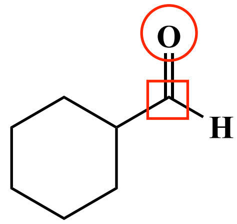
NAME (Print): ______________________________

SIGNATURE: ______________________________

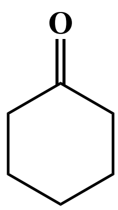
Chemistry 320N
Dr. Brent Iverson
3rd Homework
January 30, 2025

Please print the first three letters of your last name in the three boxes

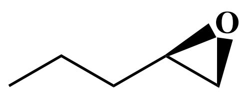
(4 pts) An important part of chemical understanding is being able to recognize the chemical reactivity of different functional groups. On the carbonyl group below, DRAW A BOX around the atom that will be attacked by nucleophiles and DRAW A CIRCLE around the atom that will be protonated in acid.



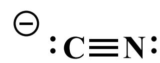
(12 pts) Being able to recognize the chemical personality of different species is one of the most important skills you can develop in Organic Chemistry. Fill in the correct circle under the structures to indicate whether that structure is considered an electrophile or nucleophile. Notice that some of the nucleophiles can also be considered bases, but we are not worrying about that for this questions.



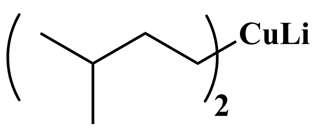
● **electrophile**
○ **nucleophile**



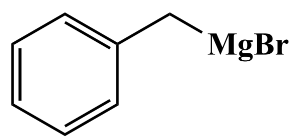
● **electrophile**
○ **nucleophile**



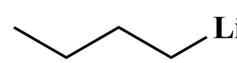
○ **electrophile**
● **nucleophile**



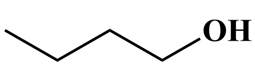
○ **electrophile**
● **nucleophile**



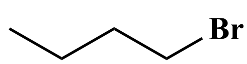
○ **electrophile**
● **nucleophile**



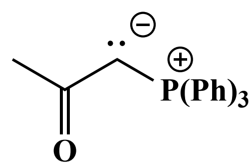
○ **electrophile**
● **nucleophile**



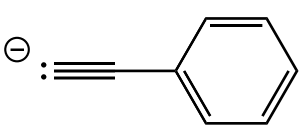
○ **electrophile**
● **nucleophile**



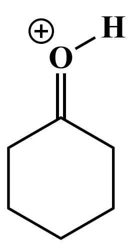
● **electrophile**
○ **nucleophile**



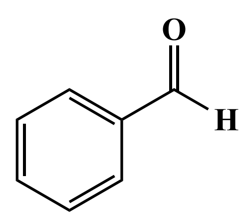
○ **electrophile**
● **nucleophile**



○ **electrophile**
● **nucleophile**

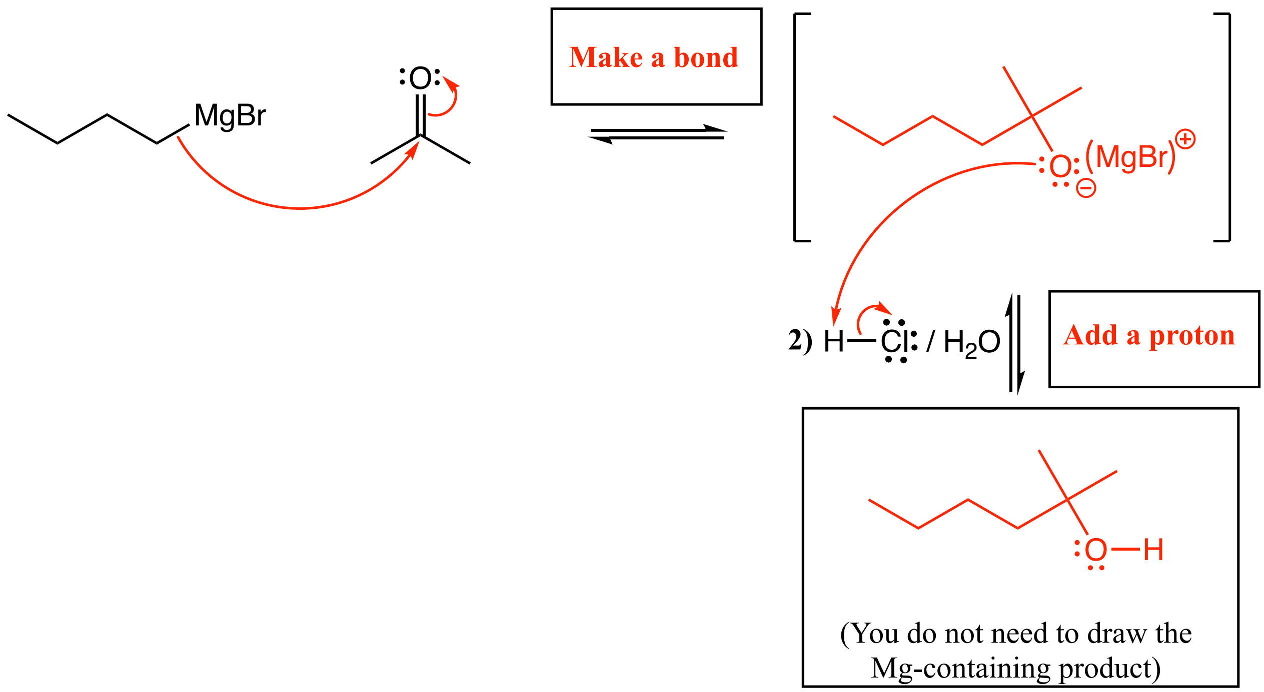


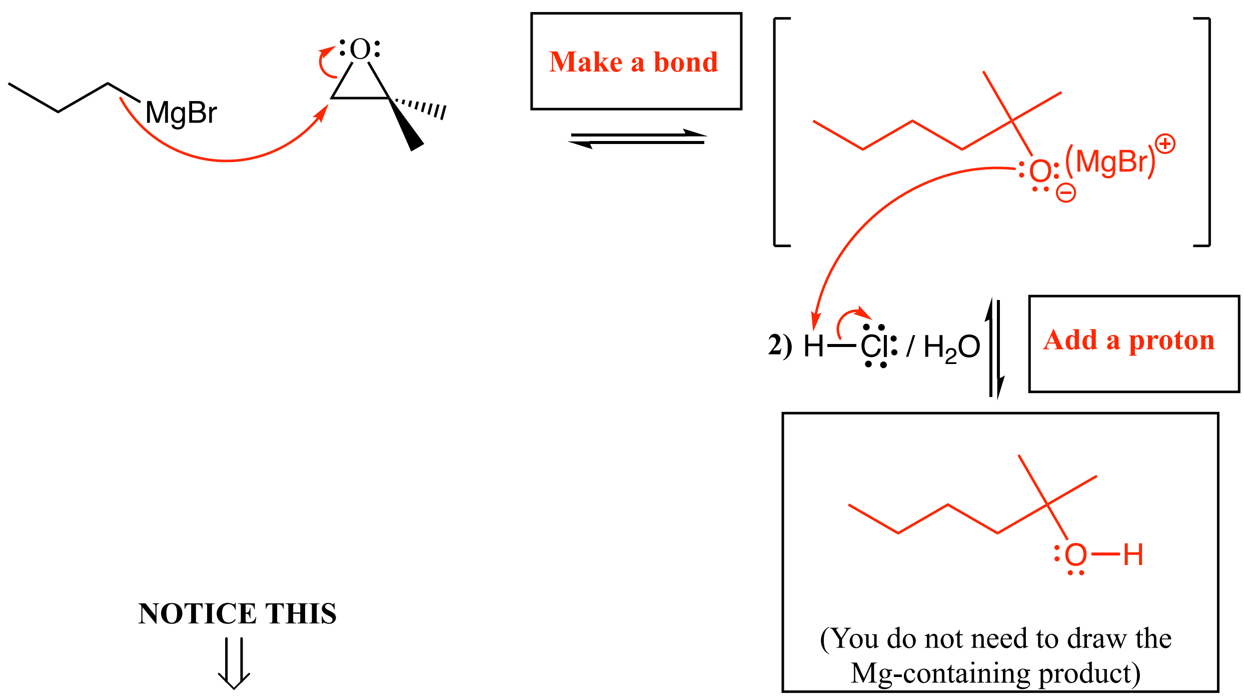
● **electrophile**
○ **nucleophile**



● **electrophile**
○ **nucleophile**

(20 pts. total) Complete the mechanism for the following two Grignard reactions. **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.



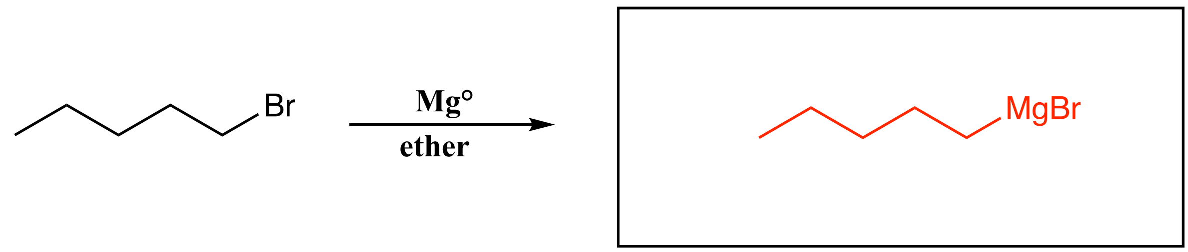


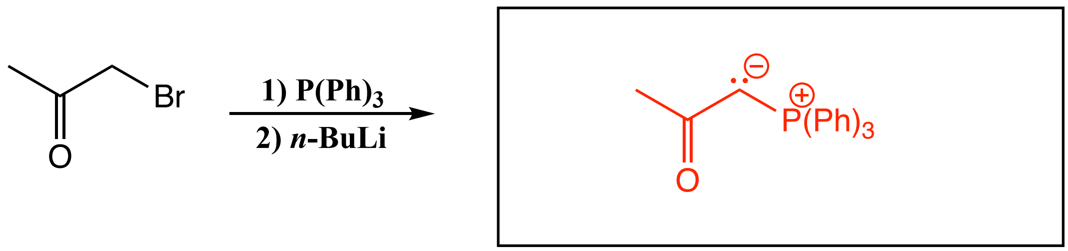
NOTICE THIS

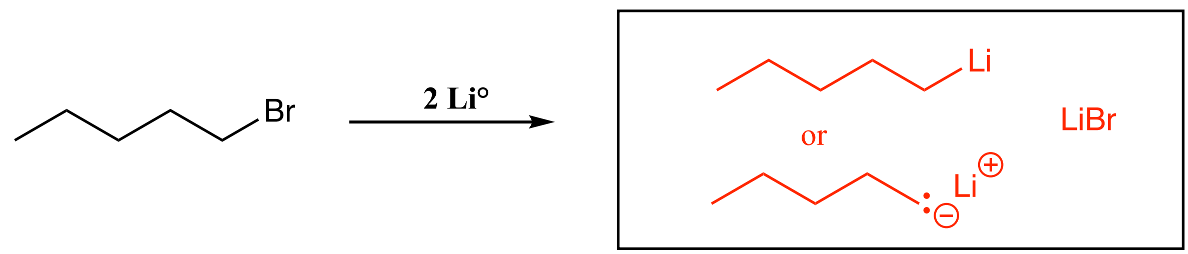
⇓

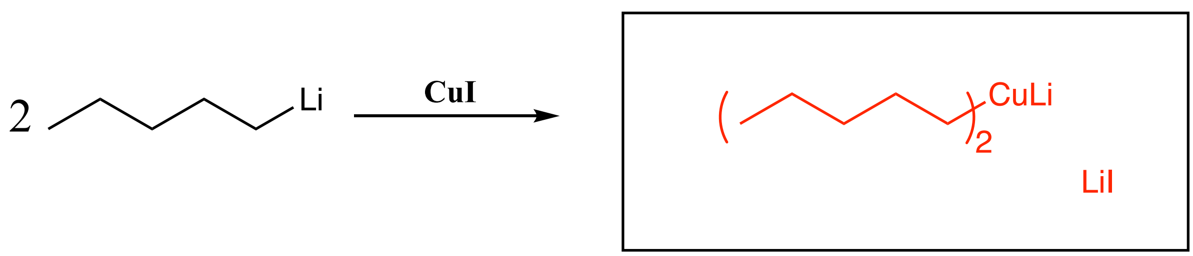
In the boxes provided adjacent to the arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.)

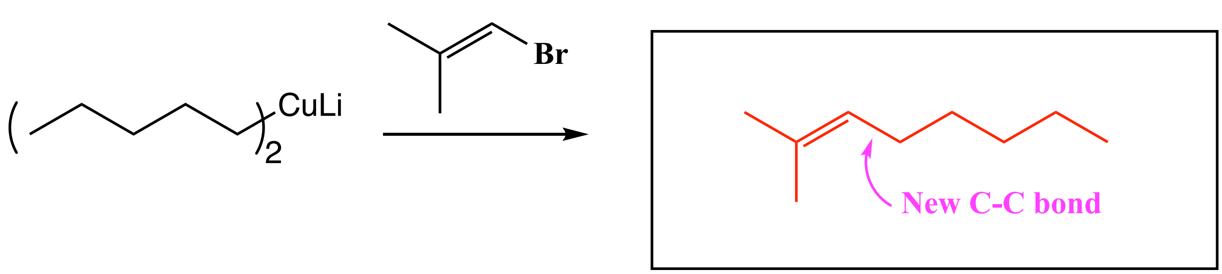
(3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges ( ) and dashes ( ) to indicate stereochemistry. To get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



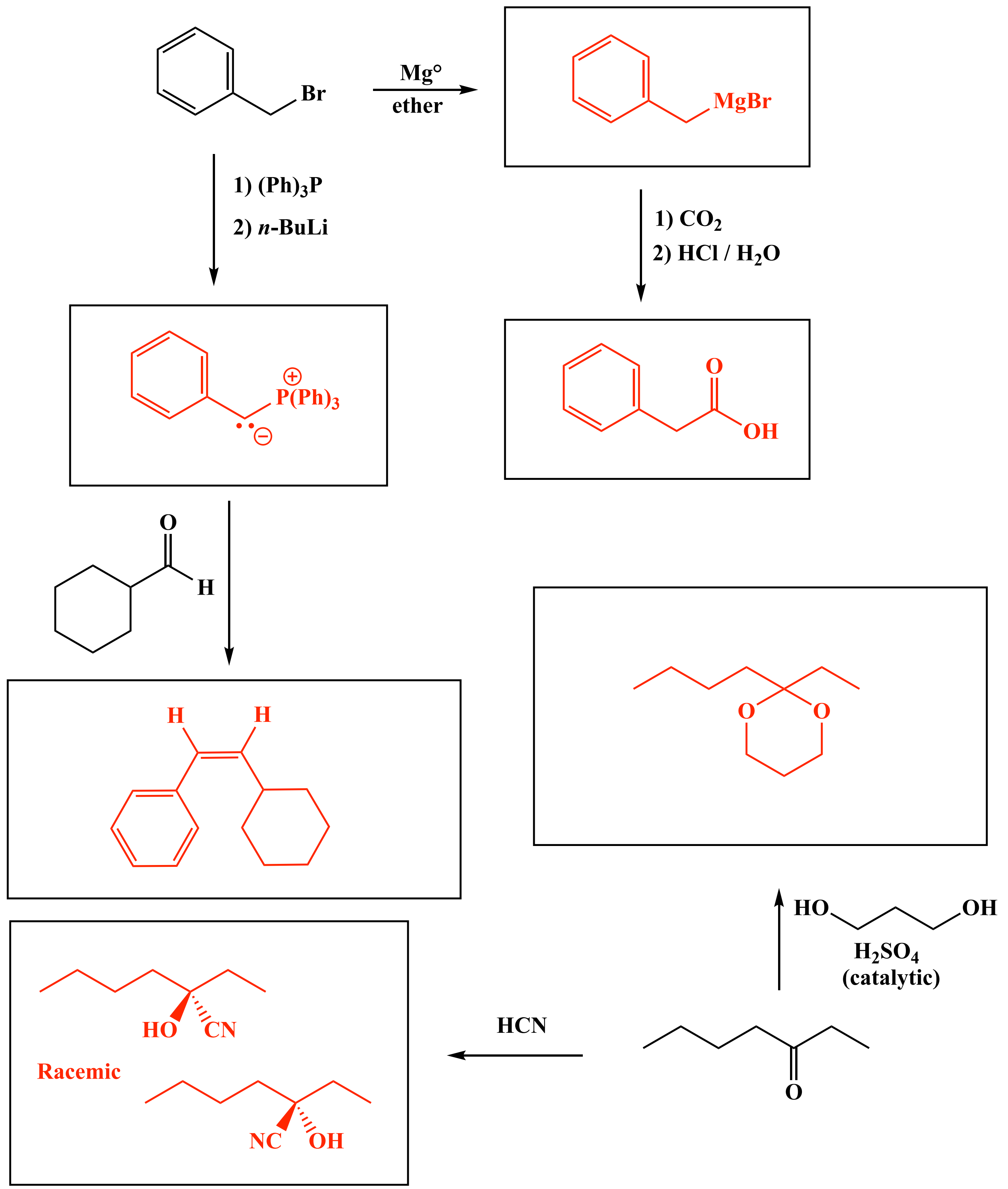




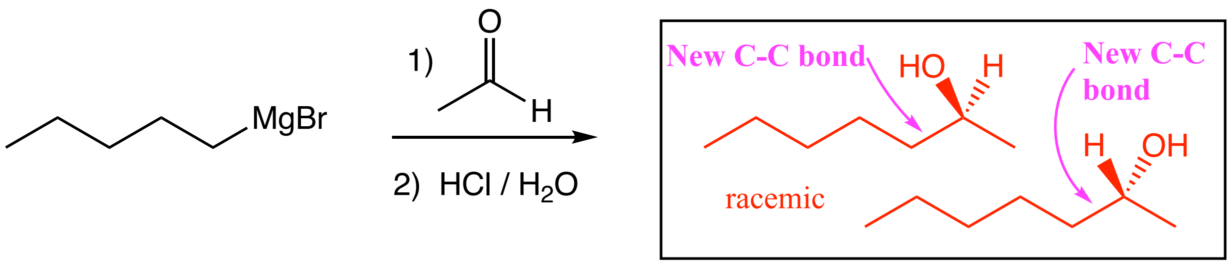


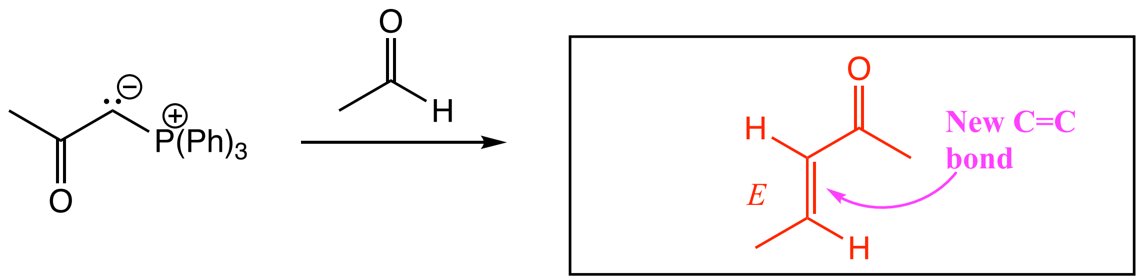


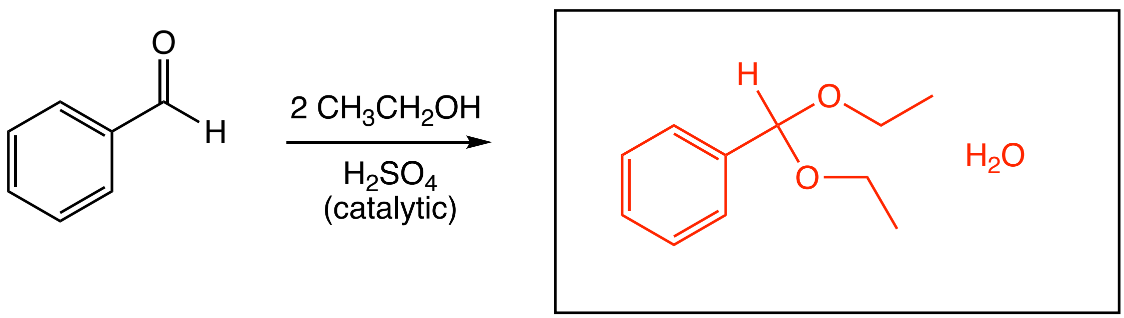
(3 or 5 pts each) Fill in the box with the product or products that are missing from the following chemical reaction equations. When a racemic mixture is formed, **you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES**. For these draw all carbon containing products.

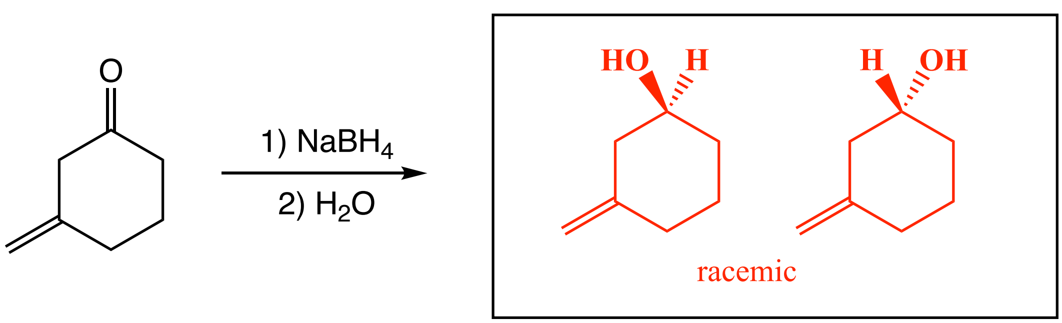


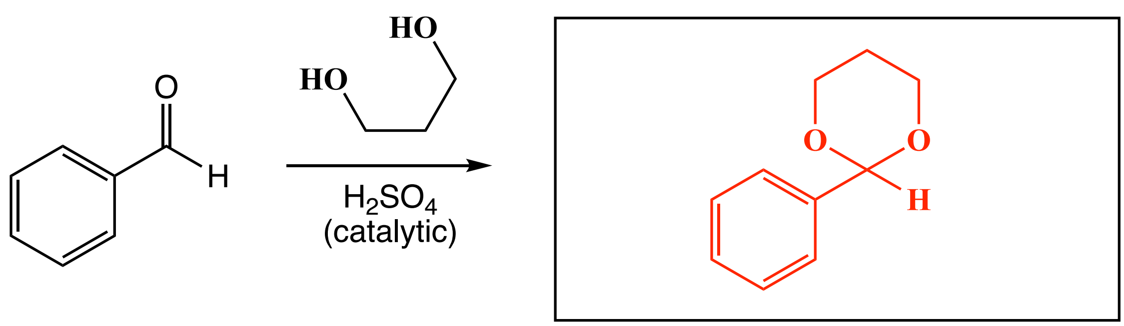
(3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges ( ) and dashes ( ) to indicate stereochemistry. To get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





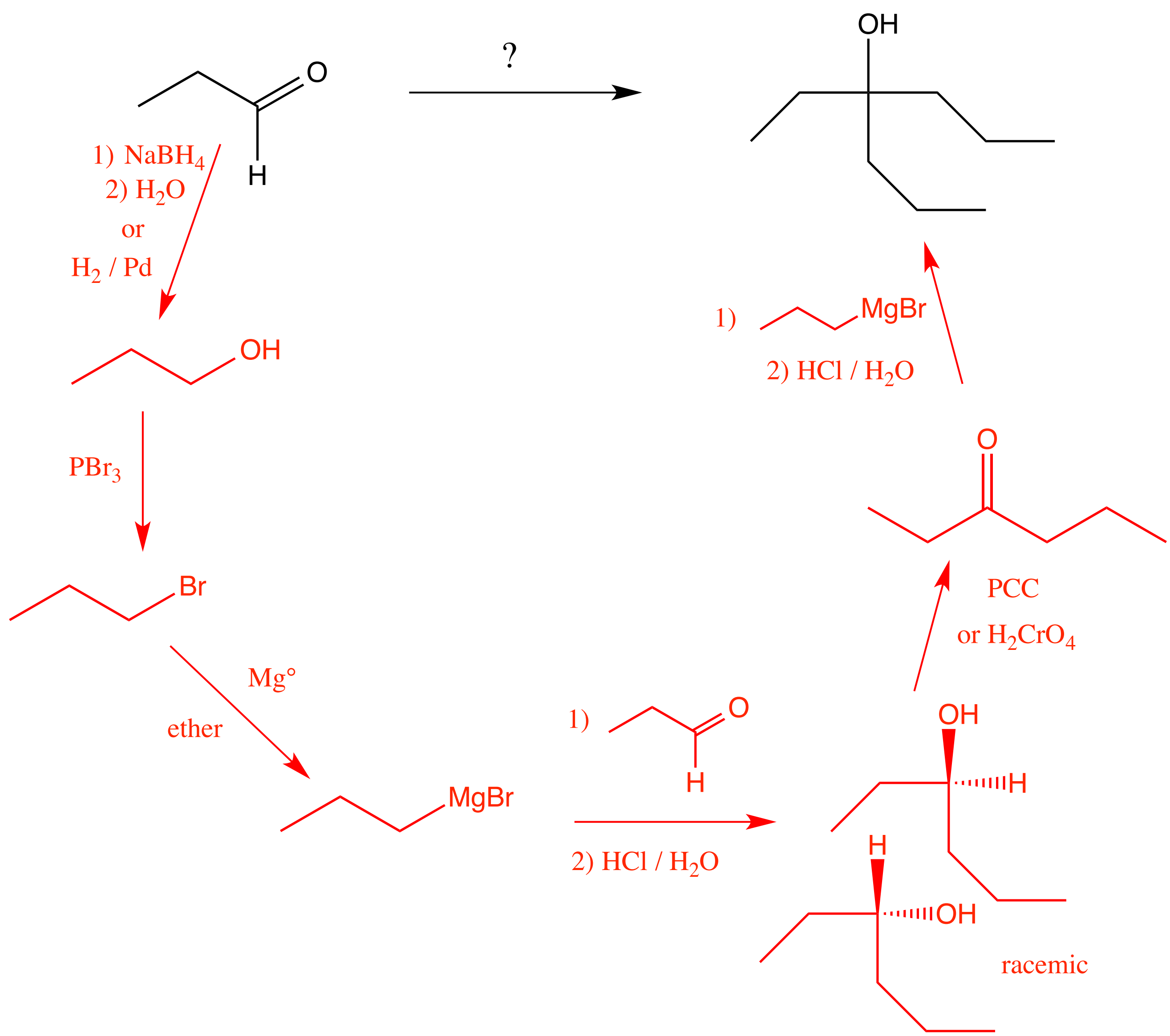






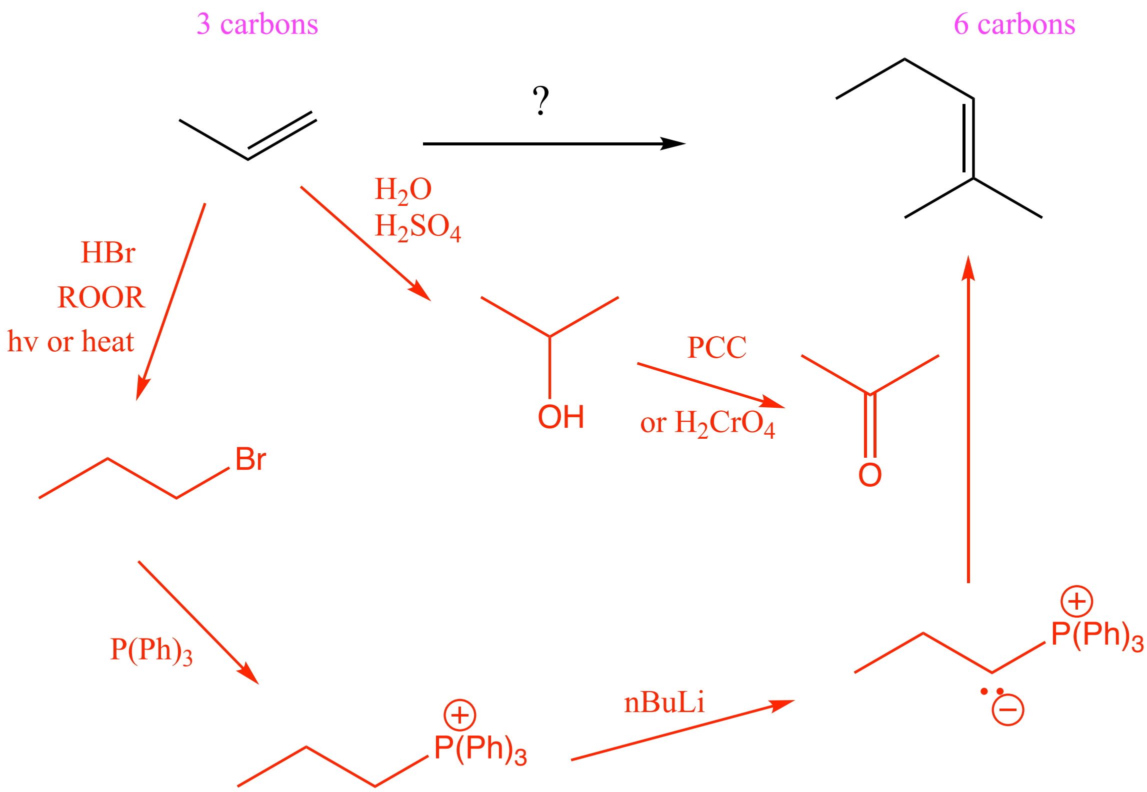
These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry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

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



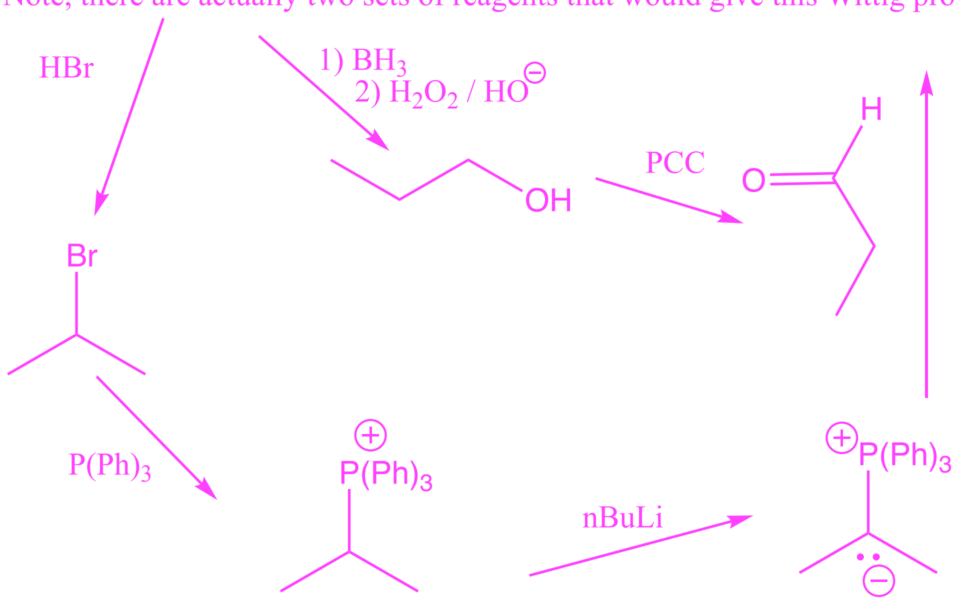
Recognize that the product alcohol has 9 carbons, meaning that three of the three carbon starting materials must be assembled to make the final product. **Recognize** further that the product is a tertiary alcohol. Hypothesize that the last reaction would be a Grinard reaction with a ketone. **Recognize** the ketone intermediate as being made from the oxidation of of the corresponding secondary alcohol, which, in turn, is derived from a Grignard reagent reacting with the starting aldehyde. Make the required Grignard reagent through the three step sequence of reduction of the starting aldehyde to a promary alcohol, conversion to an alkyl halide with PBr_3, then reaction with Mg° in ether.

(15 pts) **All of the carbon atoms of the products must come from the starting material for this one!** You have seen this before, try not to look at the answer before attempting it.

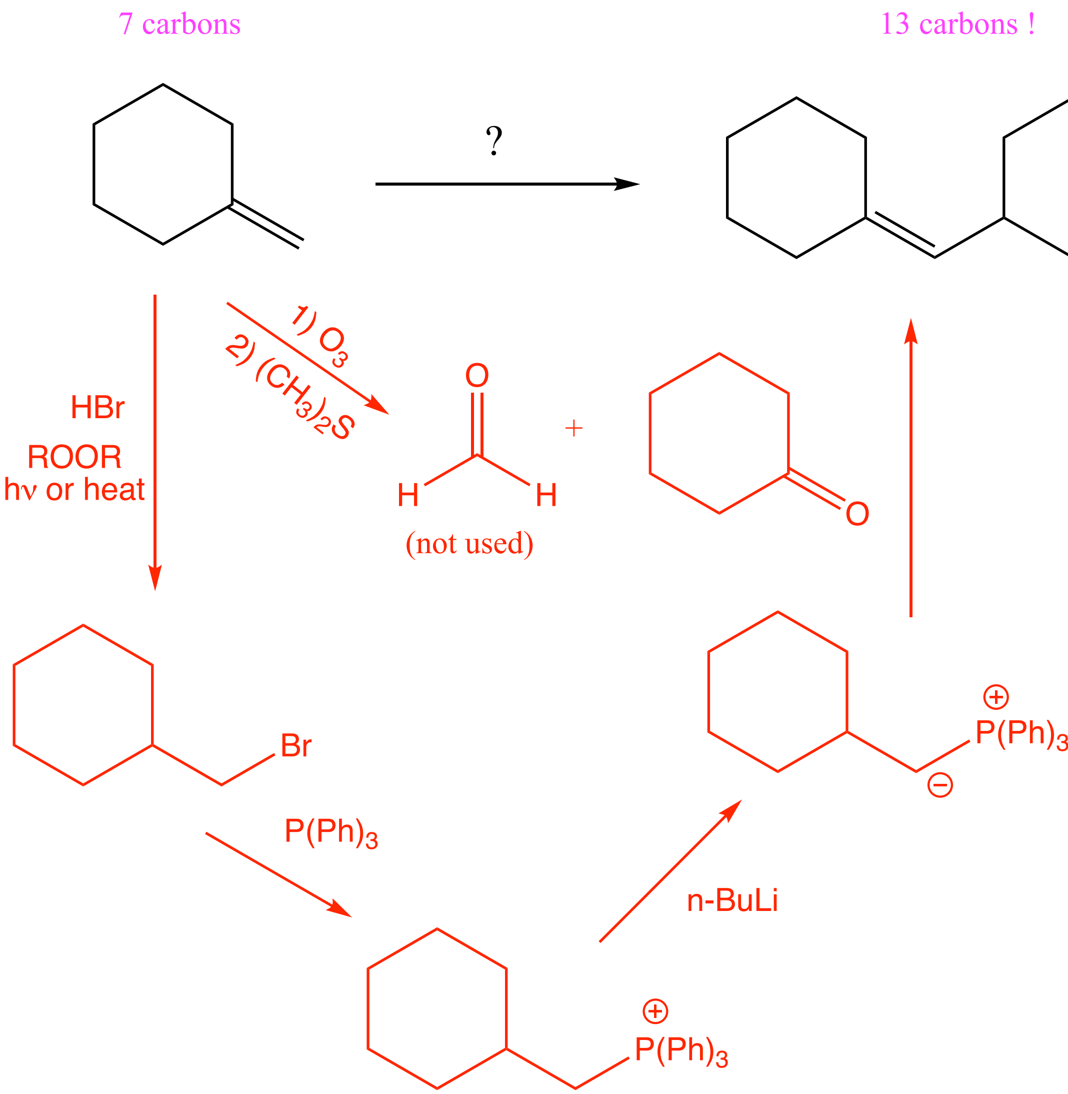


Recognize that the product is an alkene, indicating a Wittig reaction as the last step. This makes sense because the product has six carbon atoms, indicating that two molecules of the starting material were needed to create the product. **Recognize** that the acetone could be derived from propene through a combination of Markovnikov addition of water followed by oxidation. The Wittig reagent is available from non-Markovnikov addition of HBr in the presence of peroxides followed by the usual reaction with $P(Ph)_3$ and n-BuLi.

Note, there are actually two sets of reagents that would give this Wittig product.

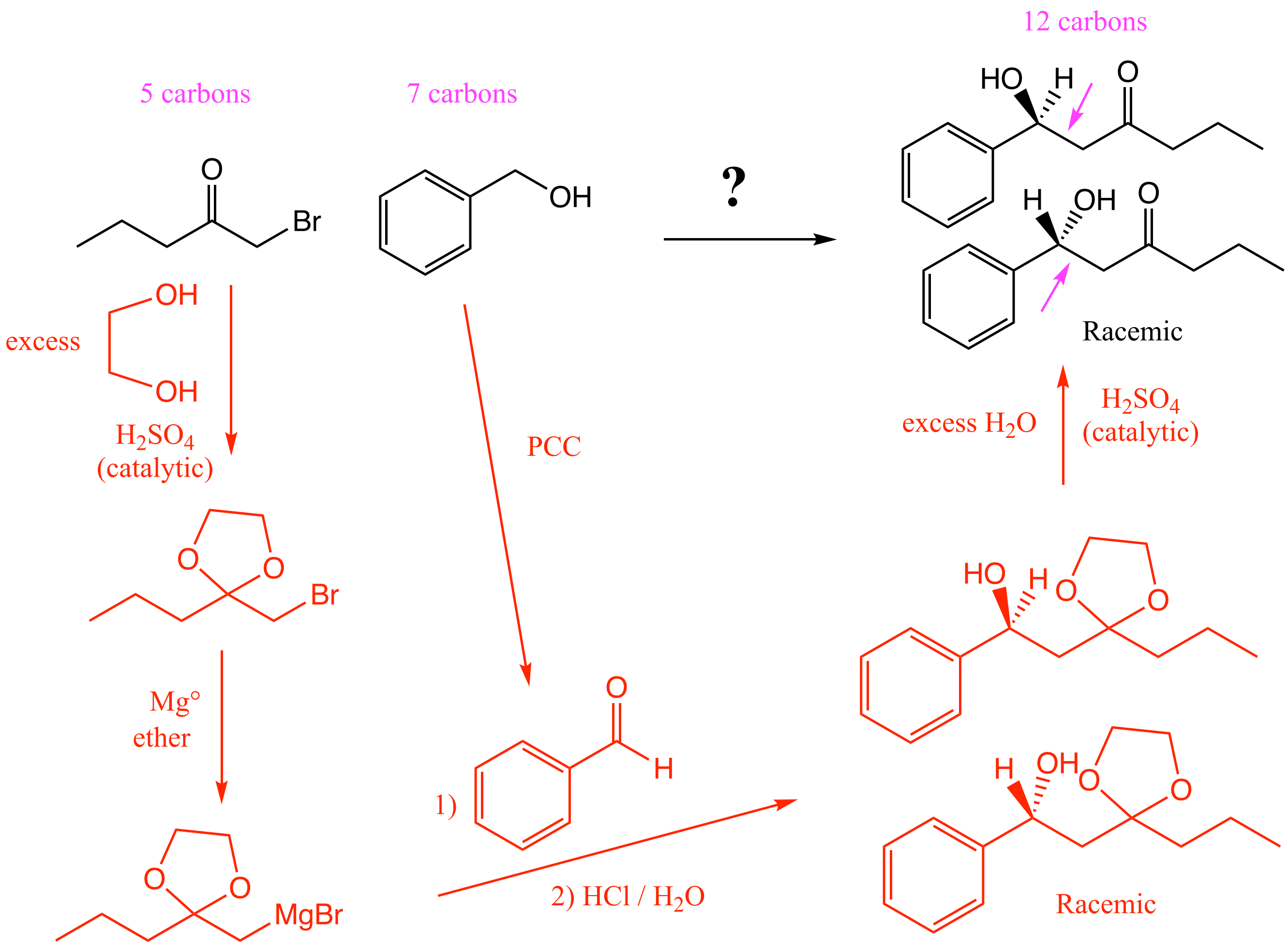


(13 pts) **All of the carbon atoms of the products must come from the starting material for this one!**



Recognize that the product is an alkene, indicating a Wittig reaction as the last step. The big story here is that the starting material has 7 carbons, but the product only has 13! The onoy way to make the final product is with a Wittig reaction between one 6 carbon and one 7 carbon piece. The only way you know to break carbon-carbon bonds is through ozonolysis, a process that generates the exact ketone you need for the final step, a Wittig reaction. **Recognize** that the Wittig you need comes from the starting alkene by reacting with HBr in the presence of peroxides and heat or light, to make the non-Markovnikov, primary haloalkane. The require Wittig reaction can be made directly from that primary haloalkane using the usual two steps of $P(Ph)_3$ followed by *n*-BuLi.

(13 pts) **All of the carbon atoms of the products must come from the starting material for this one! Note this one needs a protecting group that is not listed as a starting material because it is removed before the final product is made, so the carbons of the protecting group do not end up in the product.** In practice, protecting groups like the one you will use here can be recycled.



Recognize the product as a secondary alcohol with a new carbon-cabon bond indicatd by the arrows above. Therefore this is a KRE for a Grignard reagent reacting with an adehyde. **Recognize further** that the ketone of the 1-bromo-2-pentanone starting material must be protected as a cyclic acetal before the Grignard reagent can be made. The cyclic acetal protecting group must be removed in the last step using an excess of water and an acid catalyst such as H_2SO_4. The required aldehyde is made in one step from the starting alcohol using PCC.