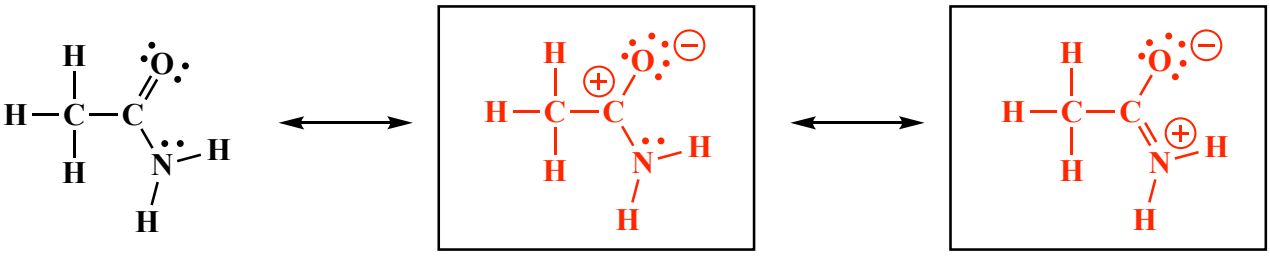
NAME (Print): _____

SIGNATURE: _____

Chemistry 320N
Dr. Brent Iverson
6th Homework
February 27, 2025

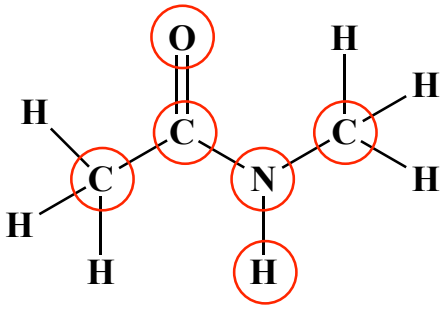
Please print the first three letters of your last name in the three boxes

On the left is drawn the Lewis structure of a simple amide. Draw the two next most important contributing structures in the spaces provided. Be sure to show all lone pairs and formal charges.

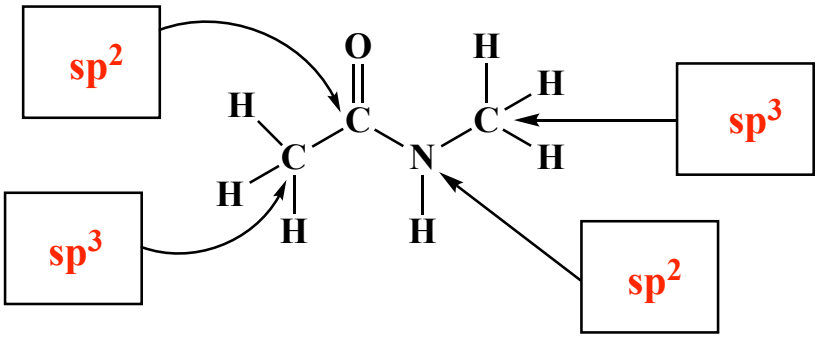


Because of the resonance you described with the above structures, several atoms of an amide bond are in the same plane. On the amide below, circle all the atoms that are in the same plane. Think carefully about this one!!

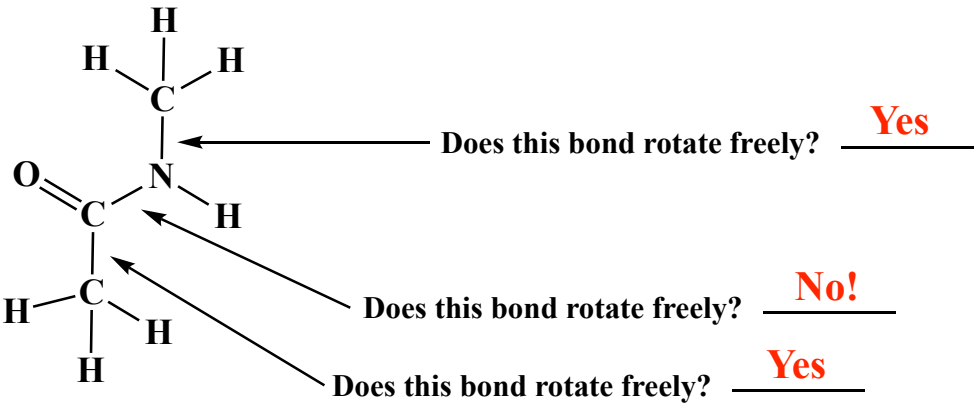
Note that one of the H atoms on the methyl groups will also be in the same plane at times, depending on the exact conformation. The atoms circled are ones that are always in the same plane.



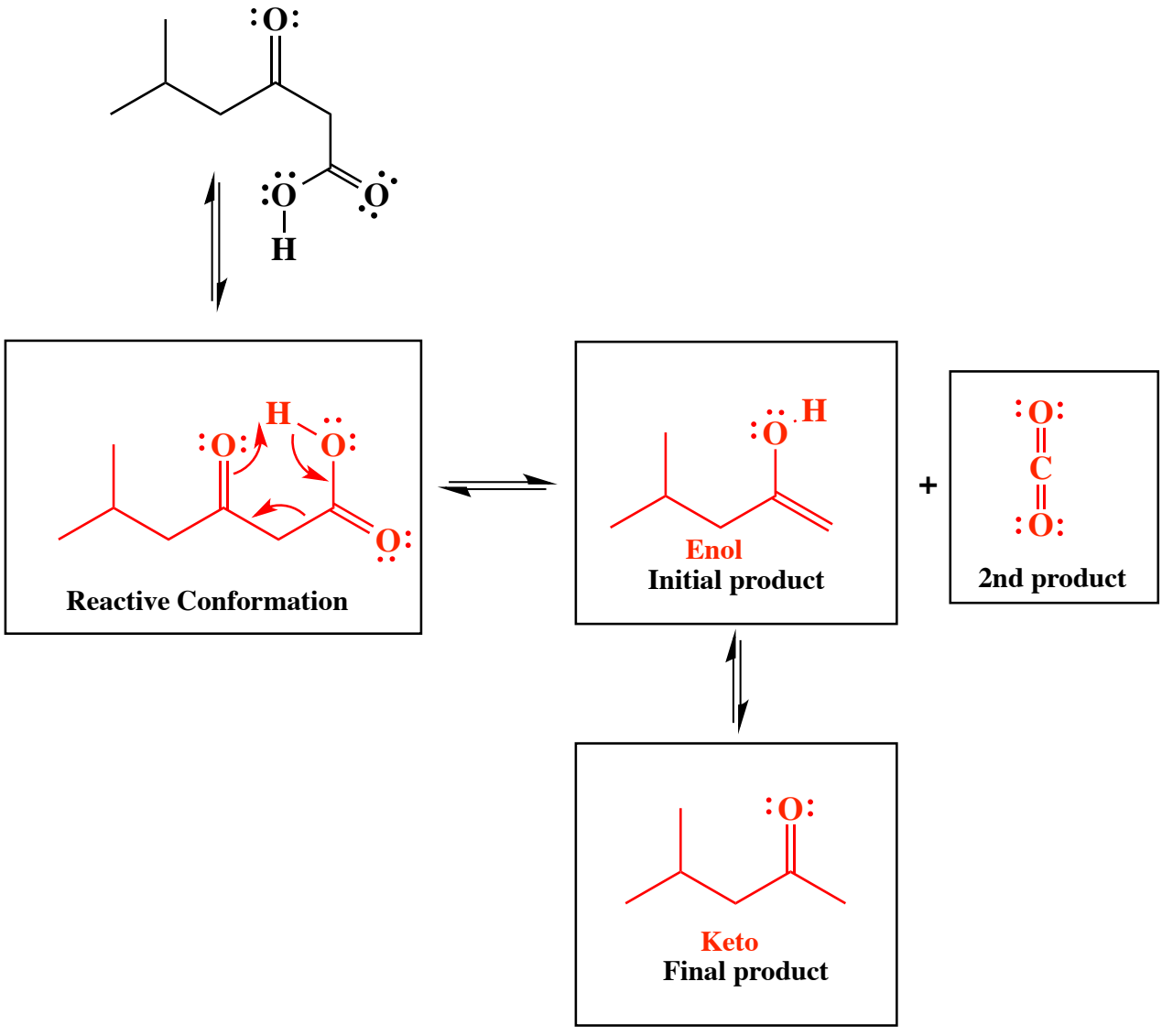
In the boxes provided, write the hybridization state of the given atoms.



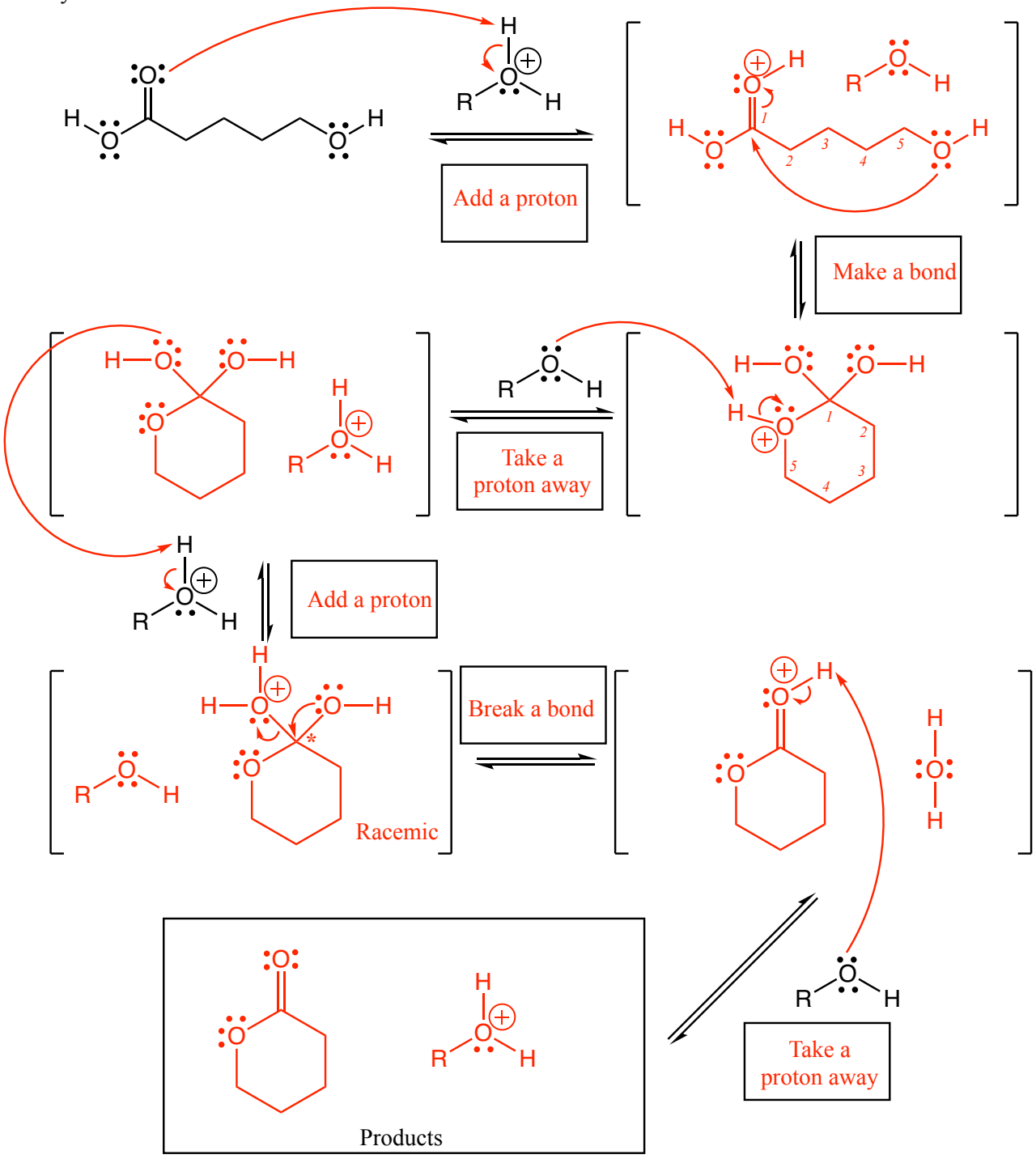
(6 pts) In the spaces given, answer the question as "yes" or "no".



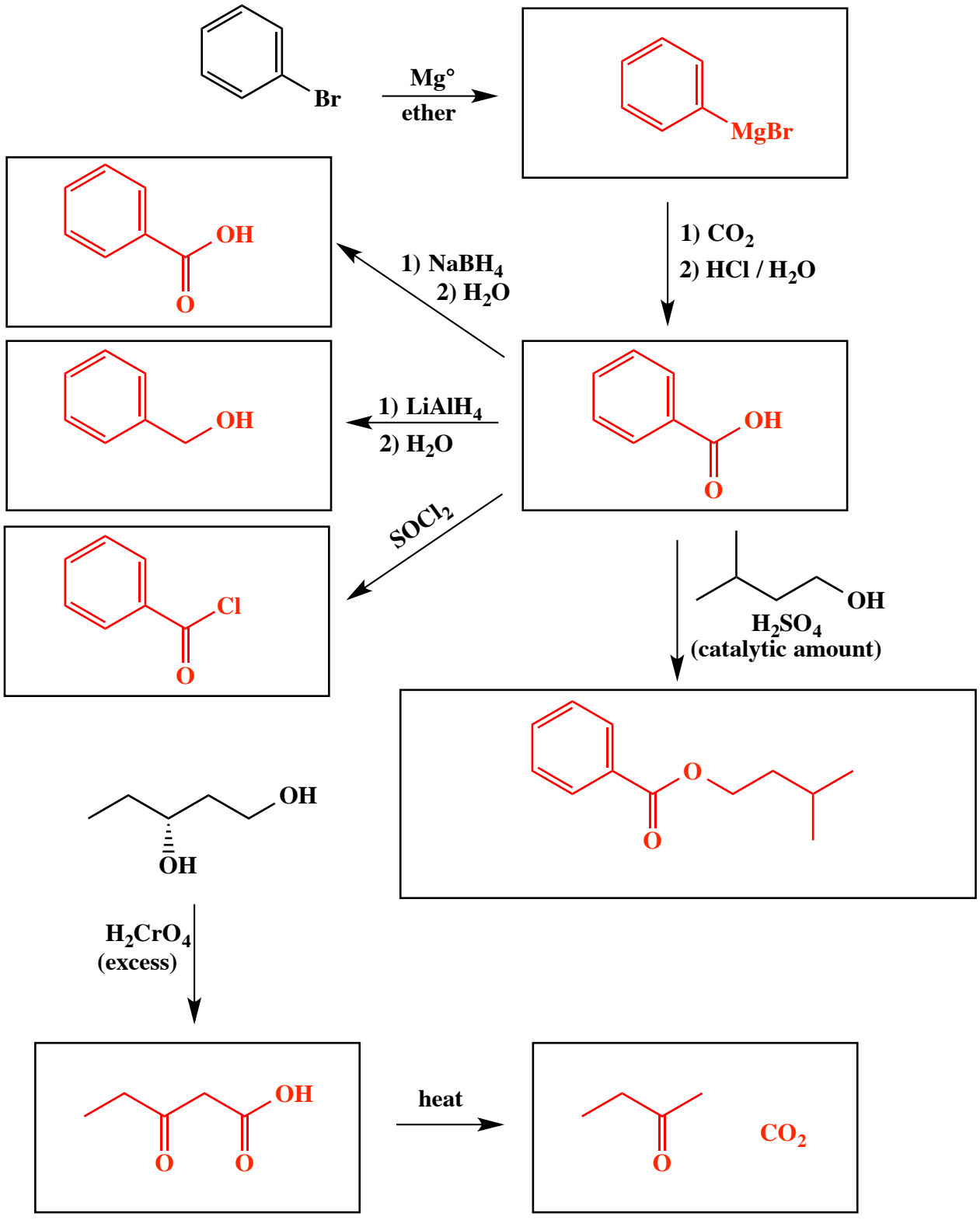
Complete the mechanism for the following decarboxylation reaction. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK. IF A CHIRAL CENTER IS CREATED IN THE PRODUCTS YOU NEED TO DRAW BOTH ENANTIONMERS, AND LABEL THE PRODUCT MIXTURE AS RACEMIC IF RELEVANT.**



Complete the mechanism for the following acid-catalyzed lactone formations 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 IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK AND LABEL AS RACEMIC IF APPROPRIATE. IF A CHIRAL CENTER IS CREATED IN THE PRODUCTS YOU NEED TO DRAW BOTH ENANTIONMERS, AND LABEL THE PRODUCT MIXTURE AS RACEMIC IF APPROPRIATE. 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.)** I realize these directions are complex, so please read them again to make sure you know what we want.



(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.



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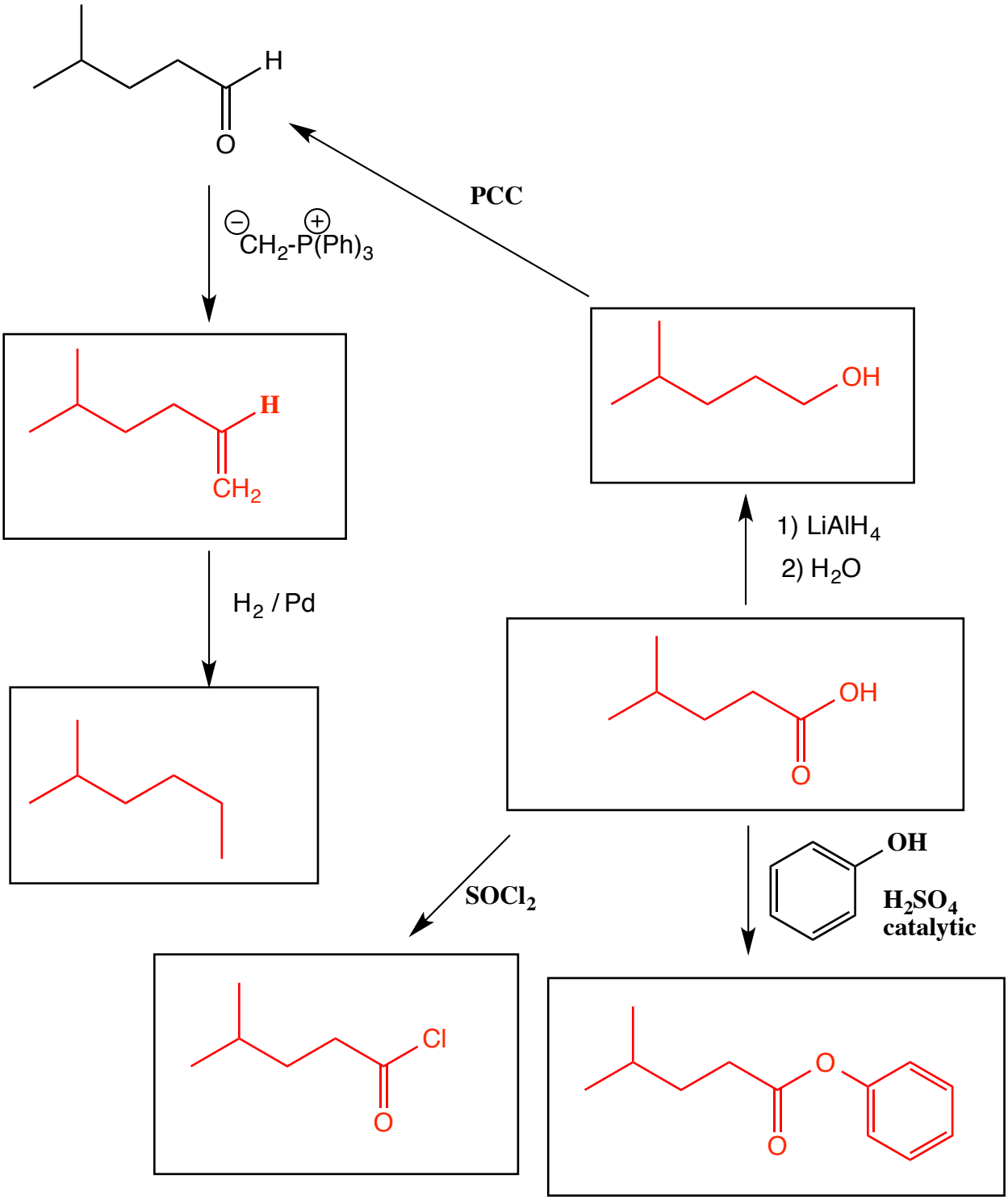
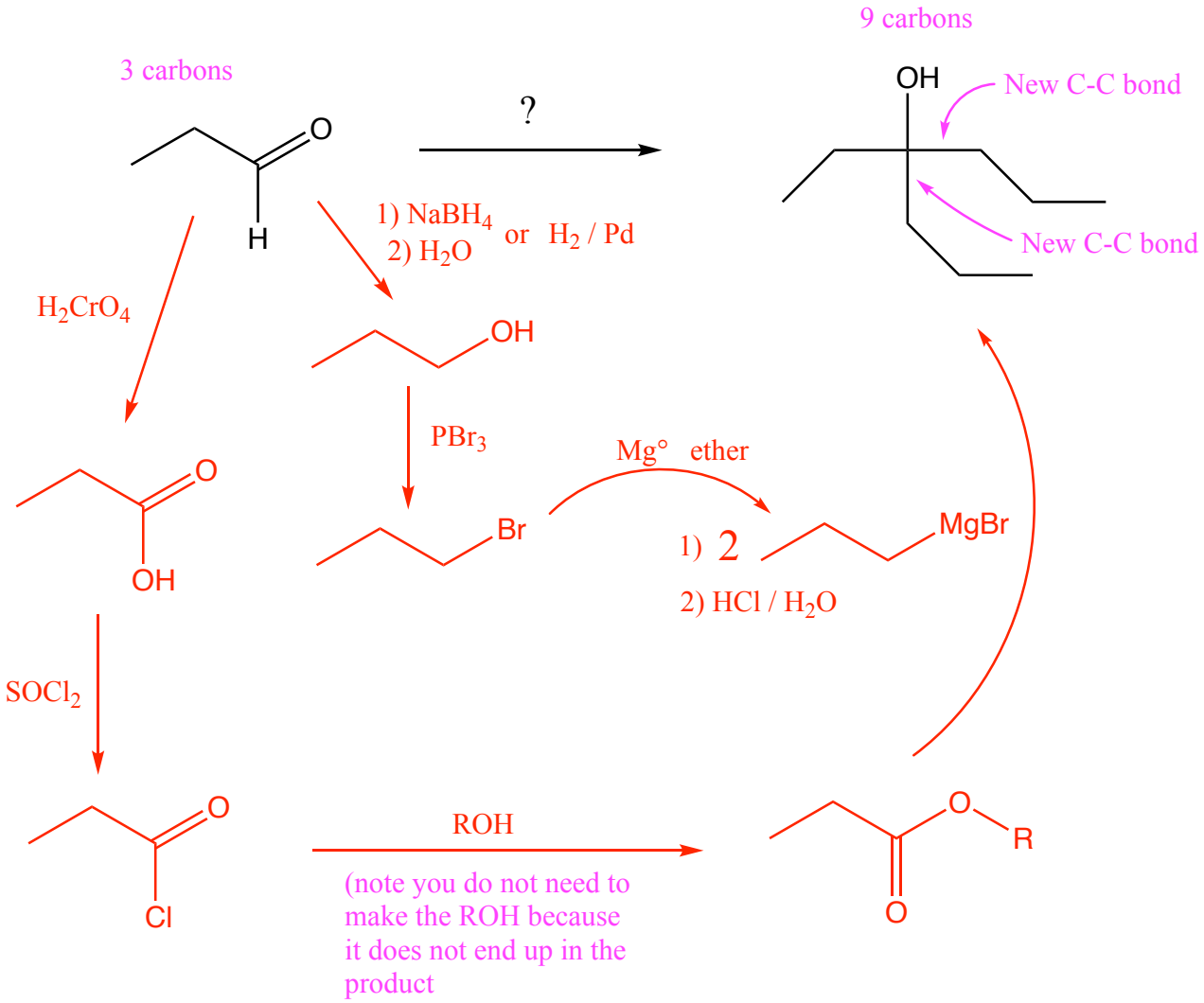


These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry 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 and two alkyl chains are the same, the KRE of an ester reacting with 2 equivalanets of a three carbon Grignard reagent. **Recognize** that you can make the required Grignard reagent through the three step sequence of reduction of the starting aldehyde to a primary alcohol, conversion to an haloalkane with PBr_3, then reaction with Mg° in ether. **Recognize** that the required ester can be made from the starting aldehyde through an oxidation to give the carboxylic acid, followed by reaction with $SOCl_2$ to give the acid chloride then reaction with an alcohol.

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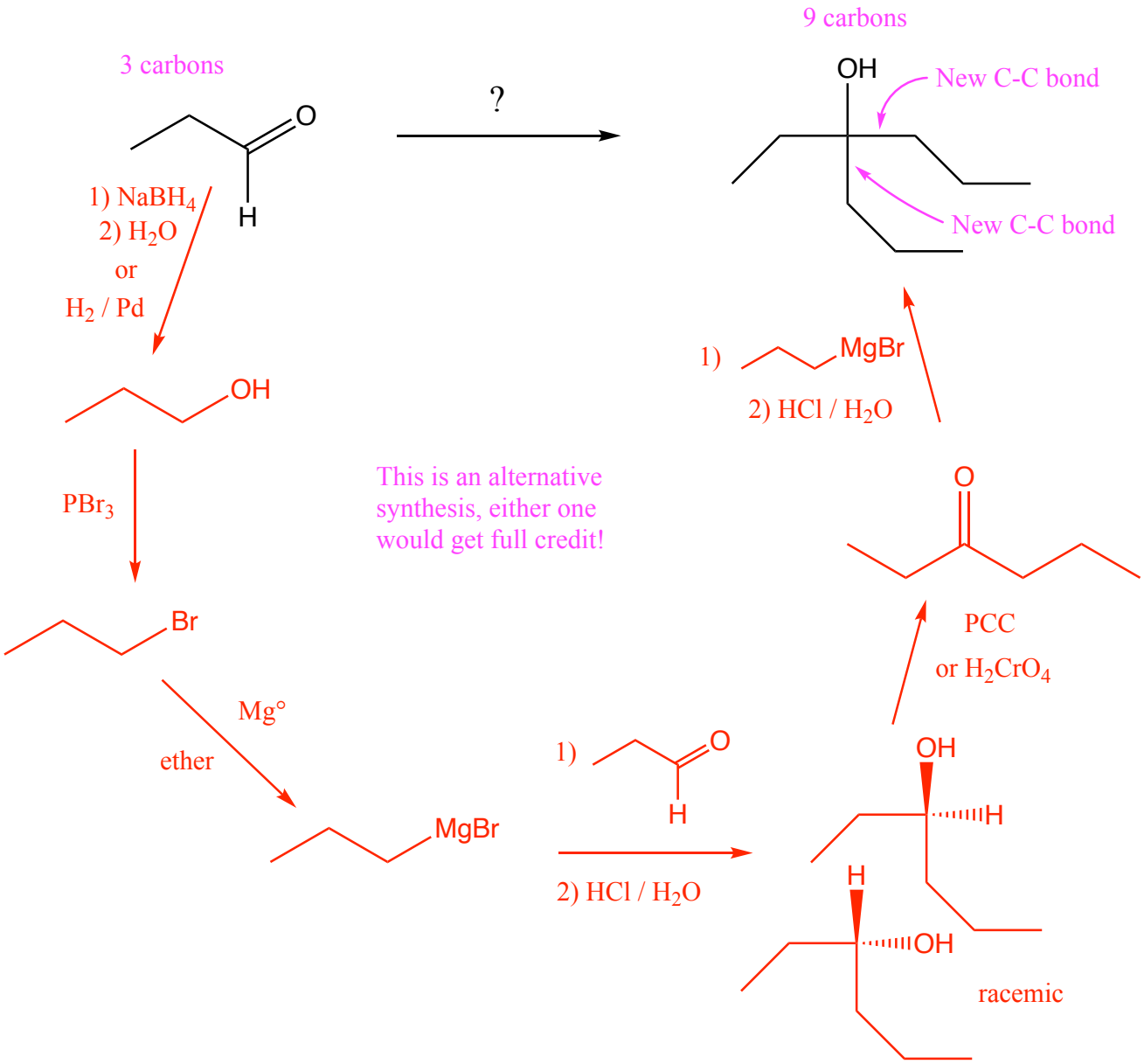
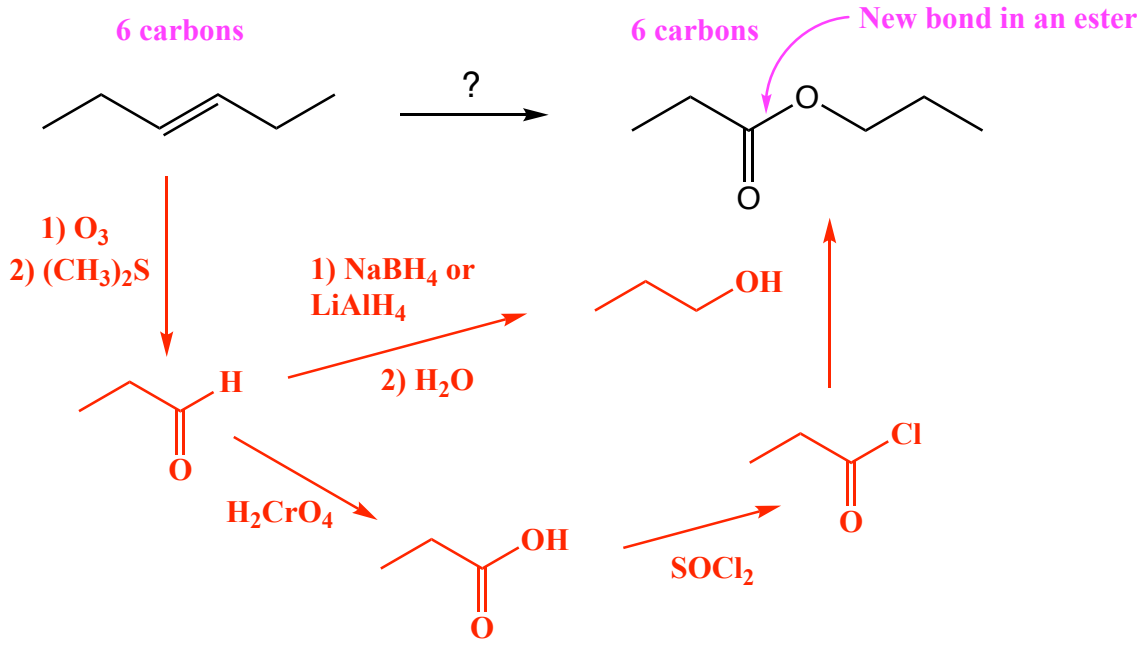


Recognize that the product alcohol has 9 carbons, meaning that three of the three carbon starting materials must be assembled to make the final product. **Recognize** further that the product is a tertiary alcohol. Hypothesize that the last reaction would be a Grinard reaction with a ketone. **Recognize** 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 primary alcohol, conversion to an haloalkane with PBr_3, then reaction with Mg° in ether.

(13 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting material. Draw all molecules synthesized along the way. When it doubt, draw the molecule! Hint: this should look familiar as a homework problem.

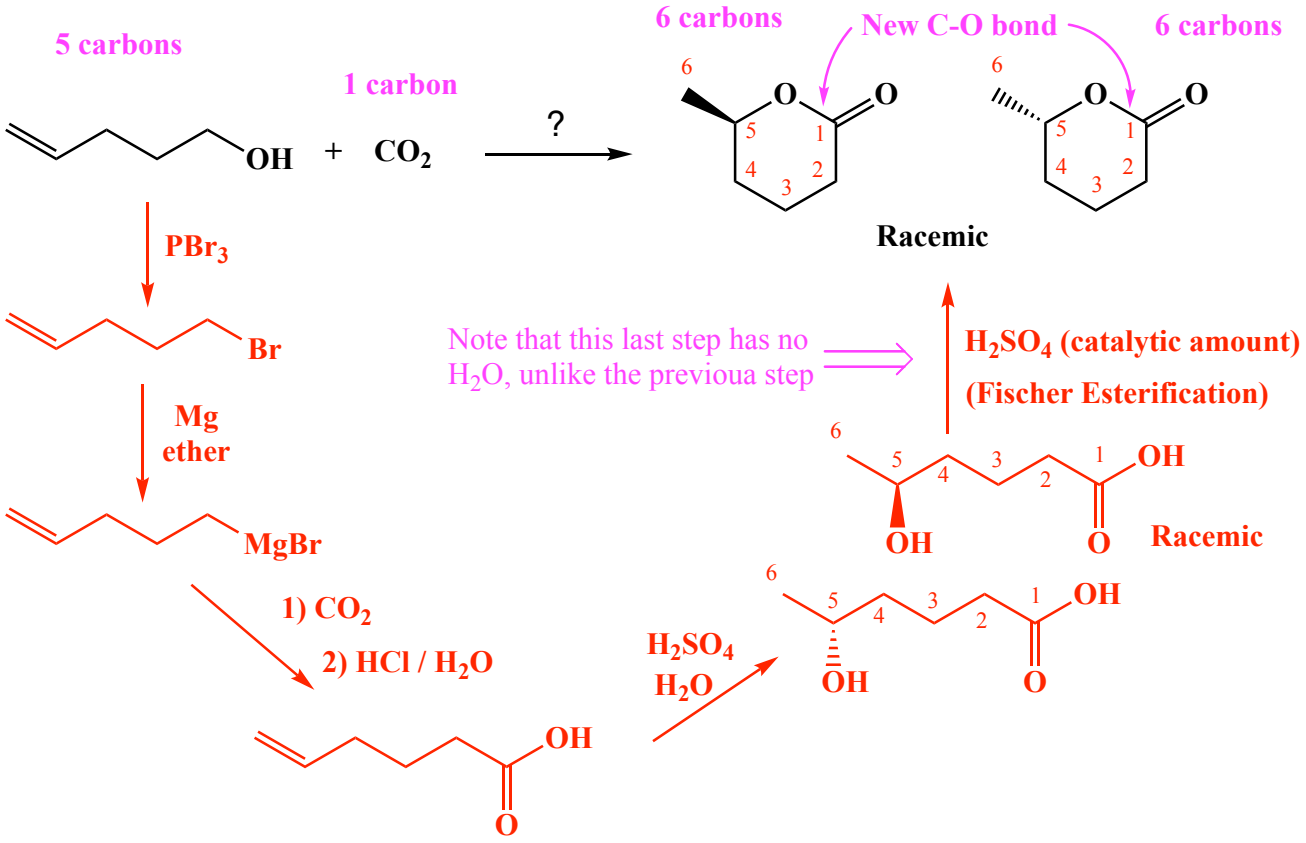
All of the carbons of the produce must come from the given starting material.



Recognize that both the starting materials have 6 carbons. **Recognize** further that the product is an ester so the new bond must be the C-O bond. In that case, the product ester is made from two three-carbon pieces, propanoyl chloride and 1-propanol. The propanoyl chloride is derived from propanoic acid. **Recognize** further that both 1-propanol and propanoic acid can be synthesized from propanal using a metal hydride reaction or H_2CrO_4, respectively. **Recognize** that propanal can be made from the starting material by ozonolysis. Note that it would be fine to create the ester from 1-propanol and propanoic acid directly using the Fischer esterification reaction.

(13 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting material. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

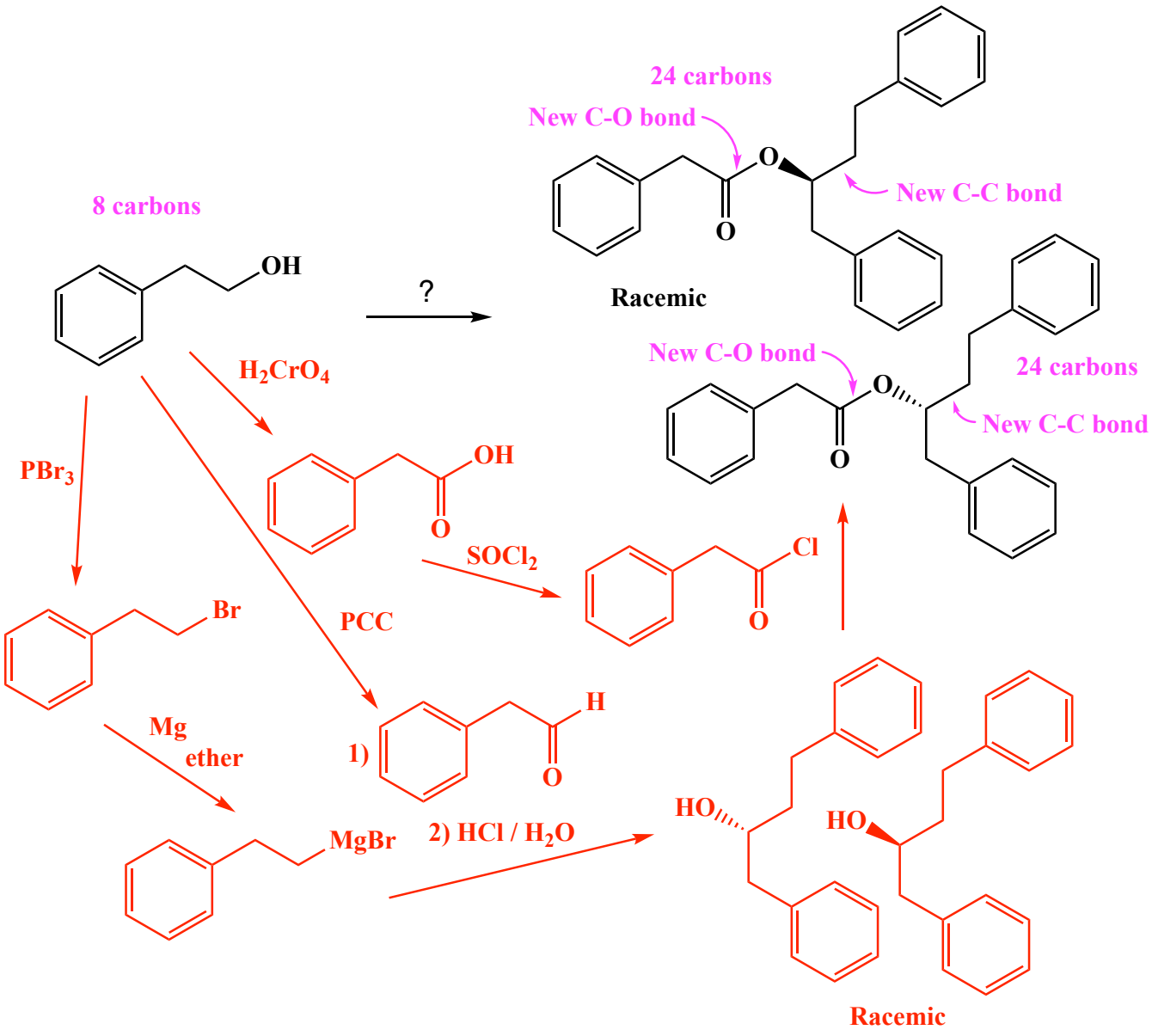
All of the carbons of the produce must come from the given starting material.



Recognize that the product is a lactone, that is a cyclic ester. It is formed by a Fischer esterification of the corresponding 5-hydroxyhexanoic acid. Counting carbons in the starting material and product indicates this must come from adding CO_2 to a Grignard reagent. **Recognize** the hard part of this problem is realizing that a Grignard reagent is too basic to be made in the presence of an -OH group in the same molecule, so the Grignard reaction used to add the extra carbon atom must take place **before** the -OH group is created,

(17 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting material. Draw all molecules synthesized along the way. When it doubt, draw the molecule! Hint: this should look familiar as a homework problem.

All of the carbons of the produce must come from the given starting material.



Recognize that the product is actually an ester, made from the corresponding alcohol and an acid chloride. Note that you would not want to carry out a Fischer esterification on this secondary alcohol because in the presence of H_2SO_4 it would probably dehydrate rather than form an ester. **Recognize** that the acid chloride can be derived from the starting alcohol via H_2CrO_4 oxidation followed by $SOCl_2$. **Recognize** the complex alcohol used in the last step is the product of a Grignard reaction between the corresponding aldehyde and Grignard reagent, which in turn come from the starting alchohol via PCC and PBr_3 followed by Mg in ether, respectively.