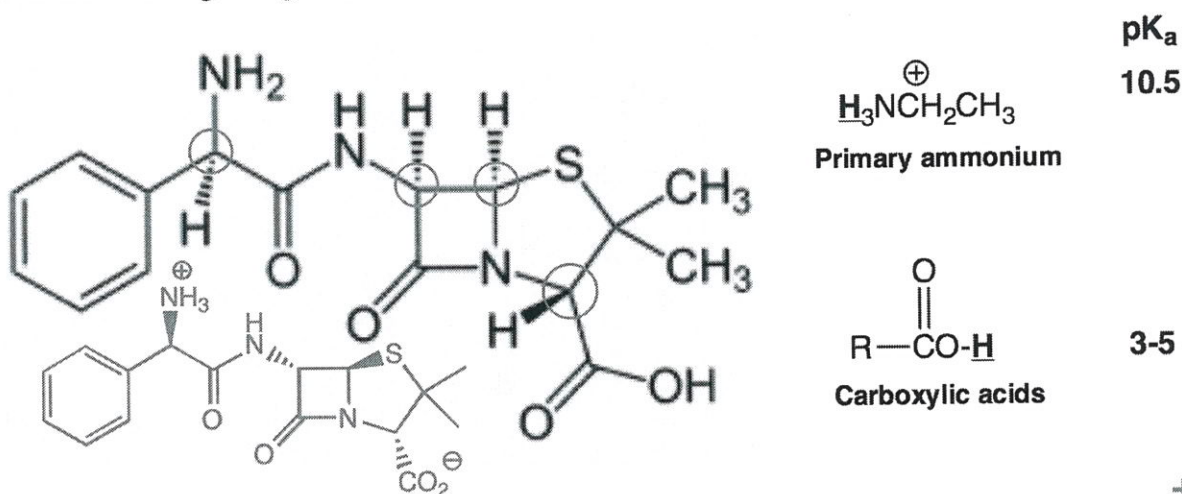


10. (10 points) The following structure is that of ampicillin, a very common antibiotic used in the treatment of many bacterial infections. The following structure was copied directly from a Wikipedia page (<http://en.wikipedia.org/wiki/Ampicillin>). To the right of the structure are listed relevant  $pK_a$  values from the table at the beginning of the exam.



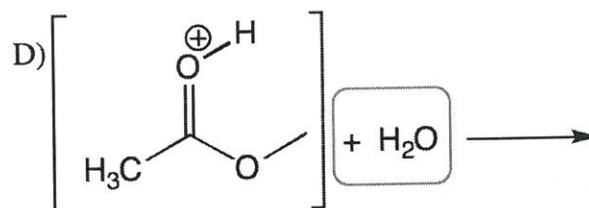
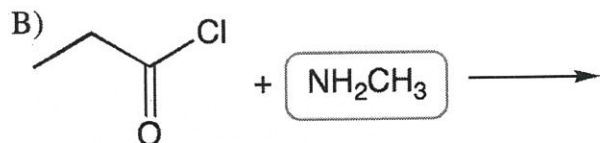
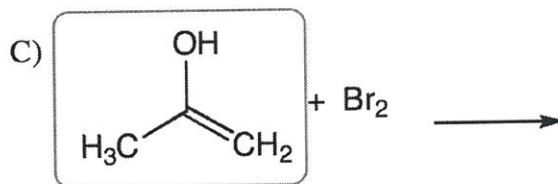
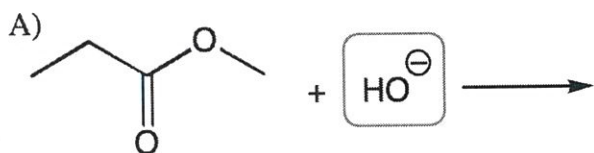
Based on the  $pK_a$  values given, what is the total charge on ampicillin in a solution of  $\text{pH} = 2.0$ ? +1  
 (Amine function will be protonated and have a positive charge and the carboxylic acid will be protonated and neutral)

Based on the  $pK_a$  values given, what is the total charge on ampicillin in a solution of  $\text{pH} = 7.0$ ? 0  
 (Amine function will be protonated and have a positive charge and the carboxylic acid will be deprotonated with a negative charge)

In only two short sentence, describe two very different things that are wrong with the format of the ampicillin structure that I copied from Wikipedia. Hint; one of the answers to this question is related to the two questions you just answered. **You can assume the atoms are all in the correct places in the structure, we do NOT assume you know the structure of ampicillin by heart!**

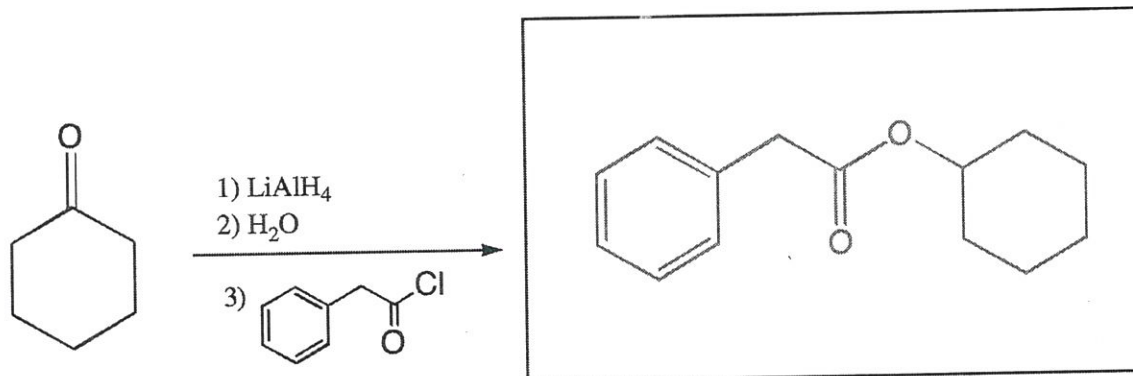
Based on the  $pK_a$  values, there is NO pH in which the carboxylic acid will be protonated but the amine function will be neutral as shown. The second problem is that the stereochemistry is ambiguous at the circled chiral centers, showing three bonds in the same plane and only one out of the plane.

11. (8 points) In the following reactions, draw a circle around the nucleophile. Note there is no reason to write any products for these.

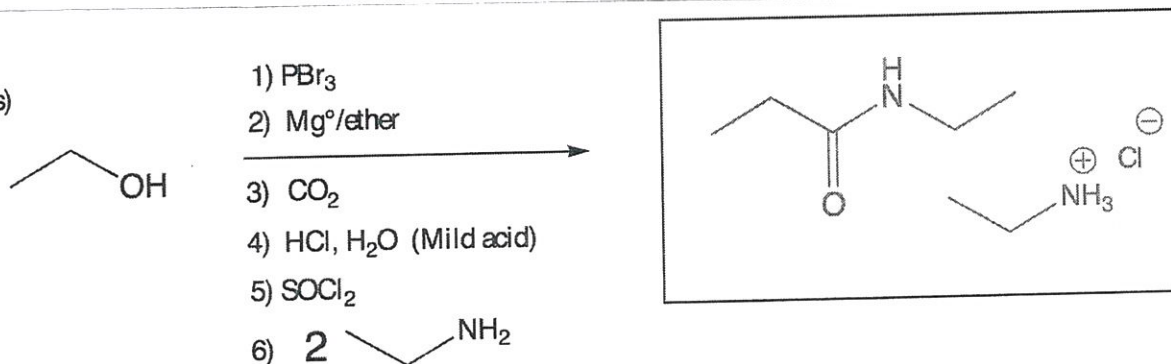


15. (14 points) For the following sequences of reactions, draw the final organic product or products after ALL the steps have been completed. You do not need to draw the molecules synthesized along the way, **only the last product that is formed**. If a new chiral center is created in the reaction that produces a racemic mixture, label the chiral center with an asterisk (\*) and write "*racemic*" underneath.

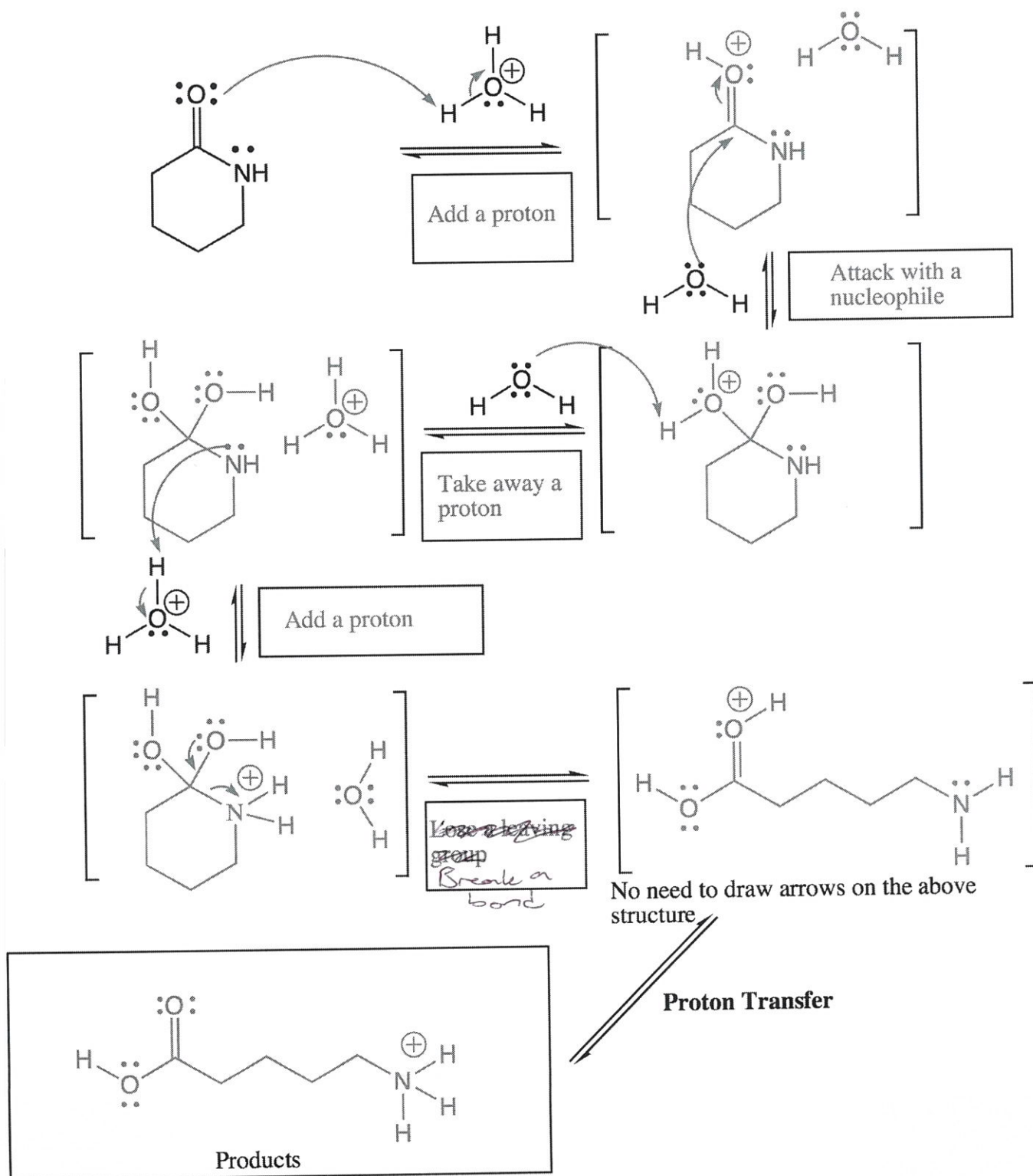
(6 pts)



(8 pts)



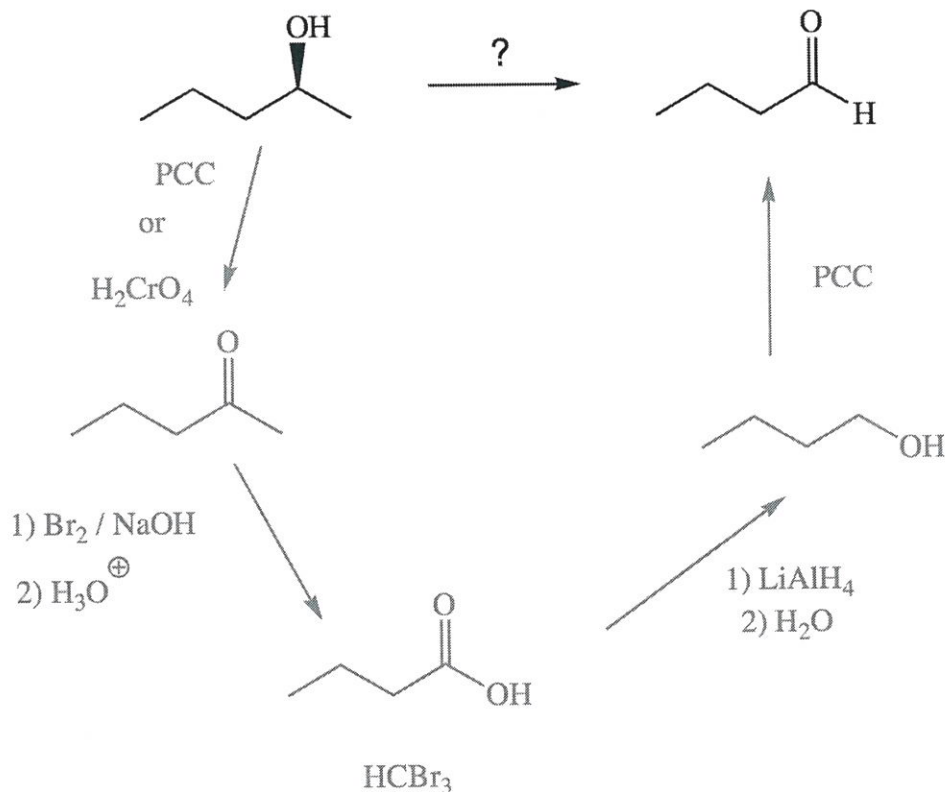
13. (29 pts.) Complete the mechanism for the following acid catalyzed lactam hydrolysis reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR THE PRODUCTS, MARK IT WITH AN ASTERISK AND LABEL AS "RACEMIC" IF RELEVANT. IN THE BOX BY EACH SET OF ARROWS, WRITE WHICH OF THE 4 MECHANISTIC ELEMENTS IS INDICATED IN EACH STEP OF YOUR MECHANISM (For example, "Add a proton").





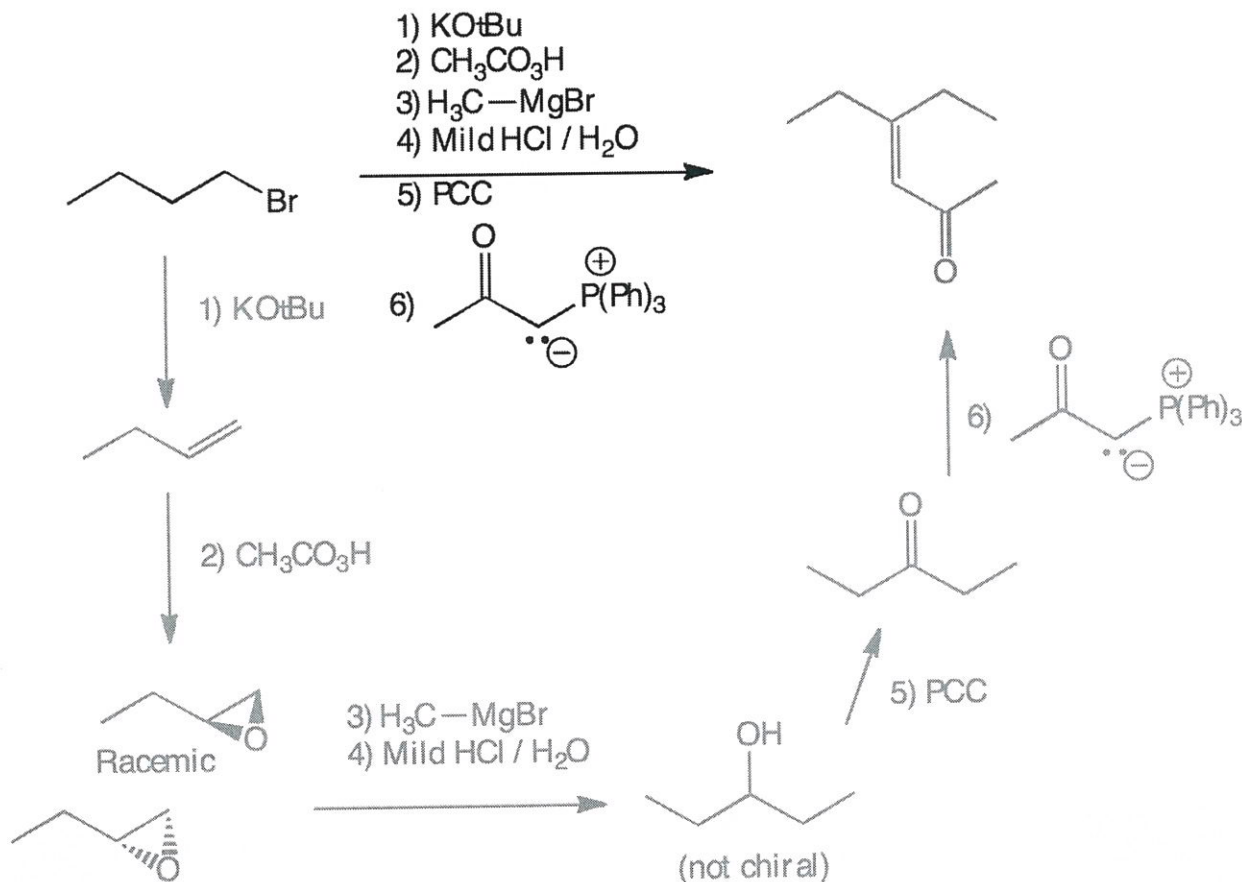
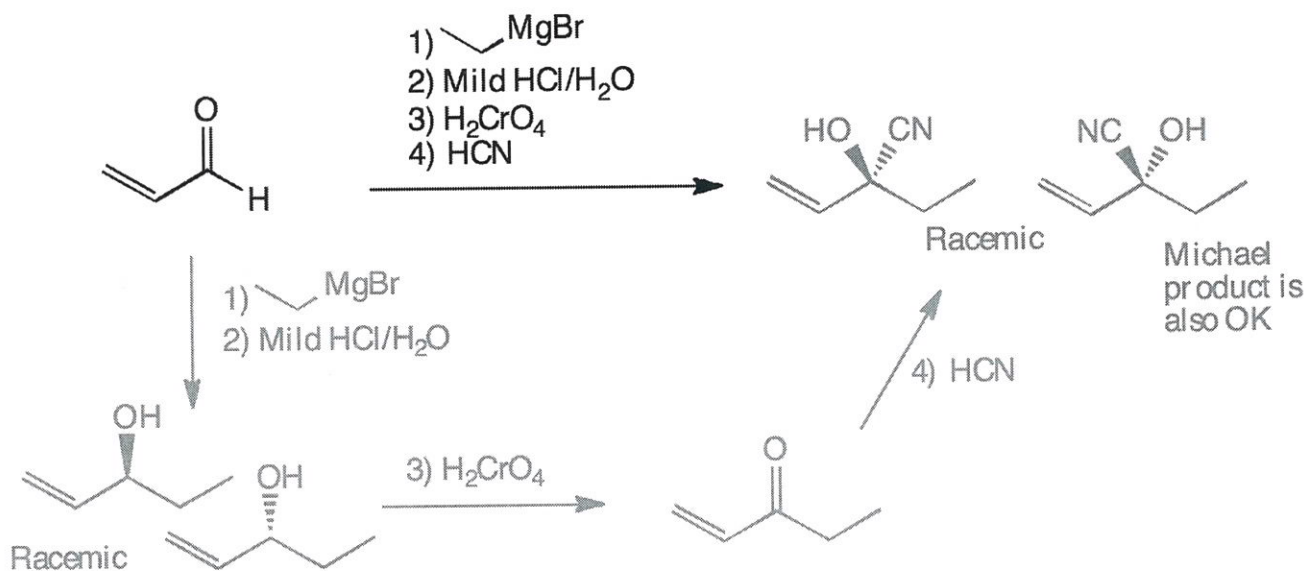
19. (10 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting material. Draw all molecules synthesized along the way. When it doubt, draw the molecule! Hint: this should look familiar as a homework problem.

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



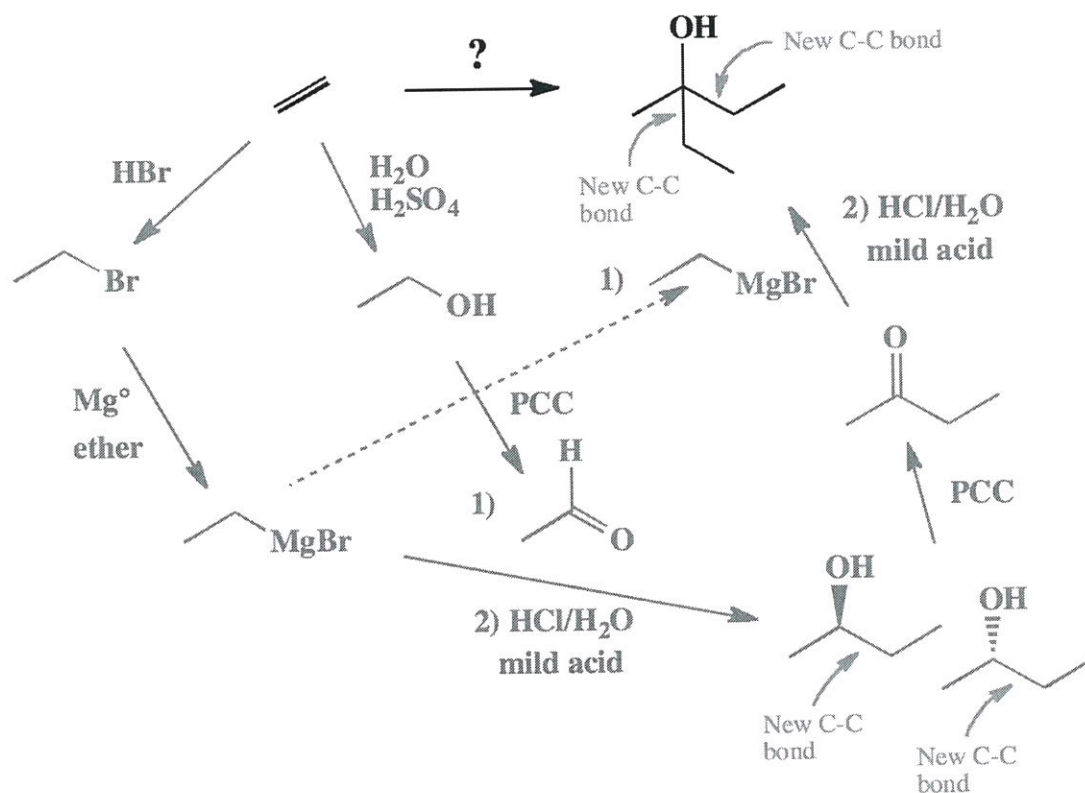
This one is pretty hard as far as we are concerned. **Recognize** that the product lost a single carbon atom compared to the starting material. You only know three ways to accomplish removal of a single carbon; ozonolysis, decarboxylation and the haloform reaction. The decarboxylation reaction is unlikely because the product is not a methyl ketone or an obvious derivative of a methyl ketone (the KRE for decarboxylation). Ozonolysis is out because there is no high yield way to give the required terminal alkene (that would be the non-Zaitsev product) On the other hand, the haloform reaction needs a methyl ketone starting material, and looking at this reaction, we **recognize** that the starting material can be easily converted to the required methyl ketone via oxidation of the OH group. Following the haloform reaction, **recognize** that reduction to butanol followed by PCC oxidation gives the product butanal.

14. (7 pts each) For the following sequences of reactions, work through all the different steps and then write the final product(s). Assume only the predominant product is formed at each step. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. We are only grading your final product(s) here.



13. 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, draw both structures and make sure to write "racemic" next to them.

(19 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 while the starting material has two. Therefore, predict that three starting material molecules combine in the product. **Predict** further that the new C-C bonds created must be as indicated by the arrows. Therefore the product has new C-C bonds connected to the same carbon atom as an -OH group, **the KRE of a alkyl Grignard reagent reacting with a ketone**. **Recognize** that the required ketone can be made from the oxidation of 2-butanol, that in turn can be made from a Grignard reaction between two two-carbon molecules; acetaldehyde reacting with ethyl Grignard. **Recognize** that acetaldehyde can be made from ethene through the two reaction sequence of hydration in acid (or oxymercuration/demercuration) followed by PCC. **Recognize** the ethyl Grignard as coming from ethene via reaction with HBr followed by Mg in ether.