NAME (Print): _____

EID _____

SIGNATURE: _____

Chemistry 320N
2nd Midterm Exam
March 13, 2025

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

Please Note: Please take your time. You have three hours to take this exam. Please do not rush, we want you to show us everything you have learned this semester so far! Making careless mistakes is not good for anyone! If you find yourself getting anxious because of a problem, skip it and come back. Please do not second guess yourself! Keep track of the questions worth a lot of points. (This does not mean they are hard, it just means we think they cover important material.)

One last thing: I recommend you close your eyes for a moment, then take some nice deep breaths before you begin. YOU GOT THIS!

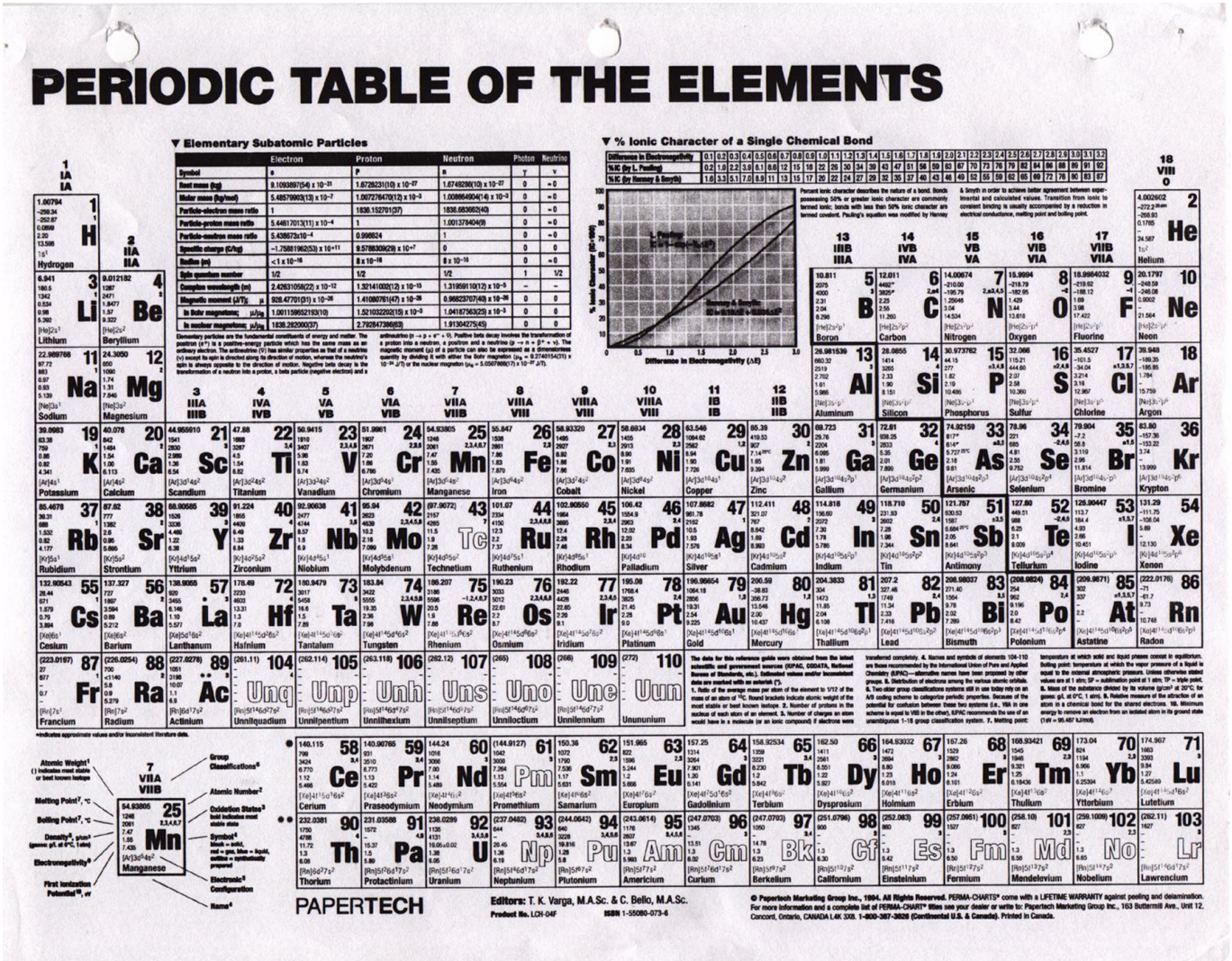
FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

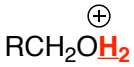
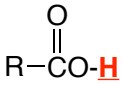
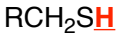
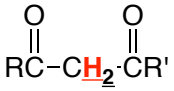
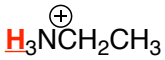
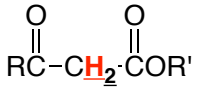
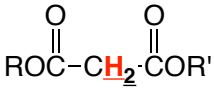
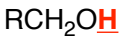
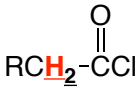
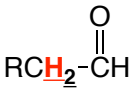
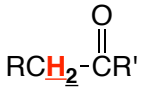
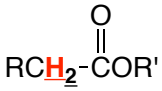
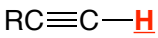
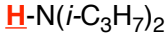
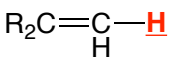
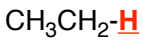
Student Honor Code

“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)



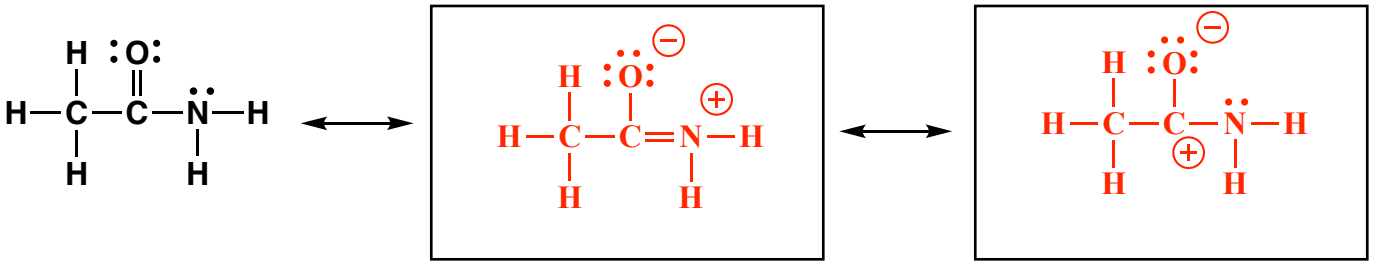
Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Carboxylic acids		3-5
Thiols		8-9
Ammonium ion		9.2
β-Dicarbonyls		10
Primary ammonium		10.5
β-Ketoesters		11
β-Diesters		13
Water		15.7
Alcohols		15-19
Acid chlorides		16
Aldehydes		18-20
Ketones		18-20
Esters		23-25
Terminal alkynes		25
LDA		40
Terminal alkenes		44
Alkanes		51

Signature_____ Pg 1 _____(27)

1. (5 pts) What is the most important question in organic chemistry?

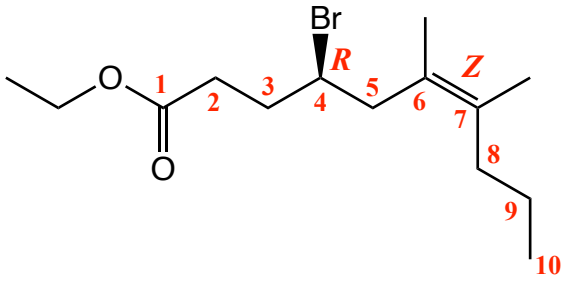
Where are the electrons?

2. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided. (No need to draw any arrows for this.)



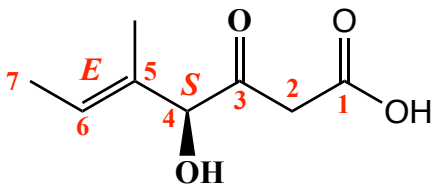
3. (6 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

A.



ethyl (*R*,*Z*)-4-bromo-6,7-dimethyldec-6-enoate
or ethyl (*R*,*Z*)-4-bromo-6,7-dimethyl-6-decenoate

B.

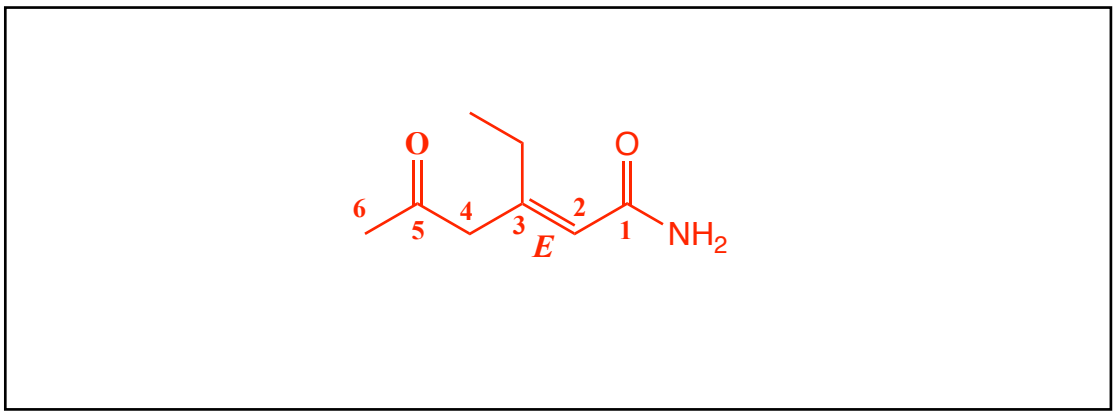


(*S*,*E*)-4-hydroxy-5-methyl-3-oxohept-5-enoic acid
or (*S*,*E*)-4-hydroxy-5-methyl-3-oxo-5-heptenoic acid

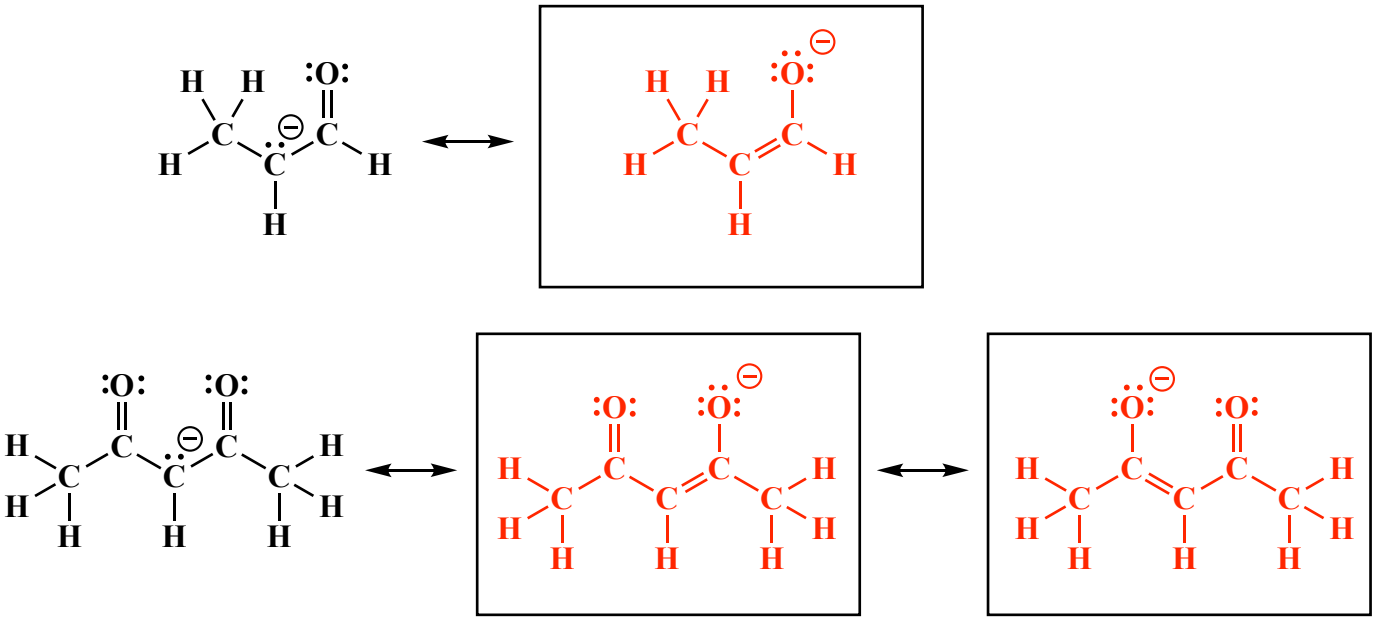
4. (6 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

In the box, draw the structure corresponding to the following IUPAC name.

(E)-3-Ethyl-5-oxohex-2-enamide
or (E)-3-Ethyl-5-oxo-2-hexenamide

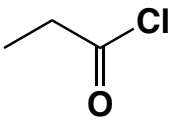


5. (9 pts each) For the two different enolates shown below, draw the other important contributing structures. Make sure to show all electrons and formal charges.

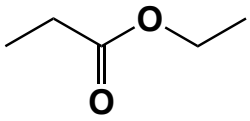


6. (14 pts) These are the ranking questions.

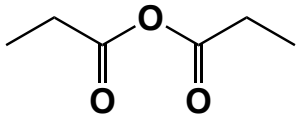
A) Rank the following with respect to reactivity with nuucleophiles, WITH A "1" UNDER THE MOST REACTIVE AND "4" UNDER THE LEAST REACTIVE, AND THEN "2" AND "3" AS APPROPRIATE.



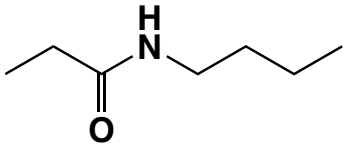
1



3

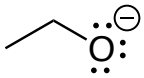


2

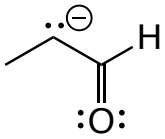


4

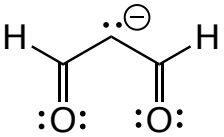
B) Rank the following with respect to anion stability, WITH A "1" UNDER THE MOST STABLE ANION AND "4" UNDER THE LEAST STABLE ANION, AND THEN "2" AND "3" AS APPROPRIATE.



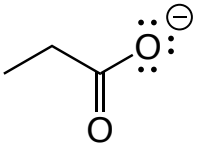
3



4

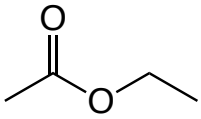


2

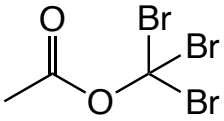


1

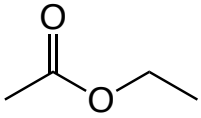
C) For each pair of molecules, fill in the circles to indicate which in each pair is more or less reactive with nucleophiles.



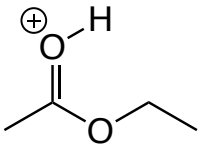
○ More reactive with nucleophiles
● Less reactive with nucleophiles



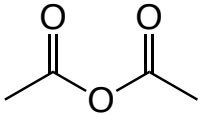
● More reactive with nucleophiles
○ Less reactive with nucleophiles



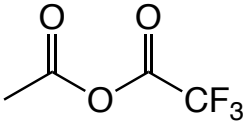
○ More reactive with nucleophiles
● Less reactive with nucleophiles



● More reactive with nucleophiles
○ Less reactive with nucleophiles

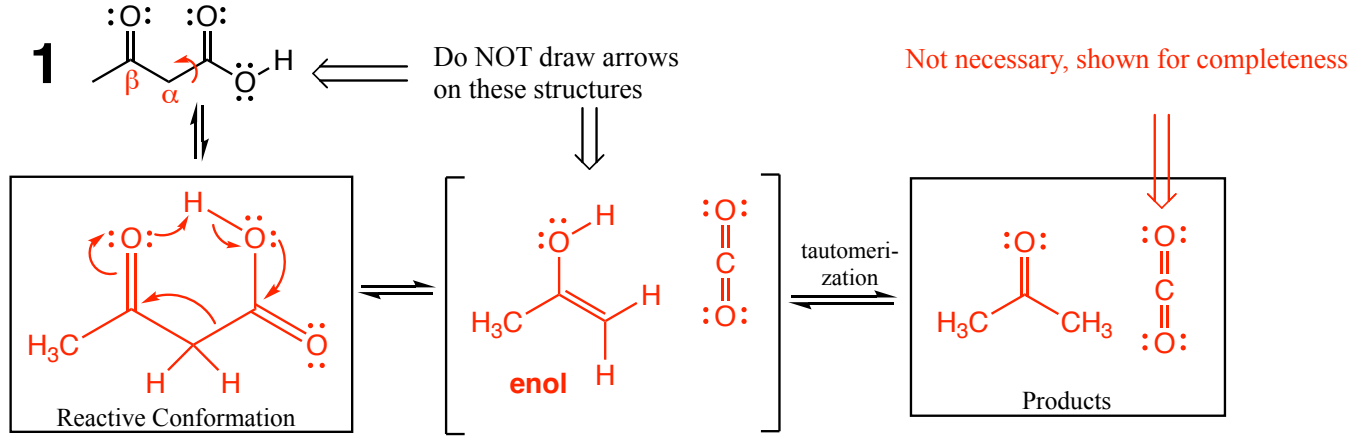


○ More reactive with nucleophiles
● Less reactive with nucleophiles



● More reactive with nucleophiles
○ Less reactive with nucleophiles

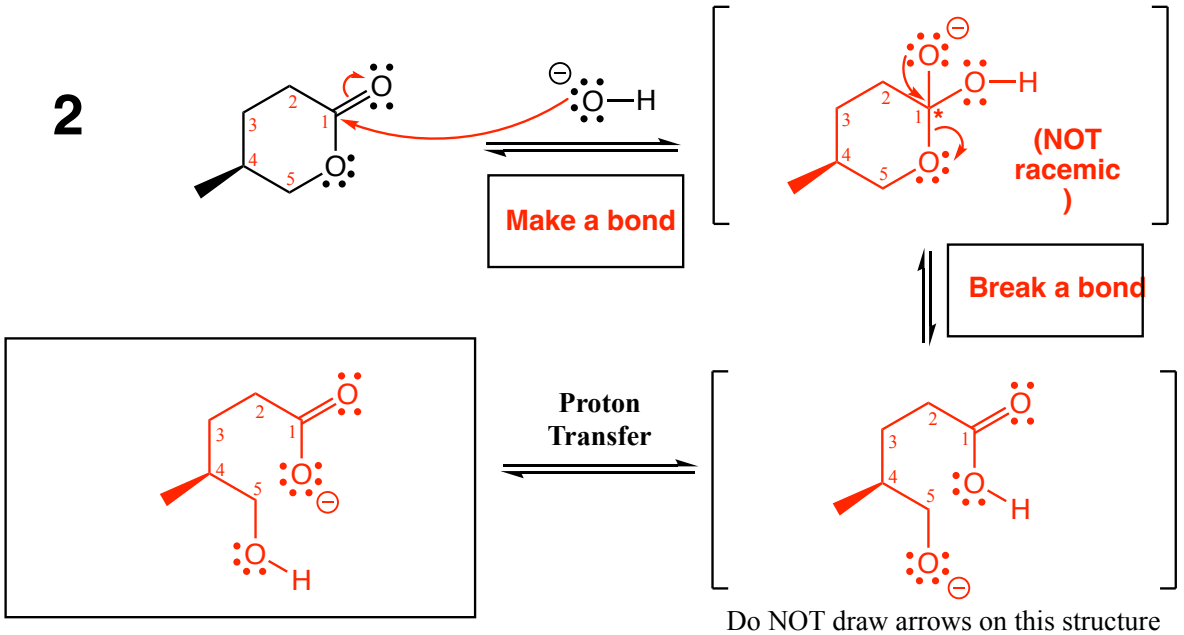
7. (12 pts) Complete the mechanism for the following decarboxylation reaction. **Be sure to show arrows to indicate movement of <u>all</u> electrons on the "Reactive Conformation", write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS RACEMIC IF APPROPRIATE.**



Draw arrows on this structure

Note you will have to write a balanced equation for the above mechanism on page 7

8. (12 pts) Complete the mechanism for the following reaction of a lactone and hydroxide. **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 OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS RACEMIC IF APPROPRIATE. In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.).**



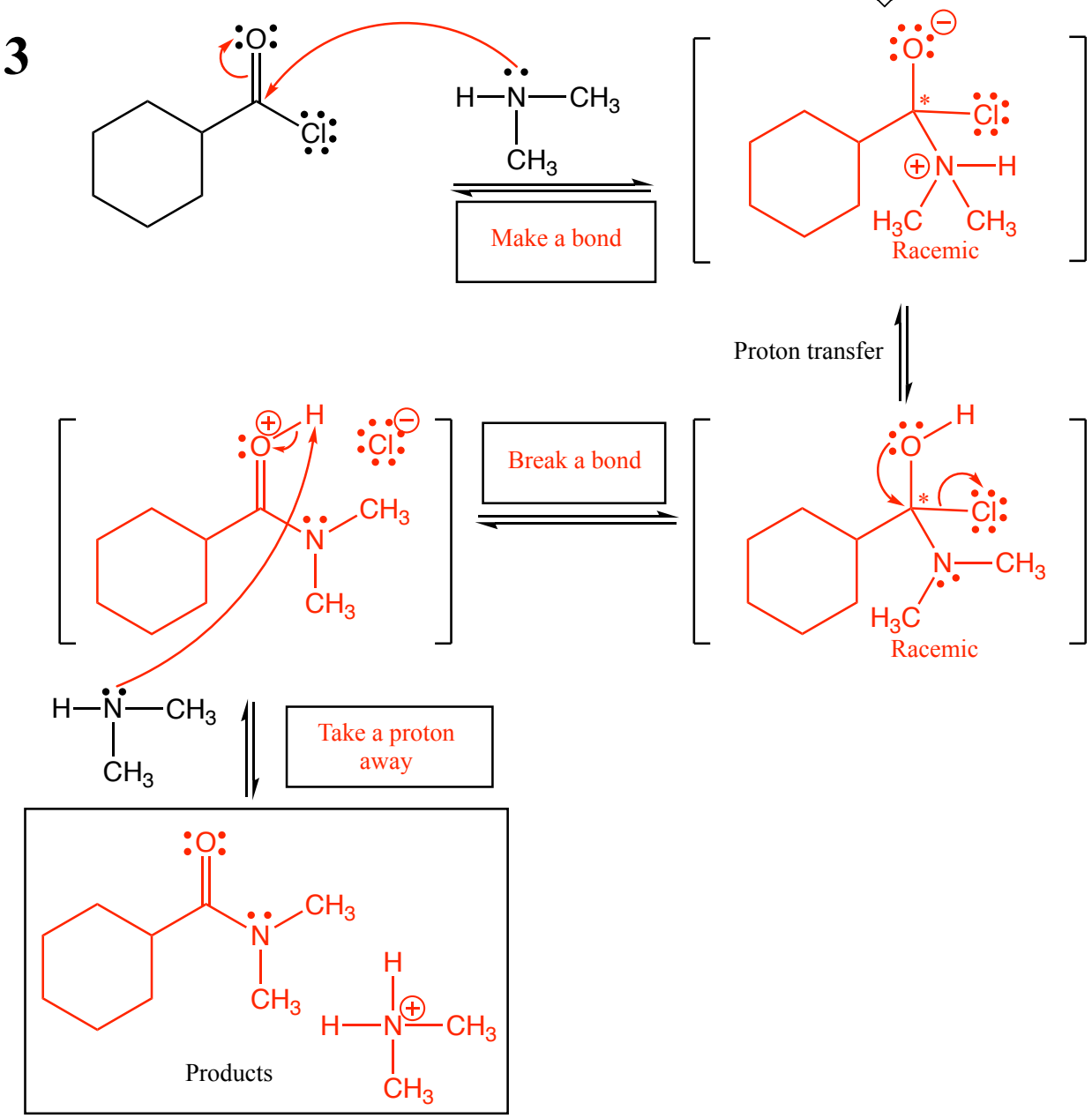
Do NOT draw arrows on this structure

Note you will have to write a balanced equation for the above mechanism on the page 7

9. (19 pts) Complete the mechanism for the following reaction of an acid chloride with an amine. **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 OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS RACEMIC IF APPROPRIATE. In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.).**

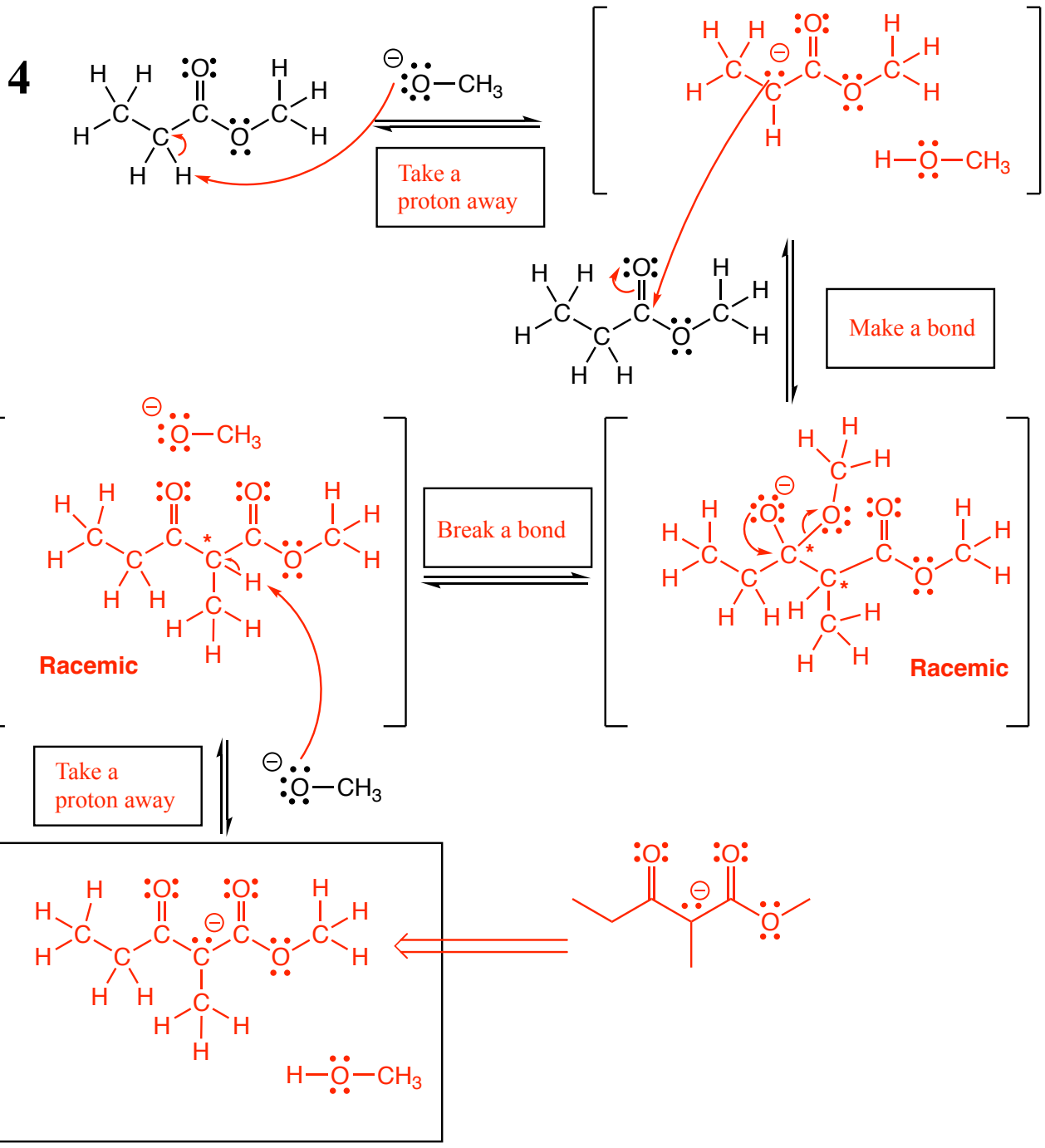
Don't write arrows on this structure

3



Note you will have to write a balanced equation for the above mechanism on PAGE 7

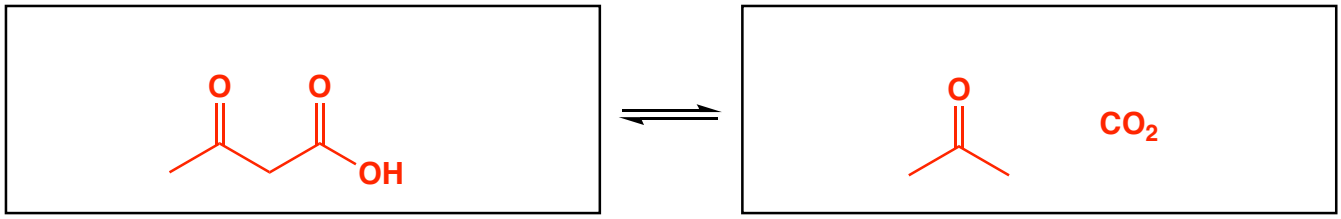
10. (23 pts) Complete the mechanism for the following Claisen condensation reaction. Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step. Remember, I said <u>all</u> the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS RACEMIC IF APPROPRIATE. In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.).



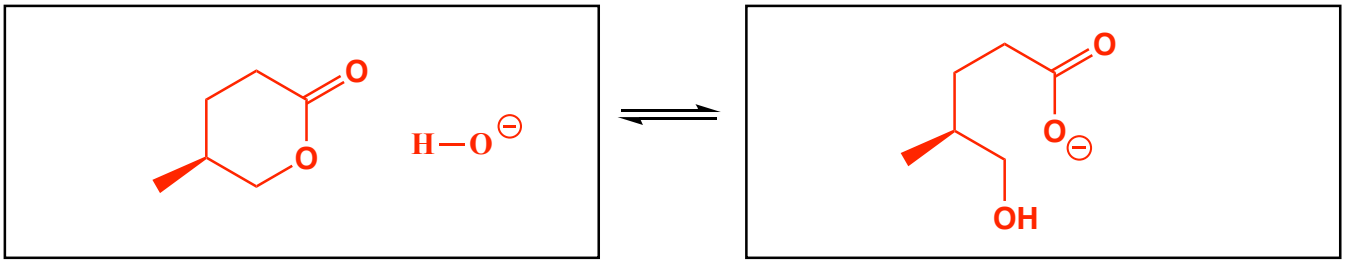
Note you will have to write a balanced equation for the above mechanism on PAGE 7

11. (17 pts) Write BALANCED equations for the four mechanisms, 1-4, that you drew on the last three pages. Only include molecules consumed or created during the reactions. In addition, you must use whole numbers when designating stoichiometries, not fractions or decimals. This is not asking to give equivalents, but rather balanced equations for each reaction.

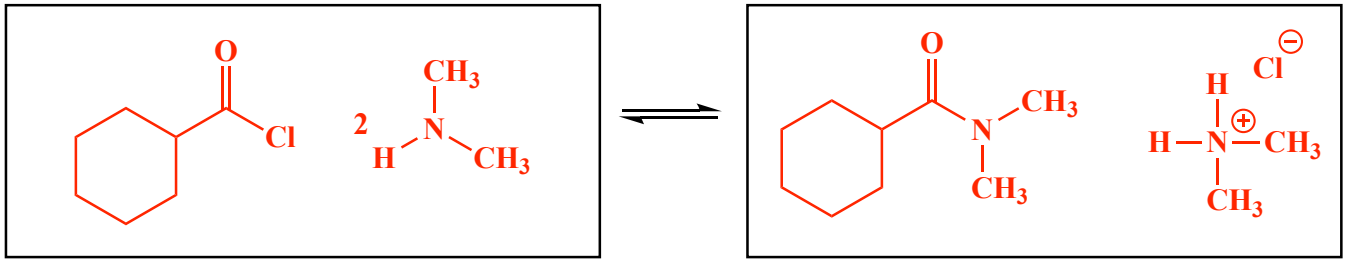
Write a balanced equation for the overall process described by mechanism 1 from page 4



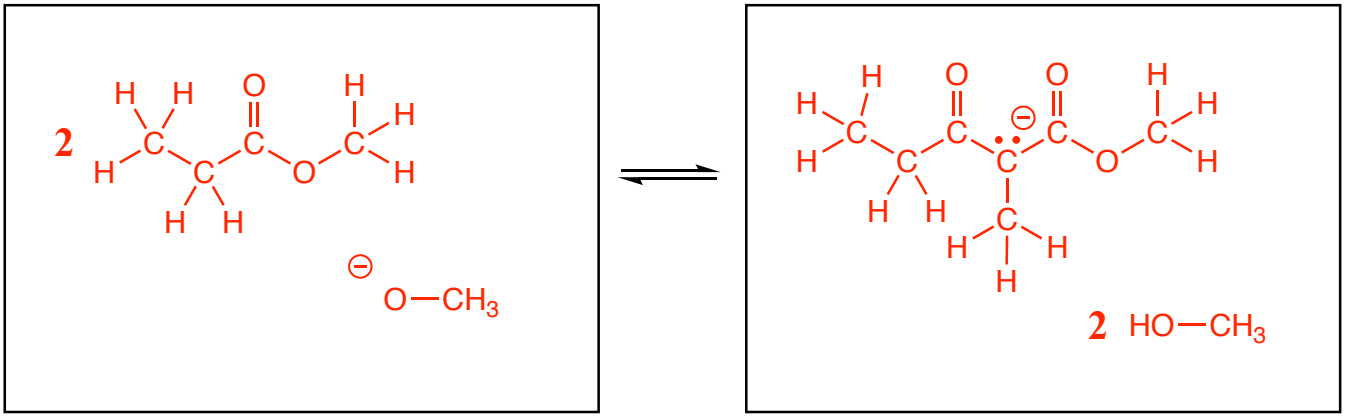
Write a balanced equation for the overall process described by mechanism 2 from page 4



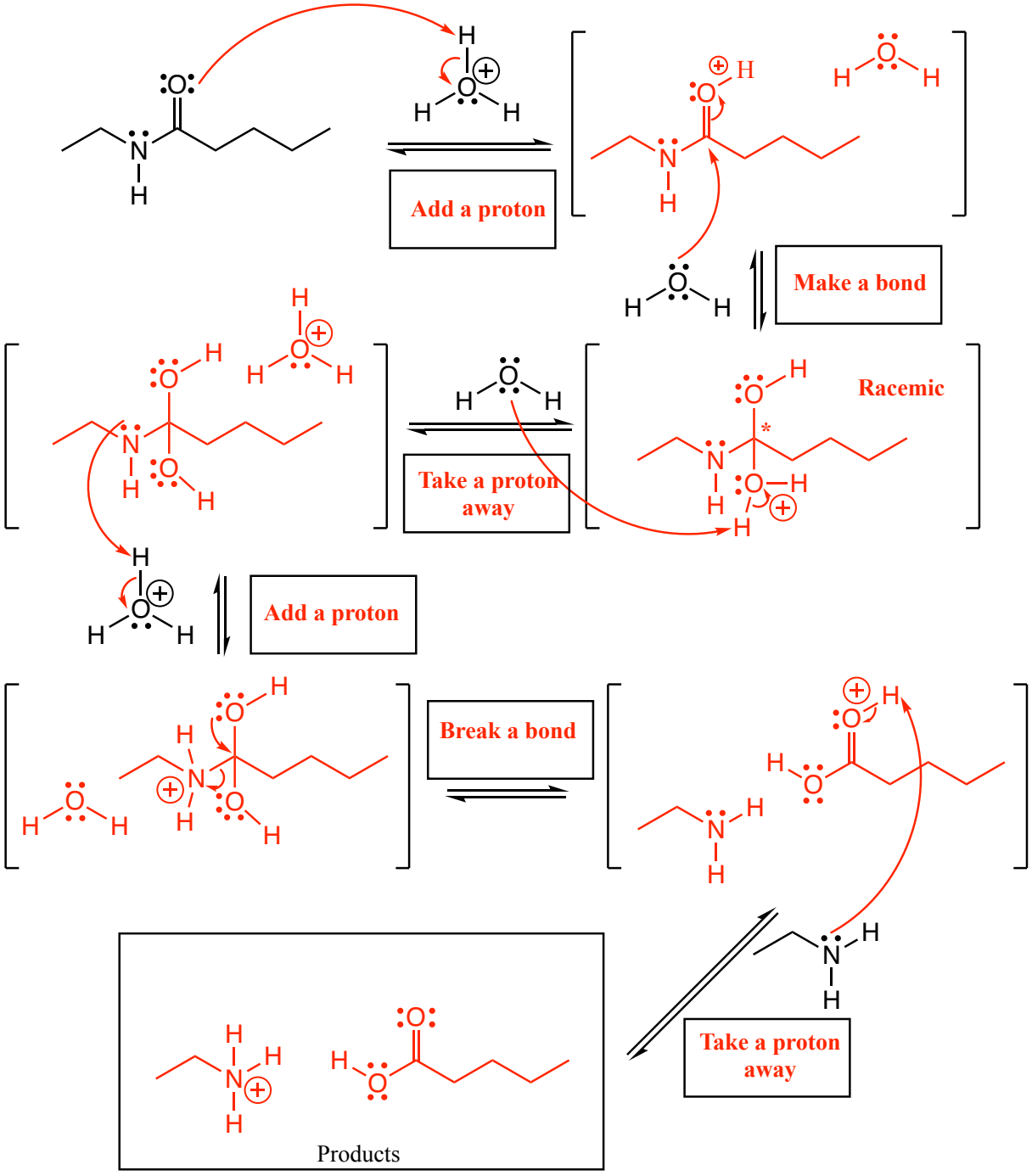
Write a balanced equation for the overall process described by mechanism 3 from page 5



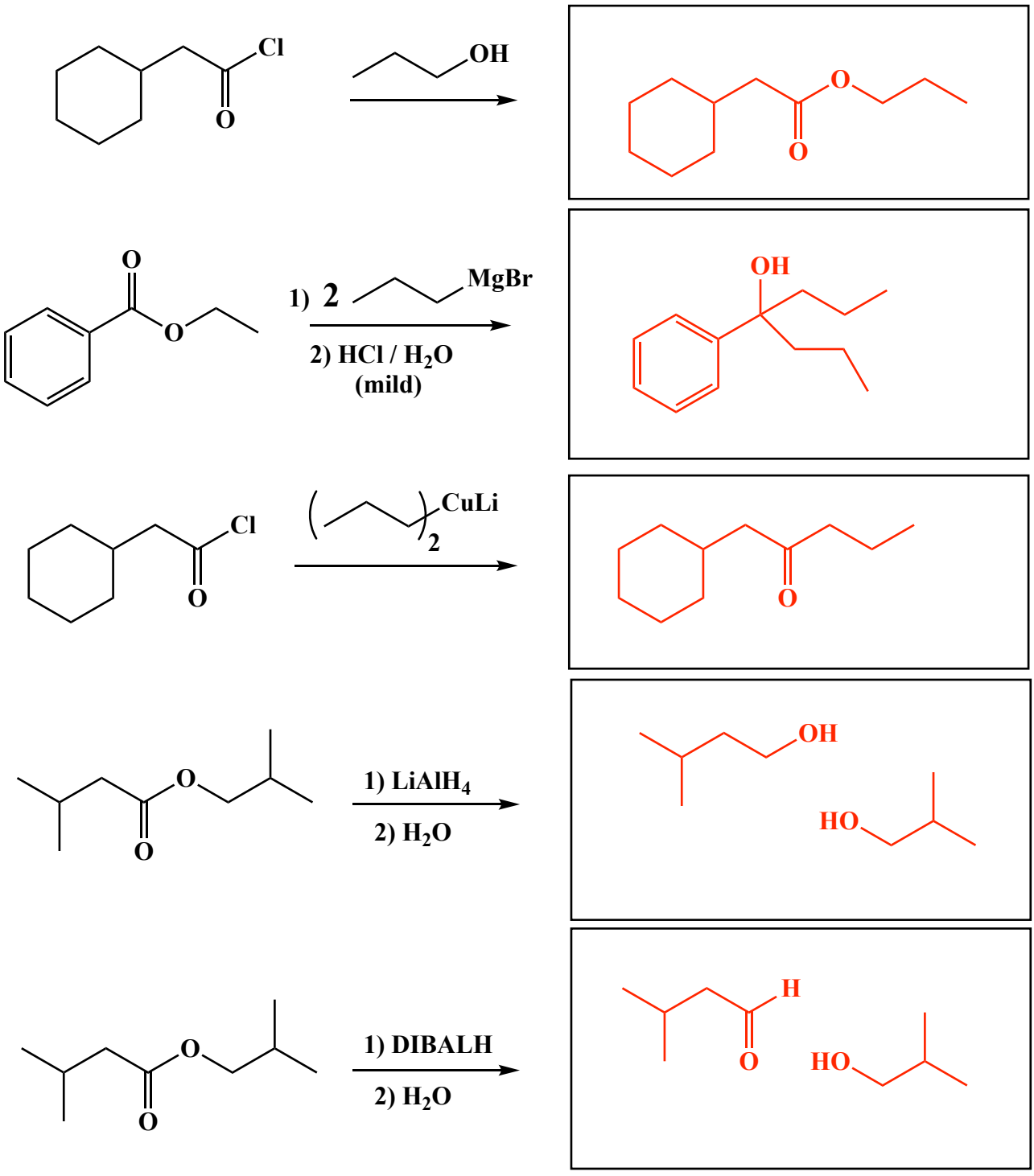
Write a balanced equation for the overall process described by mechanism 4 from page 6



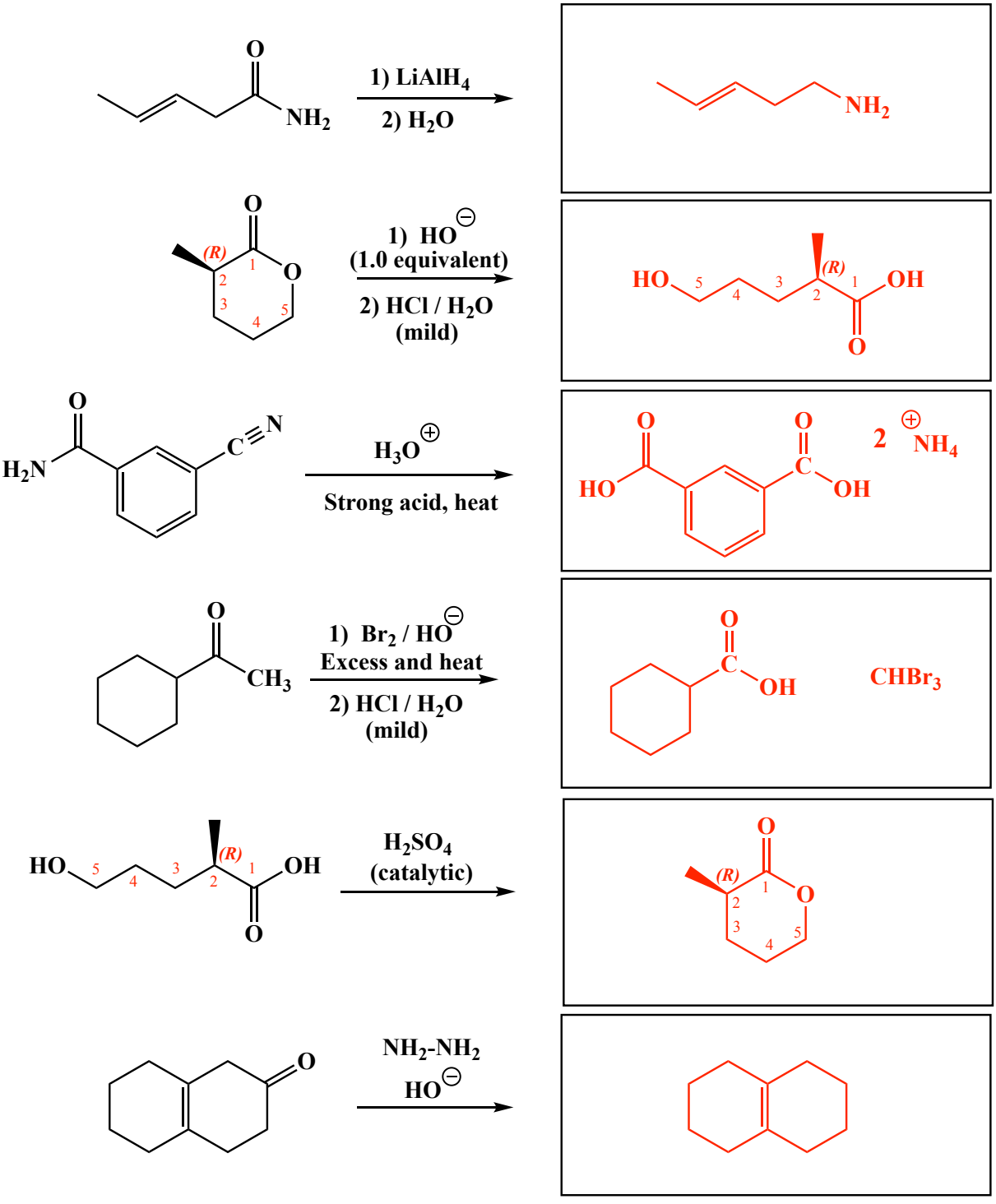
12. (35 pts) For this acid promoted amide hydrolysis reaction, use **arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. <u>FOR ALL CHIRAL PRODUCTS YOU MUST DRAW ALL ENANTIOMERS WITH WEDGES AND DASHES AND WRITE "RACEMIC' IF APPROPRIATE</u>. In the boxes provided by the arrows, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).**



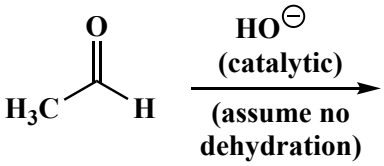
13. (3 or 5 pts.) Write all of the organic product(s) that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. **For these, you need to write all of the products of the reactions except for the products containing metals.**

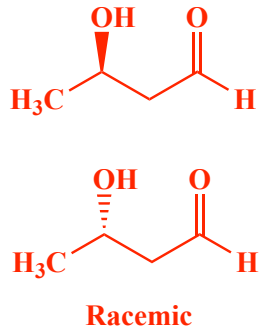


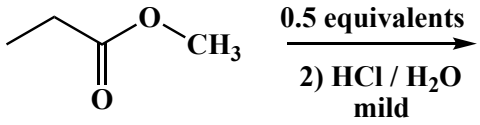
14. (3 or 5 pts.) Write all of the organic product(s) that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. **For these, you need to write all of the products of the reactions except for the products containing metals.**

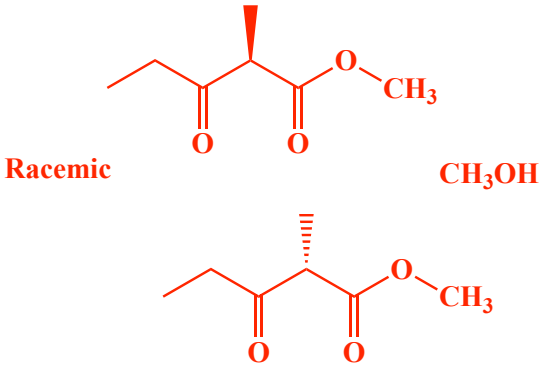


15. (5 or 9 pts.) Write all of the organic product(s) that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. **For these, you need to write all of the products of the reactions except for the products containing metals.**

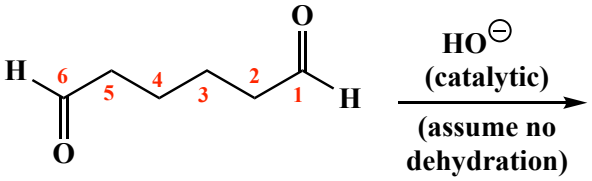


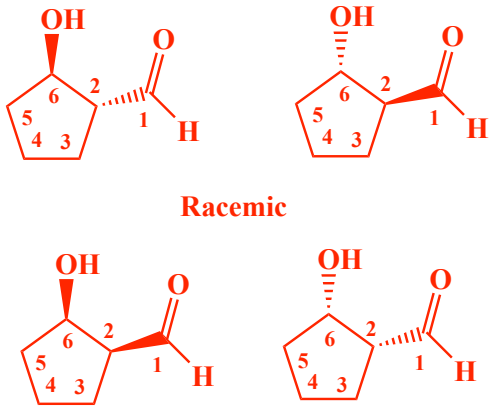






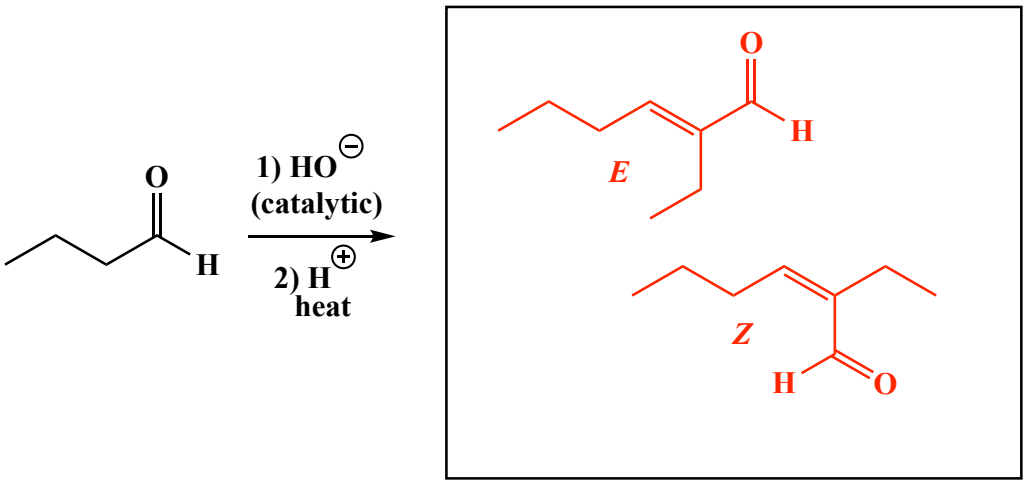
This is a hard one!!

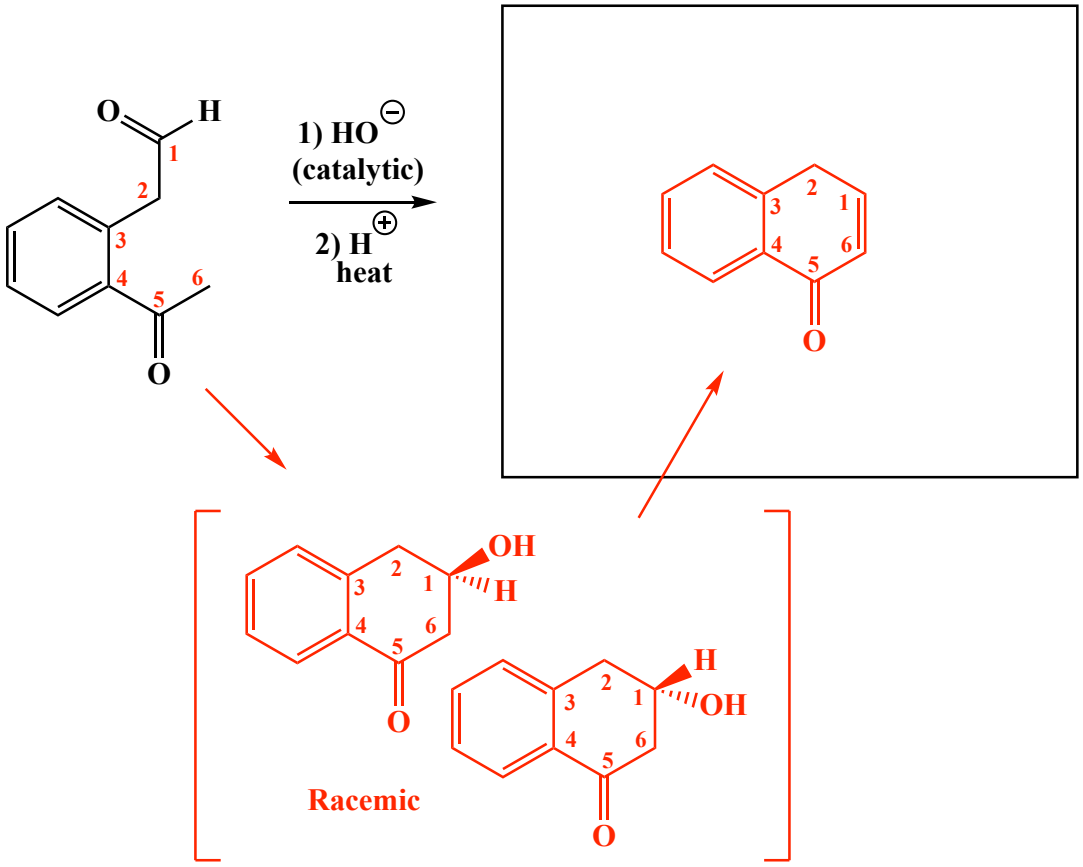




16. (4 or 6 pts.) Write the predominant product that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. **For these, you need to write all of the products of the reactions except for the products containing metals.**

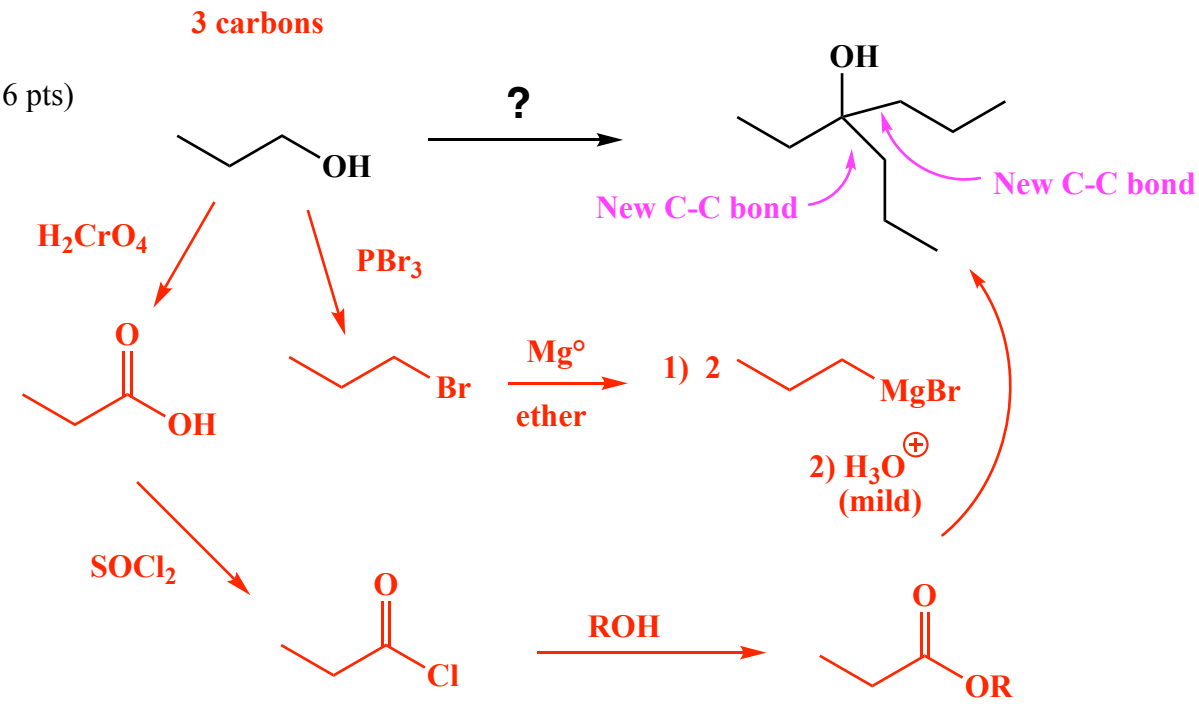
There is a lot to think about here. Please take your time. ASSUME THESE DEHYDRATES.





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 provided that the product(s) you draw for each step is/are the predominant one(s). 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. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

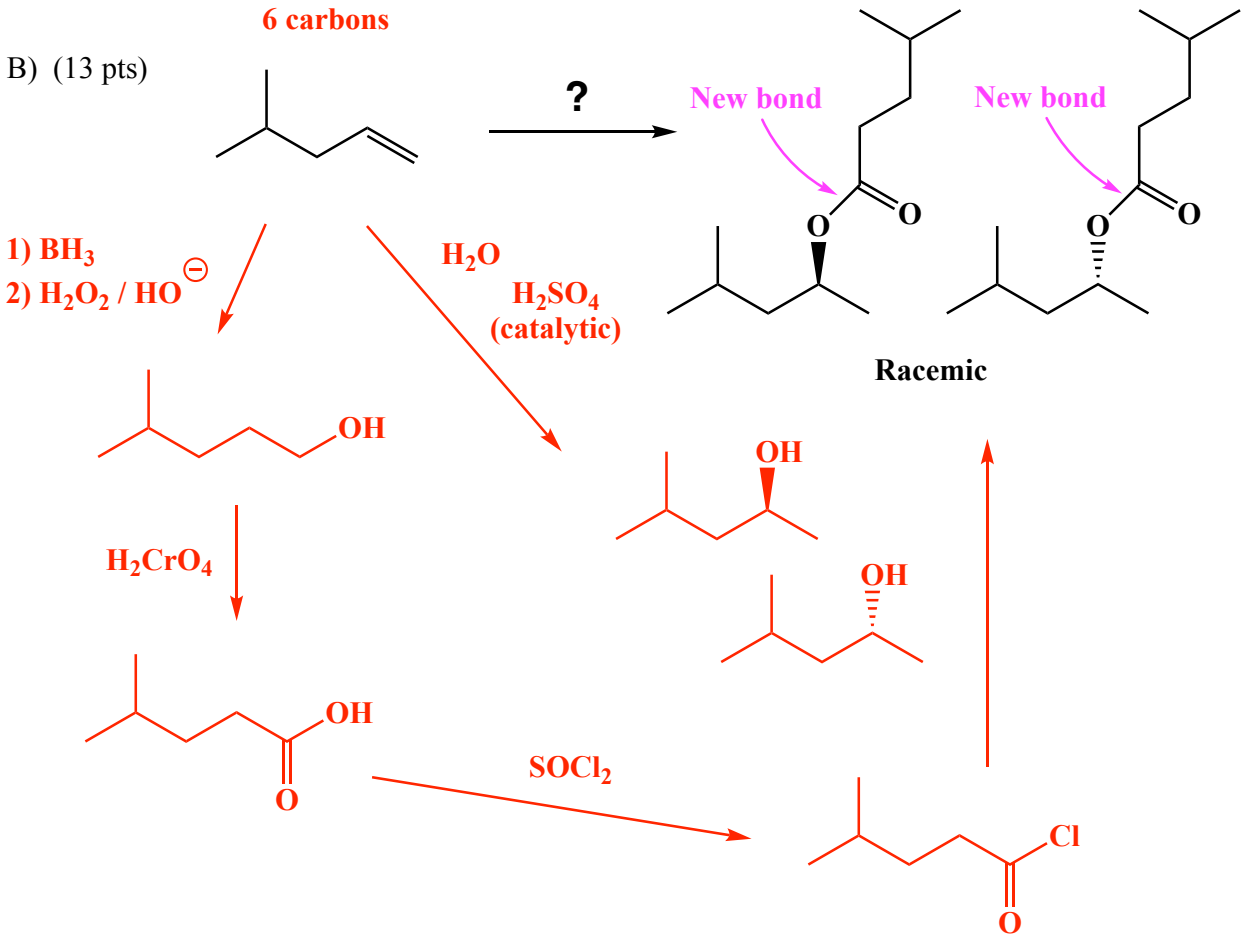
A) (16 pts)



Recognize that the product is an ester with 9 carbon atoms, and the starting material has 3 carbon atoms. Therefore, three starting material molecules will be combined in the product. **Recognize** also that the product is a tertiary alcohol with two new carbon-carbon bonds on the same carbon as the OH group, and the two new bonds are made to two identical groups. That is the KRE of a Grignard reacting with an ester! Therefore, propose that the last step is the ester shown reacting with two equivalents of a three-carbon Grignard reagent. **Recognize** that the required Grignard reagent can be made from the starting alcohol through a reaction with PBr_3 followed by reaction with Mg° in ether. **Recognize** further that the required ester can be made from the starting alcohol through the sequence of oxidation with H_2CrO_4 to give the carboxylic acid, followed by reaction with $SOCl_2$ to give the acid chloride that reacts with any alcohol to give the ester. Note we do not care which ROH is used to make the ester because those carbons do not end up in the product.

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 provided that the product(s) you draw for each step is/are the predominant one(s). 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. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

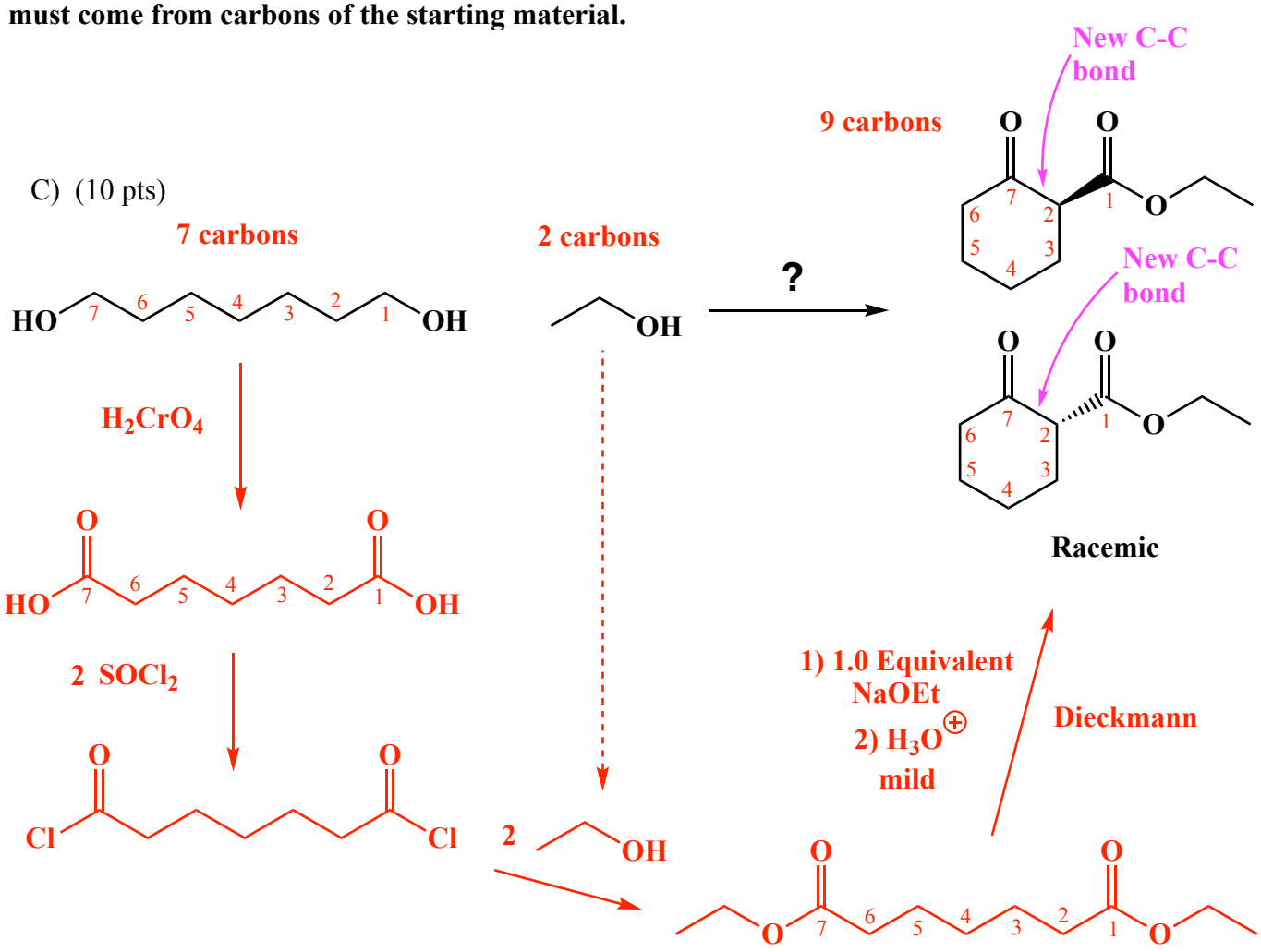
B) (13 pts)



Recognize that the product is an ester with 12 carbon atoms, and the starting material has 6 carbon atoms. Therefore, two starting material molecules will be combined in the product. **Recognize** also that the C-O single bond next to the carbonyl of an ester is the one that can be made. Therefore, the last reaction is between an acid chloride and an alcohol as shown (also could be Fischer esterification using a carboxylic acid and an alcohol with catalytic H_2SO_4). The alcohol can be made from the starting alkene using hydroboration/ oxidation (BH_3 / H_2O_2 and $HO^{\ominus}$), and the acid can be made from oxidizing that alcohol with H_2CrO_4. The acid chloride is made from the acid using $SOCl_2$. **Recognize** that the secondary alcohol needed to make the ester is made from the starting alkene in one step using the acid-catalyzed hydration reaction that gives Markovnikov regiochemistry as shown. Note, in this case we will not want you to use teh Fischer esterification reaction because of competition with the dehydration of the secondary alcohol if H_2SO_4 were added.

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 provided that the product(s) you draw for each step is/are the predominant one(s). 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. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

C) (10 pts)



Recognize that the product is a cyclic β-keto ester with 9 carbon atoms, and the starting materials have 7 carbon atoms and 2 carbon atoms, respectively. **Recognize** further that a cyclic β-keto ester is the KRE of a Dieckmann condensation with a new C-C bond as shown. **Recognize** that the required diester needed for the Dieckmann condensation is a diethyl ester, so assume the ethanol starting material is used to create the ester from the 7-carbon diacid chloride as shown. **Recognize** that the required 7-carbon diacid chloride can be made from starting 7-carbon diol from the sequence of reacting with H_2CrO_4 to give the diacid followed by reaction with $SOCl_2$ to give the diacid chloride. Note that it would have been fine to react the 7-carbon diacid with ethanol in the presence of catalytic H_2SO_4 (Fischer esterification) instead of making the diacid choride.

I hope you all have a wonderful spring break. Please make a promise to yourself to take some time to do things you really enjoy. YOU DESERVE IT, after all, you are in OChem II! And, of course, all of next week make sure to EXERCISE EVERY CHANCE YOU GET. Our 3.1 mile challenge is coming up the first week of April!