NAME (Print): _____

SIGNATURE: _____

Chemistry 310N
Dr. Brent Iverson
2nd Midterm
March 26, 2009

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.

For synthesis problems GO FOR PARTIAL CREDIT EVEN IF YOU DO NOT KNOW THE ENTIRE ANSWER!!!WRITE DOWN WHAT YOU DO KNOW IS IN THE REACTION SEQUENCE SOMEWHERE. YOU WILL GET PARTIAL CREDIT IF IT IS CORRECT

Note: You must have your answers written in pen if you want a regrade!!!!

Page	Points	
1		(26)
2		(22)
3		(21)
4		(23)
5		(18)
6		(29)
7		(19)
8		(26)
9		(35)
10		(25)
11		(9)
12		(10)
13		(16)
14		(15)
15		(20)
Total		(314)
%		
T Score		
HW		
Total Grade		

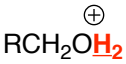
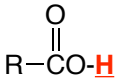
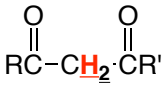
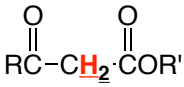
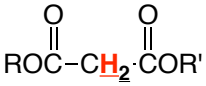
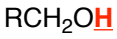
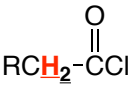
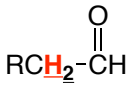
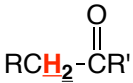
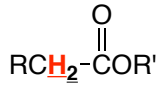
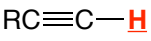
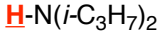
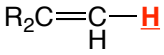
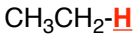
(HW score + Exam Grade) ⟹

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.

_____

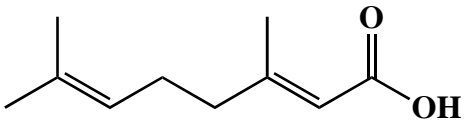
(Your signature)

Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Carboxylic acids		3-5
Ammonium ion		9.2
β-Dicarbonyls		10
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

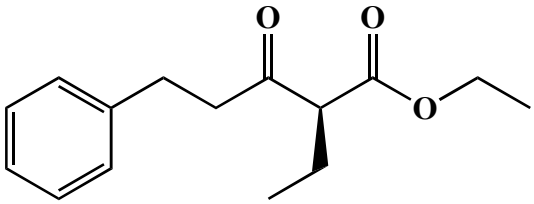
1. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We wil be looking for a minumum of 7 key points here.

The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on the **same principles as NMR**, namely the **flipping (i.e. resonance) of nuclear spins of protons** by **radio frequency irradiation** when a patient is placed in a **strong magnetic field**. **Magnetic field gradients** are used to gain imaging information, and **rotation of the gradient around the center of the object** gives imaging in an entire plane **(i.e. slice inside patient)**. In an MRI image, you are looking at **individual slices** that **when stacked make up the three-dimensional image** of **relative amounts of protons, especially the protons from water and fat, in the different tissues**.

2. (4 pts each) In the space provided, write the IUPAC name (including stereochemistry where appropriate) for the following two molecules:



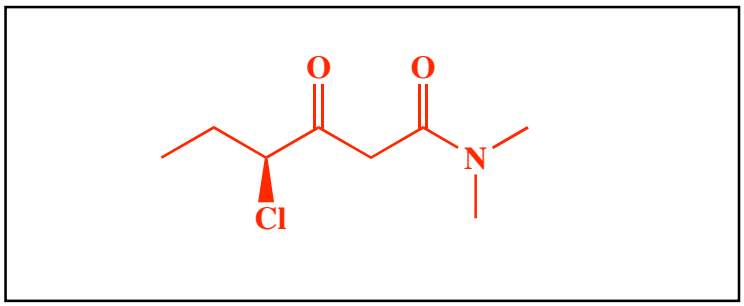
(*E*)-3,7-Dimethyl-2,6-octadienoic acid



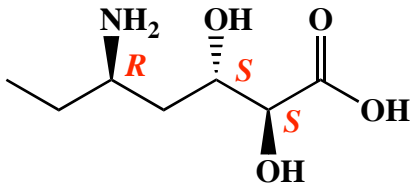
(*S*)-Ethyl 2-ethyl-3-oxo-5-phenylpentanoate

3. (4 pts) In the space provided, draw the following molecule:

(*S*)-4-Chloro-*N*,*N*-dimethyl-3-oxohexanamide

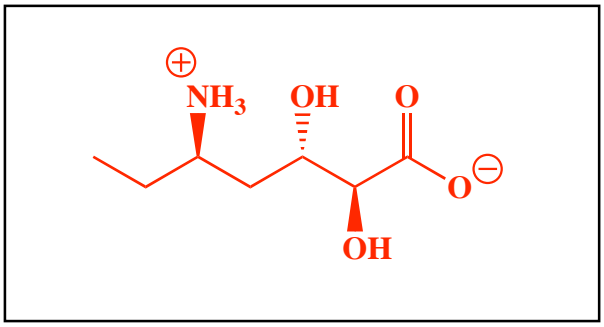


4 A) (4 points) In the space provided, write the IUPAC name (including stereochemistry where appropriate) of the following molecule.

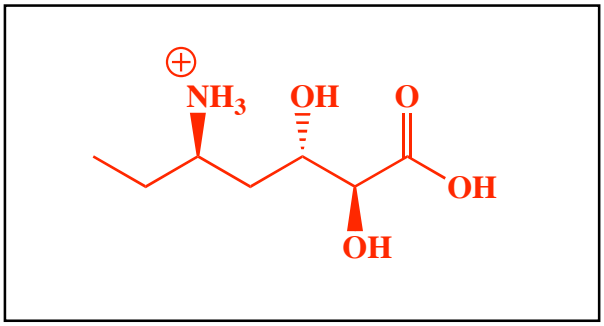


(2*S*,3*S*,5*R*)-5-Amino-2,3-dihydroxyheptanoic acid

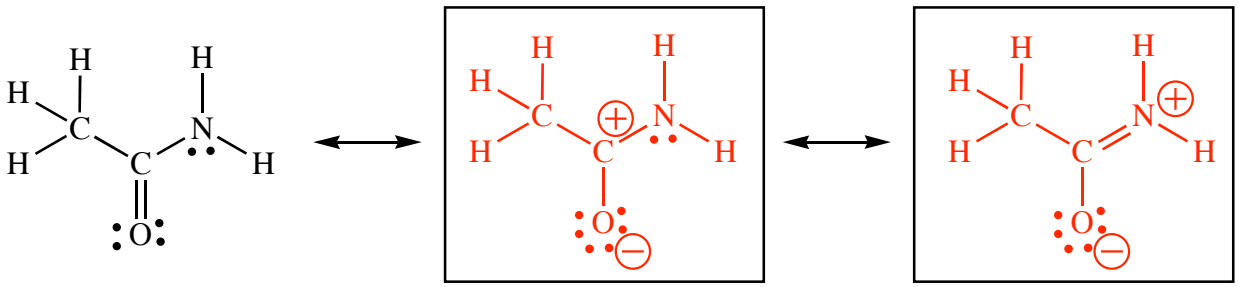
B) (5 points) Although the molecule above can be drawn and named as shown, it would actually never exist in this form. In the space provided, draw the structure of the molecule as it would exist in water at pH = 7.0.



C) (5 points) In the space provided, draw the structure of the molecule as it would exist in water at pH = 1.0.



5. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.

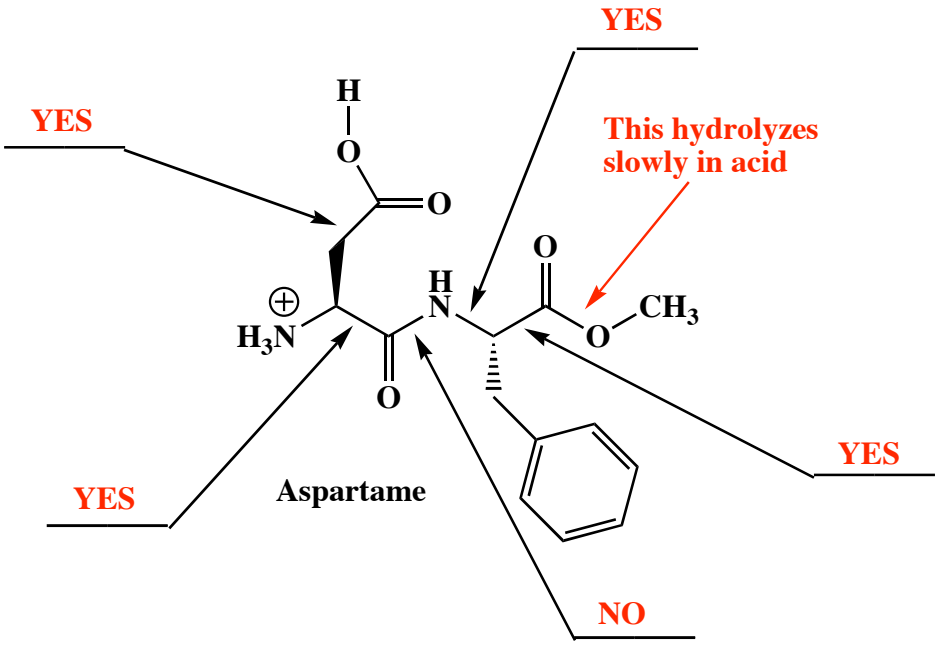


6. (6 pts) List two attributes of amide bonds that lead to stabilization of the folded structures of proteins.

1) The amide carbonyl oxygen and hydrogen on nitrogen can make strong hydrogen bonds

2) The C-N bond cannot rotate freely, so the backbone of proteins is relatively rigid (less flexible) and easier to stabilize in a folded conformation.

7. (15 points) Aspartame is the sweetner used in diet coke. Its structure is shown below. Because of carbonation and added phosphoric acid, the pH of diet coke is relatively acidic, near 2.0.



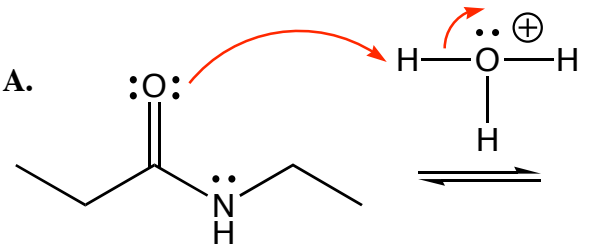
A) (5 pts) For each bond indicated by the arrows on the above drawing, write "YES" or "NO" in the spaces provided to say whether the given bond can rotate (YES) or not (NO) at room temperature.

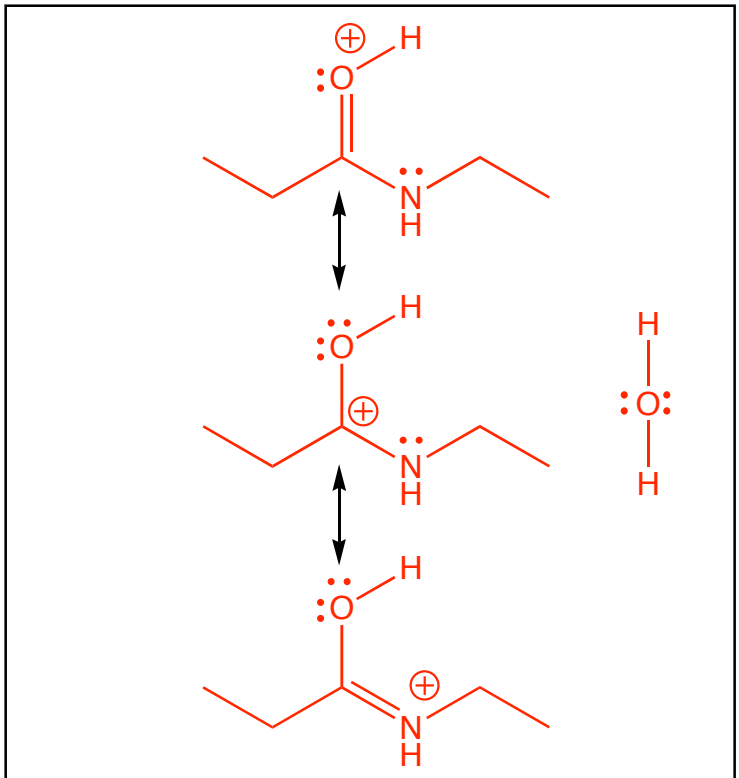
B) (10 pts) Diet coke loses its sweetness over time, especially if heated. Can you suggest a likely reason for this based on the chemistry you have learned? We are only looking for two sentences or less here.

The methyl ester hydrolyzes in the acidic pH and the free carboxylic acid is not sweet.

8. (23 points) In many of the mechanisms we have seen, there are charged intermediates encountered that are stabilized by resonance delocalization. For the following steps that come from different mechanisms, **place arrows on the structures on the left to show the flow of electrons that lead to a charged intermediate.** Next **draw all the intermediates created as well as the indicated number of major contributing structures.** Be sure so show all charges and lone pairs. Note, you only have to place arrows on the structures on the left side, not any of the contributing structures. **Finally make sure you show all intermediates made in the steps indicated.**

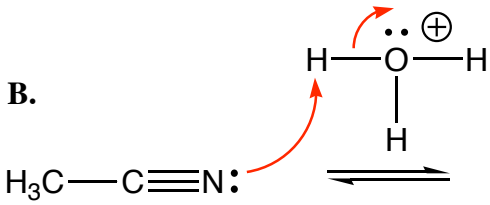
A.

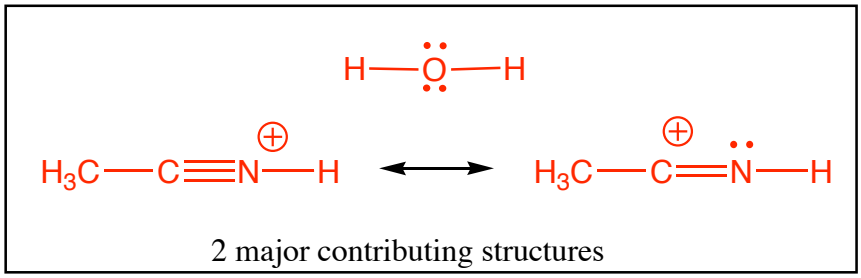




3 major contributing structures

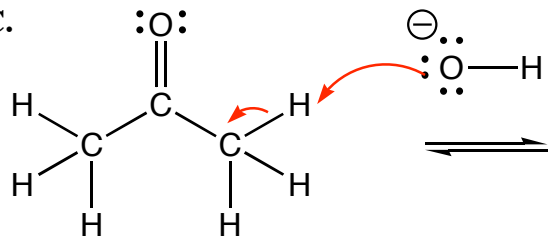
B.

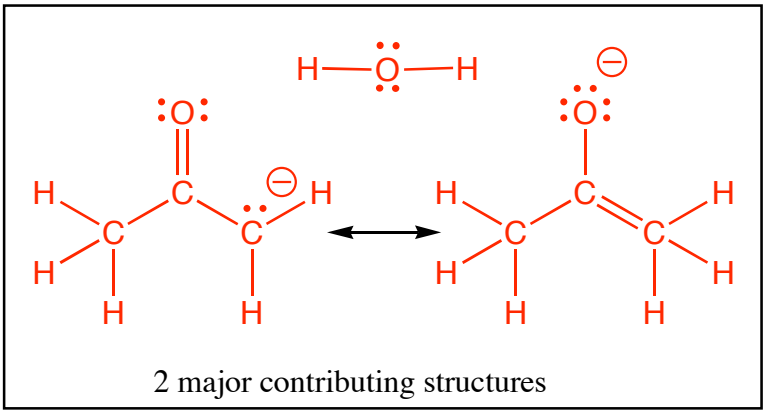




2 major contributing structures

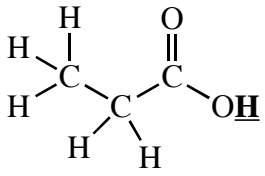
C.



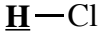


2 major contributing structures

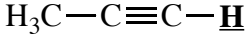
9. (5 pts) Rank all of the following with respect to relative acidity. The acidic H atom in question is indicated in bold and with an underline for each molecule. **Place a 1 under the most acidic molecule, and a 5 under the least acidic molecule.**



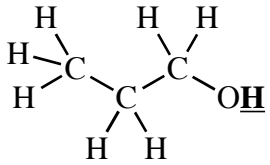
2



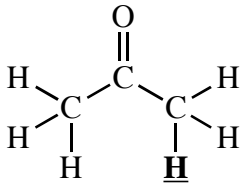
1



5

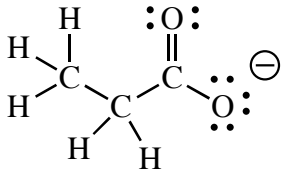


3



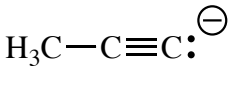
4

10. (5 pts.) Rank the following in terms of anion stability, with a **1 under the anion that is the most stable** and a **5 under the anion that is least stable.**

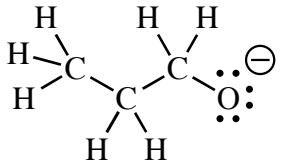


2

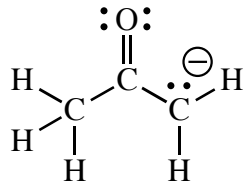
1



5

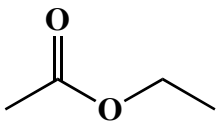


3

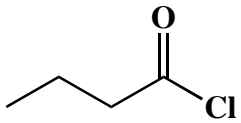


4

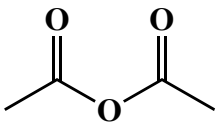
11. (4 pts.) Rank the following in terms of reaction with a strong nucleophile such as HO-, with a **1 under the molecule that is most reactive**, and a **4 under the molecule that is least reactive**.



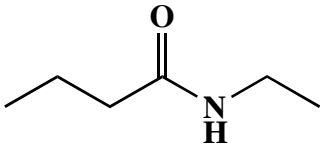
3



1

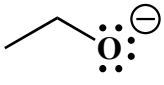


2



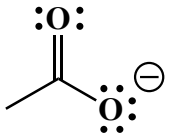
4

12. (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.**

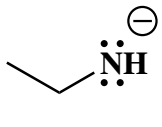


3

1



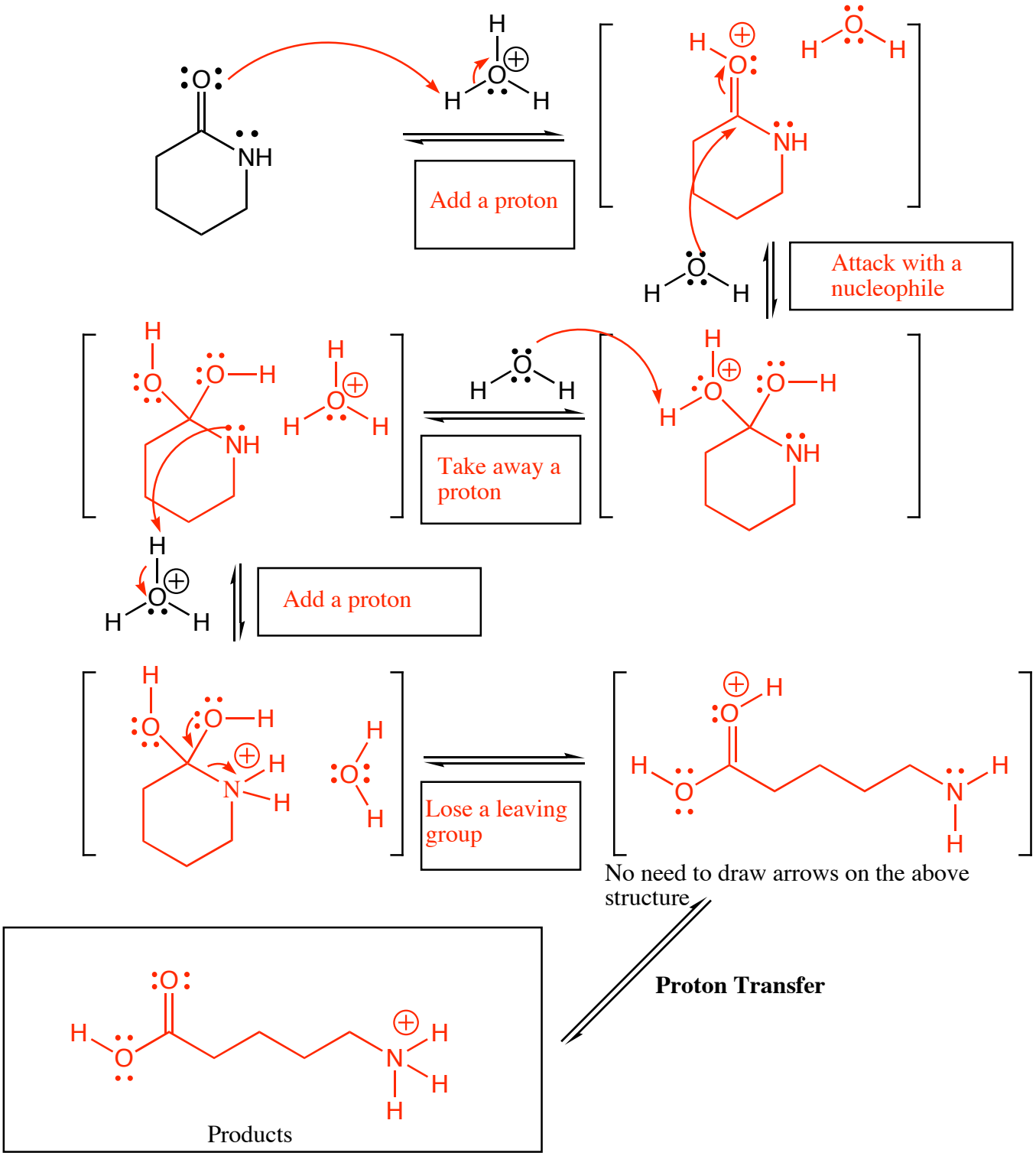
2



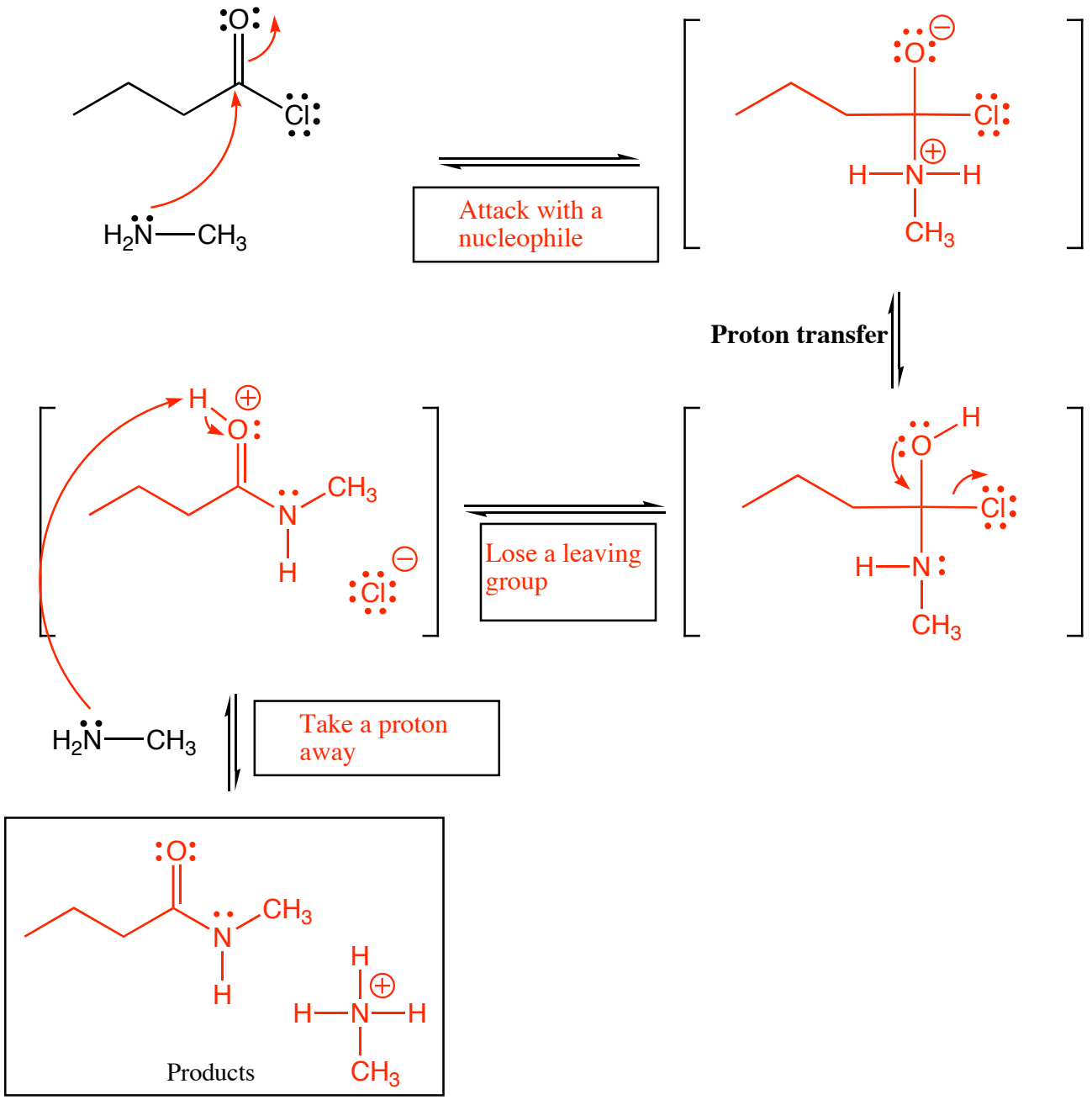
4

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

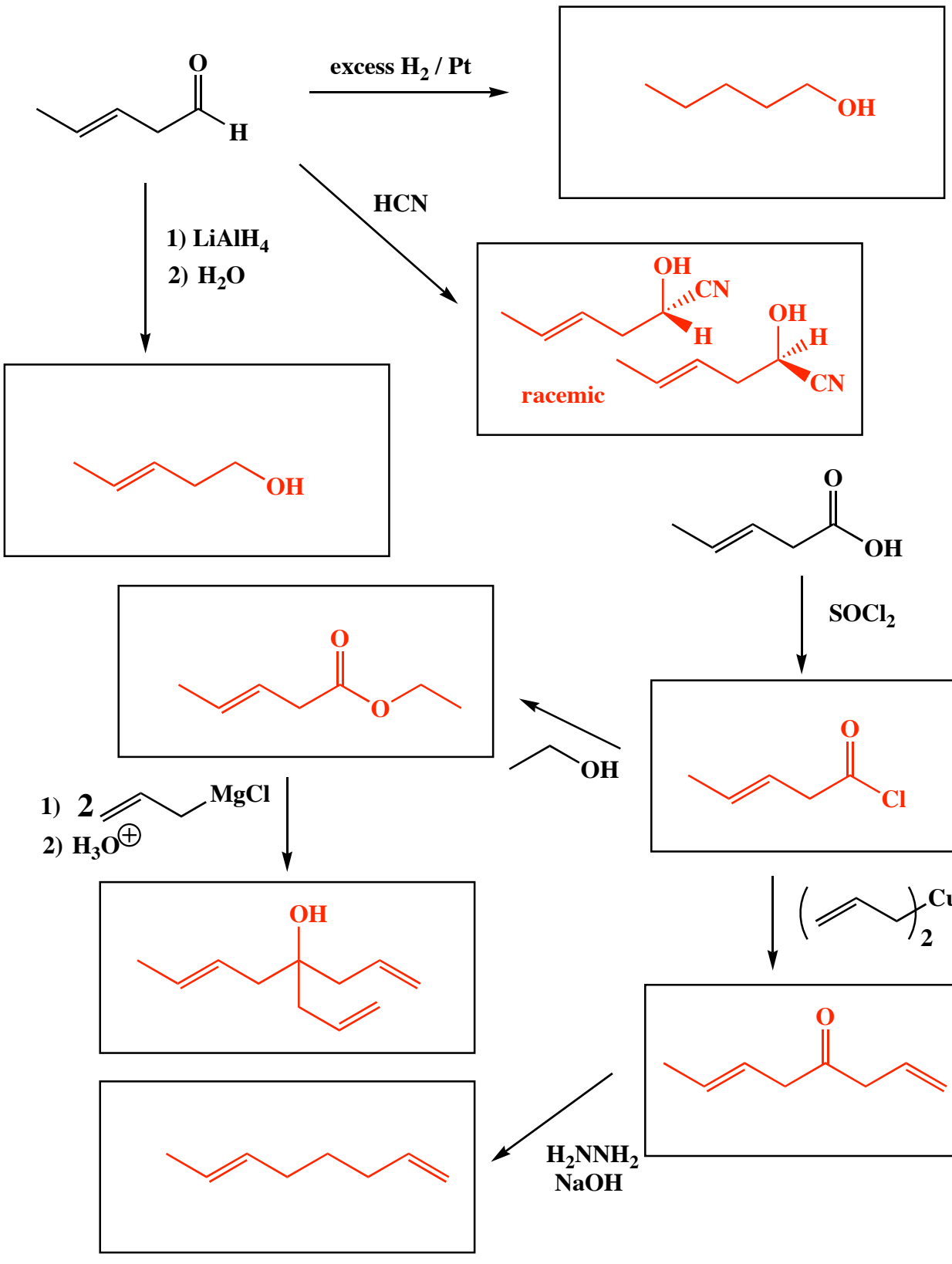
13. (29 pts.) Complete the mechanism for the following acid catalyzed lactam hydrolysis reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL 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").***



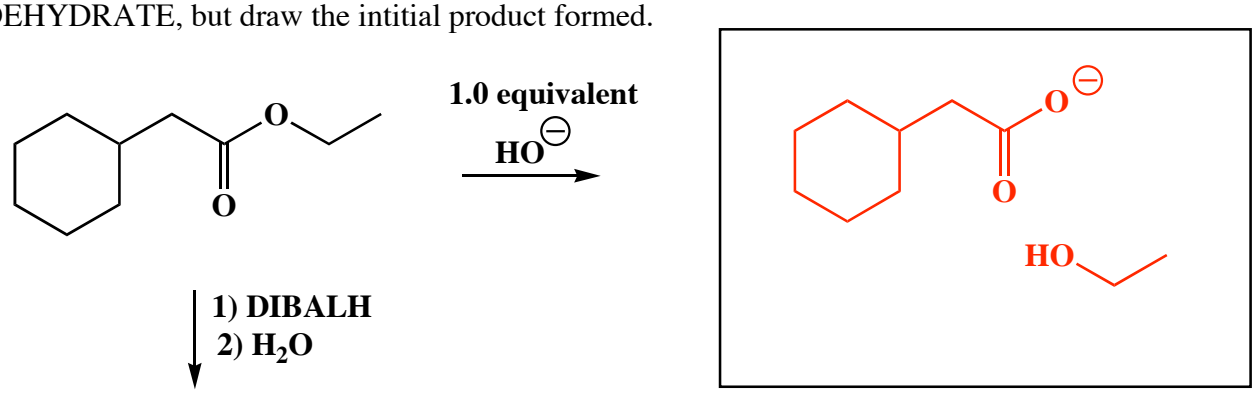
14. (19 pts.) Complete the mechanism for the following reaction between an acid chloride and an amine. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW 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").***

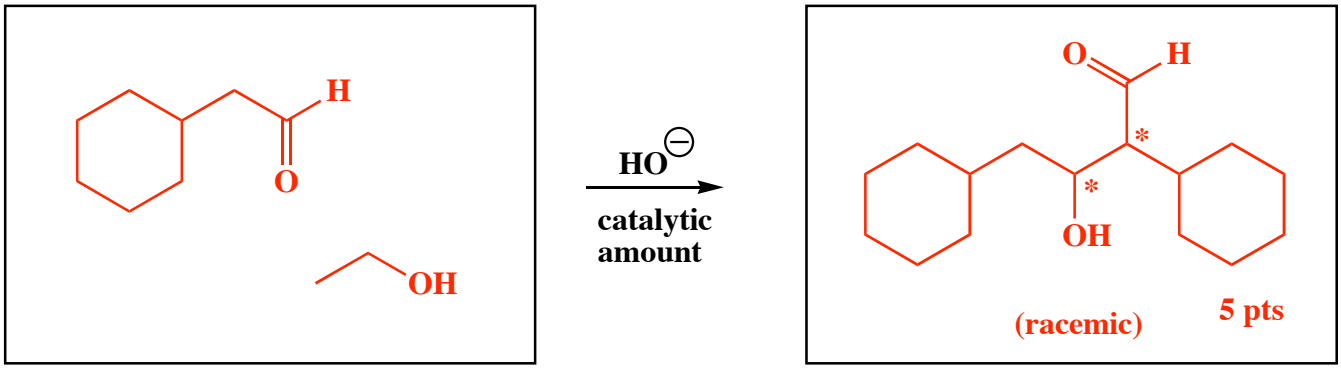


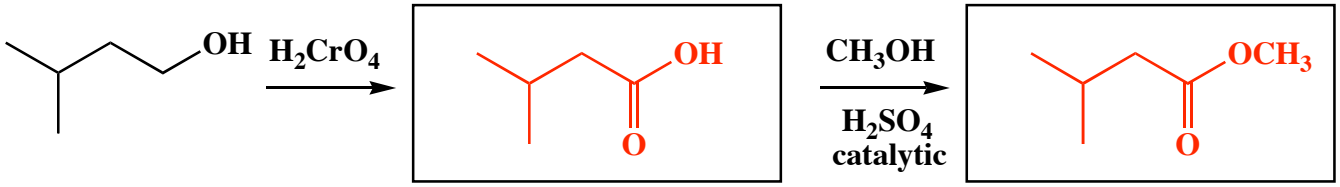
16. (26 pts) In the spaces provided, draw all products containing C atoms from the starting material. When in doubt, draw them! When a new chiral center is created put an asterisk next to the chiral ocenter and write "racemic" when racemic mixtures are formed. Also, for aldol reactions DO NOT DEHYDRATE, but draw the intitial product formed.

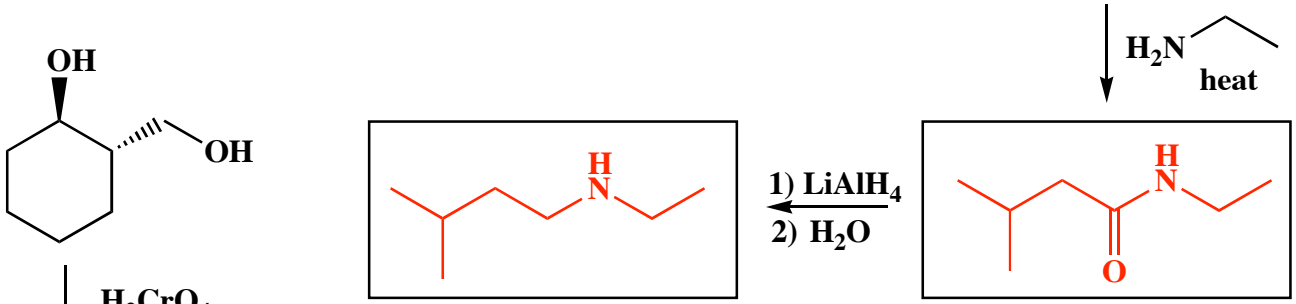


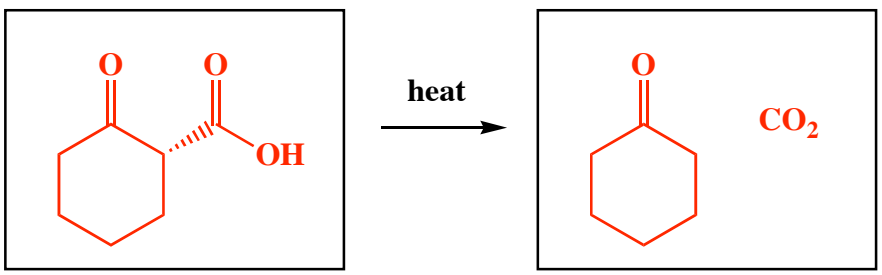
16. (35 pts) In the spaces provided, draw all products containing C atoms from the starting material. When in doubt, draw them! When a new chiral center is created put an asterisk next to the chiral center and write "racemic" when racemic mixtures are formed. Also, for aldol reactions DO NOT DEHYDRATE, but draw the intitial product formed.



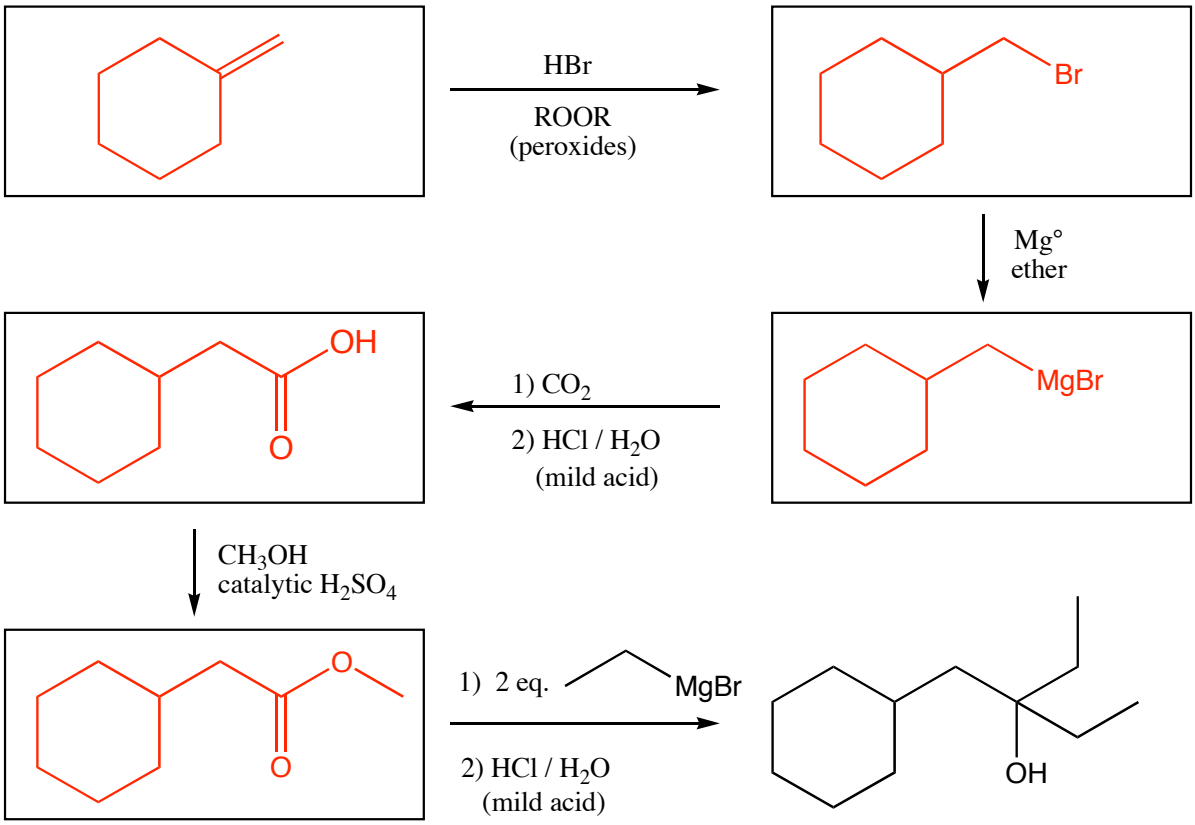




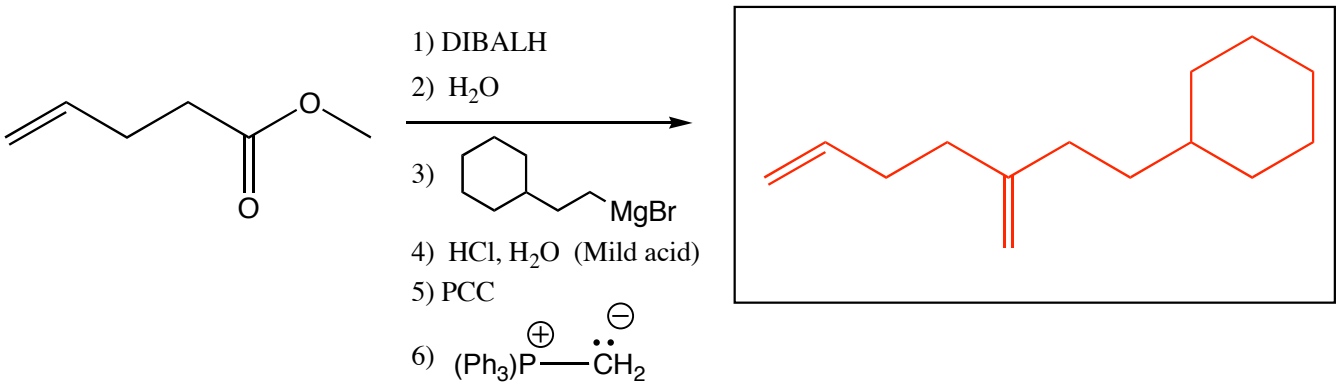




17. (15 pts) This is the same but backwards. In the spaces provided, draw all synthetic intermediates containing C atoms, working backwards from the product. When in doubt, draw them! When a new chiral center is created put an asterisk next to the chiral center and write "racemic" when racemic mixtures are formed. Also, for aldol reactions DO NOT DEHYDRATE, but draw the intitial product formed.



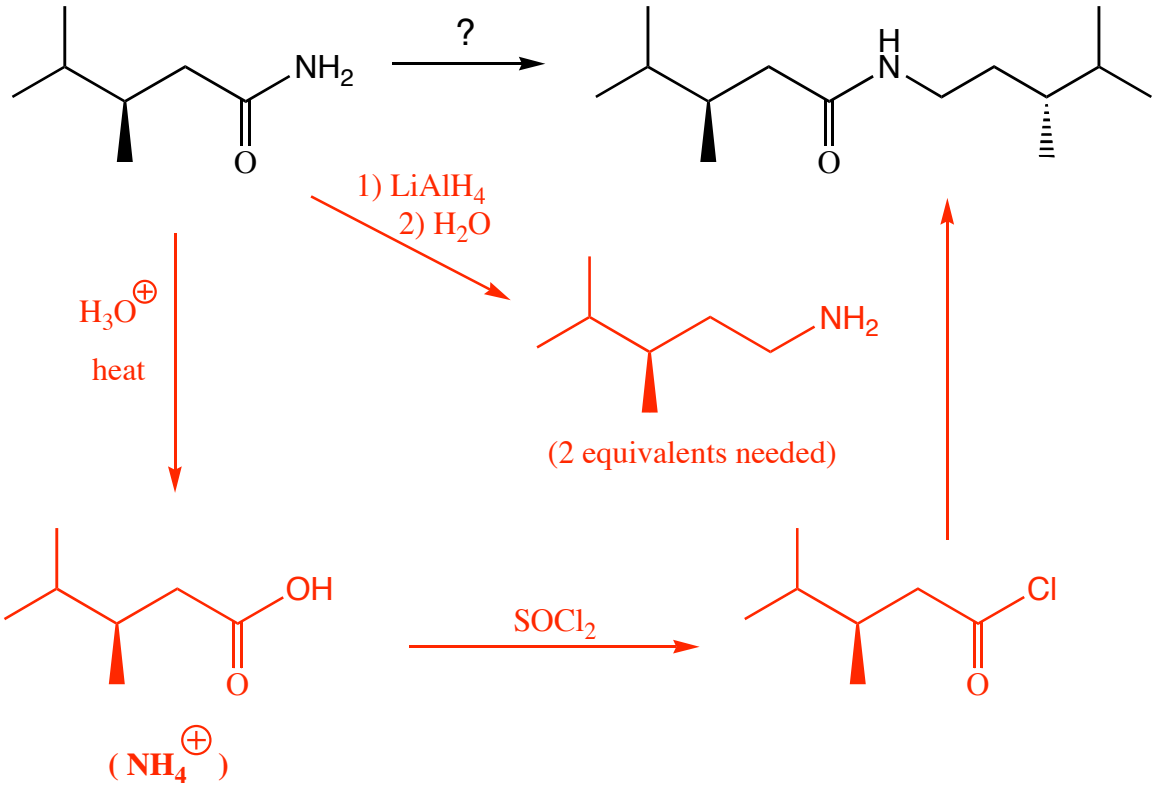
18. (10 points) For the following sequences of reactions, draw the predominant organic product or products after ALL the steps. You do not need to draw the intermediates formed along the way. If a new chiral center is created in the reaction that produces a racemic mixture, label the chiral center with an asterisk (*) and write "***racemic***" underneath. You do not have to draw all of the enantiomers.



You can use the back of the previous page as scratch paper

18. (9 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.

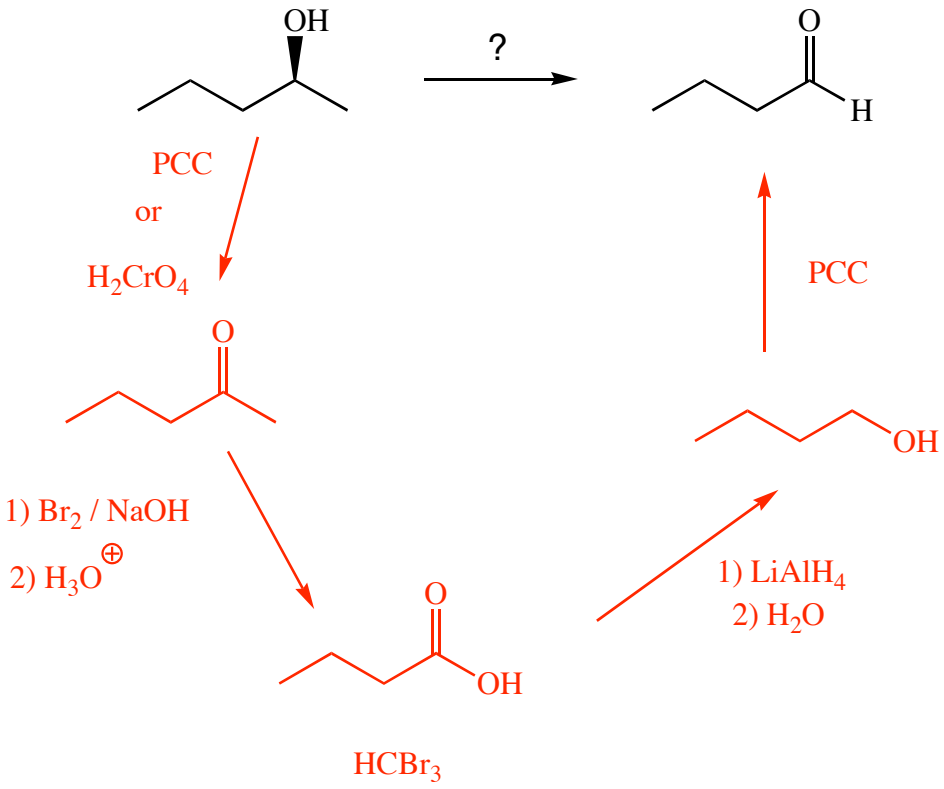
All of the carbons of the product must come from the given starting material.



Recognize the product as a amide, so the C-N bond is "in play", namely it will be made in the last step through the reaction of an acid chloride and an amine. **Recognize** the acid chloride as coming from a corresponding carboxylic acid, that happens to be the one created through hydrolysis of the starting amide. **Recognize** that the amine needed for the last step can be conveniently prepared through redution of the starting amide.

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.

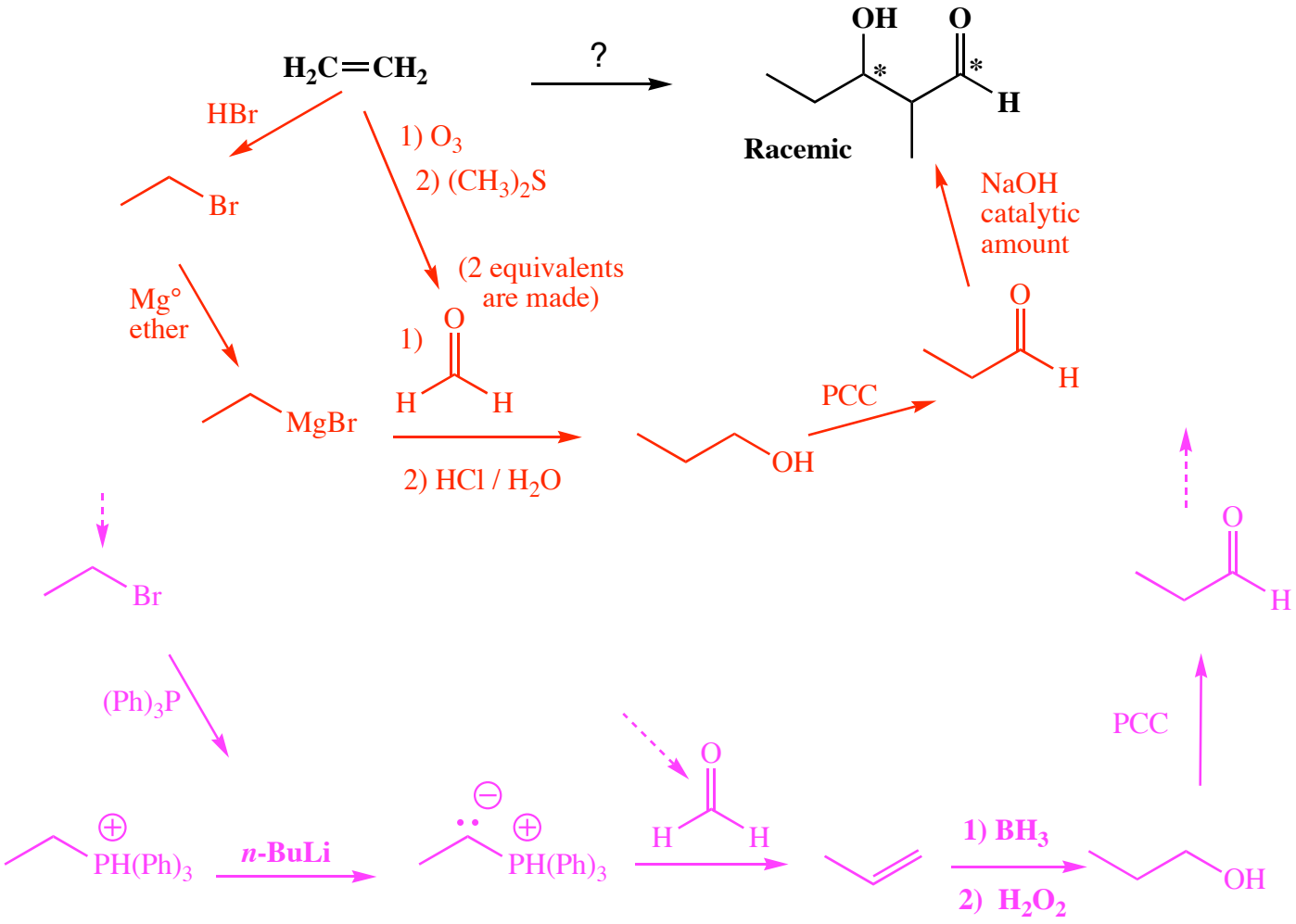
All of the carbons of the product must come from the given starting material.



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 becausethere 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.

20. (16 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.

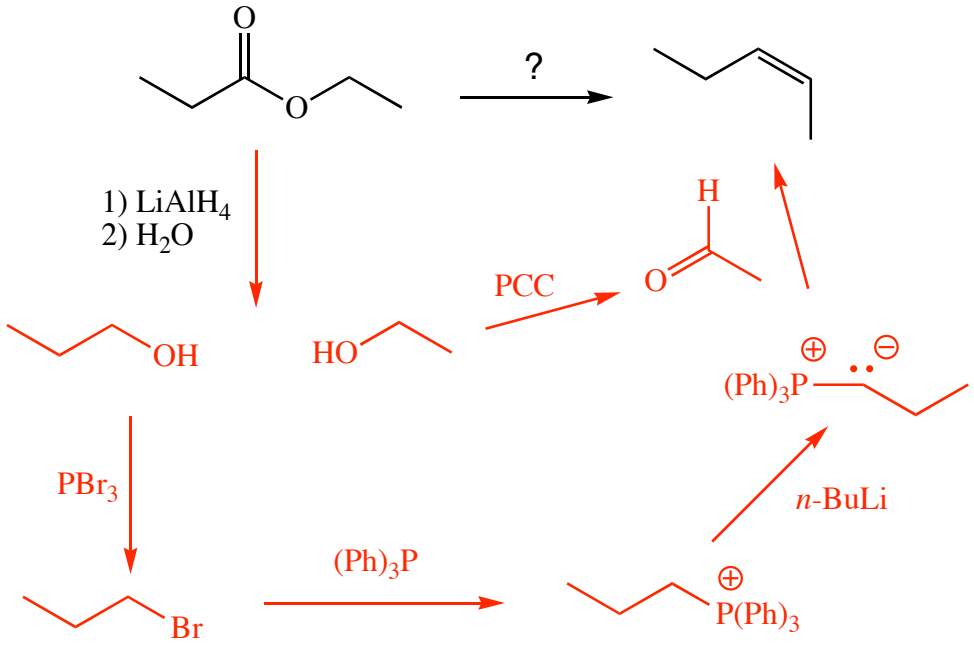
All of the carbons of the product must come from the given starting material.



Recognize that the product has the β-keto aldehyde functional group, the KRE of an aldol reaction. Further, it has 6 carbons so predict it is the result of an aldol using propanal. **Recognize** you need to add one carbon to the starting material to get propanal from ethylene, You can do this a couple of ways, but in either case, you need to carry out ozonlysis to create the one carbon fragment in the form of formaldehyde. One approach to propanal uses ethyl bromide, created from ethylene plus HBr, to make a Grignard that reacts with formaldehyde to give propanol, followed by PCC oxidation to give propanal. Another approach (not shown) uses the formaldehyde in a Wittig reaction that uses the Wittig reagent created from ethyl bromide. Following the Wittig reaction, the propene undergoes hydroboration to give propanol, followed by PCC oxidation to give propanal.

20. (15 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.

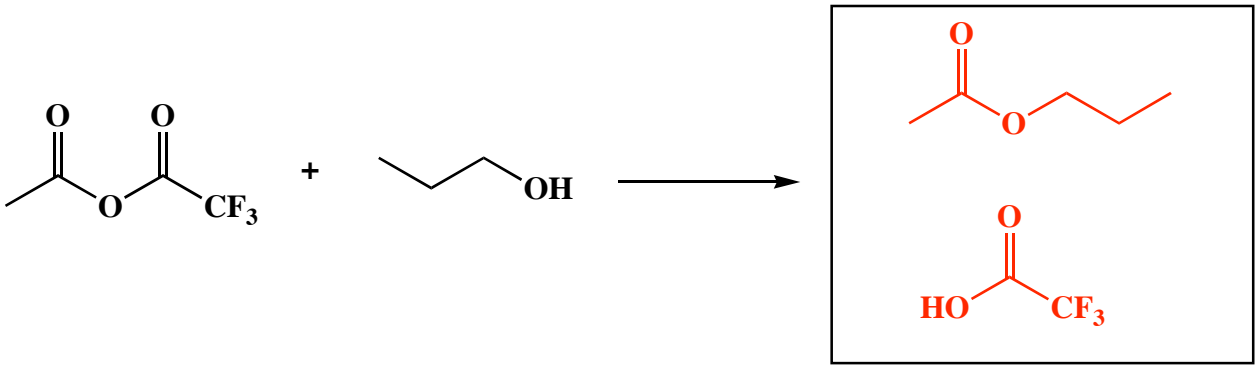
All of the carbons of the product must come from the given starting material.



Recognize the product as a cis alkene, the KRE of a Wittig using an alkyl Wittig reagent. **Recognize** further that the product has the same number of carbons as the starting ester, but that we need to make a carbon-carbon bond between a two and a three carbon piece. This can best be accomplished by reducing the ester to give two alcohols. One alcohol is oxidized to an aldehyde with PCC, while the other is converted to a Wittig reagent via the alkyl halide. Notice that either combination of aldehyde and Wittig regent will work just fine, I only show one combination here.

20. (20 pts) Here is an apply what you know question. You have not seen this reagent before, but you have learned fundamental principles of reactivity that will lead you to the correct answer.

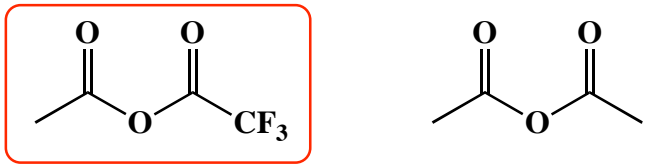
A. (5 pts) Write all of the products for the predominant reaction that takes place when the following reagents are added together.



B. (5 pts) In no more than two sentences explain your answer to part A.

The key to carboxylic acid derivatives is relative leaving group ability. The CF_3 group stabilizes the CF_3CO_2 anion leaving group via the inductive effect, so it preferentially departs during the reaction with 1-propanol.

C. (5 pts) Draw a circle around the reagent that reacts faster with various nucleophiles.



D. (5 pts) In no more than two sentences explain your answer to part C.

The key to carboxylic acid derivatives is relative leaving group ability. The CF_3 group stabilizes the CF_3CO_2 anion leaving group via the inductive effect, so the mixed anhydride containng the -CF_3 group reacts faster.