

NAME (Print): _____

Chemistry 310N
Dr. Brent Iverson
2nd Midterm
March 27, 2008

SIGNATURE: _____

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

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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 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		(29)
3		(24)
4		(12)
5		(16)
6		(35)
7		(18)
8		(22)
9		(22)
10		(26)
11		(14)
12		(7)
13		(19)
14		(13)
15		(17)
Total		(300)
%		
T Score		
HW		
Total Grade		

(HW score + Exam Grade) \implies

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.

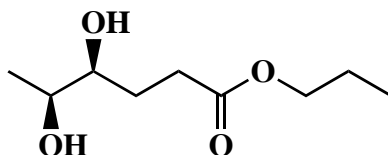
(Your signature)

Compound		pK _a
Hydrochloric acid	H-Cl	-7
Protonated alcohol	$\text{RCH}_2\text{OH}_2^+$	-2
Hydronium ion	H_3O^+	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-5
Ammonium ion	H_4N^+	9.2
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	10
β-Ketoesters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	11
β-Diesters	$\text{ROC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	16
Aldehydes	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	18-20
Ketones	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	18-20
Esters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\text{H}$	25
LDA	$\text{H}-\text{N}(i\text{-C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{H}$	44
Alkanes	$\text{CH}_3\text{CH}_2-\text{H}$	51

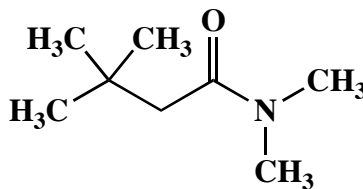
1. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

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:



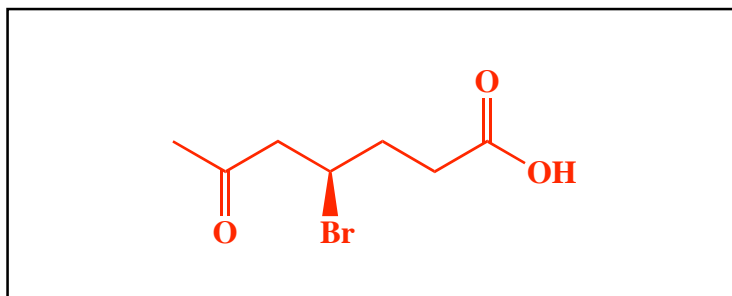
(4S,5S)-Propyl-4,5-dihydroxyhexanoate



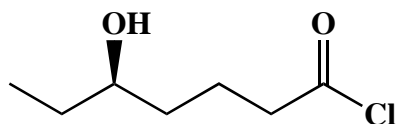
N,N-Dimethyl-3,3-dimethylbutanamide

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

(R)-4-Bromo-6-oxoheptanoic acid



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

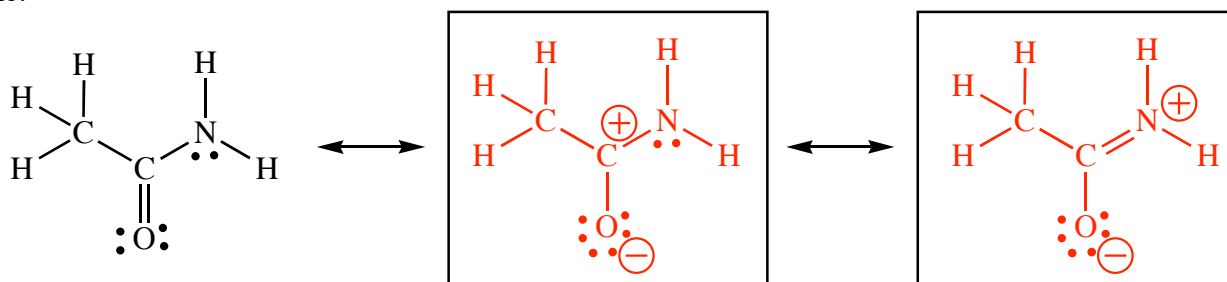


(R)-5-Hydroxyheptanoyl chloride

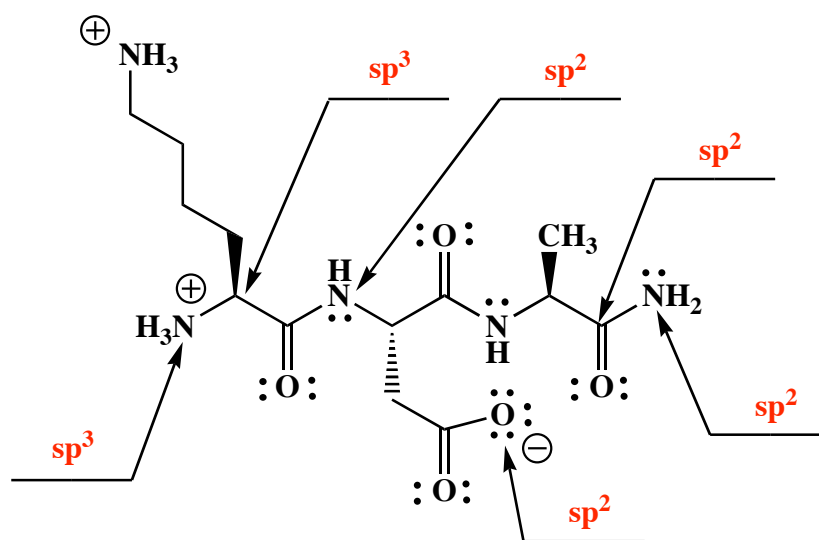
B) (5 points) Although the molecule above can be drawn and named, it actually could never be prepared and placed in a flask. In no more than two sentences, explain why the molecule shown above could never be isolated.

Alcohols react with acid chloride groups to give an ester. Therefore, a hydroxyl group could never exist in the same molecule as an acid chloride group.

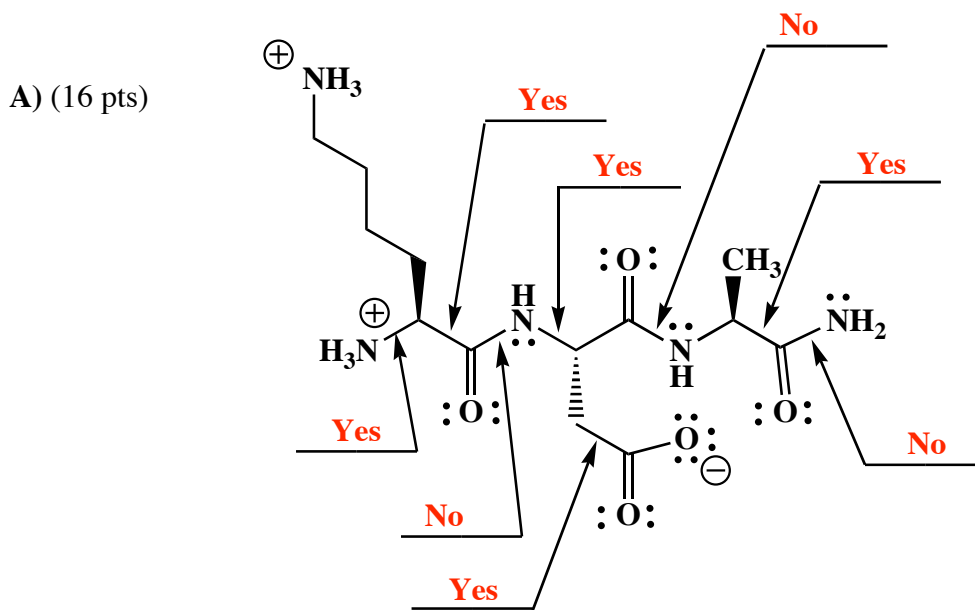
5. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



5. (12 points) On the lines, indicate the hybridization state of each atom indicated by the arrows.



6. On the lines, write either "YES" or "NO" to indicate whether the bonds indicated by the arrows can rotate freely or not.



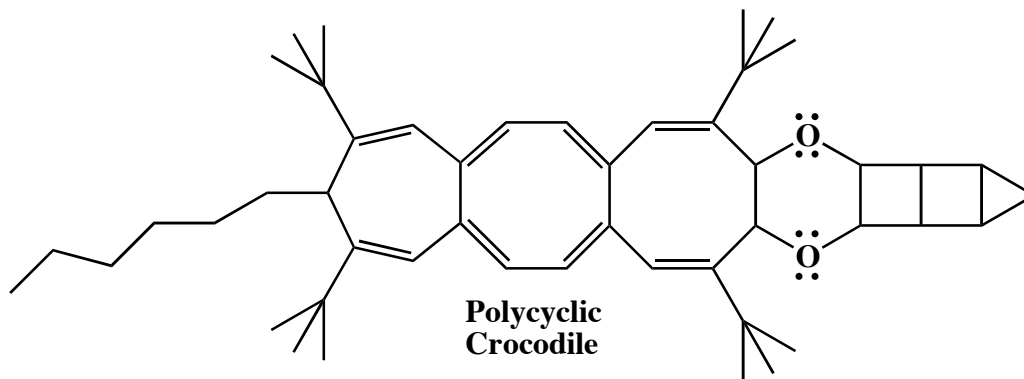
B) (2 pts) Is the above structure in the protonation state that would exist at pH 2.0, 7.0, or 11.0?

7.0

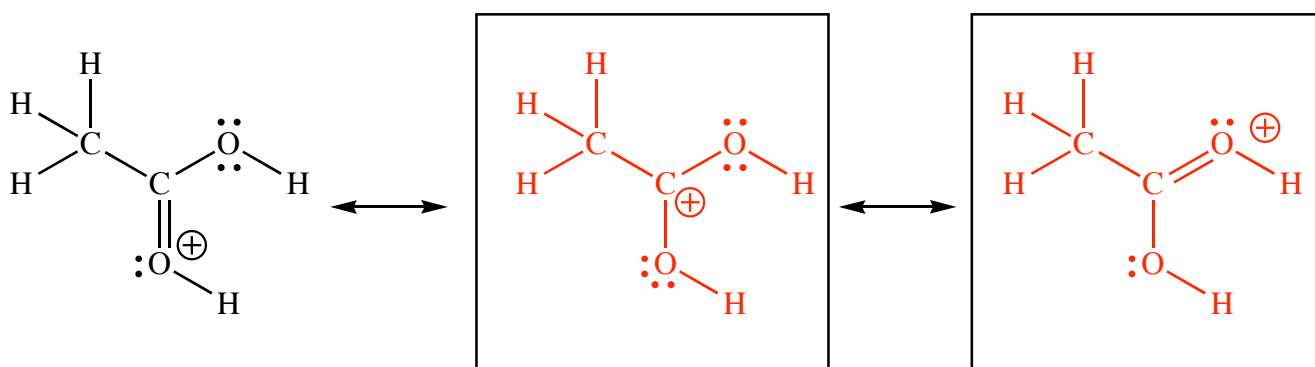
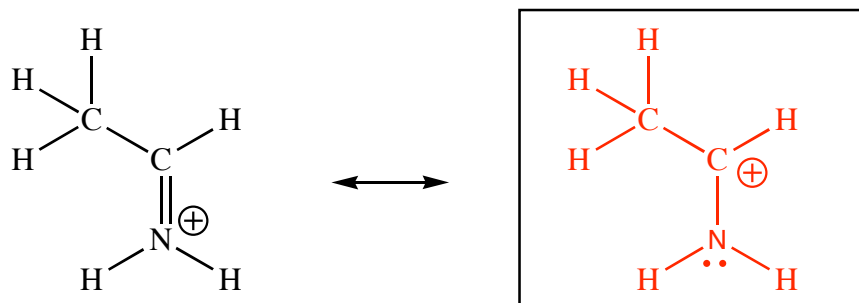
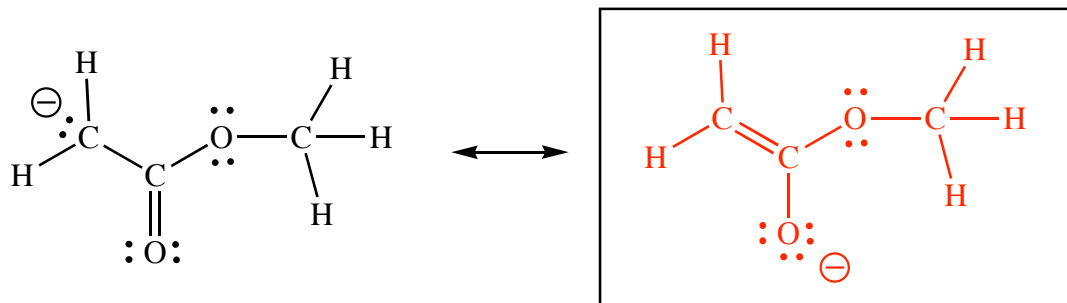
←←←← NOTICE THIS

7. (6 pts) List two attributes of amide bonds that lead to stabilization of the folded structures of proteins.

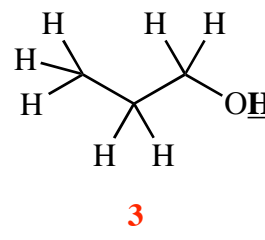
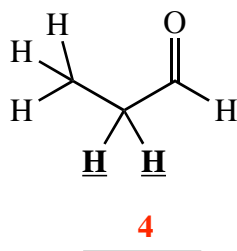
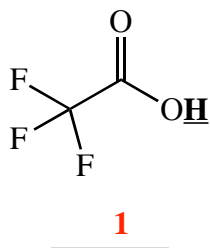
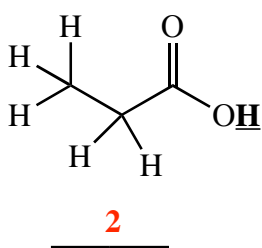
- 1) The amide carbonyl oxygen and hydrogen on nitrogen can make strong hydrogen bonds
- 2) The C-N bond cannot rotate freely, so the backbone of proteins is relatively rigid (less flexible) and easier to stabilize in a folded conformation.



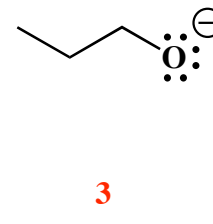
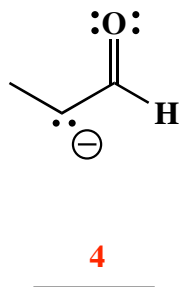
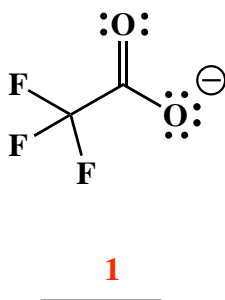
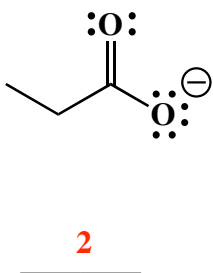
9. (12 points) For each of the following molecules, draw the indicated number of MOST important resonance contributing structures. Be sure to show all lone pairs and formal charges. You do not have to draw any arrows for this question.



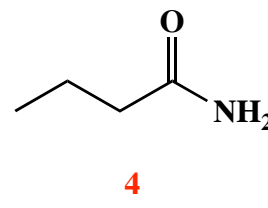
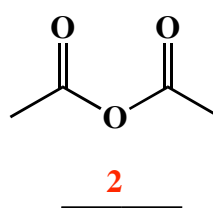
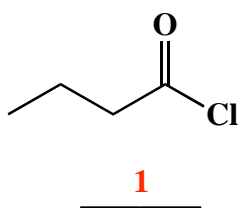
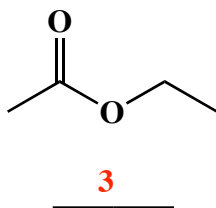
10. (4 pts.) Rank all of the following with respect to relative acidity. The acidic H atom in question is indicated in bold and with an underline for each molecule. Place a **1** under the most acidic molecule, and a **4** under the least acidic molecule.



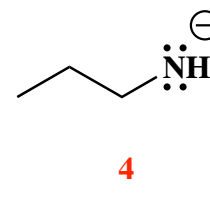
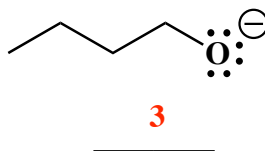
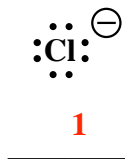
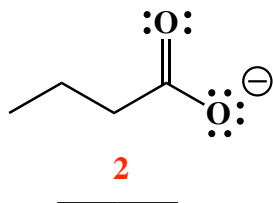
11. (4 pts.) Rank the following in terms of anion stability, with a **1** under the anion that is the most stable and a **4** under the anion that is least stable.



12. (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.

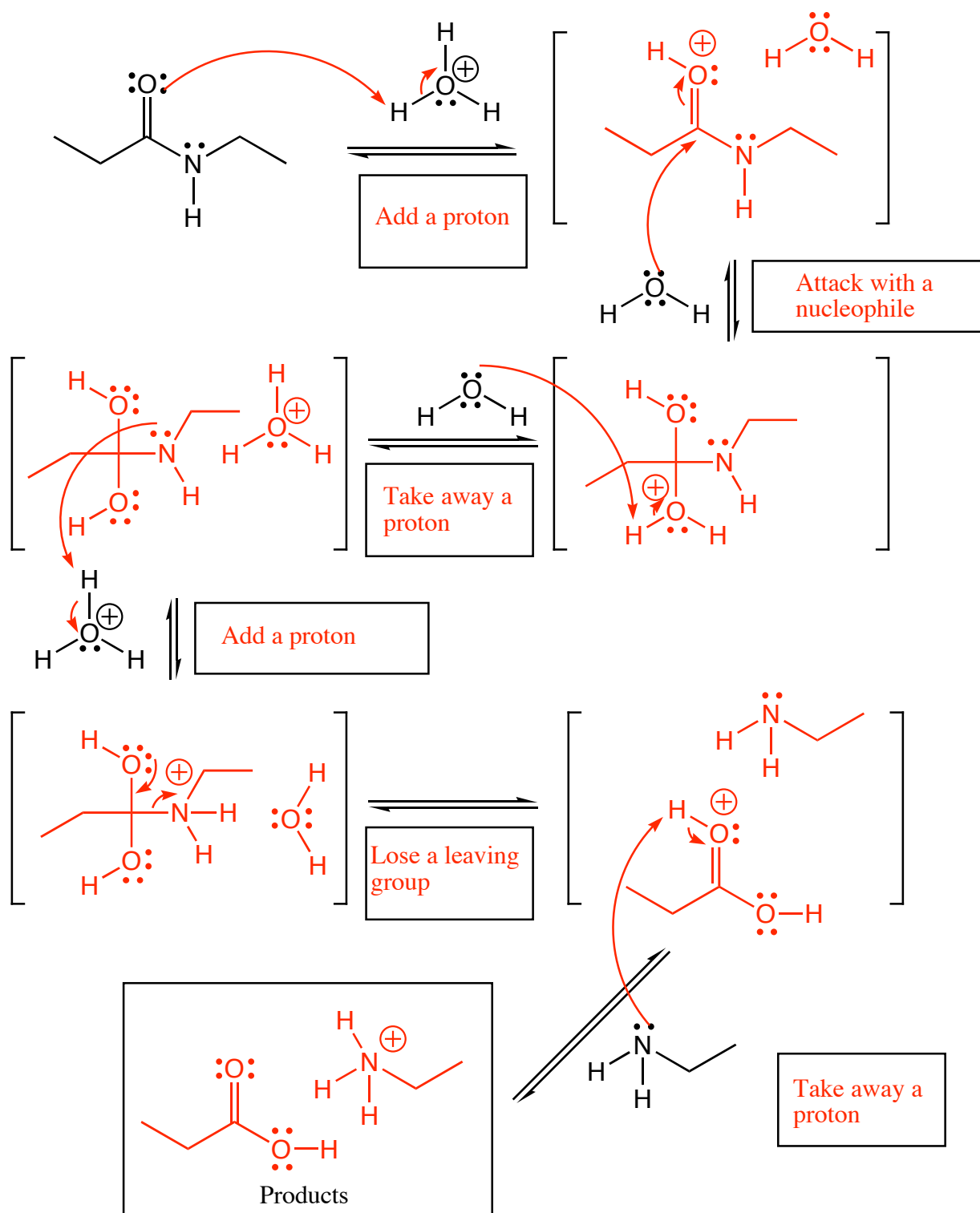


13. (4 pts.) Rank the following in terms of anion stability, with a **1** under the anion that is the most stable and a **4** under the anion that is least stable.

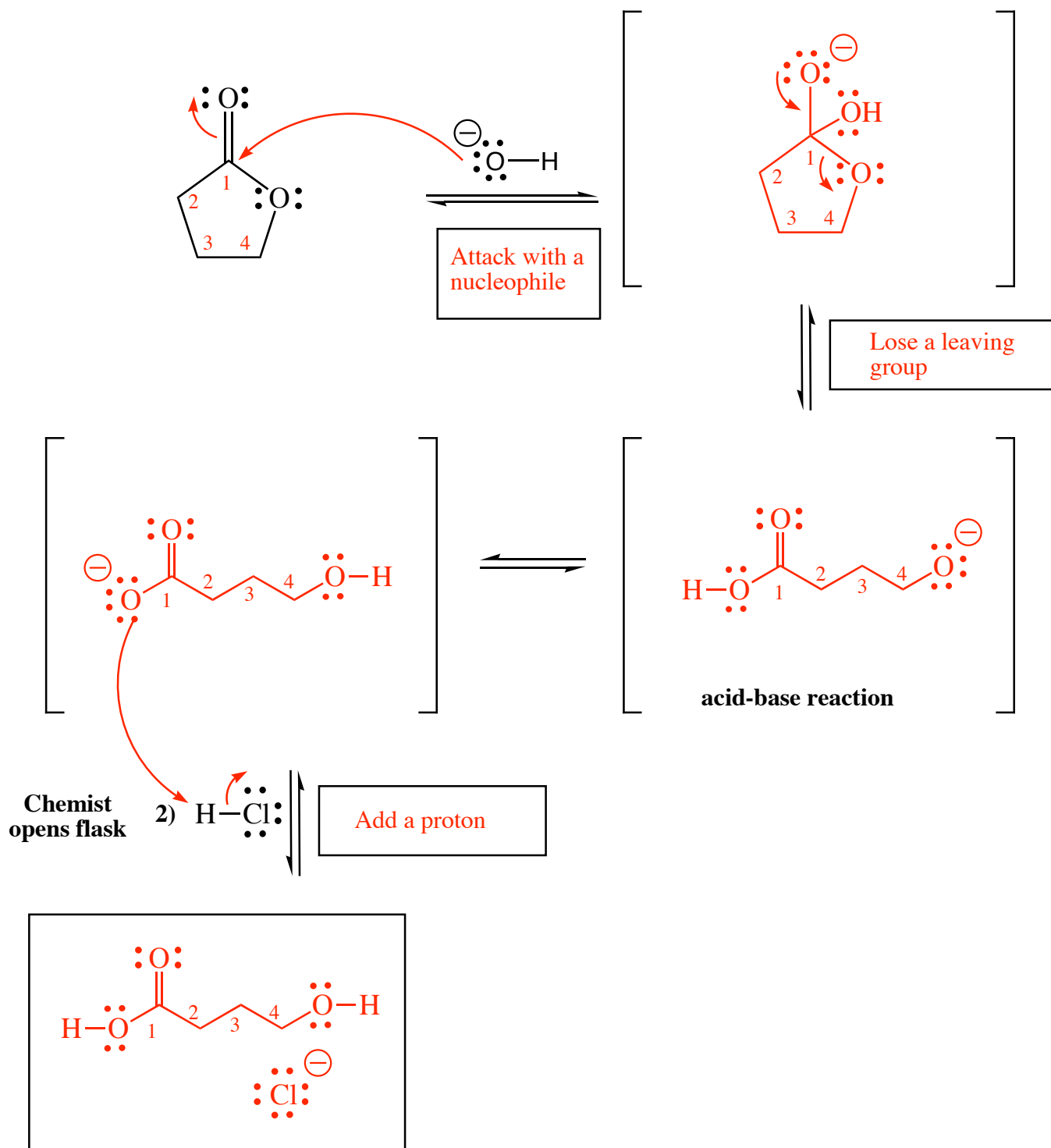


Please reread the directions to make sure you did not rank backwards!

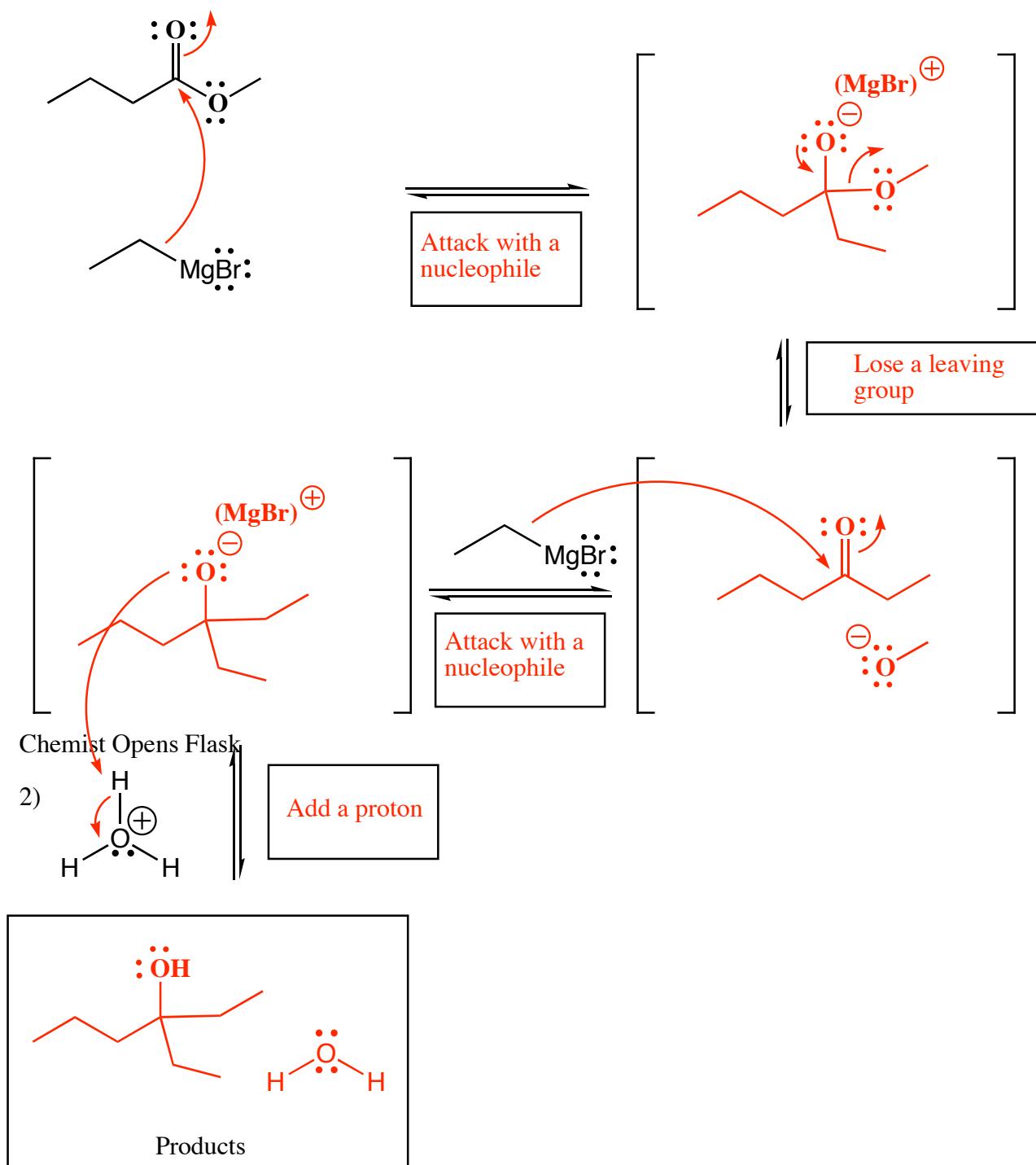
14. (35 pts.) Complete the mechanism for the following acid catalyzed amide hydrolysis reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL 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").



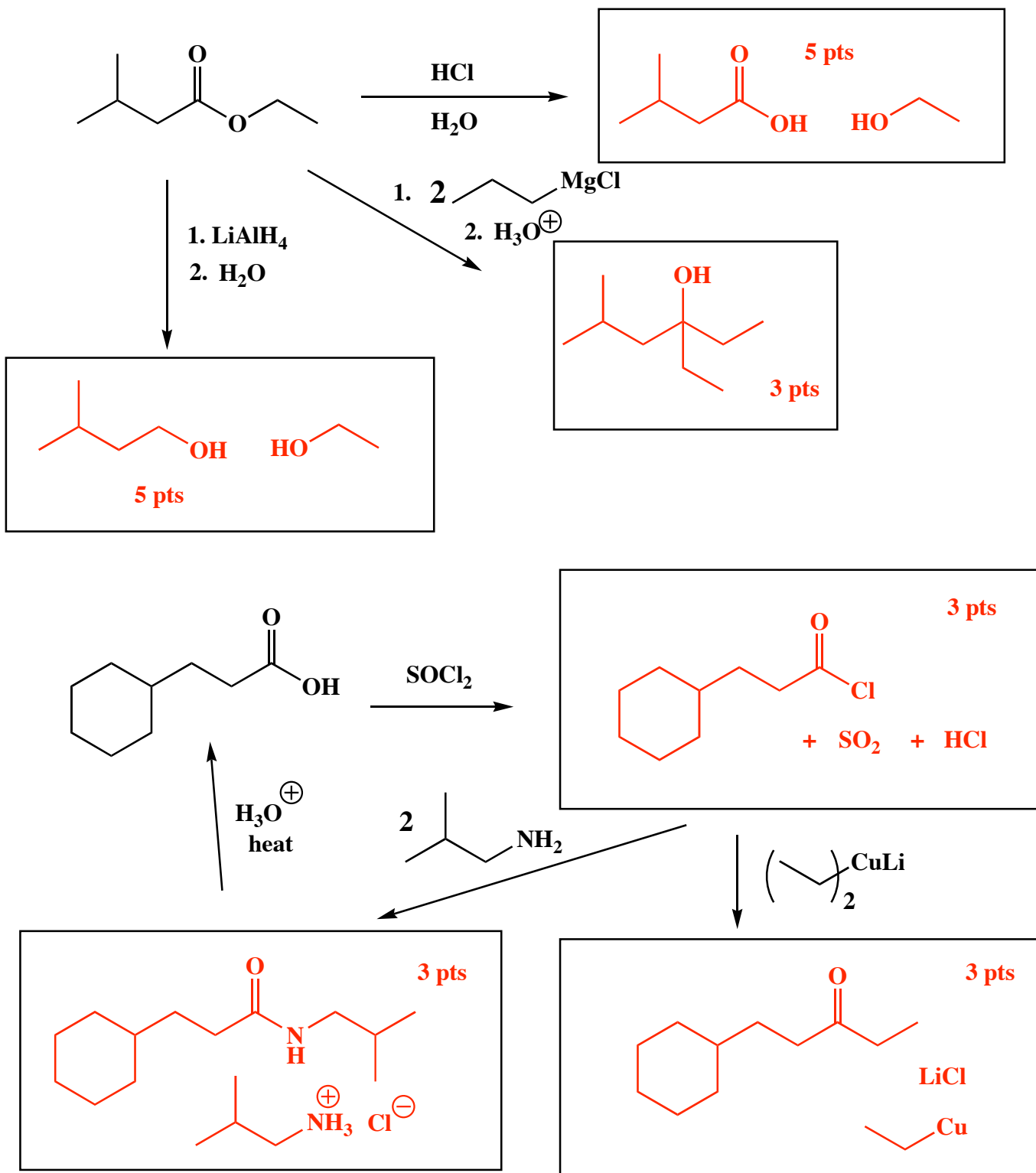
14. (cont.) (18 pts.) Complete the mechanism for the following base promoted ester hydrolysis reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, 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").



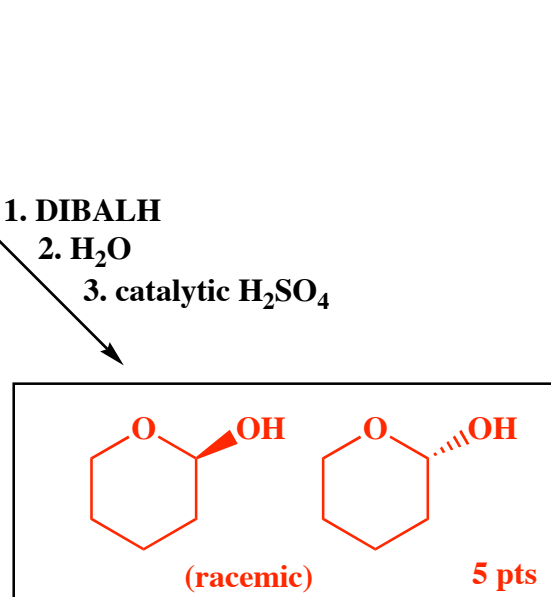
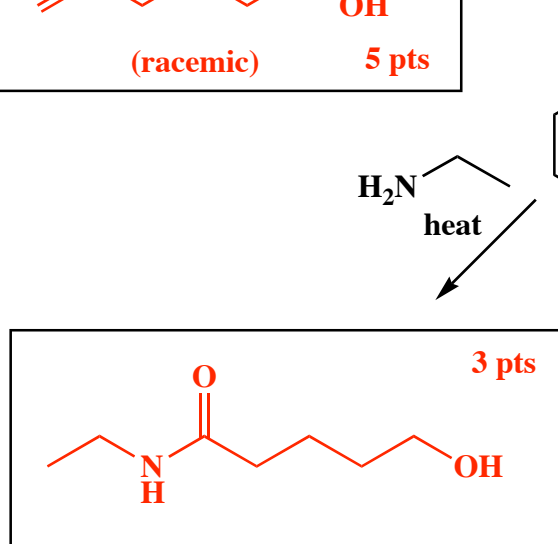
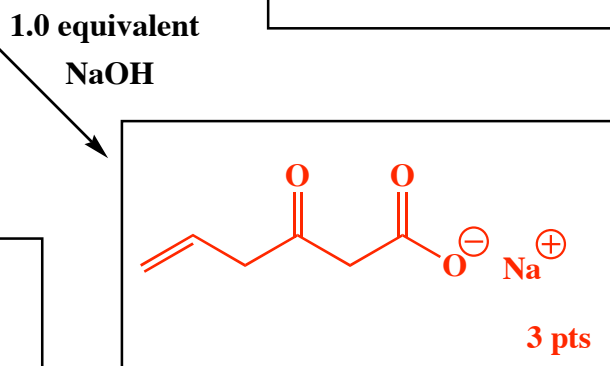
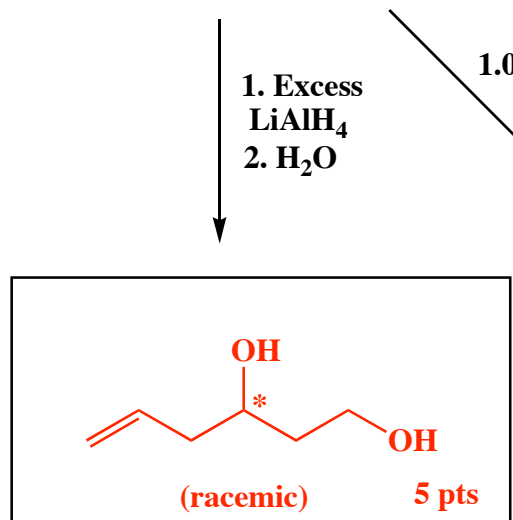
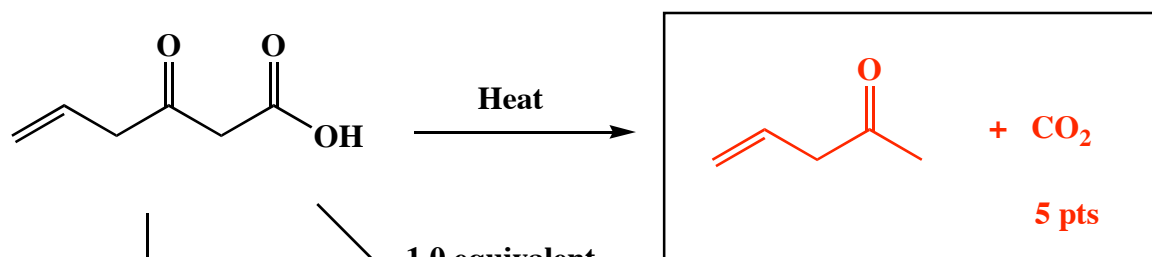
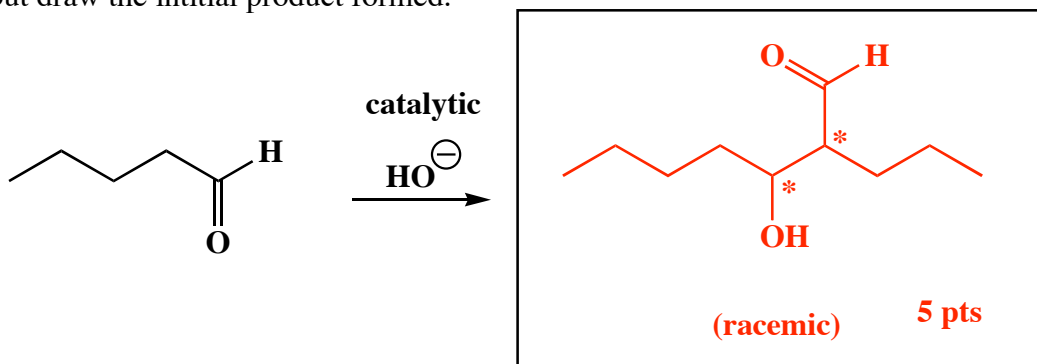
14. (cont.) (22 pts.) Complete the mechanism for the following reaction involving a Grignard reagent. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, 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").*



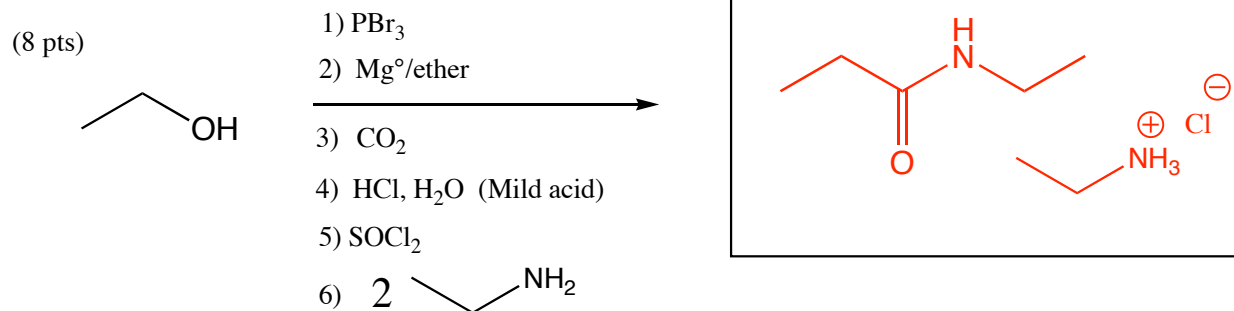
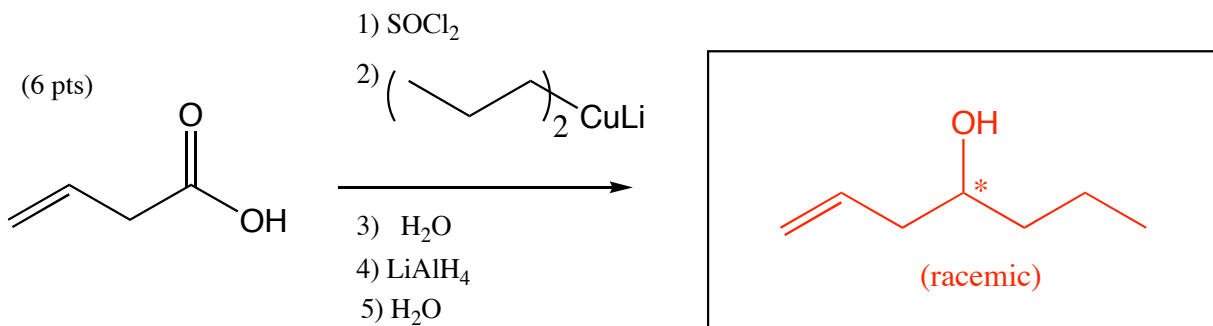
16. (22 pts) In the spaces provided, draw all products containing C atoms from the starting material. When in doubt, draw them! When a new chiral center is created put an asterisk next to the chiral center and write "racemic" when racemic mixtures are formed. Also, for aldol reactions DO NOT DEHYDRATE, but draw the initial product formed.



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 center and write "racemic" when racemic mixtures are formed. Also, for aldol reactions DO NOT DEHYDRATE, but draw the initial product formed.

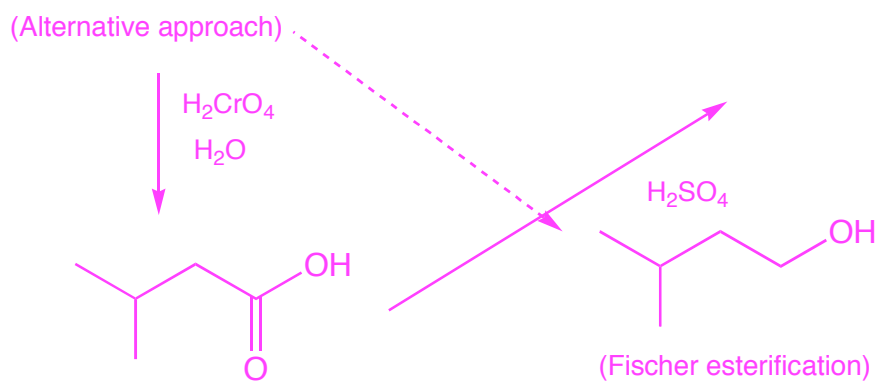
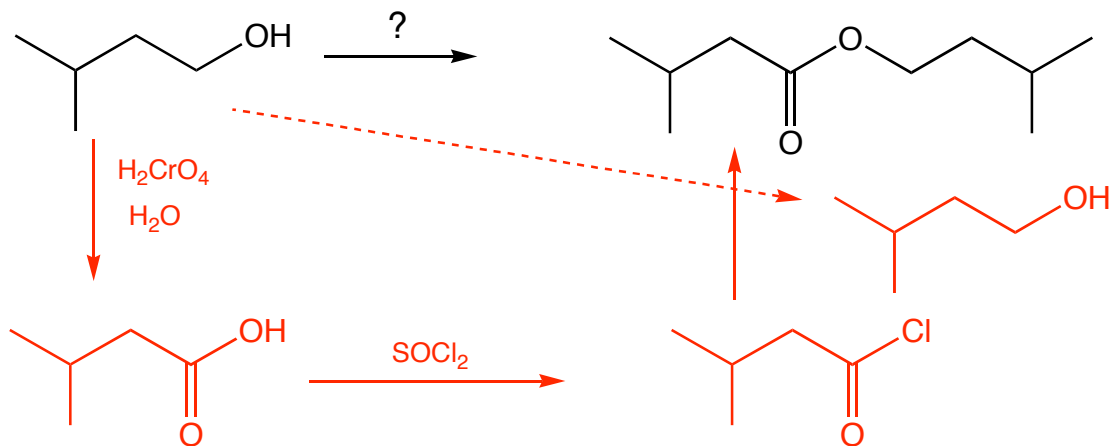


17. (14 points) For the following sequences of reactions, draw the predominant organic product or products after ALL the steps. You do not need to draw the intermediates formed along the way. If a new chiral center is created in the reaction that produces a racemic mixture, label the chiral center with an asterisk (*) and write "*racemic*" underneath. You do not have to draw all of the enantiomers.



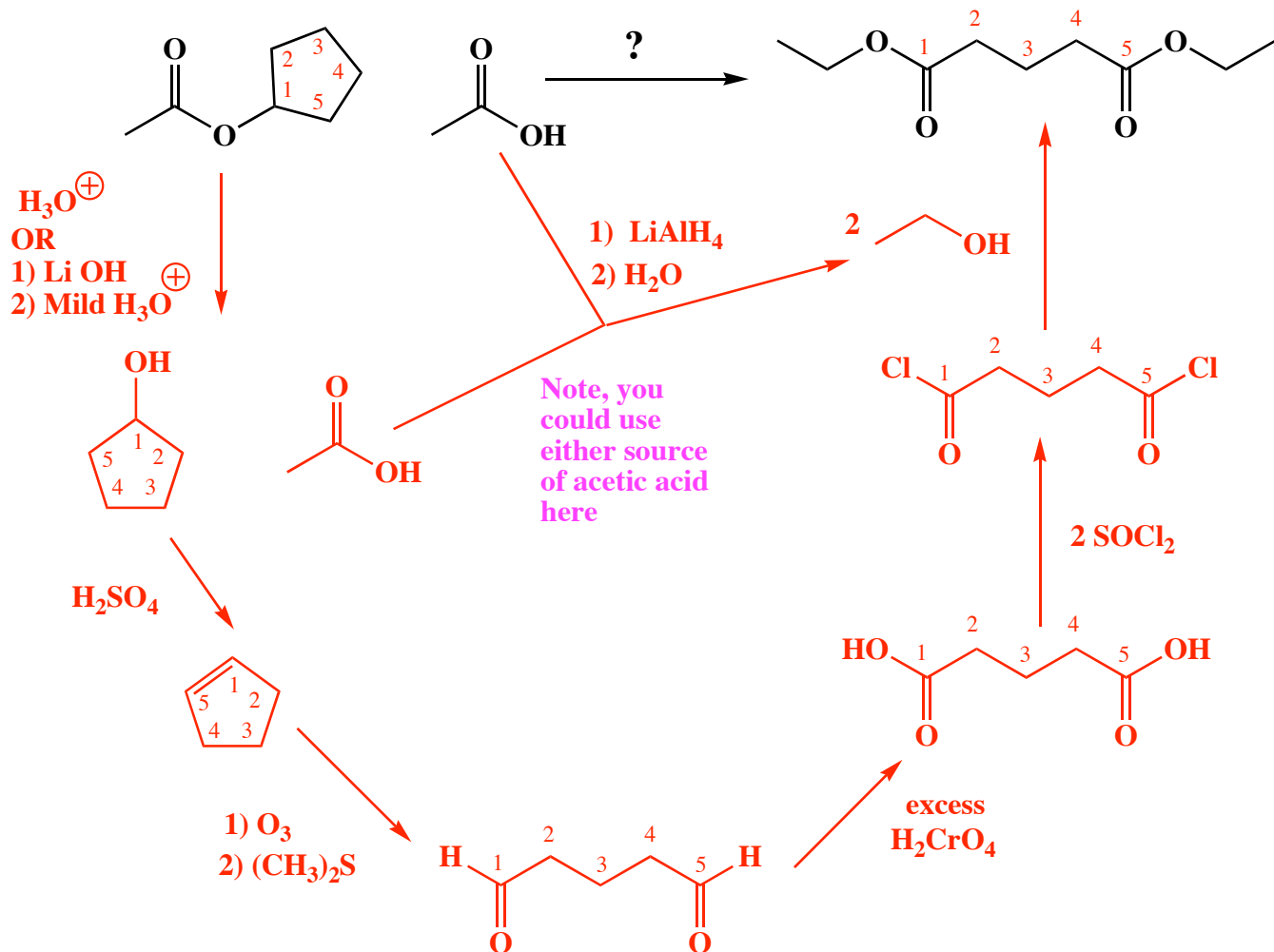
17. (7 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Hint: this should look familiar as a homework problem.

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



17. (cont.) (19 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 in doubt, draw the molecule!

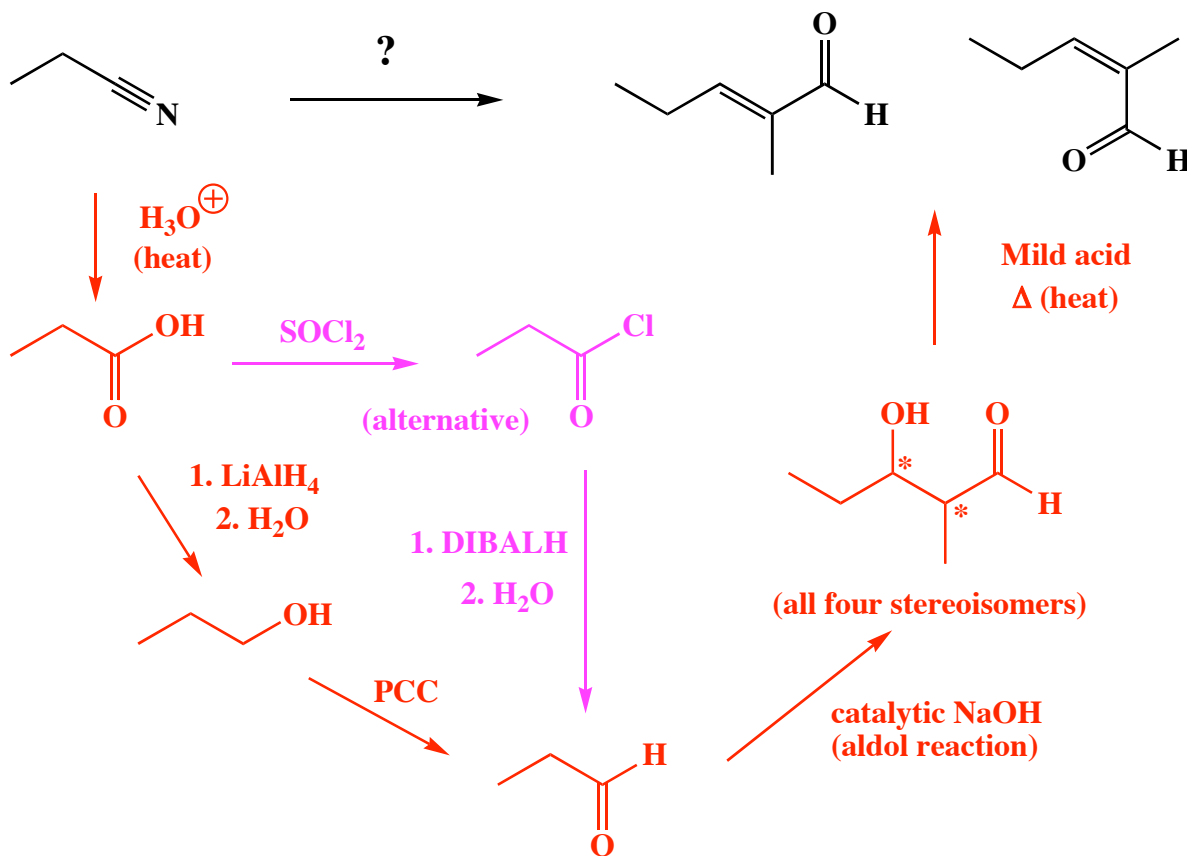
All of the carbons of the product must come from the given starting materials.



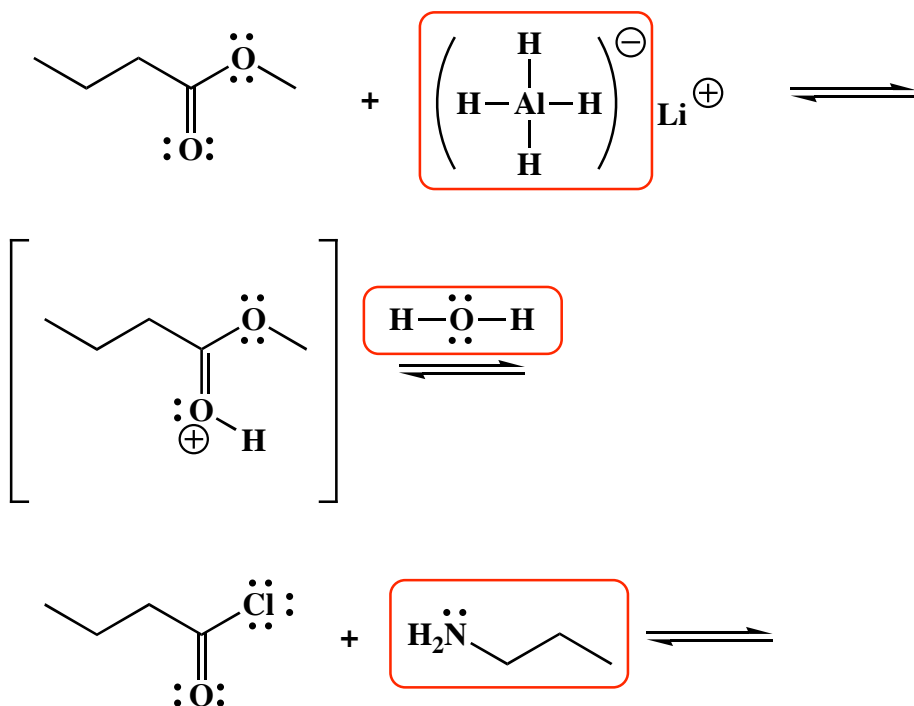
Alternatively, you could have used the diacid with 2 equivalents of ethanol in the presence of catalytic H₂SO₄ (Fischer esterification) instead of making the acid chloride.

17. (cont.) (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 in doubt, draw the molecule!

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



18. (9 points) Below are written individual steps of different reaction mechanisms we have learned. Each of these involve a nucleophile reacting with an electrophile. For each step, DRAW A CIRCLE AROUND the nucleophile. No tricks, this is simply here to make sure you can identify nucleophiles versus electrophiles. You do not have to draw any arrows or even draw the products of these steps.



19. (8 pts) Definitely save this until the end. Acid anhydrides are often used in place of acid chlorides because a less acidic carboxylic acid, not the much stronger acid HCl, is the byproduct of the reaction. In the following reaction of a carbohydrate derivative, acetic anhydride is used to obtain the product in 99% yield as a single stereoisomer. Note that the stereochemistry of the starting cyclic hemiacetal carbon is not indicated. Draw the product of the following transformation in a CHAIR FORM and show the single stereoisomer product of this transformation AS A CHAIR, which is also the most stable possible CHAIR species.

