NAME (Print): _____

SIGNATURE: _____

Chemistry 310N
Dr. Brent Iverson
2nd Midterm
March 29, 2007

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!!!!

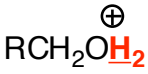
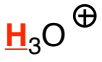
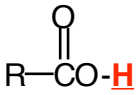
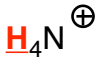
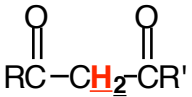
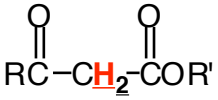
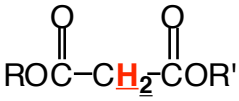
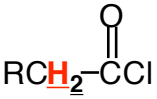
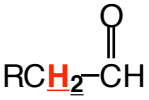
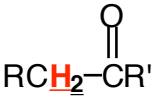
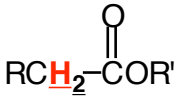
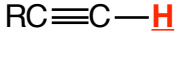
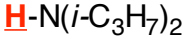
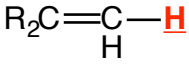
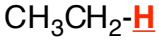
Page	Points	
1		**(26)**
2		**(34)**
3		**(19)**
4		**(18)**
5		**(29)**
6		**(19)**
7		**(19)**
8		**(25)**
9		**(17)**
10		**(21)**
11		**(14)**
12		**(7)**
13		**(16)**
14		**(16)**
15		**(18)**
16		**(6)**
Total		**(304)**
HW		
T Score		

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.

_____

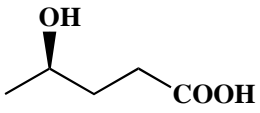
(Your signature)

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

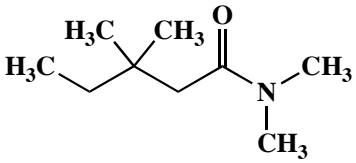
1. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We wil be looking for a minumum of 7 key points here.

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:



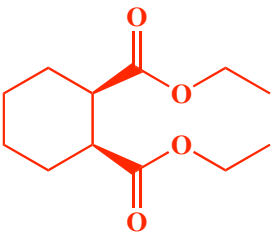
(R)-4-Hydroxypentanoic acid



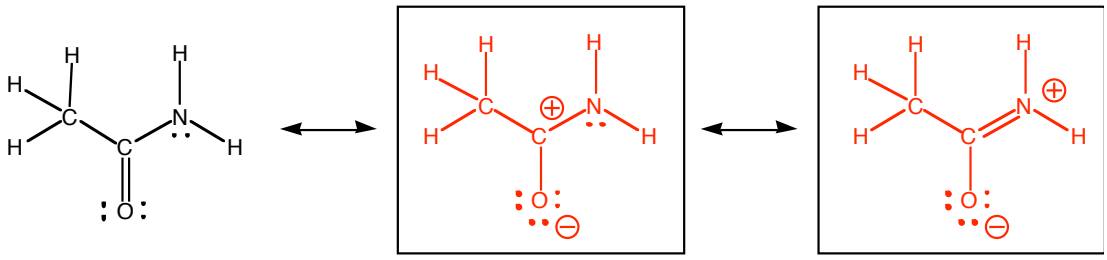
***N,N*-Dimethyl-3,3-dimethylpentanamide**

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

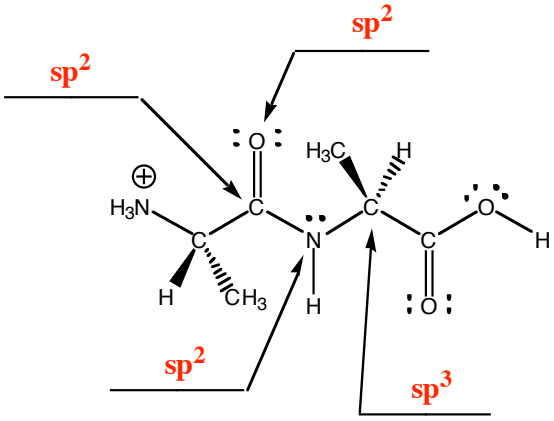
Diethyl cis-1,2-cyclohexanedicarboxylate



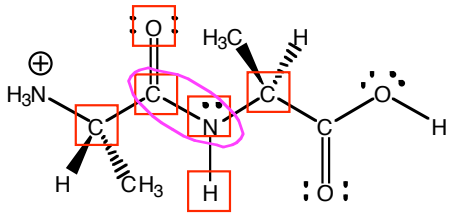
4. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



5. (8 points) On the lines, indicate the hybridization state of each atom indicated by the arrows.



6. (14 points) On the following structure **1) Draw a box around all the atoms that are ALWAYS in the same plane as the amide carbonyl group (C=O) and 2) circle all of the C-N bonds that DO NOT ROTATE.**

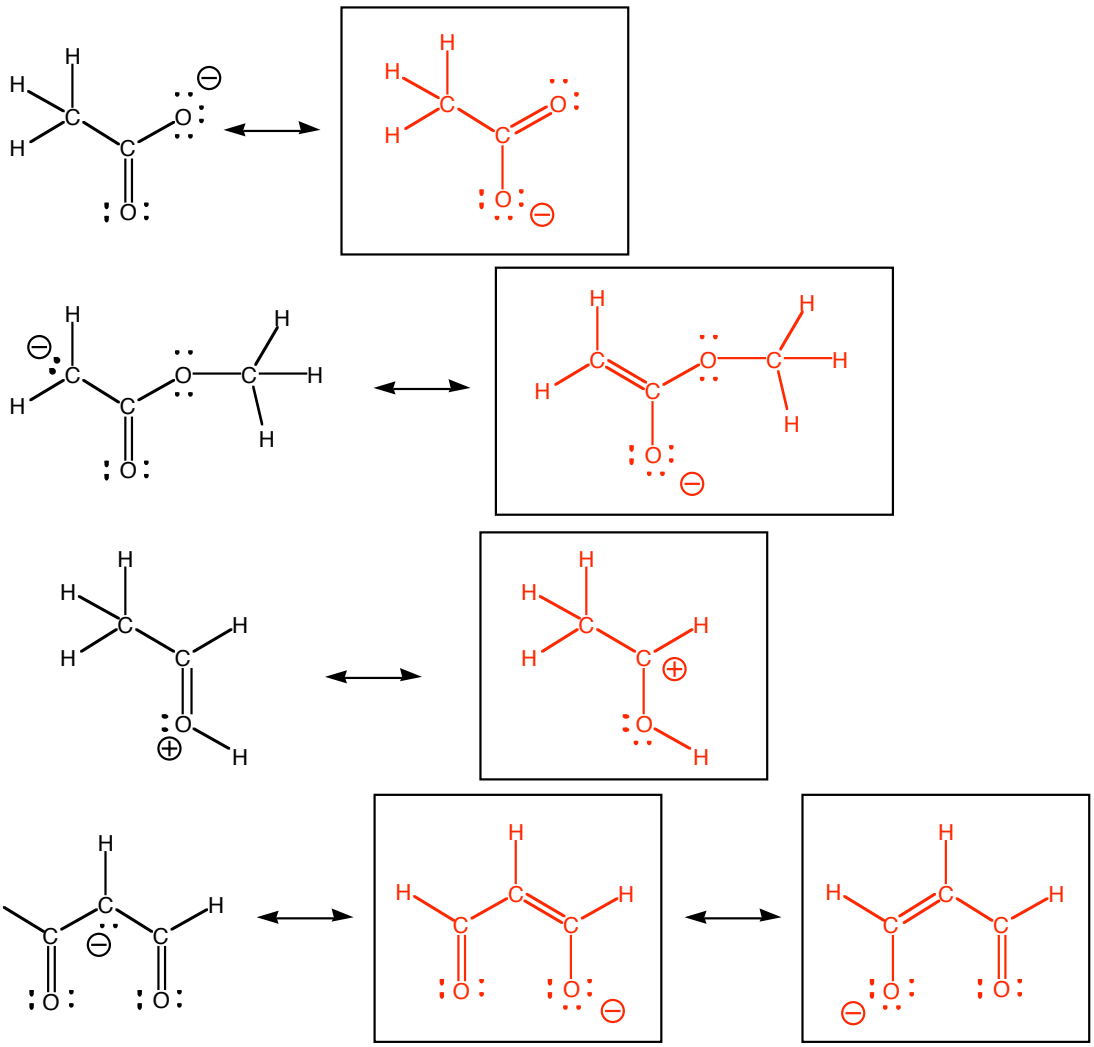


(4 pts) For the above stucture, is this the appropriate protonation state for pH 2.0, 7.0, or 10.0?

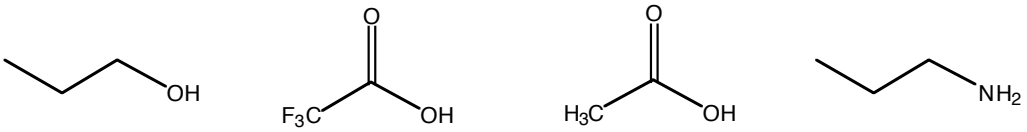
2.0

⟸ Notice This

7. (15 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 arrows on this one.

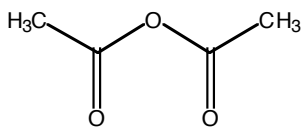


8. (4 points) Rank the following in terms of relative acidity, with a 1 under the most acidic, and a 4 under the least acidic molecule.

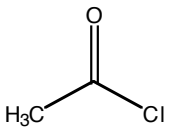


3 **1** **2** **4**

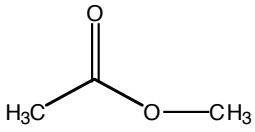
9. (4 points) Rank the following carboxylic acid derivatives with respect to reactivity with a nucleophile. Write a 1 under the most reactive, and a 4 under the least reactive derivative.



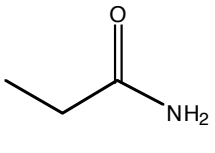
2



1

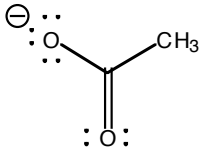


3



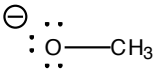
4

10. (4 points) Rank the following with respect to anion stability. Write a 1 under the most stable anion, and a 4 under the least stable anion.



2

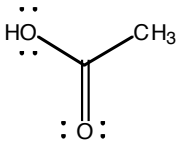
1



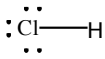
3

4

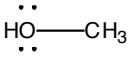
11. (4 points) Rank the following in terms of relative acidity, with a 1 under the most acidic, and a 4 unde the least acidic molecule.



2



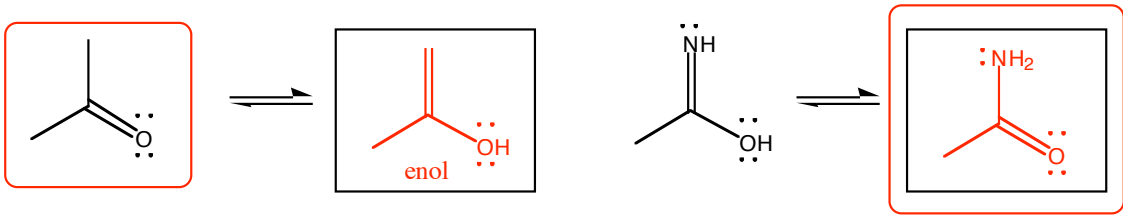
1



3

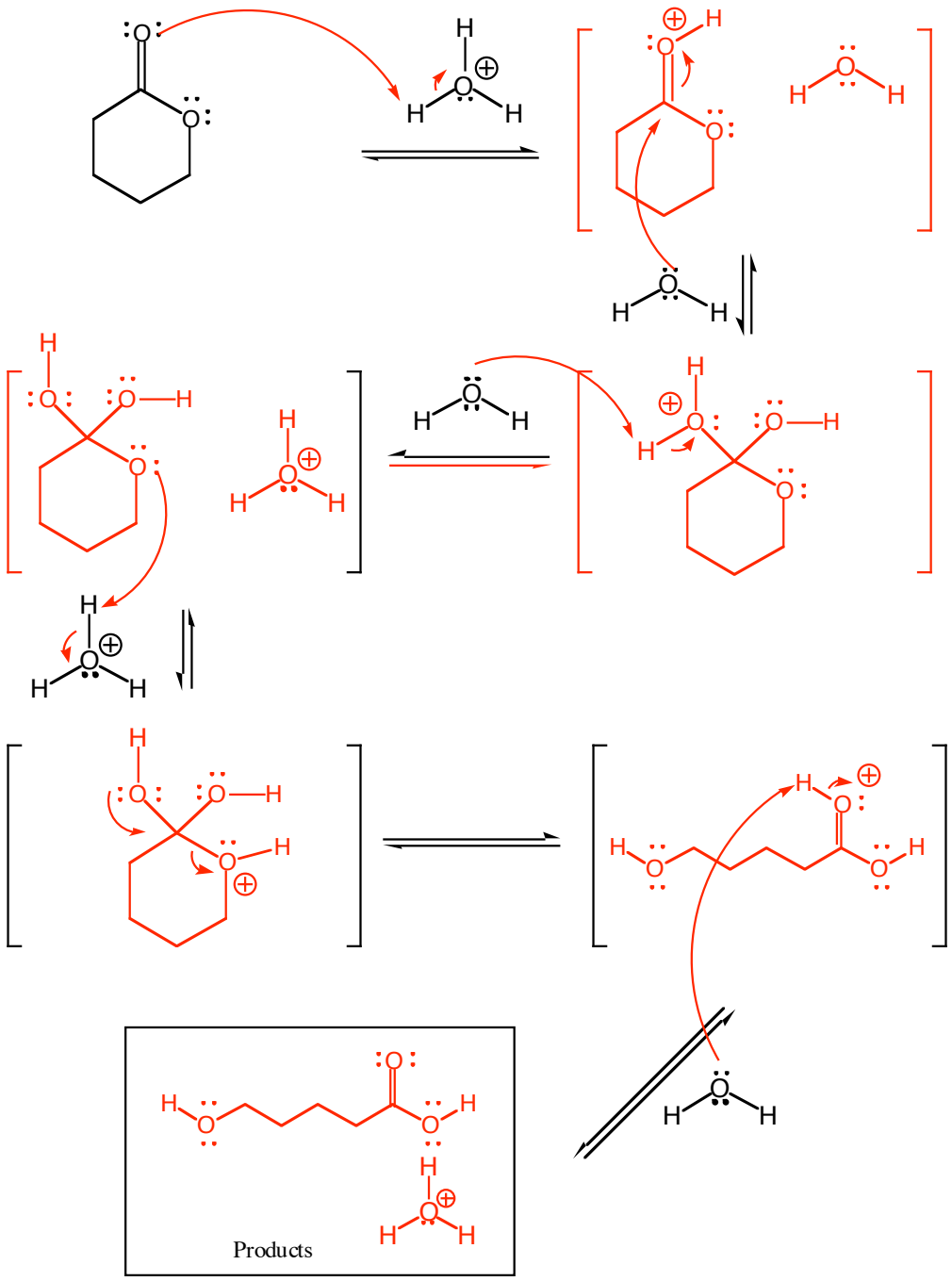
4

12. (6 points) Each of the following undergo the process of tautomerization. For each draw the other major tautomer, then for each pair, circle the one that is more stable.



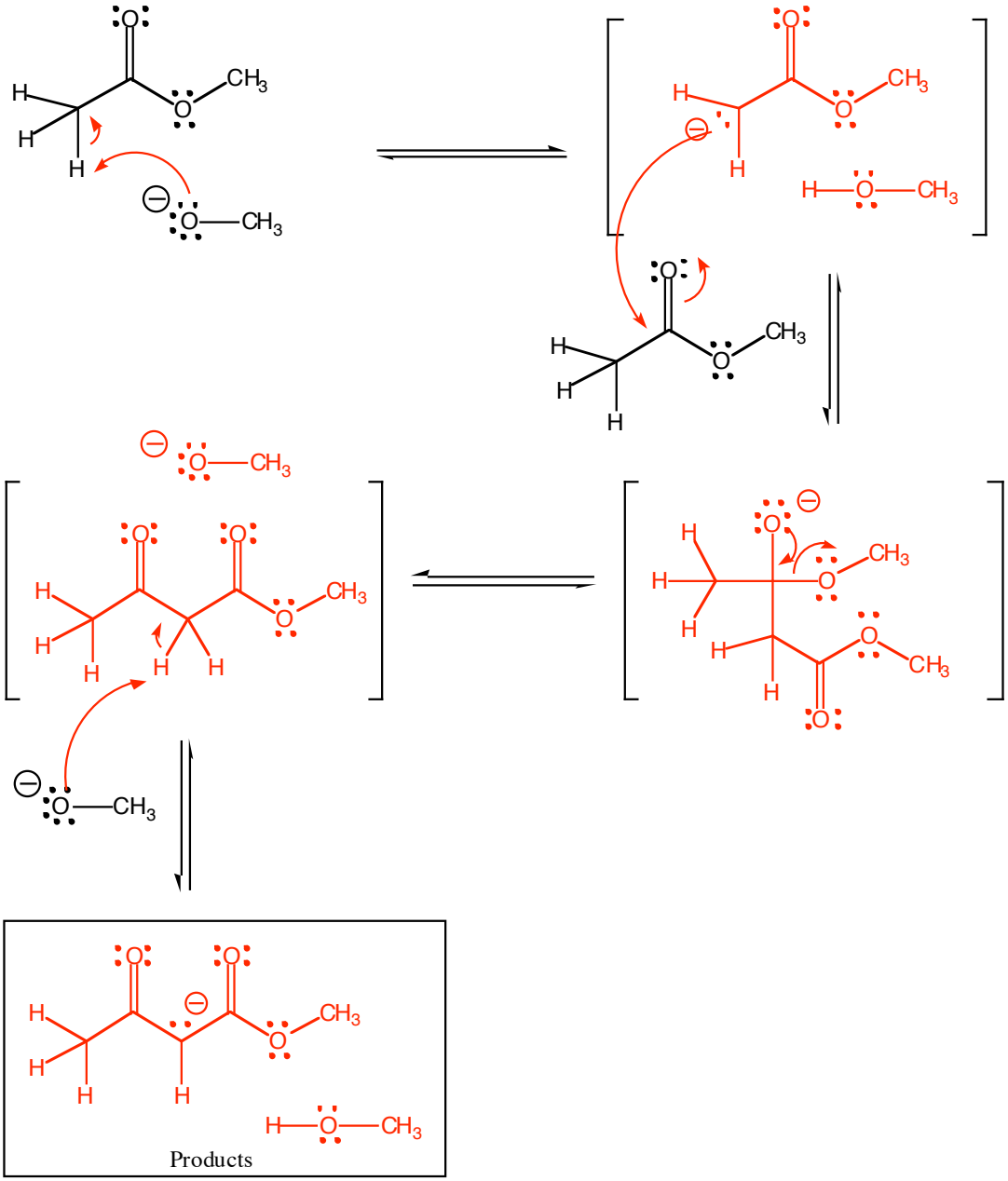
13. (29 points) Complete the following mechanism. Be sure to use arrows to indicate movement of all electrons and show all lone pairs and formal charges. Also, you must show all the products of each step. For resonance stabilized intermediates, you only need to draw one important contributing structure.

Acid Catalyzed Ester Hydrolysis



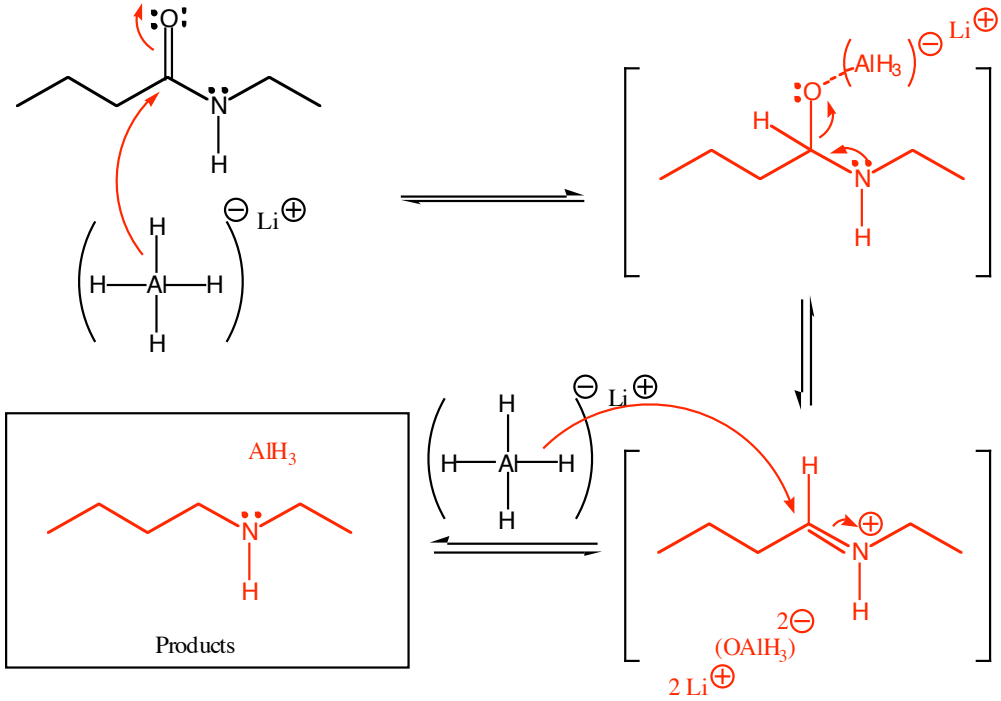
14. (19 points) Complete the following mechanism. Be sure to use arrows to indicate movement of all electrons and show all lone pairs and formal charges. Also, you must show all the products of each step. For resonance stabilized intermediates, you only need to draw one important contributing structure.

Claisen Condensation



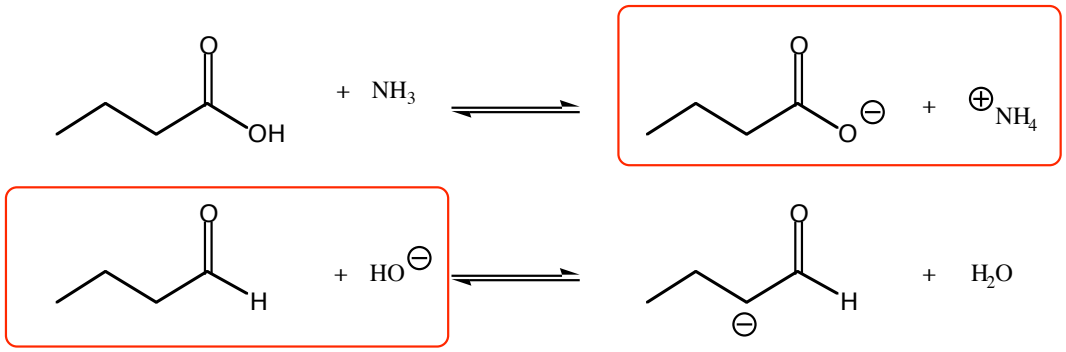
15. (13 points) Complete the following mechanism. Be sure to use arrows to indicate movement of all electrons and show all lone pairs and formal charges. Also, you must show all the products of each step. For resonance stabilized intermediates, you only need to draw one important contributing structure.

Reduction of Amides with $LiAlH_4$

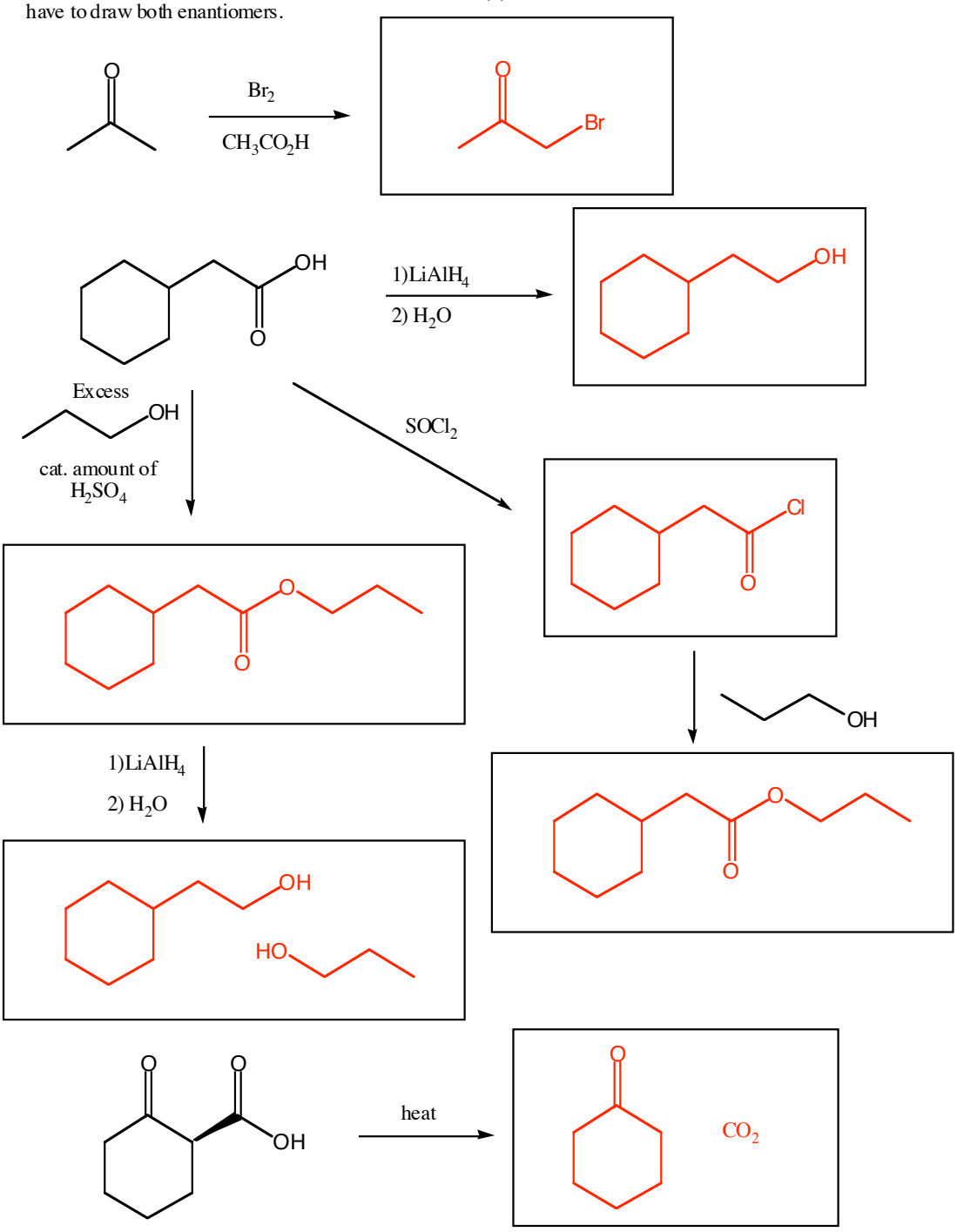


Note: In this reaction the chemist opens the flask and adds water in a second step that quenches any excess $LiAlH_4$. Therefore, you need a second step to add water when using this reaction in synthesis even though it is not shown in the mechanism above.

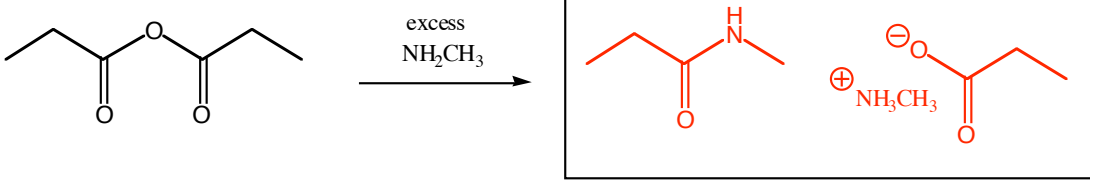
16. (6 pts) For the following equations that describe acid-base reactions, **circle the side that predominates at equilibrium.**

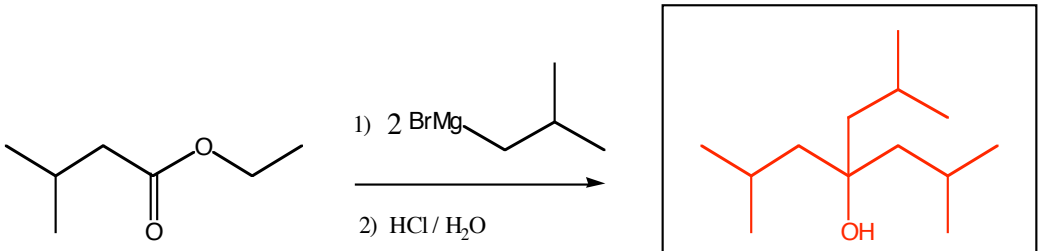


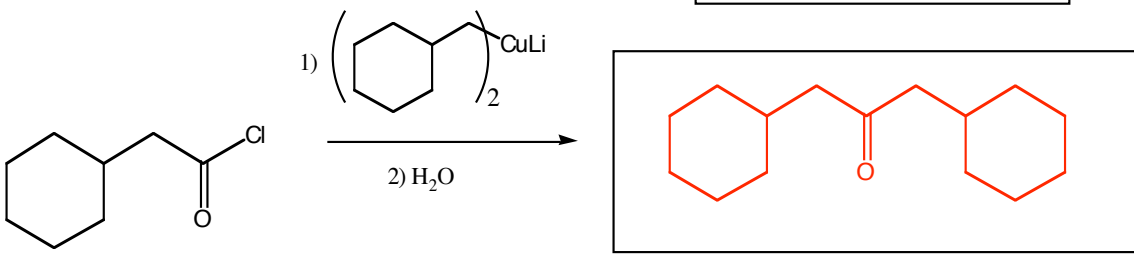
17. (25 points) Complete the following reactions. Draw the predominant carbon-containing organic product or products that will be formed. If a new chiral center is created in the reaction that produces a racemic mixture, label the chiral center with an asterisk (*) and write "***racemic***" underneath. You do not have to draw both enantiomers.

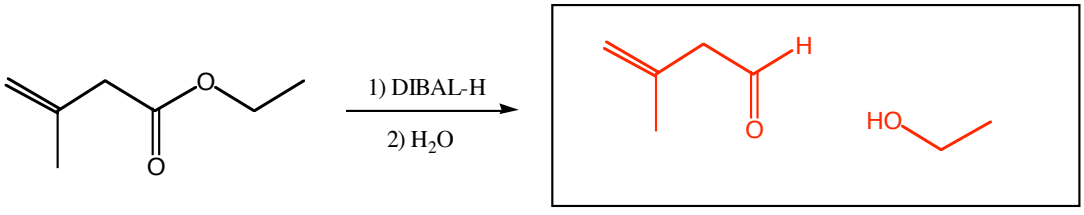


18. (15 points) Complete the following reactions. Draw the predominant carbon-containing organic product or products that will be formed. If a new chiral center is created in the reaction that produces a racemic mixture, label the chiral center with an asterisk (*) and write "***racemic***" underneath. You do not have to draw both enantiomers.

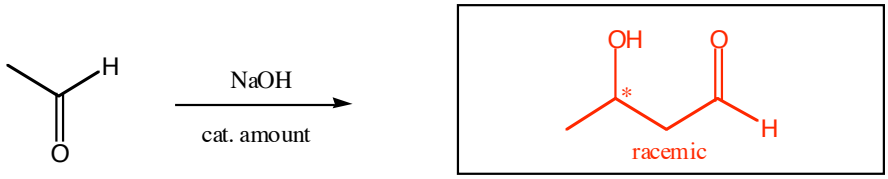


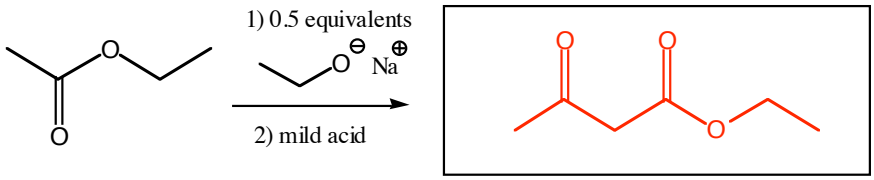


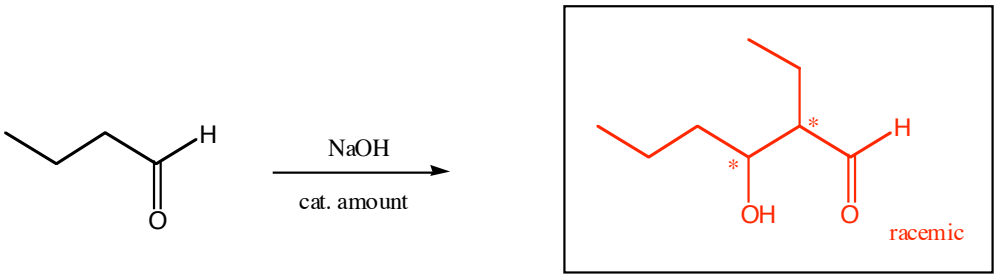


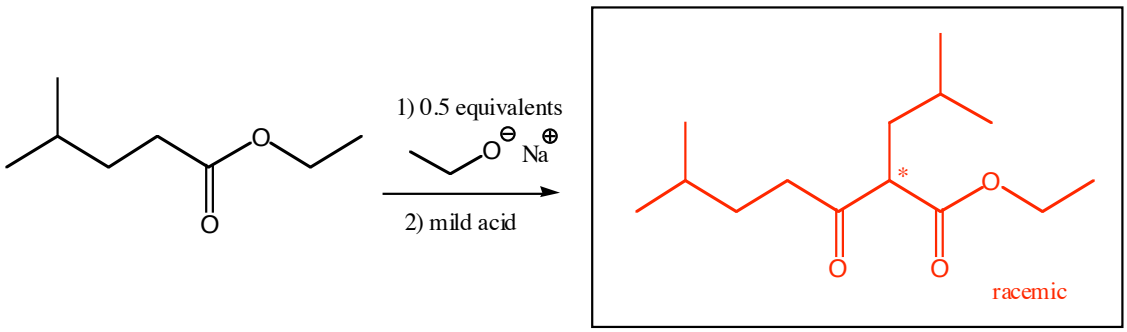


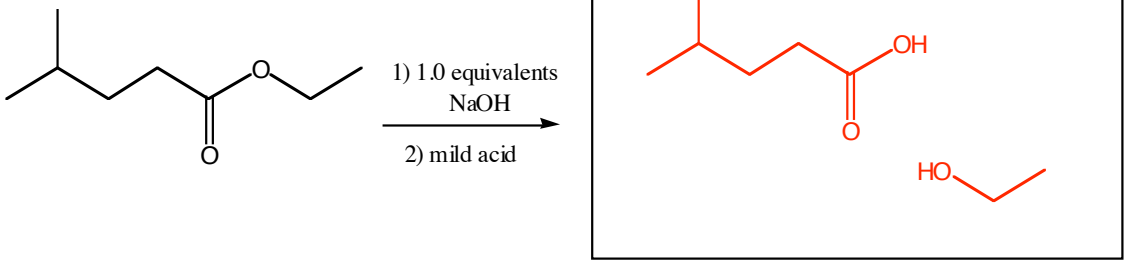
19. (21 points) Complete the following reactions. Draw the predominant carbon containing organic product or porducts that will be formed. If a new chiral center is created in the reaction that produces a racemic mixture, label the chiral center with an asterisk (*) and write "***racemic***" underneath. You do not have to draw all of the enantiomers. For aldol reactions, DO NOT DEHYDRATE. **For aldol reactions, DO NOT DEHYDRATE (it was worth repeating).**





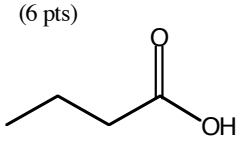




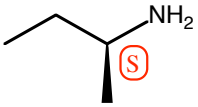


20. (14 points) For the following sequences of reactions, draw the predominant organic product or products after ALL the steps. You do not need to draw the intermediates formed along the way. If a new chiral center is created in the reaction that produces a racemic mixture, label the chiral center with an asterisk (*) and write "***racemic***" underneath. You do not have to draw all of the enantiomers.

(6 pts)

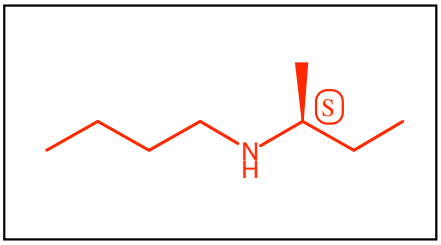


1) $SOCl_2$

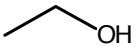
2) 

3) $LiAlH_4$

4) H_2O

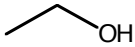


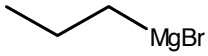
(8 pts)



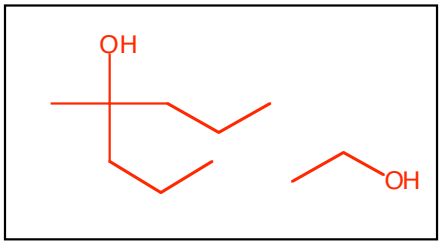
1) H_2CrO_4

2) $SOCl_2$

3) 

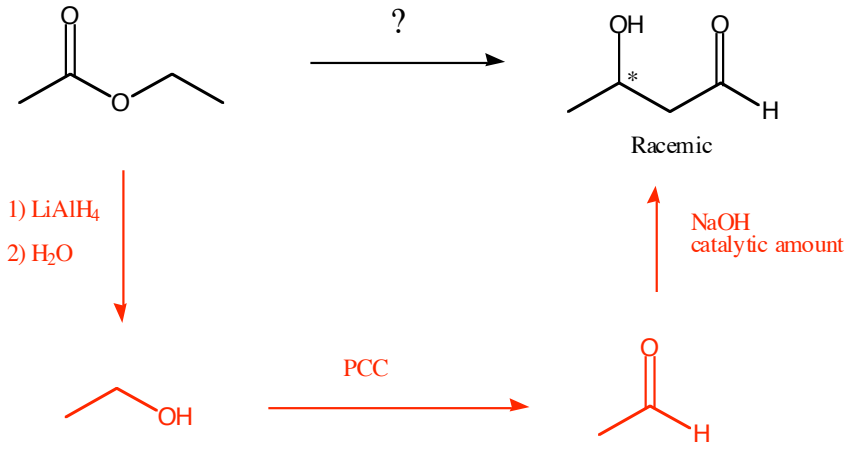
4) 2 

5) HCl, H_2O (Mild acid)



21. For the following synthesis questions, show how the starting material can be converted into the product. Show ALL intermediate molecules synthesized along the way, and show the reagents needed for each step. To get full credit, you must use the predominant product expected for each step. All of the carbon atoms of the product must come from the starting material(s).

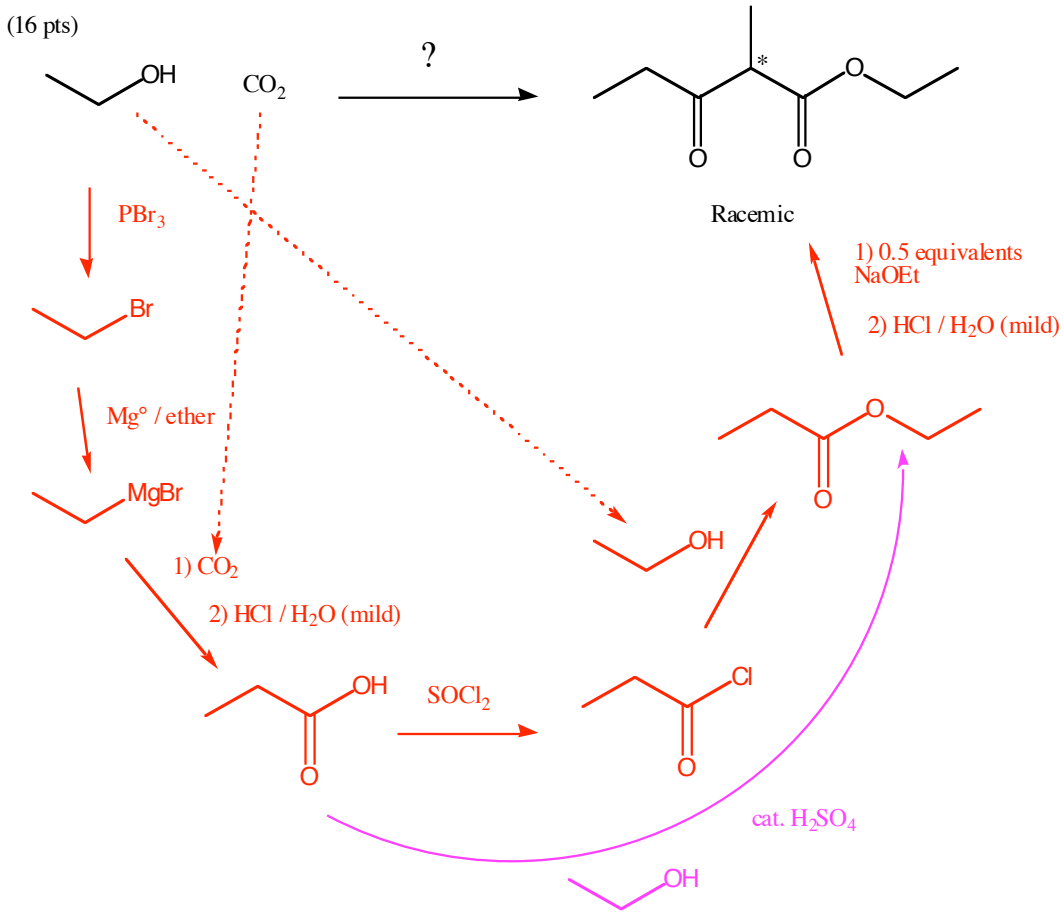
(7 pts)



Recognize the product as a β–hydroxy aldehyde, which is the product of an aldol reac tion before dehydration. This aldo requires acetaldehyde, which is made conveniently from reduction of the ethyl acetate starting material using $LiAlH_4$, followed by oxidation using PCC. Note there are several acceptable alternative ways to make the acetaldhyde from ethyl acetate including DIBAL-H reduction or hydrolysis followed by oxidation/reduction.

21. For the following synthesis questions, show how the starting material can be converted into the product. Show ALL intermediate molecules synthesized along the way, and show the reagents needed for each step. To get full credit, you must use the predominant product expected for each step. All of the carbon atoms of the product must come from the starting material(s).

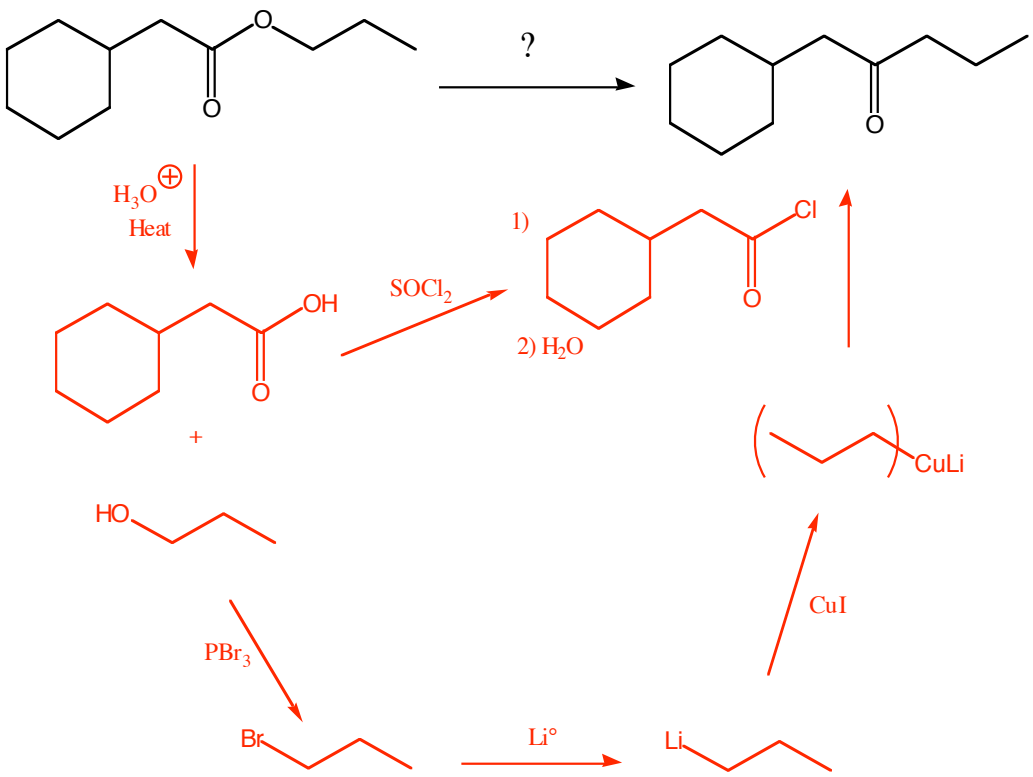
(16 pts)



Recognize the product as that of a Claisen reaction using ethyl propanoate. To make the three carbon acid, you need to add one carbon to ethanol , the easiest way to do this is via the Grignard and CO2. The resulting propanoic acid is then converted to the ethyl ester using either $SOCl_2$ then ethanol, or just ethanol and acid catalysis (Fischer esterification)

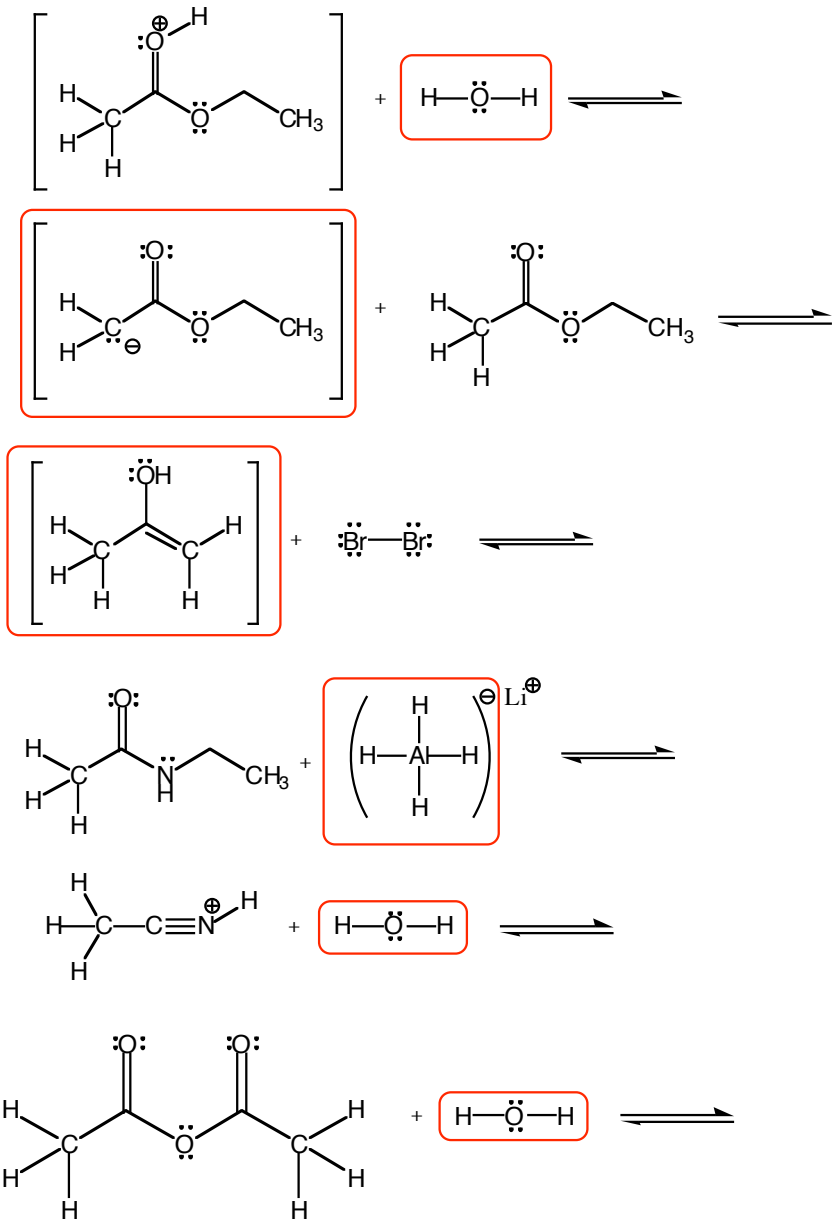
21. For the following synthesis questions, show how the starting material can be converted into the product. Show ALL intermediate molecules synthesized along the way, and show the reagents needed for each step. To get full credit, you must use the predominant product expected for each step. All of the carbon atoms of the product must come from the starting material(s).

(16 pts)

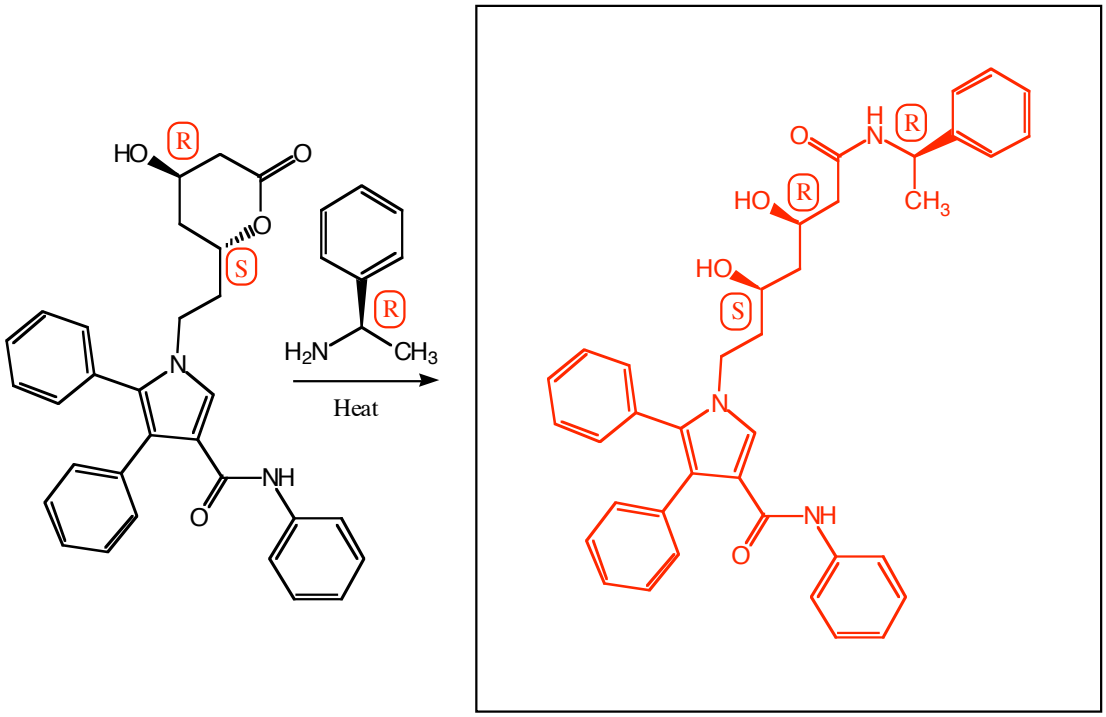


Recognize the product as being a ketone, the only reaction that creates a ketone with carbon-carbon bond formation is a acid chloride plus a Gilman reagent. The required acid chloride and Gilman reaction can be derived from the ester starting material via hydrolysis, formation of an acid chloride from the acid portion, and formation of a Gilman from the alcohol portion. Alternatively, the product ketone could be made from the oxidation of the corresponding secondary alcohol, which was synthesized using a Grignard reaction. The components of the Grignard reaction could once again come from hydrolysis of the starting ester.

22. (3 pts each) The mechanisms we have been studying largely involve nucleophiles of various types attacking electrophiles of various types, with protons being transferred quite often as well. The following reagents represent individual steps from some of these mechanisms. **For each pair of molecules, draw a circle around the nucleophile.** DO NOT DRAW THE PRODUCTS OF THESE STEPS. Do not make this hard. We are just checking that you are understanding these mechanisms, not just memorizing them.



23. (6 pts) One of the fundamental paradigms of organic chemistry is that a functional group reacts the same in a complex molecule as it does in a simple molecule. The following step was used in the synthesis of atorvastatin (Lipitor). Write the predominant product of the following transformation, including the correct stereochemistry. This will take you a while to draw and it is not worth that many points, so definitely leave it until the end.



The key to this problem is to realize that the upper cyclic portion of the starting molecule is a lactone, a cyclic ester. Esters react with amines with heating to give amides as shown in the product. Keeping track of the stereochemistry ca be accomplished by labeling each chiral center.