NAME (Print): _____

SIGNATURE: _____

Chemistry 310N
Dr. Brent Iverson
2nd Midterm
March 30, 2006

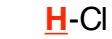
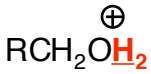
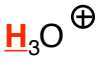
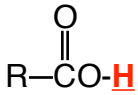
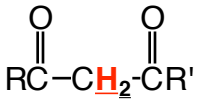
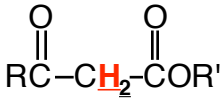
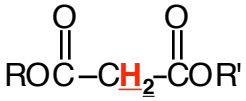
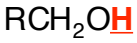
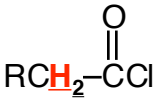
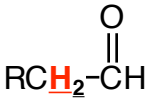
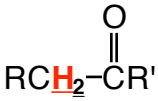
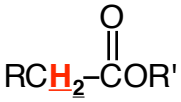
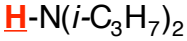
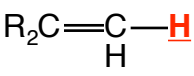
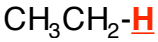
Please print the first three letters of your last name in the three boxes

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. **I recommend saving questions marked "challenge" until you are finished with all of the other questions.**

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!!!!

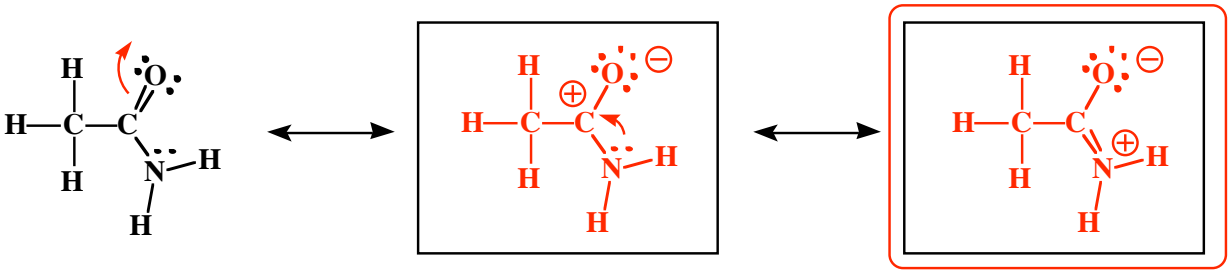
Page	Points	
1		(27)
2		(16)
3		(22)
4		(24)
5		(29)
6		(24)
7		(33)
8		(22)
9		(23)
10		(17)
11		(19)
12		(15)
Total		(271)
T Score		

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

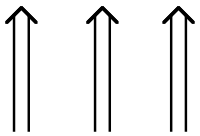
1. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We wil be looking for a minumum of 7 key points here.

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. (10 pts) On the left is drawn the Lewis structure of a simple amide. Draw the two next most important contributing structures in the spaces provided. Be sure to show all lone pairs and formal charges. You do not need to draw arrows on the structures, but you can if it helps you.



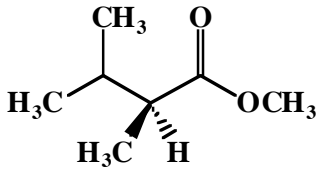
3. (3 pts) An important feature of an amide bond is that there is a partial double bond between the carbonyl carbon and nitrogen. For the contributing structures you drew in Problem **2.**, draw a circle around the one that predicts this partial double bond.



Notice This

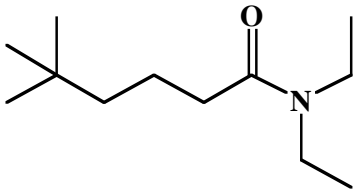
4. (4 pts each) Write an acceptable IUPAC name for the following molecules on the line provided.

A)



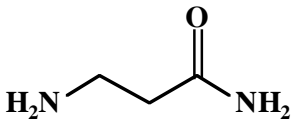
Methyl (S)-2,3-dimethylbutanoate

B)



***N,N*-diethyl-5,5-dimethylhexanamide**

C)



3-Aminopropanamide

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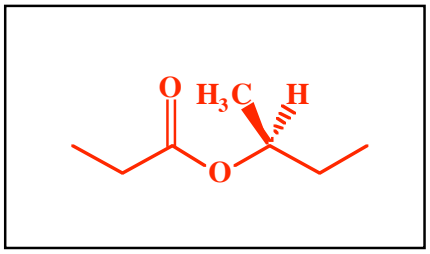
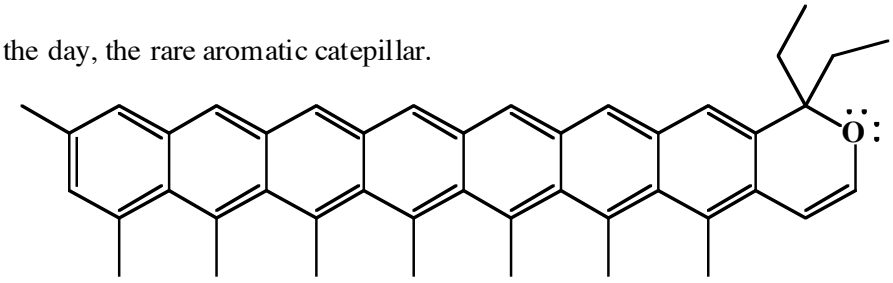
5. (4 pts each) Write the correct structure for the IUPAC name provided.

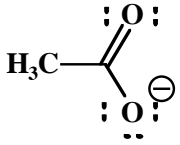
A) (S)-1-Methylpropyl propanoate



Molecule of the day, the rare aromatic catepillar.



6. (5 pts) Rank the following in terms of **relative anion stability with a 1 under the least stable anion** and a **5 under the most stable anion**.



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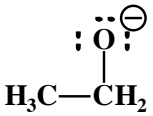
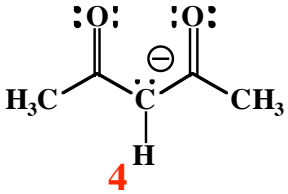


3



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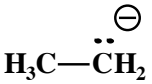
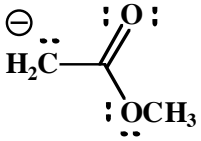
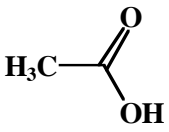


1

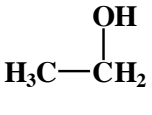


2

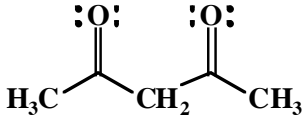
7. (5 pts) Rank the following in terms of **relative acidity with a 1 under the least acidic** and a **5 under the most acidic**



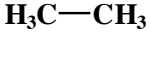
5



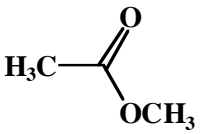
3



4

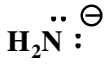


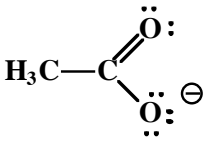
1

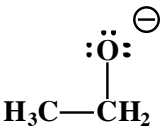


2

8. (8 pts) On the upper lines, rank the following with respect to relative anion stability, with a **1 under the least stable anion** (i.e. most reactive with a proton) and a **4 under the most stable anion** (*i.e.* least reactive with an proton). On the lower lines, rank the following with respect to leaving group ability, with a **1 under the worst leaving group**, and a **4 under the best leaving group**.



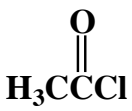




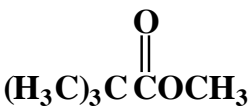
Anion Stability	4	1	3	2
Leaving Group Ability	4	1	3	2

9. (4 pts) Rank the following in terms of **relative reactivity with a nucleophile without acid catalysis**. **Place a 1 under the least reactive** and a **4 under the most reactive species**.

2



4

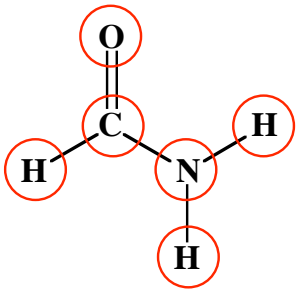


1

3

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

11. (6 pts) Because of the resonance you described earlier on page 1 of this exam, several atoms of an amide bond are in the same plane. On the amide below, circle all the atoms that are always in the same plane. Think carefully about this one!!

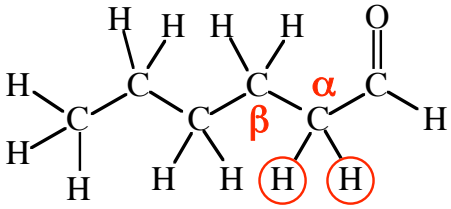


12. (6 pts) List two attributes of amide bonds that lead to stabilization of the folded structures of proteins.

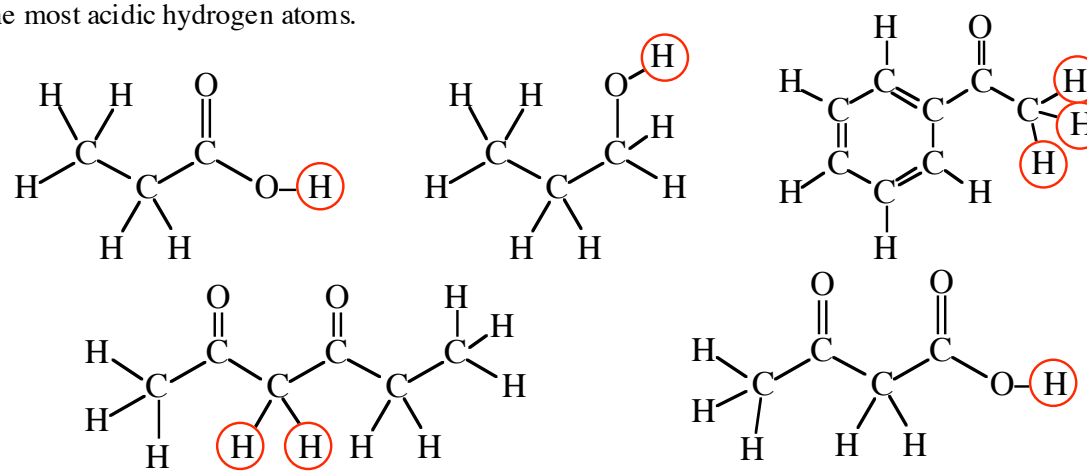
1) The amide carbonyl oxygen and hydrogen on nitrogen can make strong hydrogen bonds

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.

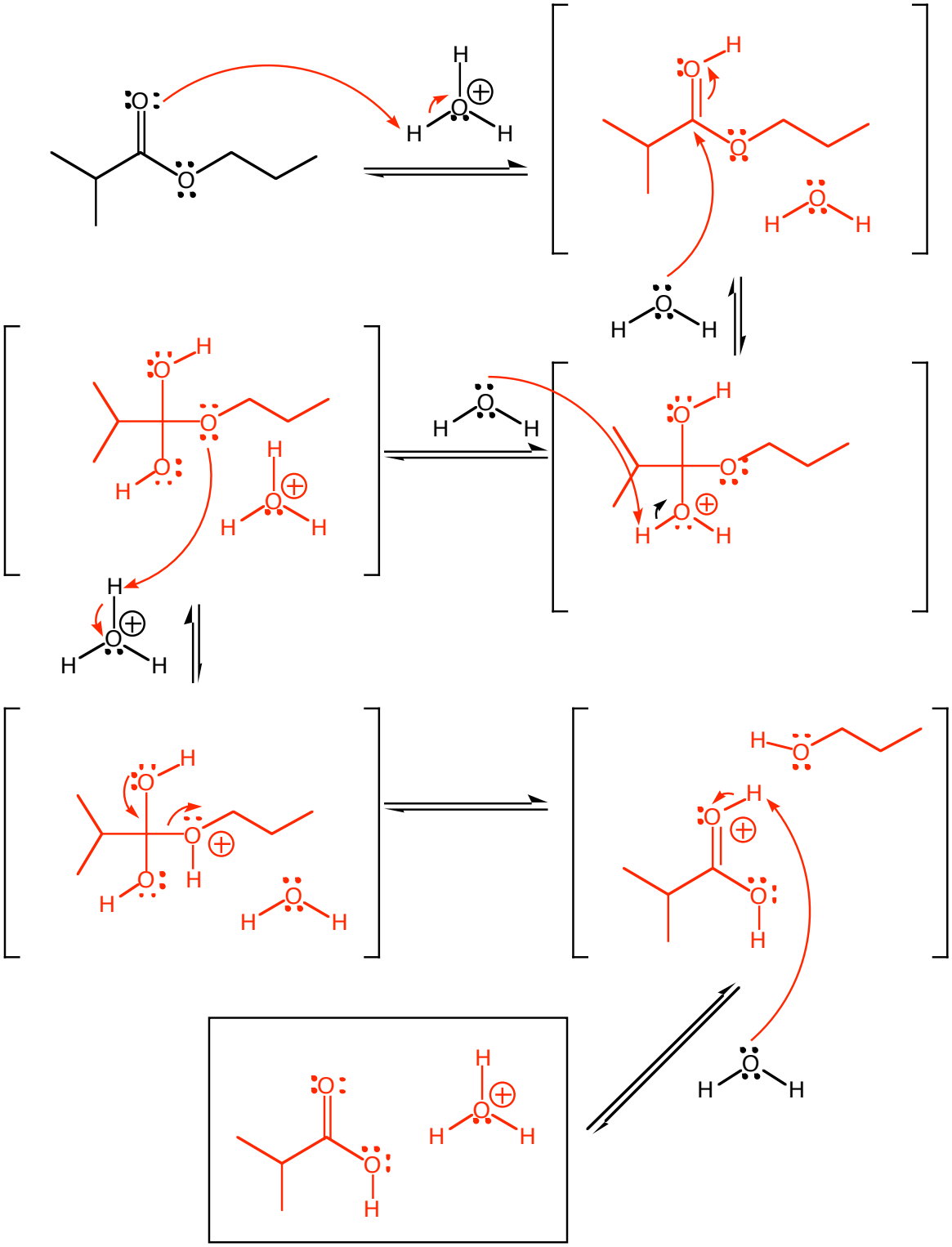
13. (4 pts) **A)** On the following molecule label the alpha carbon by putting an "α" next to it, and label the beta carbon by putting a "β" next to it. Draw a circle around the most acidic H atom(s) in the molecule. If there is a "tie" circle all the most acidic hydrogen atoms.



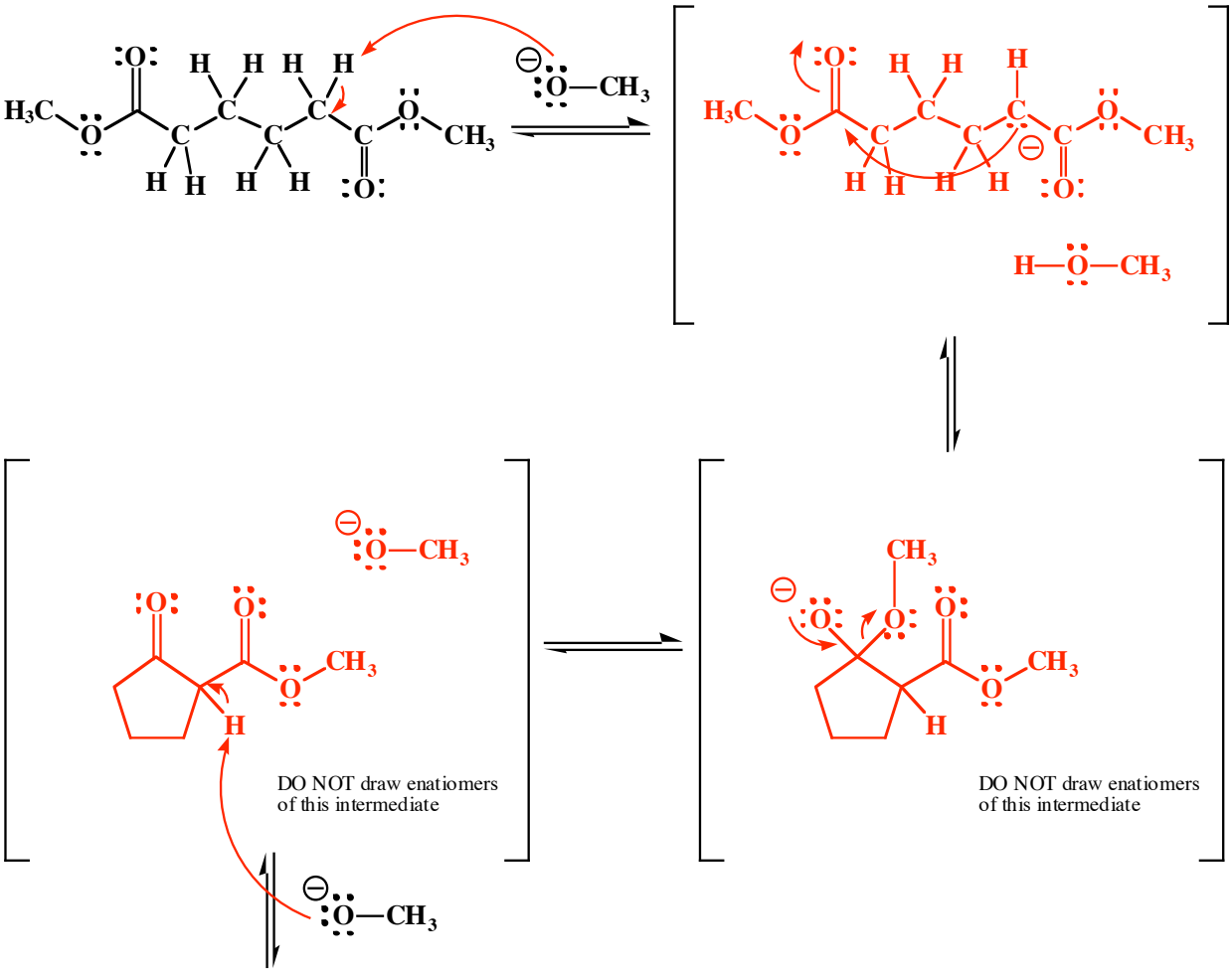
B) (8 pts) Draw a circle around the most acidic H atom(s) on each molecule. If there is a "tie" circle all the most acidic hydrogen atoms.

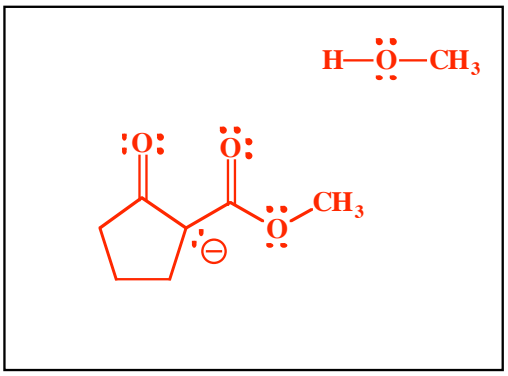


14. (29 pts.) Complete the mechanism for this lactone hydrolysis is aqueous acid. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.**



16. (19 pts) Fill in the missing structures for this Dieckmann reaction. **Draw arrows for each step to indicate the flow of electrons. Remember to draw all lone pairs and all formal charges. Remember to draw all the products for each step. Notice that for this one, you DO NOT need to draw the different enantiomers of the intermediates or products. It would take too much space.**

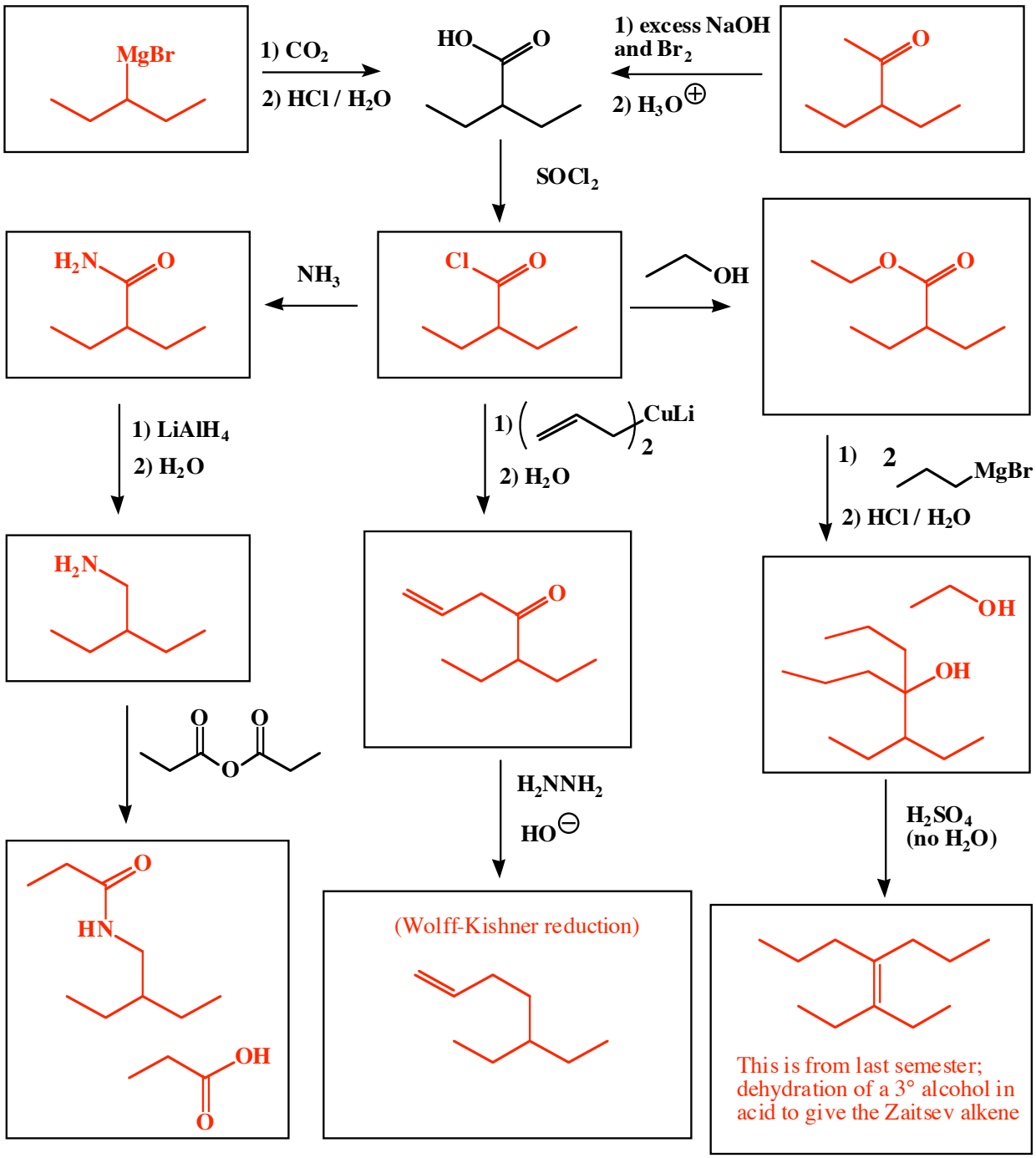




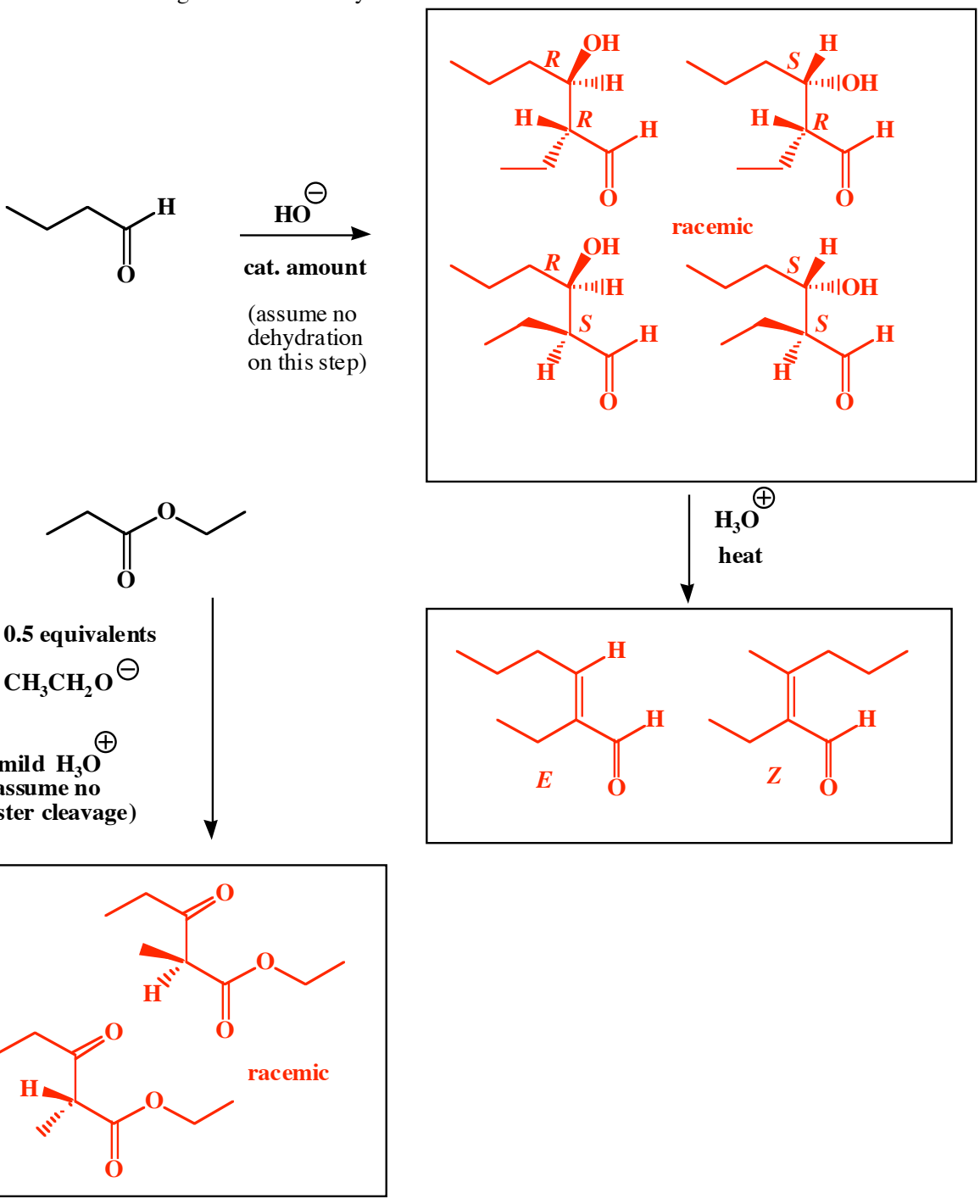
(5 pts) On the line below, based on your mechanism, state how many equivalents of methoxide ($CH_3O^{\ominus}$) relative to the starting diester are the minimum required for this reaction to go to completion.

1 Equivalent

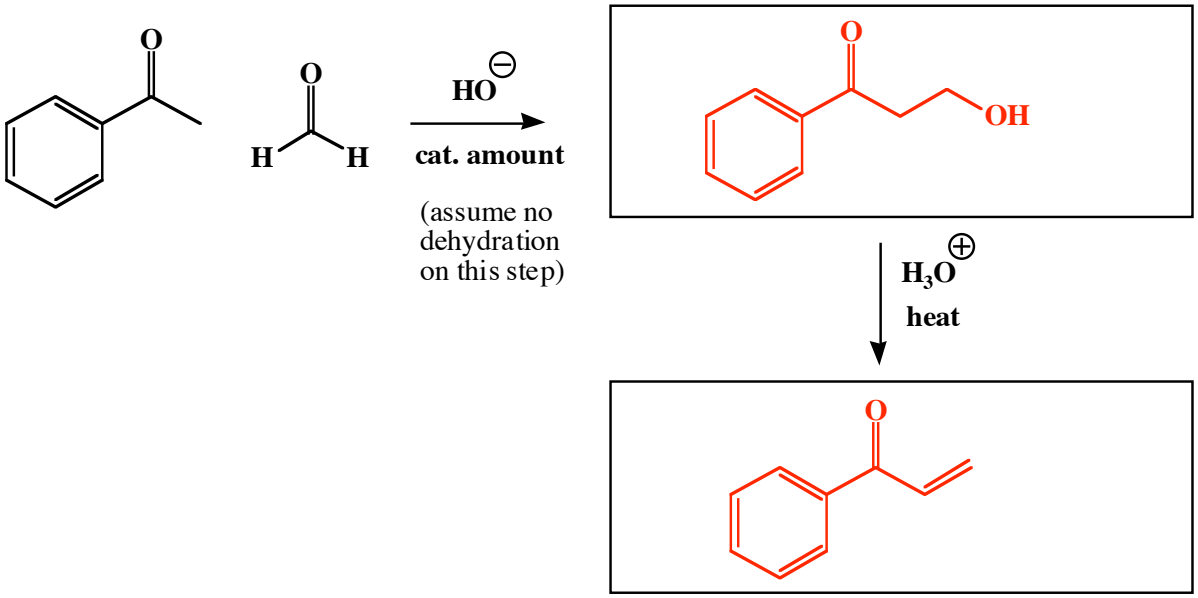
16. (3 or 5 pts each) Fill in the box with the product or products that are missing from the following chemical reaction equations. When a racemic mixture is formed, **you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES**.



16. (22 pts) Fill in the box with the product or products that are missing from the following chemical reaction equations. When a racemic mixture is formed, **you must DRAW ALL the STRUCTURES FORMED, then write "racemic" EVEN THOUGH YOU DREW all of the product enantiomers.** Assume that in the first step of the aldol reaction, there is no dehydration (loss of H_2O). If an E,Z mixture is formed as your product in any step **you must draw both the E and Z products.** These are a little harder due to the nature of the chemistry so take your time. These directions are new to you, so you might want to read them again to make sure you know what we want here.

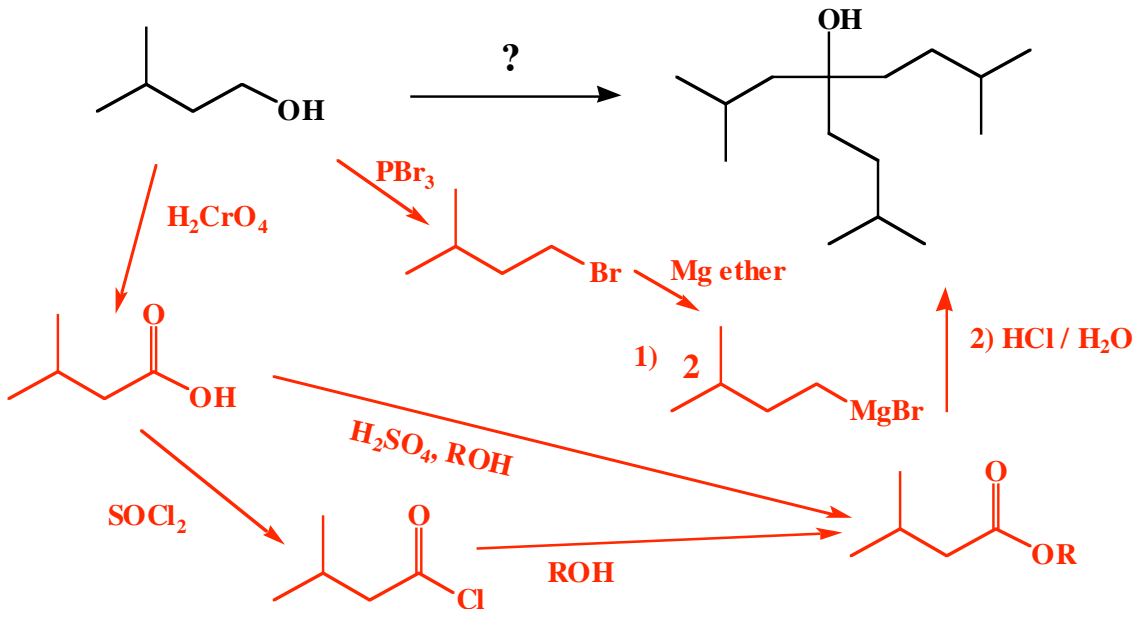


17. (3 or 5 pts each) Fill in the box with the product or products that are missing from the following chemical reaction equations. When a racemic mixture is formed, **you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES**. If an E,Z mixture is formed as your product in any step **you must draw both the E and Z products.**



18. (17 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.

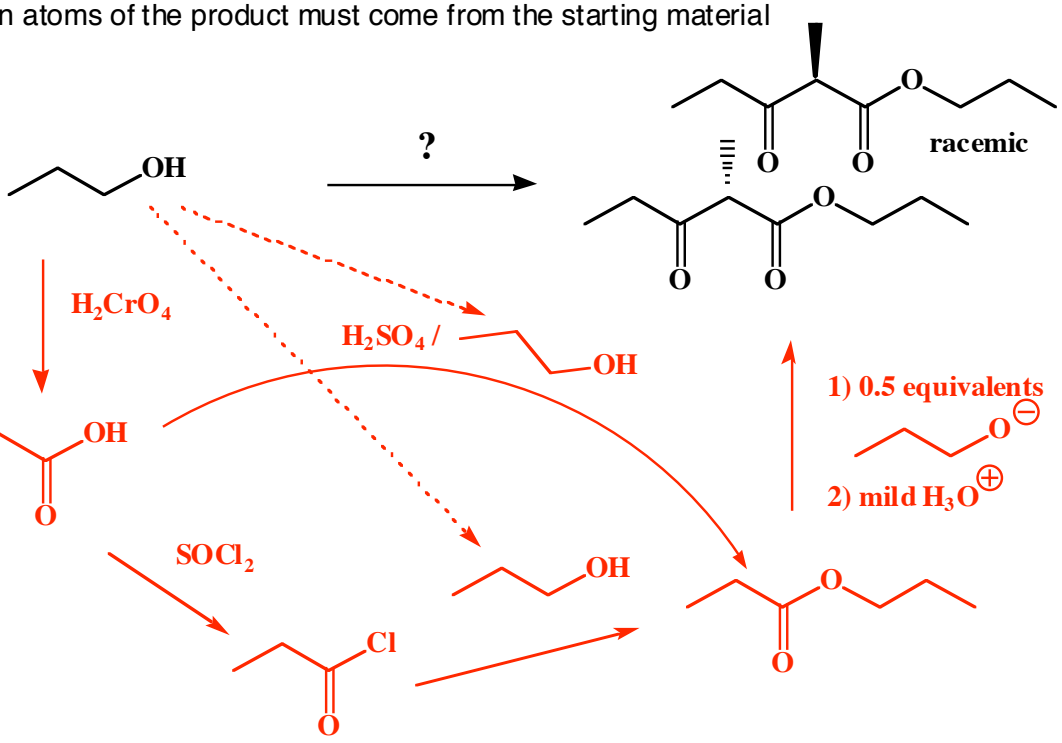
All the carbon atoms of the product must come from the starting material



18 (cont.) 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!

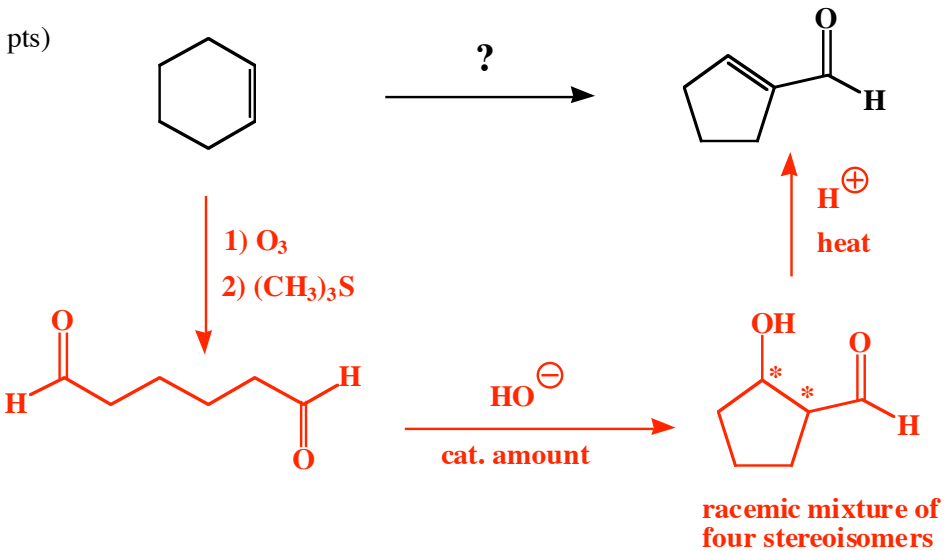
All the carbon atoms of the product must come from the starting material

(10 pts)



All the carbon atoms of the product must come from the starting material

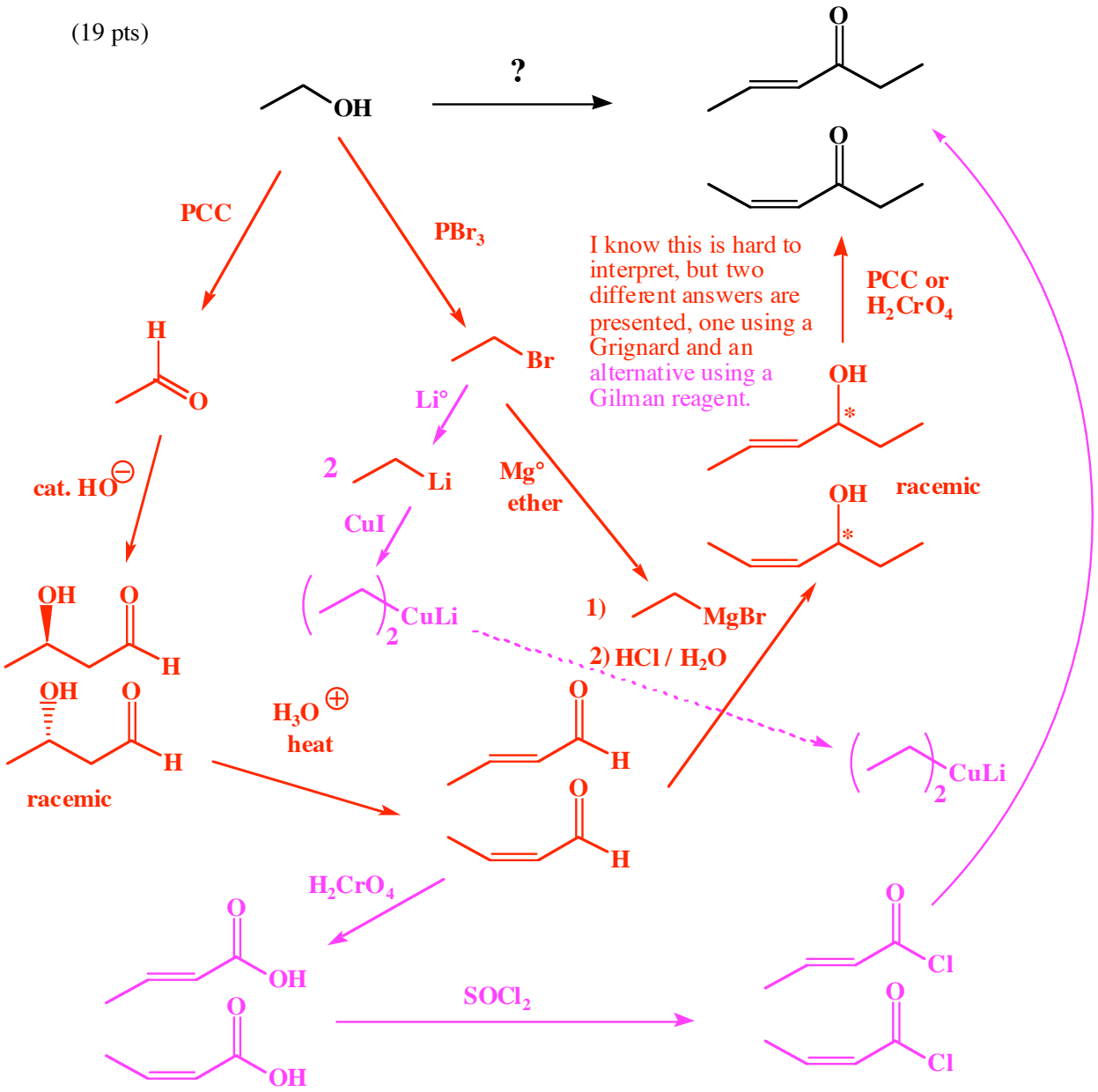
(7 pts)



18 (cont.) 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!

All the carbon atoms of the product must come from the starting material

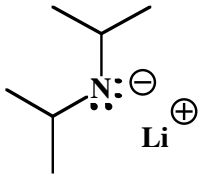
(19 pts)



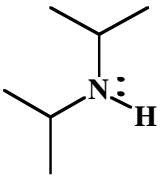
I know this is a tough one, but think about it systematically. You should be familiar with all of the chemistry required. It provides a nice example of how organic synthesis can be used to convert a relatively inexpensive and simple starting material such as ethanol into a relatively complex product such as the α,β-unsaturated ketone.

19. (15 pts) Save this until the end, it is an "apply what you know" question. Here is what you need to know; in most cases such as the examples below, **proton transfer takes place much, much faster than other types of reactions such as nucleophiles reacting with carbonyl groups**. Here is what you also do not know yet; LDA is a base that is used a great deal in organic synthesis because it is so sterically hindered by the isopropyl groups that it **cannot act as a nucleophile.** The pKa of the conjugate acid of LDA has been provided for your reference, it is also in the table at the front of the test.

(Challenge!)



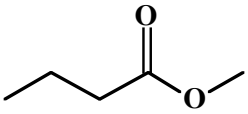
LDA



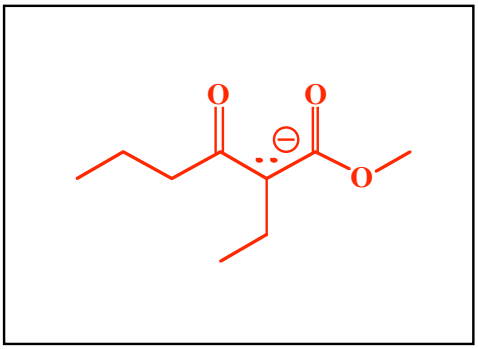
pK_a = 40

Given this information and your knowledge of the mechanism of the Claisen reaction, complete the following reactions by drawing the predominant product or products formed under the specified conditions.

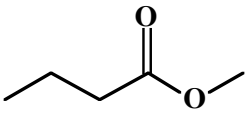
The key to this is pKa. LDA is such a strong base that it quantitatively converts the starting ester to an enolate.



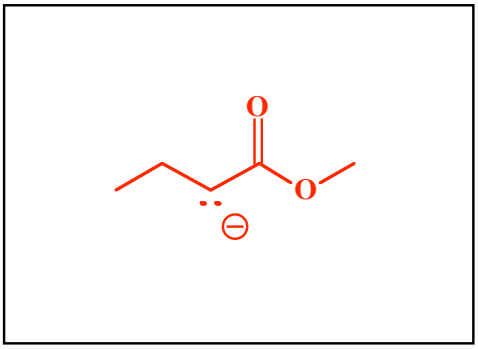
0.5 equivalent of LDA →



If 0.5 equivalents of LDA is used, only half of the ester is converted to enolate. The remaining half of the ester sample can react with the enolate to give the Claisen product.

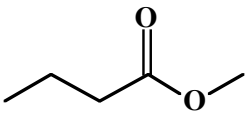


1.0 equivalent of LDA →

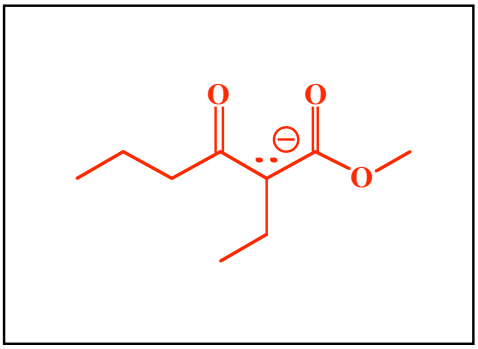


If 1.0 equivalents of LDA are used, the ester sample is completely converted to an enolate. With no ester to react with, the enolate itself is the product of this process.

Much weaker base



1.0 equivalent of $CH_3O^{\ominus}$ →



Even if 1.0 equivalents of $CH_3O^{\ominus}$ are used, equilibrium still favors ester starting material (by a lot), so the small amount of enolate that forms has plenty of ester to react with. leading to complete conversion to the Claisen product.