

NAME (Print): \_\_\_\_\_

Chemistry 310N  
Dr. Brent Iverson  
2nd Midterm  
March 25, 2010

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.

**You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK will be regraded.**

**Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.**

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

Page	Points
1	(26)
2	(28)
3	(18)
4	(18)
5	(18)
6	(18)
7	(16)
8	(33)
9	(28)
10	(17)
11	(14)
12	(10)
13	(0)
14	(18)
15	(10)
16	(16)
17	(6)
Total	(294)
%	
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.

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(Your signature)

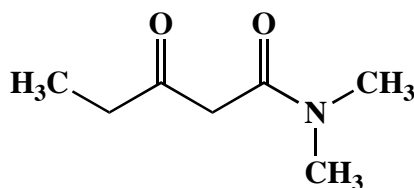
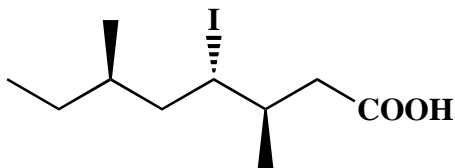
Compound		pK <sub>a</sub>
Hydrochloric acid	$\text{H-Cl}$	-7
Protonated alcohol	$\text{RCH}_2\text{OH}_2^{\oplus}$	-2
Hydronium ion	$\text{H}_3\text{O}^{\oplus}$	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-5
Ammonium ion	$\text{H}_4\text{N}^{\oplus}$	9.2
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CR}'$	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	$\text{HOH}$	15.7
Alcohols	$\text{RCH}_2\text{OH}$	15-19
Acid chlorides	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	16
Aldehydes	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	18-20
Ketones	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CR}'$	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	$\text{H}-\text{N}(\text{i-C}_3\text{H}_7)_2$	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

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Pg 1 \_\_\_\_\_(26)

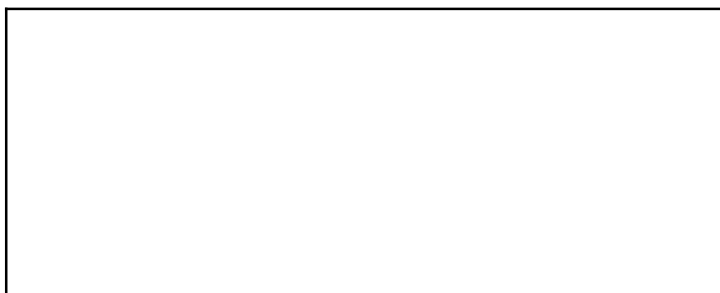
1. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

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

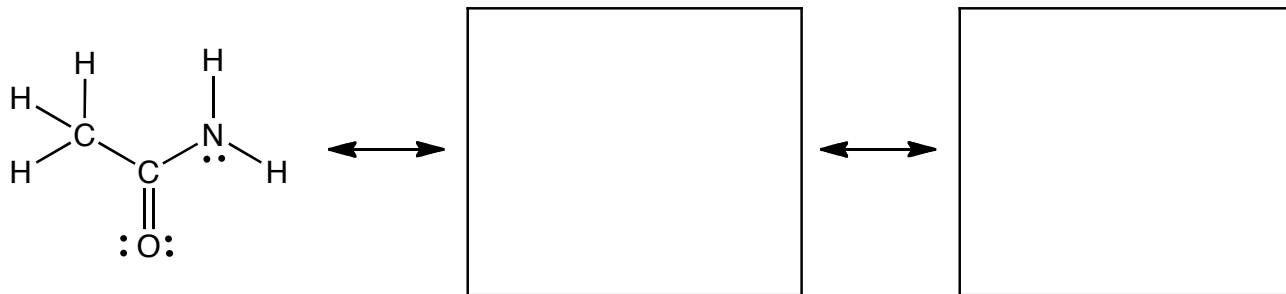


3. (4 pts) In the space provided, draw the following molecule:

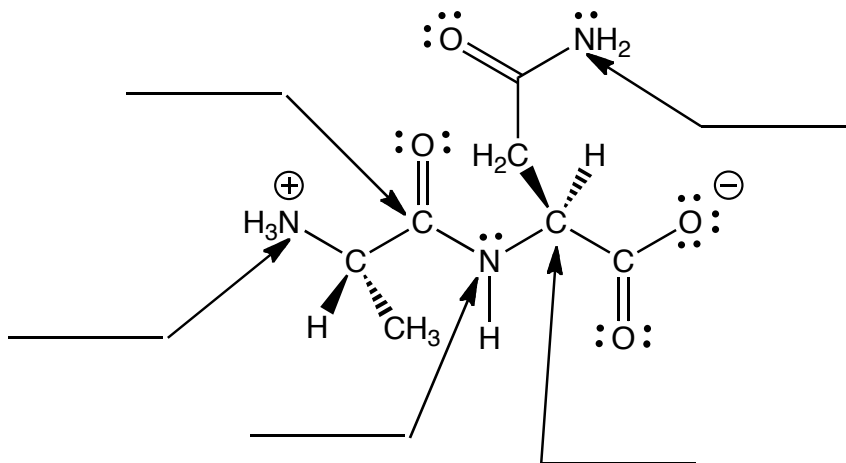
*Cis*-Diisopropyl cyclopentane-1,3-dicarboxylate



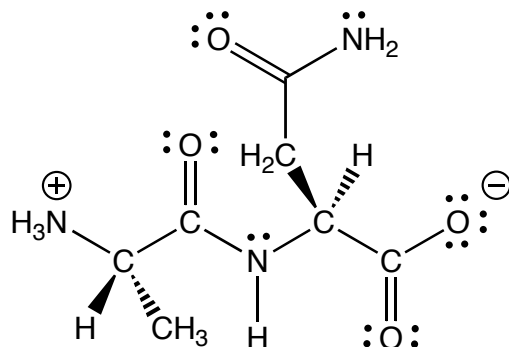
4. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



5. (10 points) On the lines, indicate the hybridization state of each atom indicated by the arrows.



6. (6 points) On the following structure circle all of the C-N bonds that DO NOT ROTATE.

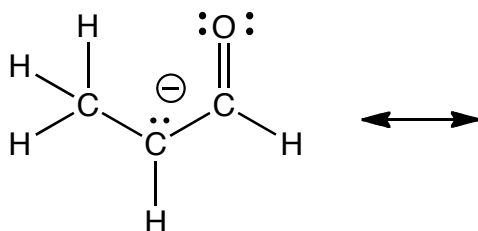
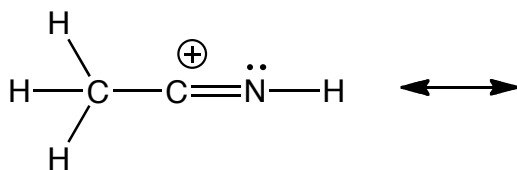
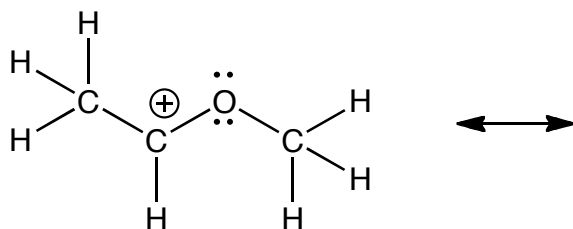
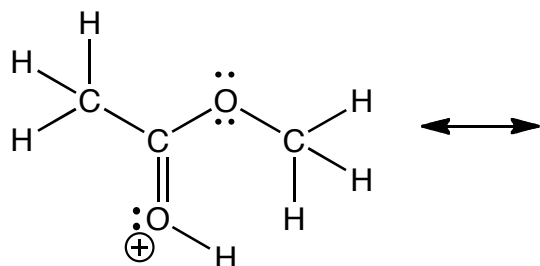


(4 pts) For the above structure, is this the appropriate protonation state for pH 2.0, 7.0, or 10.0?

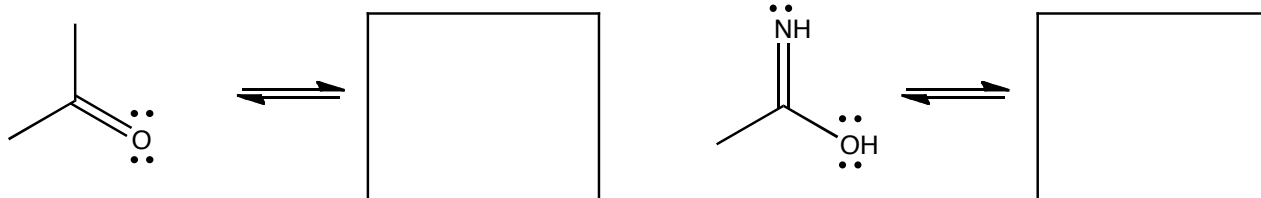
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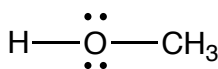
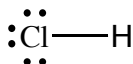
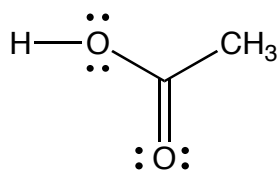
7. (18 points) For each of the following molecules, draw the other important resonance contributing structure. Be sure to show all lone pairs and formal charges. **In each case, add arrows to the structure on the left to indicate electronic rearrangement leading to the structure you drew on the right.**



8. (6 points) Each of the following undergo the process of tautomerization. For each draw the other major tautomer, then for each pair, circle the tautomer that is more stable.



9. (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.



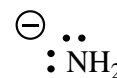
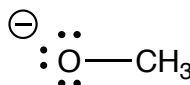
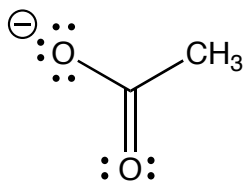
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10. (4 points) Rank the following with respect to anion stability. Write a 1 under the most stable anion, and a 4 under the least stable anion.



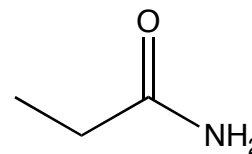
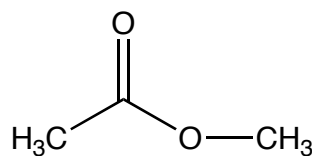
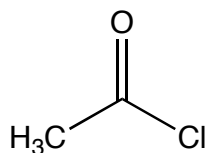
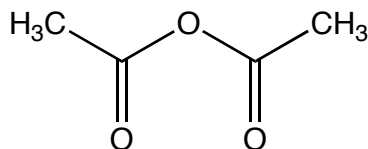
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11. (4 points) Rank the following carboxylic acid derivatives with respect to reactivity with a nucleophile. Write a 1 under the most reactive, and a 4 under the least reactive derivative.



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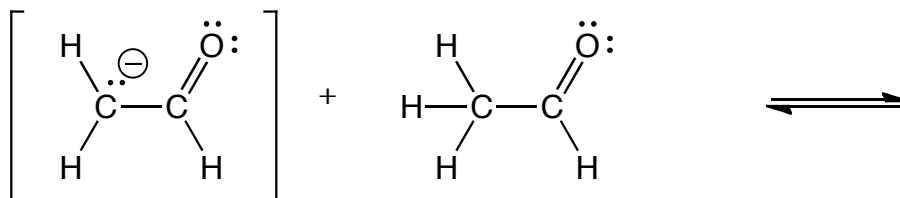
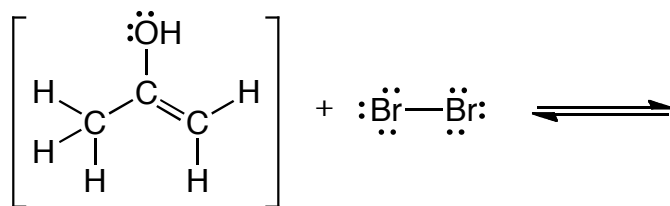
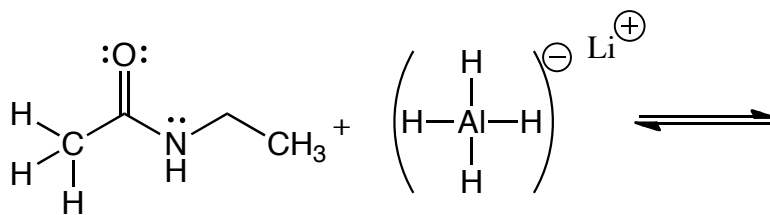
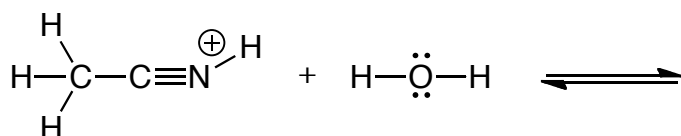
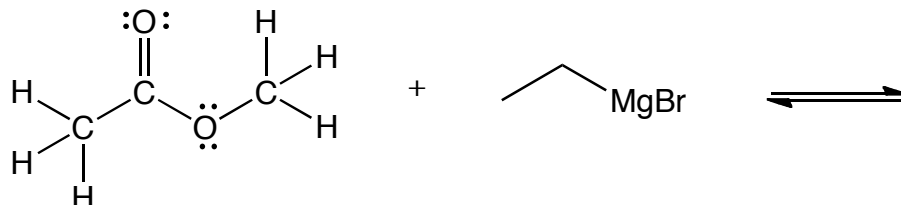
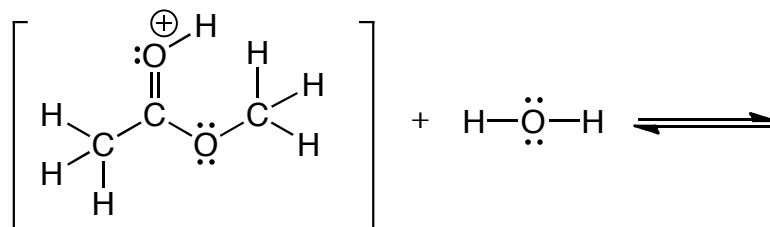
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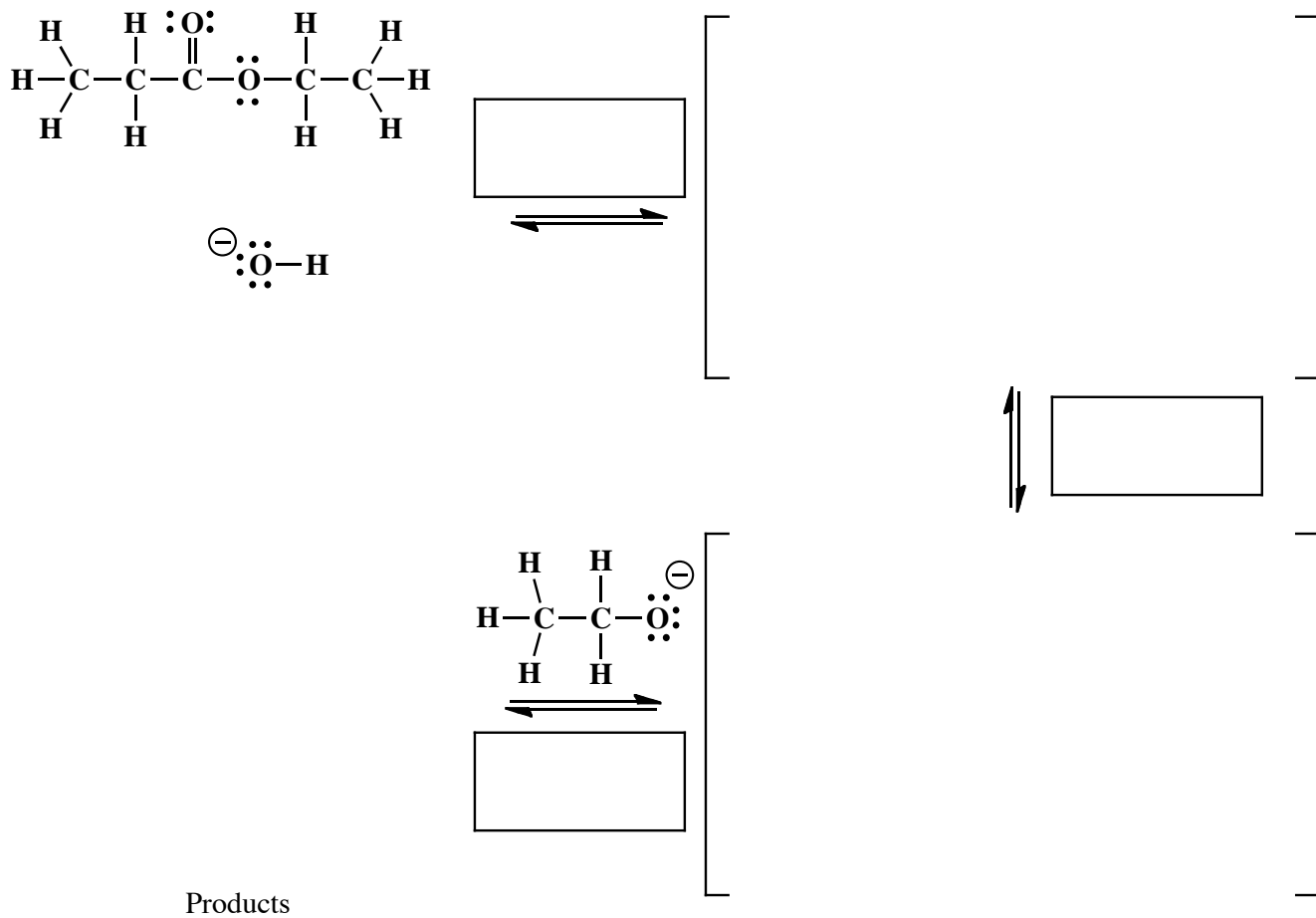
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12. (3 pts each) The mechanisms we have been studying largely involve nucleophiles of various types attacking electrophiles of various types, with protons being transferred quite often as well. The following reagents represent individual steps from 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.



13. (18 pts. total) 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 THE PRODUCTS, MARK IT WITH AN ASTERISK and WRITE RACEMIC IF RELEVANT.**

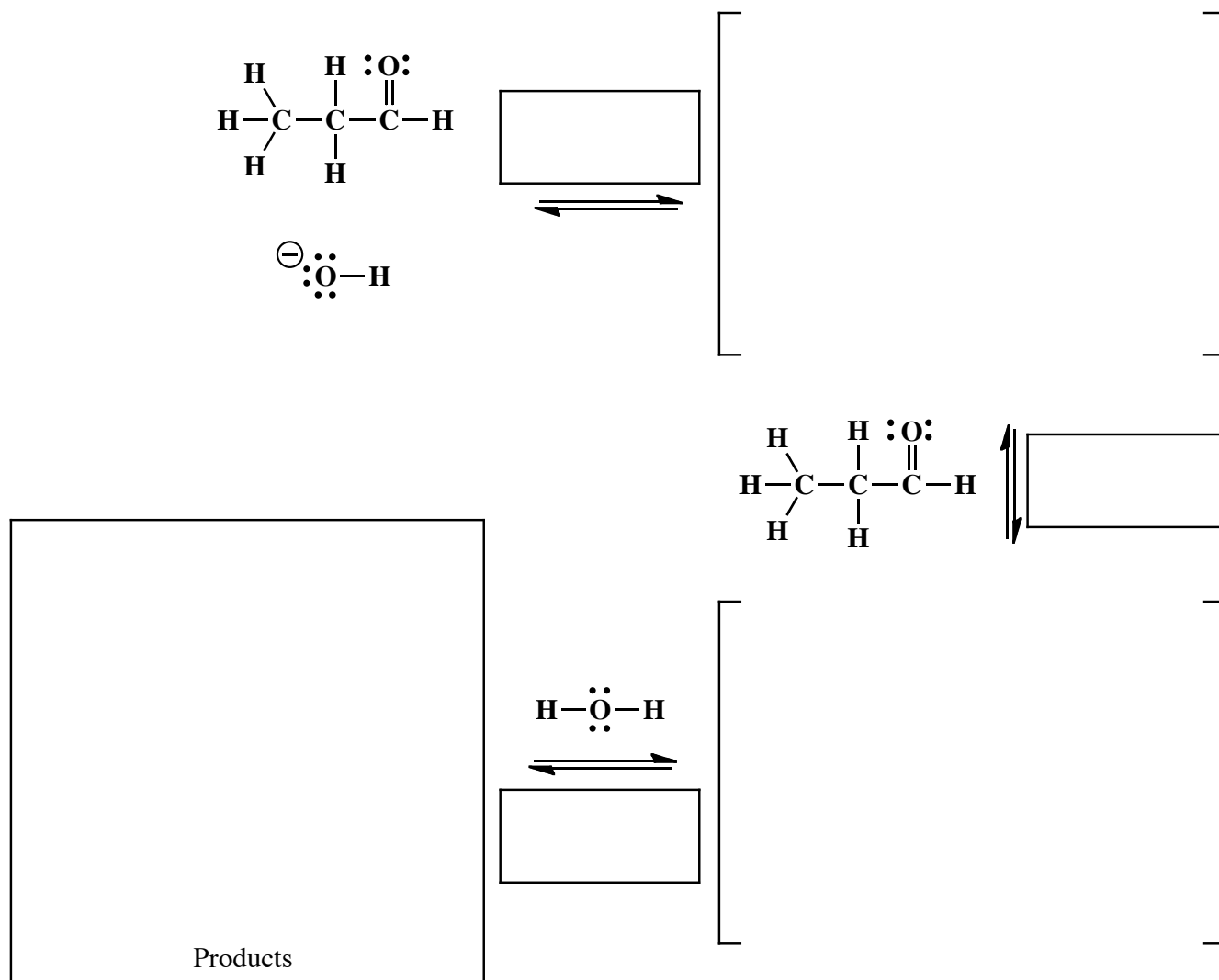


(1 pt each) In the boxes provided adjacent to the arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.)

**NOTICE THESE**

(4 Pts) In one sentence explain why this reaction is referred to as base "promoted" rather than base "catalyzed".

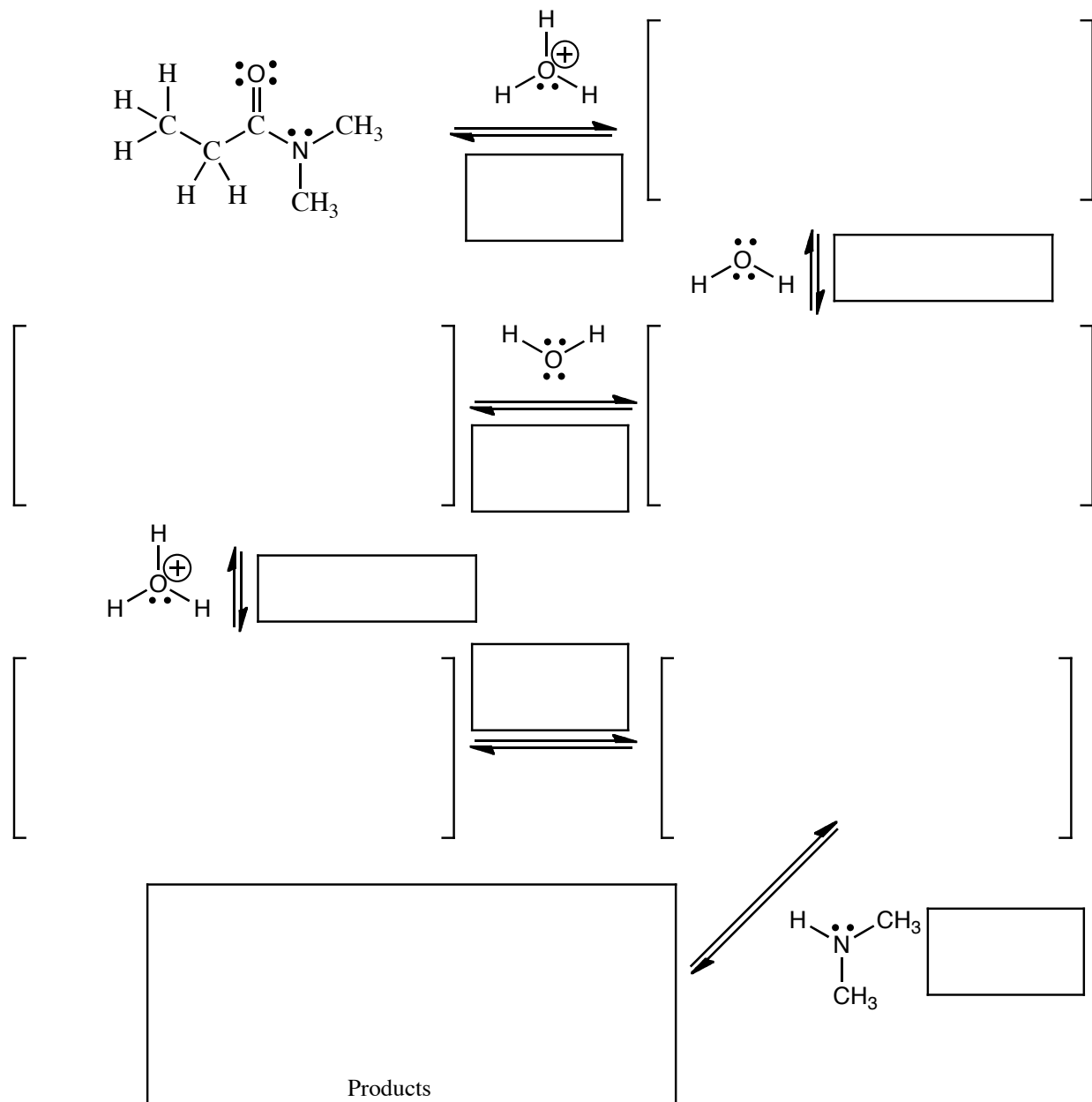
13. (16 pts. total) Complete the mechanism for the following **aldol** reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR THE PRODUCTS, MARK IT WITH AN ASTERISK and WRITE RACEMIC IF RELEVANT.**



(1 pts each) **In the boxes provided adjacent to the arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.)**

↖ **NOTICE THIS**

13. (33 pts. total) Complete the mechanism for the following **acid promoted 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 WRITE RACEMIC IF RELEVANT.**

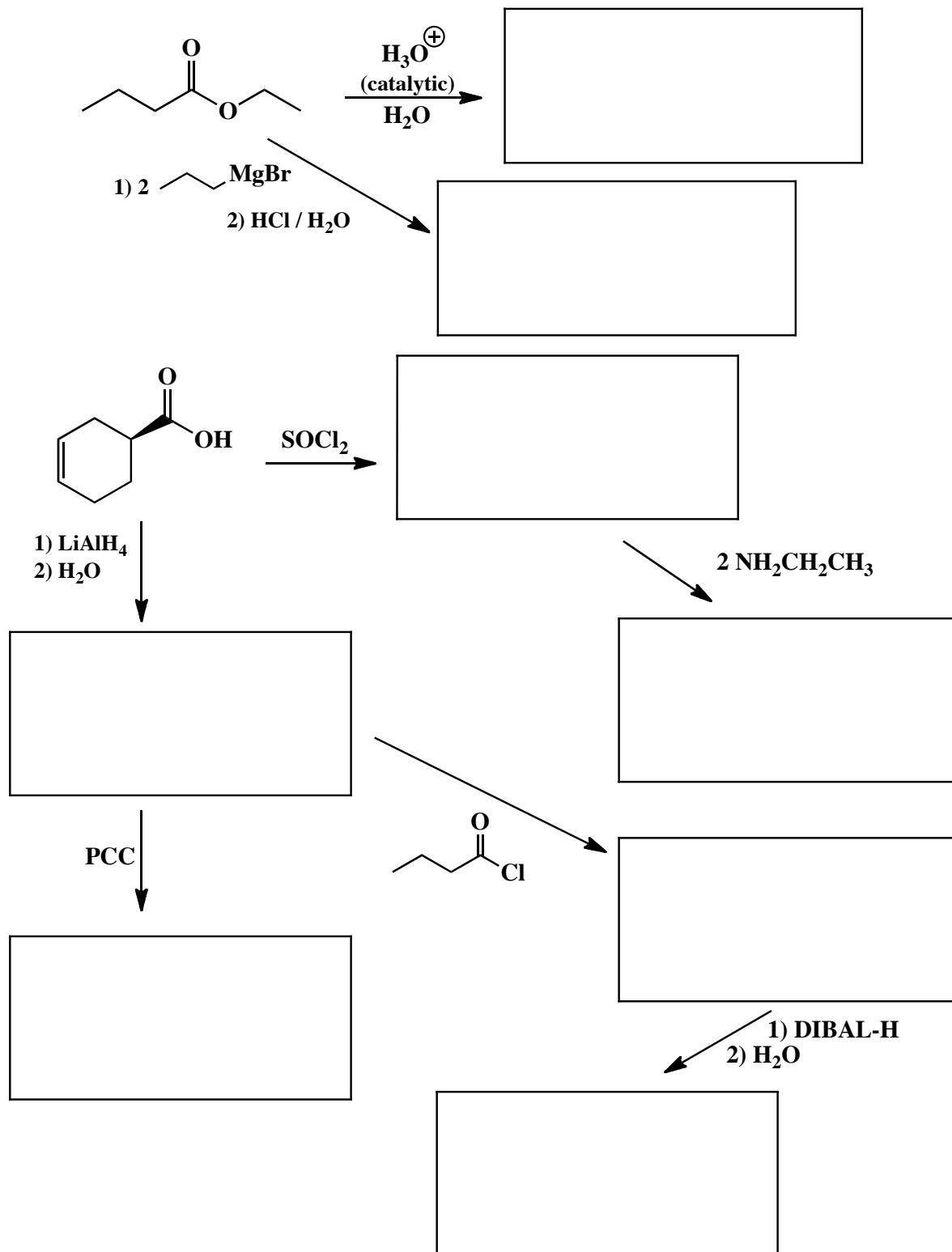


(1 pt each) In the boxes provided adjacent to the arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.)

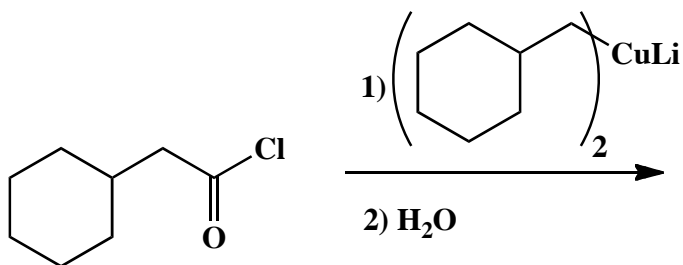
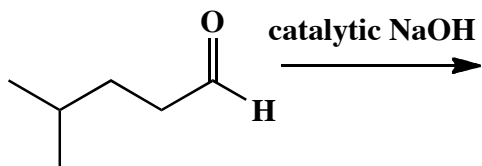
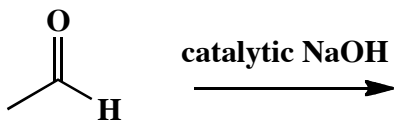
**NOTICE THESE**

(4 Pts) In one sentence explain why this reaction is referred to as acid "promoted" rather than acid "catalyzed".

14. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw all enantiomers and write "racemic" under the structure. Use wedges (  $\blacktriangleleft$  ) and dashes (  $\dashv$  ) to indicate stereochemistry. To get full credit, you must write products that account for ALL of the carbon atoms of the starting material even in multi-step reactions. DO NOT DEHYDRATE DURING AN ALDOL REACTION -WRITE THE NON-DEHYDRATED PRODUCT.

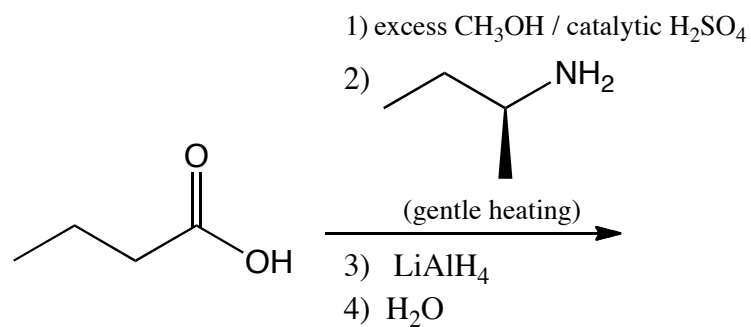


15. (3, 5 or 9 pts) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw all enantiomers and write "racemic" under the structure. Use wedges (  $\blacktriangleleft$  ) and dashes (  $\cdots$  ) to indicate stereochemistry. **DO NOT DEHYDRATE DURING AN ALDOL REACTION -WRITE THE NON-DEHYDRATED PRODUCT.****

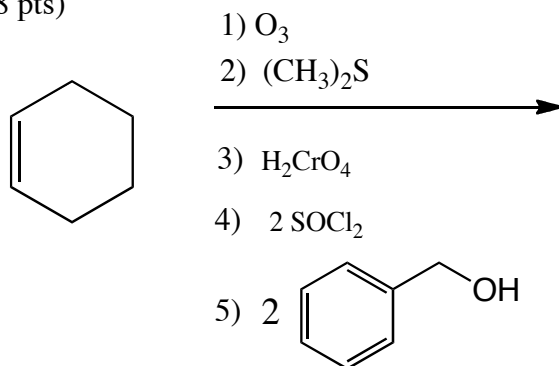


16. (14 points) For the following sequences of reactions, draw the final organic product or products after ALL the steps have been completed. You do not need to draw the molecules synthesized along the way, **only the last product that is formed**. If a new chiral center is created in the reaction that 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 this one.

(6 pts)



(8 pts)

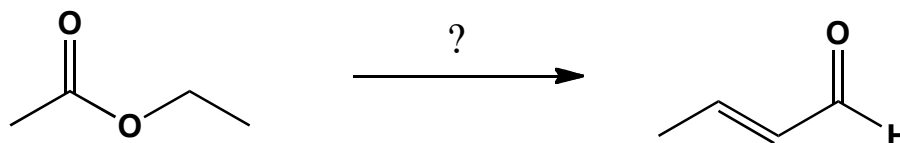


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Pg 12 \_\_\_\_\_(10)

17. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction.

(10 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**



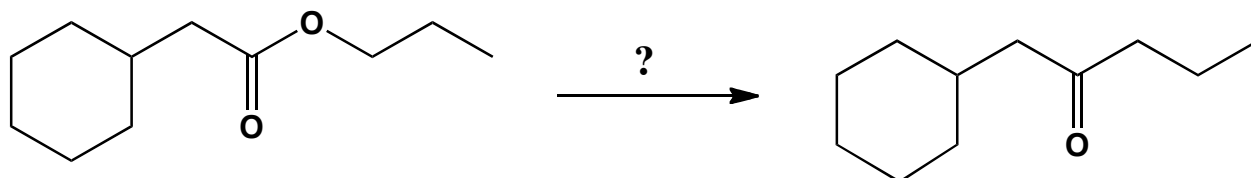


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Pg 14 \_\_\_\_\_(18)

17. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction.

(18 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**

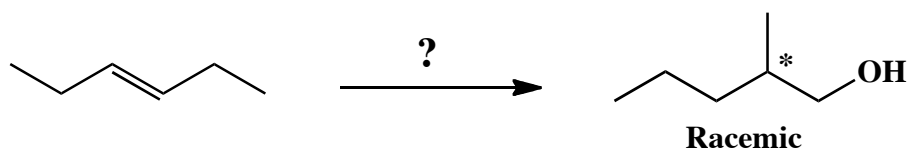


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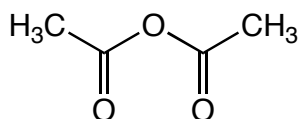
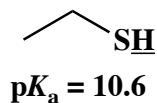
Pg 15 \_\_\_\_\_(10)

17. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction.

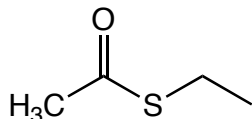
(10 pts) **All of the carbon atoms of the products must come from the starting materials for this one!**



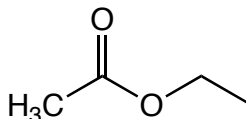
18. (16 pts) Here is an "apply what you know" question. The pK<sub>a</sub> for a thiol is given below. Given this information, predict the relative reactivities with nucleophiles of all of the following four carboxylic acid derivatives. Place a "1" under the most reactive and a "4" under the least reactive species.



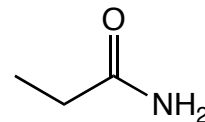
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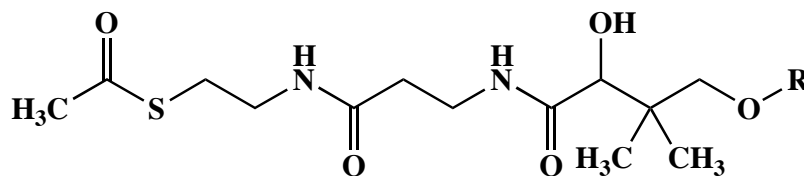
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In no more than three sentences explain your reasoning for the rankings you gave above.

The molecule AcetylCoA is very important in biochemistry. It reacts to make new bonds to carbon using mechanisms very similar to those we have seen for the carboxylic acid derivatives discussed in this class. On the following structure of Acetyl CoA, DRAW A CIRCLE AROUND THE ATOM that you predict will be attacked by nucleophiles to make new bonds. Base your answer on your responses to the first two parts of this question.



**Acetyl CoA**

In no more than two sentences explain your reasoning for the atom you circled.

19. (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.

