

NAME (Print): _____

Chemistry 320N
Dr. Brent Iverson
2nd Midterm
March 20, 2014

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	(25)
3	(16)
4	(18)
5	(35)
6	(30)
7	(35)
8	(19)
9	(15)
10	(10)
11	(13)
12	(22)
13	(4)
14	(12)
Total	(280)

Student Honor Code

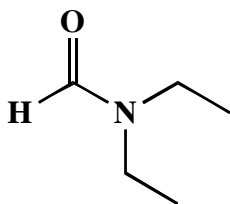
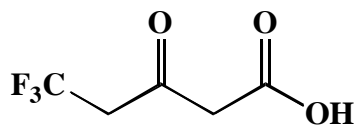
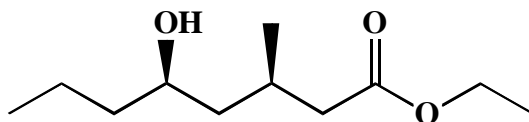
“As a student of The University of Texas at Austin, I shall abide by the core values of the University and uphold academic integrity.”

(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
Primary ammonium	$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_3$	10.5
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	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}-\text{Cl}$	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	$\text{H}-\text{N}(\text{i-C}_3\text{H}_7)_2$	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

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 each) In the space provided, draw the following molecule:

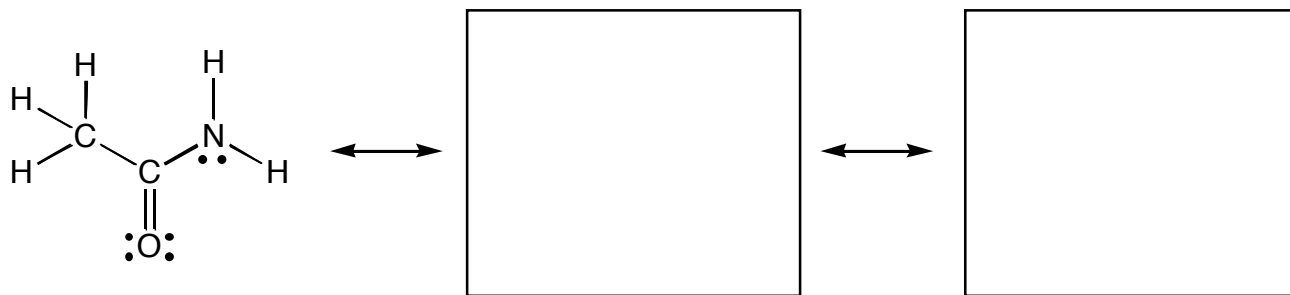
(R)-Isopropyl 3-methyl-4-oxohexanoate



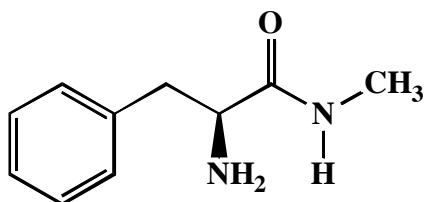
(3E,5Z)-3-Methyl-3,5-heptadienoic acid



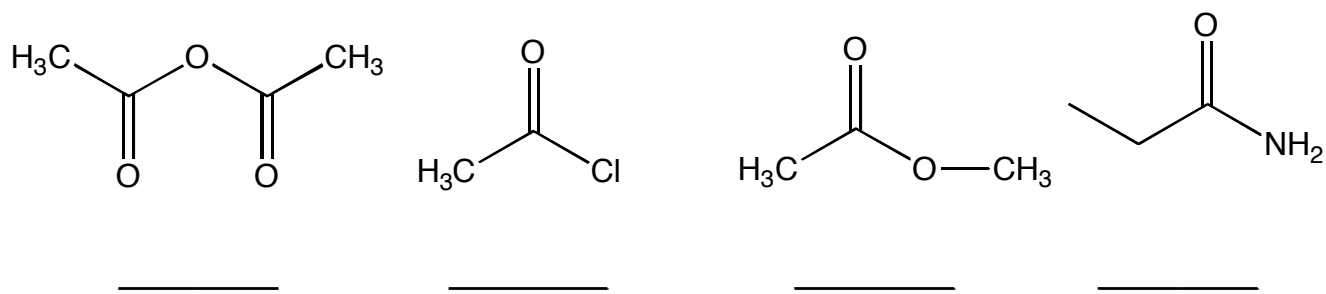
4. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



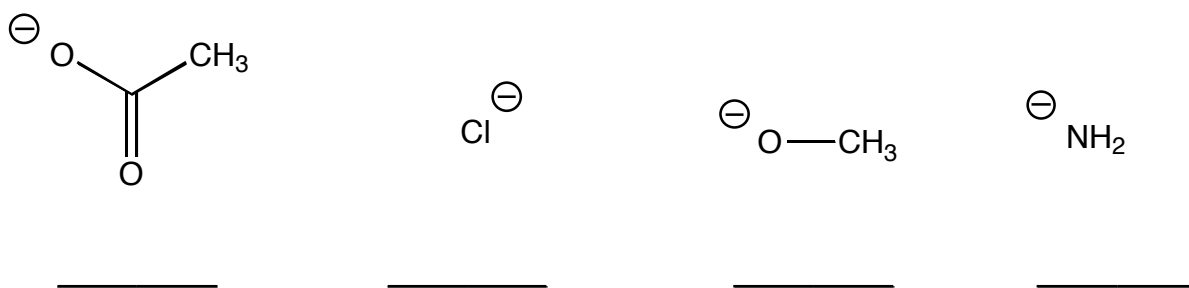
5. (9 points) Shown below is an amide formed between methyl amine and the amino acid phenylalanine. Draw a small circle around each sp^2 hybridized atom in the molecule.



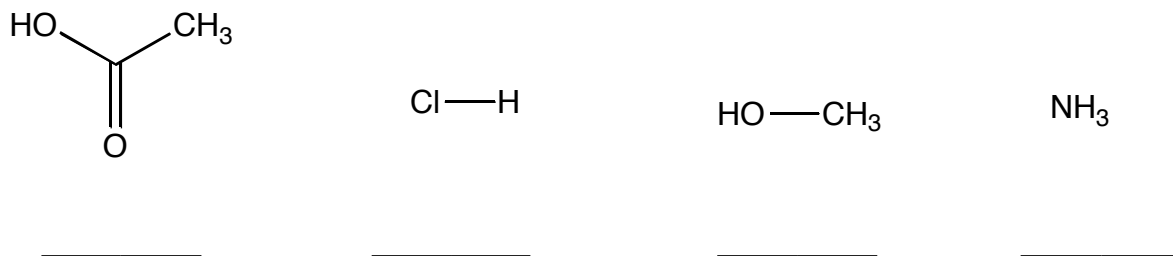
6. (4 points) Rank the following carboxylic acid derivatives with respect to reactivity with a nucleophile. Write a 1 under the most reactive, and a 4 under the least reactive derivative.



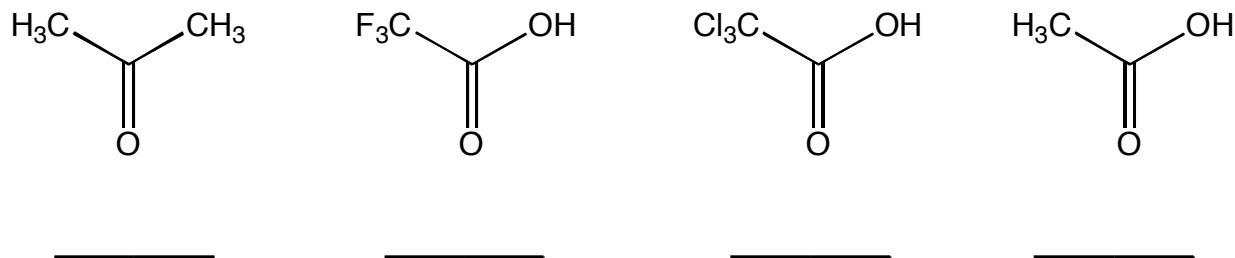
7. (4 points) Rank the following with respect to anion stability. Write a 1 under the most stable anion, and a 4 under the least stable anion.



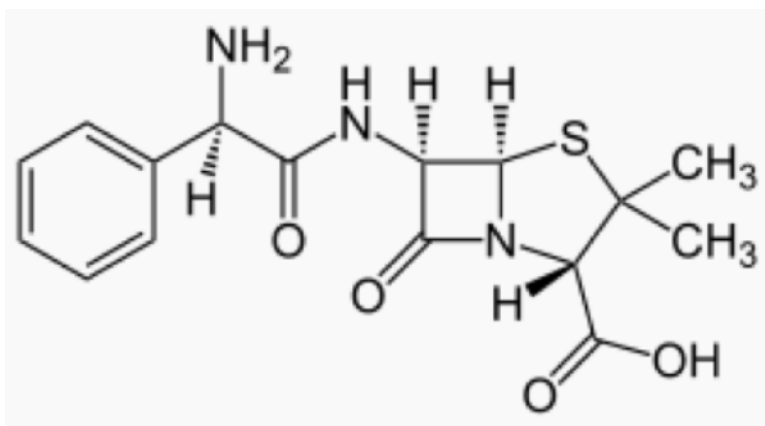
8. (4 points) Rank the following in terms of relative acidity, with a 1 under the most acidic, and a 4 under the least acidic molecule.



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.



10. (10 points) The following structure is that of ampicillin, a very common antibiotic used in the treatment of many bacterial infections. The following structure was copied directly from a Wikipedia page (<http://en.wikipedia.org/wiki/Ampicillin>). To the right of the structure are listed relevant pK_a values from the table at the beginning of the exam.



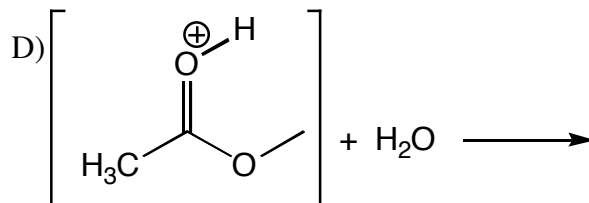
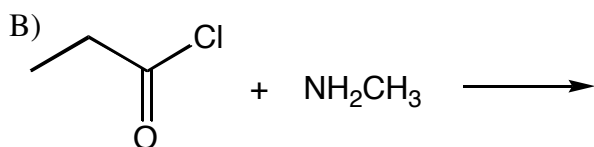
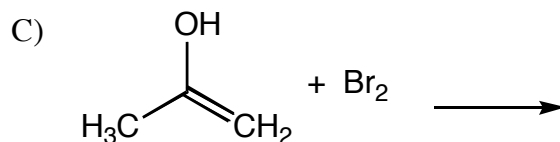
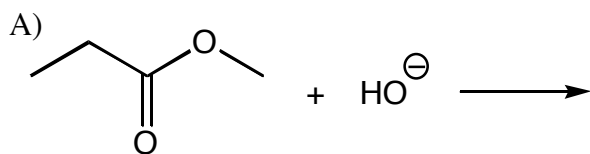
$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_3$	pK_a
Primary ammonium	10.5
$\text{R}-\text{C}(=\text{O})-\text{H}$	
Carboxylic acids	3-5

Based on the pK_a values given, what is the total charge on ampicillin in a solution of $\text{pH} = 2.0$? _____

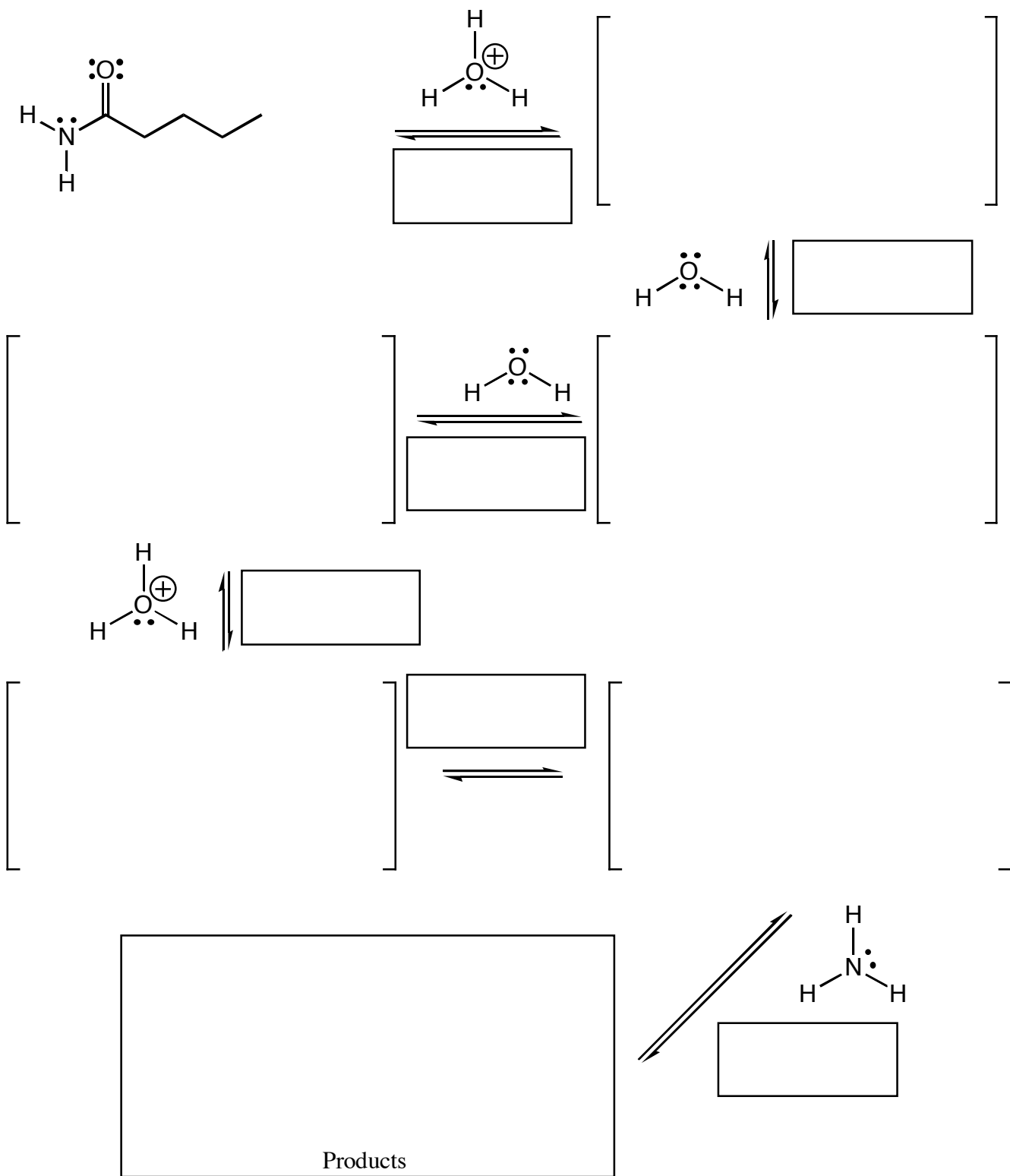
Based on the pK_a values given, what is the total charge on ampicillin in a solution of $\text{pH} = 7.0$? _____

In only two short sentences, describe two very different things that are wrong with the format of the ampicillin structure that I copied from Wikipedia. Hint; one of the answers to this question is related to the two questions you just answered. **You can assume the atoms are all in the correct places in the structure, we do NOT assume you know the structure of ampicillin by heart!**

11. (8 points) In the following reactions, draw a circle around the nucleophile. Note, there is no reason to write any products for these.

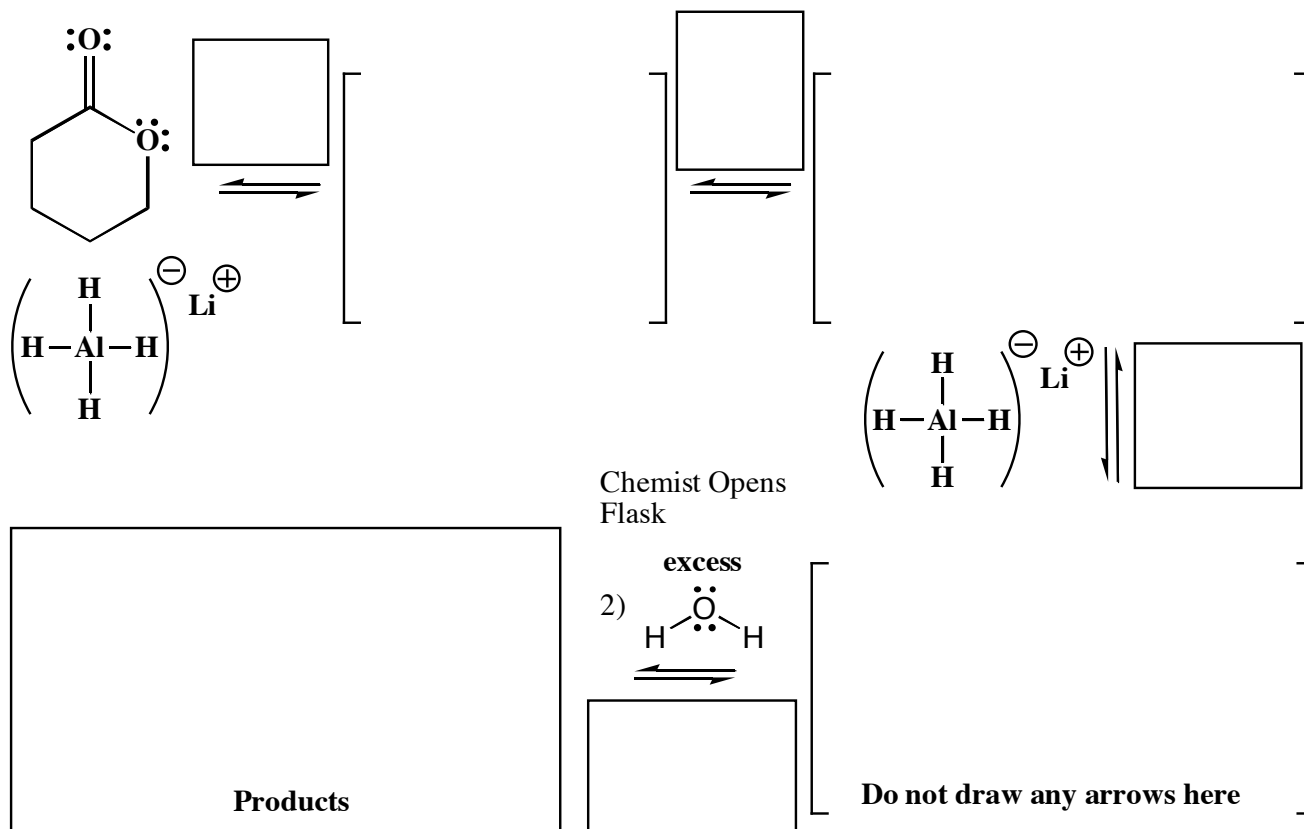
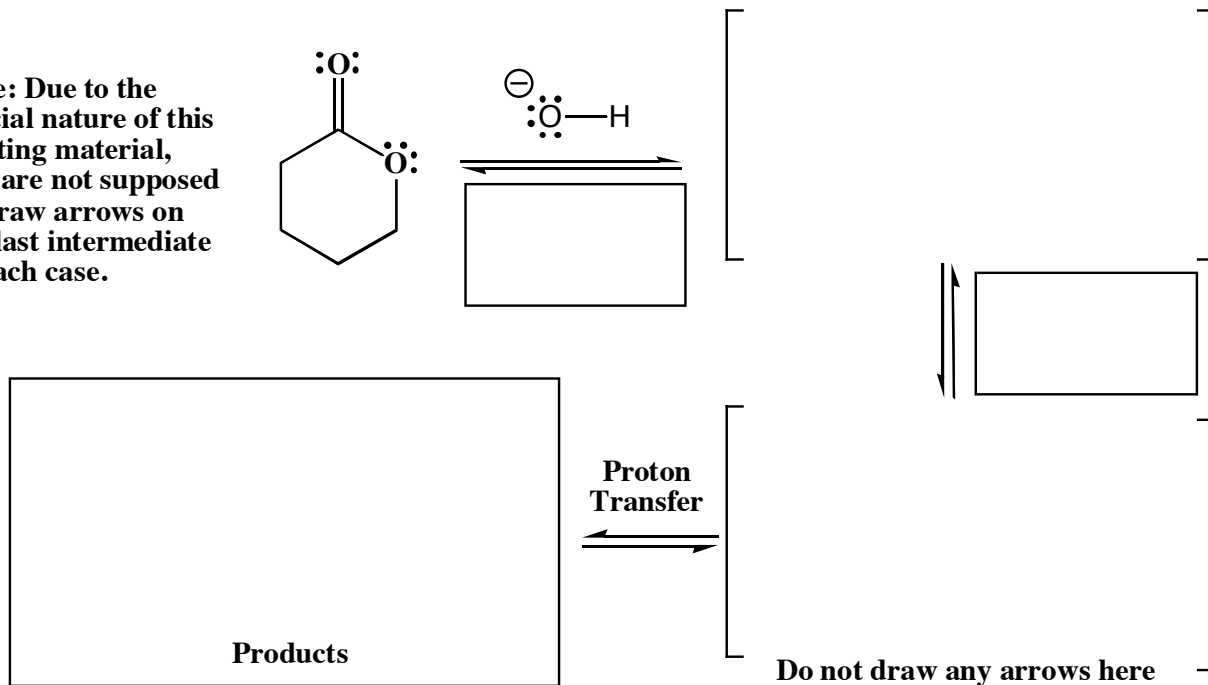


12. (35 pts) Complete the mechanism for the following amide hydrolysis reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL IT AS RACEMIC IF APPROPRIATE.** In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.).

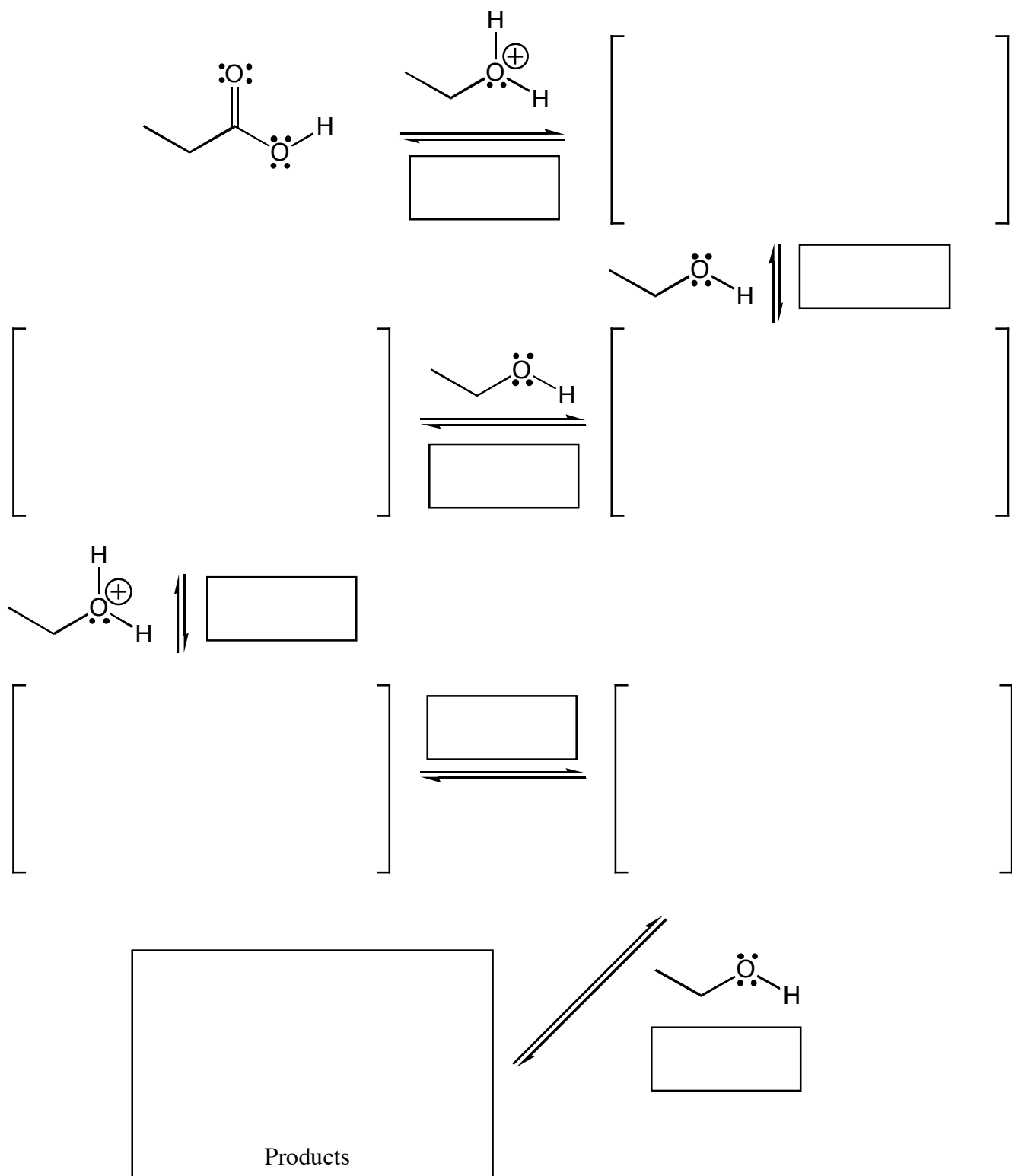


13. (30 pts) Complete the mechanisms for the following two lactone reactions. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL IT AS RACEMIC IF APPROPRIATE.** In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.).

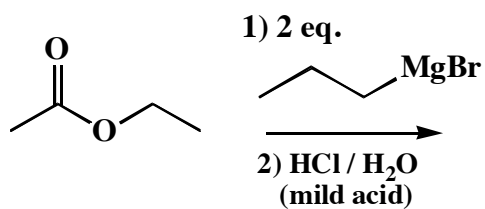
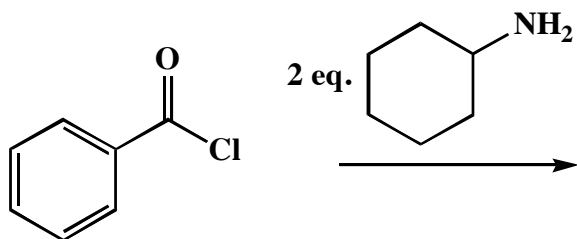
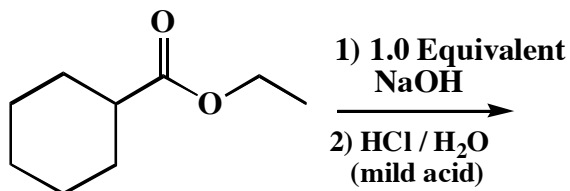
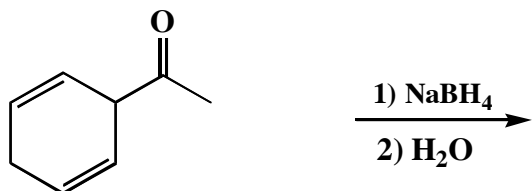
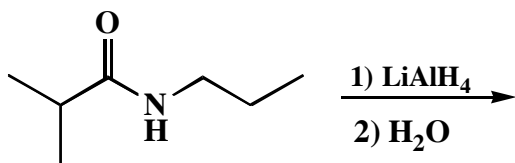
Note: Due to the special nature of this starting material, you are not supposed to draw arrows on the last intermediate in each case.



14. (35 pts) Complete the mechanism for the following Fischer esterification 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 IT AS RACEMIC IF APPROPRIATE.** In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.).

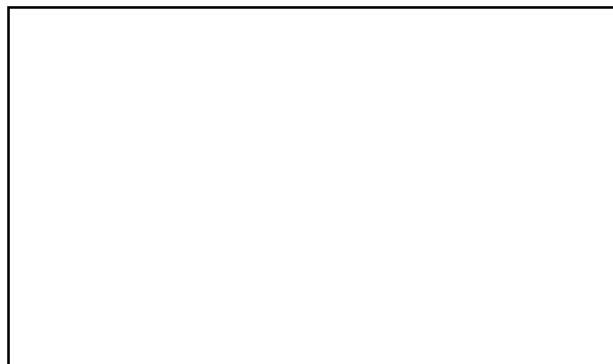
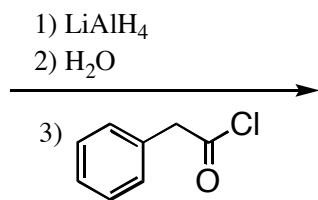
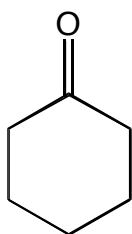


15. (3, 4 or 5 pts.) Write the predominant carbon containing product or products that will occur for each transformation. If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and write racemic. No need for wedges and dashes.

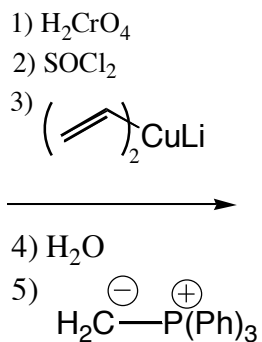
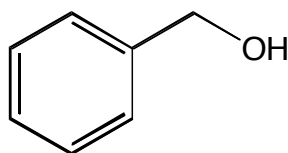


15. (14 points) For the following sequences of reactions, draw the final organic product or products after ALL the steps have been completed. You do not need to draw the molecules synthesized along the way, **only the last product that is formed**. If a new chiral center is created in the reaction that produces a racemic mixture, label the chiral center with an asterisk (*) and write "*racemic*" underneath.

(6 pts)



(9 pts)

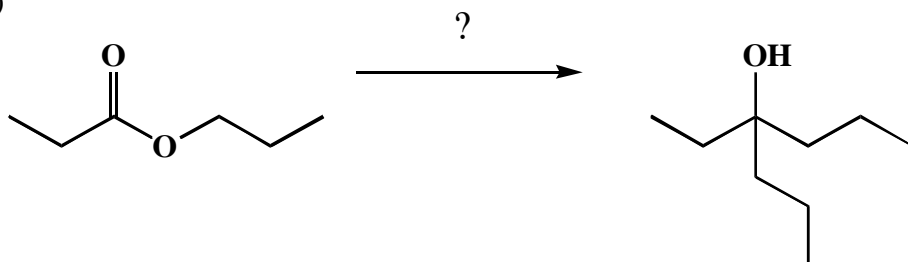


17. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" where appropriate. Hint: this should look familiar as a homework problem.

Remember, all of the carbons of the product must come from the given starting material.

(10 pts)

A)

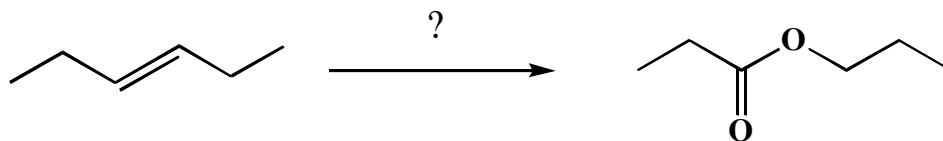


17. Using any reagents turn the starting material into the indicated product. All carbon atoms of the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" where appropriate. Hint: this should look familiar as a homework problem.

Remember, all of the carbons of the product must come from the given starting material.

(13 pts)

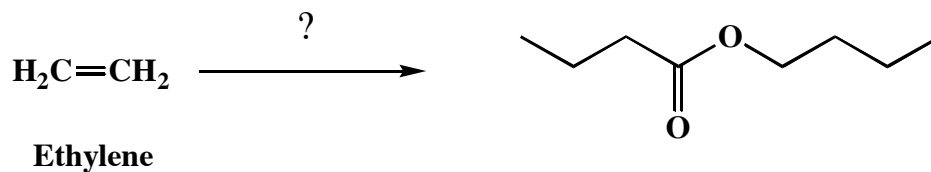
B)



17. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" where appropriate. Hint: this should look familiar as a homework problem.

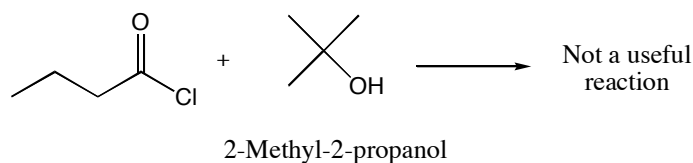
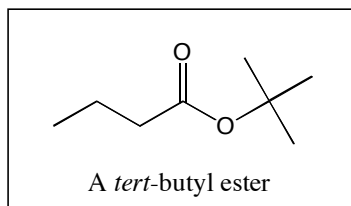
Remember, all of the carbons of the product must come from the given starting material.

(22 pts)
C)



18. (16 pts total) Here is an MCAT question in multiple choice format. You have not seen this chemistry before, but you have learned fundamental principles of reactivity that will lead you to the correct answers. In each case, **you should circle the correct answer**.

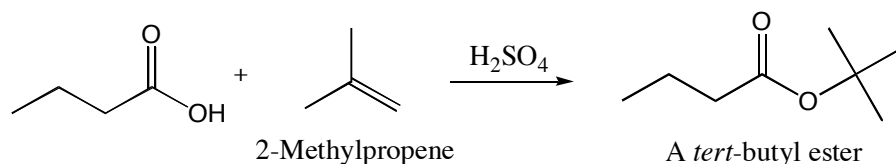
Tert-butyl esters are interesting for many reasons. Unfortunately, *tert*-butyl esters CANNOT be synthesized from the reaction of an acid chloride with 2-methyl-2-propanol.



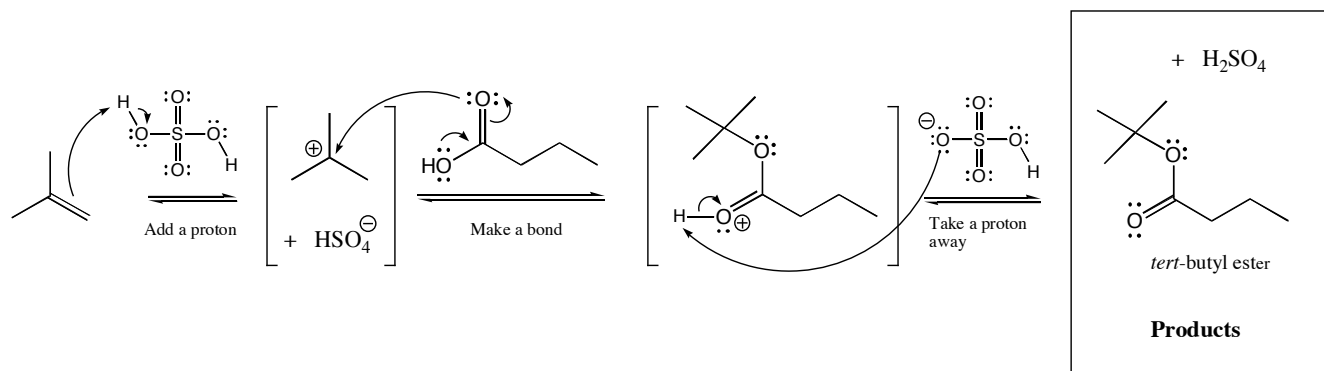
Which of the following best explains why the above reaction does not work.

- A. The 2-methyl-2-propanol has too much steric hindrance to react as a nucleophile.
- B. Alcohols are weak nucleophiles, so they need acid catalysis to react with acid chlorides.
- C. Alcohols are weak electrophiles, so they need acid catalysis to react with acid chlorides.
- D. Both A. and B. are equally responsible for the lack of reaction.

Tert-butyl esters are synthesized in high yield from a carboxylic acid and 2-methylpropene in the presence of a strong anhydrous acid such as H_2SO_4 .



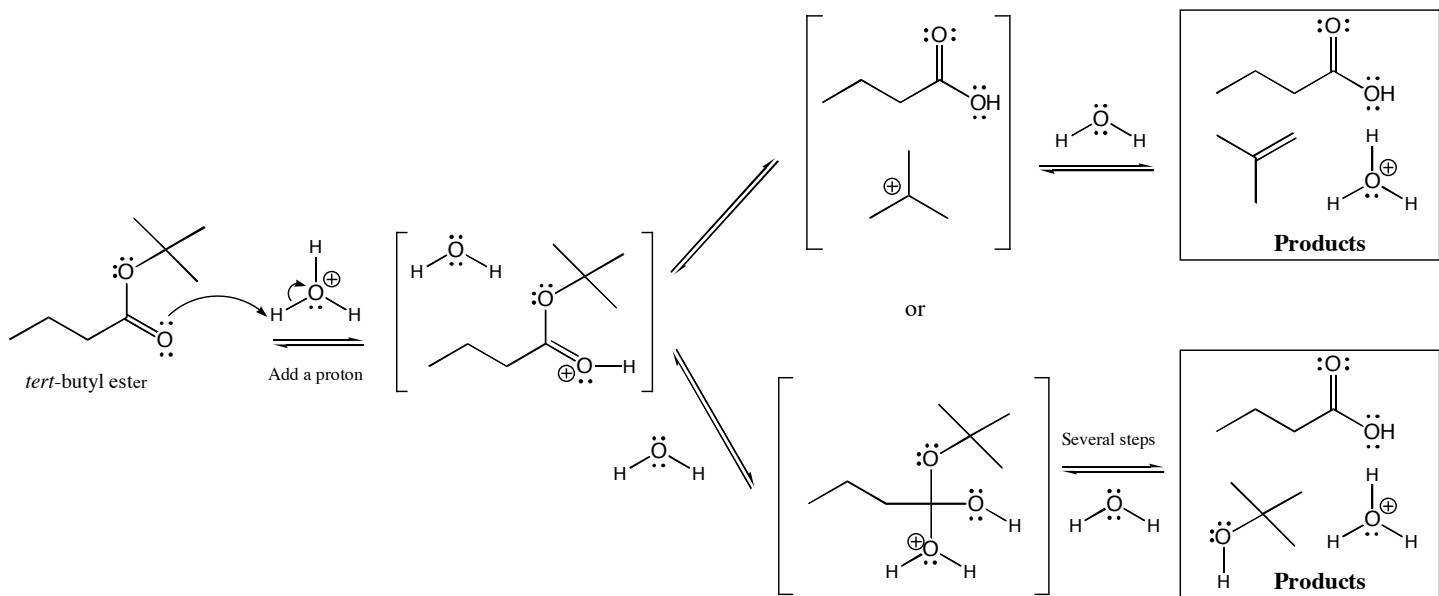
The mechanism of this reaction involves a carbocation intermediate as shown:



Which is true for the above mechanism:

- A. The pH of the reaction does not change.
- B. The pH decreases during the reaction.
- C. The reaction is catalytic in acid.
- D. Both A. and C. are true.

Tert-butyl esters can be hydrolyzed in strong acid in the presence of water. Shown below are two possible mechanisms, only one of which is correct.



Which of the following is true:

- A. The reaction follows the upper pathway involving the carbocation intermediate.
- B. The reaction follows the lower pathway involving an initial attack by water.
- C. The mechanism you chose follows directly from the mechanism for *tert*-butyl ester formation according to the law of microscopic reversibility.
- D. Both A. and C. are true.

Given your answer immediately above, which is true?

- A. The pH of the *tert*-butyl ester hydrolysis reaction does not change.
- B. The pH of the *tert*-butyl ester hydrolysis decreases during the reaction.
- C. The *tert*-butyl ester hydrolysis reaction is catalytic in acid.
- D. Both A. and C. are true.