NAME (Print): _____

SIGNATURE: _____

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

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.

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 INCIDENCTS 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!!!

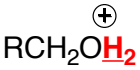
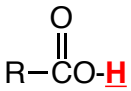
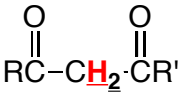
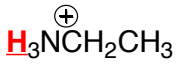
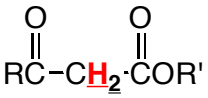
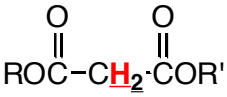
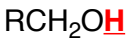
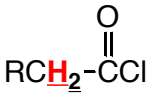
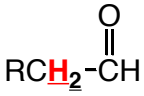
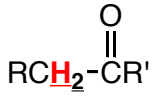
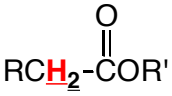
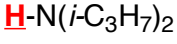
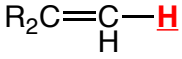
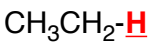
Page	Points	
1		(26)
2		(25)
3		(16)
4		(18)
5		(35)
6		(30)
7		(35)
8		(19)
9		(15)
10		(10)
11		(13)
12		(22)
13		(4)
14		(12)
Total		(280)

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.

_____

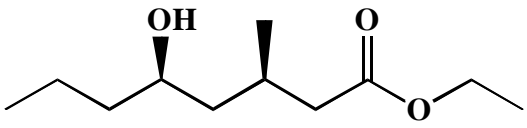
(Your signature)

Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Carboxylic acids		3-5
Ammonium ion		9.2
β-Dicarbonyls		10
Primary ammonium		10.5
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

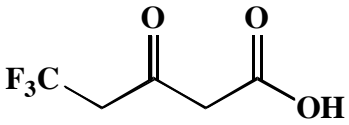
1. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We wil be looking for a minumum of 7 key points here.

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**.

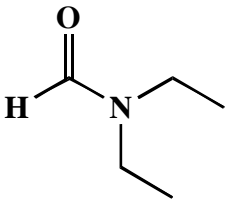
2. (4 pts each) In the space provided, write the IUPAC name (including stereochemistry where appropriate) for the following two molecules:



(3*R*,5*R*)-Ethyl 5-hydroxy-3-methyloctanoate



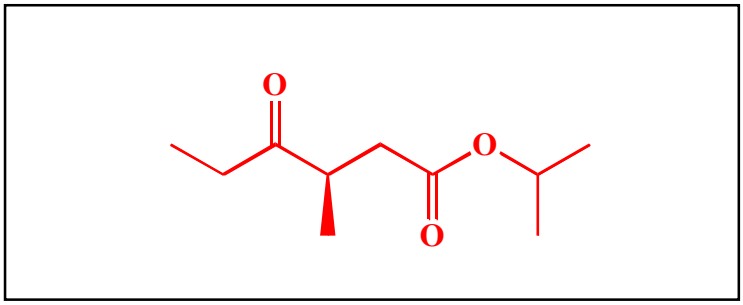
5,5,5-Trifluoro-3-oxopentanoic acid



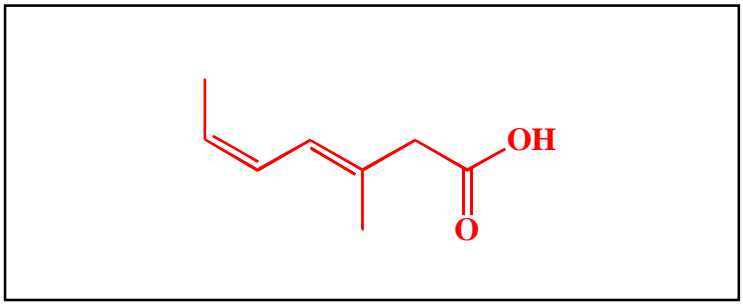
***N*,*N*-Diethylformamide**

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

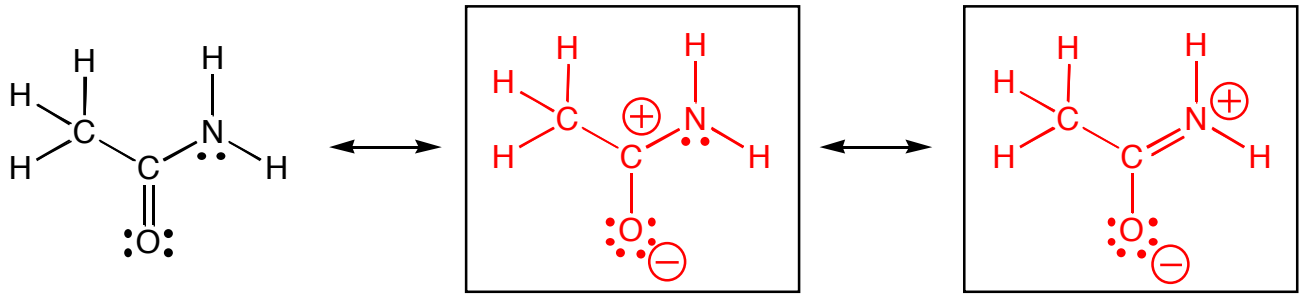
(*R*)-Isopropyl 3-methyl-4-oxohexanoate



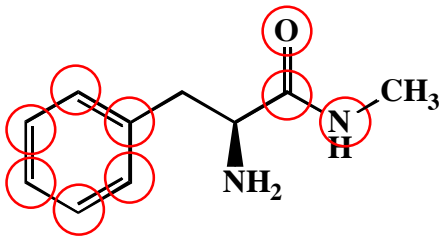
(3*E*,5*Z*)-3-Methyl-3,5-heptadienoic acid



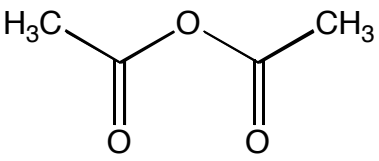
4. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



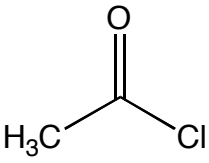
5. (9 points) Shown below is an amide formed between methyl amine and the amino acid phenylalanine. Draw a small circle around all sp^2 hybridized atoms in the molecule.



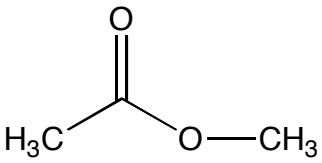
6. (4 points) Rank the following carboxylic acid derivatives with respect to reactivity with a nucleophile. Write a 1 under the most reactive, and a 4 under the least reactive derivative.



2



1



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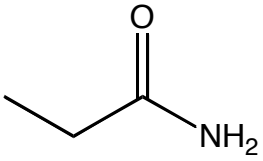
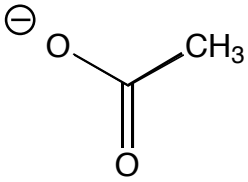


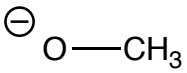
4

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.

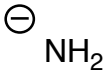


2

1

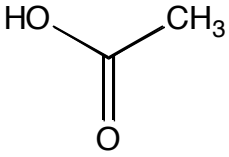


3

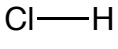


4

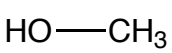
8. (4 points) Rank the following in terms of relative acidity, with a 1 under the most acidic, and a 4 under the least acidic molecule.



2



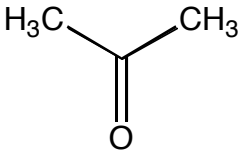
1



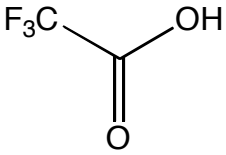
3

4

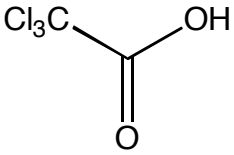
9. (4 points) Rank the following in terms of relative acidity, with a 1 under the most acidic, and a 4 under the least acidic molecule.



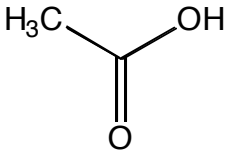
4



1

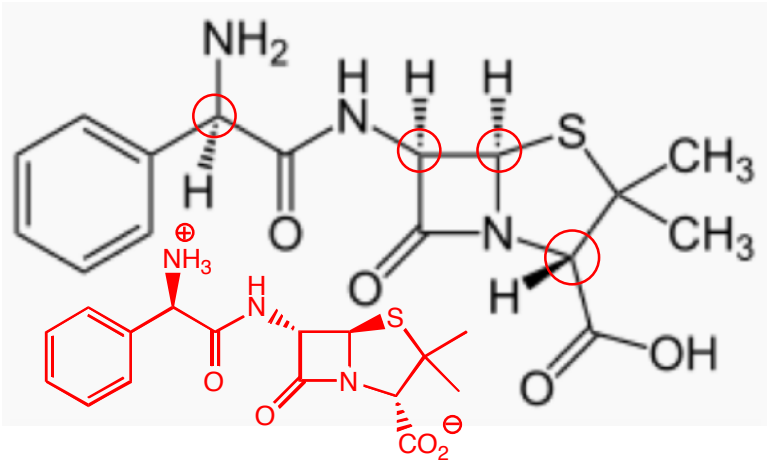


2



3

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.



	pK_a
$\underline{H}_3\overset{\oplus}{N}CH_2CH_3$ **Primary ammonium**	**10.5**
R—CO-**H** **Carboxylic acids**	**3-5**

Based on the pK_a values given, what is the total charge on amplicillin in a solution of pH = 2.0? **+1**

(Amine function will be protonated and have a positive charge and the carboxylic acid will be protonated and neutral)

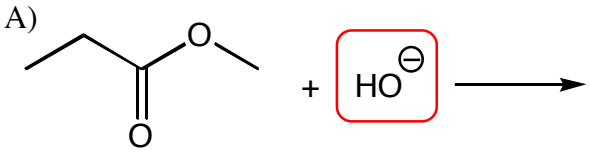
Based on the pK_a values given, what is the total charge on amplicillin in a solution of pH = 7.0? **0**

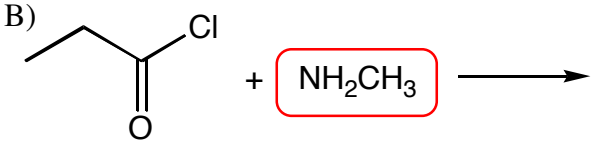
(Amine function will be protonated and have a positive charge and the carboxylic acid will be deprotonated with a negative charge)

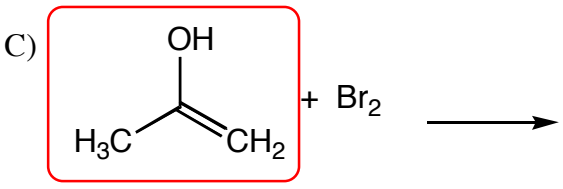
In only two short sentence, describe two very different things that are wrong with the format of the ampicillin structure that I copied from Wikipedia. Hint; one of the answers to this question is related to the two questions you just answered. **You can assume the atoms are all in the correct places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

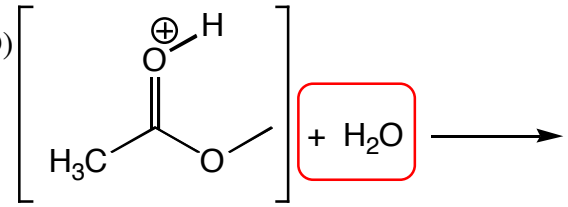
Based on the pK_a values, there is NO pH in which the carboxylic acid will be protonated but the amine function will be neutral as shown. The second problem is that the stereochemistry is ambiguous at the circled chiral centers, showing three bonds in the same plane and only one out of the plane.

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

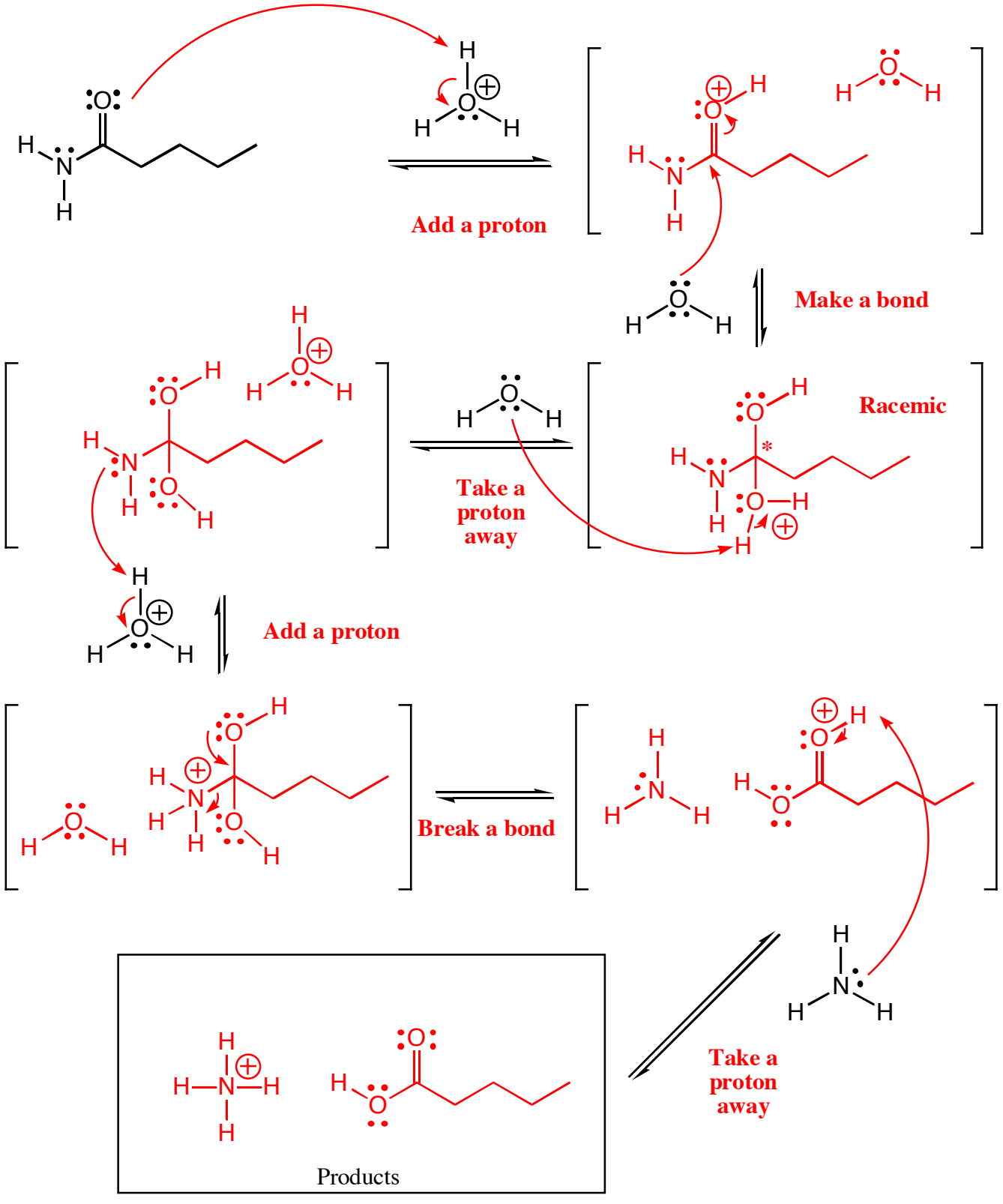
A) 

B) 

C) 

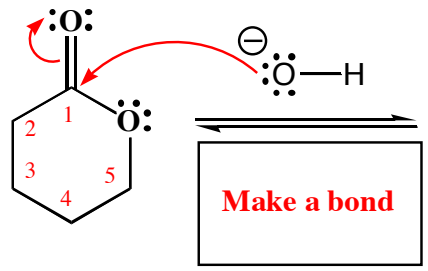
D) 

12. (35 pts) Complete the mechanism for the following amide hydrolysis reaction. **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.** Remember, I said <u>all</u> 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.).**

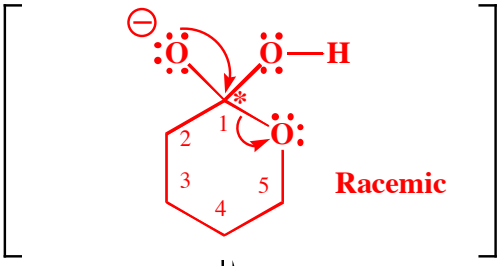


13. (30 pts) Complete the mechanisms for the following two lactone reactions. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **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.

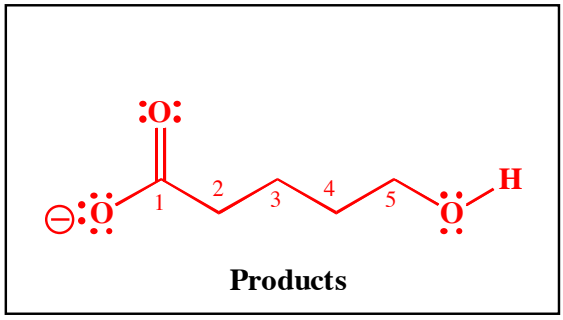


Make a bond



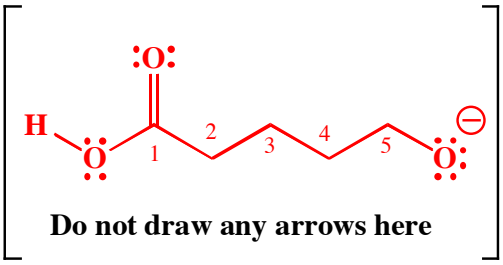
Racemic

Break a bond

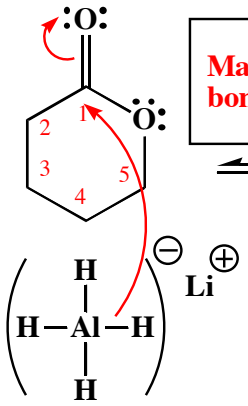


Products

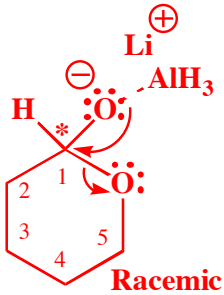
Proton Transfer



Do not draw any arrows here

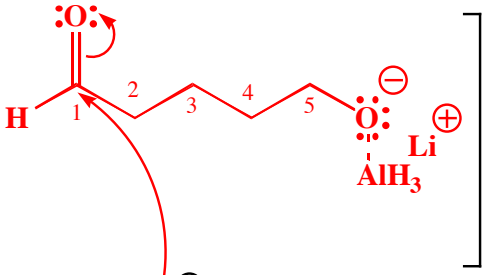


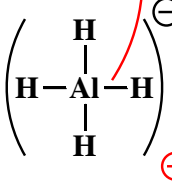
Make a bond



Racemic

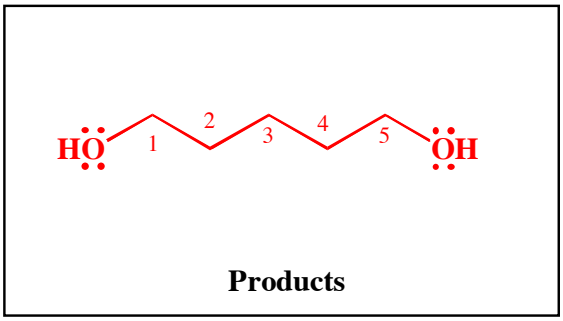
Break a bond





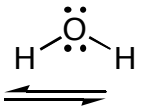
Make a bond

Chemist Opens Flask

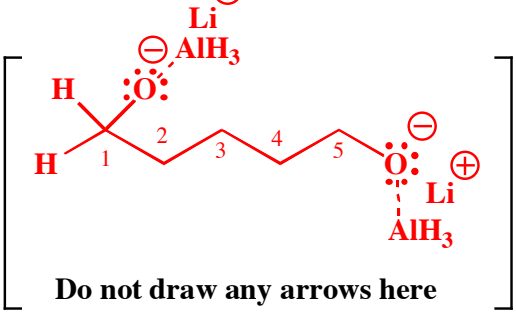


Products

2) excess

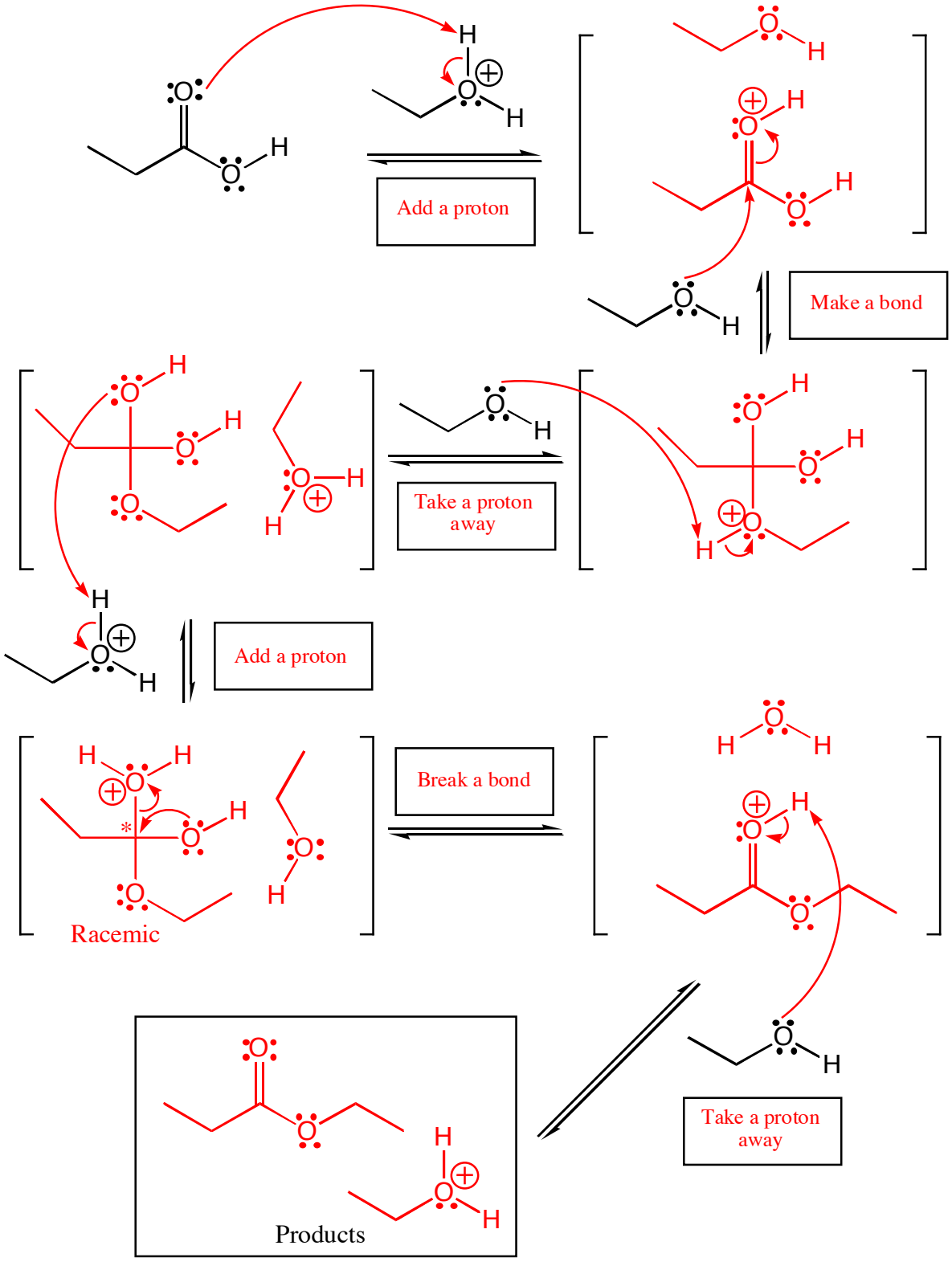


Add a proton

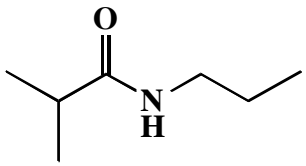


Do not draw any arrows here

14. (35 pts) Complete the mechanism for the following Fischer esterification reaction. **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.** Remember, I said <u>all</u> 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.).**

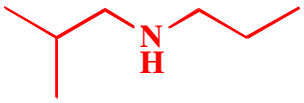


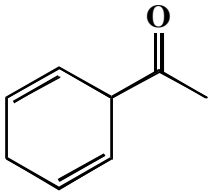
15. (3 or 5 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and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



1) $LiAlH_4$

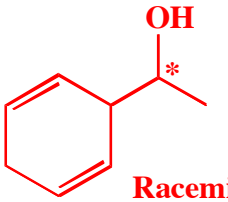
2) H_2O



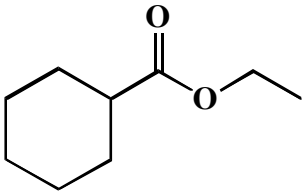


1) $NaBH_4$

2) H_2O

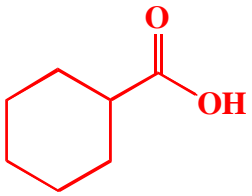


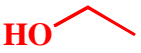
Racemic

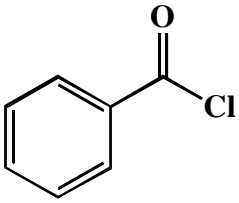


1) 1.0 Equivalent NaOH

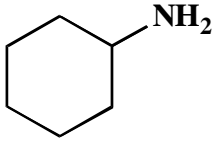
2) HCl / H_2O (mild acid)

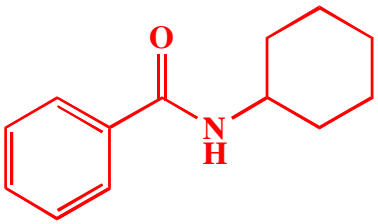


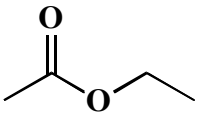




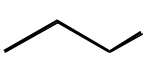
2



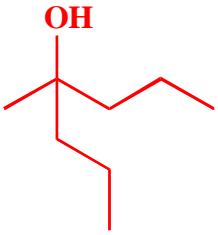


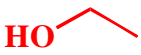


1) 2 eq.



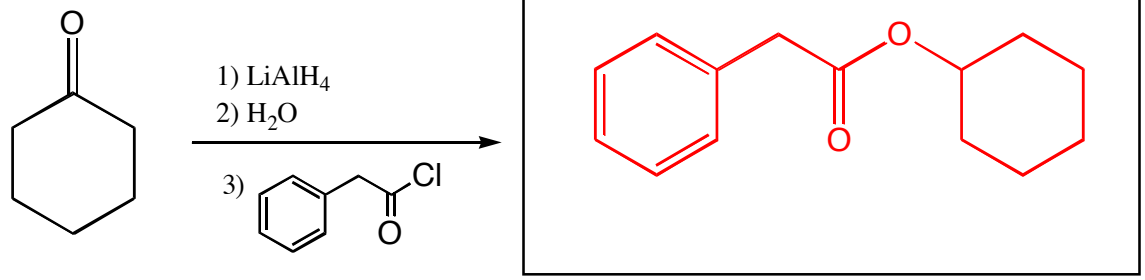
2) HCl / H_2O (mild acid)



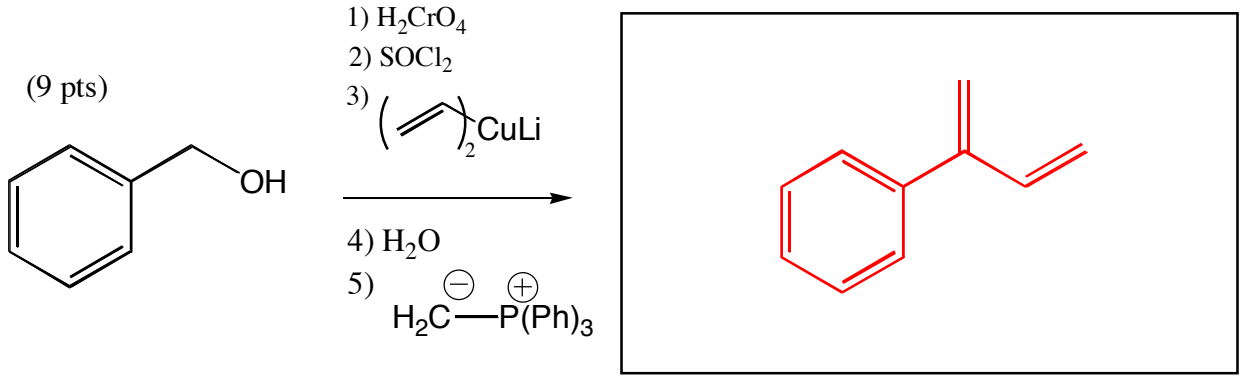


15. (14 points) For the following sequences of reactions, draw the final organic product or products after ALL the steps have been completed. You do not need to draw the molecules synthesized along the way, **only the last product that is formed**. If a new chiral center is created in the reaction that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

(6 pts)



(9 pts)

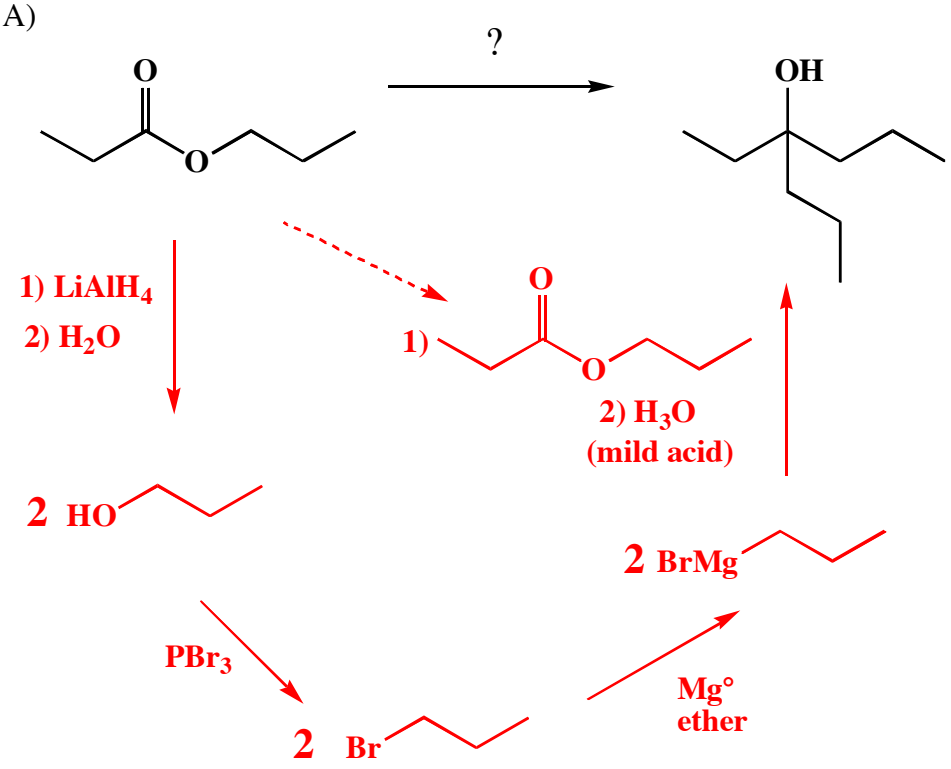


17. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" 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)

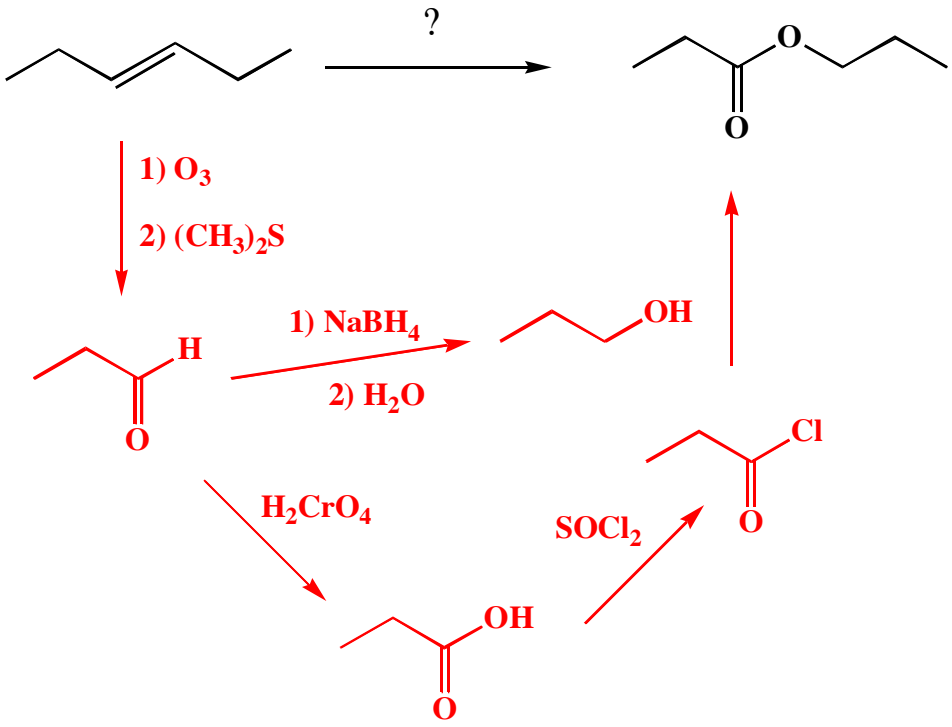


17. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" 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.

(13 pts)

B)

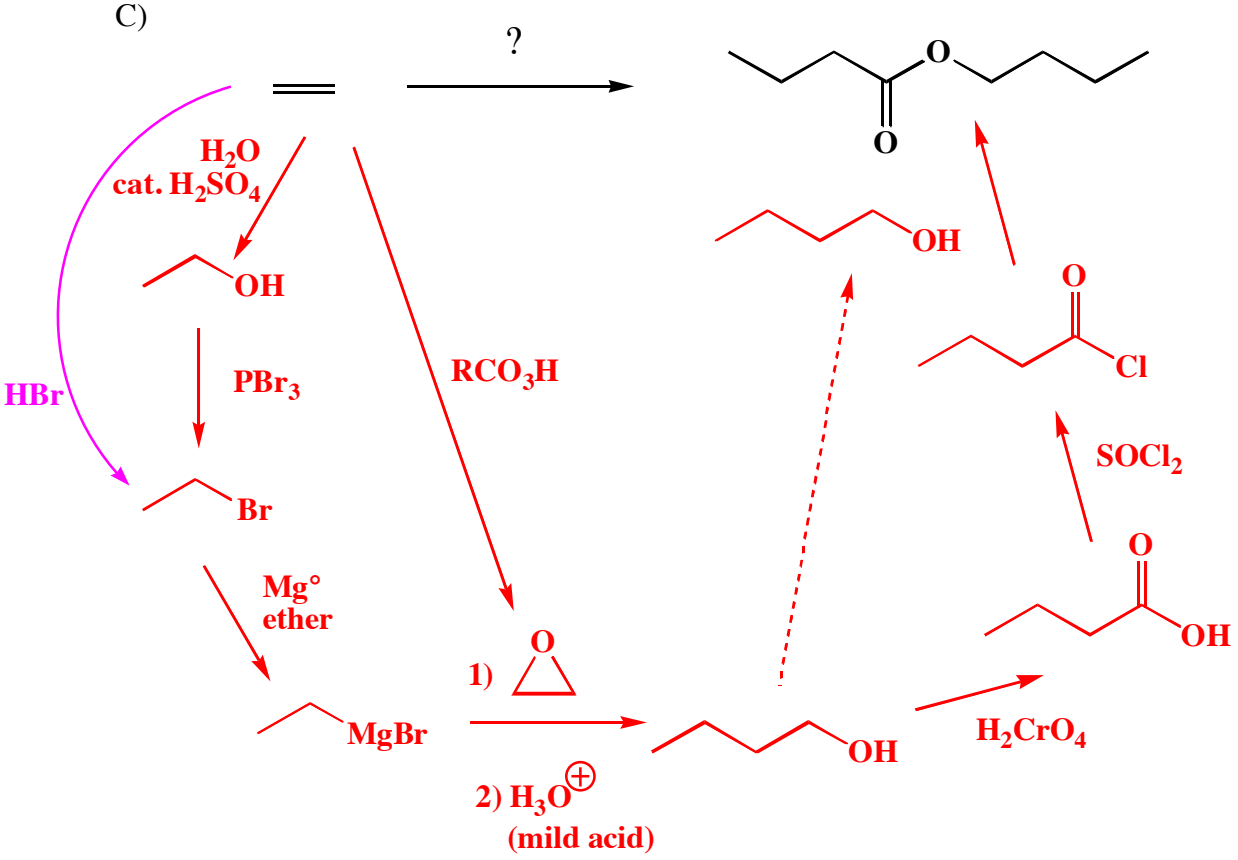


17. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" 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.

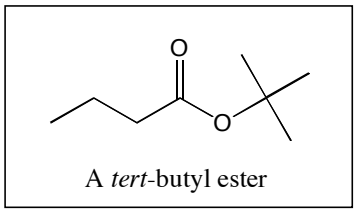
(22 pts)

C)

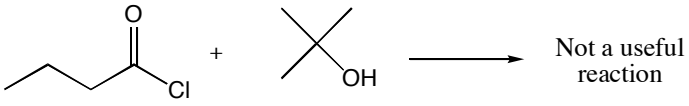


18. (16 pts total) Here is an MCAT question in multiple choice format. You have not seen this chemistry before, but you have learned fundamental principles of reactivity that will lead you to the correct answers. In each case, **you should circle the correct answer**.

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.



A *tert*-butyl ester



2-Methyl-2-propanol

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

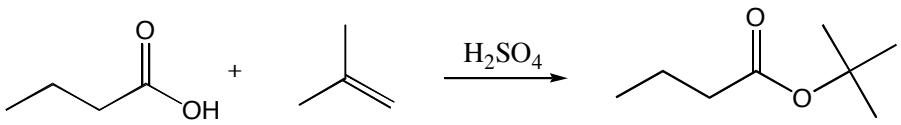
A. The 2-methyl-2-propanol has too much steric hindrance to react as a nucleophile.

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.

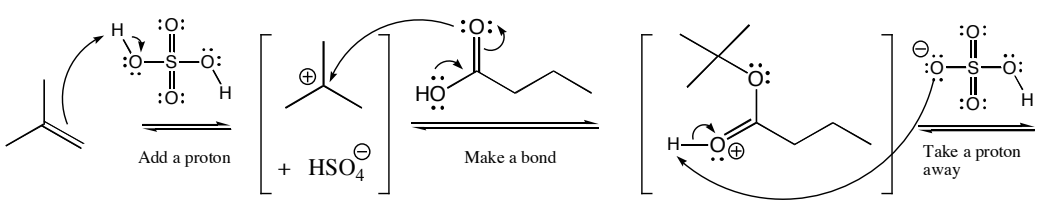
D. Both A. and B. are equally responsible for the lack of reaction.

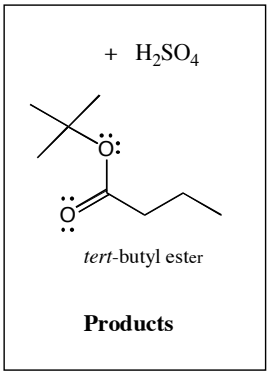
Tert-butyl esters are synthesized in high yield from a carboxylic acid and 2-methylpropene in the presence of a strong anhydrous acid such as H_2SO_4.



2-Methylpropene A *tert*-butyl ester

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





Which is true for the above mechanism:.

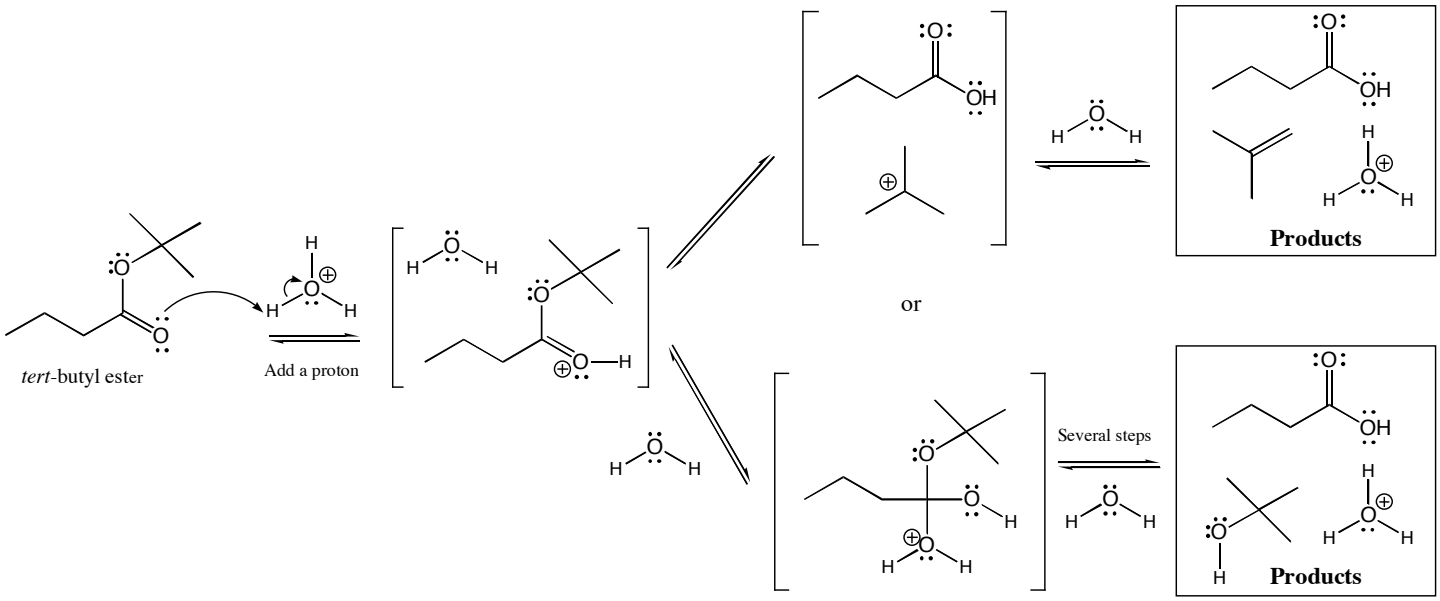
A. The pH of the reaction does not change.

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 use 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.