NAME (Print): _____

SIGNATURE: _____

Chemistry 320N
Dr. Brent Iverson
2nd Midterm
March 24, 2016

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!!!

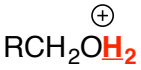
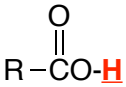
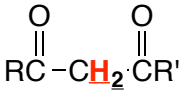
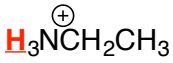
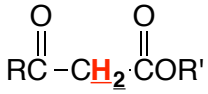
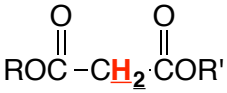
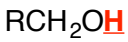
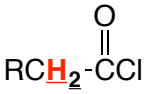
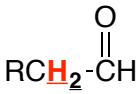
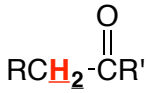
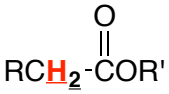
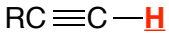
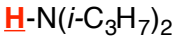
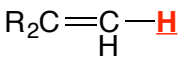
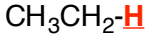
Page	Points	
1		**(63)**
6		**(30)**
7		**(12)**
8		**(35)**
9		**(19)**
10		**(12)**
11		**(12)**
12		**(17)**
13		**(23)**
14		**(21)**
15		**(10)**
16		**(16)**
17		**(4)**
18		**(10)**
Total		**(284)**

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		-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

Signature_____ Pg 1 _____(63)

DO NOT TEAR OUT THIS PAGE!!

You must write the answers for the questions on the next four pages on this single sheet.

Question 1, page 2 (5 pts) Write the correct letter, A), B), C), D) or E) corresponding to the order of acidity of the molecules, listed from most to least acidic.

____

Question 2, page 2 (5 pts) Write the correct letter, A), B), C), D) or E) corresponding to the order of anion stability, listed from most to least stable.

____

Question 3, page 3 (5 pts) Write the correct letter, A), B), C), D) or E) corresponding to the order of reactivty with nucleophiles, listed from most to least reactive.

____

Question 4, page 3 (5 pts) Write the hybridization state of the atoms indicated by the arrows.

a) ____ b) ____ c) ____ d) ____ e) ____

Question 5, page 4 (5 pts) Write""yes" or "no" corresponding to whether the bond indicated by the arrows does ("yes") or does not ("no") rotate freely at room temperature.

a) ____ b) ____ c) ____ d) ____ e) ____

Question 6, page 4 (5 pts) What pH (2.0, 7.0, or 11.0) corresponds to the stucture from question 5?

____

Question 7, page 4 (5 pts) Write the correct letter, A), B), C), D) or E) corresponding to the order of acidity, listed from most to least acidic.

____

Question 8, page 5 (2 pts each word) Fill in the appropriate two words on the lines provided.

_____ _____

Question 9, page 5 (4 pts each) Write "Make a Bond", "Break a Bond", "Add a Proton" or "Take a Proton Away"

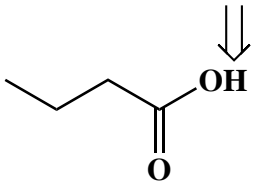
9.1 _____ 9.4 _____

9.2 _____ 9.5 _____

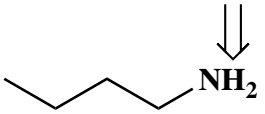
9.3 _____ 9.6 _____

Write the answers to these questions on the answer sheet on page 1

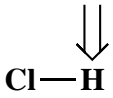
1. (5 pts) Rank order all of the following with respect to relative acidity. The acidic H atom in question is indicated with the arrow for each molecule. **On the answer sheet on page 1 write the letter corresponding to the correct order of acidity,** ranked from most to least acidic for the molecules labeled as (a) - (d).



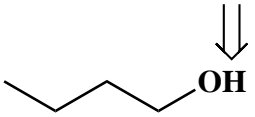
(a)



(b)



(c)



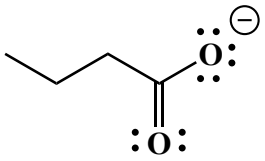
(d)

most acidic least acidic

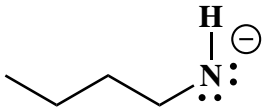
A)	**(a)**	**(b)**	**(c)**	**(d)**
B)	**(b)**	**(a)**	**(d)**	**(c)**
C)	**(c)**	**(a)**	**(d)**	**(b)**
D)	**(c)**	**(b)**	**(a)**	**(d)**
E)	**(c)**	**(d)**	**(b)**	**(a)**

2. (5 pts.) Rank order the following in terms of anion stability. **On the answer sheet on page 1 write the letter corresponding to the correct order of anion stability,** ranked from most to least stable for the molecules labeled as (a) - (e).

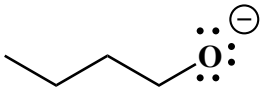
(a)



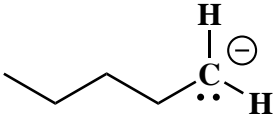
(b)



(c)



(d)



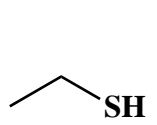
(e)

most stable least stable

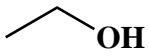
A)	**(a)**	**(b)**	**(c)**	**(d)**	**(e)**
B)	**(e)**	**(a)**	**(b)**	**(d)**	**(c)**
C)	**(a)**	**(e)**	**(b)**	**(d)**	**(c)**
D)	**(a)**	**(b)**	**(d)**	**(c)**	**(e)**
E)	**(b)**	**(a)**	**(e)**	**(d)**	**(c)**

Write the answers to these questions on the answer sheet on page 1

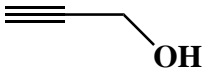
3. (5 pts) You are going to have to think about this one! The following pK_a values will help in your analysis:



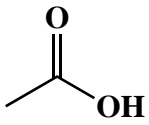
pK_a **= 10.61**



pK_a **= 15.50**

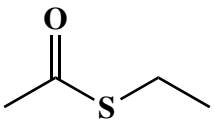


pK_a **= 13.60**

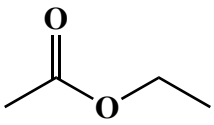


pK_a **= 4.75**

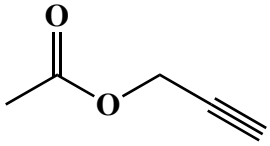
Rank order all of the following with respect to relative reactivity with a nucleophile such as NH_3. O**n the answer sheet on page 1 write the letter corresponding to the predicted order of reactivity,** ranked from most to least reactive for the molecules labeled as (a) - (d).



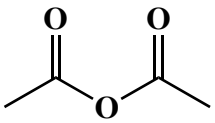
(a)



(b)



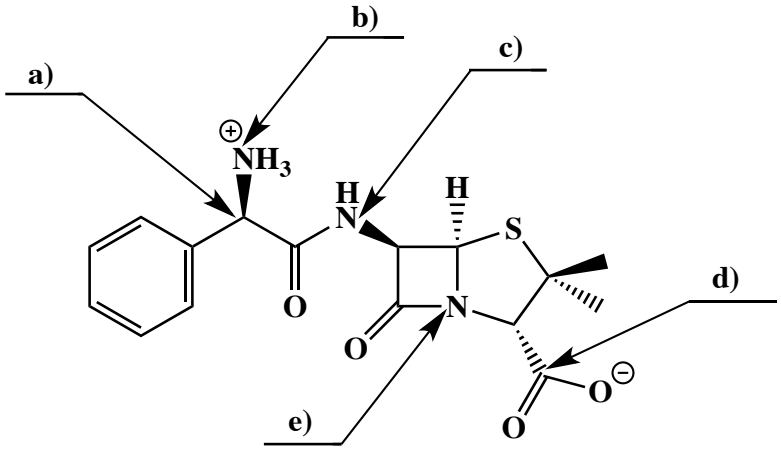
(c)



(d)

	most reactive			least reactive
A)	**(b)**	**(c)**	**(a)**	**(d)**
B)	**(d)**	**(a)**	**(c)**	**(b)**
C)	**(c)**	**(a)**	**(d)**	**(b)**
D)	**(c)**	**(b)**	**(a)**	**(d)**
E)	**(d)**	**(a)**	**(b)**	**(c)**

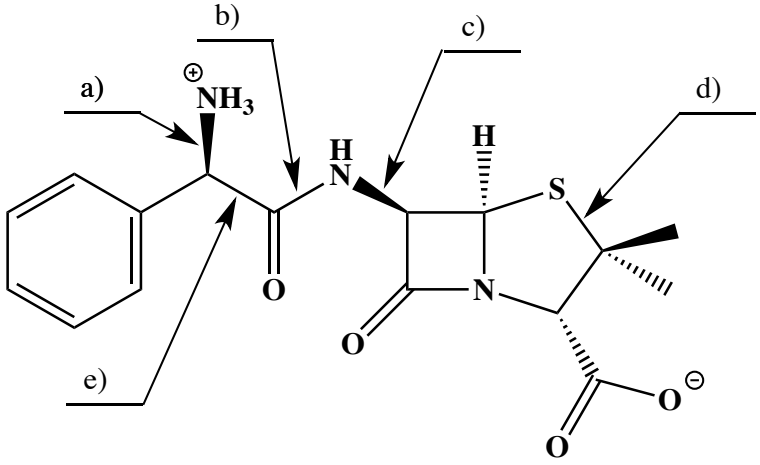
4. (5 points) On the answer sheet on page 1, indicate the hybridization state of each atom identified by the arrows.



Ampicillin - a common antibiotic used often in research

Write the answers to these questions on the answer sheet on page 1

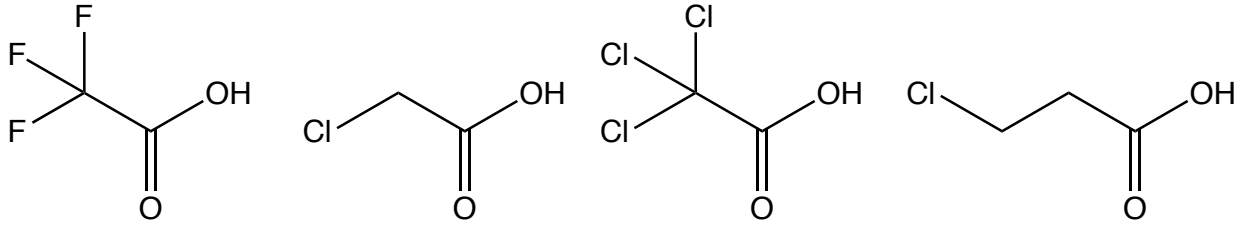
5. (5 pts) **On the answer sheet on page 1 write "yes" or "no" to indicate whether the bond identified by the arrow does (yes) or does not (no) rotate freely at room temperature.**



Ampicillin - a common antibiotic used often in research

6. (5 pts) For the above structure (problem 5), is the molecule drawn in the correct protonation state for pH 2.0, 7.0, or 11.0? Write 2.0, 7.0 or 11.0 on the answer sheet on page 1.

7. (5 pts) Rank the following molecules with respect to overall acidity. **On the answer sheet on page 1, write the letter corresponding to the correct order of acidity,** ranked from most to least acidic for the molecules labeled as (a) - (d).



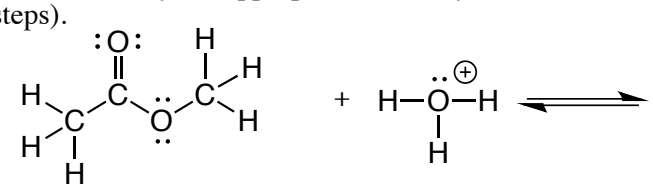
(a) **(b)** **(c)** **(d)**

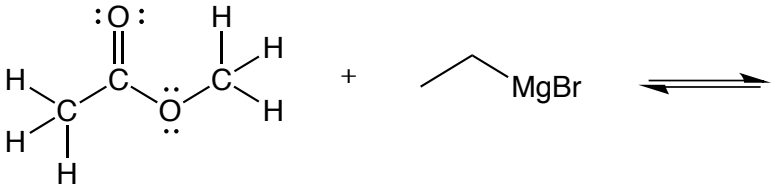
	most acidic			least acidic
A)	**(a)**	**(c)**	**(b)**	**(d)**
B)	**(a)**	**(b)**	**(d)**	**(c)**
C)	**(c)**	**(a)**	**(b)**	**(d)**
D)	**(c)**	**(d)**	**(b)**	**(a)**
E)	**(d)**	**(b)**	**(c)**	**(a)**

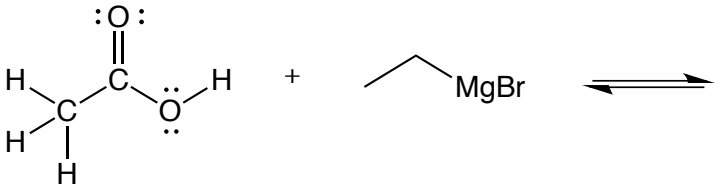
Write the answers to these questions on the answer sheet on page 1

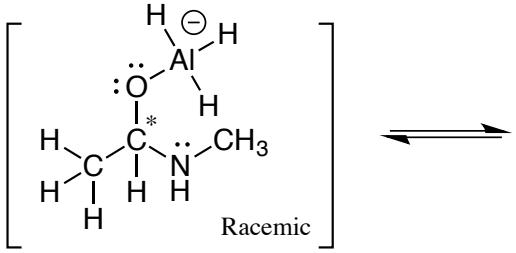
8. (2 pts each word) The mechanisms of reversible reactions are the same in either direction, meaning the same intermediates are encountered in either direction. A great illustration of this principle involves the mechanisms we have encountered for the Fischer esterification and acid catalyzed ester hydrolysis. The principle that indicates reaction mechanisms are the same in both directions of a reversible reaction is known as the principle of _____ _____. (write the two appropriate words on the answer sheet of page 1.

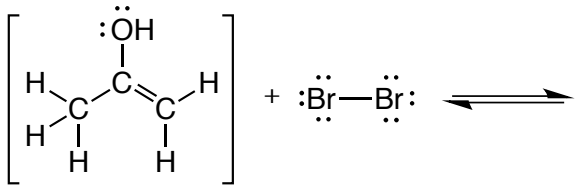
9. (4 pts each) Predict which of the four mechanistic elements describe the **next mechanism step** indicated by the following reagent or reagents. On page 1 write "Make a Bond", "Break a Bond", "Add a Proton" or "Take a Proton Away" as appropriate. (Note you do NOT need to draw any arrows or products for these steps).

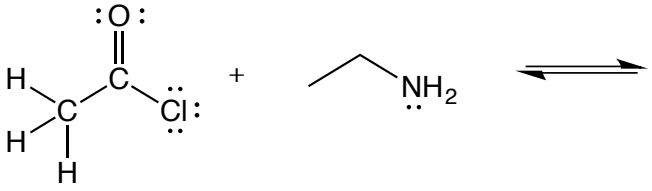
9.1 

9.2 

9.3 

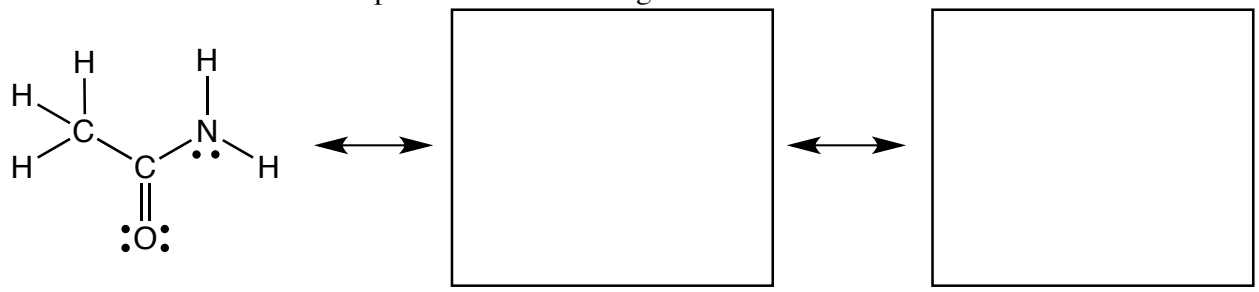
9.4 

9.5 

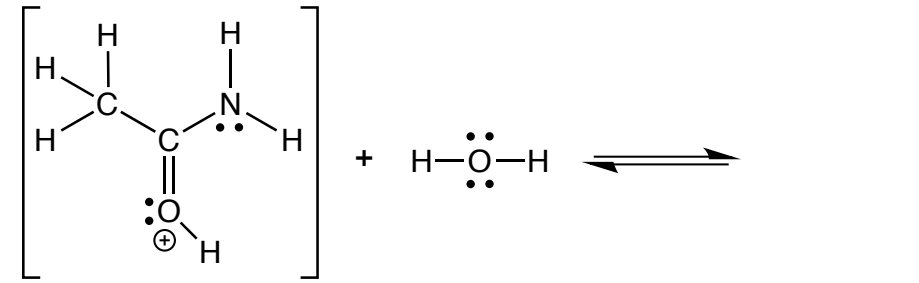
9.6 

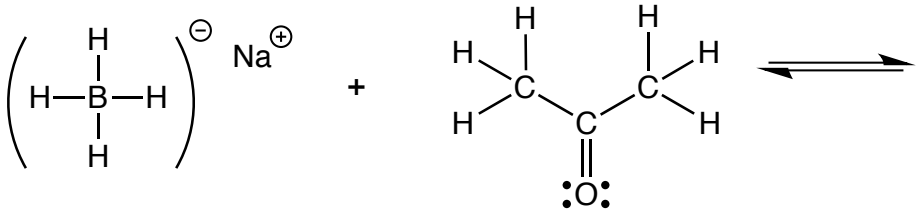
10. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We wil be looking for a minimum of 7 key points here.

11. (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.

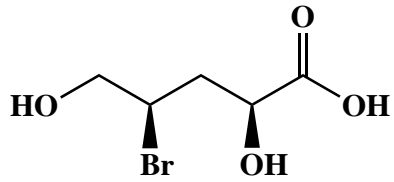


12. (4 pts each) For the following two pairs of reagents, **circle** the nucleophile.

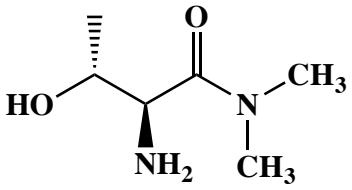




13. (4 pts each) In the space provided, write the IUPAC name (including stereochemistry where appropriate) for the following two molecules:



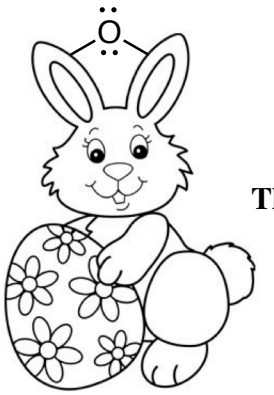
_____



_____

14. (4 pts) In the space provided, draw the following molecule:

Isopropyl (*E*)-2-ethyl-2-butenoate

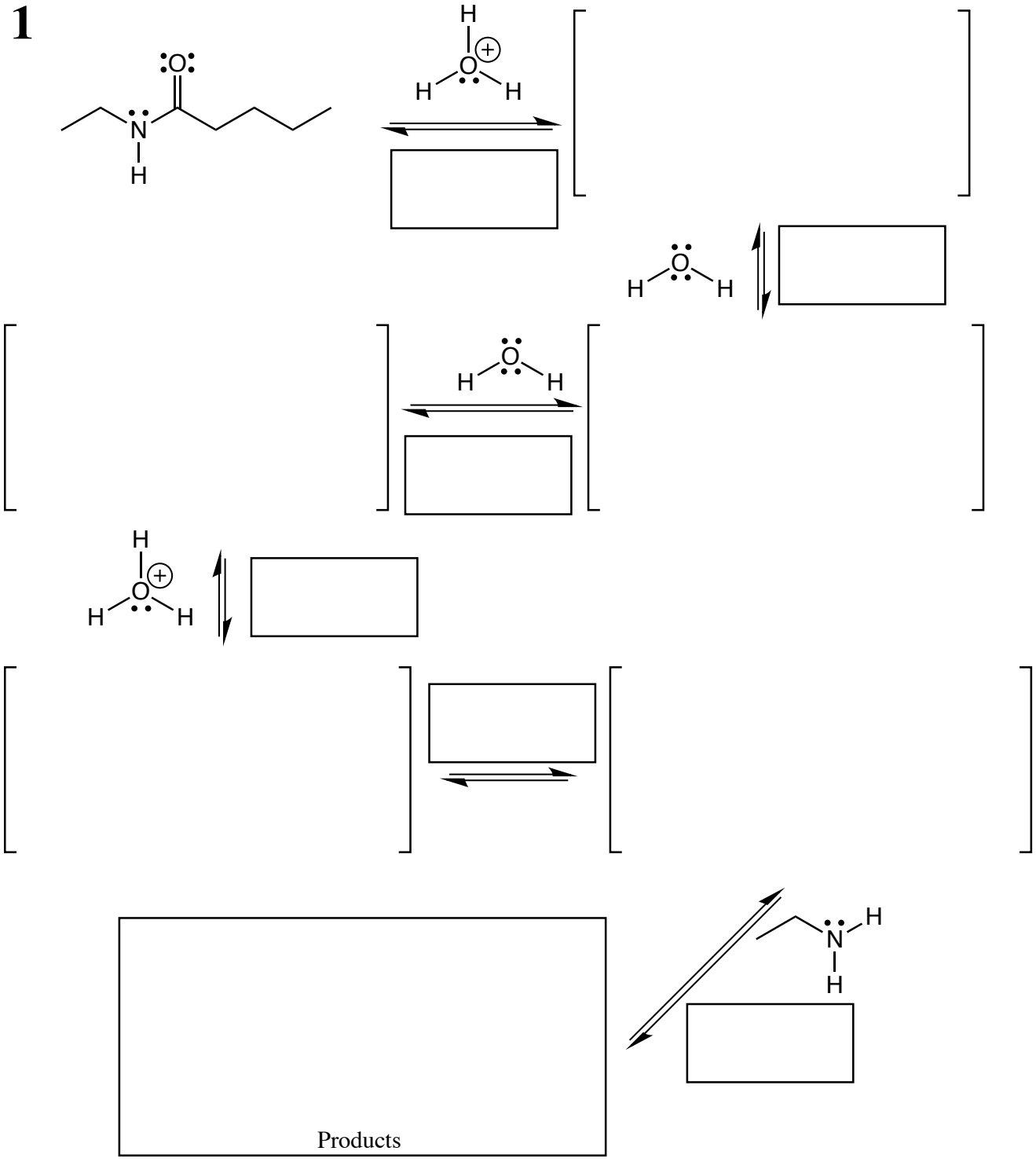


The Ether Bunny

The Ester Bunny

15. (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 THE MOLECULE 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.).**

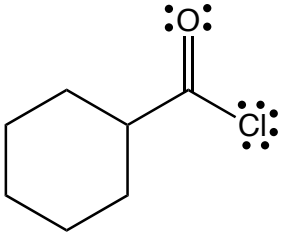
1

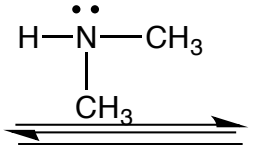


Note you will have to write a balanced equation forthe above mechanism on PAGE 11

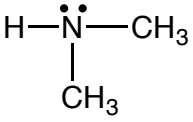
16. (19 pts) Complete the mechanism for the following reaction of an acid chloride with an amine. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE 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.).**

2





Proton transfer

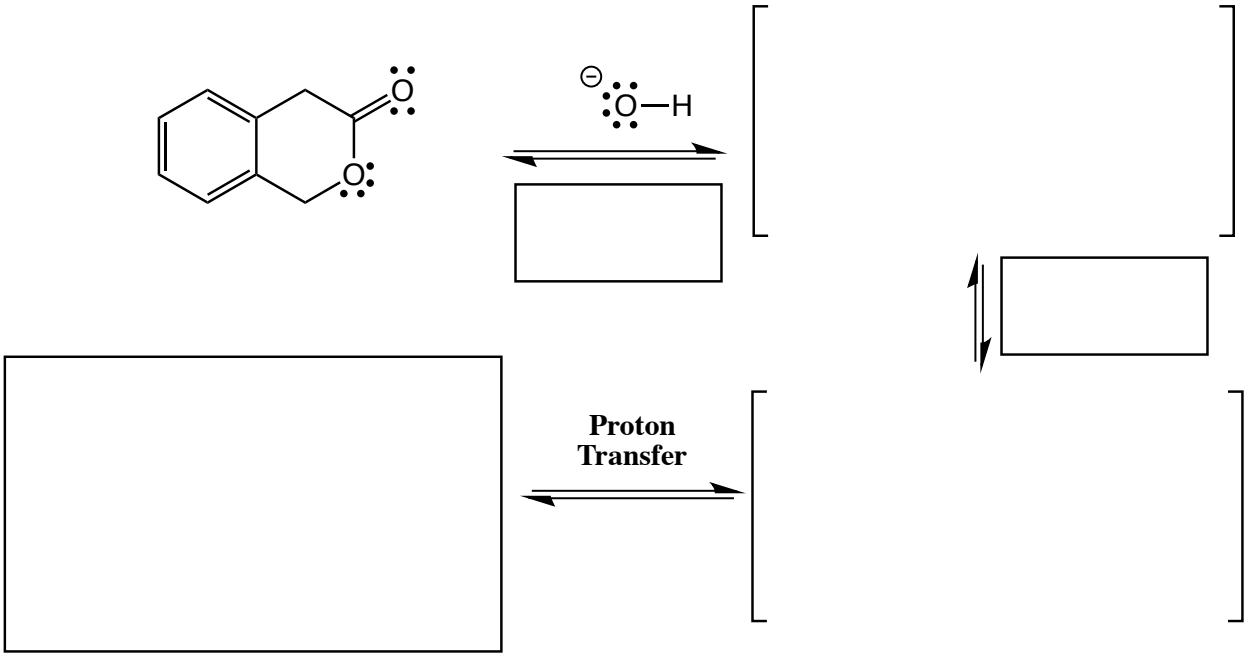


Products

Note you will have to write a balanced equation for the above mechanism on PAGE 11

17. (12 pts) Complete the mechanism for the following reaction a lactone and hydroxide. **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 THE MOLECULE 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.).**

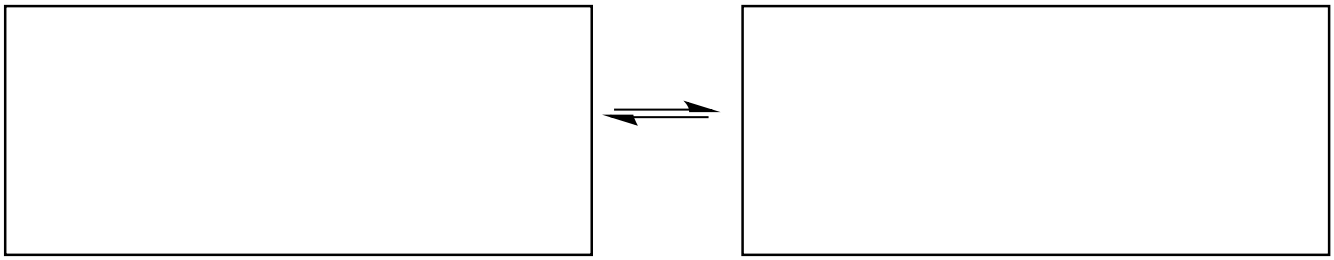
3



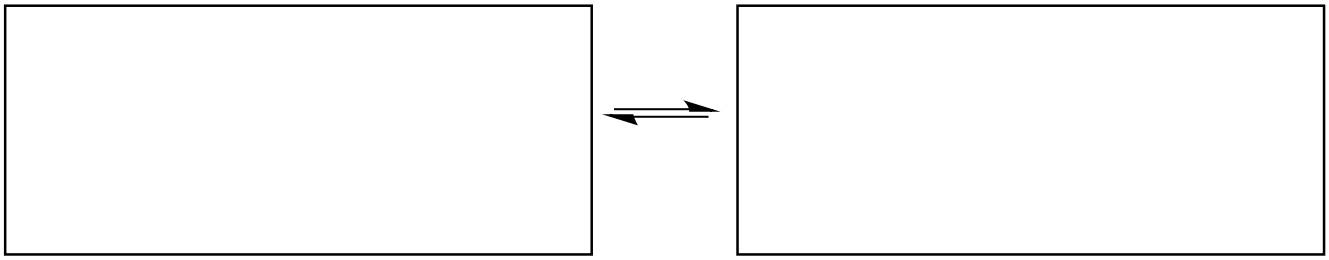
Note you will have to write a balanced equation for the above mechanism on the NEXT page

18. (12 pts) Write BALANCED equations for the three mechanisms, 1-3, that you drew on the last three pages.

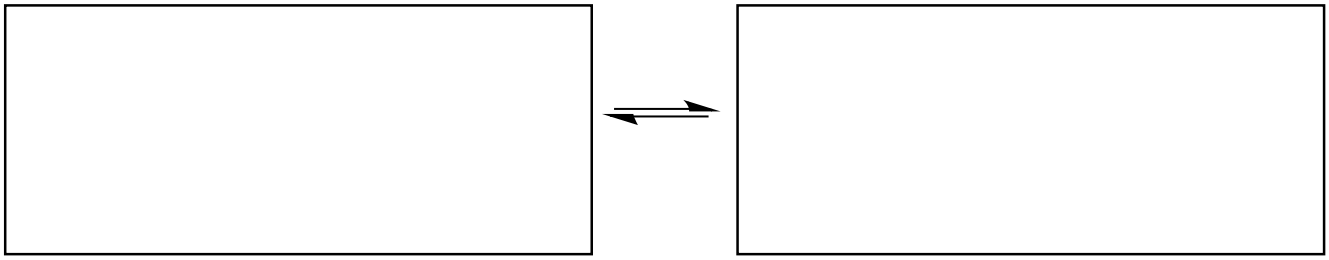
Write a balanced equation for the overall process described by mechanism 1 from page 8



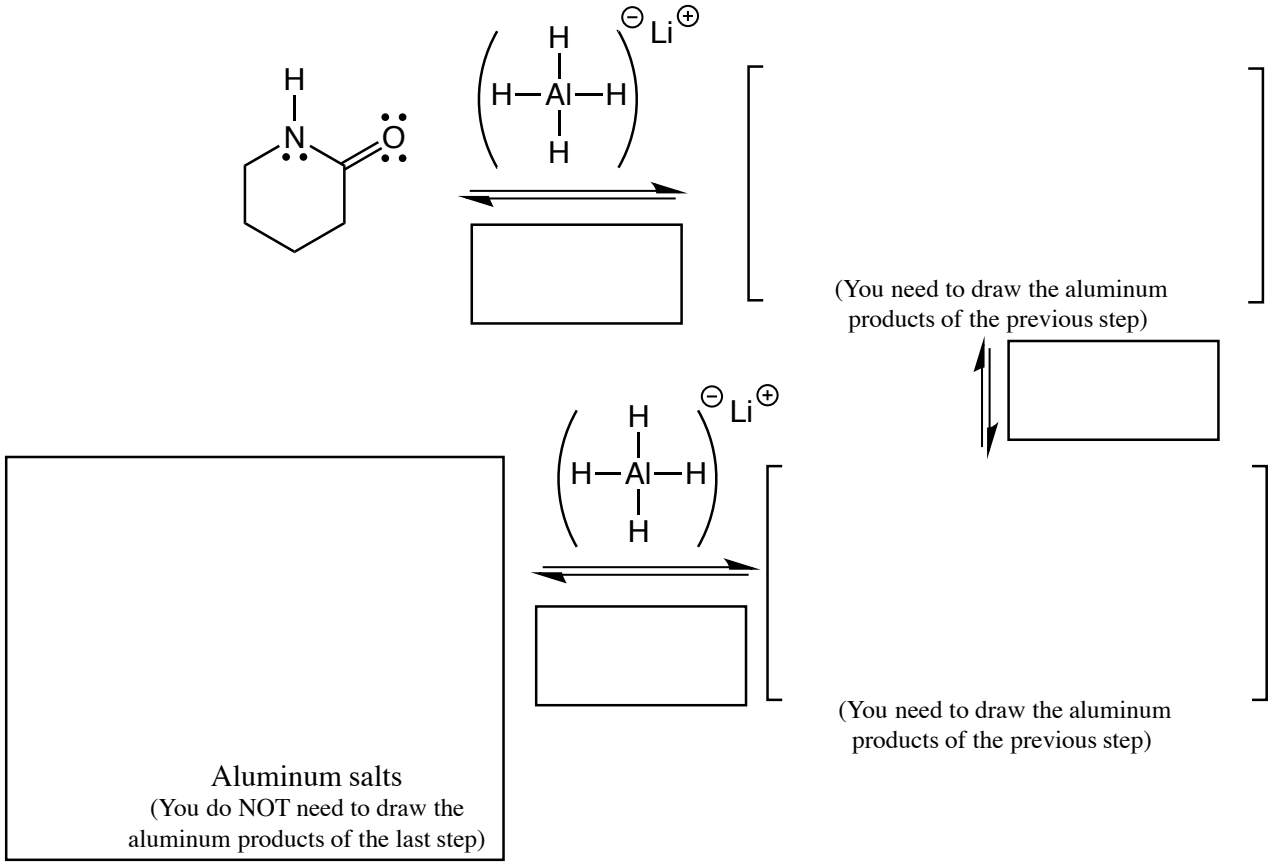
Write a balanced equation for the overall process described by mechanism 2 from page 9



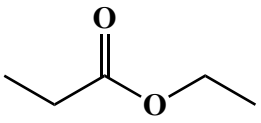
Write a balanced equation for the overall process described by mechanism 3 from page 10



19. (17 pts) Complete the mechanism for the reduction of the following lactam. **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 carbon containing products for each step.** Remember, I said <u>all</u> the carbon containing products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE 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.).**

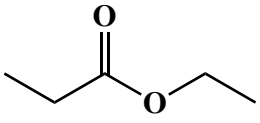


20. (3 or 5 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and write racemic. No need for wedges and dashes. Also, do not worry about balancing these equations, you just need to show us the major carbon-containing products of these transformations.**



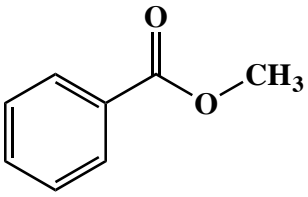
H_2N → heat

Draw all the organic products made from the ester starting material



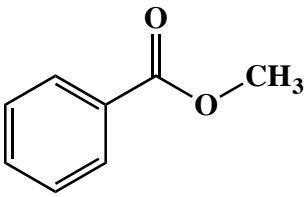
H_2O → H_2SO_4 catalytic

Draw all the organic products made from the ester starting material



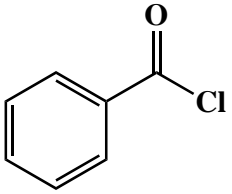
1) $LiAlH_4$ → 2) H_2O

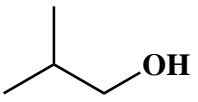
Draw all the organic products made from the ester starting material



1 eq. NaOH →

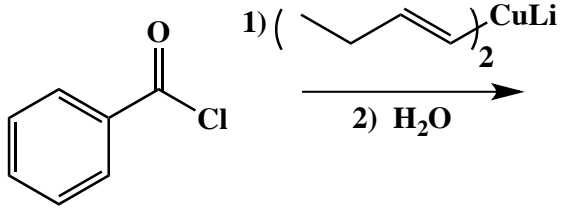
Draw all the organic products made from the ester starting material

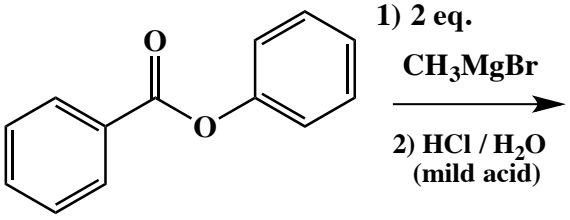




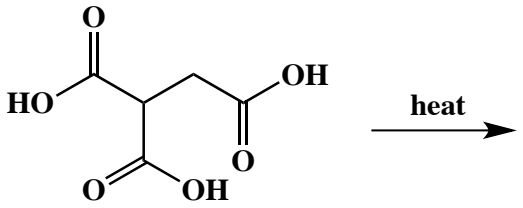
→

22. (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. Also, do not worry about balancing these equations, you just need to show us the major organic products of these transformations.**

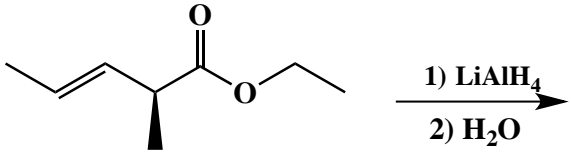




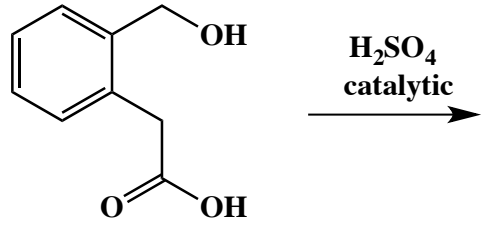
Draw all the carbon containing products made from the ester starting material



Draw all the carbon containing products made from the triacid starting material



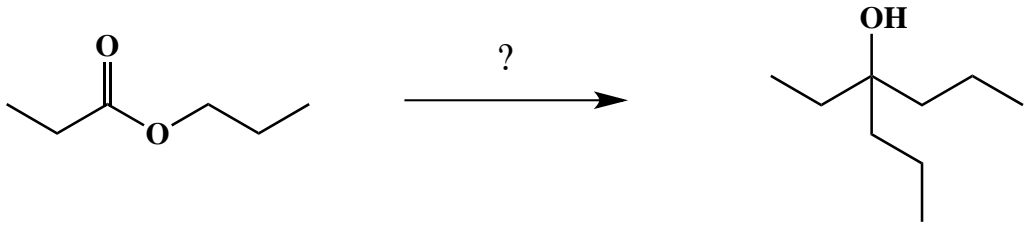
Draw all the carbon containing products made from the ester starting material



23. 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 write "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)

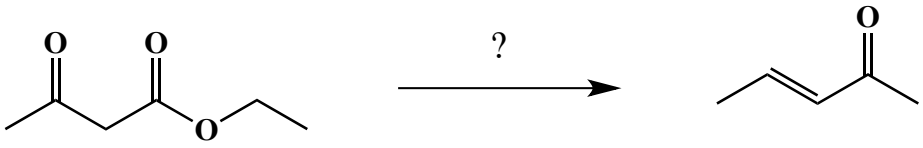
A)



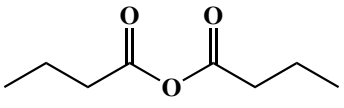
23. You might want to save this until last. I consider it to be challenging. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to write "Racemic" where appropriate.

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

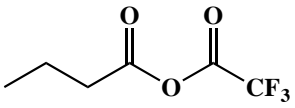
(16 pts)

B) 

24. Here is an MCAT style "Passage" question. Read the passage then answer the multiple choice questions. The anhydrides you have seen thus far are symmetrical, meaning both halves are derived from the same carboxylic acid. It is possible to make unsymmetrical anhydrides. They are produced by reacting acid chlorides derived from one carboxylic acid with the carboxylate of a different carboxylic acid.

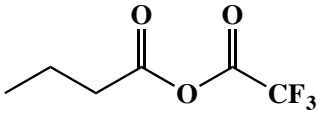


Symmetrical anhydride

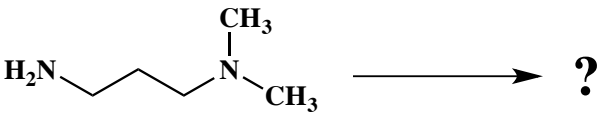


Unsymmetrical anhydride

Unsymmetrical anhydrides react with nucleophiles according to mechanism B. Based on what you know about reactivity, predict the product of the following reaction of an unsymmetrical anhydride with a diamine.



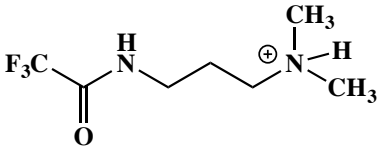
Unsymmetrical anhydride



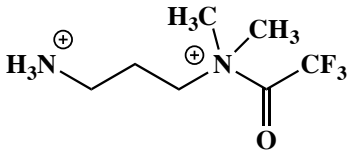
***N*,*N*-dimethylpropane-1,3-diamine**

Question 1 (4 pts) Circle the predominant product of the above reaction:

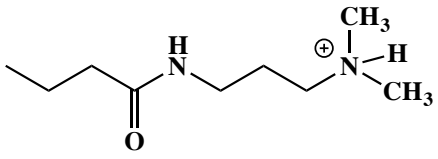
A)



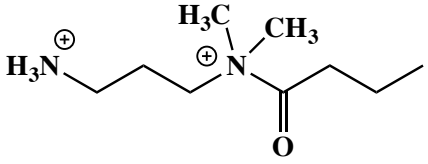
B)



C)



D)



Question 2 (6 pts) For the following question, you can only circle ONE answer. Let us consider the answer you chose for the first part (Question 1) of this problem. Select which of the following arguments supported your selection of the major reaction product you chose.

A) The three fluorine atoms stabilize an anion via the inductive effect so $CF_3CO_2^{\ominus}$ is the better leaving group.

B) The three fluorine atoms destabilize an anion via the inductive effect so $CH_3CH_2CH_2CO_2^{\ominus}$ is the better leaving group.

C) The primary amine is the better nucleophile because there is less steric hindrance and the product amide functional group is neutral.

D) The tertiary amine is the better nucleophile because there is more steric hindrance and product amide functional group has a positive charge.

E) Both A) and C)

F) Both B) and D)

Question 3 (4 pts) Think through the reaction mechanism. Select the MINIMUM number of equivalents of the *N*,*N*-dimethylpropane-1,3-diamine you would need to complete the reaction if we assume 1.0 equivalent of unsymmetrical anhydride is used as starting material.

A) 1.0 Equivalent

B) 2.0 Equivalents

C) 3.0 Equivalents

D) 4.0 Equivalents