NAME (Print): _____

SIGNATURE: _____

Chemistry 320N
Dr. Brent Iverson
2nd Midterm
March 26, 2015

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!!!

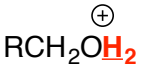
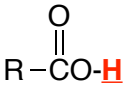
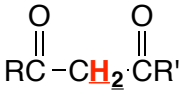
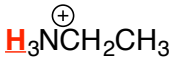
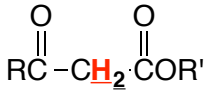
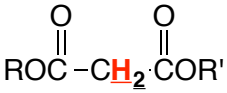
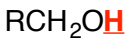
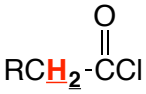
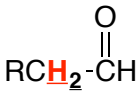
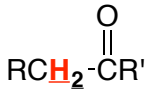
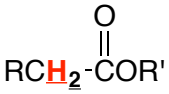
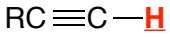
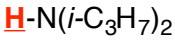
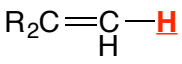
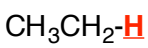
Page	Points	
1		**(57)**
6		**(34)**
7		**(35)**
8		**(36)**
9		**(12)**
10		**(17)**
11		**(17)**
12		**(19)**
13		**(10)**
14		**(19)**
15		**(4)**
16		**(8)**
17		**(5)**
Total		**(273)**

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

DO NOT TEAR OUT THIS PAGE!!

We are trying something new to improve grading accuracy. 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.

B)

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.

B)

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.

D)

Question 4, page 3 (6 pts) Write the hybridization state of the atoms indicated by the arrows.

a) sp^2 b) sp^3 c) sp^2 d) sp^3 e) sp^2 f) sp^2

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) yes b) no c) yes d) yes e) no

Question 6, page 4 (1 pt) What pH (2.0, 7.0, or 11.0) corresponds to the stucture from question 5?

2.0

Question 7, page 4 (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.

A)

Question 8, page 5 (4 pts each) Write "A" or "B" in each blank to indicate which structure is the nucleophile and which is the electrophile.

8.1 The nucleophile is B and the electrophile is A

8.2 The nucleophile is B and the electrophile is A

8.3 The nucleophile is B and the electrophile is A

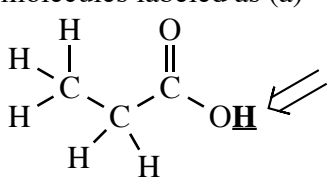
8.4 The nucleophile is B and the electrophile is A

8.5 The nucleophile is A and the electrophile is B

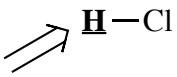
8.6 The nucleophile is B and the electrophile is A

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

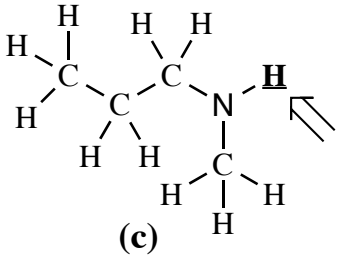
1. (5 pts) Rank order all of the following with respect to relative acidity. The acidic H atom in question is indicated in bold and with an underline for each molecule. **On the answser sheet on page 1 write the letter corresponding to the correct order of acidity,** ranked from most to least acidic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



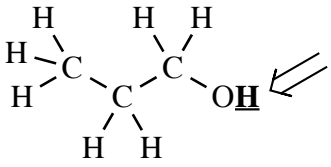
(a)



(b)



(c)

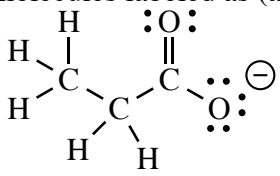


(d)

most acidic least acidic

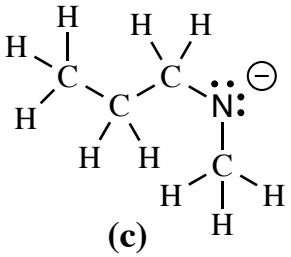
A)	**(a)**	**(b)**	**(c)**	**(d)**
B)	**(b)**	**(a)**	**(d)**	**(c)**
C)	**(c)**	**(a)**	**(d)**	**(b)**
D)	**(b)**	**(c)**	**(a)**	**(d)**
E)	**(d)**	**(c)**	**(b)**	**(a)**

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) - (d).

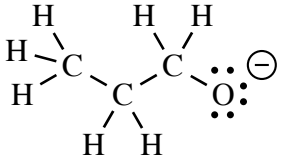


(a)

(b)



(c)



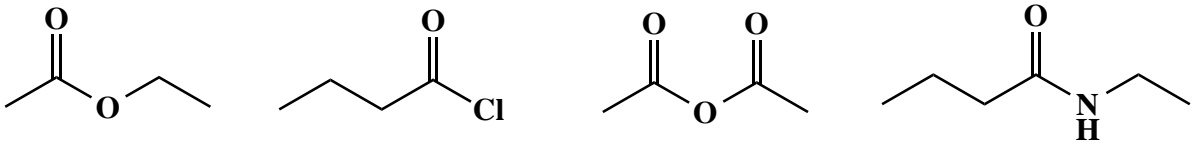
(d)

most stable least stable

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

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

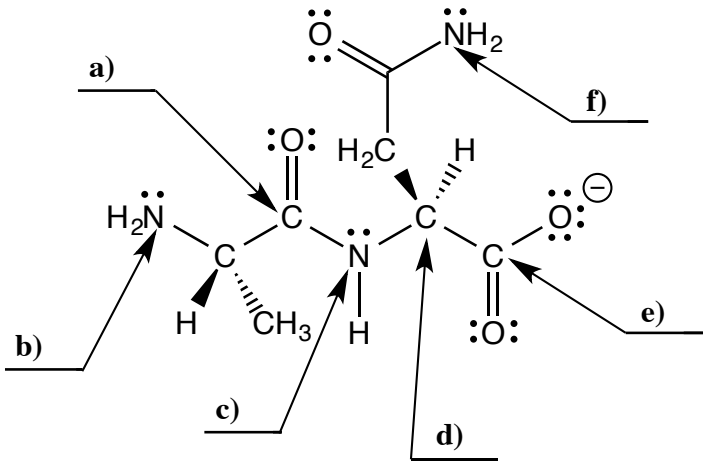
3. (5 pts) Rank order all of the following with respect to relative reactivity with a nucleophile such as NH_3. **On the answer sheet on page 1 write the letter corresponding to the correct order of reactivity,** ranked from most to least reactive for the molecules labeled as (a) - (d).



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

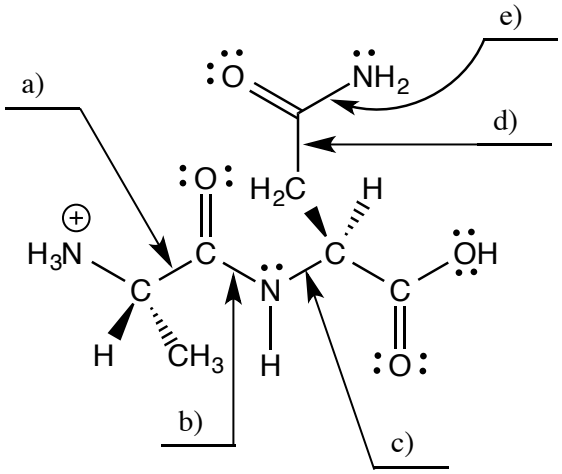
	most reactive			least reactive
A)	**(a)**	**(b)**	**(c)**	**(d)**
B)	**(b)**	**(a)**	**(d)**	**(c)**
C)	**(c)**	**(a)**	**(d)**	**(b)**
D)	**(b)**	**(c)**	**(a)**	**(d)**
E)	**(d)**	**(c)**	**(b)**	**(a)**

4. (6 points) On the answer sheet on page 1, indicate the hybridization state of each atom identified by the arrows.



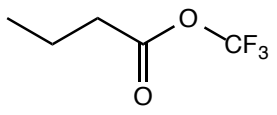
Write the answers to these questions on the answer sheet on page 1

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.**

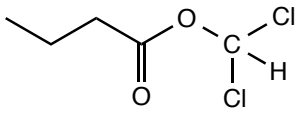


6. (1 pt) For the above structure (problem 5), is the molecule drawn in the correct protonation state for pH 2.0, 7.0, or 11.0? Write 2.0, 7.0 or 11.0 on the answer sheet on page 1.

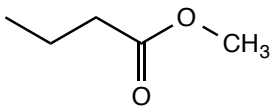
7. (5 pts) You will have to think about this one a little. Rank the following molecules with respect to overall reactivity with nucleophiles such as NH_3. **On the anwer sheet on page 1, write the letter corresponding to the correct order of reactivity,** ranked from most to least reactive for the molecules labeled as (a) - (d).



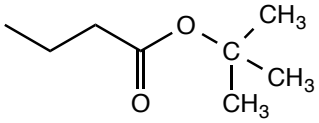
(a)



(b)



(c)

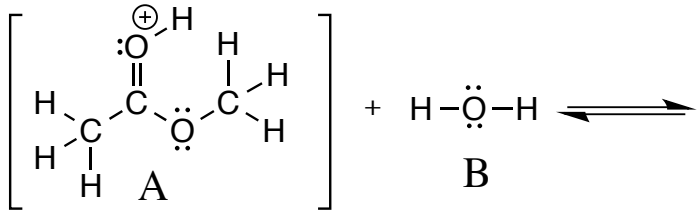


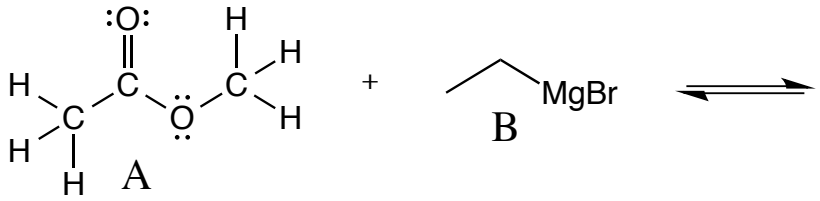
(d)

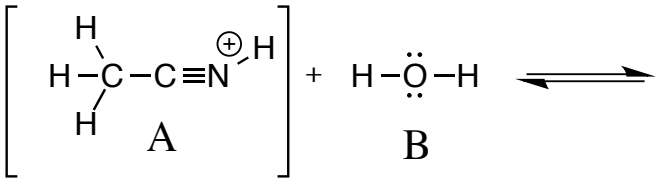
	most reactive			least reactive
A)	**(a)**	**(b)**	**(c)**	**(d)**
B)	**(b)**	**(a)**	**(d)**	**(c)**
C)	**(c)**	**(a)**	**(d)**	**(b)**
D)	**(b)**	**(c)**	**(a)**	**(d)**
E)	**(d)**	**(c)**	**(b)**	**(a)**

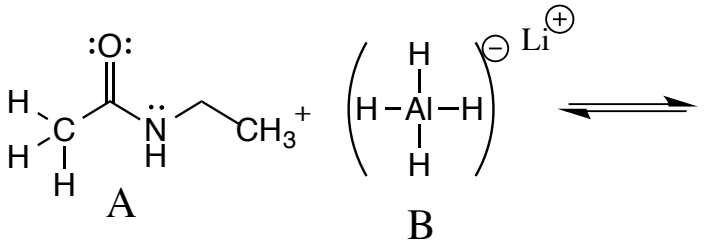
Write the answers to these questions on the answer sheet on page 1

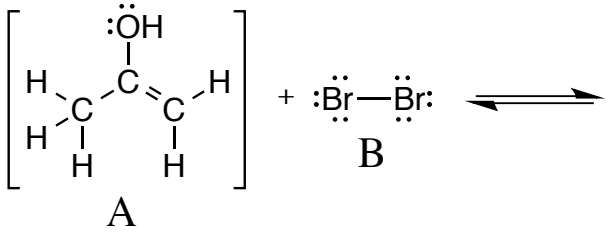
8. (4 pts each) The mechanisms we have been studying largely involve nucleophiles of various types attacking electrophiles of various types, with protons being transferred quite often as well. The following reagents represent individual steps from some of these mechanisms. **For each pair of reacting molecules, one is labeled A and the other B. On the page 1 answer sheet, indicate whether A or B is the nucleophile and whether A or B is the electrophile.**

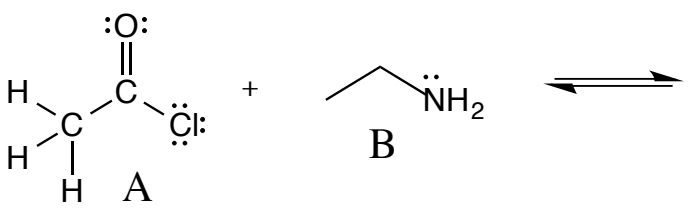
8.1 

8.2 

8.3 

8.4 

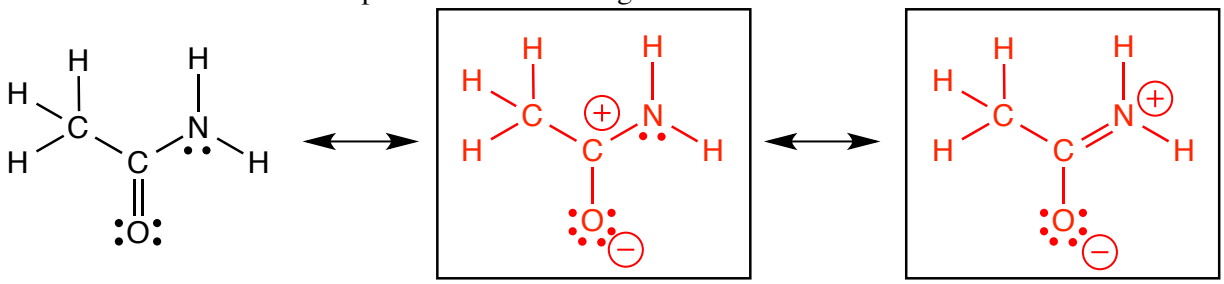
8.5 

8.6 

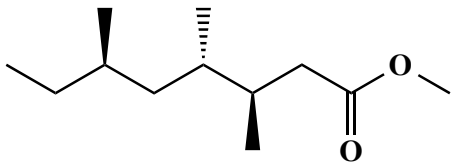
9. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We wil be looking for a minumum of 7 key points here.

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**.

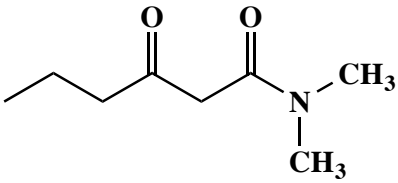
10. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



11. (4 pts each) In the space provided, write the IUPAC name (including stereochemistry where appropriate) for the following two molecules:

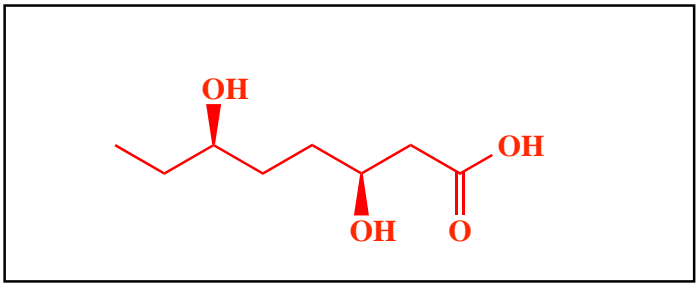


methyl (3*R*,4*S*,6*R*)-3,4,6-trimethyloctanoate

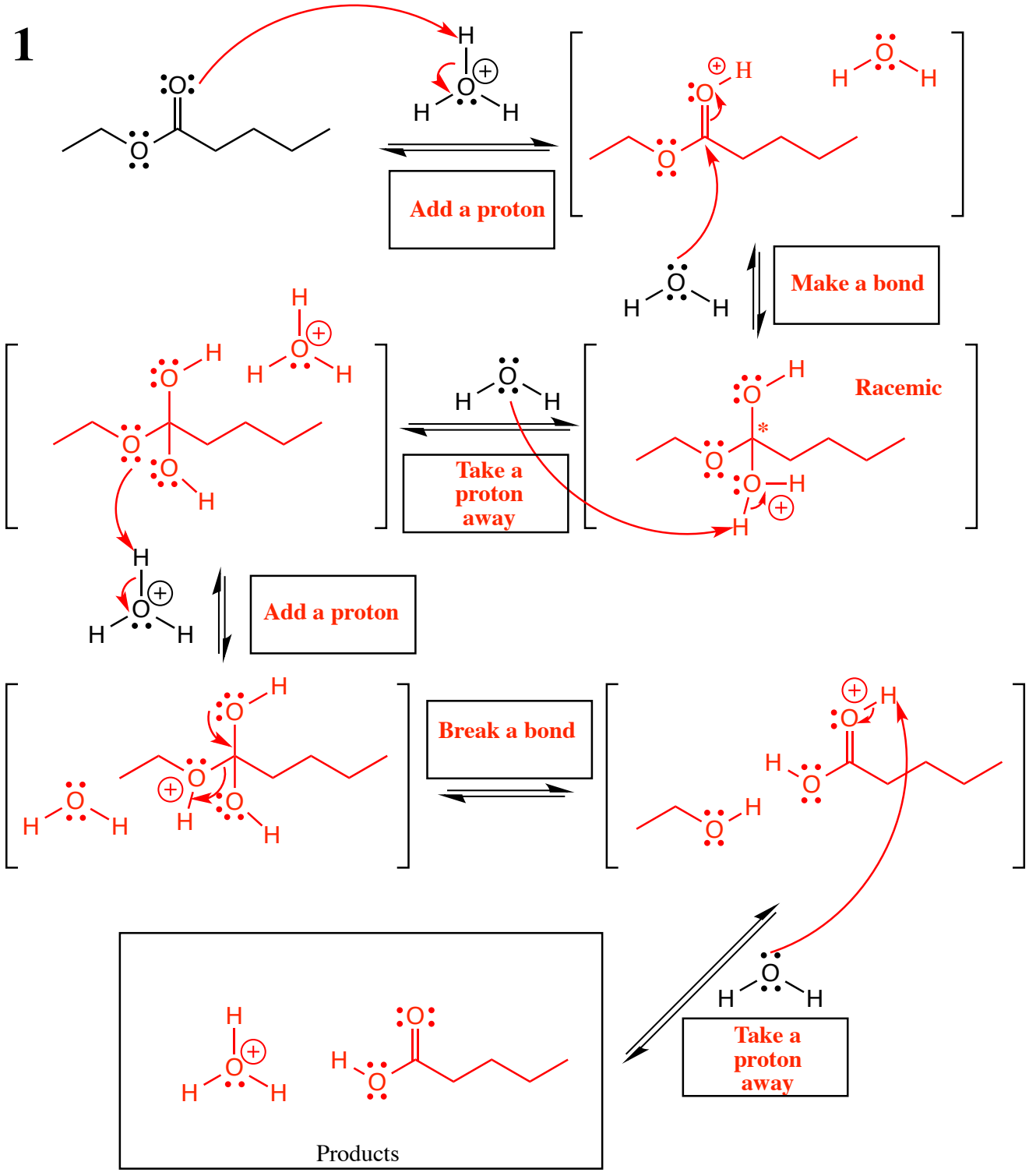


***N*,*N*-dimethyl-3-oxohexanamide**

12. (4 pts) In the space provided, draw the following molecule: (3*S*,6*R*)-3,6-dihydroxyoctanoic acid



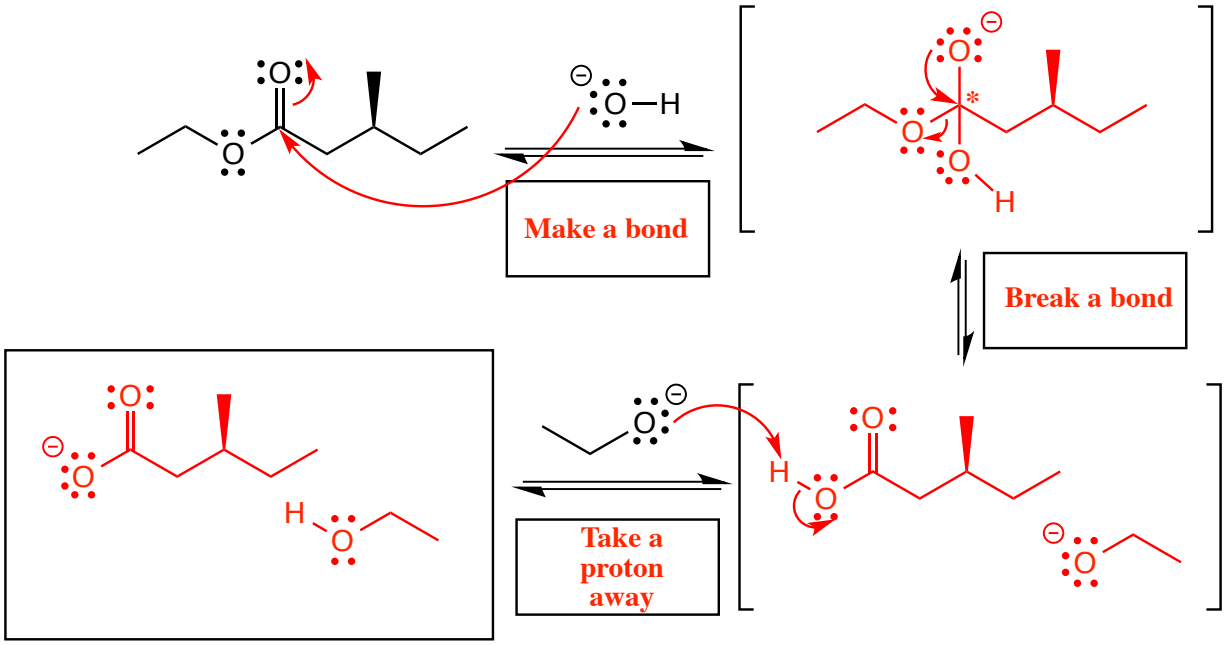
13. (35 pts) Complete the mechanism for the following ester hydrolysis reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR 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.).**



Note you will have to write a balanced equation forthe above mechanism on PAGE 9

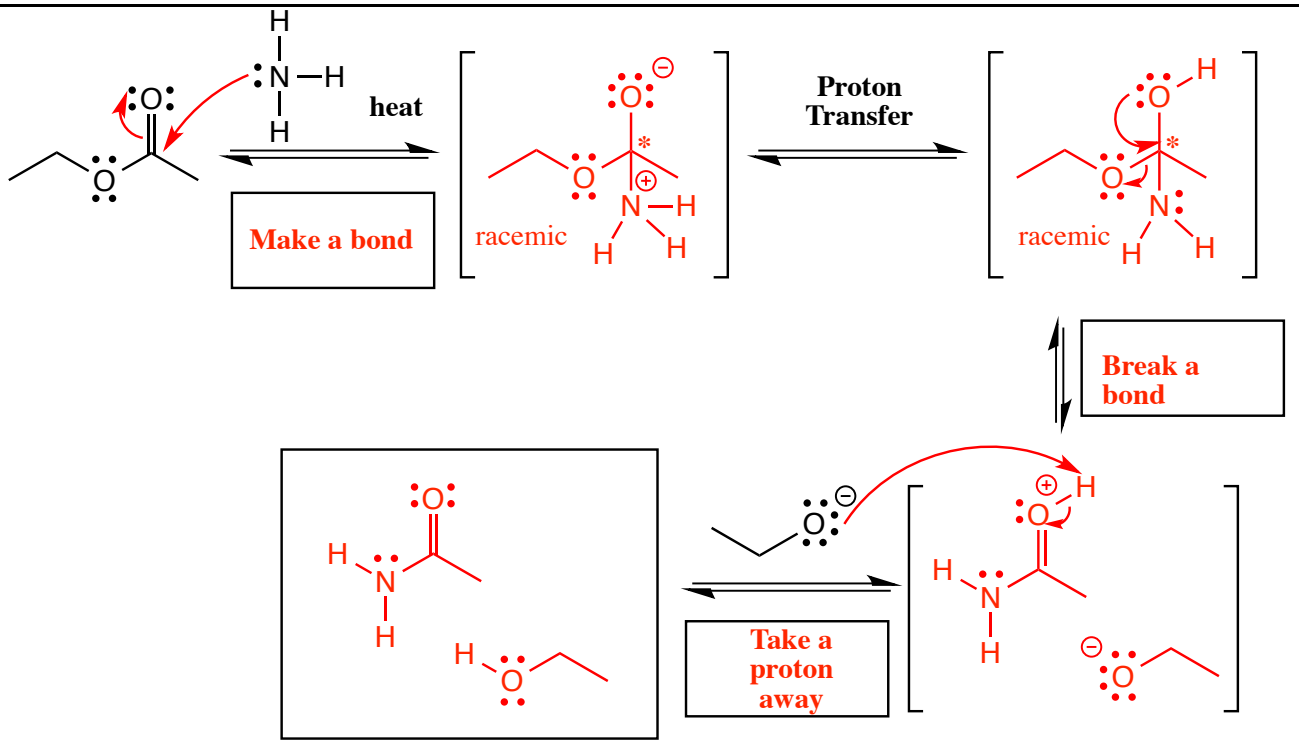
15. (36 pts) Complete the mechanism for the following two reactions of esters. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each 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



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

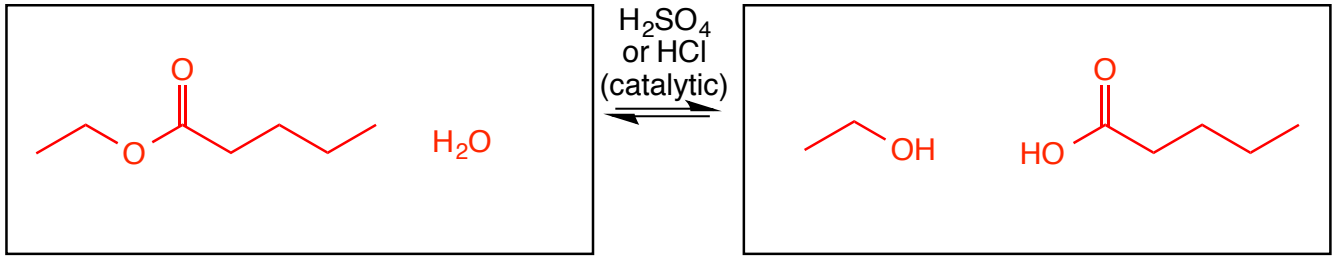
3



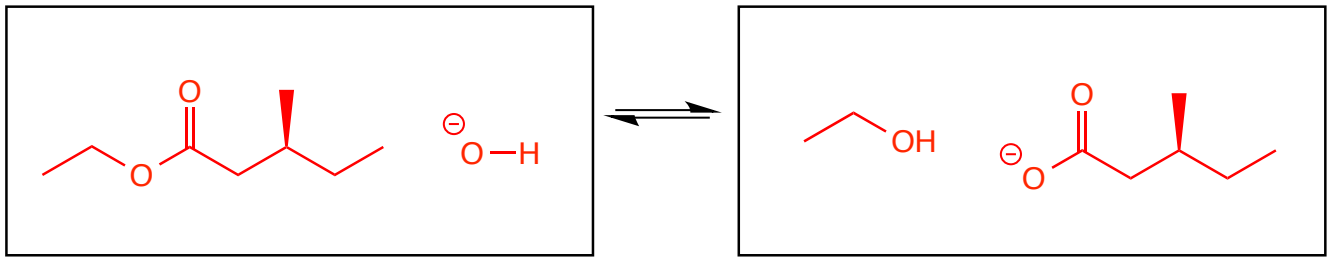
Note you will have to write a balanced equation for the above mechanism on the NEXT page

16. (12 pts) Write BALANCED equations for the three mechanisms, 1-3, that you drew on the last three pages.

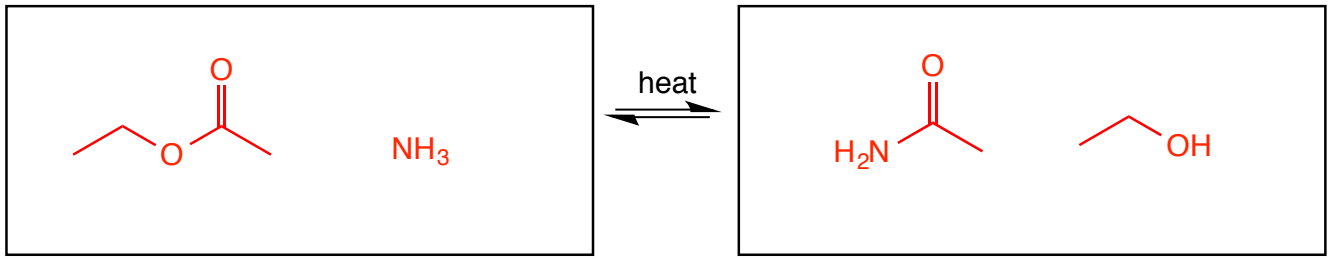
Write a balanced equation for the overall process described by mechanism 1 from page 7



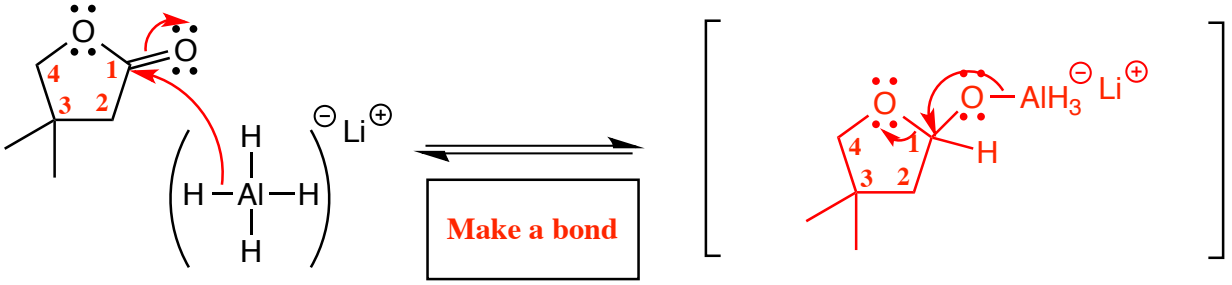
Write a balanced equation for the overall process described by mechanism 2 from page 8

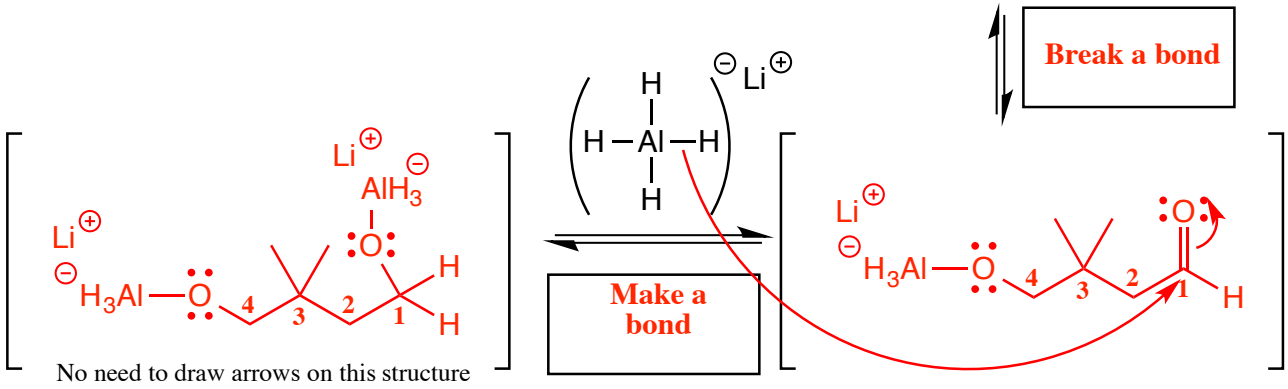


Write a balanced equation for the overall process described by mechanism 3 from page 8

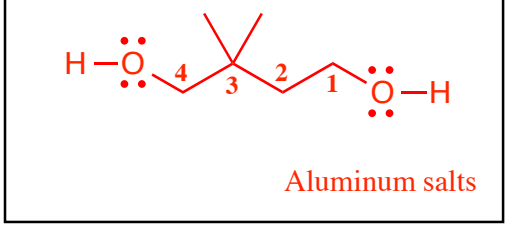


14. (17 pts) Complete the mechanism for the reduction of the following lactone. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the carbon containing products for each step.** Remember, I said <u>all</u> the 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.).**

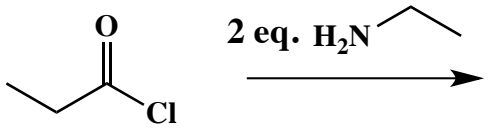


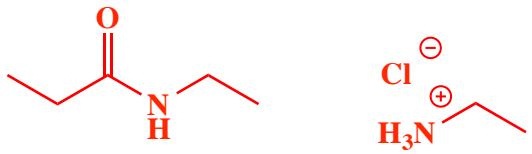


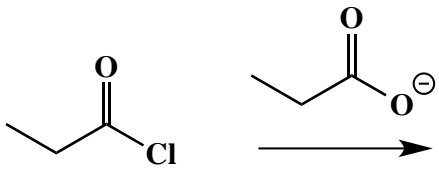
2) Chemist opens flask and adds excess

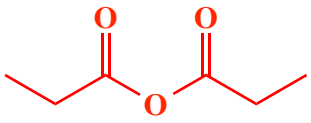


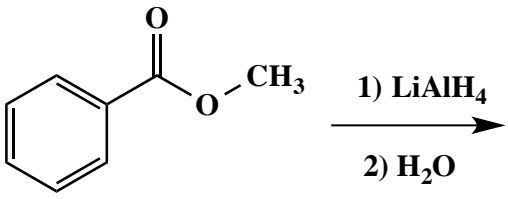
16. (3 or 5 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and 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.**

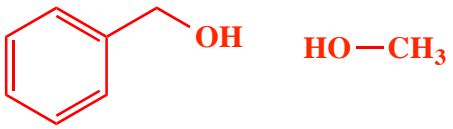




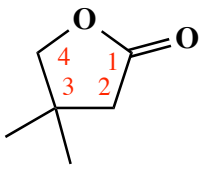


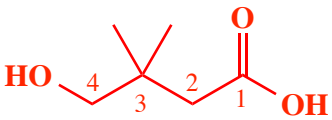


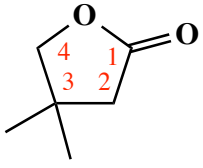


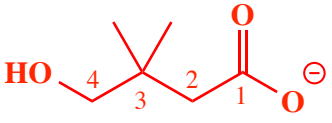


Draw all the organic products made from the ester starting material

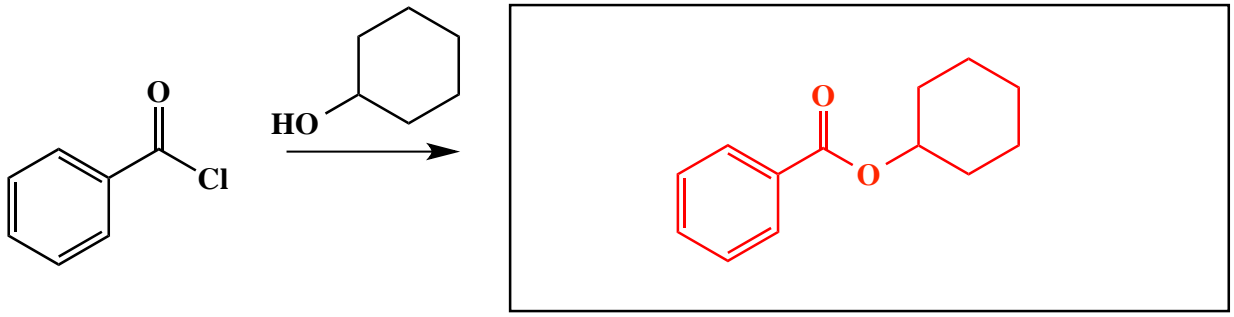


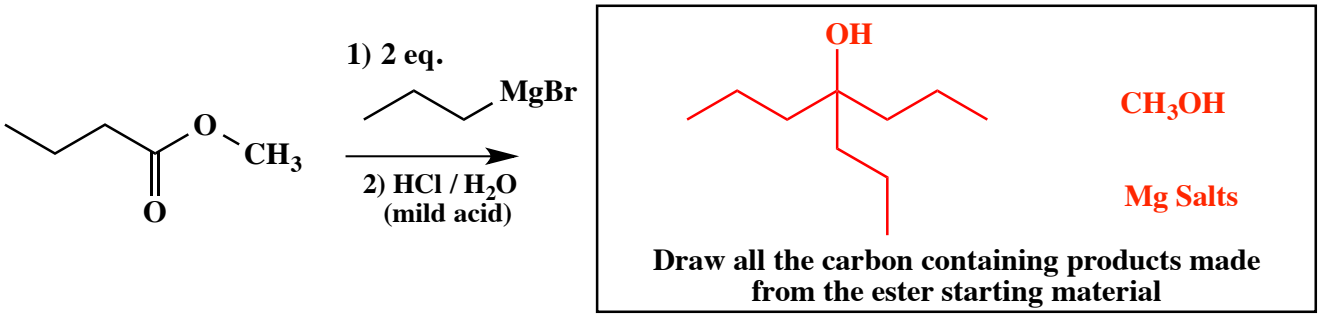


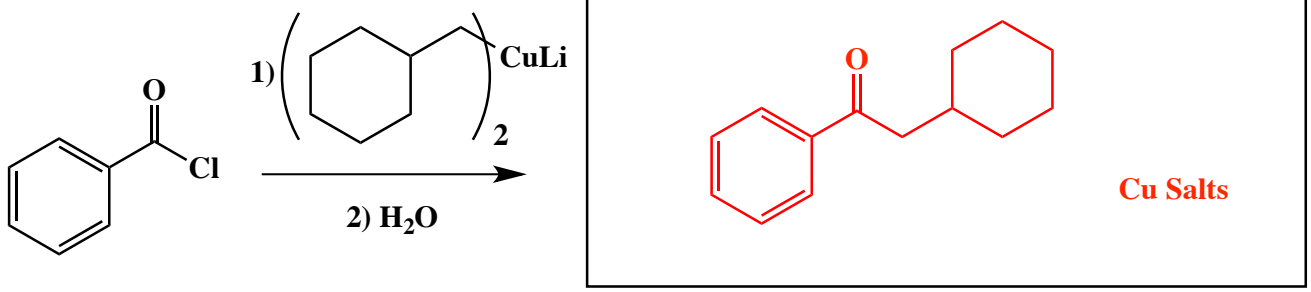


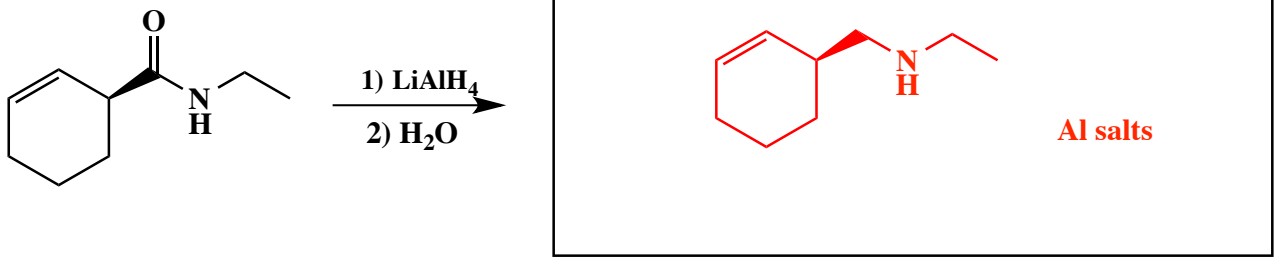


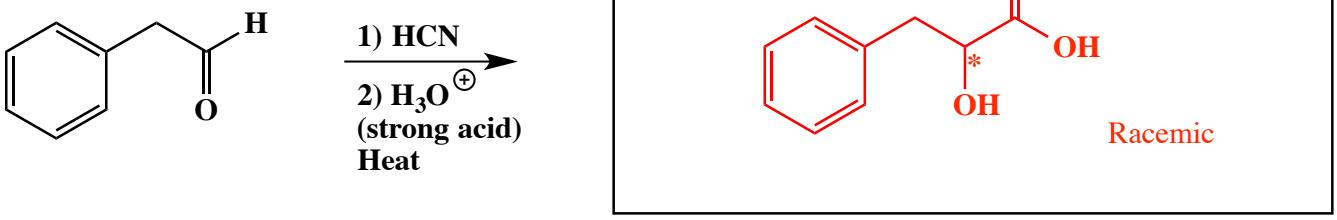
16. (3 or 5 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and 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.**









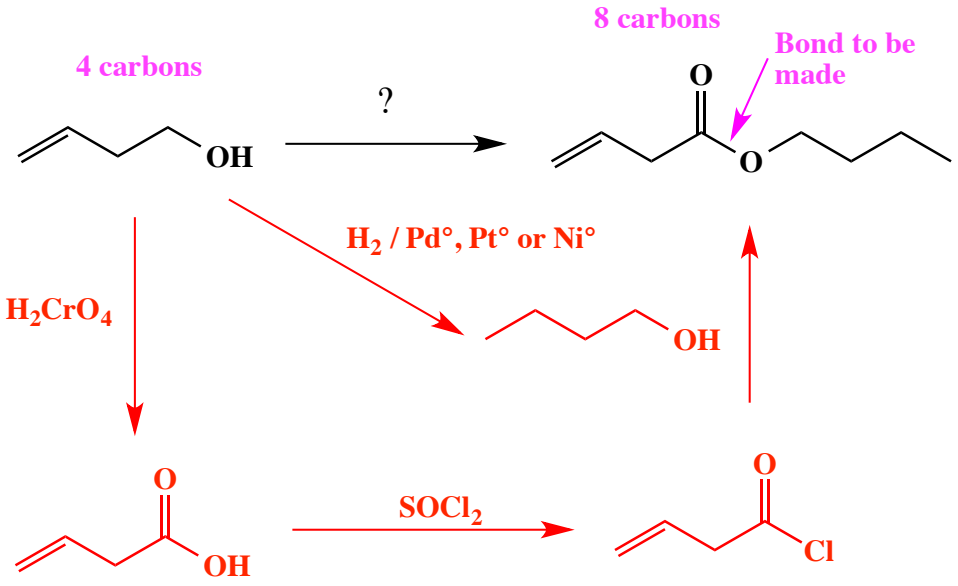


17. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic"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



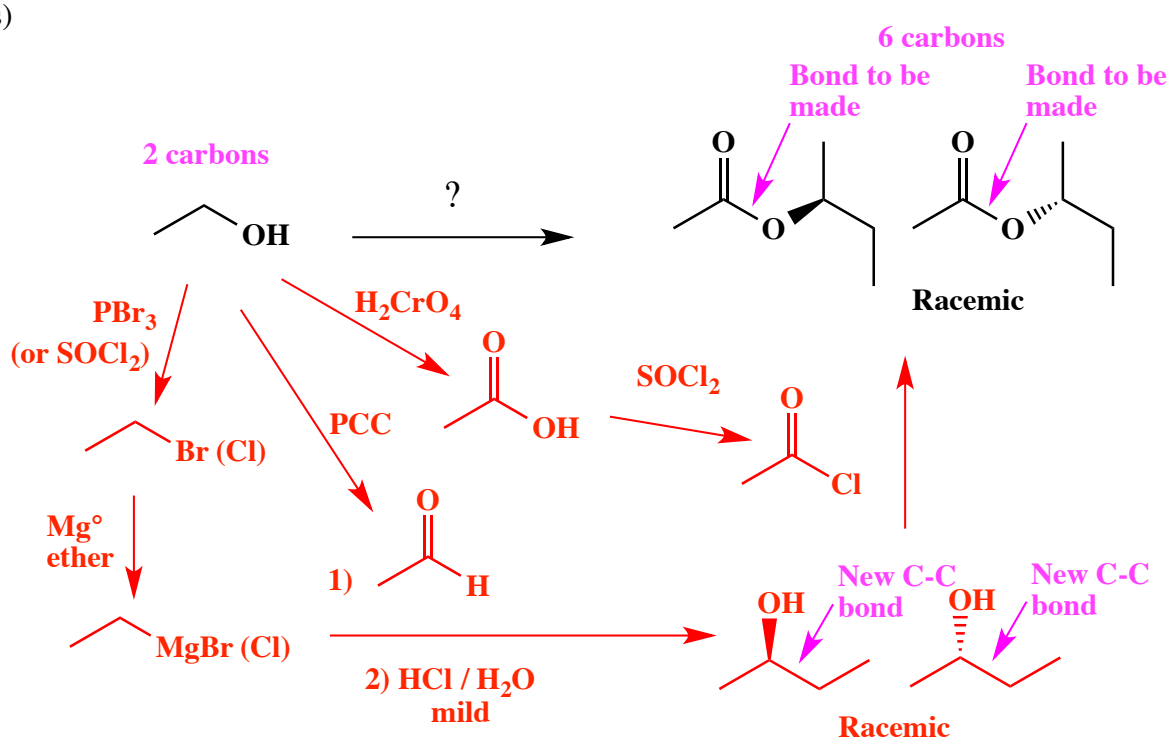
Recognize there are 8 carbons in the product, but 4 carbons in the starting material so 2 molecules of starting material must be assembled into the product. **Recognize** further the final product as an ester, so the bond to be made is between an acid chloride and an alcohol. **Recognize** the acid chloride as being derived from oxidation of the starting alcohol. **Recognize** the alcohol as coming from reduction of the C=C bond of the starting alcohol

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.

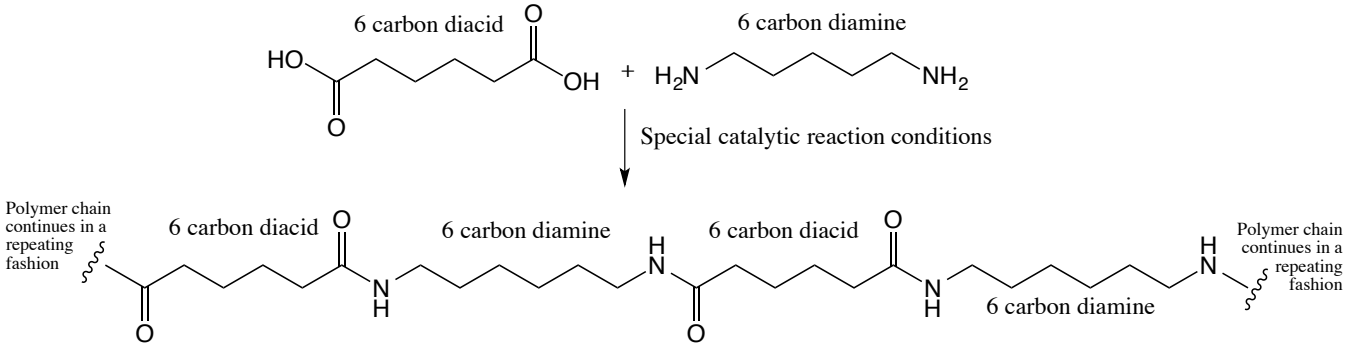
(19 pts)

B)



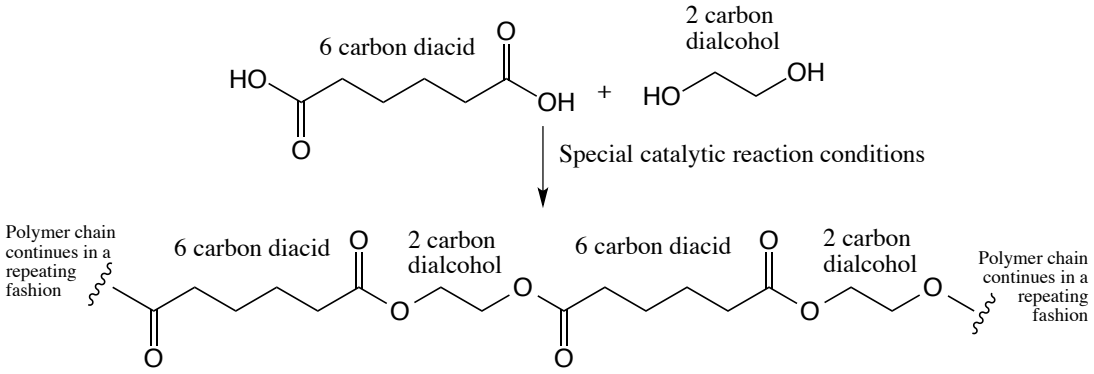
Recognize there are 6 carbons in the product, but 2 carbons in the starting material so three molecules of starting material must be assembled into the product. **Recognize** further the final product as an ester, so the bond to be made is between an acid chloride and an alchohol. **Recognize** the acid chloride as being derived from acetic acid, which comes from the starting ethanol via oxidation with chromic acid. **Recognize** the reacemic four carbon alcohol as the KRE of a Grignard reaction between acetaldehyde and an ethyl Grignard, both of which can be made from ethanol as shown.

18. Here is an MCAT style "Passage" question. Read the passage then answer the multiple choice questions. Synthetic fibers are used in everything from modern fabrics for clothes to synthetic ropes and even bullet proof vests and clothes. The first commercially important synthetic fiber, Nylon 66, was created right after World War II at the DuPont company. Nylon 66 is so-named because it is synthesized as a polymer from a 6-carbon diacid and a 6-carbon diamine. These molecules are reacted to give amide bonds. Because both the diacid and diamine have two functional groups, the result is a very long chain molecule called a polymer.



Nylon 66

Nylon 66 was made at the same time as analogous polyester polymers, such as the one shown here made from the same 6-carbon diacid and a 2-carbon dialcohol.



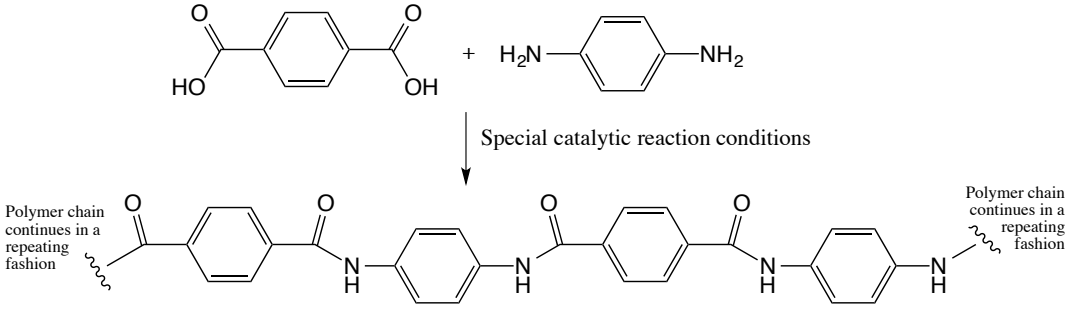
One of the first polyester polymer fibers

For the following three questions, circle the single best choice among the four answers:

1) Nylon 66 makes strong fibers suitable for creating durable fabrics among many other items. The first polyesters, on the other hand, turned out to melt too easily and are not used for any useful fibers or other products. Fibers made from Nylon 66 are strong and useful while the polyester fibers are not because:

   A) The amide bond does not rotate as easily as ester bonds making the nylon polymer molecules less flexible
   B) Amides can hydrogen bond between polymer chains, while polyesters cannot
   C) Amides are more basic than esters
   D) Both A) and B)

Kevlar is an important fiber that is also composed of diacids and diamines linked by amides to make long polymer molecules as shown below. Kevlar fibers are so strong they are used to make bullet-proof vests and more recently bullet-proof clothes. Many celebrities and politicians wear suits made from Kevlar every day and no one can usually tell their stylish suit jacket would stop a bullet!

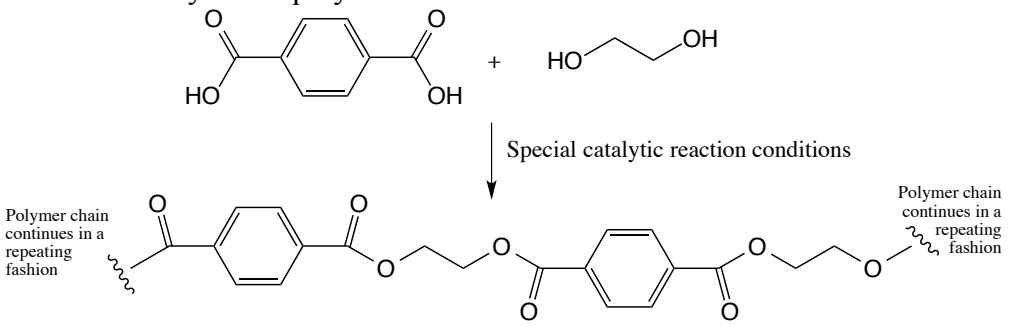


Kevlar

2) Kevlar makes fibers that are much stronger than Nylon 66 because:

A) The rings make the amides more basic in Kevlar compared to Nylon 66
B) The rings make the Kevlar polymer chain much more rigid than the Nylon 66 polymer chain
C) The Kevlar amides make hydrogen bonds between polymer chains, while the amides in Nylon 66 do not make hydrogen bonds.
D) Kevlar was brought to Earth by Superman, explaining why his suit stops bullets.

Dacron and Mylar are polyesters made from the same diacid used to make Kevlar

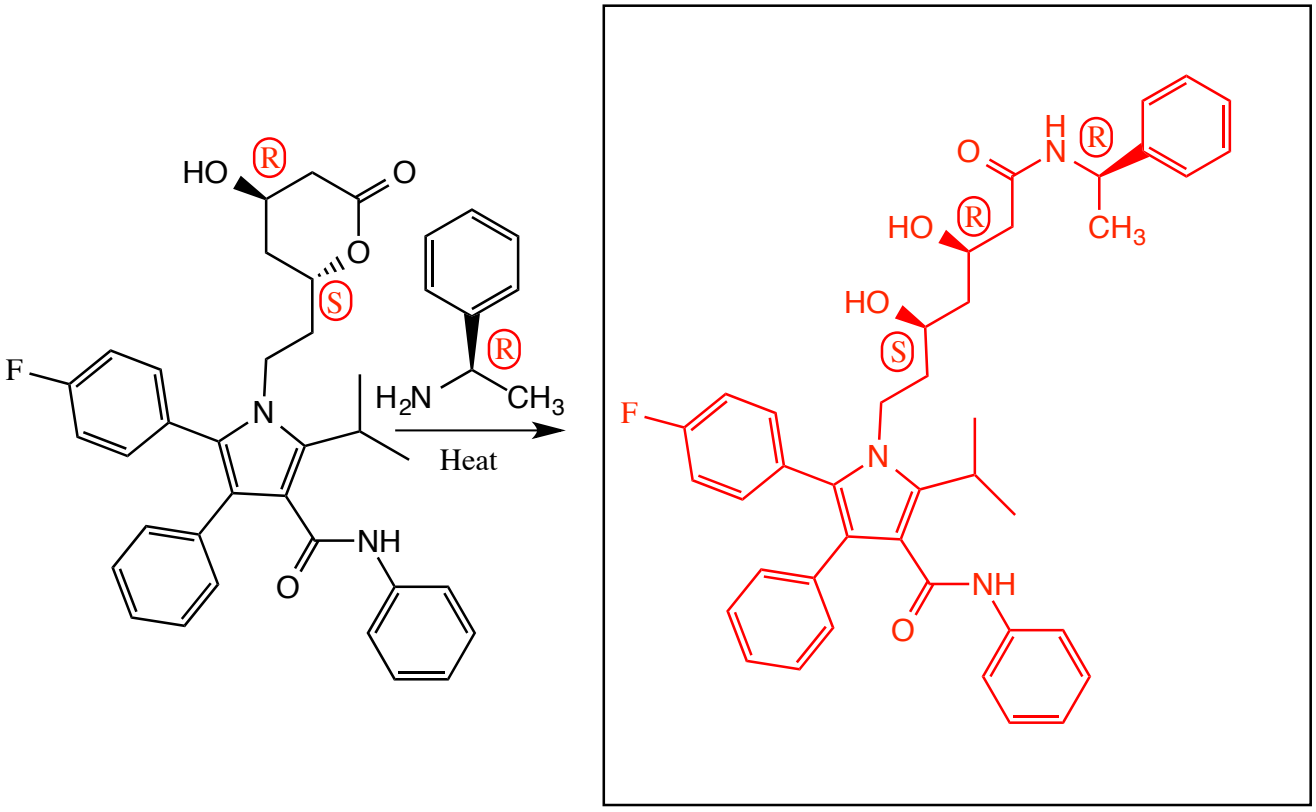


Dacron and Mylar

3) Dacron and Mylar make much stronger fibers and films compared to the polyester on the previous page because:

A) The rings make the esters more basic in Dacron and Mylar compared to ester polymers with no rings
B) The rings make the Dacron and Mylar polymer chain much more rigid compared to ester polymers with no rings
C) The Dacron and Mylar esters make hydrogen bonds between polymer chains, while the polymers made from esters with no rings do not make hydrogen bonds
D) Dacron was brought to Earth by aliens bent on colonizing our planet. In the 1980's the aliens tried to convince all males to buy polyester "leisure suits" and thus become unattractive to all human females. It almost worked. Check out some old photos of your father!!

19. (10 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.



The key to this problem is to realize that the upper cyclic portion of the starting molecule is a lactone, a cyclic ester. Esters react with amines with heating to give amides as shown in the product. Keeping track of the stereochemistry can be accomplished by labeling each chiral center.