NAME (Print): _____

SIGNATURE: _____

Chemistry 320N
Dr. Brent Iverson
2nd Midterm
March 21, 2013

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		(17)
2		(21)
3		(18)
4		(18)
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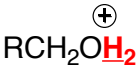
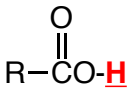
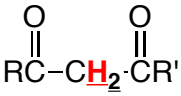
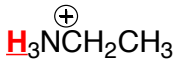
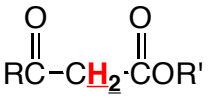
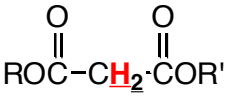
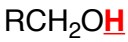
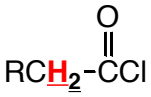
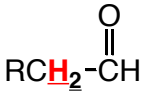
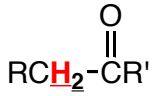
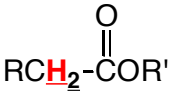
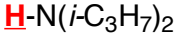
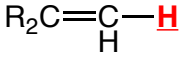
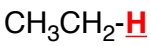
6		(34)
7		(22)
8		(25)
9		(23)
10		(14)
11		(7)
12		(18)
13		(10)
14		(8)
15		(8)
Total		(272)

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

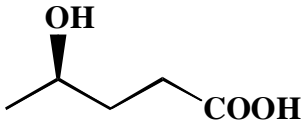
Signature_____ Pg 1 _____(17)

1. (3 pts) The most important question in organic chemistry is:

_____

2. (3 or 4 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

A.



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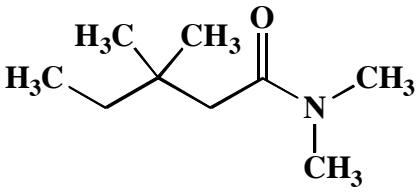
B.

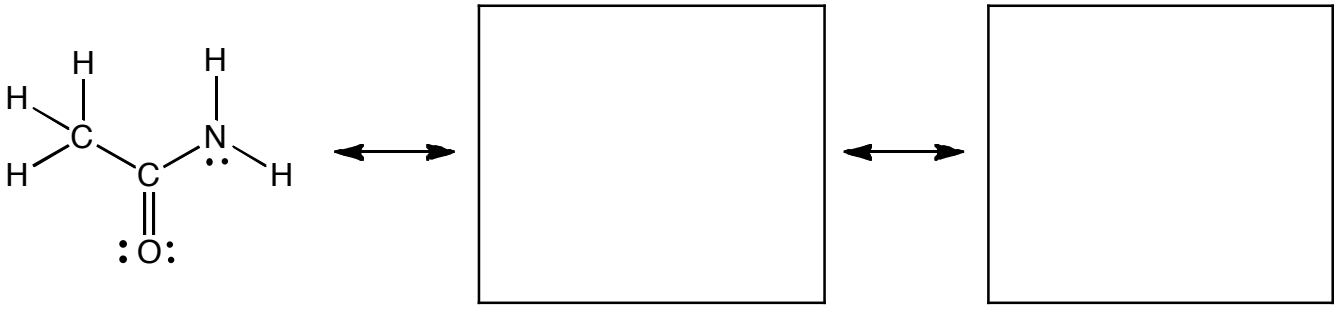


_____

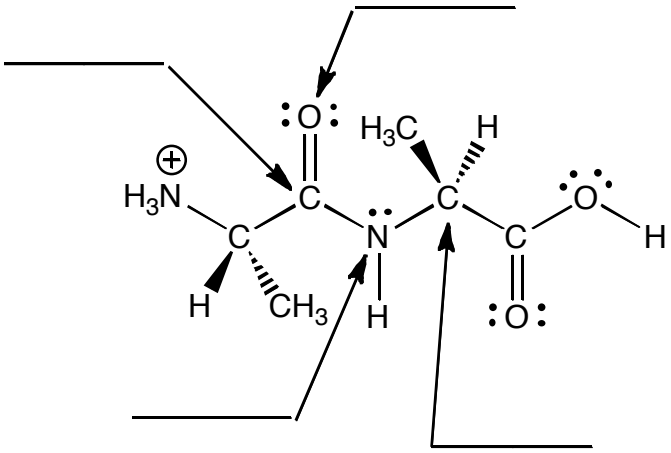
C. **Diethyl cis-1,2-cyclohexanedicarboxylate**

D. **(*3S,4S*)-3-Chloro-4-methylhexanoyl chloride**

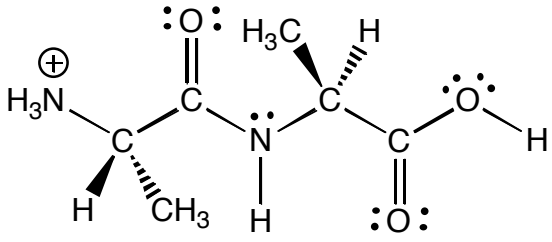
3. (10 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



4. (4 points) On the lines, indicate the hybridization state of each atom indicated by the arrows.



5. (5 points) On the following structure **1) Draw a box around all the atoms that are ALWAYS in the same plane as the amide carbonyl group (C=O) and 2) circle all of the C-N bonds that DO NOT ROTATE.**

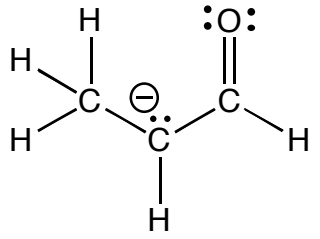


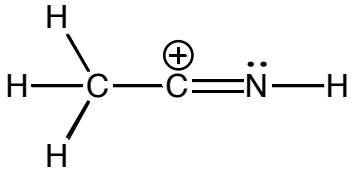
(2 pts) For the above stucture, is this the appropriate protonation state for pH 2.0, 7.0, or 10.0?

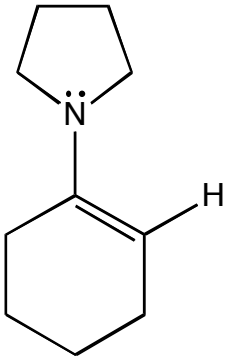
_____

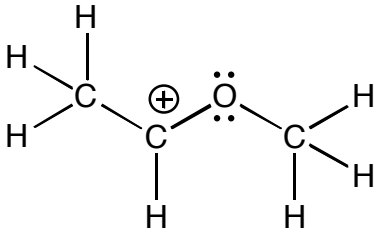
⟸ Notice This

6. (16 points) For each of the following molecules, draw the other important resonance contributing structure. Be sure to show all lone pairs and formal charges. **In each case, add arrows to the structure on the left to indicate the flow of electrons leading to the structure you drew on the right.**

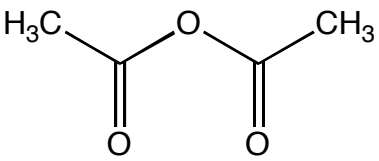


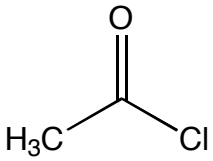


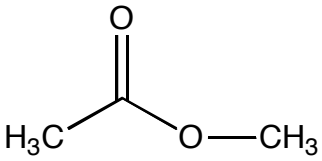


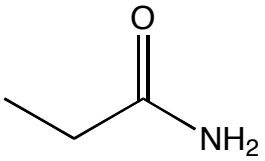


7. (4 points) Rank the following carboxylic acid derivatives with respect to reactivity with a nucleophile. Write a 1 under the most reactive, and a 4 under the least reactive derivative.



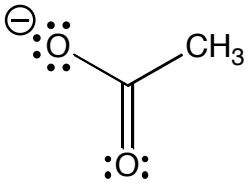


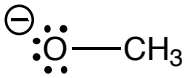


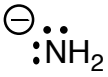


_____ _____ _____ _____

8. (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.

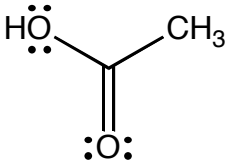


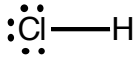


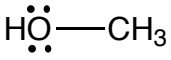


_____ _____ _____ _____

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

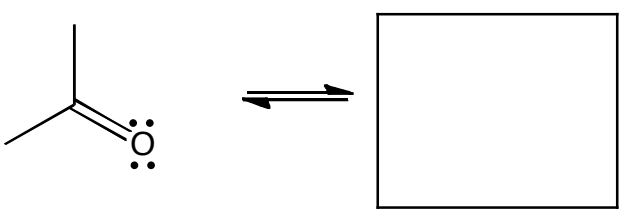


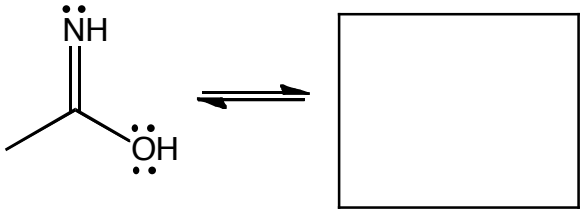




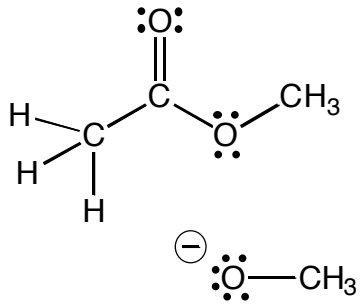
_____ _____ _____ _____

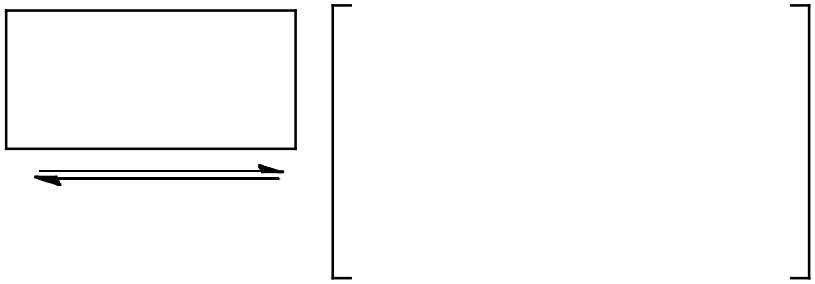
10. (6 points) Each of the following undergo the process of tautomerization. For each draw the other major tautomer, then for each pair, circle the one that is more stable.

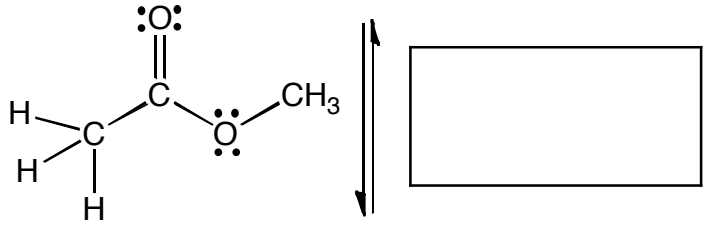


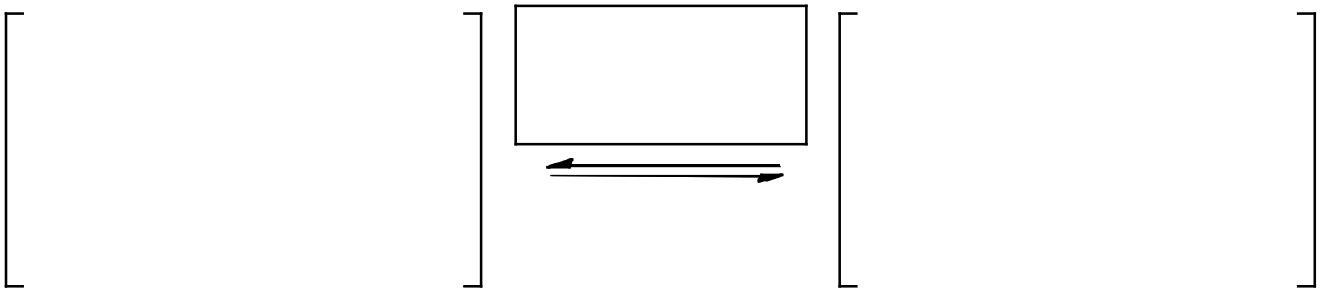


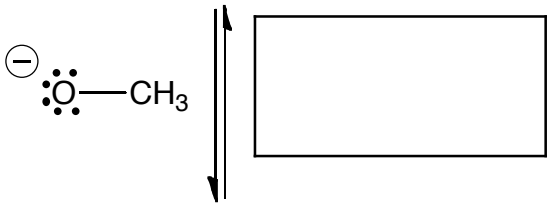
11. (29 pts.) Complete the mechanism for the following Claisen condensation reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR THE PRODUCTS, MARK IT WITH AN ASTERISK AND LABEL AS "RACEMIC" IF RELEVANT. ***IN THE BOX BY EACH SET OF ARROWS, WRITE WHICH OF THE 4 MECHANISTIC ELEMENTS IS INDICATED IN EACH STEP OF YOUR MECHANISM (For example, "Add a proton").***











Products

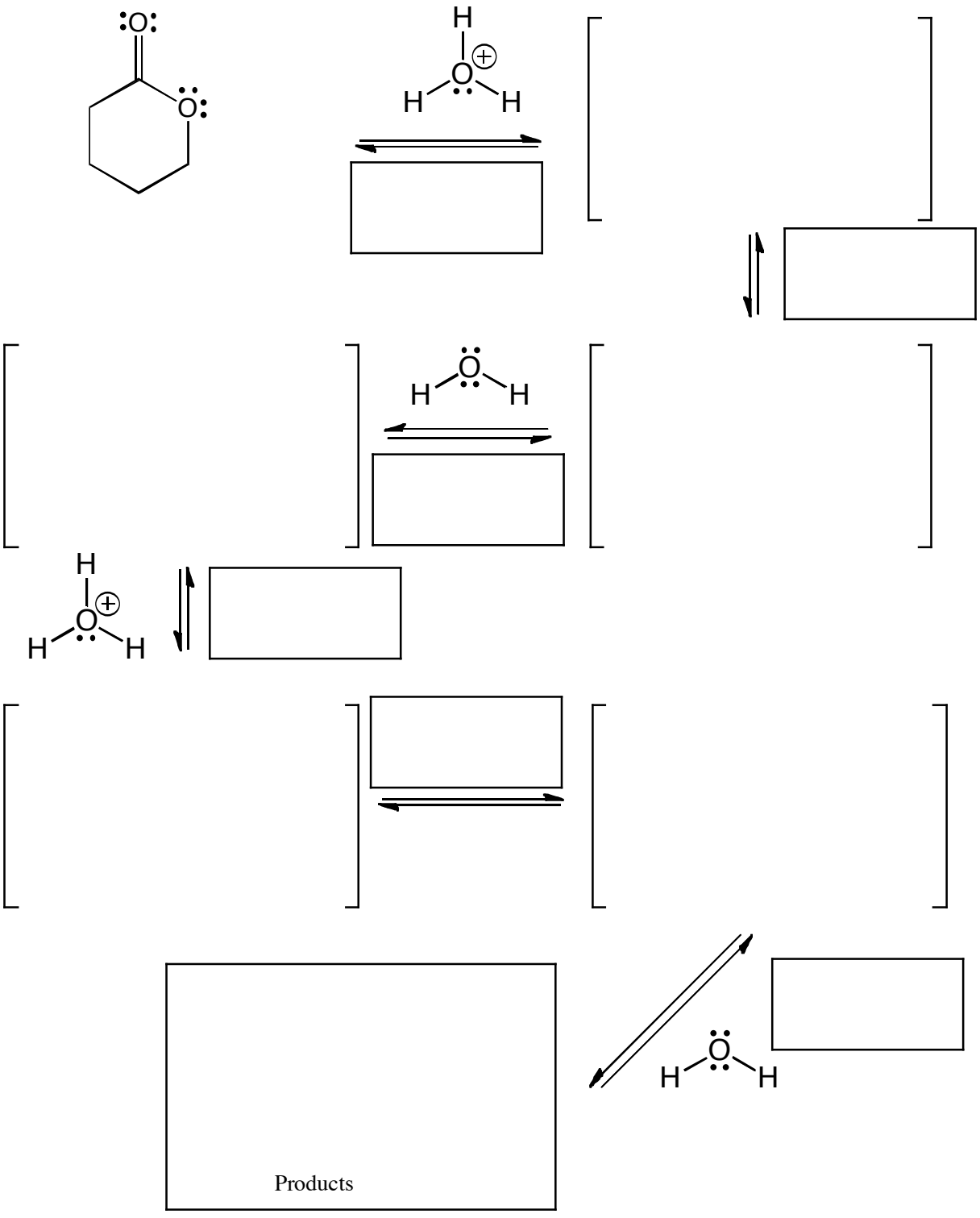
(2 pts) Based on the mechanism you just drew, what is the MINIMUM number of equivalents of $NaOCH_3$ you need to get a 100% yield of product?

_____

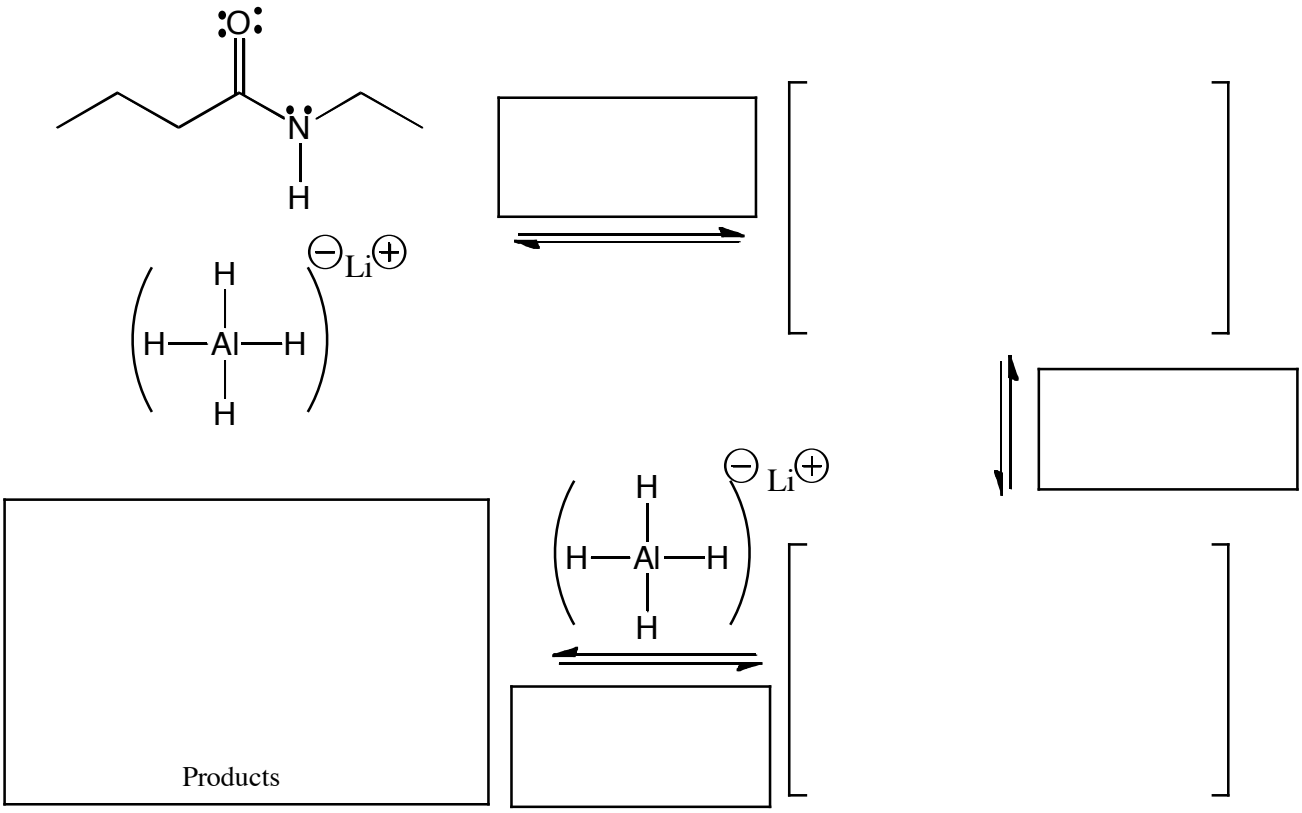
*******NOTICE THESE********

(4 pts) For any mechanism steps above that you labeled as "Make a bond", draw a CIRCLE around the molecule that is acting as the nucleophile, and a BOX around the molecule that is acting as the electrophile for that step.

12. (34 pts.) Complete the mechanism for the following acid catalyzed ester hydrolysis reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR THE PRODUCTS, MARK IT WITH AN ASTERISK AND LABEL AS "RACEMIC" IF RELEVANT. ***IN THE BOX BY EACH SET OF ARROWS, WRITE WHICH OF THE 4 MECHANISTIC ELEMENTS IS INDICATED IN EACH STEP OF YOUR MECHANISM (For example, "Add a proton").***

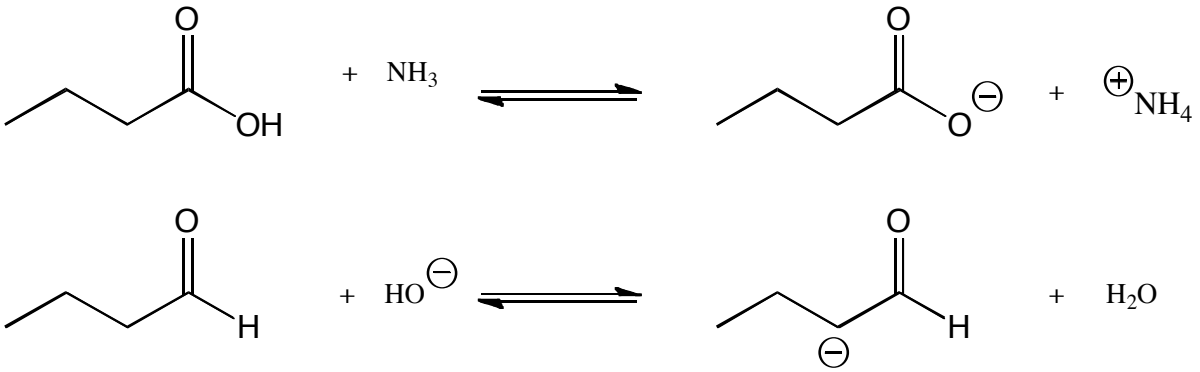


13. (16 pts.) Complete the mechanism for the following reduction of an amide using $LiAlH_4$. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR THE PRODUCTS, MARK IT WITH AN ASTERISK AND LABEL AS "RACEMIC" IF RELEVANT. ***IN THE BOX BY EACH SET OF ARROWS, WRITE WHICH OF THE 4 MECHANISTIC ELEMENTS IS INDICATED IN EACH STEP OF YOUR MECHANISM (For example, "Add a proton").***

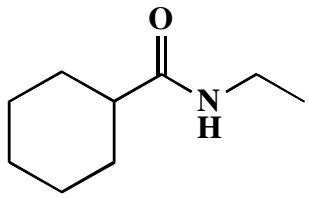


Note: In this reaction the chemist opens the flask and adds water in a second step that quenches any excess $LiAlH_4$. Therefore, you need a second step to add water when using this reaction in synthesis even though it is not shown in the mechanism above.

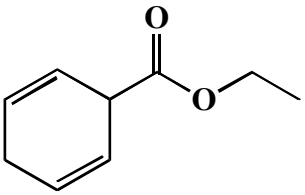
14. (6 pts) For the following equations that describe acid-base reactions, **circle the side that predominates at equilibrium.**



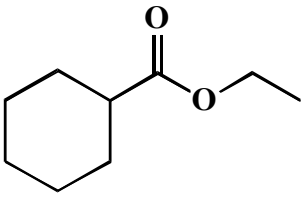
15. (3 or 5 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and write racemic. No need for wedges and dashes. DO NOT DEHYDRATE DURING AN ALDOL REACTION -WRITE THE NON-DEHYDRATED PRODUCT.**



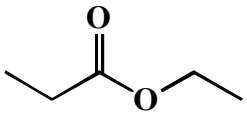
4 eq. HCl
H_2O
heat



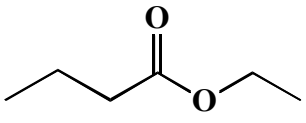
1) $LiAlH_4$
2) H_2O

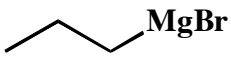


1) 1.0 Equivalent NaOH
2) HCl / H_2O (mild acid)



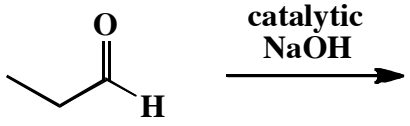
1) 0.5 Equivalent NaOEt
2) HCl / H_2O (mild acid)

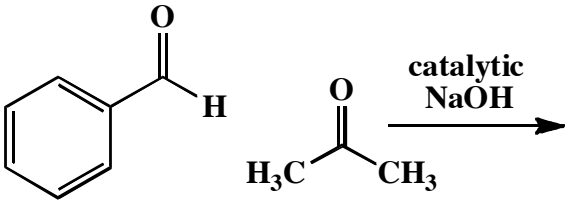


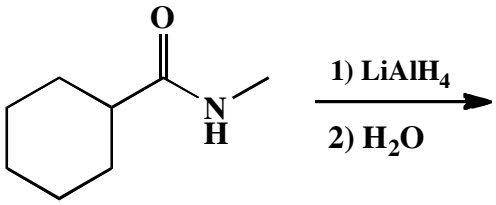
1) 2 eq.


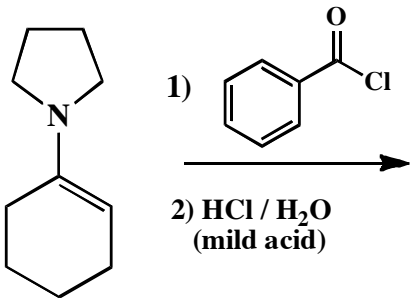
2) HCl / H_2O (mild acid)

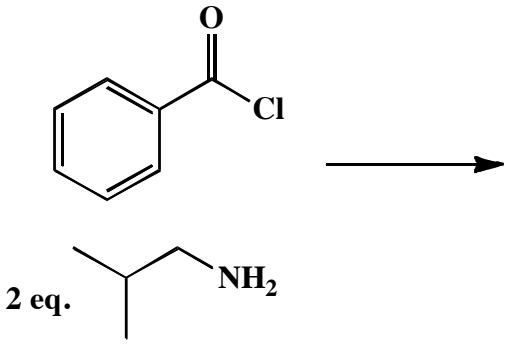
15 (cont. 3 or 5 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and write racemic. No need for wedges and dashes. DO NOT DEHYDRATE DURING AN ALDOL REACTION -WRITE THE NON-DEHYDRATED PRODUCT.**





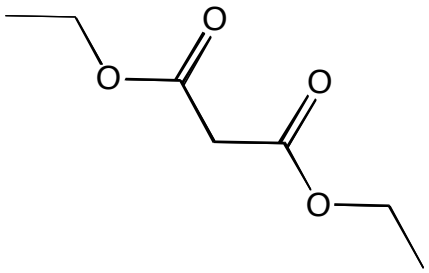




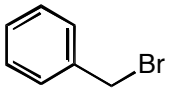


16. (14 points) For the following sequences of reactions, draw the final organic product or products after ALL the steps have been completed. You do not need to draw the molecules synthesized along the way, **only the last product that is formed**. If a new chiral center is created in the reaction that produces a racemic mixture, label the chiral center with an asterisk (*) and write "***racemic***" underneath.

(6 pts)



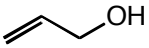
1) 1.0 eq. NaOEt

2) 

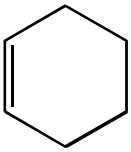
3) H_2SO_4/H_2O (Strong acid)

4) Heat

5) $SOCl_2$

6) 

(8 pts)



1) O_3

2) $(CH_3)_2S$

3) catalytic NaOH

4) $H_3O^{\oplus}$, heat

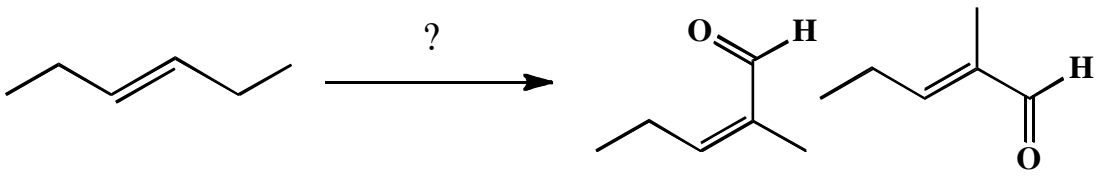
5) $H_2C^{\ominus}—P^{\oplus}(Ph)_3$

17. (7 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms 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.

(7 pts)

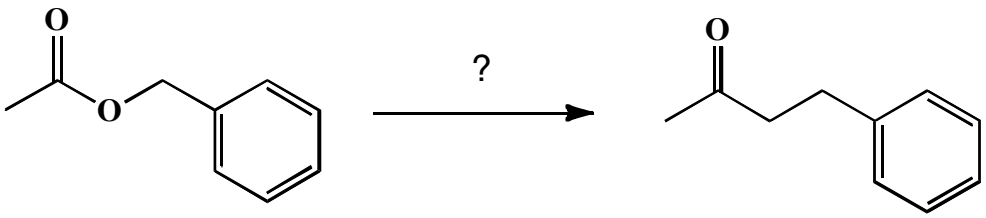
A)



***E,Z* Mixture**

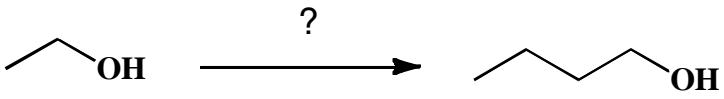
17. (cont. 18 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" where appropriate.

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



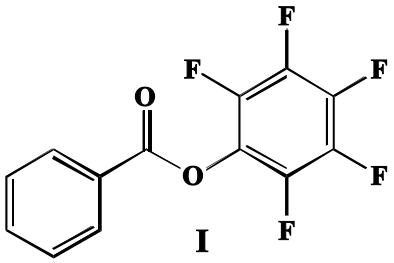
17. (cont. 10 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" where appropriate.

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

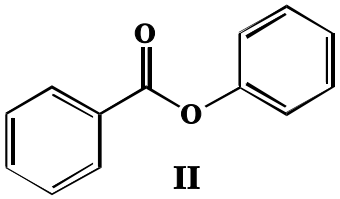


18. (16 pts total) Here is an MCAT question in multiple choice format. You have not seen this chemistry before, but you have learned fundamental principles of reactivity that will lead you to the correct answers. In each case, you should circle the correct answer.

The carboxylic acid derivatives we discussed in class represent only the tip of the iceberg of those that have been developed. For example, there are a variety of different carboxylic acid derivatives that have F atoms attached to modulate reactivity. One of these is the ester shown below on the left.



I



II

Suppose both of these esters are reacted with CH_3NH_2. Which one of the following statements is true?

A. Molecule I reacts faster to create an amide product.

B. Molecule II reacts faster to create an amide product.

C. Molecules I and II react at the same rate to create an amide product.

D. Neither molecule I or II will react with CH_3NH_2.

Select the statement that best explains your answer to the previous question.

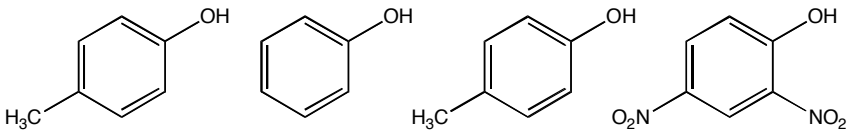
A. Molecule I reacts faster primarily because of the inductive effect.

B. Molecule I reacts faster primarily because of hyperconjugation.

C. Molecule II reacts faster primarily because of the inductive effect.

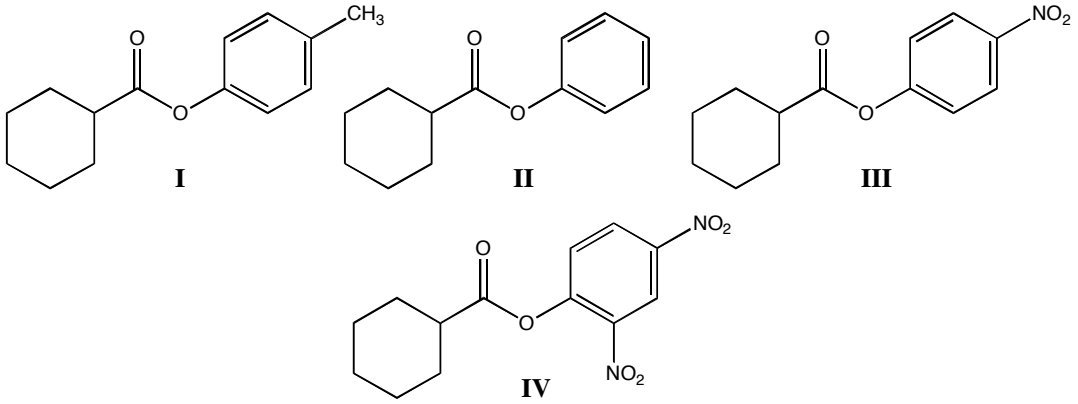
D. Molecule II reacts faster primarily because of hyperconjugation.

Following are the pK_a values for four different alcohols.



pK_a = 10.3 pK_a = 10 pK_a = 7.2 pK_a = 4.1

All of these alcohols are commonly used to make esters. Examples of these esters are shown below.



Given the above pK_a values, which one of the following statements is true?

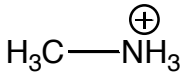
A. Ester **I** will react the fastest with CH_3NH_2 to create an amide.

B. Ester **II** will react the fastest with CH_3NH_2 to create an amide.

C. Ester **III** will react the fastest with CH_3NH_2 to create an amide.

D. Ester **IV** will react the fastest with CH_3NH_2 to create an amide.

Given the following pK_a value:



$pK_a = 10.7$

How many equivalents of CH_3NH_2 will you need to get a 100% yield of amide when reacting with ester **III**?

A. You only need a catalytic amount

B. You need at least 0.5 equivalents

C. You need at least 1.0 equivalent

D. You need at least 2.0 equivalents