

NAME (Print): _____

Chemistry 310N
Dr. Brent Iverson
2nd Midterm
March 22, 2012

SIGNATURE: _____

Please print the
first three letters
of your last name
in the three boxes

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Please Note: This test may be a bit long, but there is a reason. I would like to give you a lot of little questions, so you can find ones you can answer and show me what you know, rather than just a few questions that may be testing the one thing you forgot. **I recommend you look the exam over and answer the questions you are sure of first**, then go back and try to figure out the rest. Also make sure to **look at the point totals** on the questions as a guide to help budget your time.

You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK will be regraded.

Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.

FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

Page	Points	
1		(30)
2	XXXXX	(XX)
3		(20)
4		(21)
5		(18)
6		(25)
7		(29)
8		(17)
9		(20)
10		(14)
11		(10)
12	XXXXX	(XX)
13		(19)
14		(8)
15		(8)
Total		(239)
%		
T Score		
HW		
(HW score + Exam Grade) \implies	Total Grade	

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.

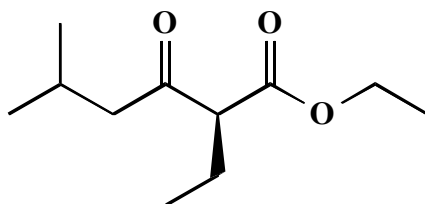
(Your signature)

Compound		pK _a
Hydrochloric acid	H-Cl	-7
Protonated alcohol	$\text{RCH}_2\text{OH}_2^+$	-2
Hydronium ion	H_3O^+	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-5
Ammonium ion	H_4N^+	9.2
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	10
Primary ammonium	$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_3$	10.5
β-Ketoesters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	11
β-Diesters	$\text{ROC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	16
Aldehydes	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	18-20
Ketones	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	18-20
Esters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\text{H}$	25
LDA	$\text{H}-\text{N}(\text{i-C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{H}$	44
Alkanes	$\text{CH}_3\text{CH}_2-\text{H}$	51

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

The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on the **same principles as NMR**, namely the **flipping (i.e. resonance) of nuclear spins of protons by radio frequency irradiation** when a patient is placed in a **strong magnetic field**. **Magnetic field gradients** are used to gain imaging information, and **rotation of the gradient around the center of the object** gives imaging in an entire plane (**i.e. slice inside patient**). In an MRI image, you are looking at **individual slices that when stacked make up the three-dimensional image of relative amounts of protons, especially the protons from water and fat, in the different tissues.**

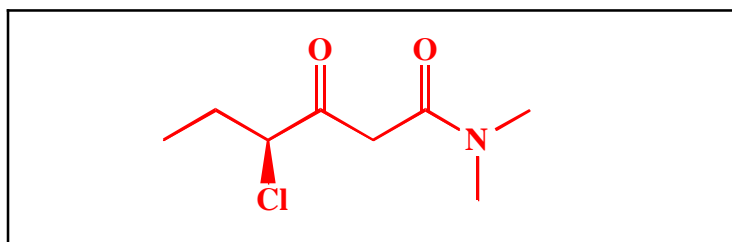
2. (4 pts) In the space provided, write the IUPAC name (including stereochemistry where appropriate) for the following two molecules:



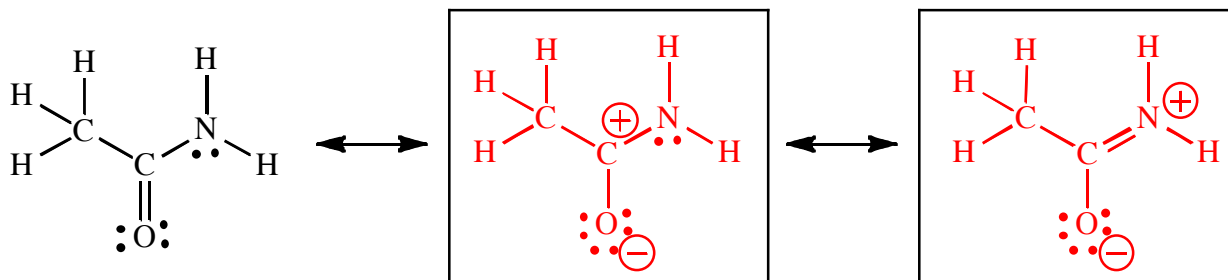
(S)-Ethyl 2-ethyl-5-methyl-3-oxohexanoate

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

(S)-4-Chloro-N,N-dimethyl-3-oxohexanamide



5. (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.

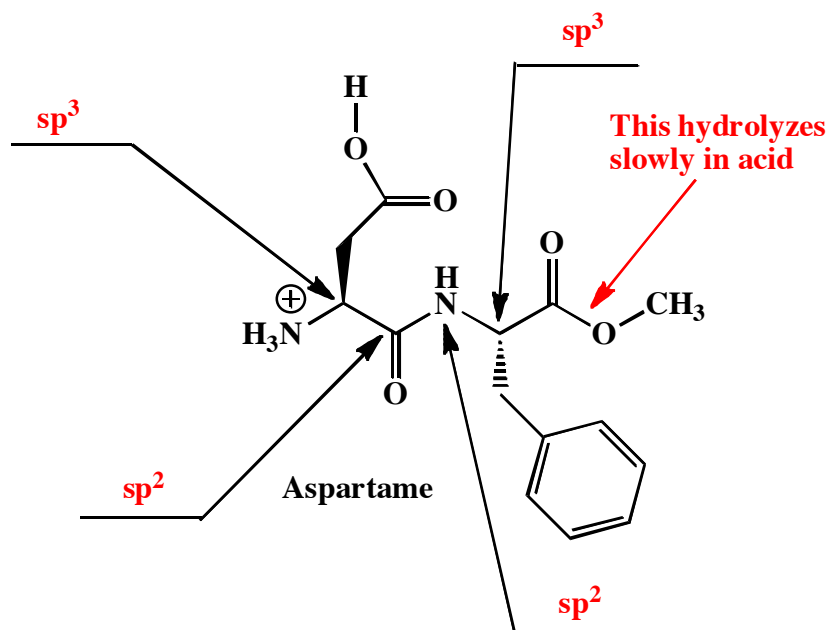


6. (6 pts) List two attributes of amide bonds that lead to stabilization of the folded structures of proteins.

1) The amide carbonyl oxygen and hydrogen on nitrogen can make strong hydrogen bonds

2) The C-N bond cannot rotate freely, so the backbone of proteins is relatively rigid (less flexible) and easier to stabilize in a folded conformation.

7. Aspartame is the sweetener used in diet coke. Its structure is shown below. Because of carbonation and added phosphoric acid, the pH of diet coke is relatively acidic, around pH 2-3.

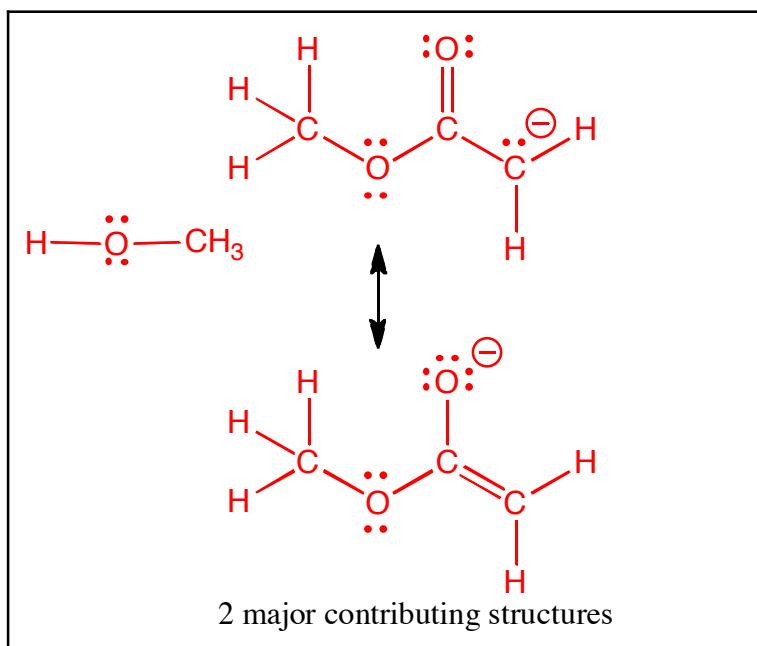
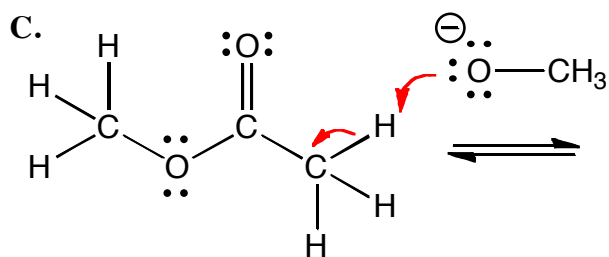
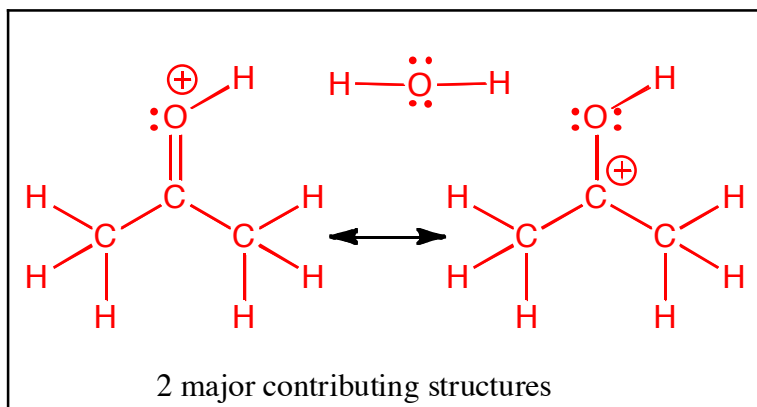
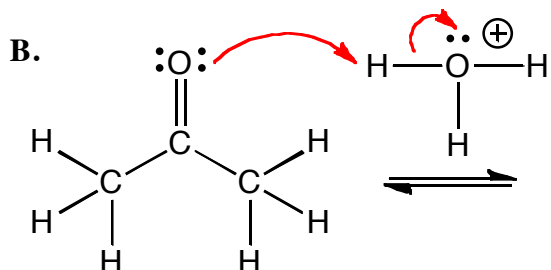
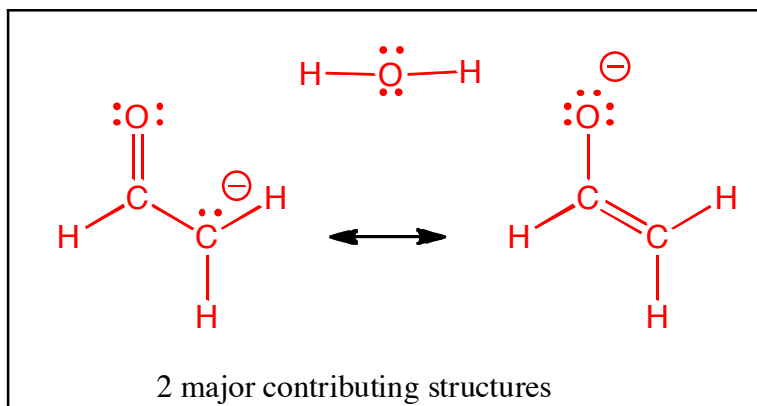
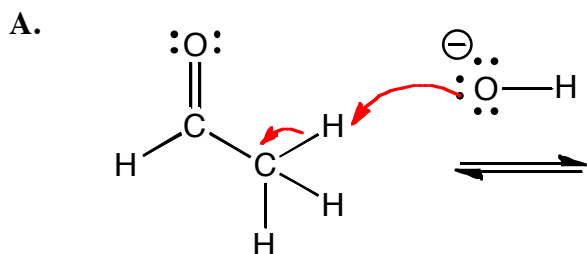


A) (4 pts) For each atom indicated by the arrows on the above drawing, write the hybridization state on the line provided.

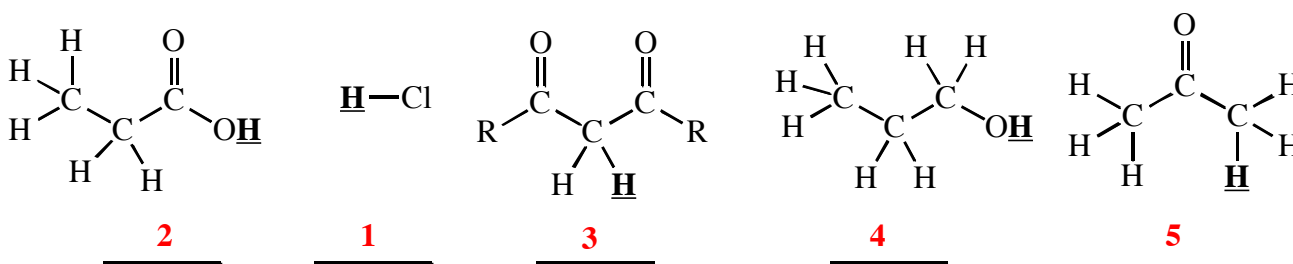
B) (5 pts) Diet coke loses its sweetness over time, especially if heated. Can you suggest a likely reason for this based on the chemistry you have learned? We are only looking for two sentences or less here.

The methyl ester hydrolyzes in the acidic pH and the free carboxylic acid is not sweet.

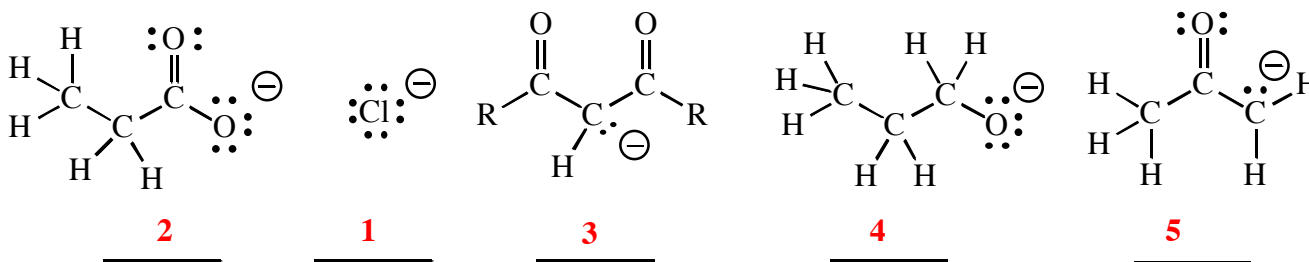
8. (21 points) In many of the mechanisms we have seen, there are charged intermediates encountered that are stabilized by resonance delocalization. For the following steps that come from different mechanisms, **place arrows on the structures on the left to show the flow of electrons that lead to a charged intermediate.** Next **draw all the intermediates created as well as the indicated number of major contributing structures.** Be sure to show all charges and lone pairs. Note, you only have to place arrows on the structures on the left side, not any of the contributing structures. **Finally make sure you show all intermediates made in the steps indicated.**



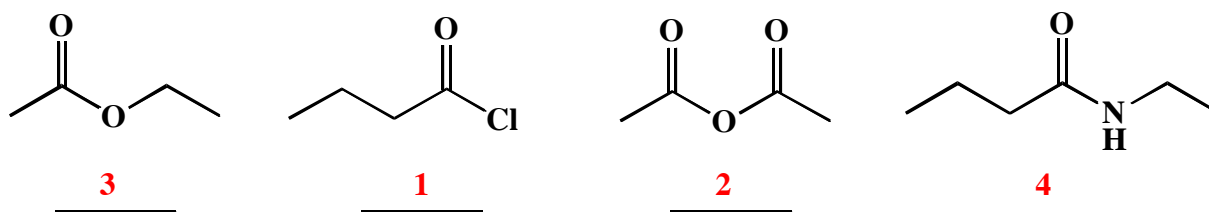
9. (5 pts) Rank all of the following with respect to relative acidity. The acidic H atom in question for each molecule is indicated in bold and with an underline. **Place a 1 under the most acidic molecule, and a 5 under the least acidic molecule.**



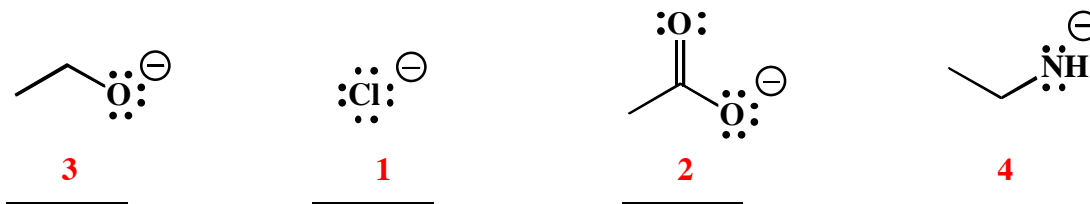
10. (5 pts.) Rank the following in terms of anion stability, with a **1 under the anion that is the most stable** and a **5 under the anion that is least stable**.



11. (4 pts.) Rank the following in terms of reaction with a strong nucleophile such as HO^- , with a **1 under the molecule that is most reactive**, and a **4 under the molecule that is least reactive**.

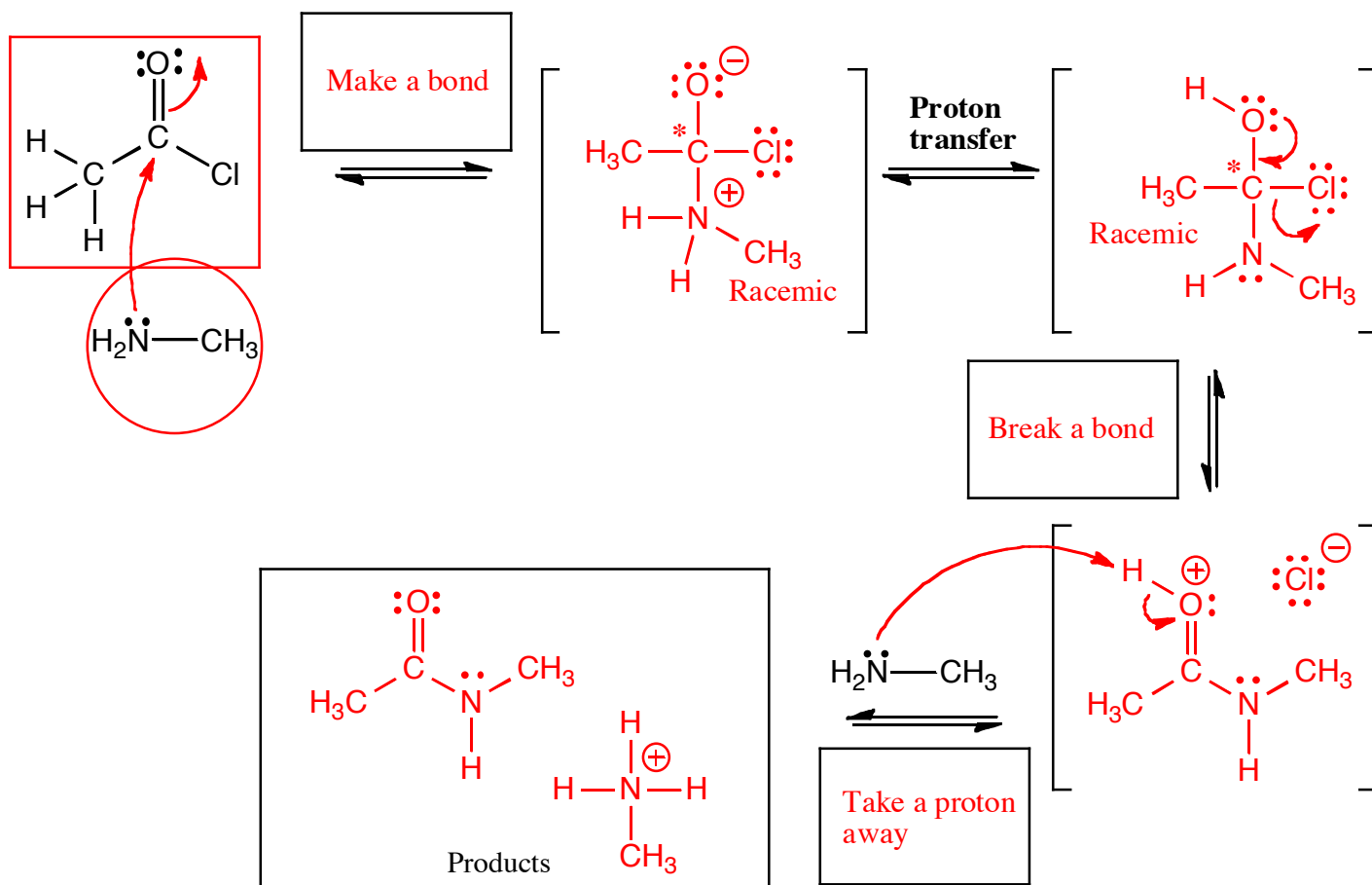


12. (4 pts.) Rank the following in terms of anion stability, with a **1 under the anion that is the most stable** and a **4 under the anion that is least stable**.



Please reread the directions to make sure you did not rank backwards!

13. (19 pts.) Complete the mechanism for the following reaction between an acid chloride and amine. 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").

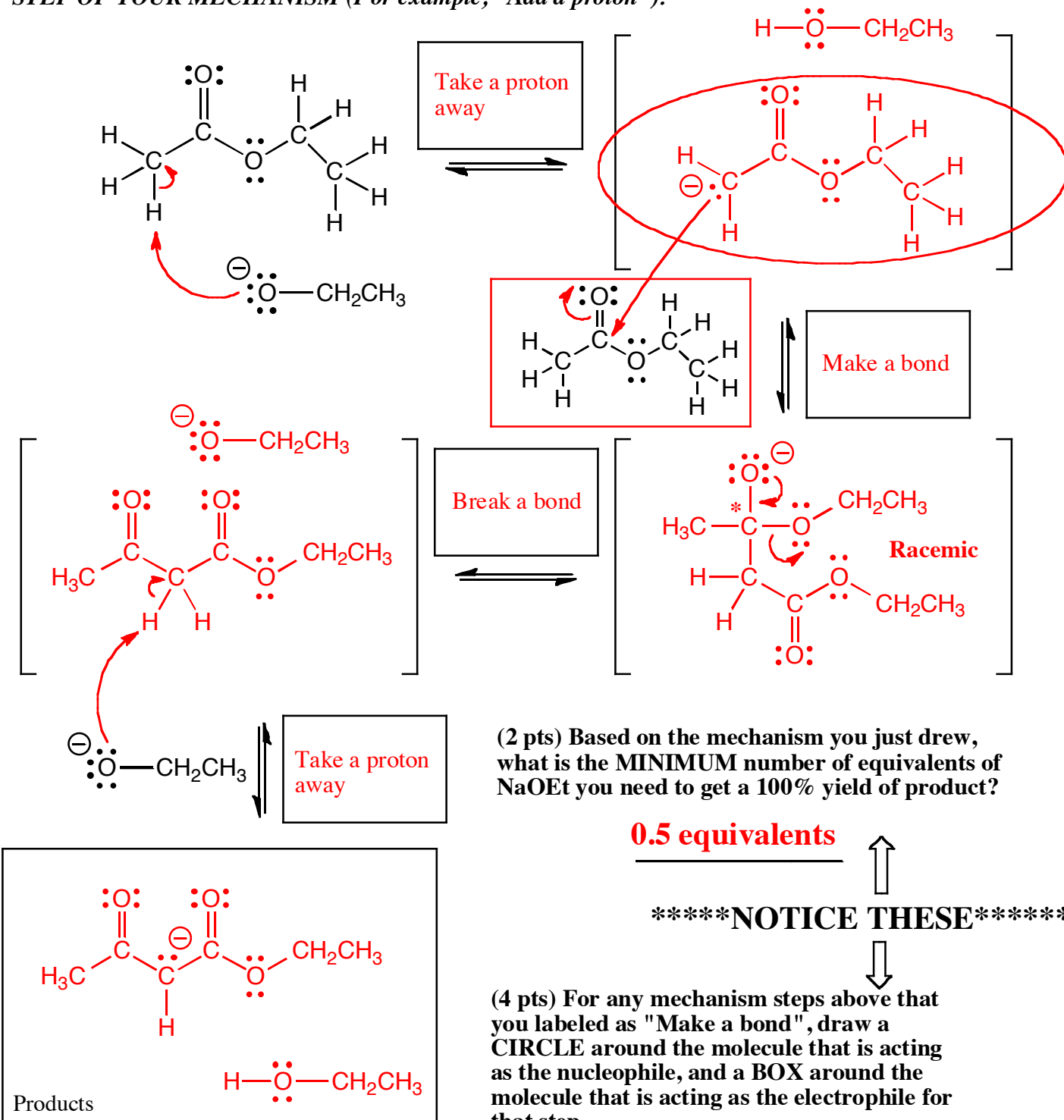


(2 pts) Based on the mechanism you just drew, what is the MINIMUM number of equivalents of $\text{H}_2\text{N}-\text{CH}_3$ you need to get a 100% yield of product? 2 equivalents

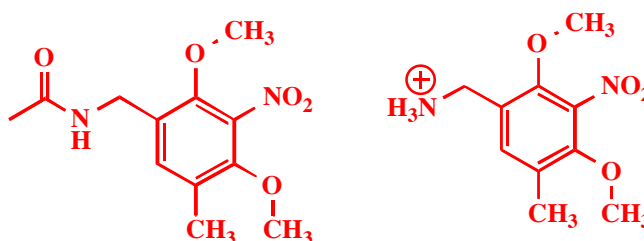
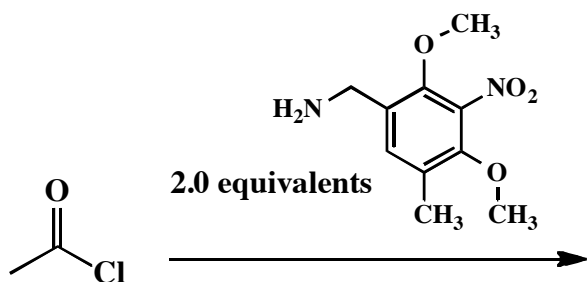
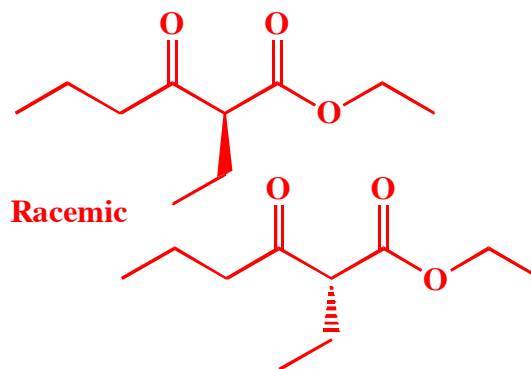
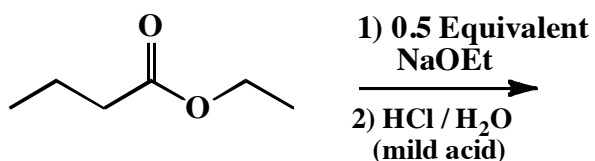
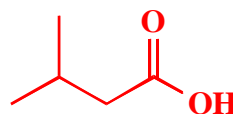
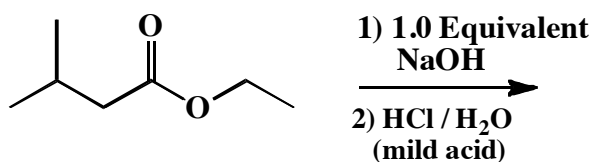
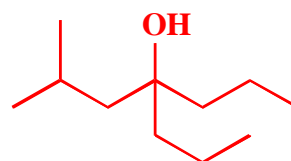
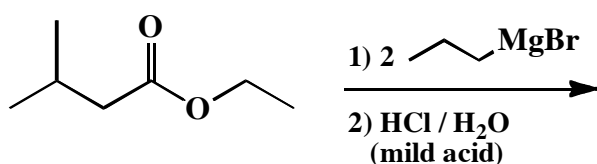
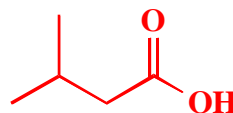
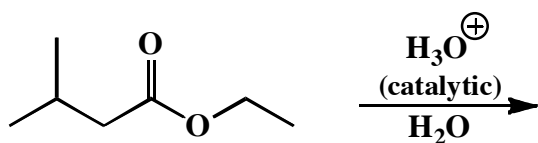
*****NOTICE THESE*****

(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.

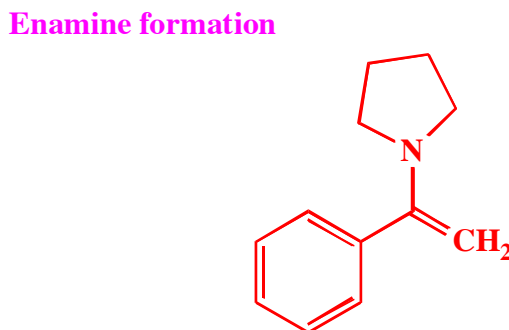
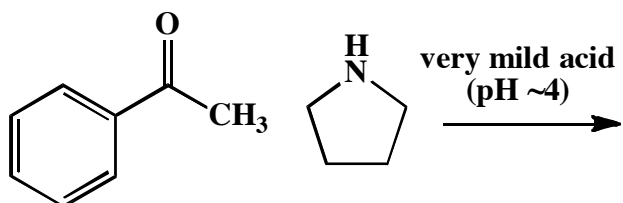
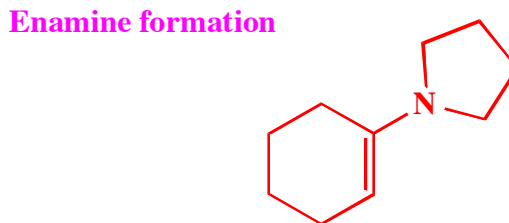
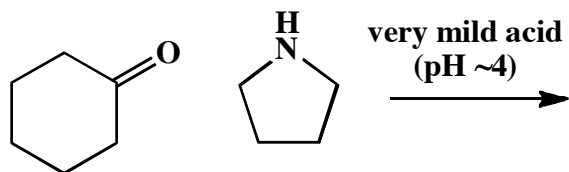
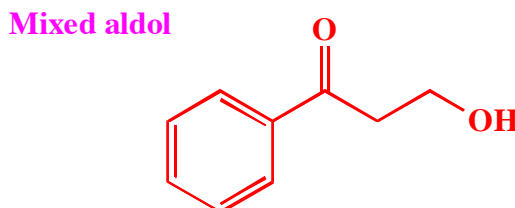
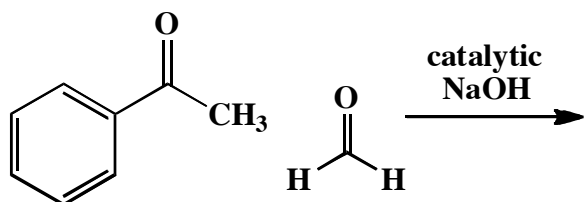
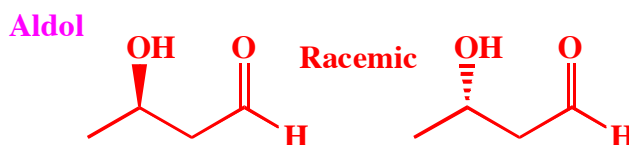
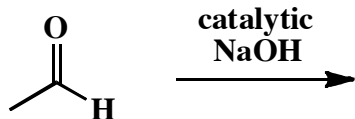
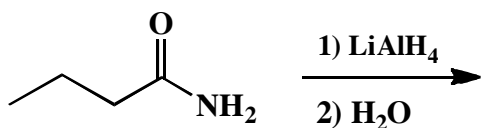
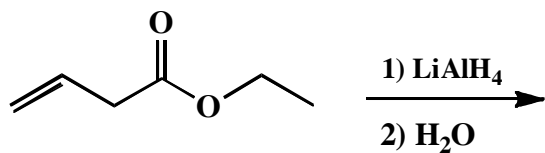
14. (23 pts.) Complete the mechanism for the following Claisen condensation reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS 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").



15. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw all enantiomers and write "racemic" under the structure. Use wedges (\blacktriangleleft) and dashes (\dashv) to indicate stereochemistry. DO NOT DEHYDRATE DURING AN ALDOL REACTION -WRITE THE NON-DEHYDRATED PRODUCT.

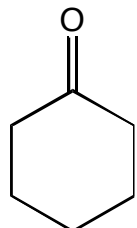


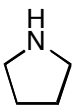
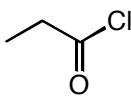
15 (cont. 3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw all enantiomers and write "racemic" under the structure. Use wedges (\blacktriangleleft) and dashes (\dashv) to indicate stereochemistry. DO NOT DEHYDRATE DURING AN ALDOL REACTION -WRITE THE NON-DEHYDRATED PRODUCT.

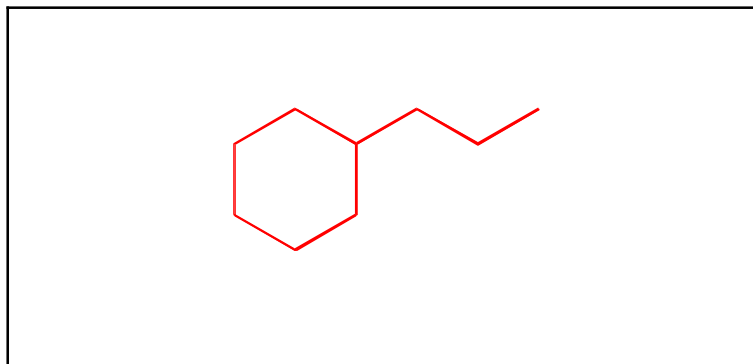


16. (14 points) For the following sequences of reactions, draw the final organic product or products after ALL the steps have been completed. You do not need to draw the molecules synthesized along the way, **only the last product that is formed**. If a new chiral center is created in the reaction that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

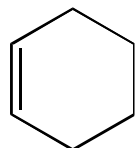
(6 pts)

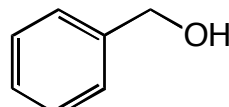


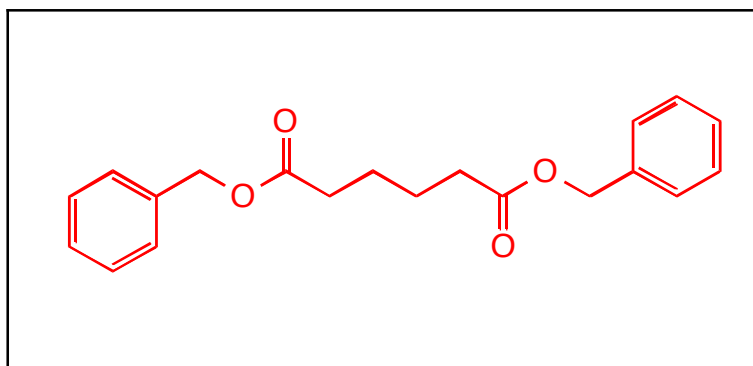
- 1)  very mild acid (pH ~4)
 - 2) 
-
- 3) $\text{H}_3\text{O}^{\oplus}$
 - 4) Excess $\text{NH}_2\text{NH}_2 / \text{NaOH}$



(8 pts)



- 1) O_3
 - 2) $(\text{CH}_3)_2\text{S}$
-
- 3) Excess H_2CrO_4
 - 4) 2 SOCl_2
 - 5) 2 

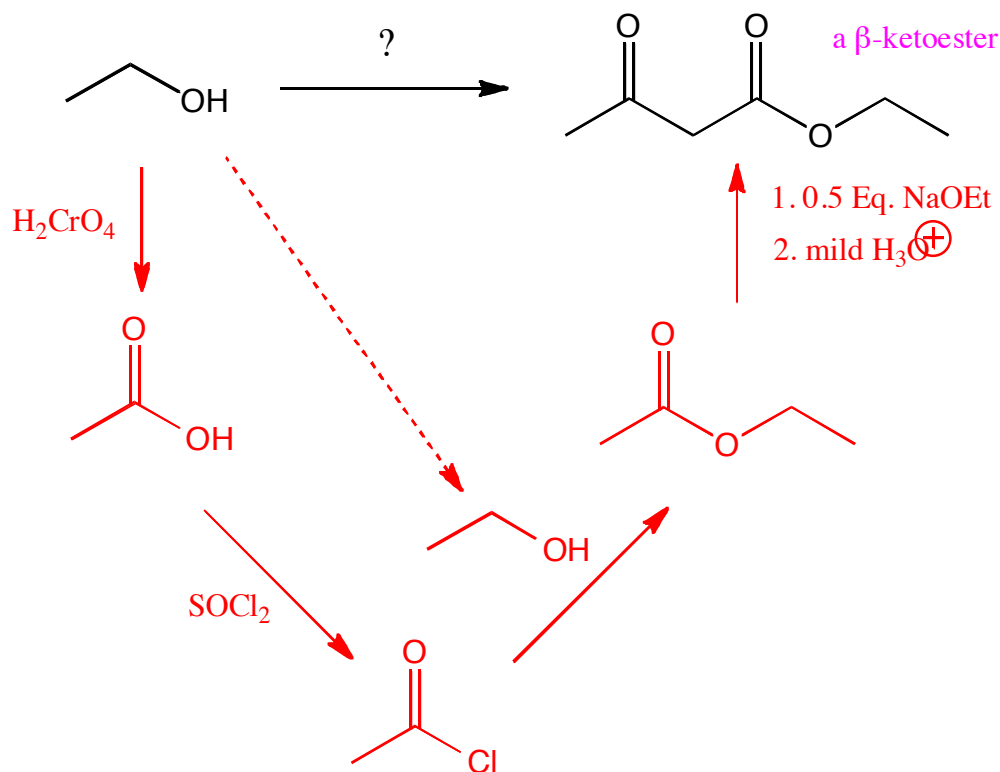


17. (10 pts) Using any reagents turn the starting material into the indicated product. All carbon atoms must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic"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

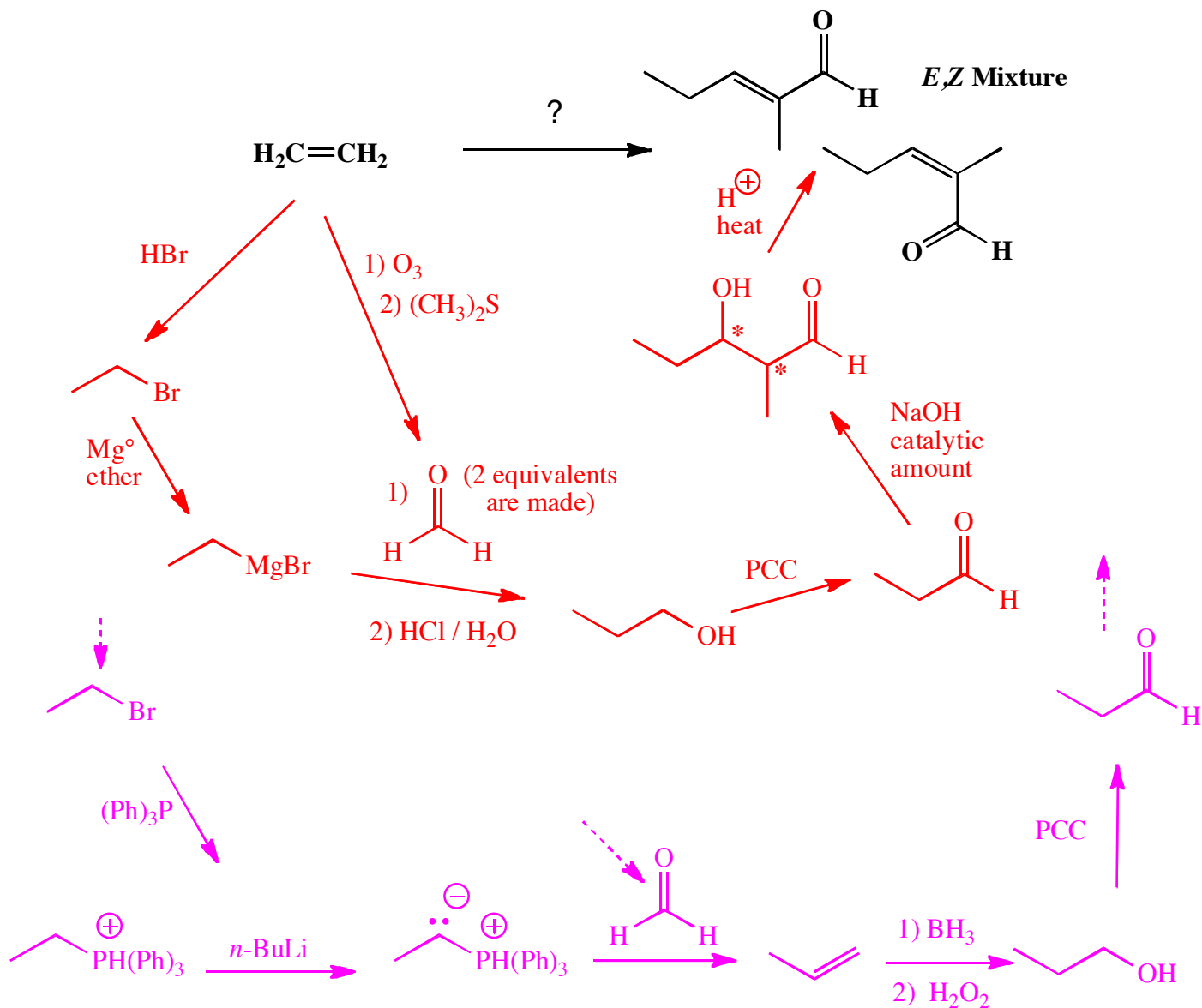
A)



Notice that the product has 6 carbon atoms, and the starting material has 2. Therefore, assume 3 molecules are reacted to make one product molecule. **Recognize** the product as a β -ketoester, the KRE for a Claisen condensation. **Recognize** that the required ester is derived from acetyl chloride reacting with ethanol. The acetyl chloride is made from acetic acid with SOCl_2 , which, in turn, comes from reaction of the starting ethanol with chromic acid.

17. (cont. 19 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.

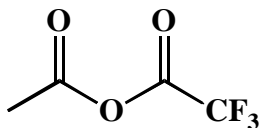


Recognize that the product has the α,β -unsaturated aldehyde functional group, the KRE of an aldol reaction followed by dehydration. Further, it has 6 carbons so predict it is the result of an aldol using propanal.

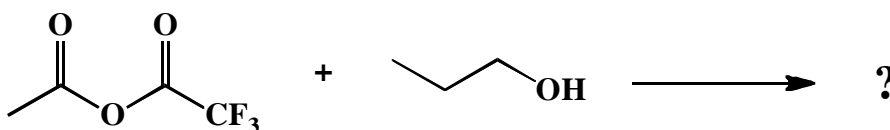
Recognize you need to add one carbon to the starting material to get propanal from ethylene. You can do this a couple of ways, but in either case, you need to carry out ozonolysis to create the one carbon fragment in the form of formaldehyde. One approach to propanal uses ethyl bromide, created from ethylene plus HBr, to make a Grignard that reacts with formaldehyde to give propanol, followed by PCC oxidation to give propanal. Another approach (below) uses the formaldehyde in a Wittig reaction that uses the Wittig reagent created from ethyl bromide. Following the Wittig reaction, the propene undergoes hydroboration to give propanol, followed by PCC oxidation to give propanal.

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.

The carboxylic acid derivatives we discussed in class represent only the tip of the iceberg of what has 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 unsymmetrical anhydride reagent shown below.

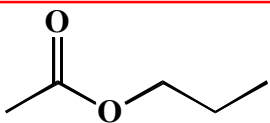


Predict what happens when this anhydride reacts with 1-propanol.



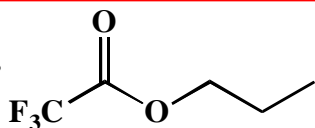
Circle the correct answers

A. The product is



C. You get a 50-50 mixture of the product in A. and the product in B.

B. The product is



D. There is no reaction between these reagents

Based on your answer to the first question, the F atoms are important because they:

A. Make the CF_3CO_2^- anion a better leaving group compared to the CH_3CO_2^- anion via hyperconjugation.

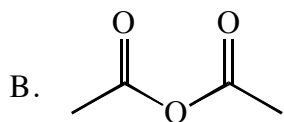
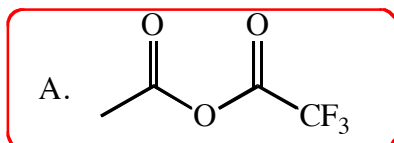
B. Make the CH_3CO_2^- anion a better leaving group compared to the CF_3CO_2^- anion via hyperconjugation.

C. Make the CF_3CO_2^- anion a better leaving group compared to the CH_3CO_2^- anion via the inductive effect.

D. Make the CH_3CO_2^- anion a better leaving group compared to the CF_3CO_2^- anion via the inductive effect.

18. (cont.)

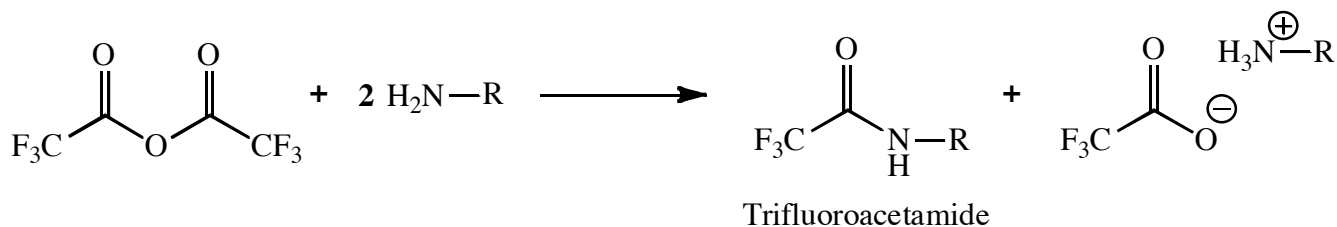
Based on your reasoning from the last part of the problem, predict which of the following reacts with an alcohol the fastest.



C. The reagents listed in parts A. and B. will react at about the same rate

D. Neither the reagent in part A. or part B. will react with an alcohol

The following anhydride reacts with amines to make an interesting type of amide called a trifluoroacetamide. Trifluoroacetamides are used as protecting groups for amines because they can be hydrolyzed more easily than other amides under certain conditions.



Based on your understanding of reactivity, suggest what conditions are used to hydrolyze trifluoroacetamides.

A. Trifluoroacetamides will hydrolyze best in aqueous acid because the F atoms make the carbonyl O atom more basic due to the inductive effect.

B. Trifluoroacetamides will hydrolyze best in aqueous base because the F atoms make the carbonyl C atom more susceptible to nucleophilic attack due to the inductive effect.

C. Trifluoroacetamides will hydrolyze best in aqueous acid because the F atoms make the carbonyl O atom more basic due to hyperconjugation.

D. Trifluoroacetamides will hydrolyze best in aqueous base because the F atoms make the carbonyl C atom more susceptible to nucleophilic attack due to hyperconjugation.