NAME (Print): _____

EID _____

SIGNATURE: _____

Chemistry 320N
2nd Midterm Exam
March 7, 2024

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

Please Note: Please take your time. You have three hours to take this exam. Please do not rush, we want you to show us everything you have learned this semester so far! Making careless mistakes is not good for anyone! If you find yourself getting anxious because of a problem, skip it and come back. Please do not second guess yourself! Keep track of the questions worth a lot of points. (This does not mean they are hard, it just means we think they cover important material.)

One last thing: I recommend you close your eyes for a moment, then take some nice deep breaths before you begin. YOU GOT THIS!

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!!!

Student Honor Code for the University of Texas at Austin

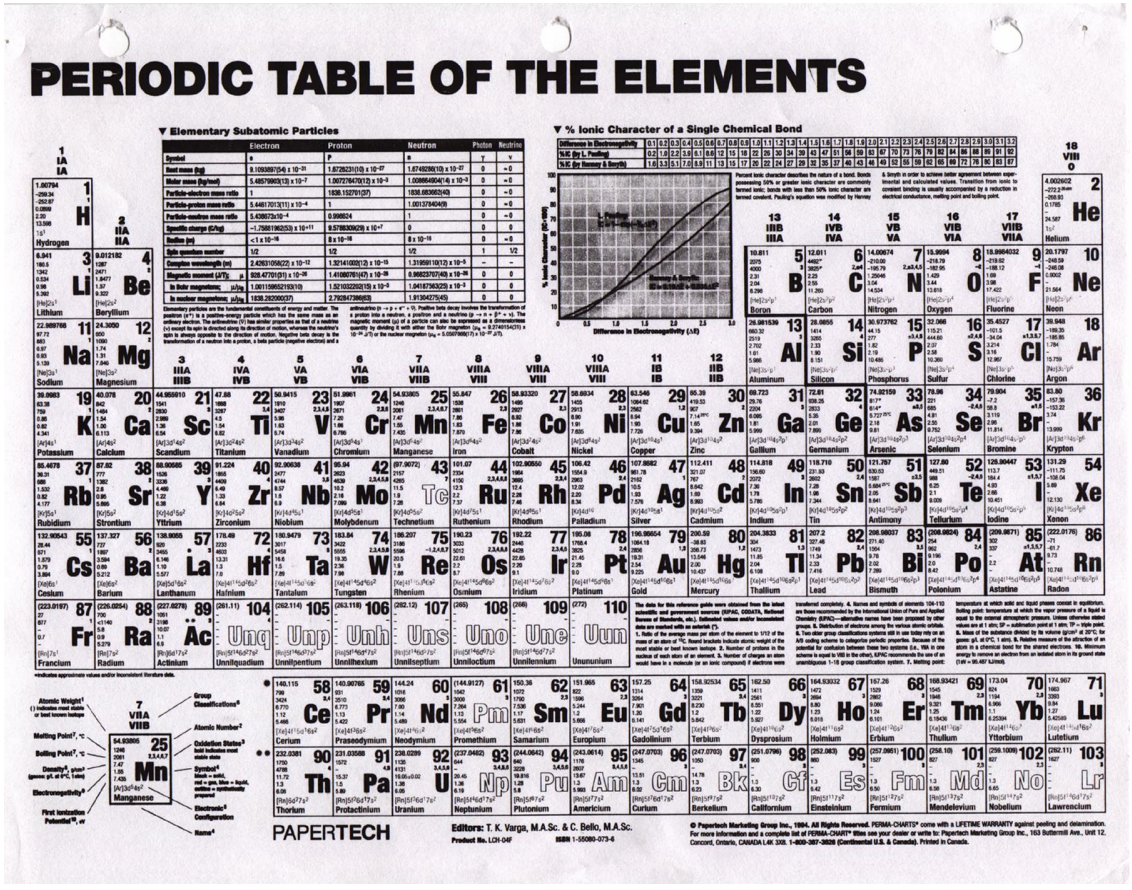
"I pledge, as a member of The University of Texas at Austin community, to do my work honestly, respectfully, and through the intentional pursuit of learning and scholarship."

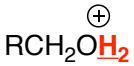
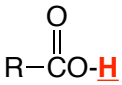
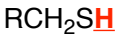
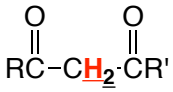
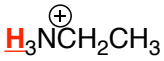
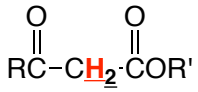
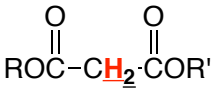
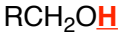
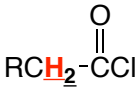
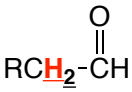
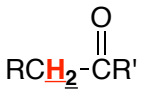
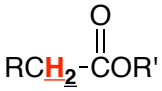
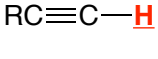
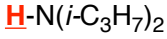
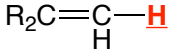
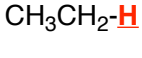
Elaboration

1. I pledge to be honest about what I create and to acknowledge what I use that belongs to others.
2. I pledge to value the process of learning in addition to the outcome, while celebrating and learning from mistakes.
3. This code encompasses all of the academic and scholarly endeavors of the university community.

_____

(Your signature)



Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Carboxylic acids		3-5
Thiols		8-9
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 _____(36)

1. (5 pts) What is the most important question in organic chemistry?

Where are the electrons?

2. (1 pt each) Fill in each blank with the word that best completes the sentences. Yep, this is the MRI paragraph!

The popular medical diagnostic technique of 1.**magnetic** 2.**resonance**

3.**imaging** (**MRI**) is based on the same principles as 4.**NMR**,

namely the flipping (i.e. 5.**resonance**) of nuclear spins of H atoms by

6.**radio** frequency irradiation when a patient is placed in a strong

7.**magnetic** 8.**field**. Magnetic field 9.**gradients**

are used to gain 10,**imaging** information, and rotation of the

11. **gradient** around the center of the object gives imaging in an entire plane (i.e.

12. **slice** inside patient). In an MRI image, you are looking at individual

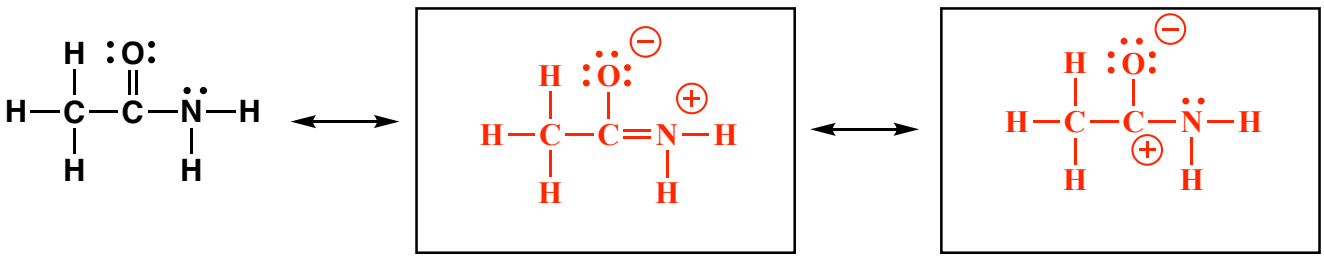
13.**slices** that when 14.**stacked** make up the three-

dimensional image of 15.**relative** amounts of 16. **H** atoms,

especially the 17.**H** atoms from 18.**water** and

19.**fat**, in the different 20.**tissues**.

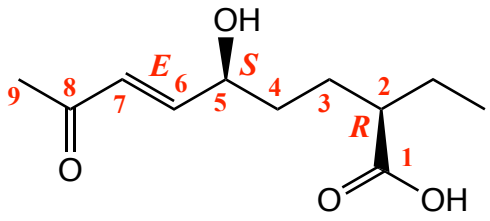
3. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided. (No need to draw any arrows for this.)



Signature_____ Pg 2_____(18)

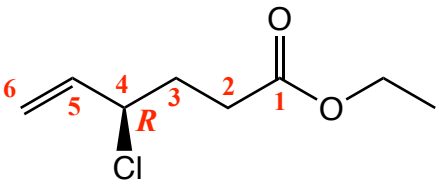
4. (6 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

A.



(*2R,5S,E*)-2-ethyl-5-hydroxy-8-oxonon-6-enoic acid
or (*2R,5S,E*)-2-ethyl-5-hydroxy-8-oxo-6-nonenoic acid

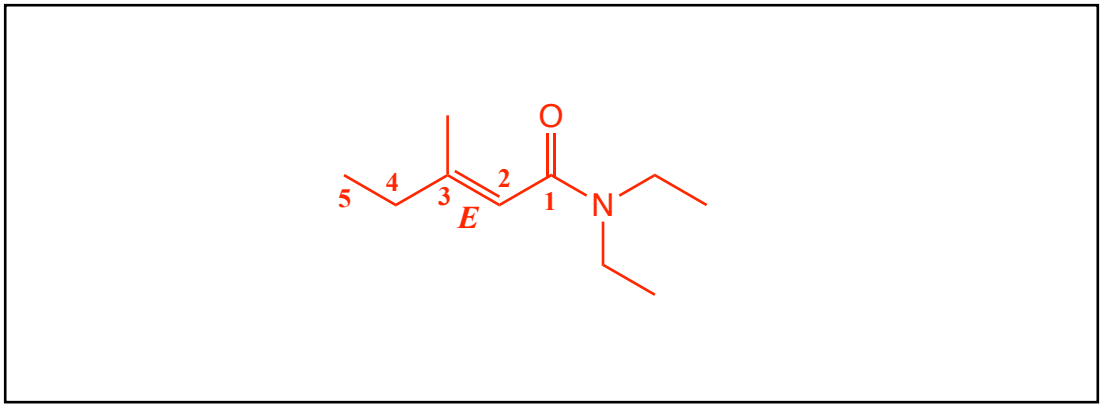
B.



ethyl (*R*)-4-chlorohex-5-enoate
or ethyl (*R*)-4-chloro-5-hexenoate

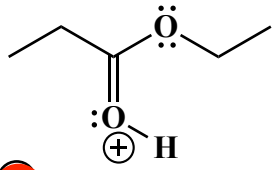
C. In the box, draw the structure corresponding to the following IUPAC name.

(*E*)-*N,N*-diethyl-3-methylpent-2-enamide
or (*E*)-*N,N*-diethyl-3-methyl-2-pentenamide



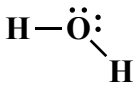
5. (12 pts) Being able to recognize the chemical personality of different species is one of the most important skills you can develop in Organic Chemistry. Fill in the appropriate circle to indicate whether each structure is a nucleophile or electrophile in the mechanisms we have seen. **Note that these species might be proton acids or bases in certain situations, but we will ignore that for this problem.**

5.1



● Electrophile
○ Nucleophile

5.2

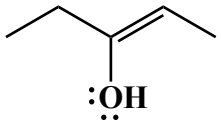


○ Electrophile
● Nucleophile

5.3 $LiAlH_4$

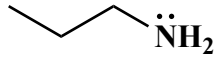
○ Electrophile
● Nucleophile

5.4



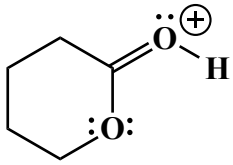
○ Electrophile
● Nucleophile

5.5



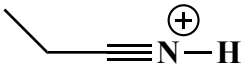
○ Electrophile
● Nucleophile

5.6



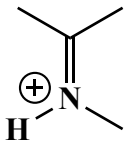
● Electrophile
○ Nucleophile

5.7



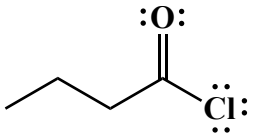
● Electrophile
○ Nucleophile

5.8



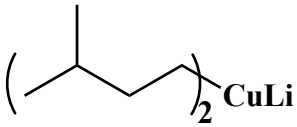
● Electrophile
○ Nucleophile

5.9



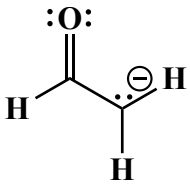
● Electrophile
○ Nucleophile

5.10



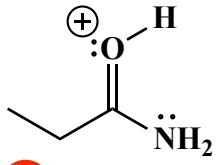
○ Electrophile
● Nucleophile

5.11



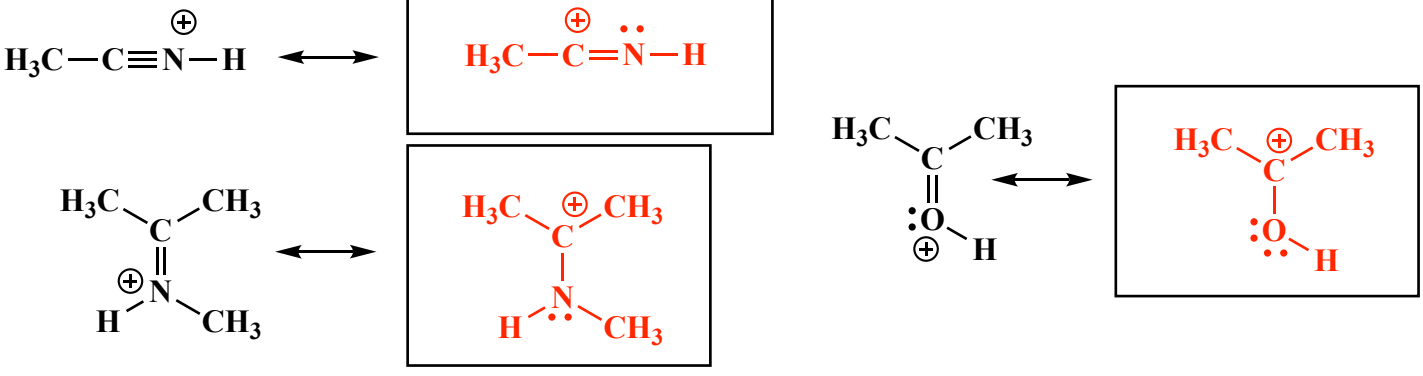
○ Electrophile
● Nucleophile

5.12

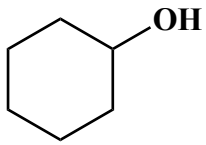


● Electrophile
○ Nucleophile

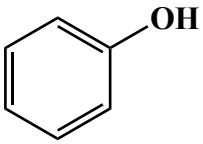
6. (6 pts) For each structure below, draw the other important contributing structure. You do not need to draw arrows anywhere, but you must include all lone pairs and formal charges.



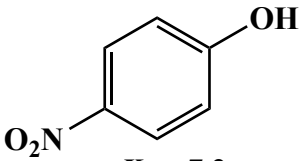
7. (16 pts) As described in class, the reactivity of carboxylic acid derivatives with nucleophiles is correlated with leaving group ablility. We also pointed out that leaving group ability can be correlated with the pK_a of the protonated form of the leaving group anion. Here are a series of related alcohols with their pK_a values listed below each one.



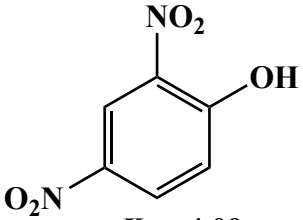
pK_a = 16.0



pK_a = 10.0

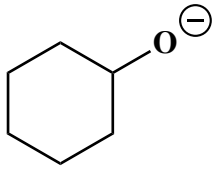


pK_a = 7.2



pK_a = 4.09

A) (1 pt each) Rank the stabilities of each of the following anions from 1-4. Put a "1" under the most stable anion, and a "4" under the least stable anion (then a "2" and "3" as appropriate).



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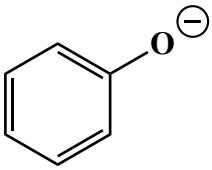

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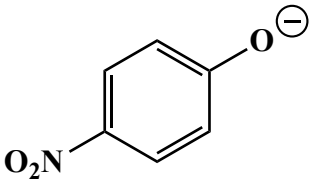

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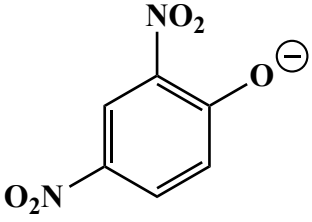
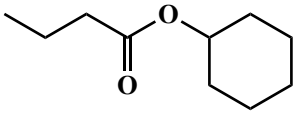


1

B) (1 pt each) Rank the following esters from 1-4 for reactivty with nucleophiles such as $HO^{\ominus}$ or an amine. Put a "1" under the most reactive with nucleophiles, and a "4" under the least reactive with nucleophiles (then a "2" and "3" as appropriate).



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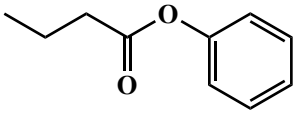

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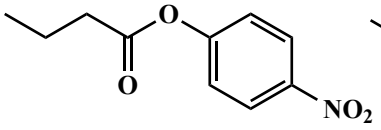

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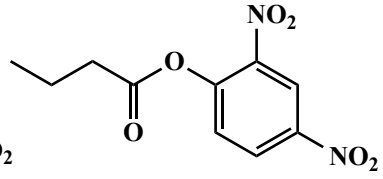
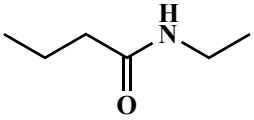


1

C) (2 pts each) Rank the following carboxylic acid derivatives from 1-4 for reactivty with nucleophiles such as water or an amine. Put a "1" under the most reactive with nucleophiles, and a "4" under the least reactive with nucleophiles (then a "2" and "3" as appropriate).



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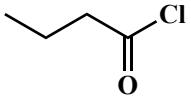

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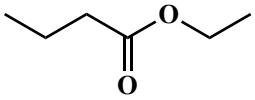

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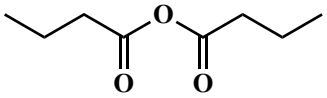
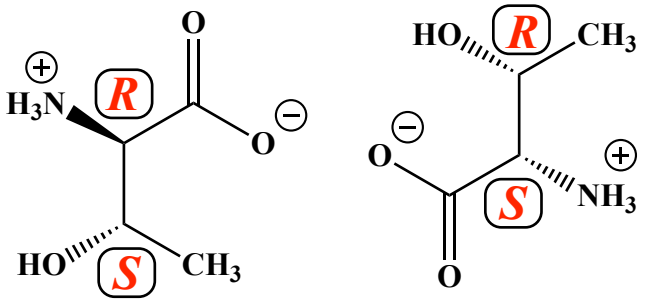
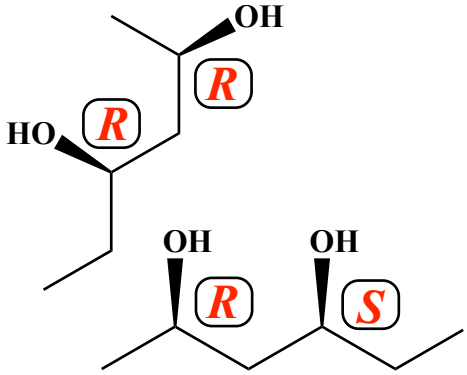


2

8. (12 pts) Being good at identifying relationships betweem molecules is an important skill in Organic Chemistry. **Fill in the circle to identify the stereochemical relationship between each pair of molecules. In the boxes provided, you need to write whether each chiral center is "R" or "S".**

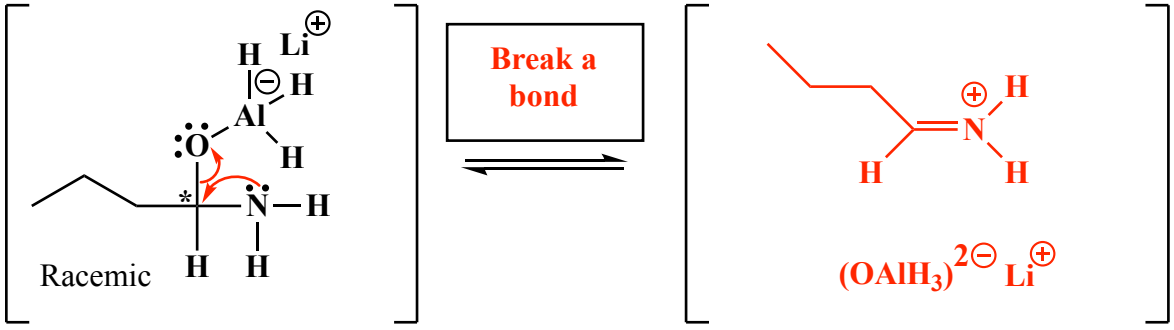


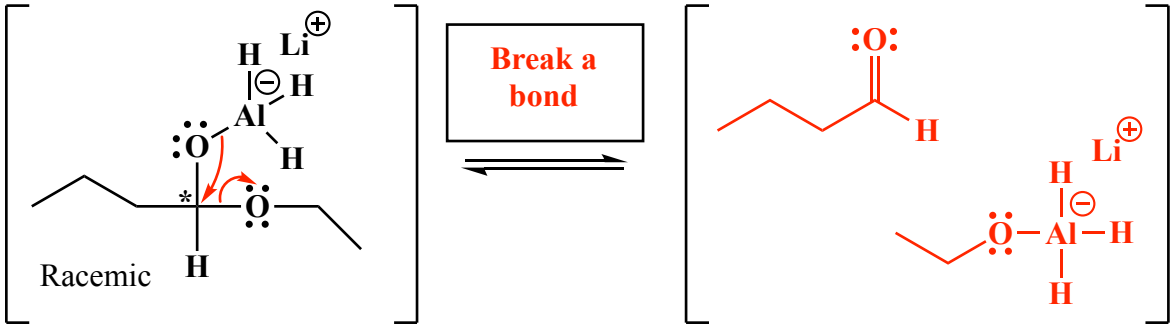
● Enantiomers
○ Diastereomers
○ Same Molecule



○ Enantiomers
● Diastereomers
○ Same Molecule

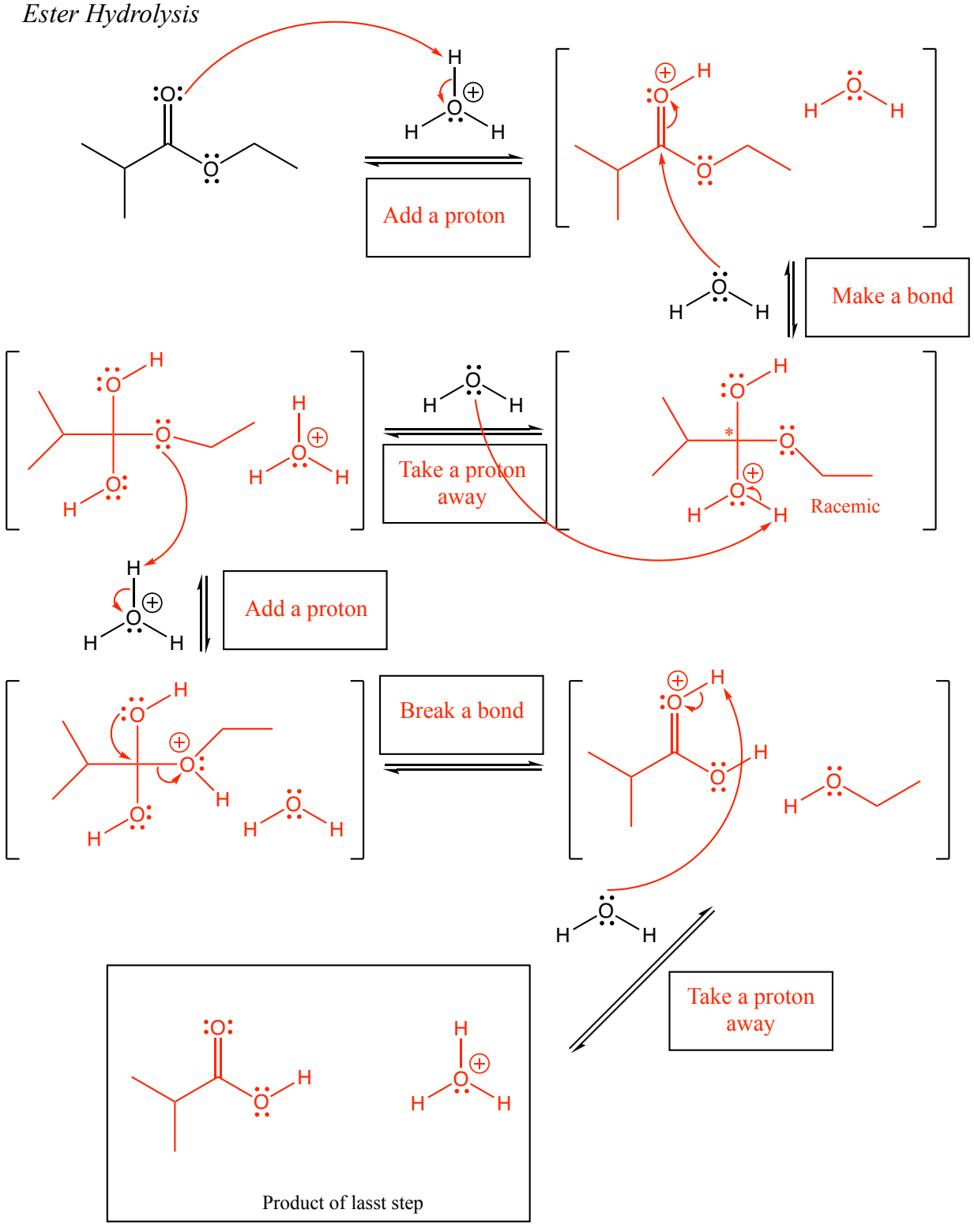
9. (14 pts) The following two intermediates are encountered in the reaction of $LiAlH_4$ with amides and esters, respectively. In each case, draw the appropriate arrows and only the next intermediate of the mechanism. No need to continue on with the mechanisms, we only want arrows on the structures we drew, and we only want you to draw the next intermediate in the mechanism. Remember to write all products of the step, and include all lone pairs and all formal charges. In the box over the arrow, indicate what type of step this is (add a proton, make a bond, etc.) HINT: *These are not the last steps of the mechanisms, so writing "Aluminum Salts" is not appropropriate, you need to indicate the structure of the Aluminum species produced in this step.*





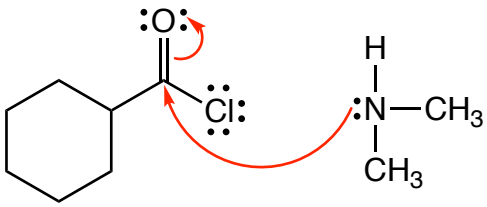
10. (35 pts) For this reaction, use **arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. <u>FOR ALL CHIRAL PRODUCTS YOU MUST DRAW ALL ENANTIOMERS WITH WEDGES AND DASHES AND WRITE "RACEMIC' IF APPROPRIATE</u>. In the boxes provided by the arrows, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).**

Ester Hydrolysis

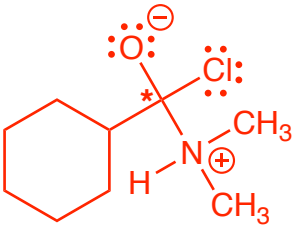


11. (24 pts) For this reaction, use **arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. <u>FOR ALL CHIRAL PRODUCTS YOU MUST DRAW ALL ENANTIOMERS WITH WEDGES AND DASHES AND WRITE "RACEMIC' IF APPROPRIATE</u>. In the boxes provided by the arrows, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).**

Acid Chlorides Reacting with Amines



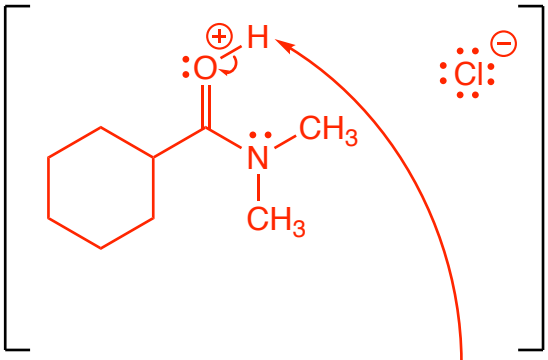
Make a bond



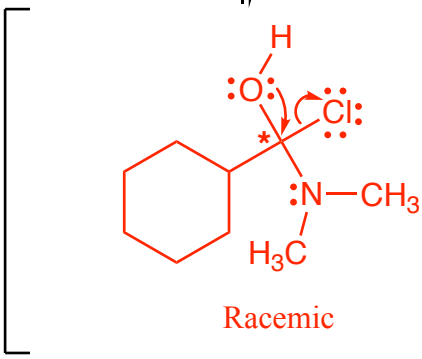
Racemic

No need to draw arrows

Proton Transfer

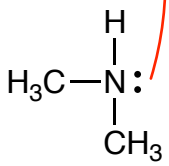


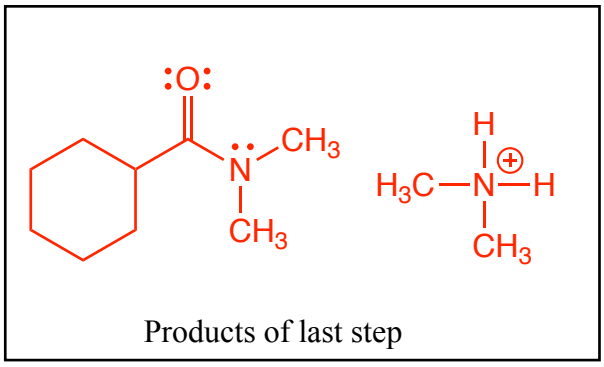
Break a bond



Racemic

Take a proton away

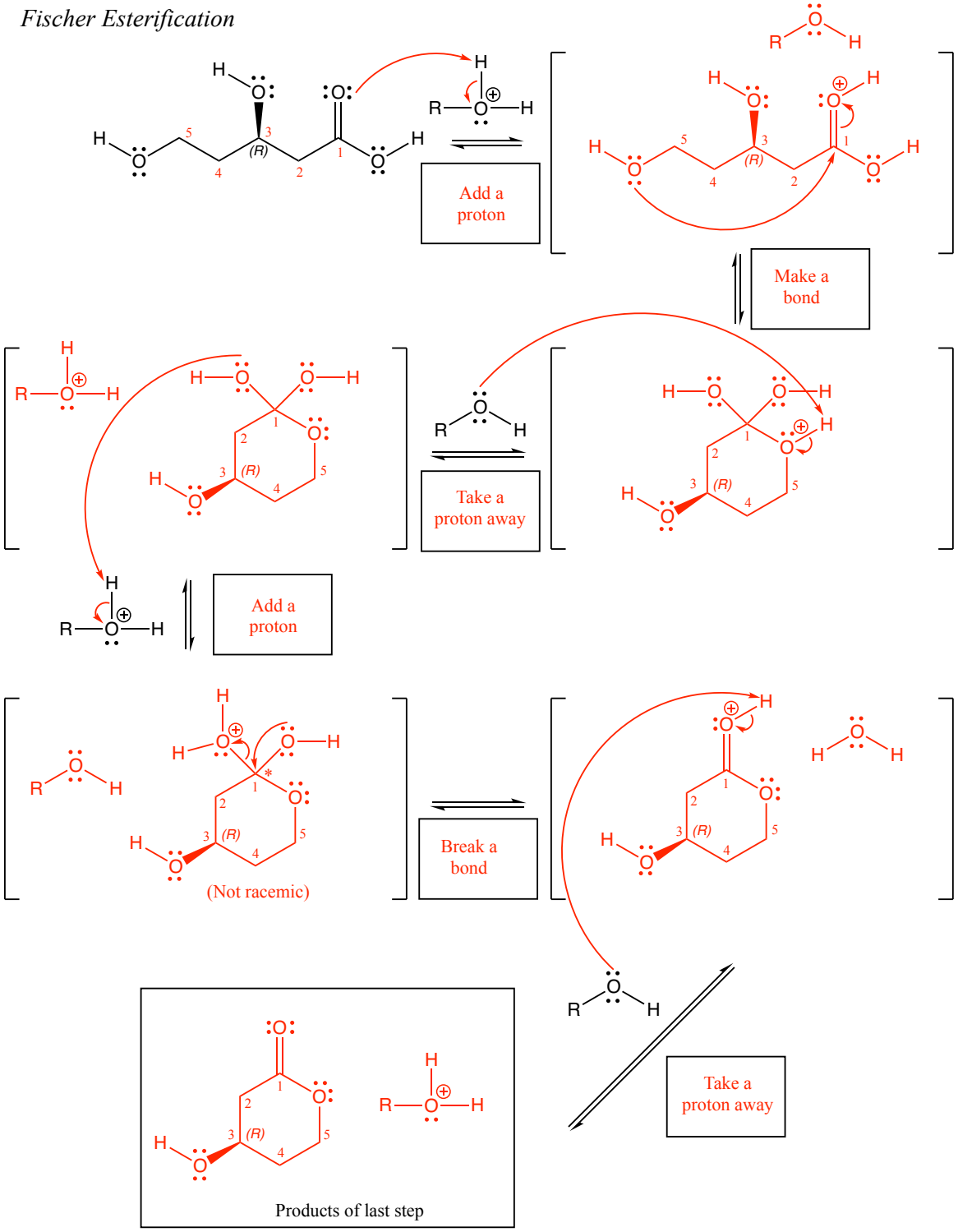




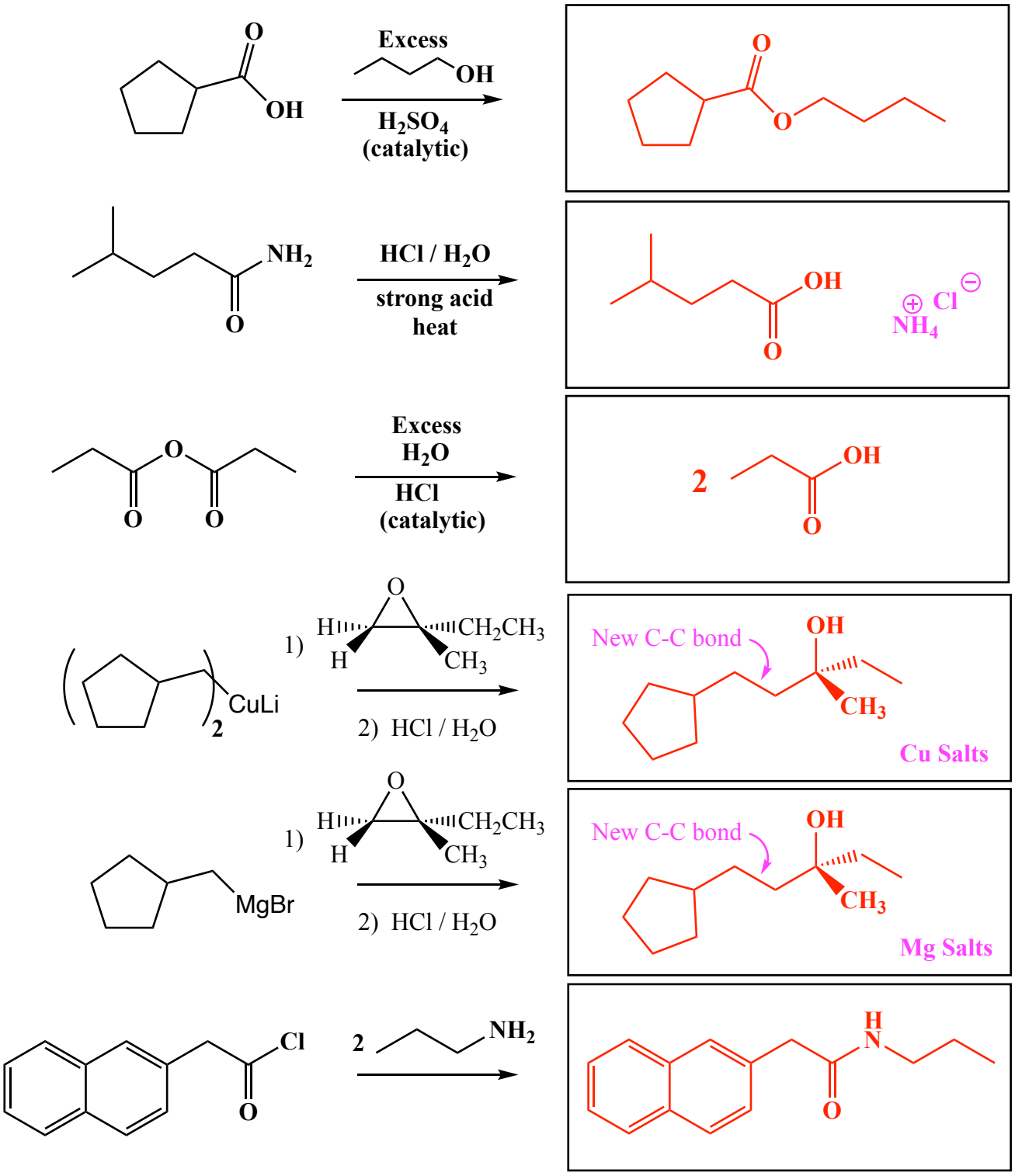
Products of last step

12. (35 pts) For this reaction, use **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, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. <u>FOR ALL CHIRAL PRODUCTS YOU MUST DRAW ALL ENANTIOMERS WITH WEDGES AND DASHES AND WRITE "RACEMIC' IF APPROPRIATE</u>. In the boxes provided by the arrows, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.). NOTE: For the chiral centers already on the starting material, you need to show them with WEDGES and DASHES, EVEN ON THE INTERMEDIATES).**

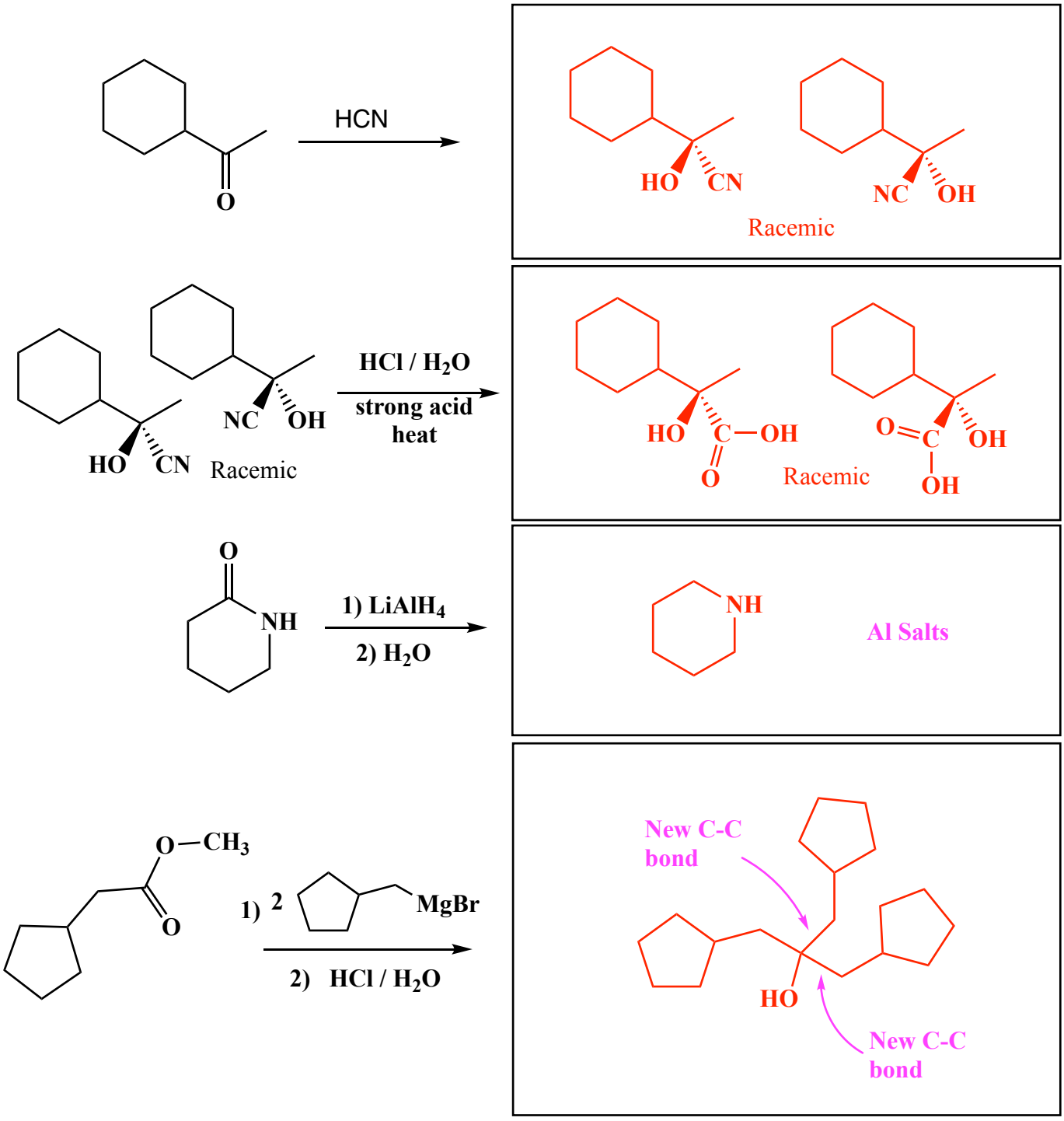
Fischer Esterification



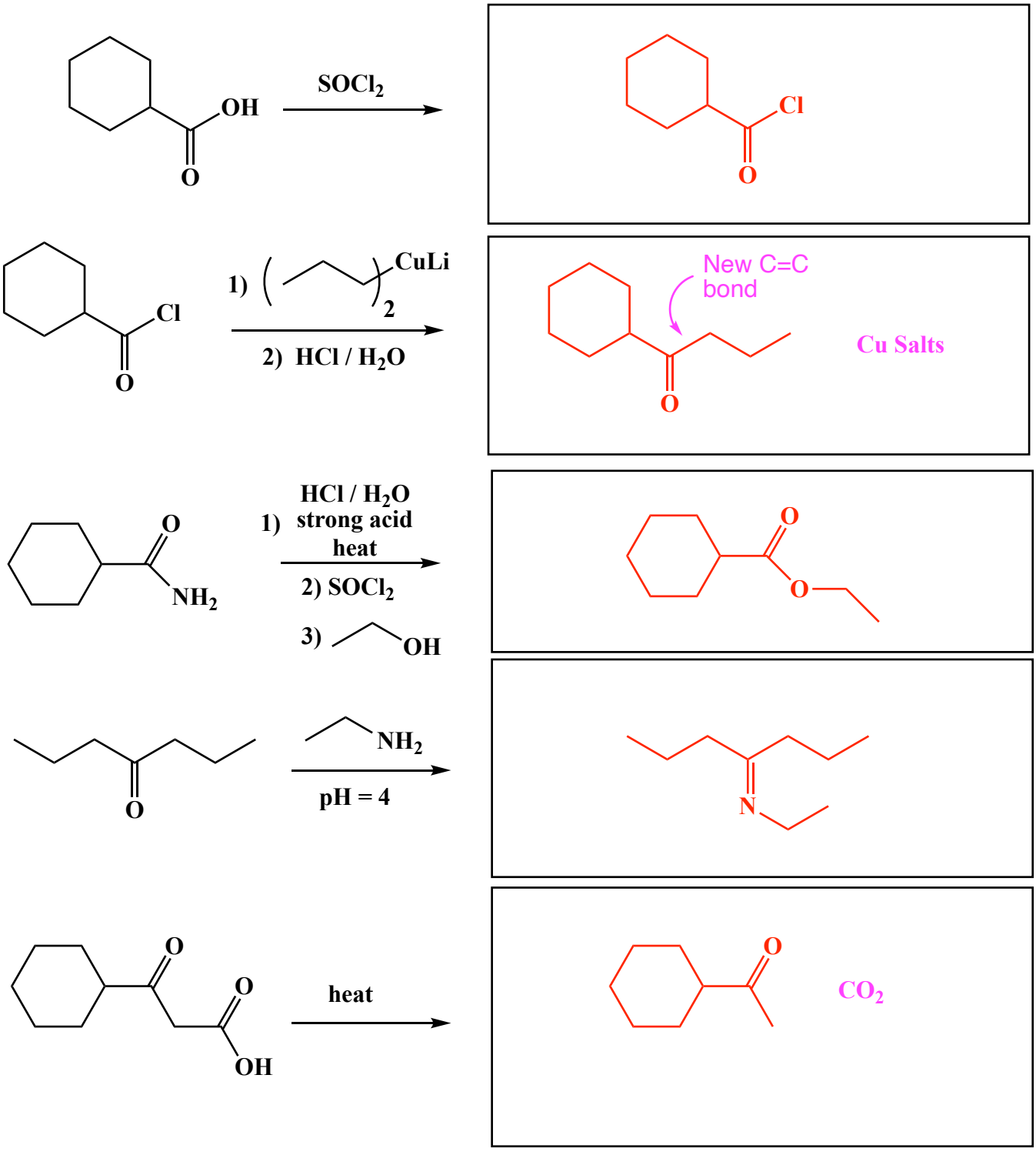
13. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. NOTE:



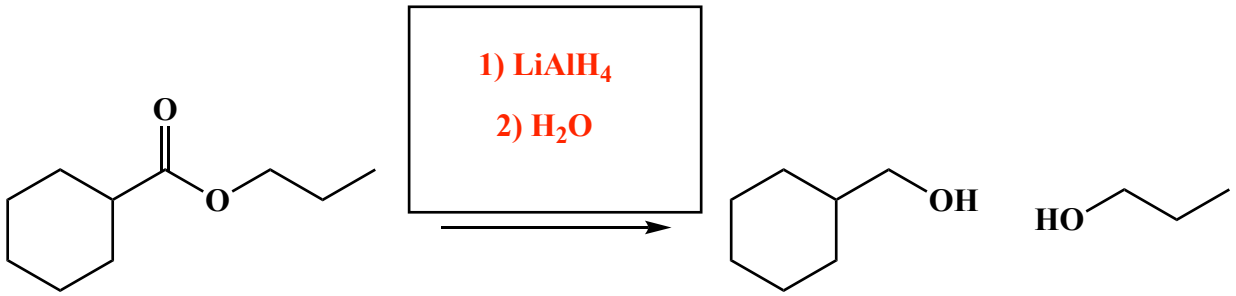
13. (cont.) (3, 4 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (····|||) to indicate stereochemistry. To get full credit, you only need to write the the major organic product for these. You do not have to worry about the other products.

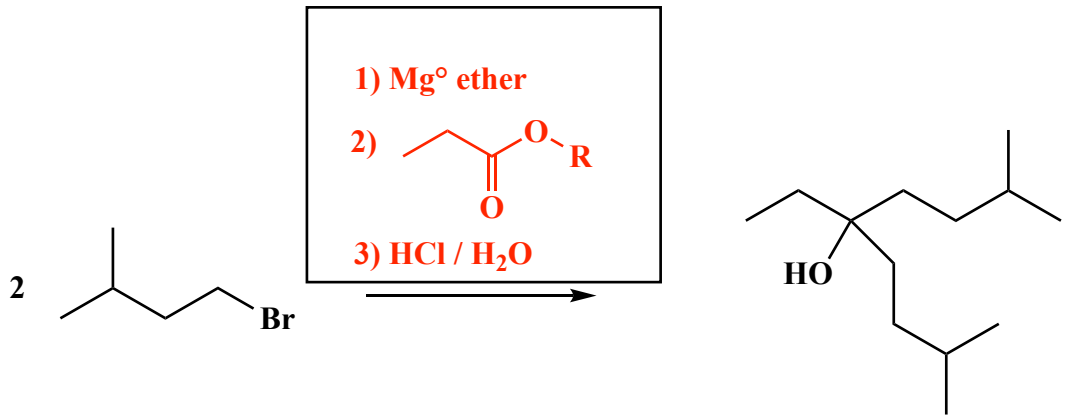


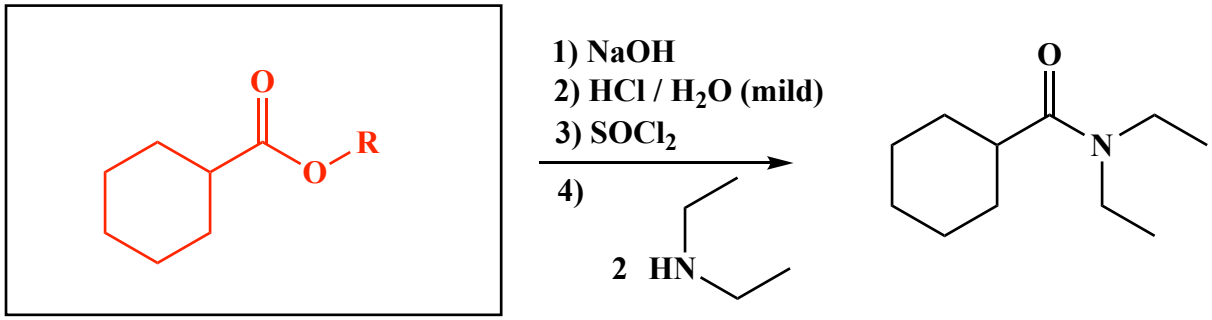
13. (cont.) (3, 4 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (····|||) to indicate stereochemistry. To get full credit, you only need to write the the major organic product for these. You do not have to worry about the other products.

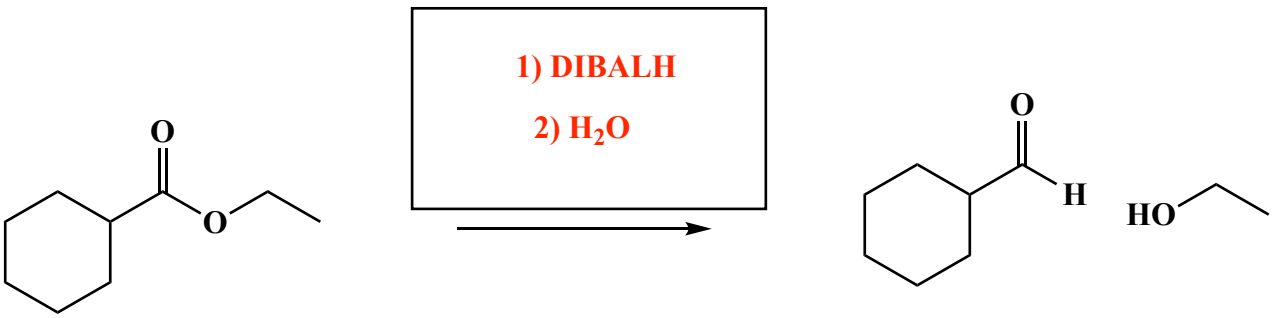


14. (13 pts) For these, you need to fill in the box with the starting material or reagents as appropriate. Note, this is **NOT** a synthesis problem, the product can contain carbon atoms from your reagent!

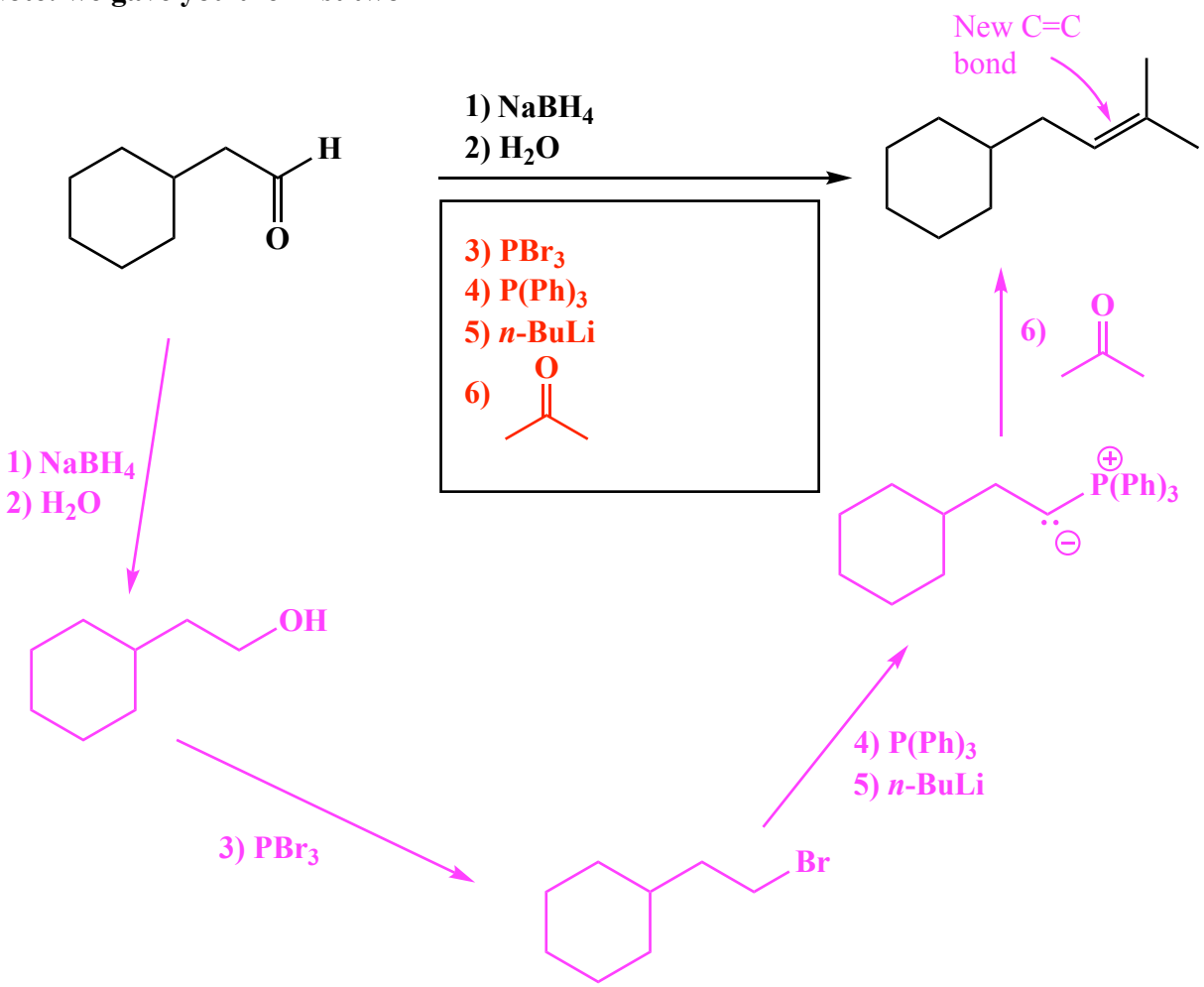






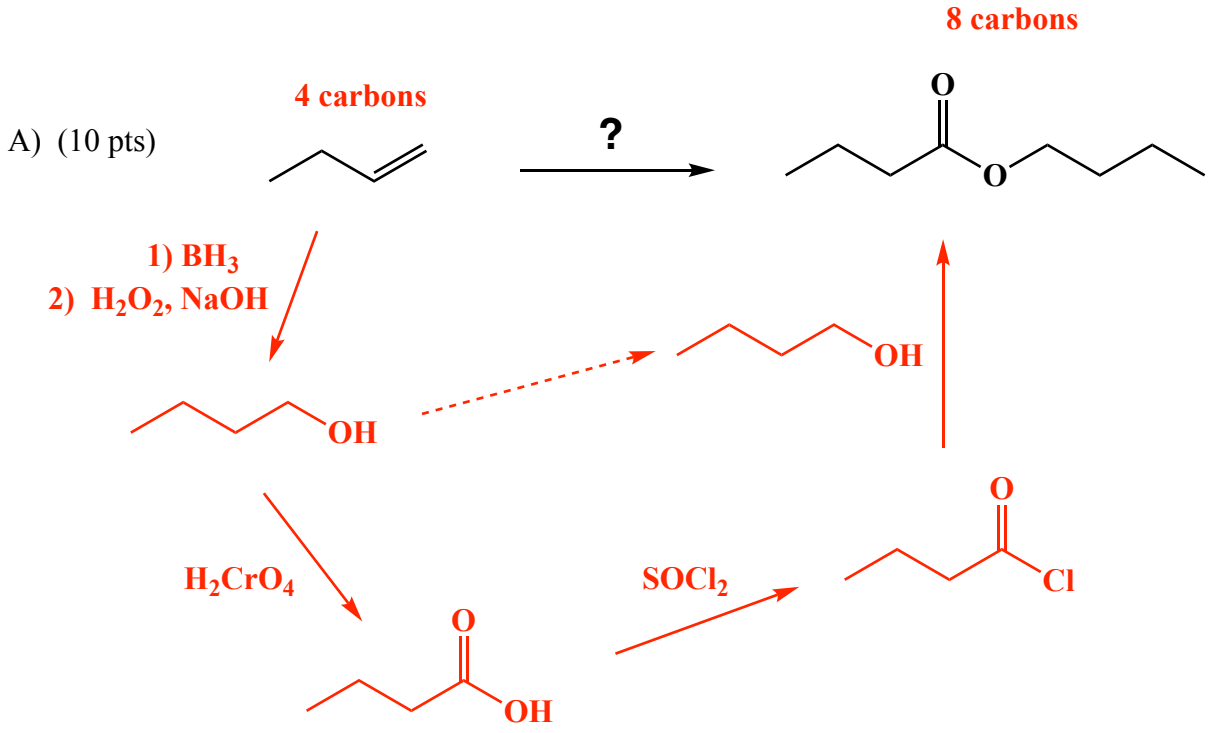


15. (8 pts) Here is a synthesis warm-up. For the following series of reactions, we have given you the final product and starting material. Work backwards and **in the box provided write the missing reagents. Note: we gave you the first two**



16. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

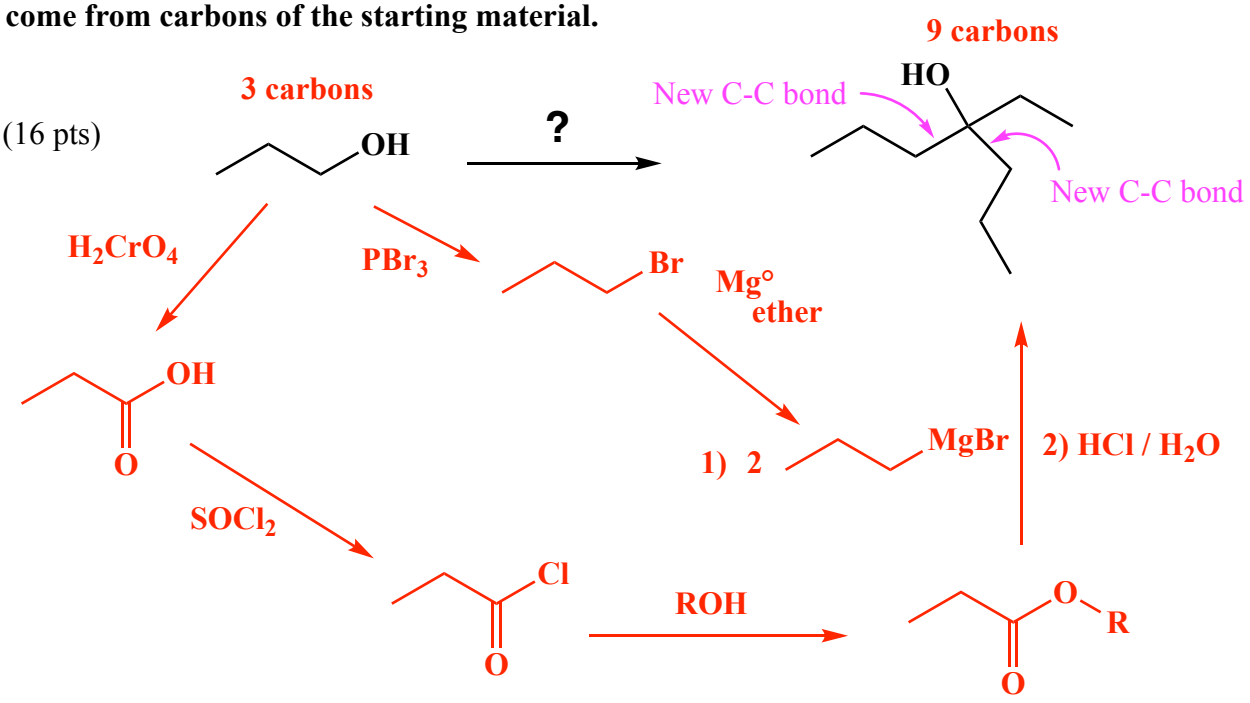
A) (10 pts)



Recognize the product as an ester, that is made from butanyl chloride and butanol (Fischer esterification between the butanoic acid and butanol with catatlytic H_2SO_4 is also OK). The butanoic acid is made from the starting alkene in two steps using hydroboration/oxidation (non-Markovnikov) to give butanol followed by oxidation using chromic acid (Jones Reagent).

16. (cont.). These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

B) (16 pts)



Recognize this as the same problem from last exam! You could use the same strategy from last time to get full credit. What we hoped was that you would **Recognize** the product as the KRE of a four-carbon Grignard reagent reacting with a four-carbon ester. Namely, the KRE is two new C-C bonds from identical groups on the same carbon as an OH group. The ester is made from the four-carbon carboxylic acid that comes from oxidation of the starting butanol with chromic acid (Jones Reagent) followed by reaction with $SOCl_2$. Note the "ROH" used to make the ester can be any alcohol (methanol, ethanol, etc.) because those carbons do not end up in the product so they didn't have to come from the starting butanol (but you certainly could have used butanol to make the ester). The four-carbon Grignard reagent can be made by reacting the starting butanol with PBr_3 followed by Mg° in ether.

Nope, there are no MCAT style questions on this exam.
Have a relaxing and safe spring break. And remember to exercise every chance you get!