NAME (Print): _____

EID _____

SIGNATURE: _____

Chemistry 320N
2nd Midterm Exam
March 9, 2023

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!

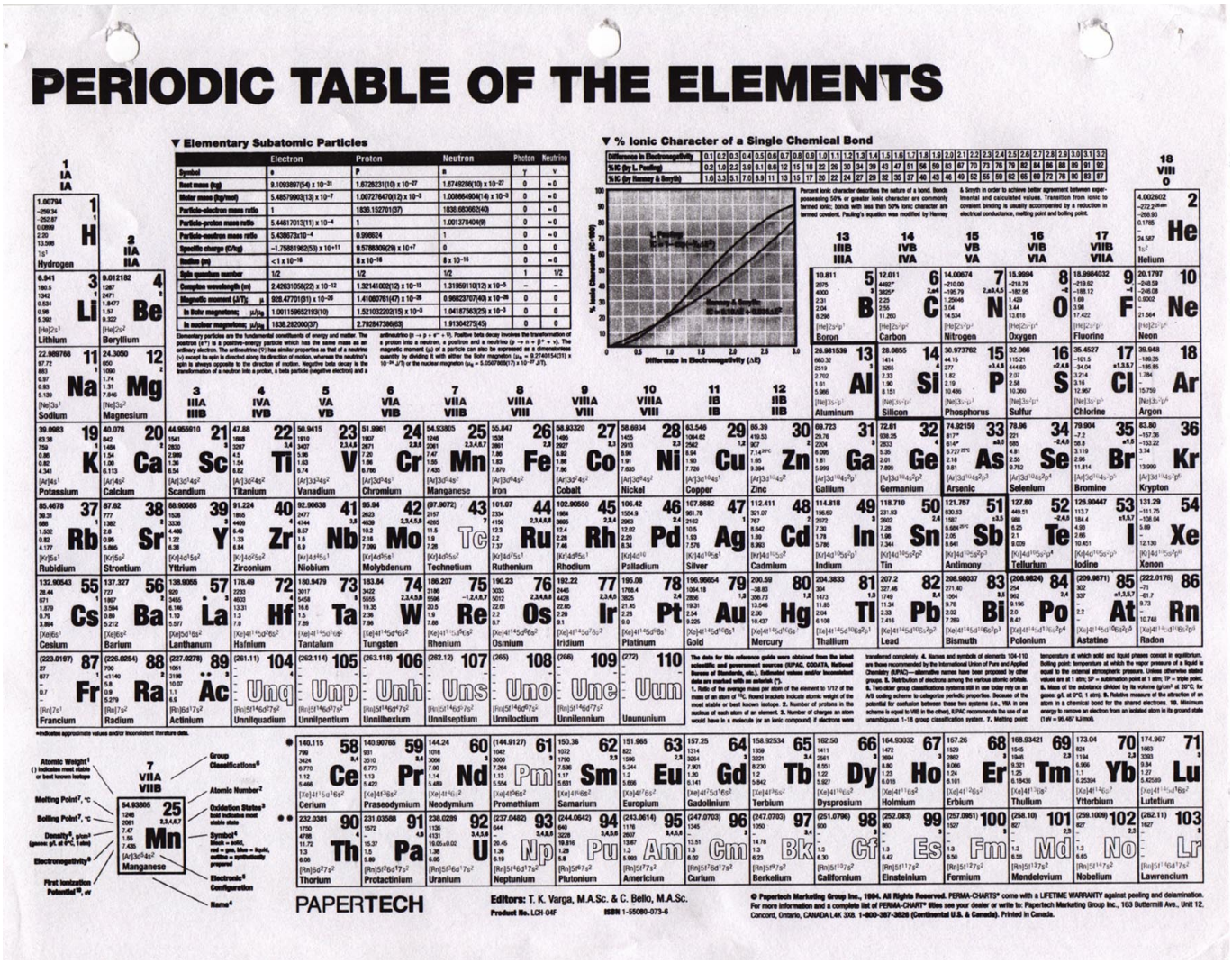
FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

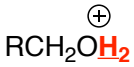
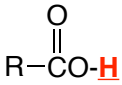
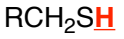
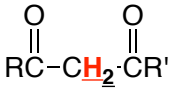
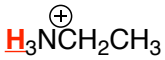
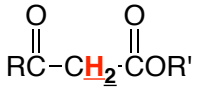
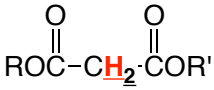
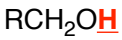
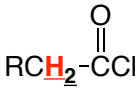
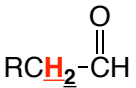
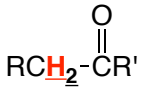
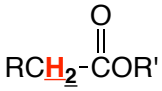
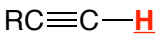
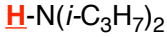
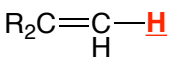
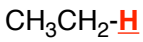
Student Honor Code

"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
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 _____(32)

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

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 1. _____ technique of 2. _____

3. _____ imaging (MRI) is based on the same principles as

4. _____ , namely the 5. _____ (i.e. 6. _____)

of nuclear 7. _____ of H atoms by radio 8. _____

irradiation when a patient is placed in a strong 9. _____ field. Magnetic field

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

11. _____ 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 12. _____

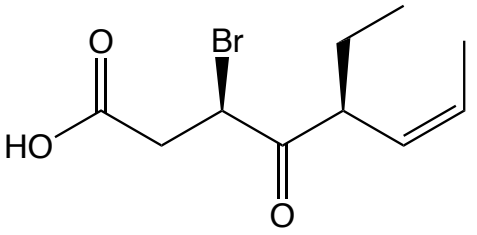
that when stacked make up the three-dimensional image of 13. _____ amounts

of 14. _____ atoms, especially the 15. _____ atoms from

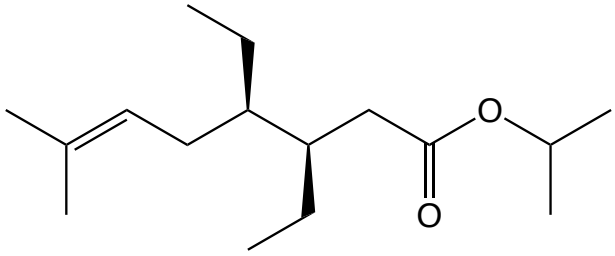
16. _____ and 17. _____ , in the different tissues.

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.

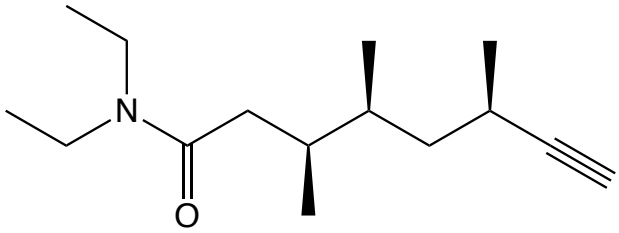
4. (6 pts each) From the list below, select the letter associated with the IUPAC name that is correct for each structure.



The letter corresponding to the IUPAC name of this molecule is ☐



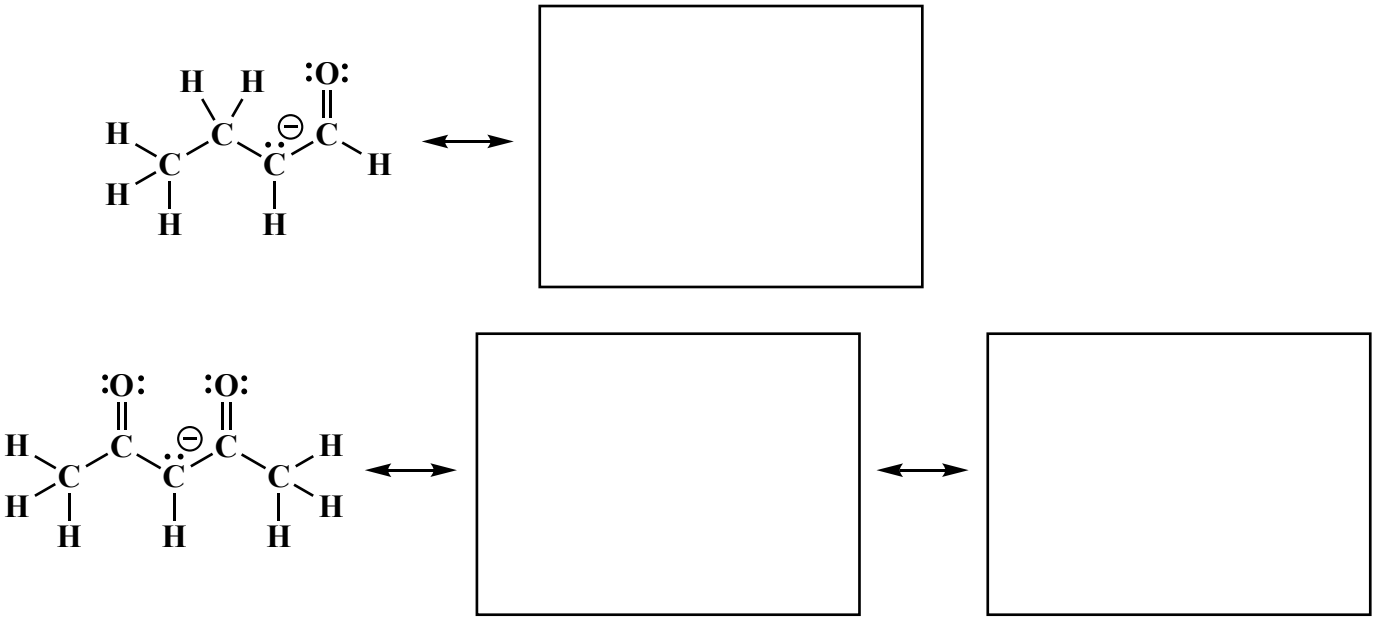
The letter corresponding to the IUPAC name of this molecule is ☐

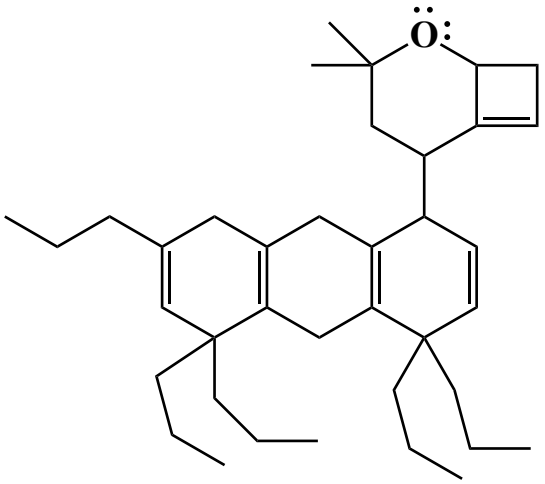


The letter corresponding to the IUPAC name of this molecule is ☐

A.	isopropyl (3*R*,4*R*)-3,4-diethyl-7-methyl-6-octenoate
B.	isopropyl (3*S*,4*R*)-3,4-diethyl-7-methyl-6-octenoate
C.	isopropyl (3*S*,4*S*)-3,4-diethyl-7-methyl-6-octenoate
D.	(*R*,*E*)-3-bromo-5-ethyl-4-oxo-5-octenoic acid
E.	(2*R*,5*S*,*Z*)-2-bromo-5-ethyl-4-oxo-6-octenoic acid
F.	(3*R*,5*S*,*Z*)-3-bromo-5-ethyl-4-oxo-6-octenoic acid
G.	(3*S*,4*S*,6*R*)-3-butyl-*N*-ethyl-4,6-dimethyl-*N*-propyl-7-octynamide
H.	(3*S*,4*S*,6*R*)-*N*,*N*-diethyl-3,4,6-trimethyl-7-octynamide
I.	(3*S*,4*R*,*E*)-3-butyl-*N*-ethyl-4,6-dimethyl-*N*-propyl-5-octenamide

5. (9 pts) For the two different enolates shown below, draw the other important contributing structures. Make sure to show all electrons and formal charges.



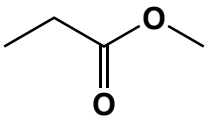


3,3-dimethyl-5-(4,4,5,5,7-pentapropyl-1,4,5,8,9,10-hexahydroanthracen-1-yl)-2-oxabicyclo[4.2.0]oct-6-ene

Also known as Fifi, a miniature, and I mean miniature, Chihuahua

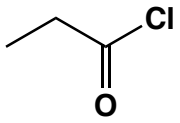
6. (17 pts) Being able to recognize the chemical personality of different species is one of the most important skills you can develop in Organic Chemistry. Fill in the appropriate circle to indicate whether each structure is a nucleophile or electrophile in bond-making ("Make a Bond") steps of mechanisms you have seen. Note that these species might be acids or bases in certain situations, but we will ignore that for this problem.

6.1



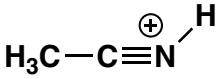
◯ Electrophile
◯ Nucleophile

6.2



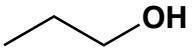
◯ Electrophile
◯ Nucleophile

6.3



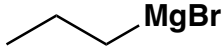
◯ Electrophile
◯ Nucleophile

6.4



◯ Electrophile
◯ Nucleophile

6.5

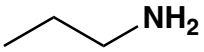


◯ Electrophile
◯ Nucleophile

6.6 $LiAlH_4$

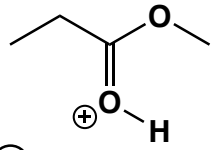
◯ Electrophile
◯ Nucleophile

6.7



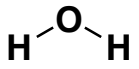
◯ Electrophile
◯ Nucleophile

6.8



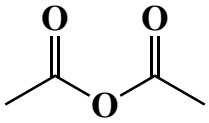
◯ Electrophile
◯ Nucleophile

6.9



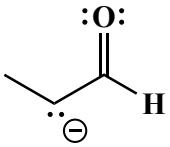
◯ Electrophile
◯ Nucleophile

6.10



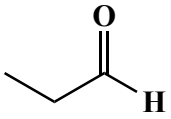
◯ Electrophile
◯ Nucleophile

6.11



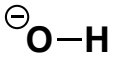
◯ Electrophile
◯ Nucleophile

6.12



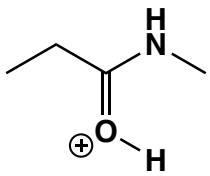
◯ Electrophile
◯ Nucleophile

6.13



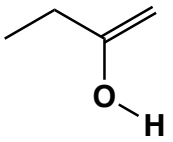
◯ Electrophile
◯ Nucleophile

6.14



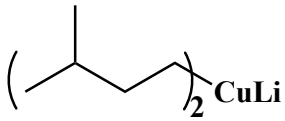
◯ Electrophile
◯ Nucleophile

6.15



◯ Electrophile
◯ Nucleophile

6.16



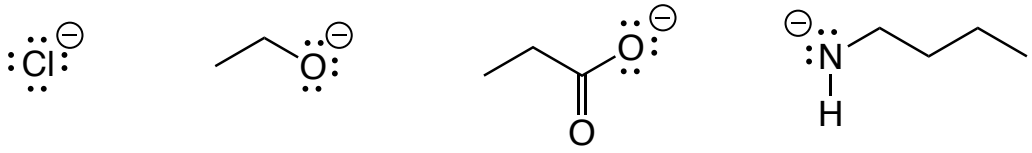
◯ Electrophile
◯ Nucleophile

6.17 $NaBH_4$

◯ Electrophile
◯ Nucleophile

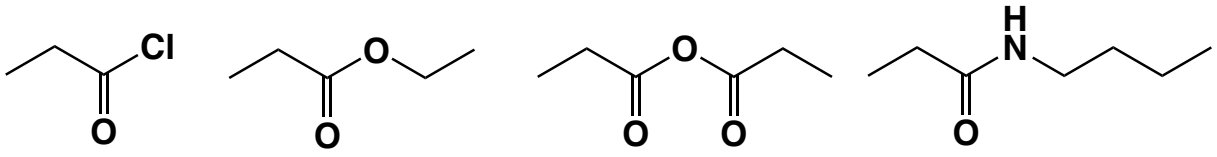
7. (12 pts) These are the ranking questions.

A) Rank the following with respect to anion stability, WITH A "1" UNDER THE MOST STABLE ANION AND "4" UNDER THE LEAST STABLE ANION, AND THEN "2" AND "3" AS APPROPRIATE.



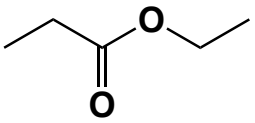
_____ _____ _____ _____

B) Rank the following with respect to reactivity with nuucleophiles, WITH A "1" UNDER THE MOST REACTIVE AND "4" UNDER THE LEAST REACTIVE, AND THEN "2" AND "3" AS APPROPRIATE.

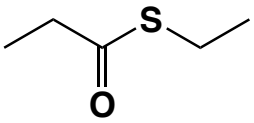


_____ _____ _____ _____

C) Thioesters (S in place of O in an ester) are important in biochemistry, being present in molecules such as Acetyl-CoA. Recall that anions increase in stability down a row of the periodic table as a function of increasing atomic radius (larger atoms have the negative charge spread over a larger area). Which of these two will be more reactive with nucleophiles?

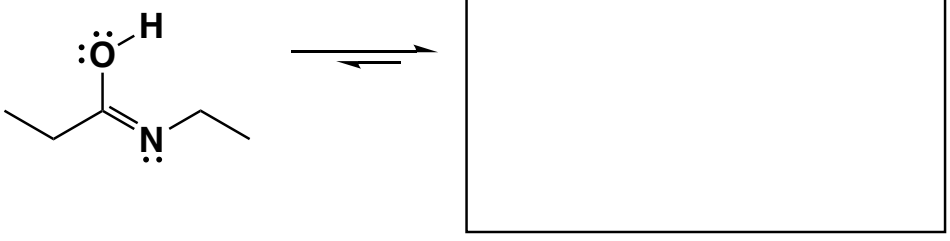


○ More reactive with nucleophiles
○ Less reactive with nucleophiles

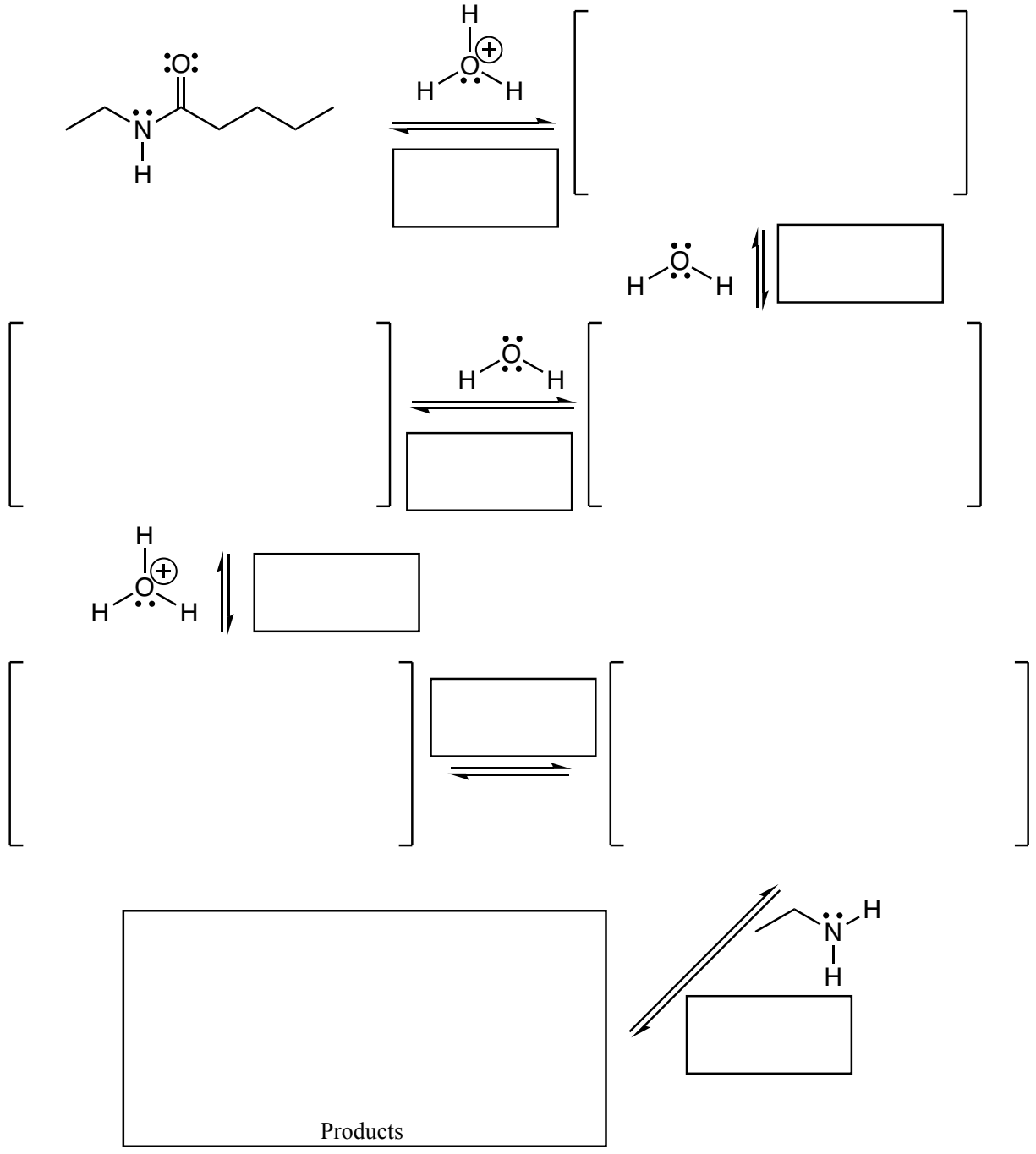


○ More reactive with nucleophiles
○ Less reactive with nucleophiles

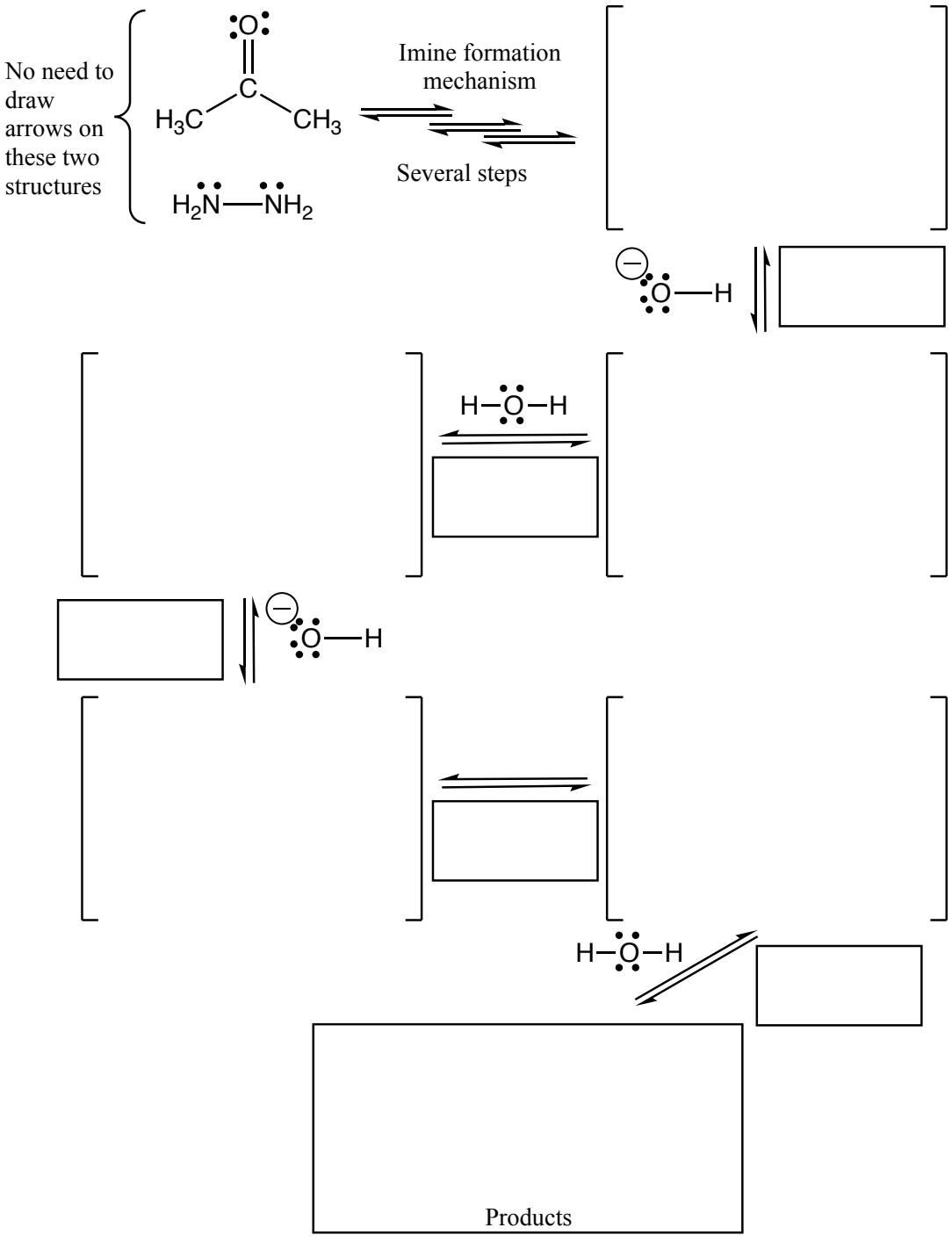
8. (4 pts) The following molecule spontaneously tautomerizes to a more stable species. **Draw the more stable species in the box provided.** There is no need to draw arrows here, but you do need to add all lone pairs and formal charges that are appropriate.



9. (36 pts) For this acid promoted amide hydrolysis 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.).**

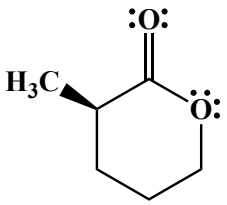


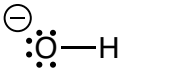
9. (34 pts) For this Wolff-Kishner reaction, use **arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE 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.).**

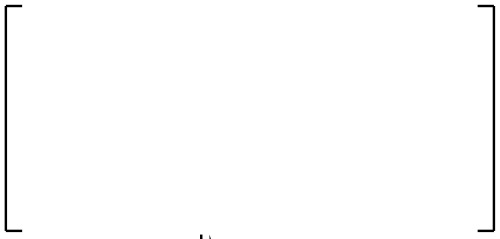


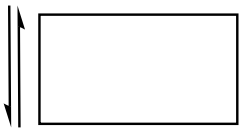
9. (34 pts) For these two reactions, use **arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" 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.).**

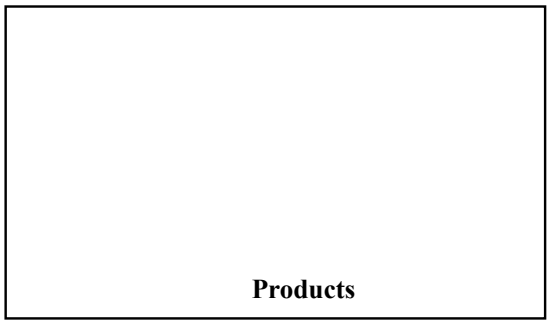
Note: Due to the special nature of the starting materials, you are not supposed to draw arrows on the last intermediate for these two mechanisms.







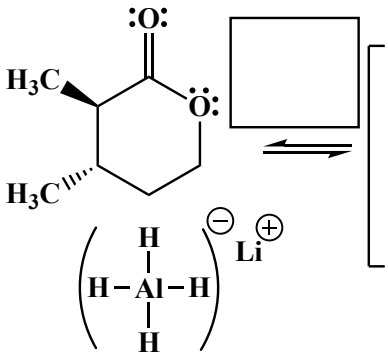


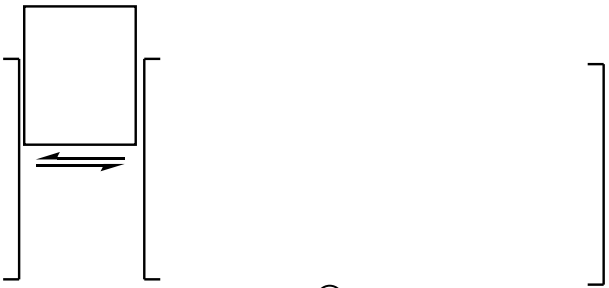


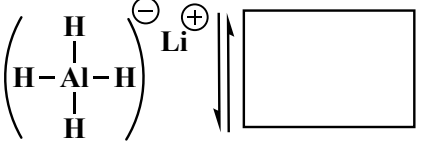
Products

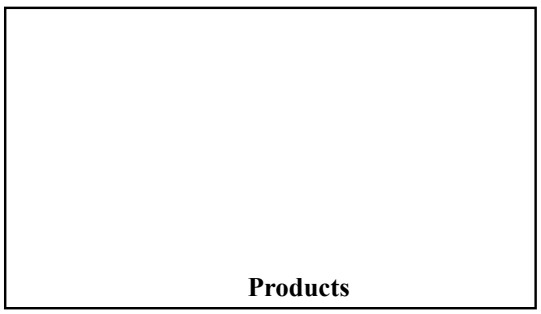
Proton Transfer

Do not draw any arrows here





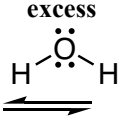




Products

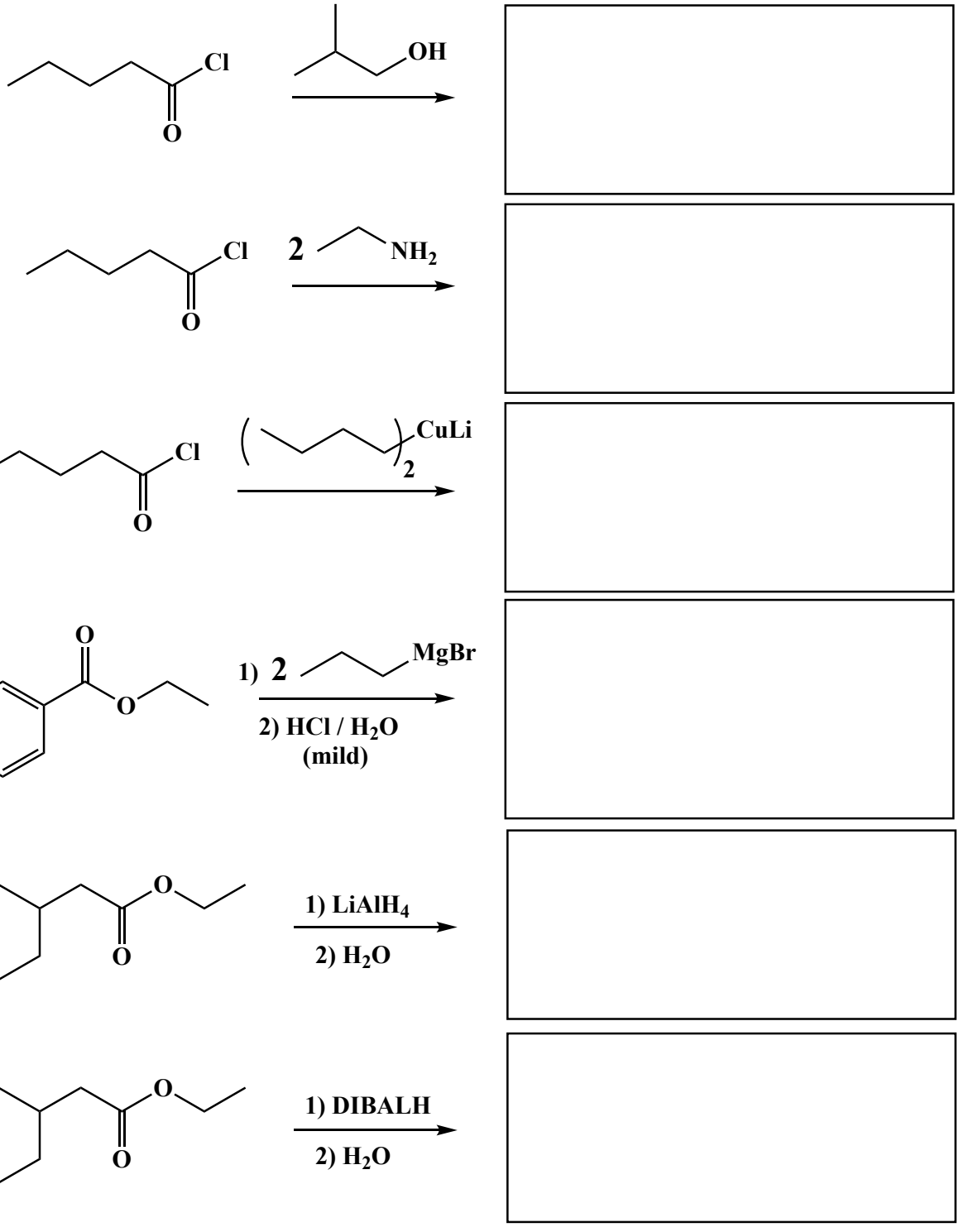
Chemist Opens Flask

2) **excess**



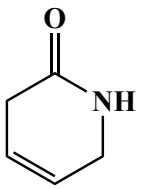
Do not draw any arrows here

10. (3 or 5 pts.) Write the predominant product 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 (····ıı) to indicate stereochemistry. For these, you do not have to worry about metal salts in the products.

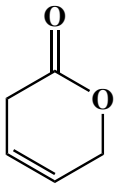


Signature_____ Pg 10 _____(18)

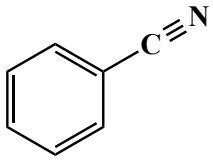
10. (3 or 5 pts.) Write the predominant product that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. For these, you do not have to worry about metal salts in the products.



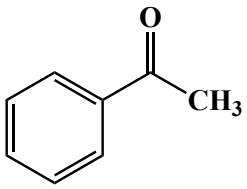
1) $LiAlH_4$
2) H_2O



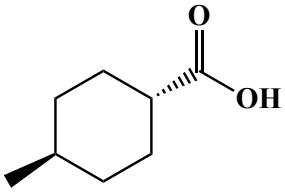
1) $HO^{\ominus}$
(1.0 equivalent)
2) HCl / H_2O
(mild)

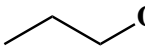


$H_3O^{\oplus}$
Strong acid, heat

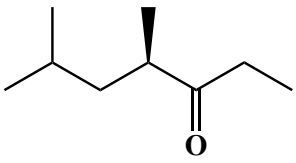


1) Br_2 / $HO^{\ominus}$
Excess and heat
2) HCl / H_2O
(mild)



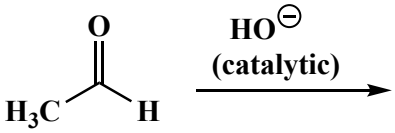


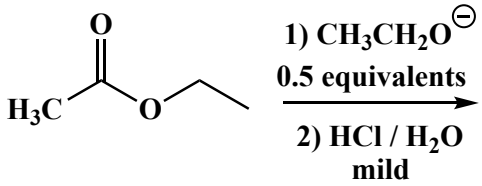
H_2SO_4
(catalytic)

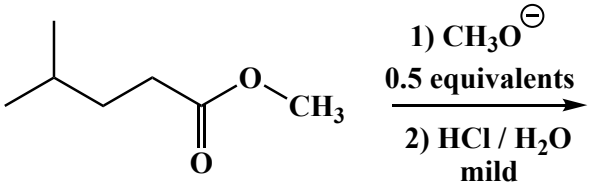


NH_2-NH_2
$HO^{\ominus}$

10. (3 or 5 pts.) Write the predominant product 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. For these, you do not have to worry about metal salts in the products.



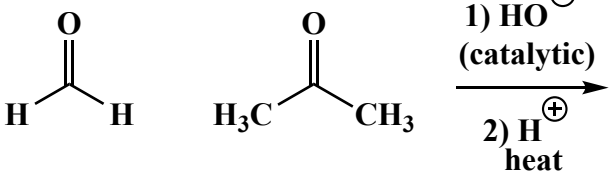


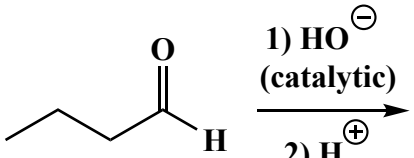


Signature_____ Pg 12 _____(10)

10. (4 or 6 pts.) Write the predominant product 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. For these, you do not have to worry about metal salts in the products.

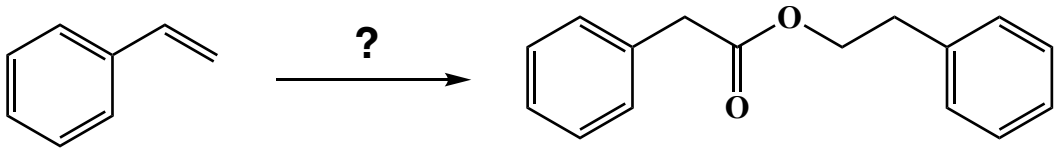
There is a lot to think about here. Please take your time. ASSUME THESE DEHYDRATE.





11. 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)



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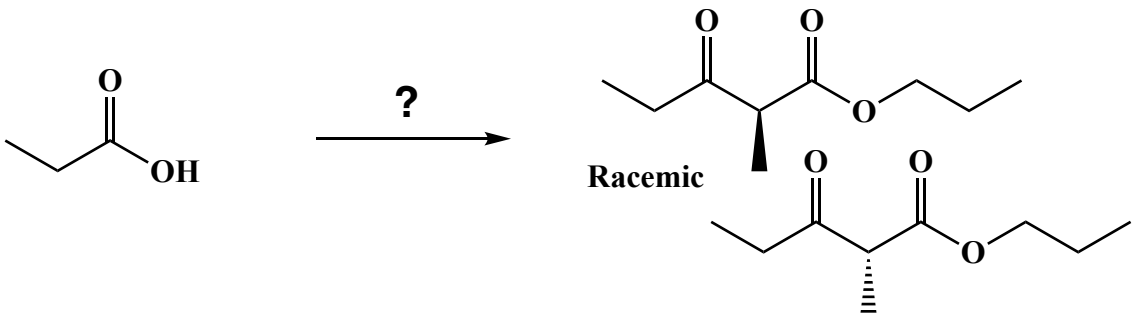
B) (10 pts)



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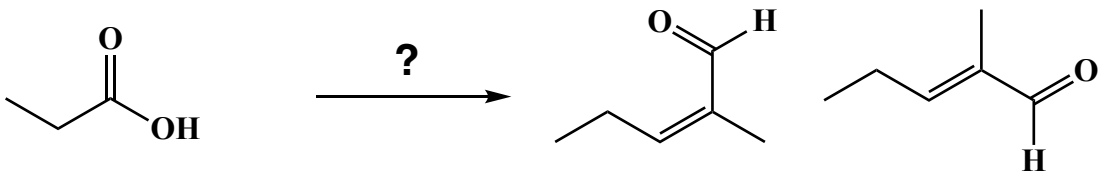
C) (12 pts)



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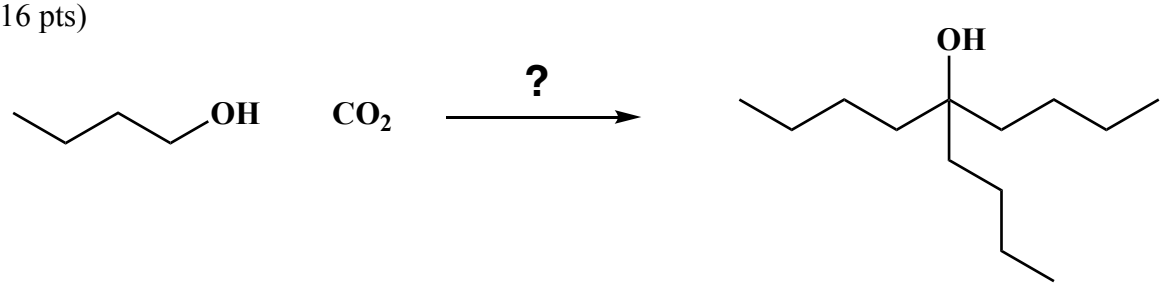
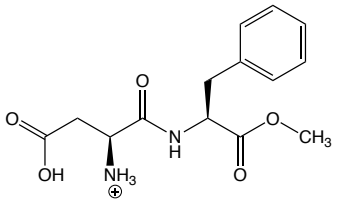
D) (16 pts)



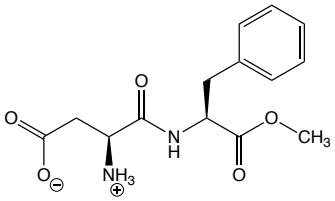
12. (16 pts) Here is an "Apply What you Know" Problem. You have not seen this directly, but based on what you know you CAN figure out the answers to the following questions. Aspartame, aka Nutrasweet® or Equal®, is one of the most popular artificial sweeteners used today. It is about 200 times sweeter than table sugar (sucrose), so very little goes a long way. According to the FDA "the use of aspartame as a general purpose sweetener… is safe." That safety makes sense in light of the structure. Instead of being an entirely synthetic framework, or even a carbohydrate derivative as one might have expected, Aspartame is composed of two common and naturally occurring *amino acids* aspartic acid and phenylalanine, connected through an ordinary amide bond. There is a methyl ester on the carboxylic acid end of the phenylalanine. Because so little needs to be used in food or drinks to provide the desired sweetness, and because the structure is composed of amino acids, the number of calories associated with aspartame in a food or drink is negligible.

Phosphoric acid is added to soda to provide tartness and prevent bacteria from growing. The phosphoric acid lowers the pH of soda to between 2.5 to 3.2. For example, Diet Coke, a product that contains aspartame in place of sugar or high fructose corn syrup, has a pH that has been measure as 3.1 (https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4808596/).

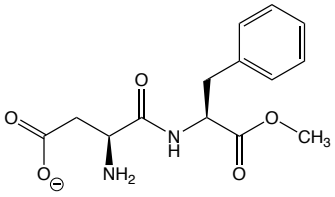
A) Aspartame has two pKa values, the first is 3.19 and the second is 7.87. At a pH of exactly 3.19, almost exactly the pH of Diet Coke, what is the protonation state of aspartame?



A



B



C

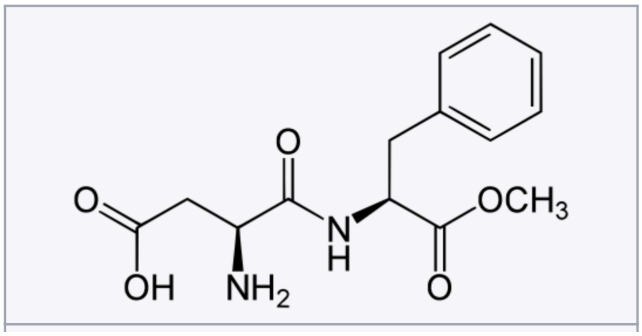
- ◯ Structure A
- ◯ Structure B
- ◯ Structure C
- ◯ A 1:1 Mixture of Structure A and Structure B

B) At pH 6.0, what is the protonation state of aspartame?

- ◯ Structure A
- ◯ Structure B
- ◯ Structure C
- ◯ A 1:1 Mixture of Structure B and Structure C

Below, I have attached a screen shot of the Wikipedia page for Aspartame (March 5, 2023).

Aspartame[1]

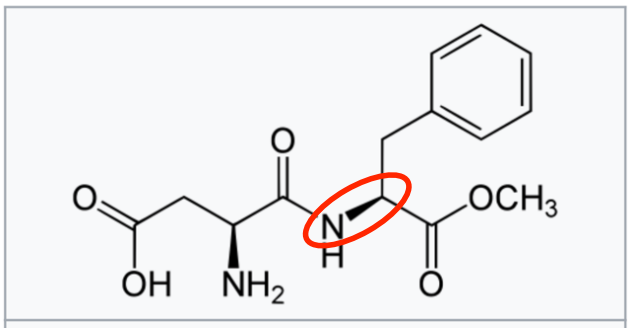


C) At what pH is the structure shown the correct protonation state of Aspartame?

- ◯ pH = 3.19
- ◯ pH = 7.0
- ◯ pH = 10
- ◯ There is no pH at which this could be the corret protonation state

Look at the C-N bond that is circled below.

Aspartame[1]



Recall that in organic chemistry, a bond that is drawn as a normal line is intended to be in the plane of the paper, a bond that is drawn as a wedge indicates that the atom at the wider end of the wedge is above the plane of the paper, and for a dashed bond, the atom at the wider end of the dash is below the plane of the paper.

D) Given what you know about the geometry of amide bonds, is the circled wedge bond an appropriate way to represent the stereochemistry in aspartame?

- ◯ Yes, all of the bonds in this Wikipedia structure are drawn appropriately
- ◯ No, the circled bond would have to be in the same plane as the paper, and therefore a normal line, because the N atom is sp^2 hybridized and planar.

E) Drinks containing aspartame need to be stored in cold temperatures to avoid losing their sweet taste. For example, if Diet Coke is stored in the Texas heat for several weeks it will rapidly lose sweetness. **Examine the Aspartame structure carefully. Inside the box provided, in no more than two sentences, explain why aspartame loses sweetness when exposed to heat.**

I hope you all have a wonderful spring break. Please make a promise to yourself to take some time to do things you really enjoy. YOU DESERVE IT, after all, you are in OChem II! And, of course, all of next week make sure to EXERCISE EVERY CHANCE YOU GET. Our 3.1 mile challenge is coming up the first week of April!