NAME (Print): _____

SIGNATURE: _____

Chemistry 310N
Dr. Brent Iverson
Final
May 18, 2009

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

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

For synthesis problems GO FOR PARTIAL CREDIT EVEN IF YOU DO NOT KNOW THE ENTIRE ANSWER!!!WRITE DOWN WHAT YOU DO KNOW IS IN THE REACTION SEQUENCE SOMEWHERE. YOU WILL GET PARTIAL CREDIT IF IT IS CORRECT

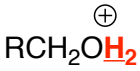
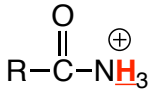
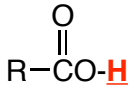
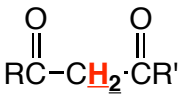
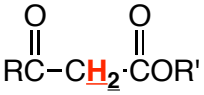
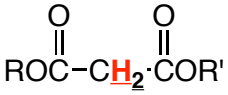
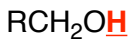
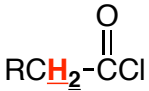
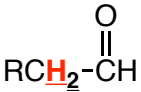
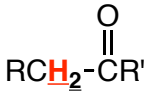
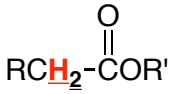
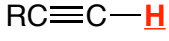
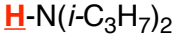
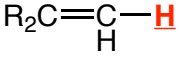
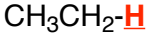
Note: You must have your answers written in pen if you want a regrade!!!!

Honor Code

The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.

_____

(Your signature)

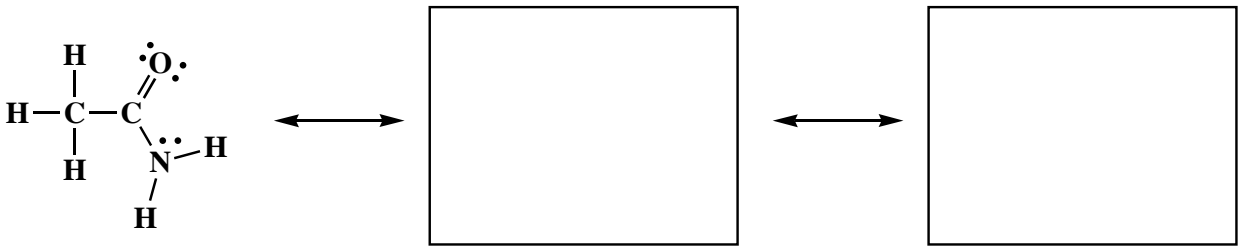
Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Protonated Amide		-0.5
Carboxylic acids		3-5
Ammonium ion		9.2
β-Dicarbonyls		10
β-Ketoesters		11
β-Diesters		13
Water		15.7
Alcohols		15-19
Acid chlorides		16
Aldehydes		18-20
Ketones		18-20
Esters		23-25
Terminal alkynes		25
LDA		40
Terminal alkenes		44
Alkanes		51

Signature_____ Pg 1 _____(36)

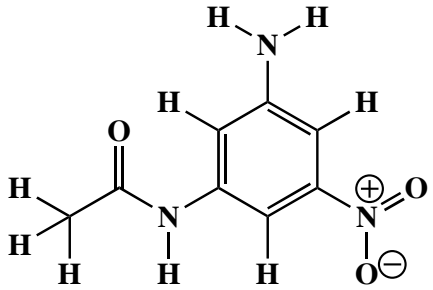
1. (4 points) What is the most important question in chemistry?

2. (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 minumum of 7 key points here.

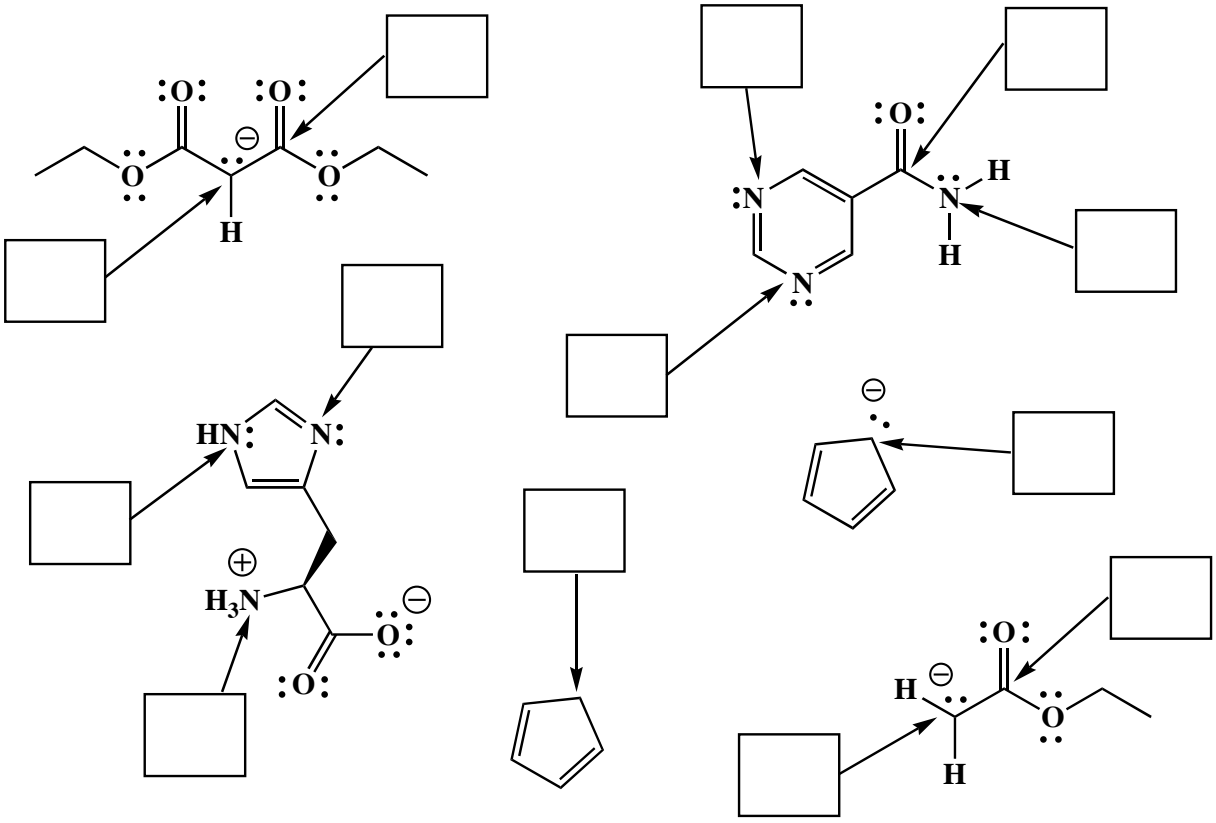
3. (8 pts) On the left is drawn the Lewis structure of a simple amide. Draw the two next most important contributing structures in the spaces provided. Be sure to show all lone pairs and formal charges. Place arrows on the two structures on the left to indicate how you are moving electrons to create the structure immediately to their right.



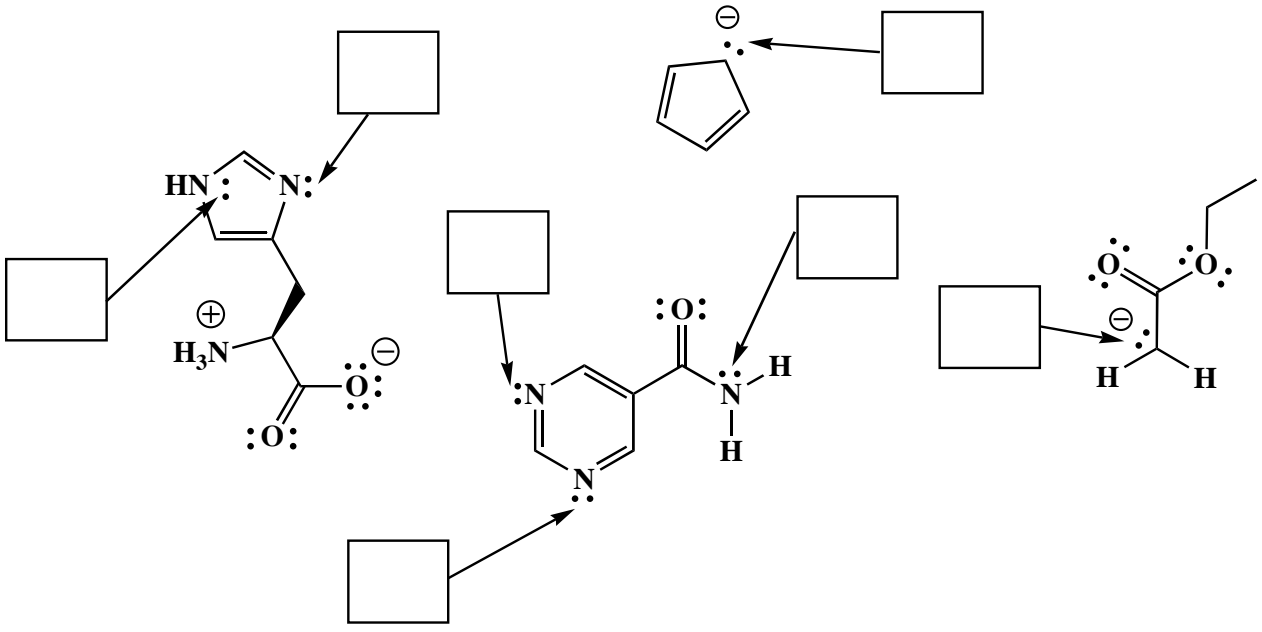
3. (10 pts) Because of pi delocalilzation,many of the atoms in the molecules below are predicted to be in the same plane. On the structures below, circle all the atoms that you believe will be located the same plane at equilibrium. Do not circle atoms that are in the same plane only temporarily as their bonds are rotating freely at room temperature.



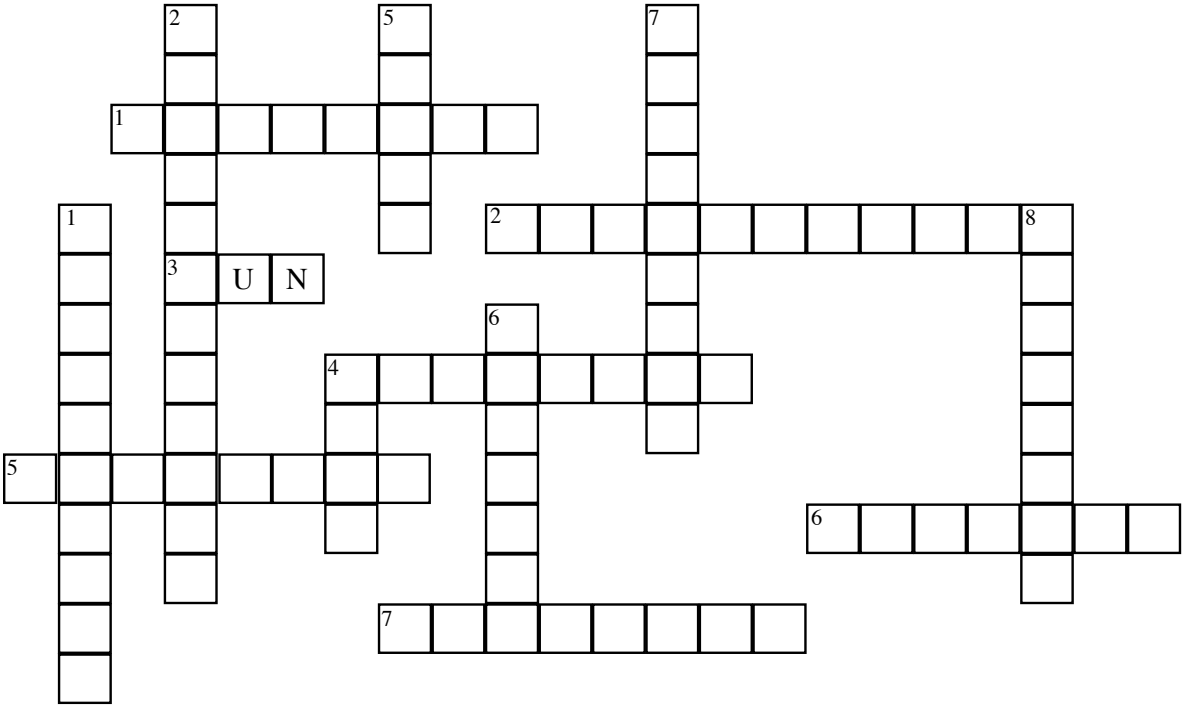
4. (13 pts) In the boxes provided, write the hybridization state of the given atoms.



5. (7 pts) In the boxes provided, according to the valence bond approach, write the type of atomic orbital that contains the indicated lone pair of electrons..



6. (14 pts)Complete the following crossword puzzle



Across

1. The distance between peaks of a signal is called the _____ constant ("J")

2. _____ tells you how many equivalent H atoms there are

3. A great way to stay fit and healthy for the rest of your life is to _____ every chance you get.

4. The more _____ the nucleus, the smaller the chemical shift

5. Physics: Moving charge generates a _____ field

6. For nonsymmetric _____ or ring structures such as cyclopropanes, the splitting does not simplify (no bond rotation)

7. THEORY: When there are two sets of adjacent H atoms, the number of peaks _____.

Down

1. _____ hydrogen atoms in a molecule give the same NMR signal.

2. The difference in energy between the +1/2 and -1/2 nuclear spin states is _____ to the strength of the magnetic field felt by the nucleus

4. Atomic nuclei, like electrons, have a quantum mechanical property of _____.

5. Chemical _____ tells you what functional groups are present

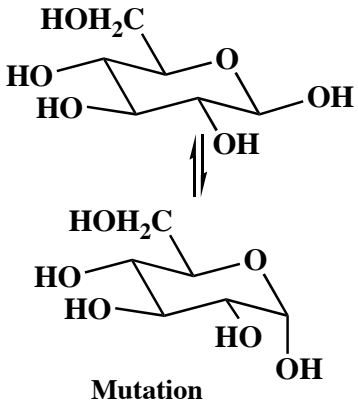
6. Non-equivalent H atoms on the same C atom can split each other (called _____ coupling), for example on alkenes or small rings.

7. Splitting patterns tell you how the atoms are _____ to each other.

8. In practice, if there are n adjacent H atoms, equivalent or not, you will see ____ _____ _____ peaks (three words)

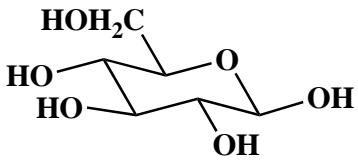
7. (2 pts each) I know you were wondering how we were going to test the carbohydrate material. Here is what we came up with. For the following structures, draw a circle around the terms that provide the most accurate description.

A.



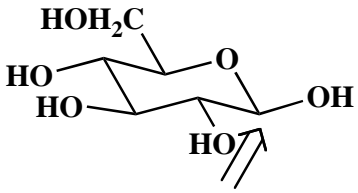
Mutation
Fermentation
Mutarotation
Mutacirculation

B.



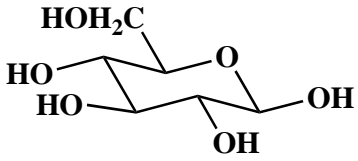
Furanose
Pyranose
Runny nose

C.



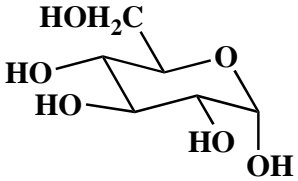
Monomeric carbon
Anomeric carbon
Polymeric carbon

D.



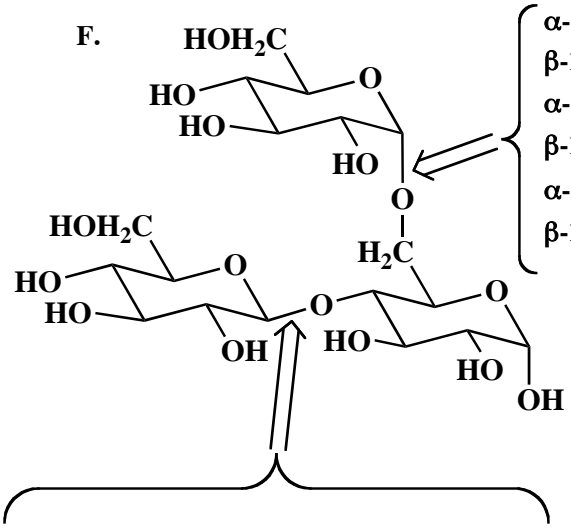
α-D-Glucose
β-D-Glucose
βββ-D-Glucose
ΣAE-D-Glucose

E.



α-D-Glucose
β-D-Glucose
βββ-D-Glucose
ΣAE-D-Glucose

F.

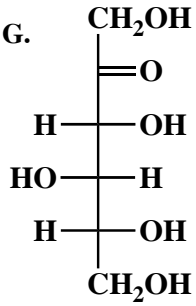


α-1,5-Glycosidic bond
β-1,5-Glycosidic bond
α-1,3-Glycosidic bond
β-1,3-Glycosidic bond
α-1,6-Glycosidic bond
β-1,6-Glycosidic bond

α-1,4-Glycosidic bond
β-1,4-Glycosidic bond
α-1,3-Glycosidic bond

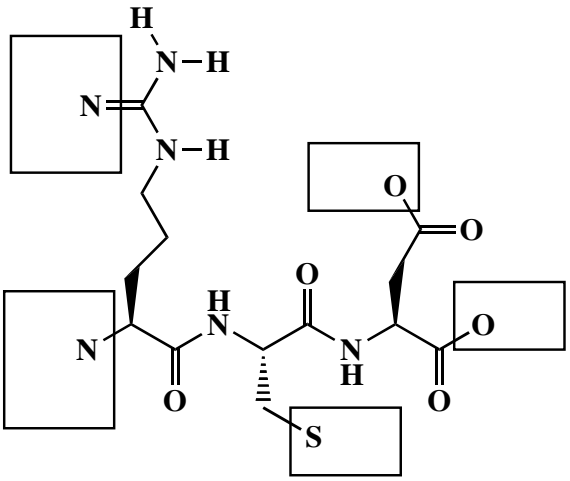
β-1,3-Glycosidic bond
α-1,5-Glycosidic bond
β-1,5-Glycosidic bond

G.



Aldohexose
Ketohexose
Aldopentose
Pointy toes

8. (16 points) **A)** This semester we have learned a great deal about carboxylic acids, guanidine groups, and amines. Here is an apply what you know problem. Charge is a major factor in determining the properties and activities of peptides. Below is the tripeptide Arginine-Cysteine-Aspartic acid (RCD). ***In the boxes provided, draw the correct protonation state of the carboxylic acid, amine, thiol and guanidine group*** **at pH, 6.0**. **You must show all protons and formal charges that are present on the functional groups within the five boxes. For this problem, assume the pK_a values of the carboxylic acids are 4.0, the pK_a value for a protonated amine (ammonium ion) is 9.2, the pK_a value for a protonated guanidine group (guanidimium ion) is 13.2 and the pKa for a thiol is 8.3.**

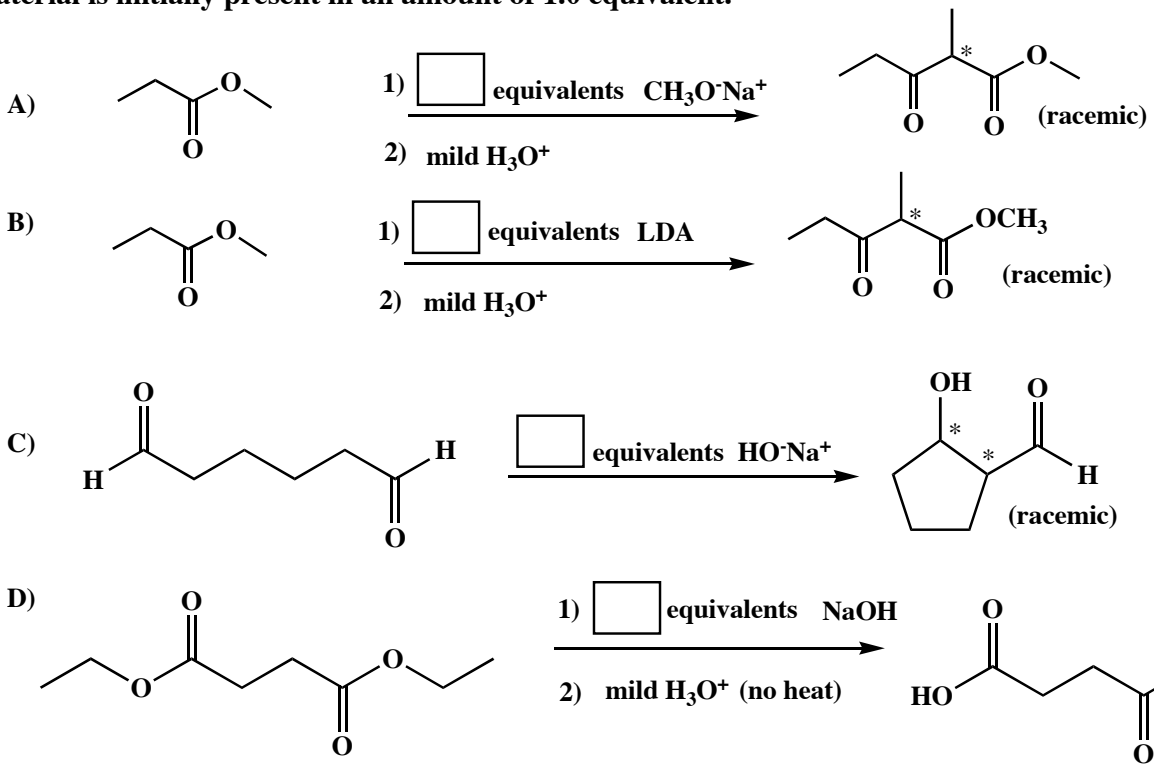


B) What is the total charge on this peptide at pH 6.0? _____

C) What is the total charge on this peptide at pH 2.0? _____

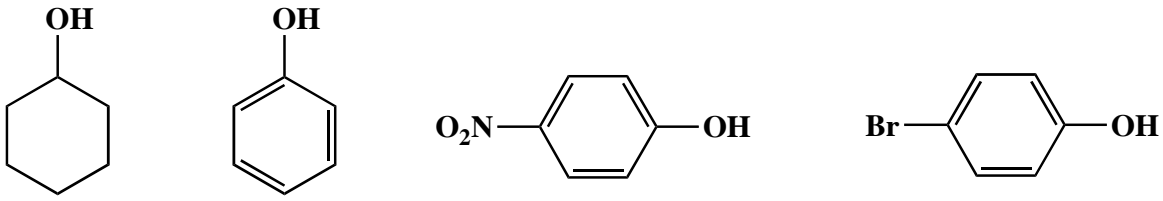
D) What is the total charge on this peptide at pH 11.2? _____

9. (2 pts each) In each of the boxes over an arrow, **write the minimum number of equivalents** of the specified reagent required to carry out the reaction shown **to completion**. If only a catalytic amount is needed, write **"CAT"**. Note: **You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent.**



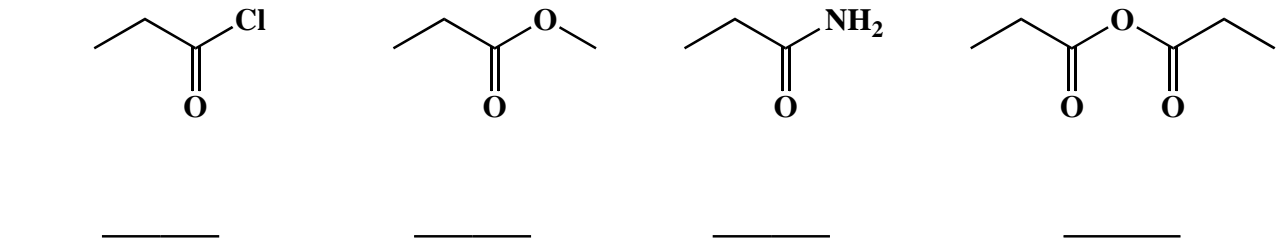
10. (3-4 pts each) For the following, rank the molecules according to the directions given.

A. Rank from least to most acidic, with a **1** under the least acidic and a **4** under the most acidic molecule.

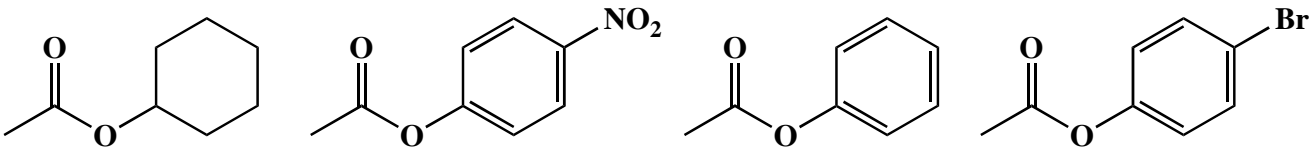


_____ _____ _____ _____

B. Rank from least to most reactive with nucleophiles, with a **1** under the least reactive and a **4** under the most reactive molecule.

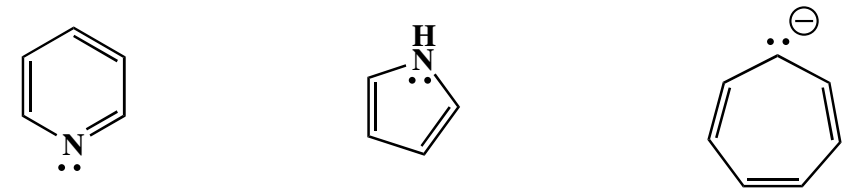


_____ _____ _____ _____



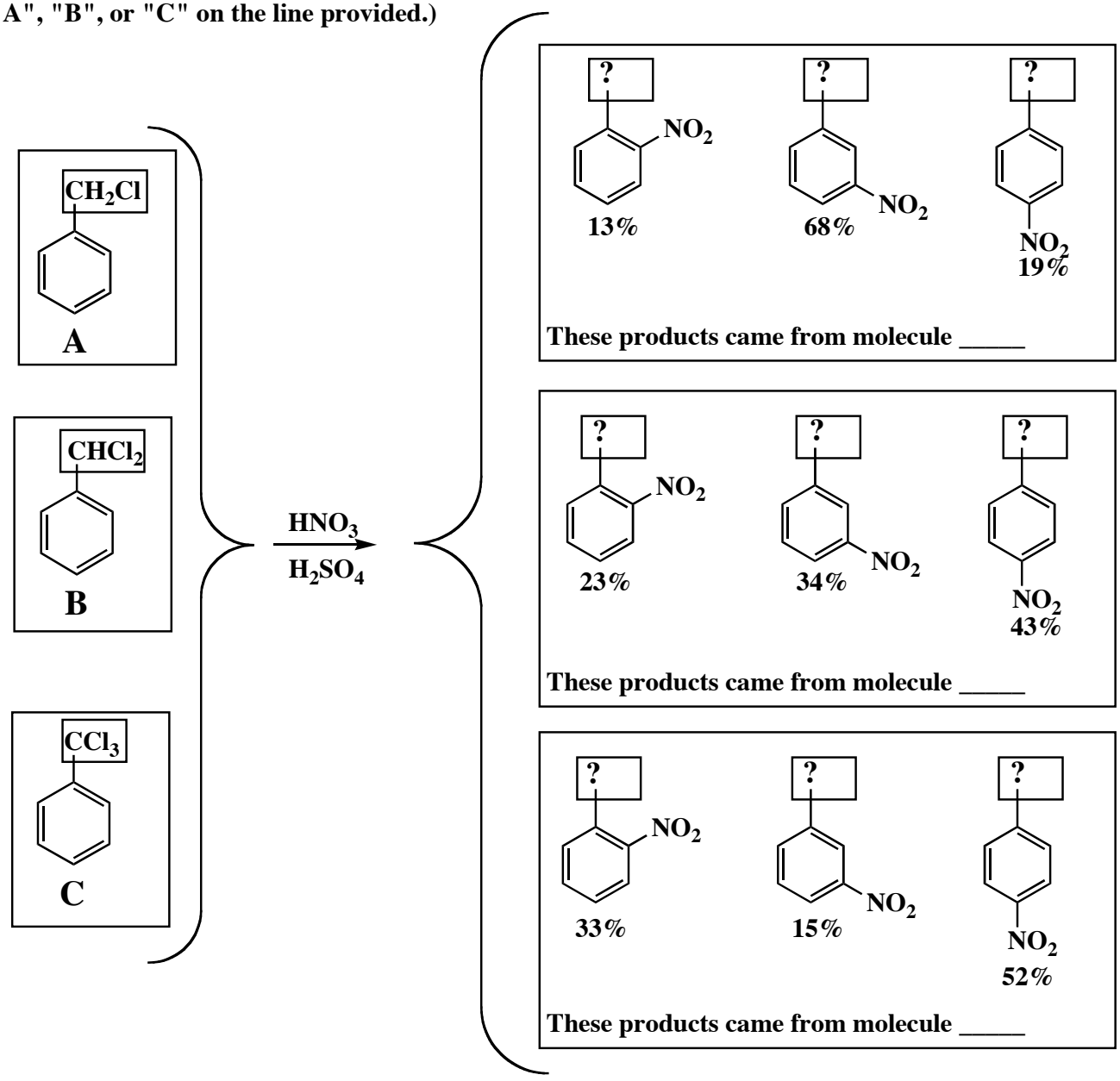
_____ _____ _____ _____

C. Rank from least to most basic, with a **1** under the least basic and a **3** under the most basic molecule.



_____ _____ _____

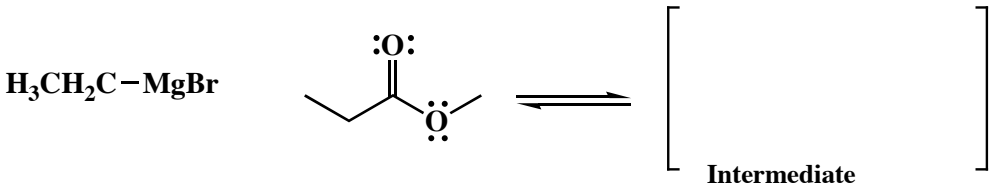
11. (13 pts) **Here is an apply what you know problem.** Below are listed three molecules, designated as **A**, **B**, or **C**. They differ in the number of chlorine atoms attached to the methyl group. We have three groups of products, and **under the structures we give you relative percentages of the ortho, para, and meta products obtained when each of these molecules undergoes the nitration reaction. Based on the percentages given, fill in the identitiy of the molecule (write A, B, or C on the line) that gave rise to each set of products. (Note: we do not want you to fill in the boxes, we want you to write the letter "A", "B", or "C" on the line provided.)**



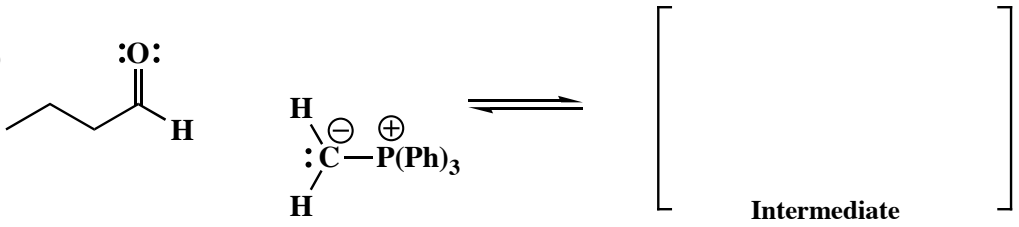
Explain your answer here (no more than two sentences):

13. (32 points) Many of the reactions we have learned this semester involve steps with nucleophiles reacting with electrophiles. For the following examples of steps in mechanisms we have seen this semester, **1) Draw the intermediate that will be formed when the two molecules react. 2) Draw all formal charges and lone pairs on the intermediates. 3) Draw arrows on the starting materials to indicate the flow of electrons that leads to the intermediate. 4) FINALLY, DRAW A BOX AROUND THE NUCLEOPHILE AND A CIRCLE AROUND THE ELECTROPHILE IN EACH CASE. There is no need to draw products or any further steps of the mechanisms.** You might want to read these directions again so you know what we want.

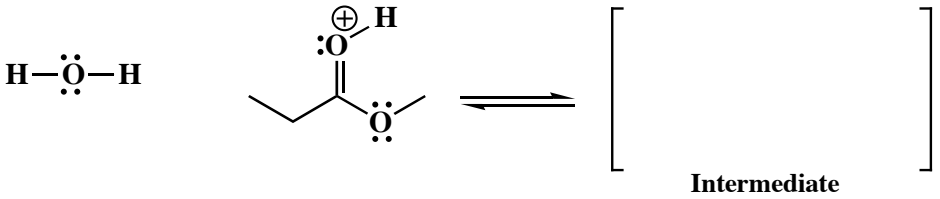
A)



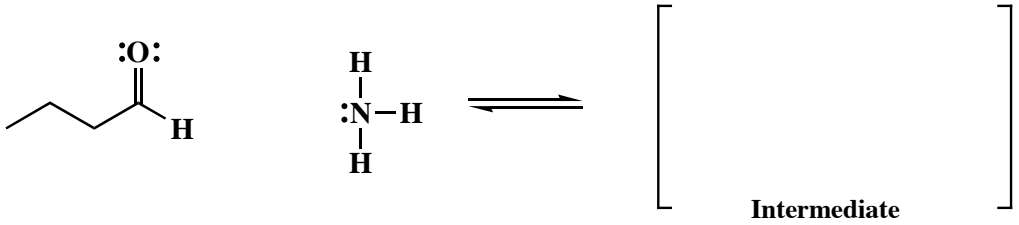
B)



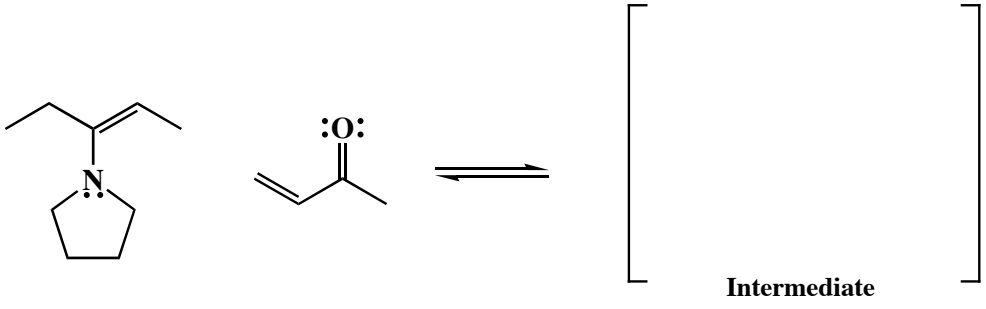
C)



D)

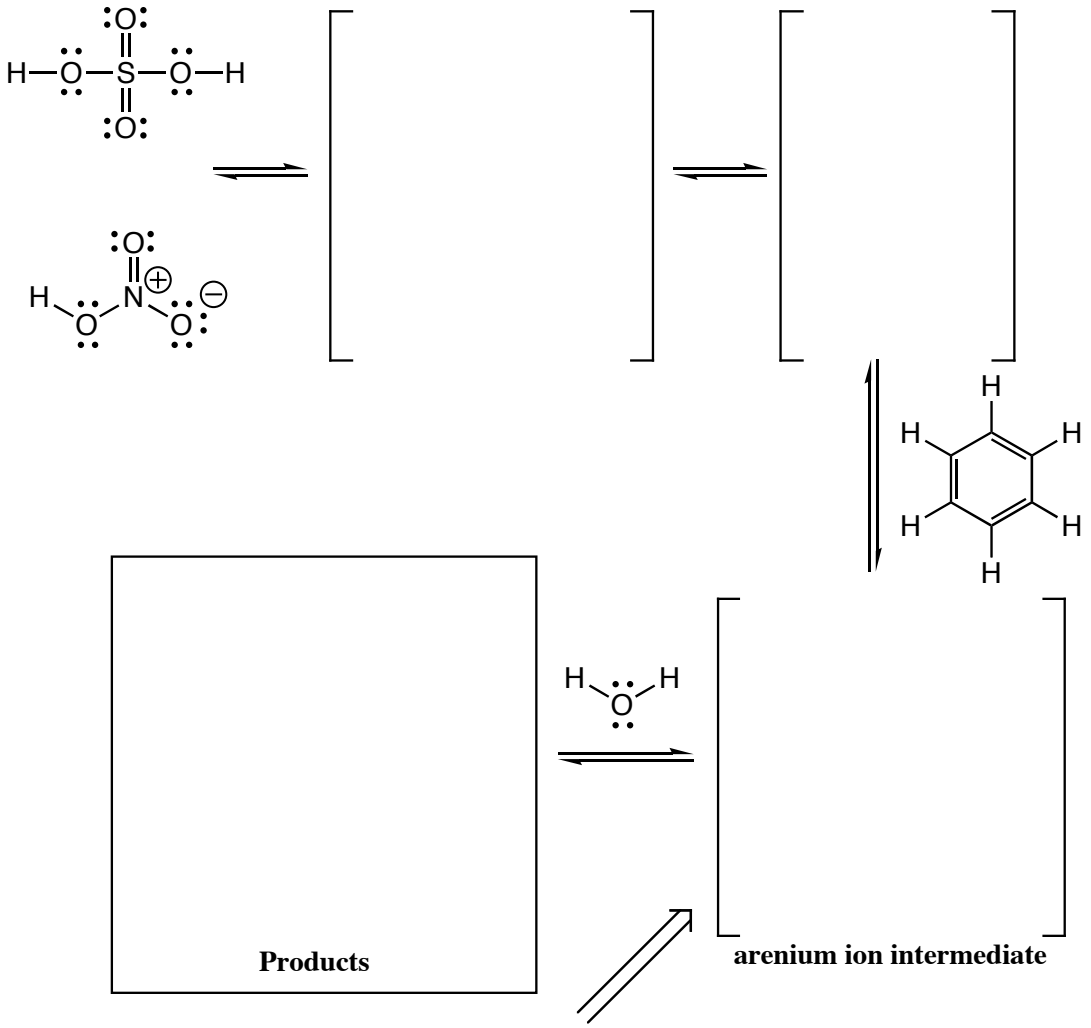


E)

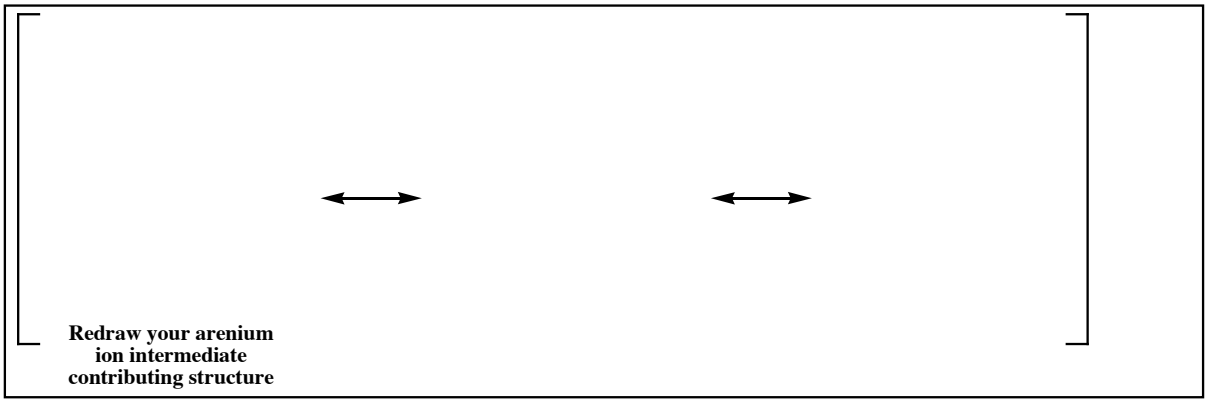


Did you remember to draw boxes and circles?

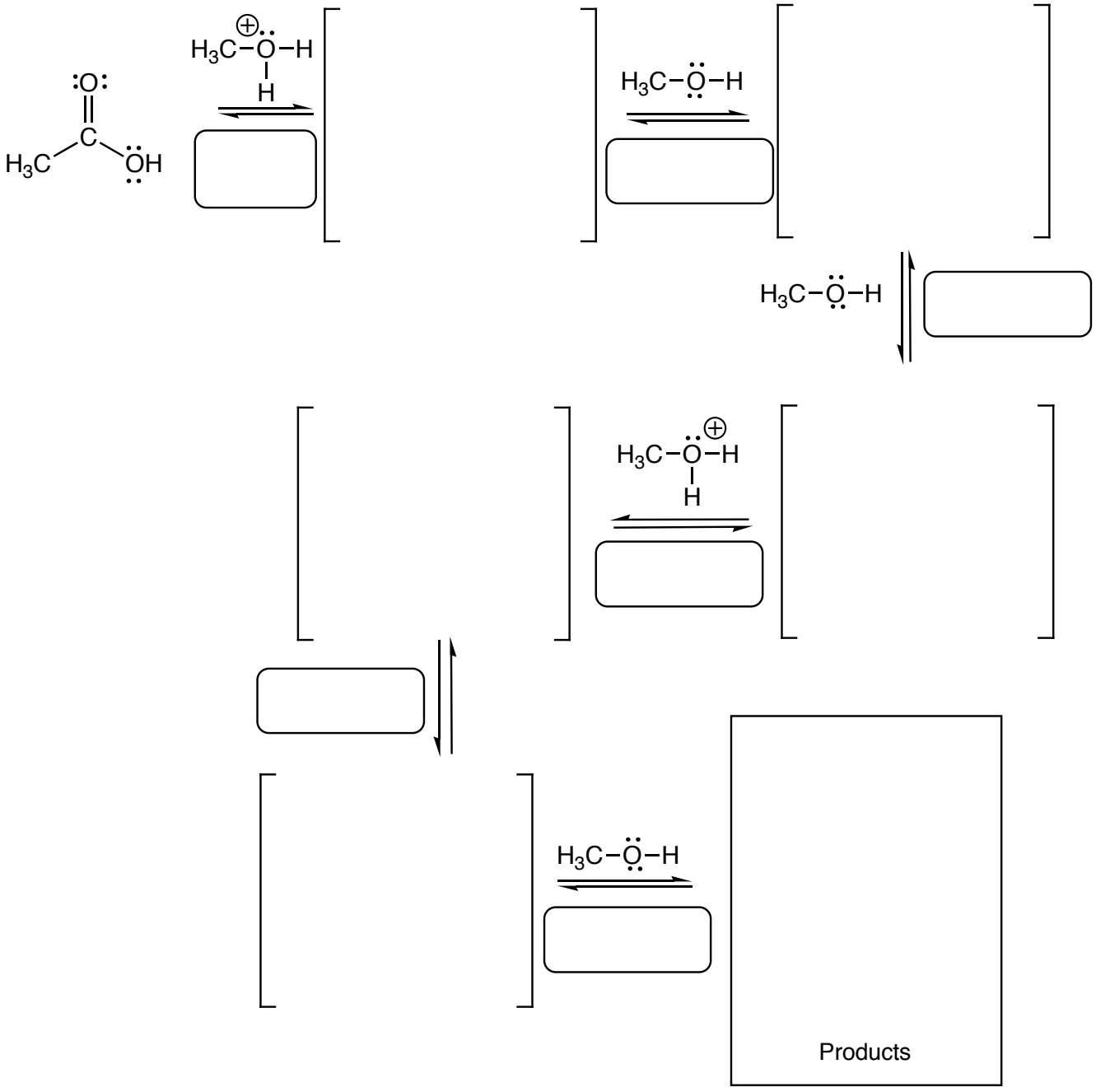
13. (27 points) Complete the mechanism below for electrophilic aromatic substitution. Use arrows to show the movement of all electrons, and be sure to draw all lone pairs of electrons and all formal charges. You do not have to worry about labeling chiral centers on this one, **but you do have to draw the three most important contributing structures**. ***Remember, you must show all products for each step.***



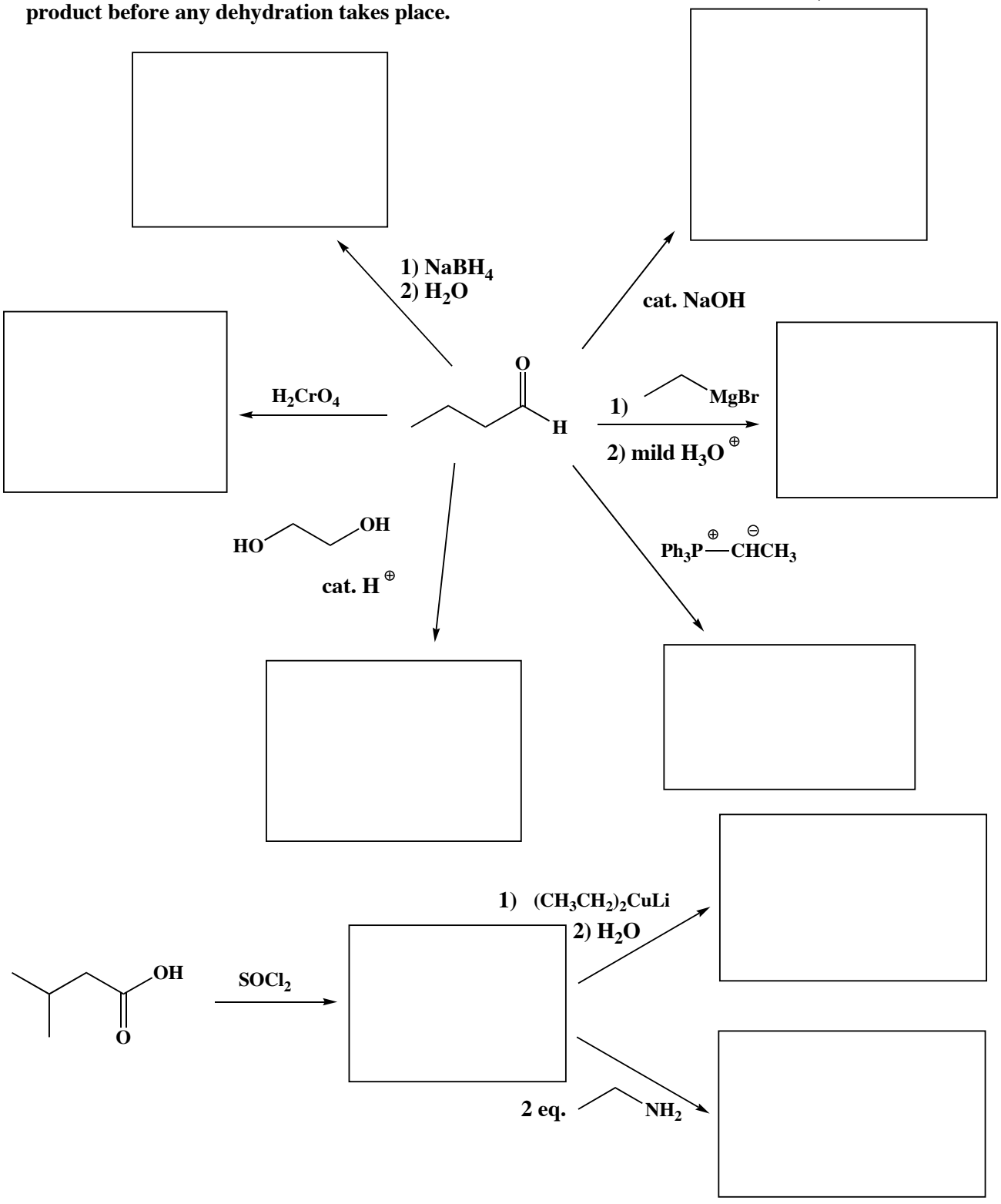
(6 pts) In the above mechanism, we only gave you enough space to draw one contributing structure of the arenium ion intermediate. In the box below, redraw the arenium ion intermediate contributing structure you drew in the mechanism, then draw two other important contributing structures.



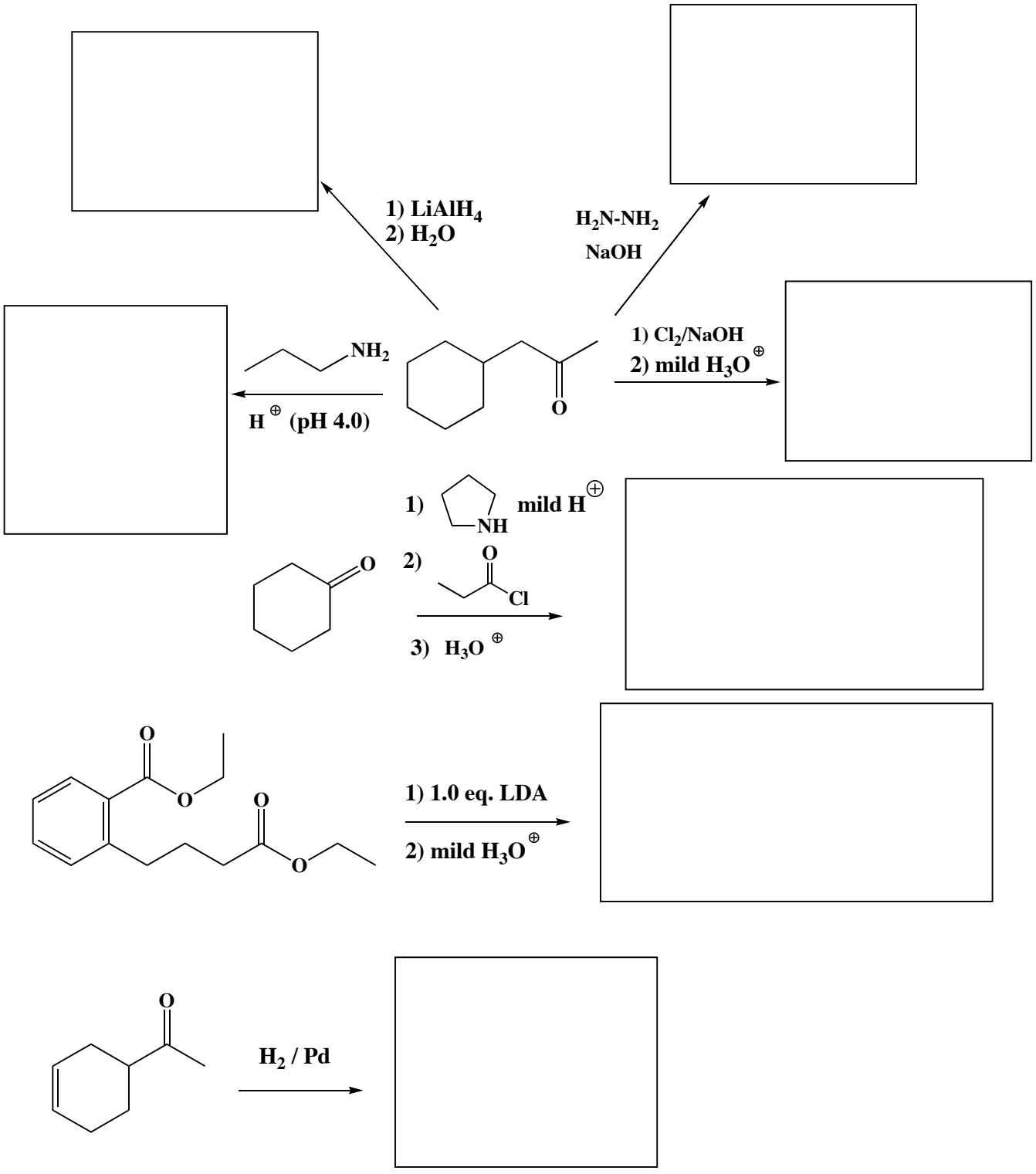
13. (35 points) Complete the mechanism below for Fisher esterification. Use arrows to show the movement of all electrons, and be sure to draw all lone pairs of electrons and all formal charges. You do not have to worry about labeling chiral centers on this one. ***Remember, you must show all products for each step.*** **Fill in the boxes below each set of arrows to indicate which type of mechanistic element is involved, i.e. "add a proton", lose a leaving group, etc.**



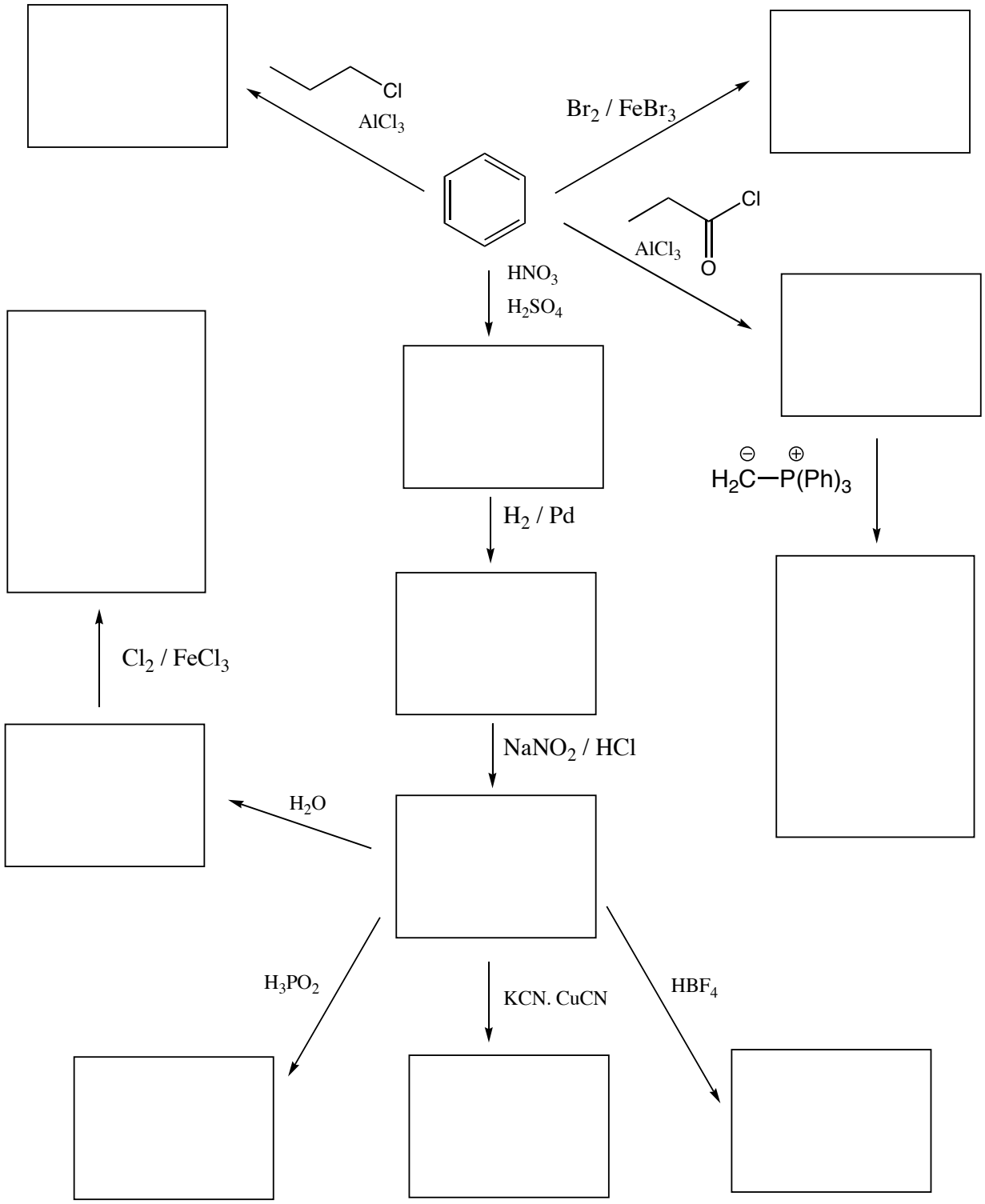
14. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, mark the chiral center with an asterisk "*" and write "racemic" under the structure. If there is an aldol reaction, draw the product before any dehydration takes place.**



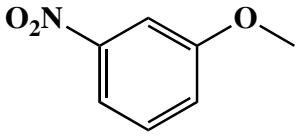
15. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, mark the chiral center with an asterisk "*" and write "racemic" under the structure. If there is an aldol reaction, draw the product before any dehydration takes place.**



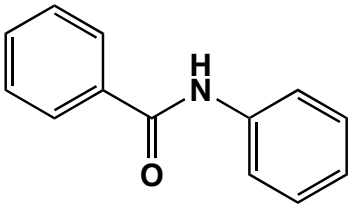
16. (2 or 4 pts.) Write the predominant product or products that will occur for each transformation. Assume each reagent only adds once to the ring. If predominantly ortho/para products are predicted, you must draw both.



17. (21 pts.) You might find these are harder so take your time. 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, mark the chiral center with an asterisk "*" and write "racemic" under the structure. If ortho/para products are made, you must draw both. Note, for this problem, aldols can dehydrate if heated in dilute acid.**

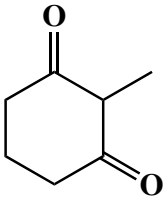


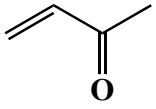
Br_2 / $FeBr_3$



Br_2 / $FeBr_3$

Assume only one Br atom adds

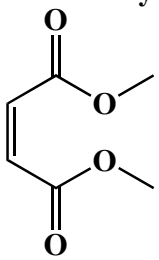


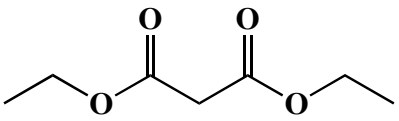


1) cat. NaOH

2) $H_3O^{\oplus}$ / heat

Be sure to indicate stereochemistry of the products on this next one.



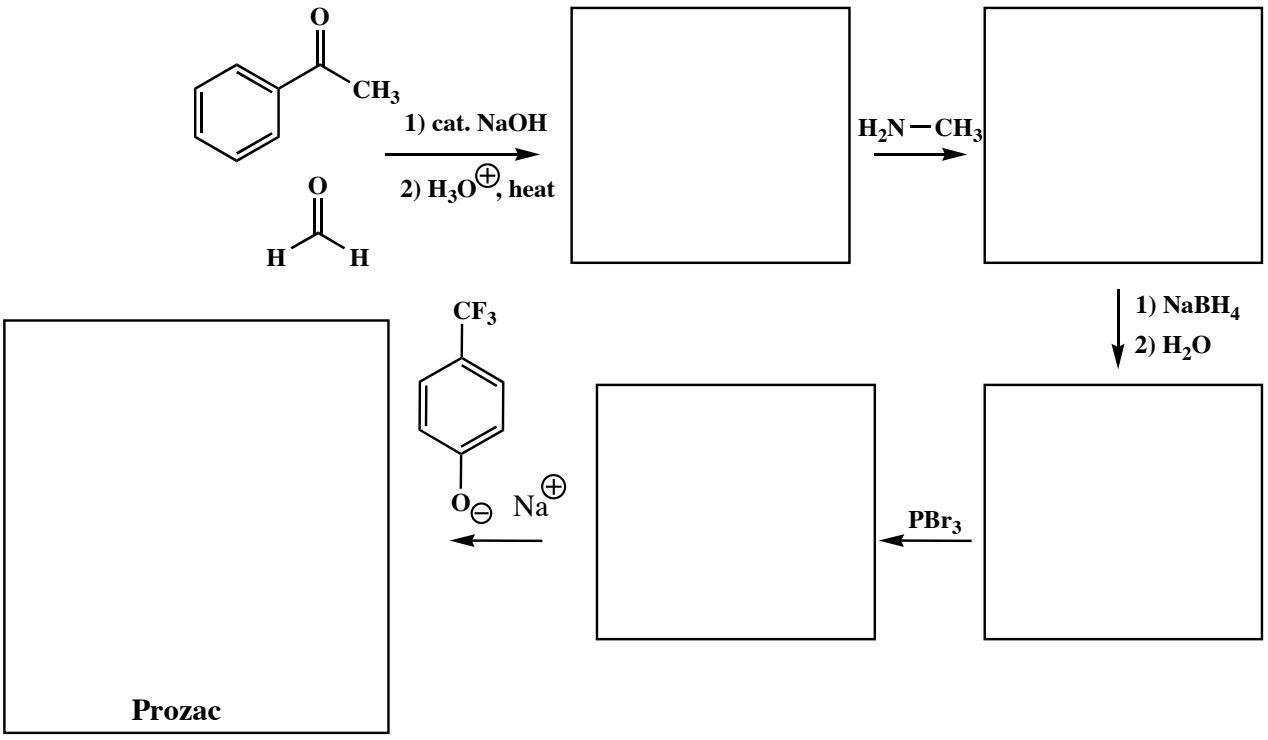


1) 1.0 Eq. NaOEt

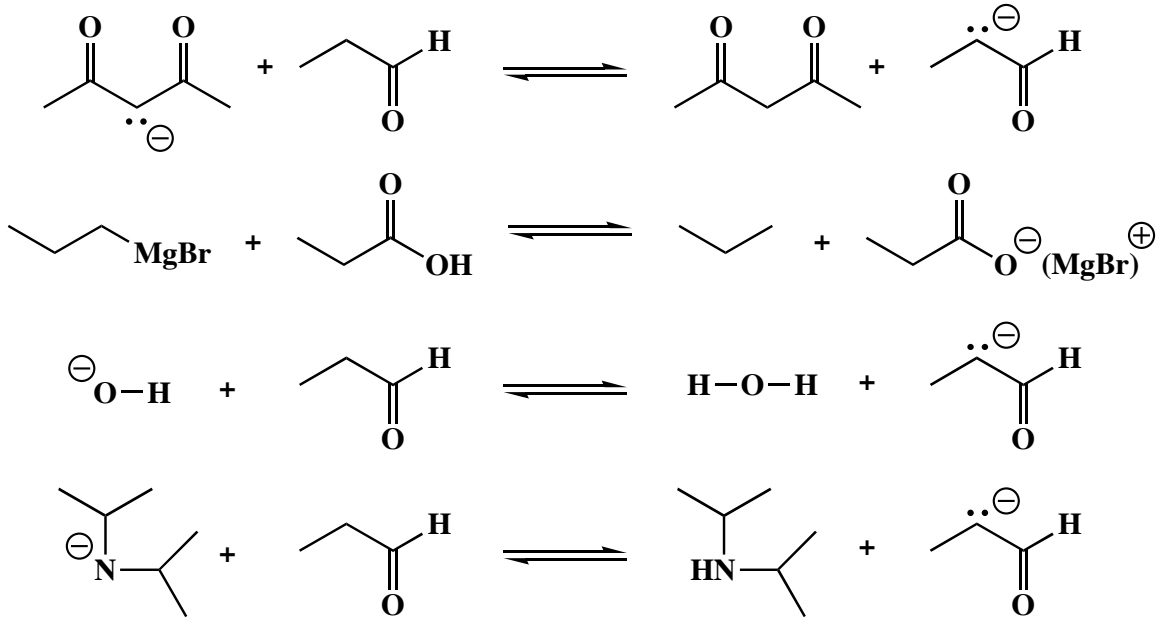
2)

3) $H_3O^{\oplus}$ / heat

17. (21 pts.) Here is the synthesis of the important pharmaceutical Prozac. You are familiar with all of the chemistry, it just might take you a while to recognize the reactions. **Fill in the boxes with the appropriate structures, and remember to use an asterisk "*" and write "racemic" to indicate any new chiral centers created along the way.**

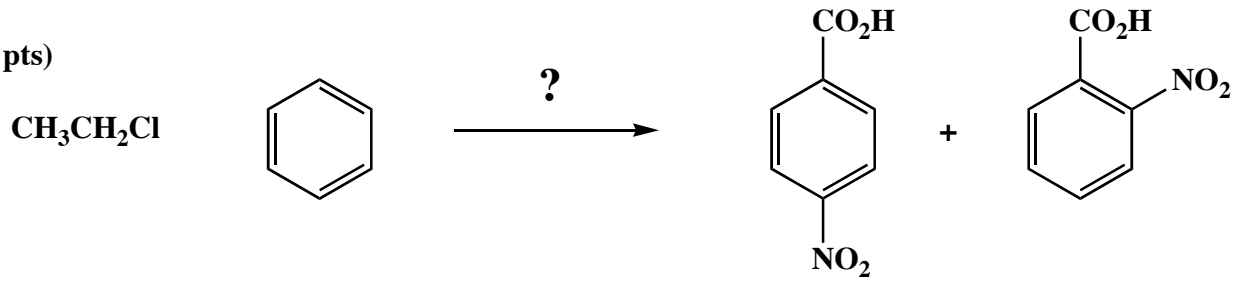


18. (8 pts) **For the following reactions, circle the side of the equation that predominates at equilibrium**

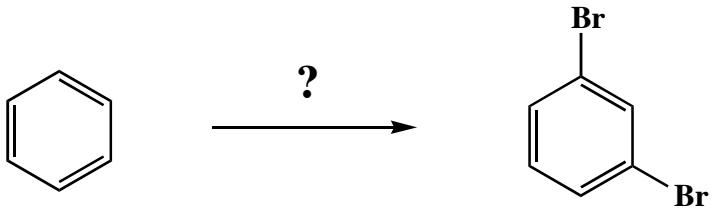


19. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

(7 pts)

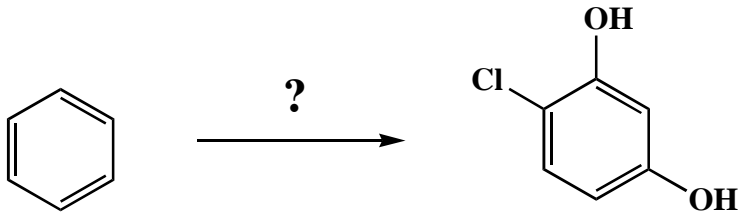


(13 pts)



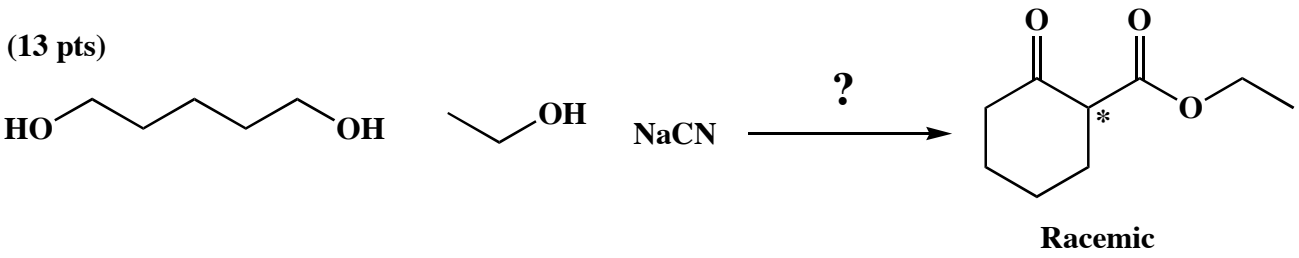
19. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule! **NOTE: For this one, you are not allowed to separate complex mixtures along the way and pull out just the isomers you want. In other words, the product isomers shown must be the only predominant isomers you make during your synthesis.**

(16 pts)



19. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

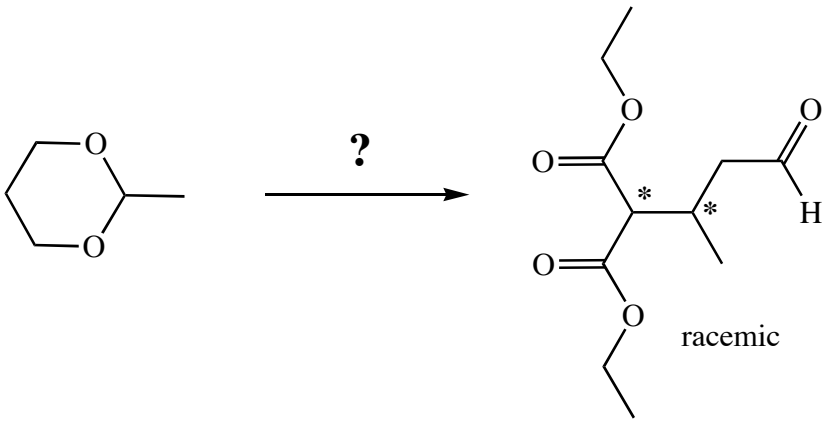
(13 pts)



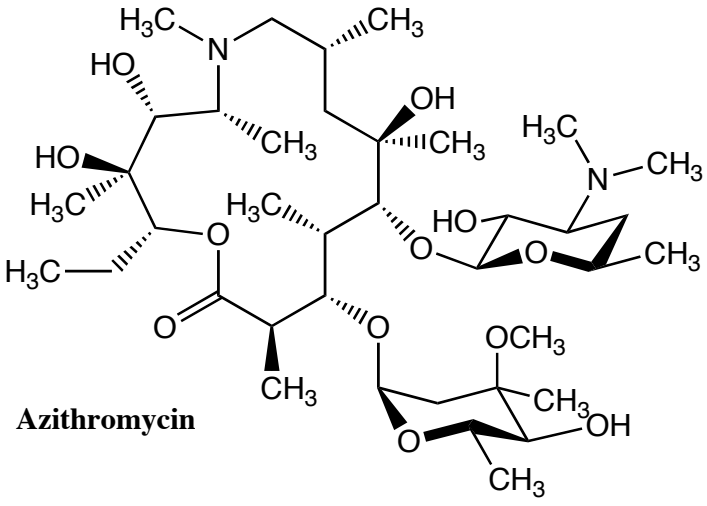
Racemic

19. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

(21 pts)



20. (12 pts.) Here is an apply what you know question. Below is the structure for the antibiotic azithromycin. Azithromycin prevents protein synthesis by binding to the 50S ribosome of bacteria and thus inhibiting translation of mRNA. This stops bacteria from growing. Although it has a complicated structure, you should be able to recognize the different functional groups of azithromycin. **If azithromycin is placed in aqueous acid, several bonds will be hydrolyzed. On the structure below, based on the chemistry you have learned this semester, circle the three bonds that will hydrolyze when azithromycin is placed in aqueous acid.**

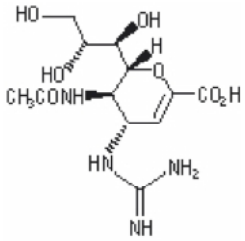


Azithromycin

21. (8 pts) Here is another apply what you know problem. The following is a portion of the official literature that accompanies the antiviral medication Relenza. Relenza is a neuraminidase inhibitor just like Tamiflu. The structure as drawn below is incorrect in some way.

11 DESCRIPTION

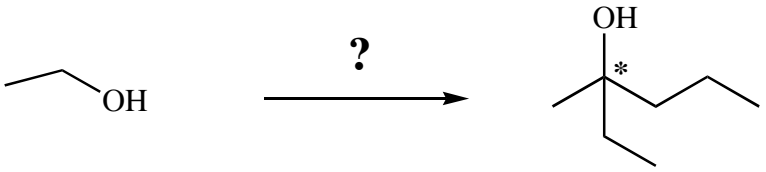
The active component of RELENZA is zanamivir. The chemical name of zanamivir is 5-(acetylamino)-4-[(aminoiminomethyl)-amino]-2,6-anhydro-3,4,5-trideoxy-D-glycero-D-galacto-non-2-enonic acid. It has a molecular formula of $C_{12}H_{20}N_4O_7$ and a molecular weight of 332.3. It has the following structural formula:



Based on what we discussed in CH310N this semester, in no more than two sentences, describe what can be viewed as inaccurate in the above molecular structure of Relenza.

22. We saved this until last. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

(25 pts)



racemic

Dear class,

The TA's and myself have very much enjoyed getting to know you this semester. You have done very well as a class on the first three exams, and we have every reason to believe you will also do well on this final. Job well done!! I was particularly pleased with the strong turnout at the 5K race. Remember, even for those of you who could not join us for the race, be sure to RUN EVERY CHANCE YOU GET. ***That is the best advice you will ever get as an adult.*** **Be safe, and never stop wondering where the electrons are.**

Brent Iverson

Page	Points	
1		(36)
2		(20)
3		(14)
4		(16)
5		(24)
6		(15)
7		(13)
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(HW score + Exam Grade) ⟹