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

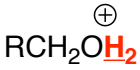
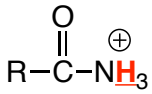
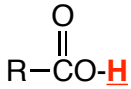
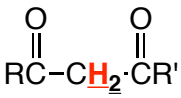
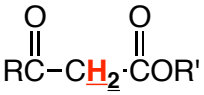
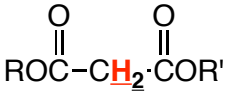
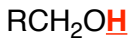
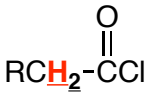
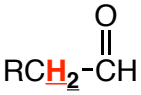
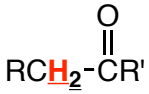
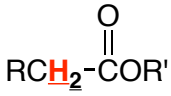
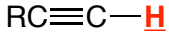
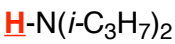
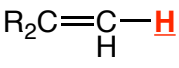
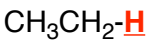
Note: You must have your answers written in pen if you want a regrade!!!!

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

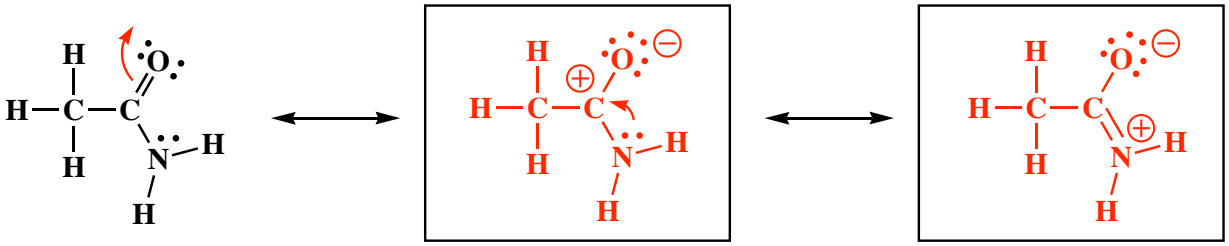
1. (4 points) What is the most important question in chemistry?

Where are the electrons?

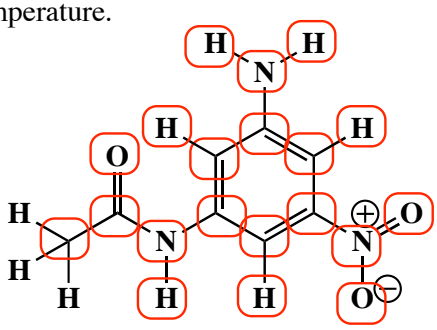
2. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minumum of 7 key points here.

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

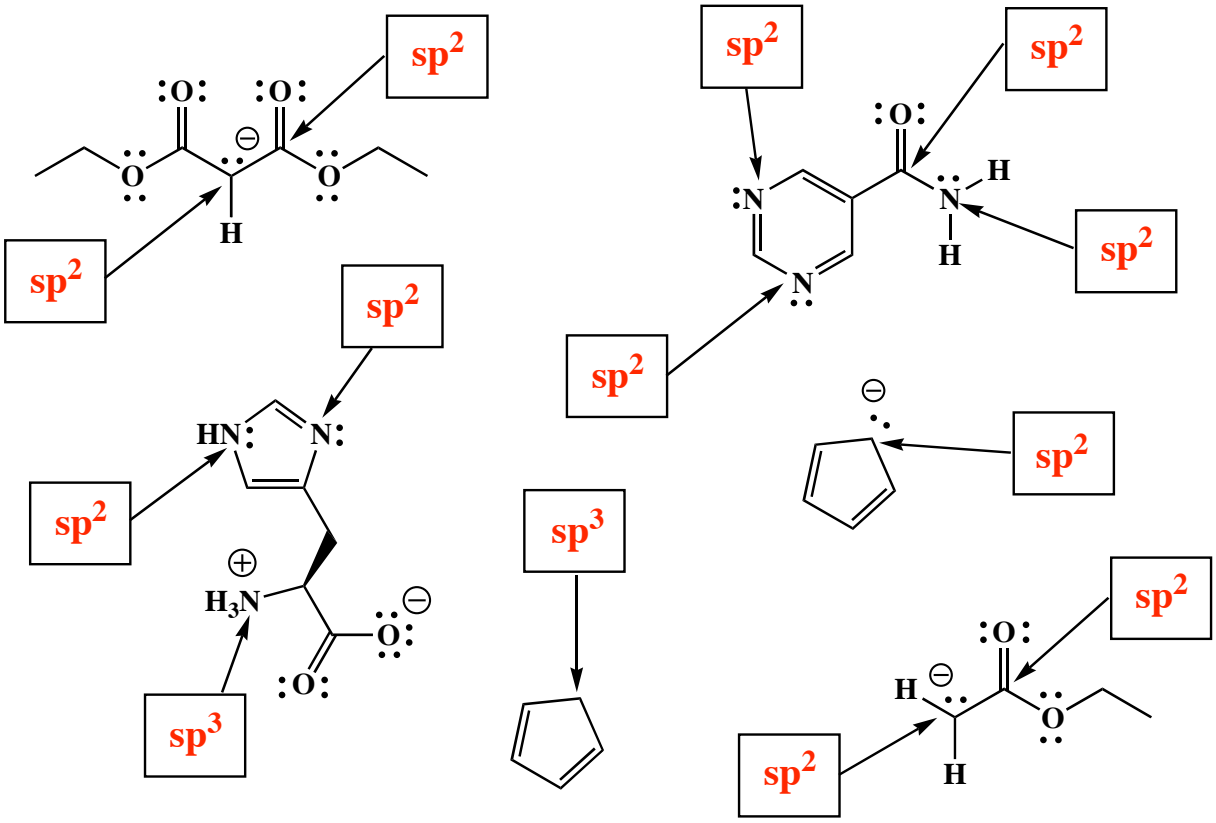
3. (8 pts) On the left is drawn the Lewis structure of a simple amide. Draw the two next most important contributing structures in the spaces provided. Be sure to show all lone pairs and formal charges. Place arrows on the two structures on the left to indicate how you are moving electrons to create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



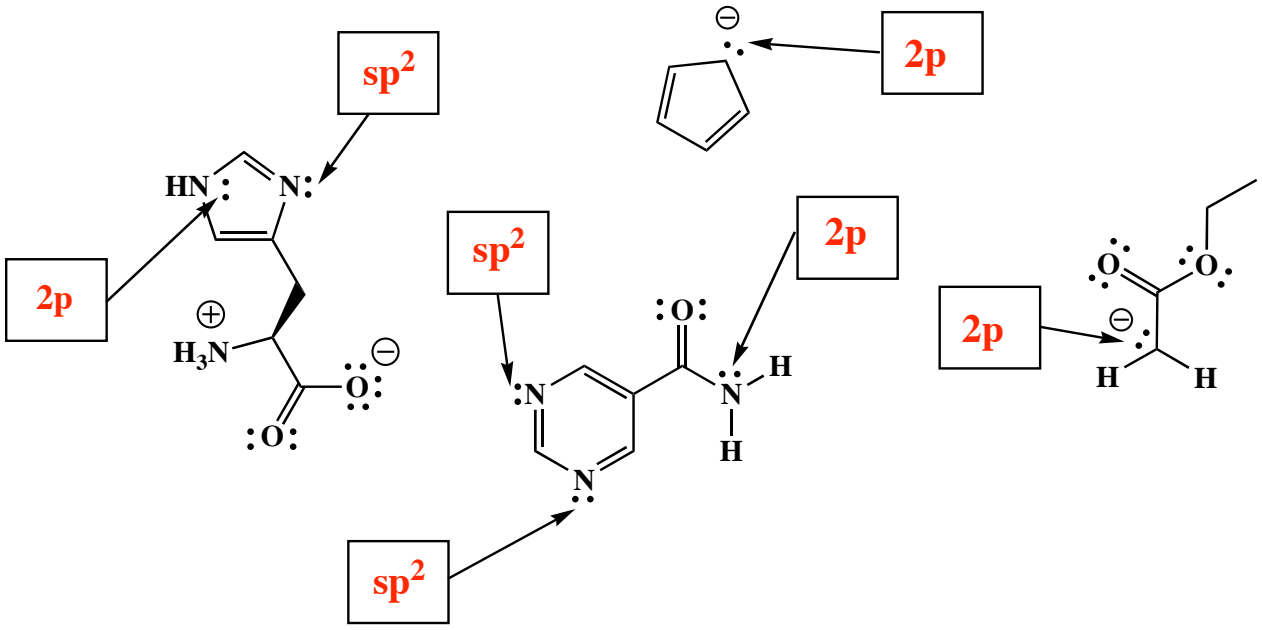
3. (10 pts) Because of pi delocalilzation,many of the atoms in the molecules below are predicted to be in the same plane. On the structures below, circle all the atoms that you believe will be located the same plane at equilibrium. Do not circle atoms that are in the same plane only temporarily as their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



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

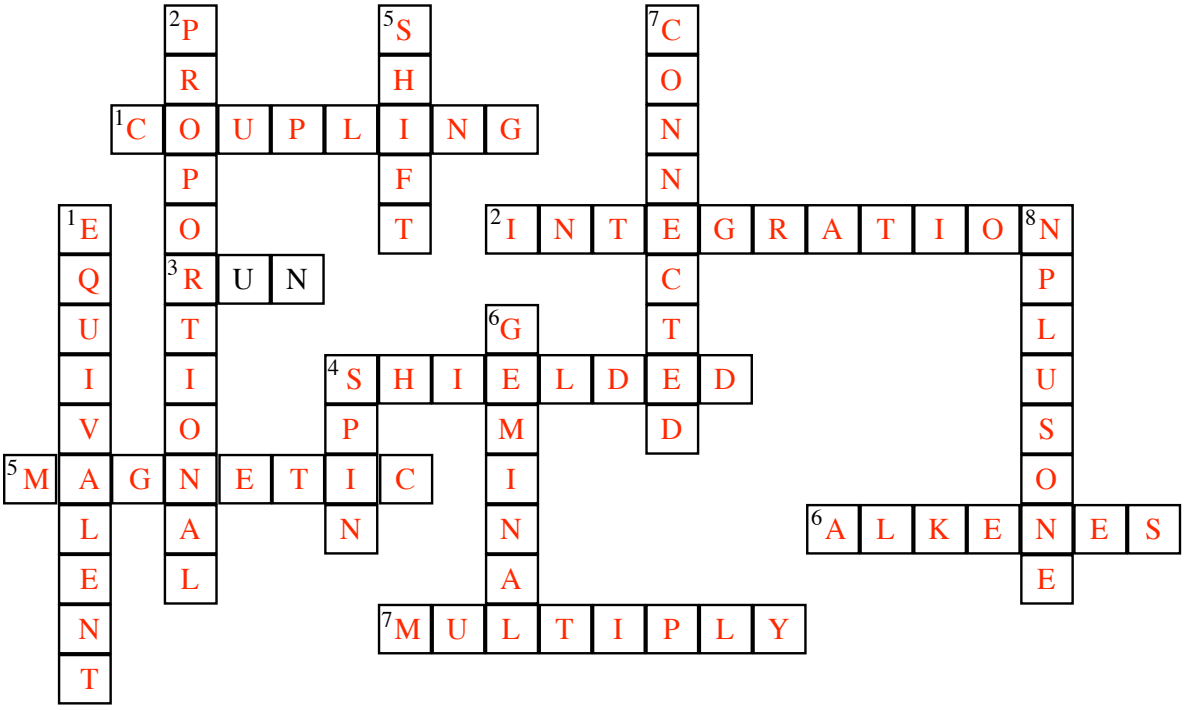


5. (7 pts) In the boxes provided, according to the valence bond approach, write the type of atomic orbital that contains the indicated lone pair of electrons..



Signature_____ Pg 3 _____(14)

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

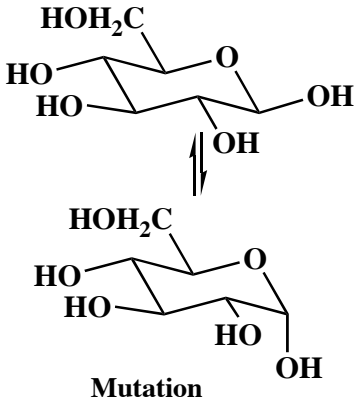
6. Non-equivalent H atoms on the same C atom can split each other (called _____ coupling), for example on alkenes or small rings.

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)

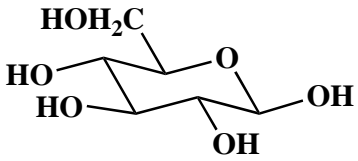
7. (2 pts each) I know you were wondering how we were going to test the carbohydrate material. Here is what we came up with. For the following structures, draw a circle around the terms that provide the most accurate description.

A.



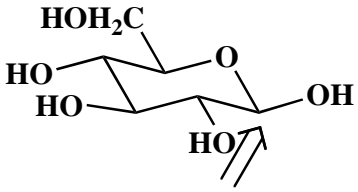
Mutation
Fermentation
Mutarotation
Mutacirculation

B.



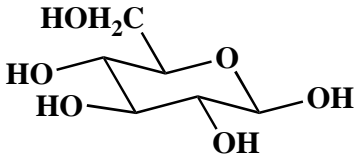
Furanose
Pyranose
Runny nose

C.



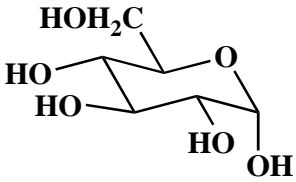
Monomeric carbon
Anomeric carbon
Polymeric carbon

D.



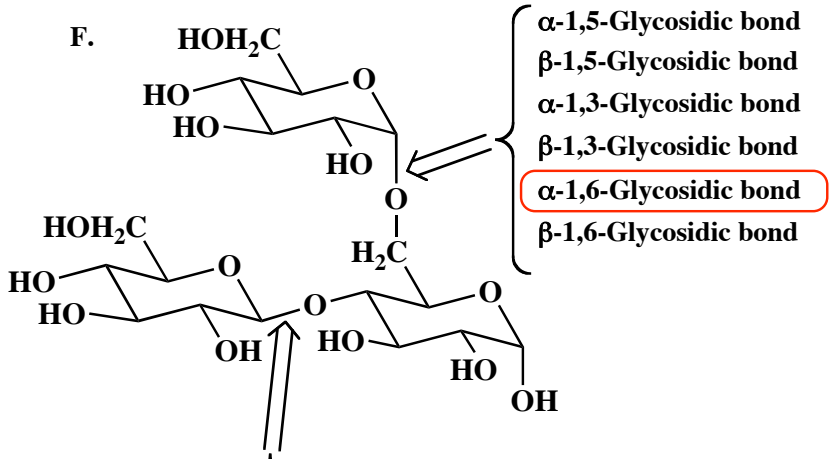
α-D-Glucose
β-D-Glucose
βββ-D-Glucose
ΣAE-D-Glucose

E.



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

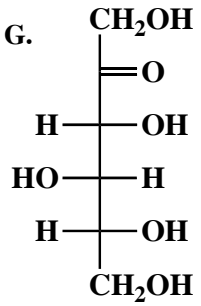
F.



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

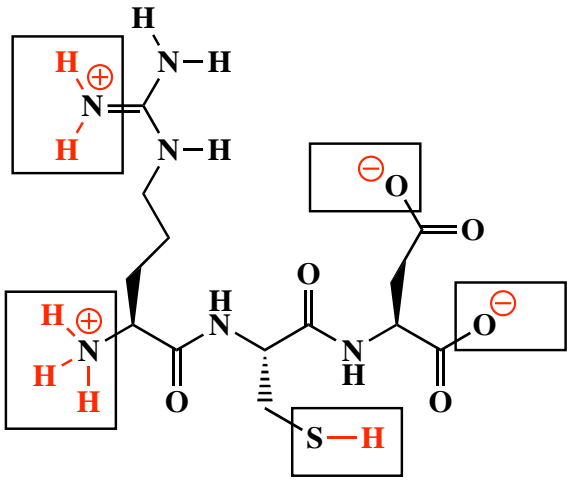
α-1,4-Glycosidic bond
β-1,4-Glycosidic bond
α-1,3-Glycosidic bond
β-1,3-Glycosidic bond
α-1,5-Glycosidic bond
β-1,5-Glycosidic bond

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.**

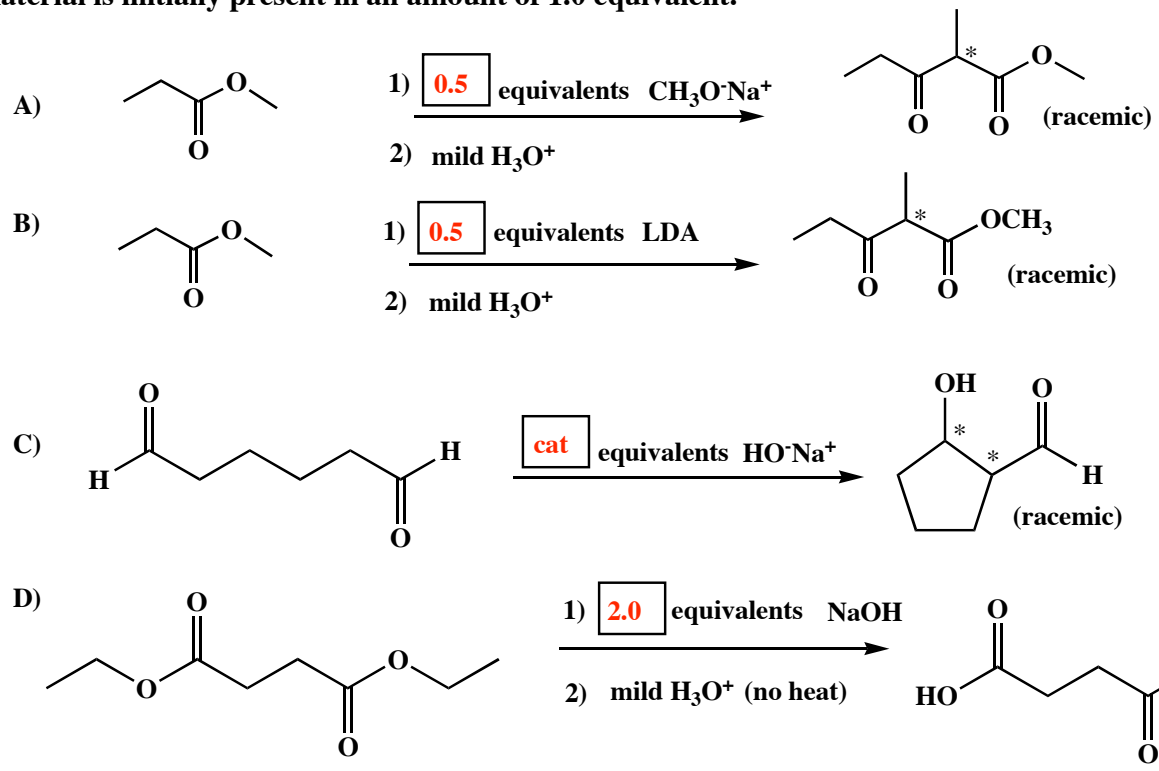


B) What is the total charge on this peptide at pH 6.0? **0**

C) What is the total charge on this peptide at pH 2.0? **+2**

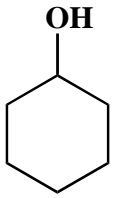
D) What is the total charge on this peptide at pH 11.2? **-2**

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.**

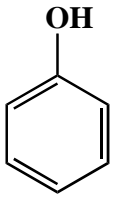


10. (3-4 pts each) For the following, rank the molecules according to the directions given.

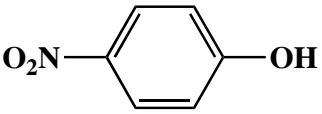
A. Rank from least to most acidic, with a **1** under the least acidic and a **4** under the most acidic molecule.



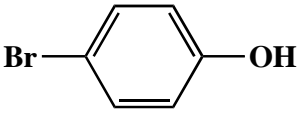
1



2

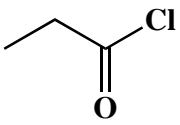


4

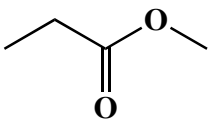


3

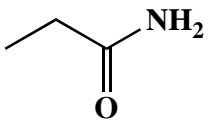
B. Rank from least to most reactive with nucleophiles, with a **1** under the least reactive and a **4** under the most reactive molecule.



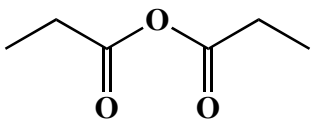
4



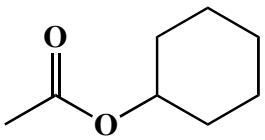
2



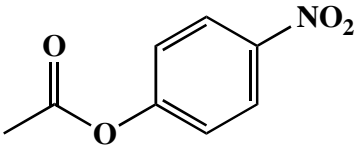
1



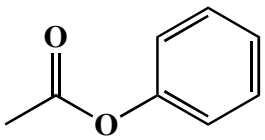
3



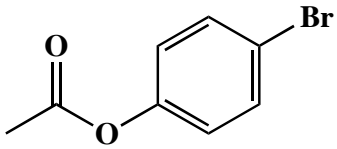
1



4

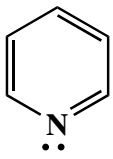


2

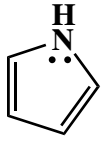


3

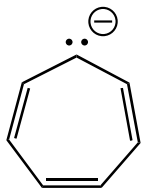
C. Rank from least to most basic, with a **1** under the least basic and a **3** under the most basic molecule.



2

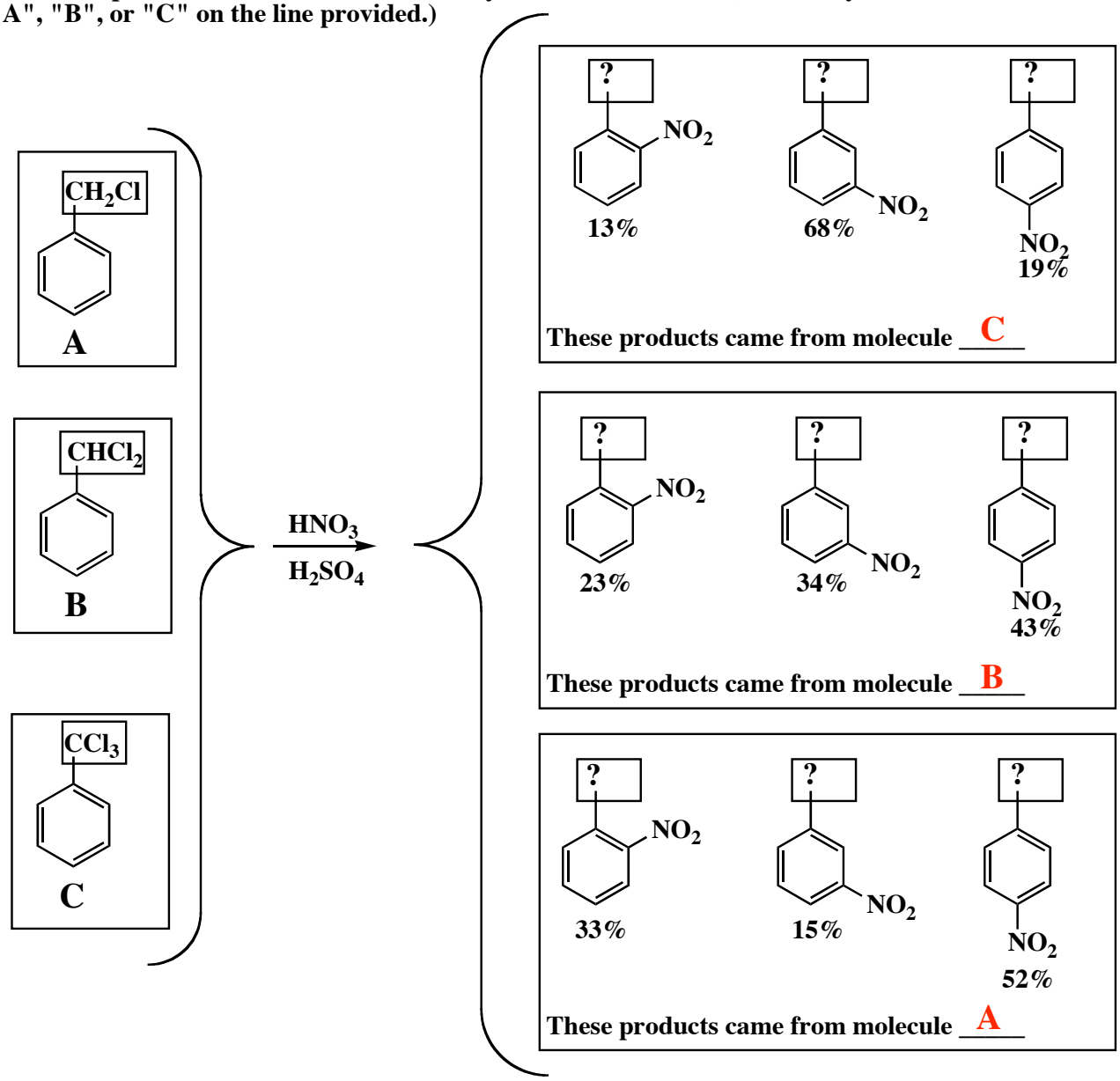


1



3

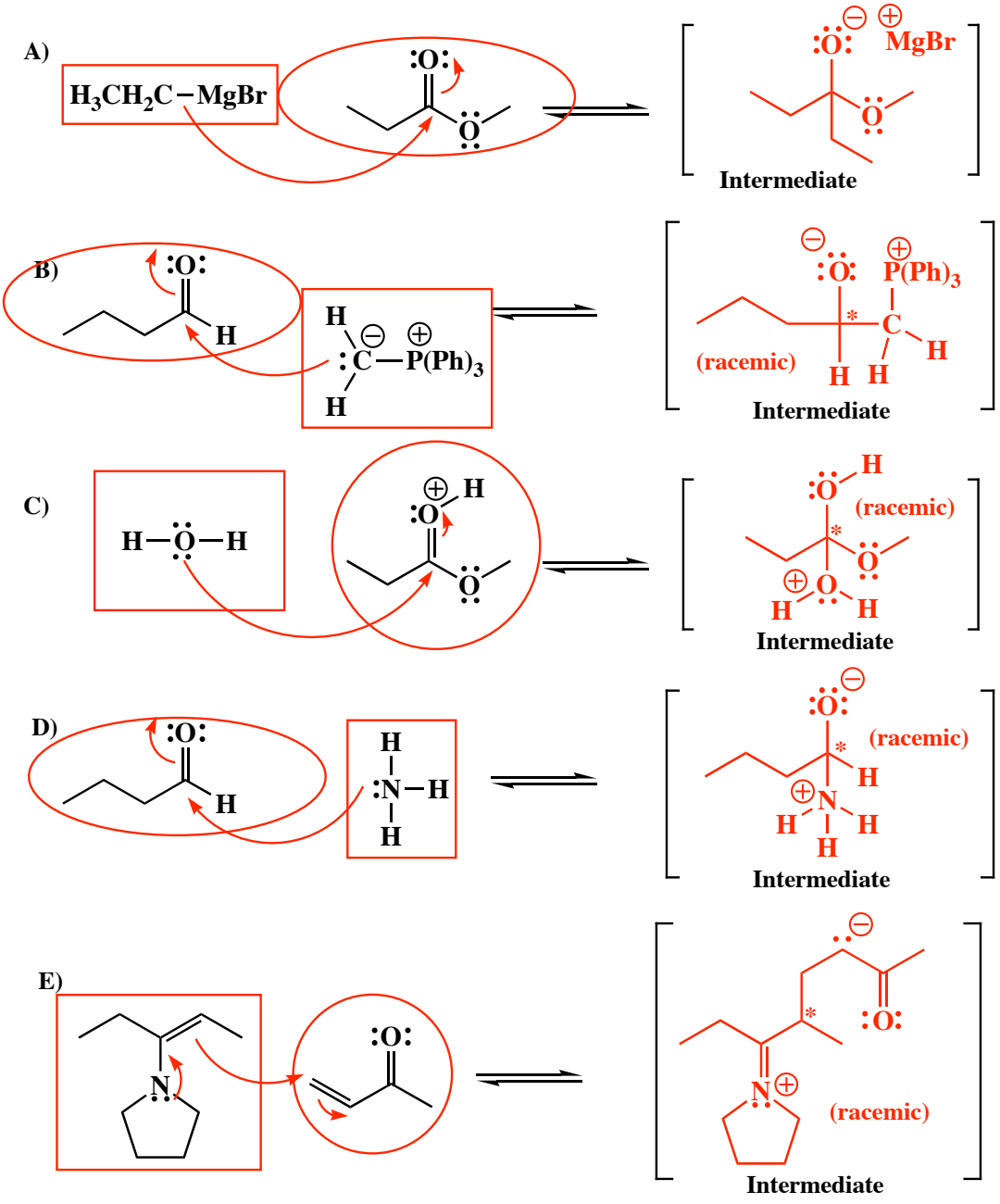
11. (13 pts) **Here is an apply what you know problem.** Below are listed three molecules, designated as **A**, **B**, or **C**. They differ in the number of chlorine atoms attached to the methyl group. We have three groups of products, and **under the structures we give you relative percentages of the 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):

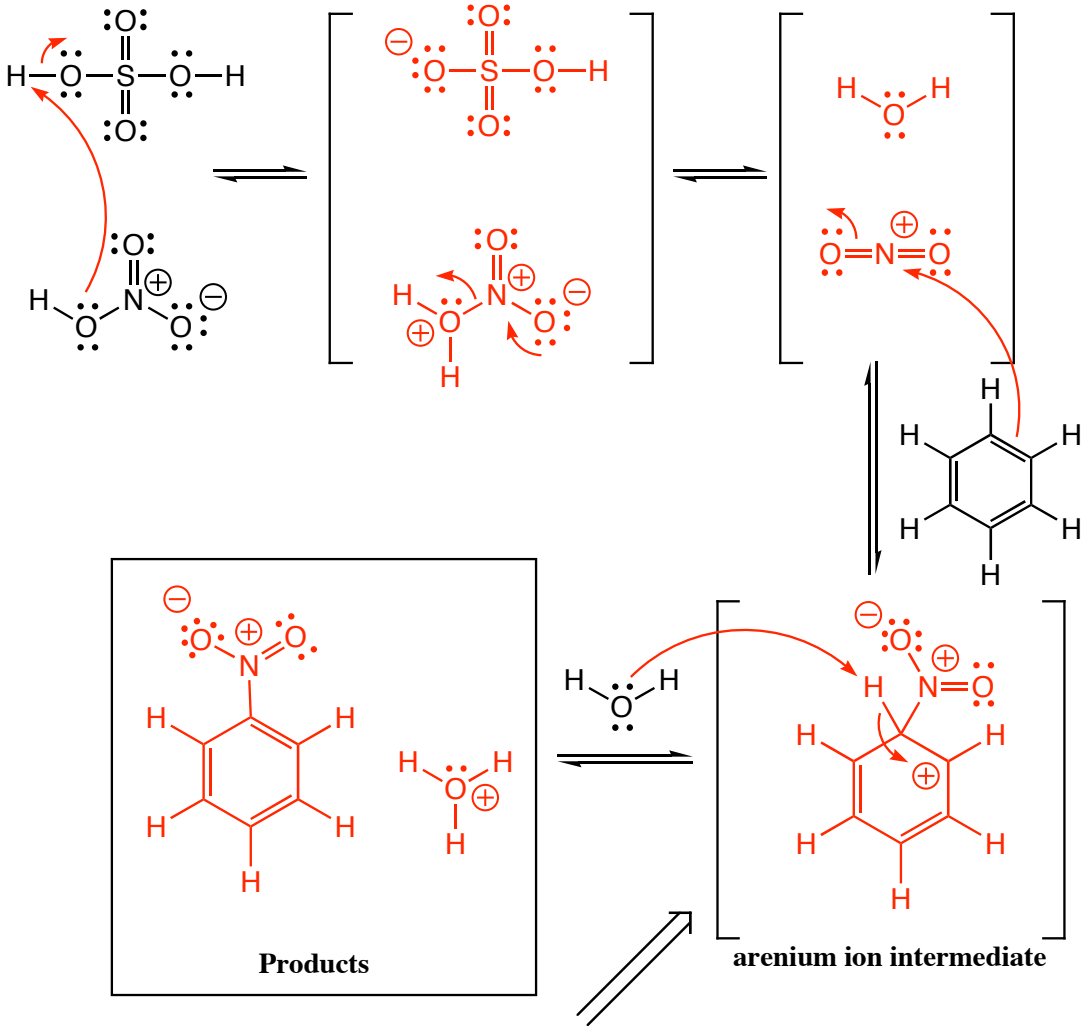
The chlorine atoms are electron withdrawing, so more chlorine atoms means the methyl group will be more electron withdrawing ("more bad"). Therefore, the highest percentage of meta product will come from the molecule, C, with the most chorine atoms because being the most electron withdrawing, it will be the most meta directing.

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.

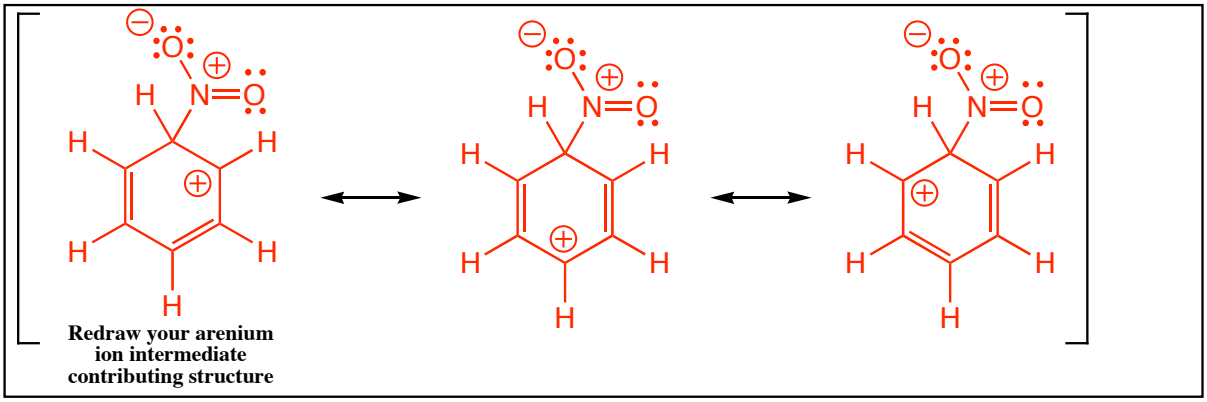


Did you remember to draw boxes and circles?

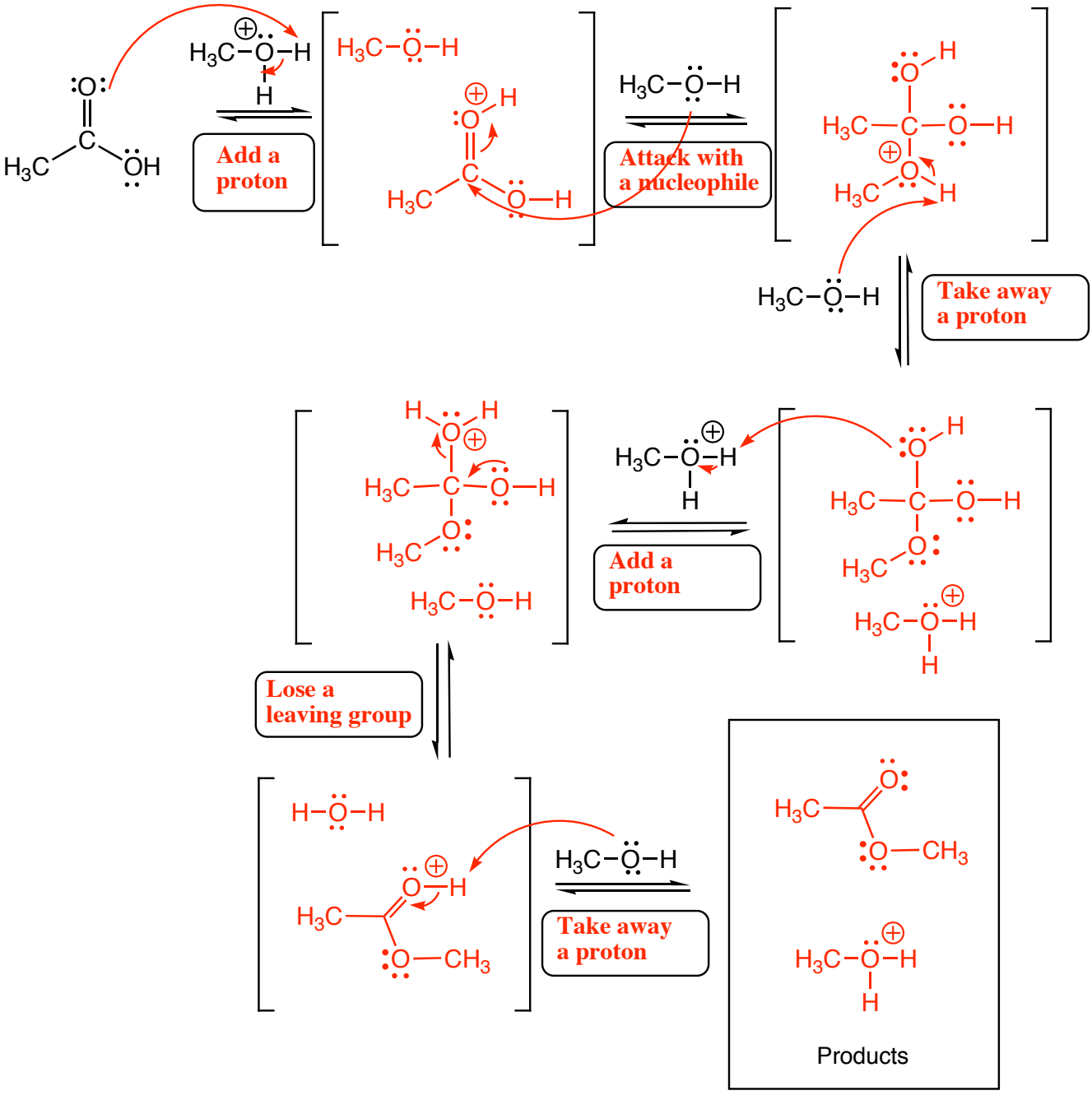
13. (27 points) Complete the mechanism below for electrophilic aromatic substitution. Use arrows to show the movement of all electrons, and be sure to draw all lone pairs of electrons and all formal charges. You do not have to worry about labeling chiral centers on this one, **but you do have to draw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



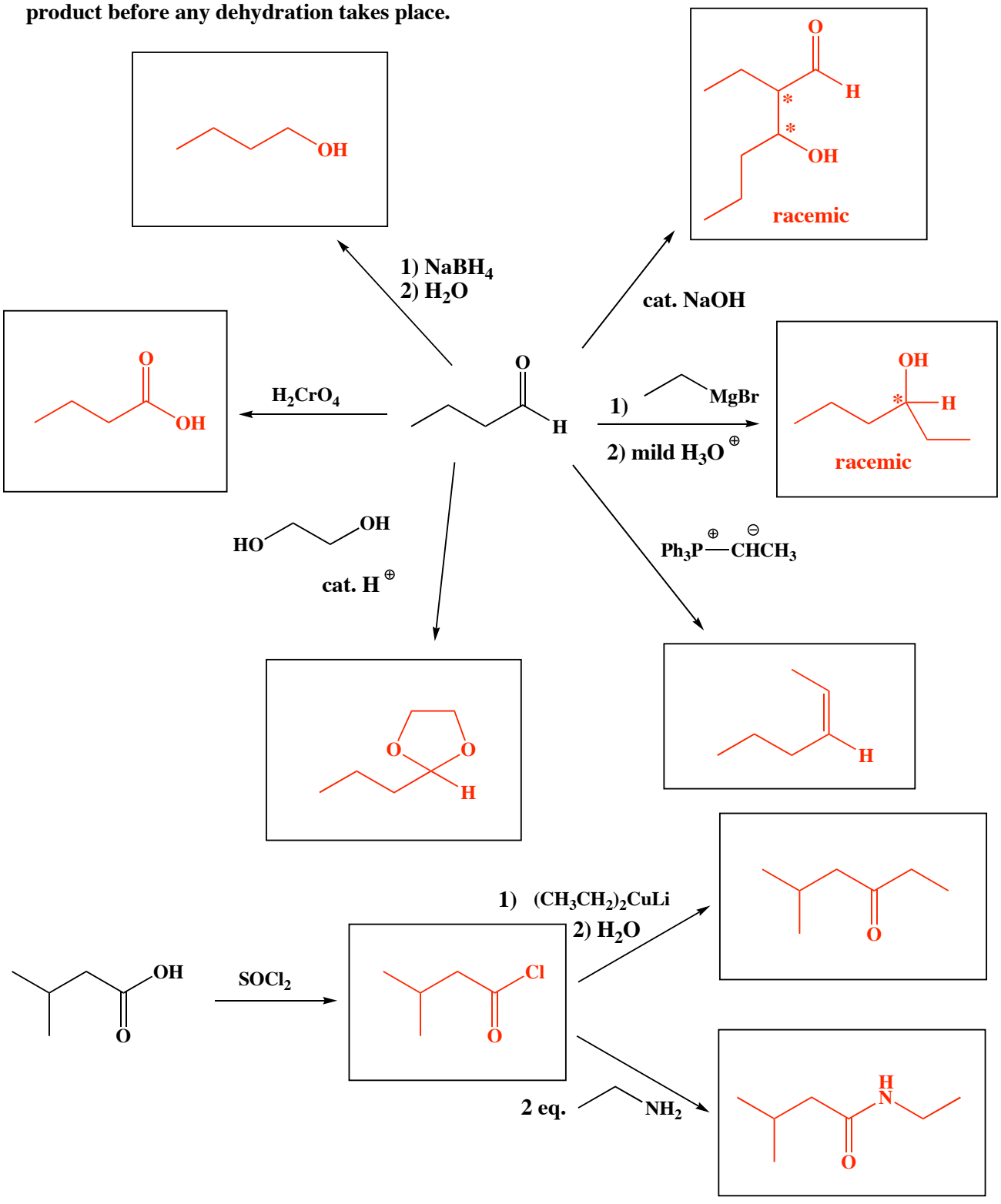
(6 pts) In the above mechanism, we only gave you enough space to draw one contributing structure of the arenium ion intermediate. In the box below, redraw the arenium ion intermediate contributing structure you drew in the mechanism, then draw two other important contributing structures.



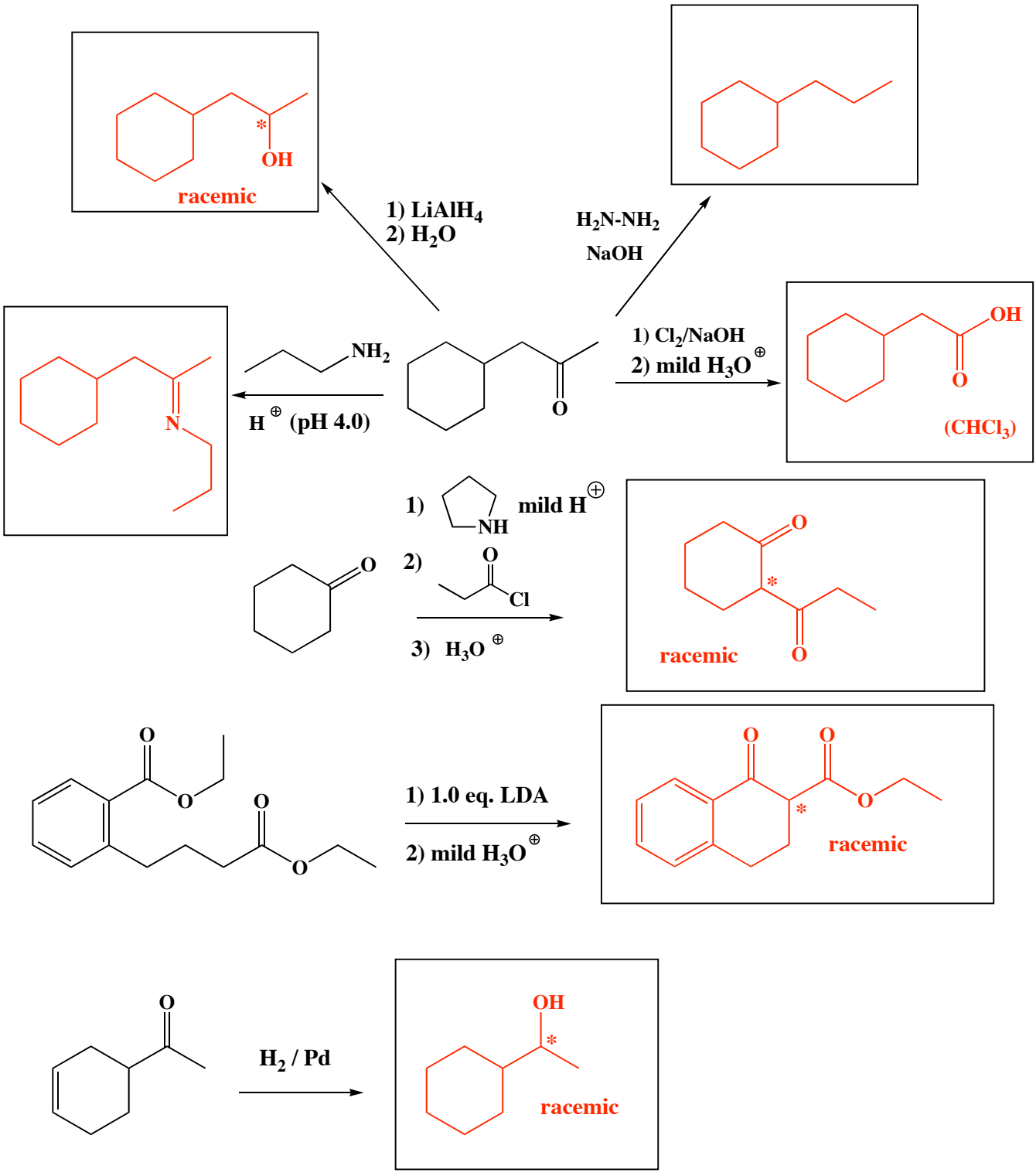
13. (35 points) Complete the mechanism below for Fisher esterification. Use arrows to show the movement of all electrons, and be sure to draw all lone pairs of electrons and all formal charges. You do not have to worry about labeling chiral centers on this one. ***Remember, you must show all products 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.**



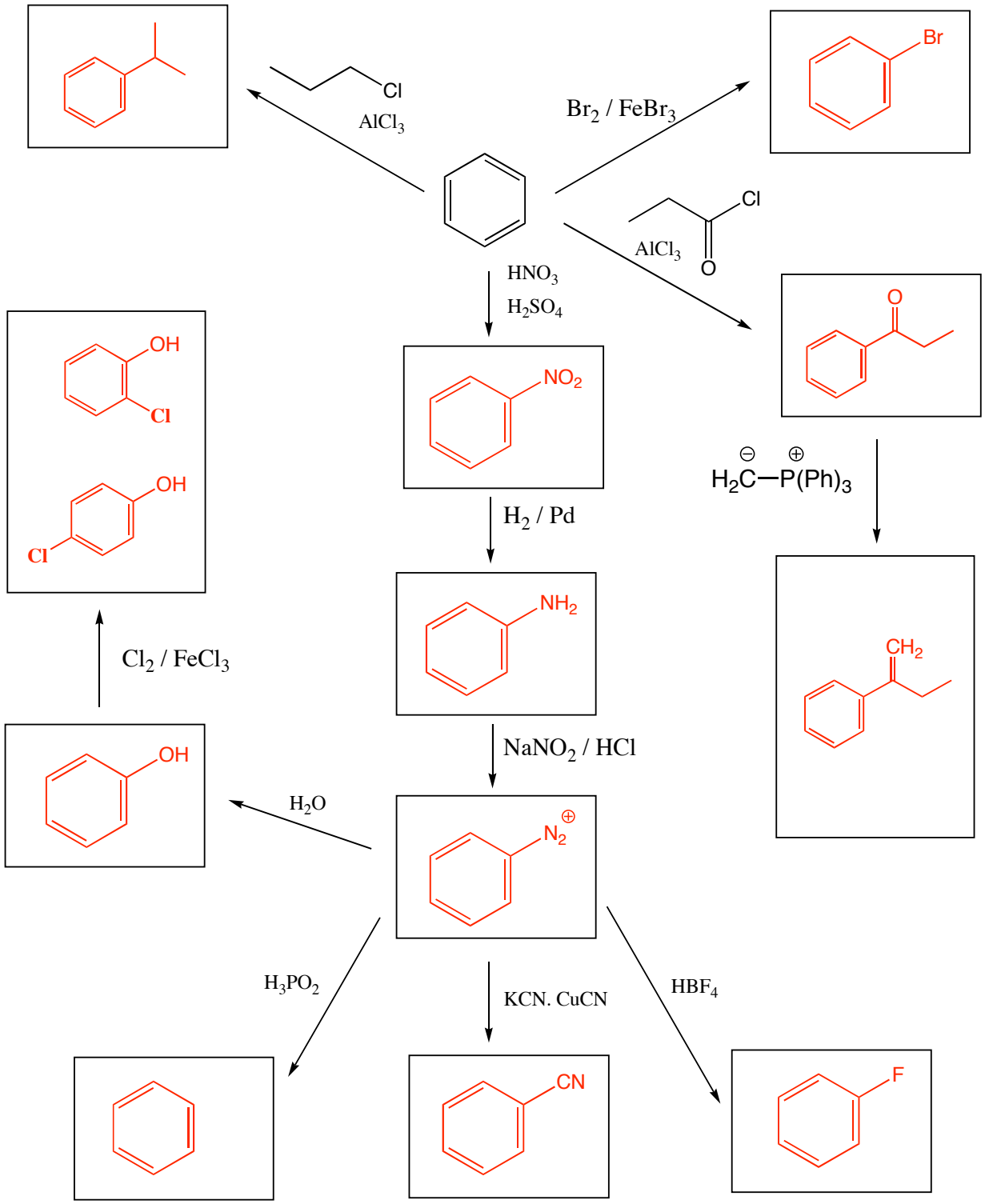
14. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, mark the chiral center with an asterisk "*" and write "racemic" under the structure. If there is an aldol reaction, draw the product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



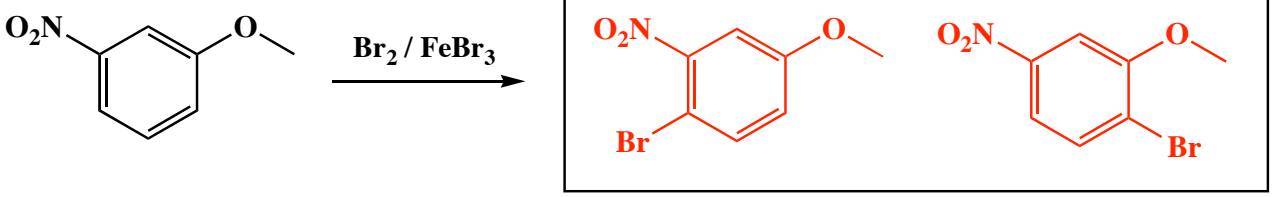
15. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, mark the chiral center with an asterisk "*" and write "racemic" under the structure. If there is an aldol reaction, draw the product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

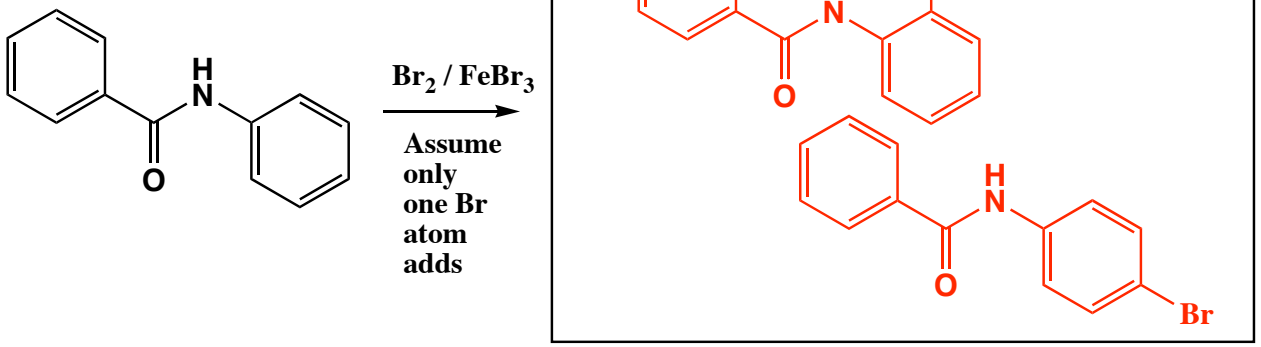


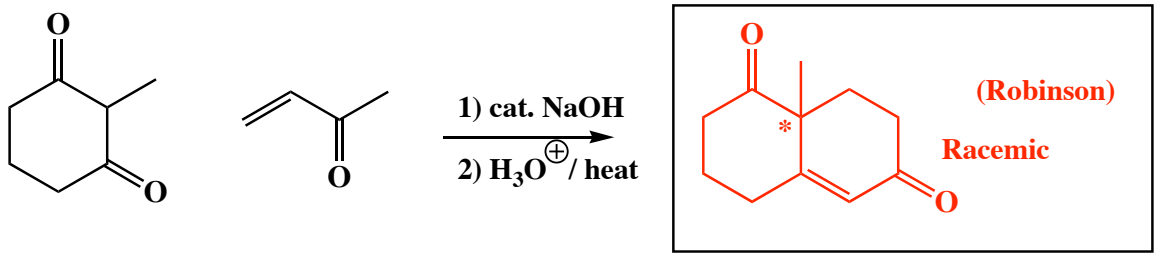
16. (2 or 4 pts.) Write the predominant product or products that will occur for each transformation. Assume each reagent only adds once to the ring. If predominantly ortho/para products are predicted, you must draw both.



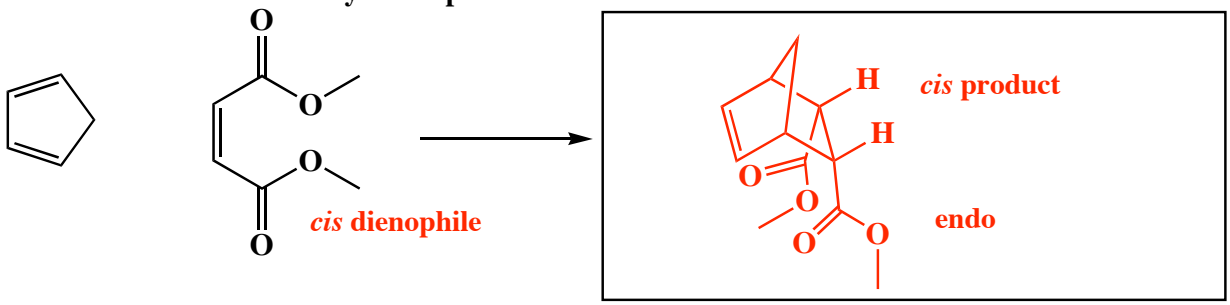
17. (21 pts.) You might find these are harder so take your time. Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, mark the chiral center with an asterisk "*" and write "racemic" under the structure. If ortho/para products are made, you must draw both. Note, for this problem, aldols can dehydrate if heated in dilute acid.**

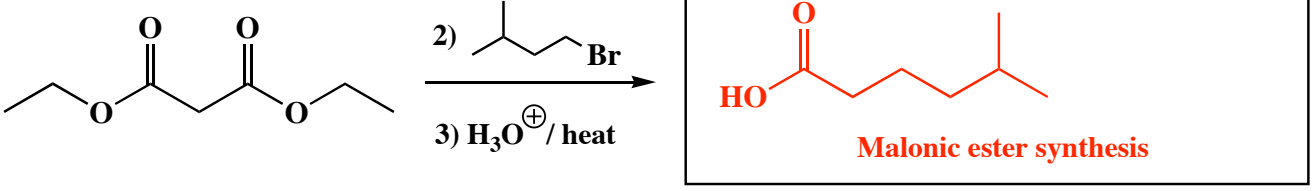




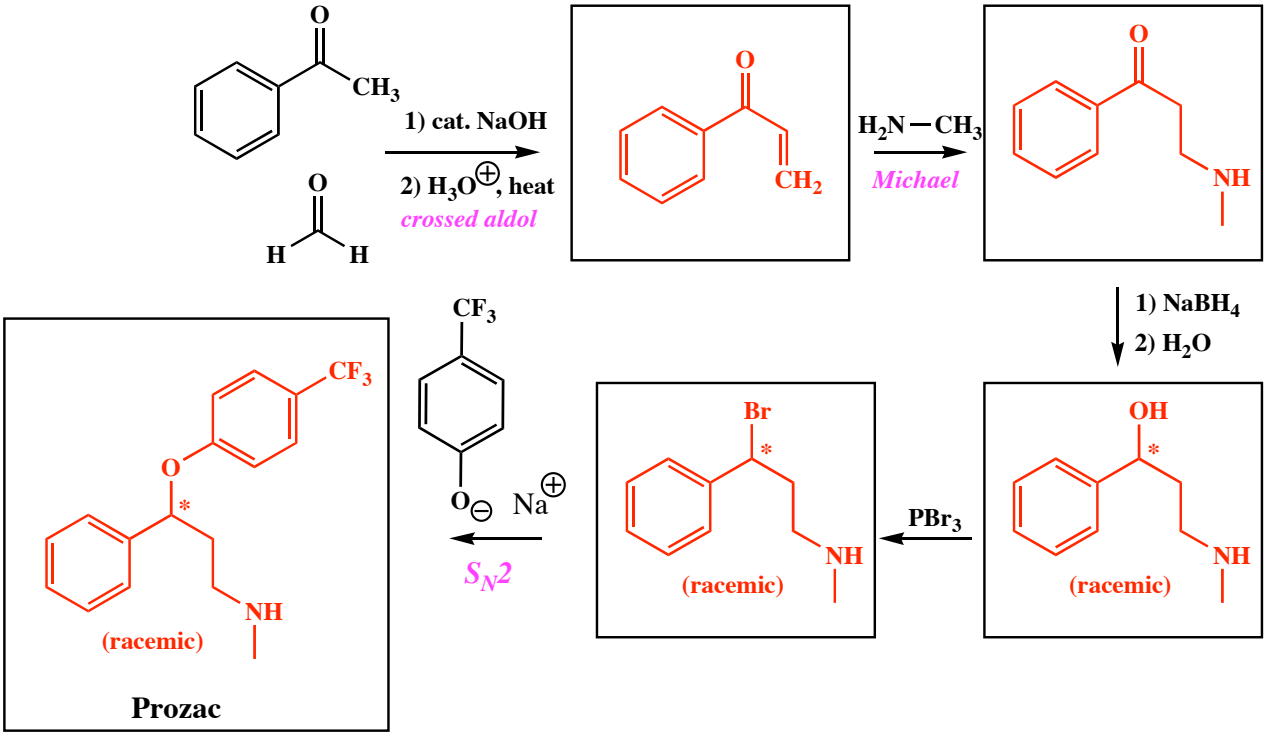


Be sure to indicate stereochemistry of the products on this next one.

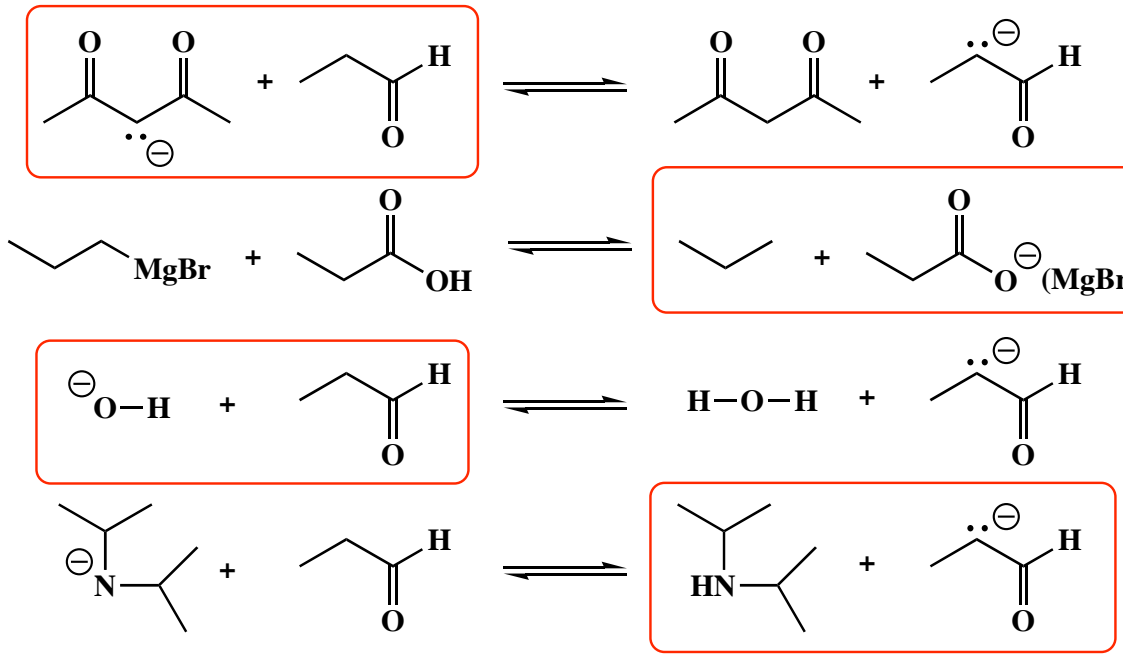




17. (21 pts.) Here is the synthesis of the important pharmaceutical Prozac. You are familiar with all of the chemistry, it just might take you a while to recognize the reactions. **Fill in the boxes with the appropriate structures, and remember to use an asterisk "*" and write "racemic" to indicate any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

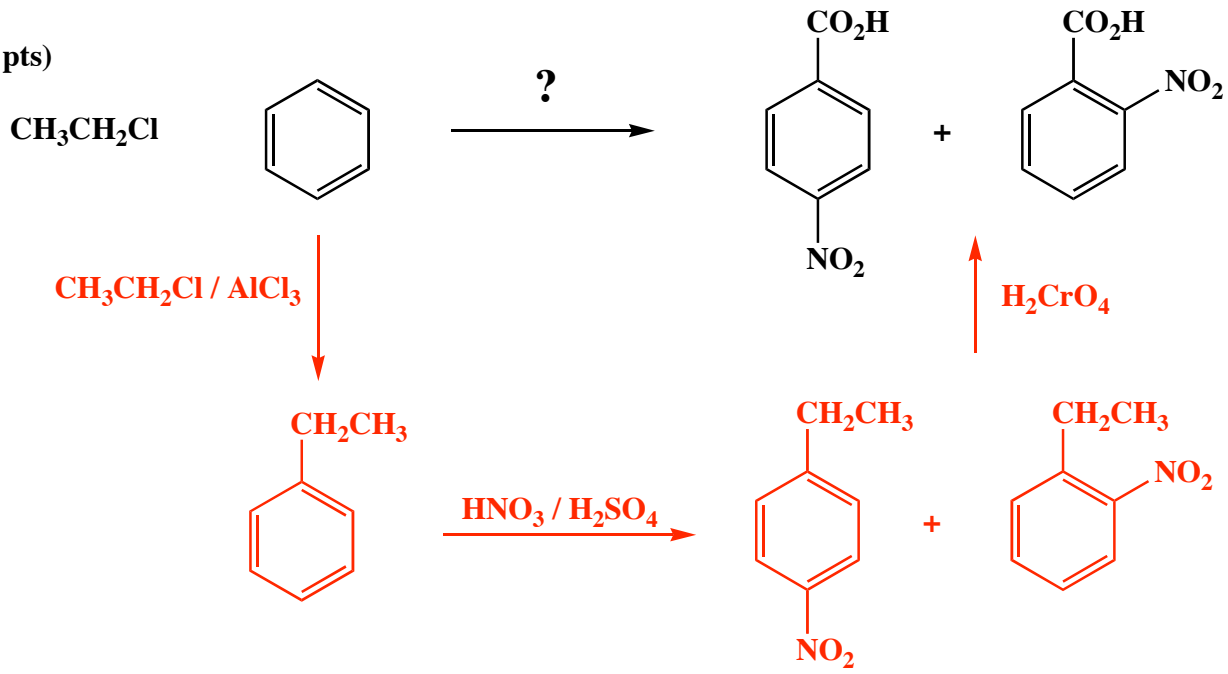


18. (8 pts) **For the following reactions, circle the side of the equation that predominates at equilibrium**

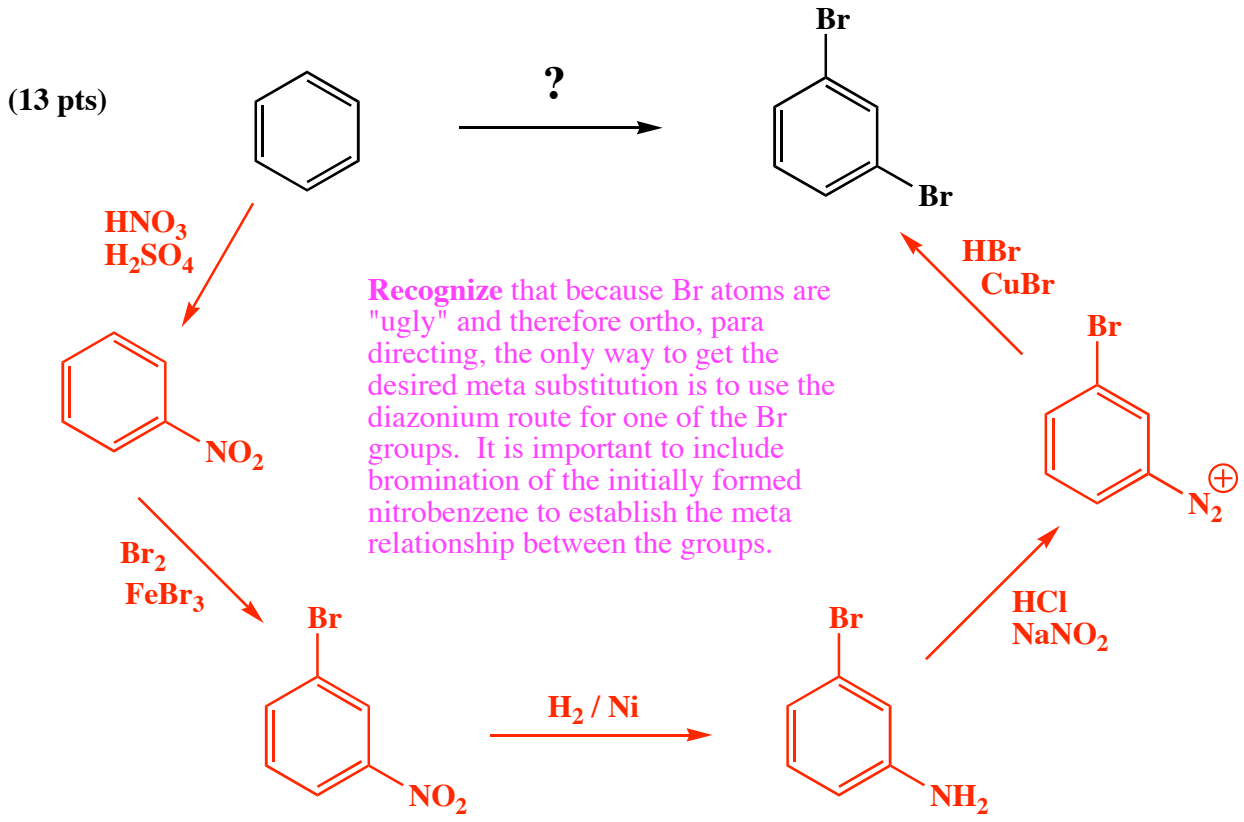


19. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

(7 pts)



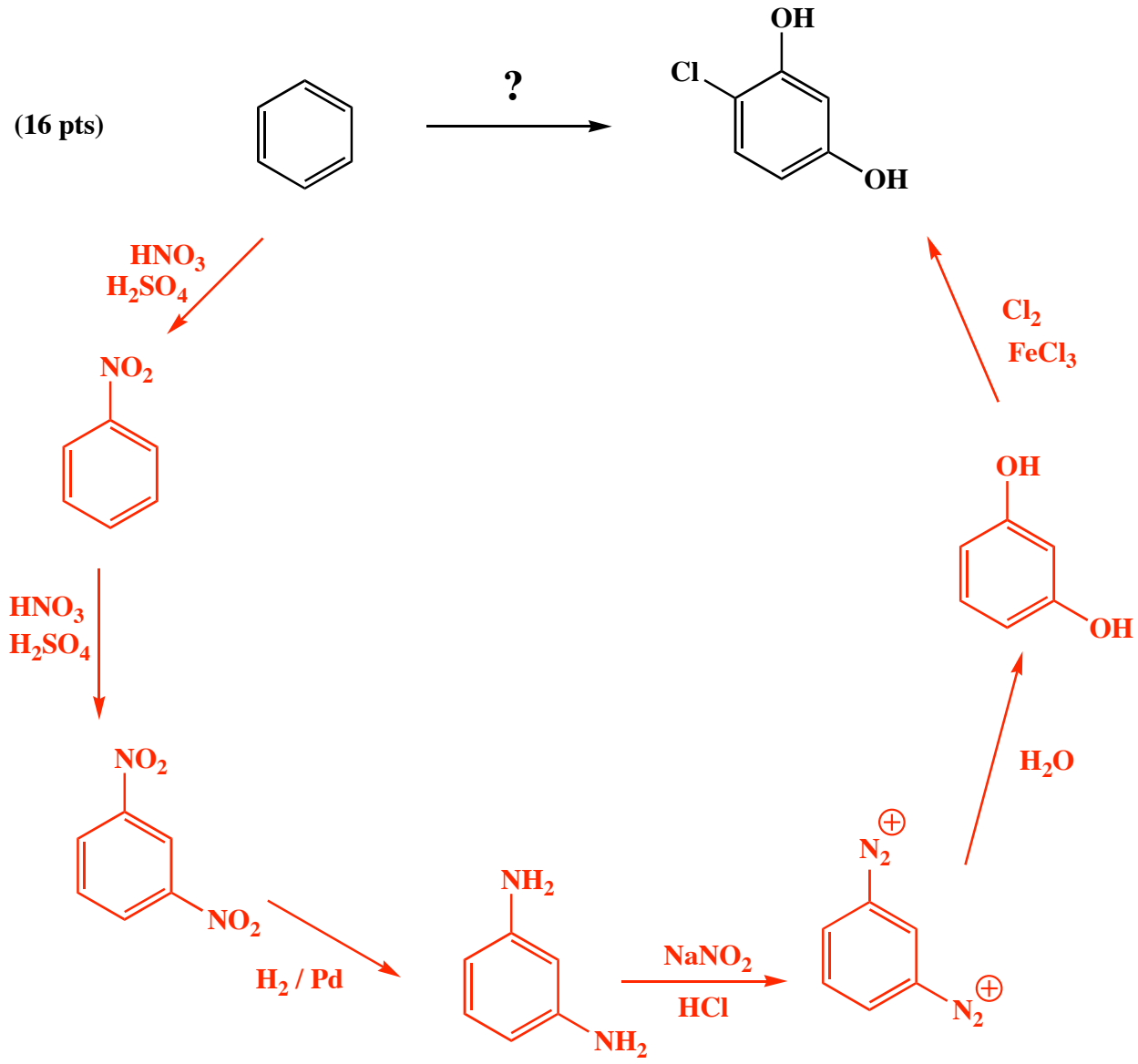
(13 pts)



Recognize that because Br atoms are "ugly" and therefore ortho, para directing, the only way to get the desired meta substitution is to use the diazonium route for one of the Br groups. It is important to include bromination of the initially formed nitrobenzene to establish the meta relationship between the groups.

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.**

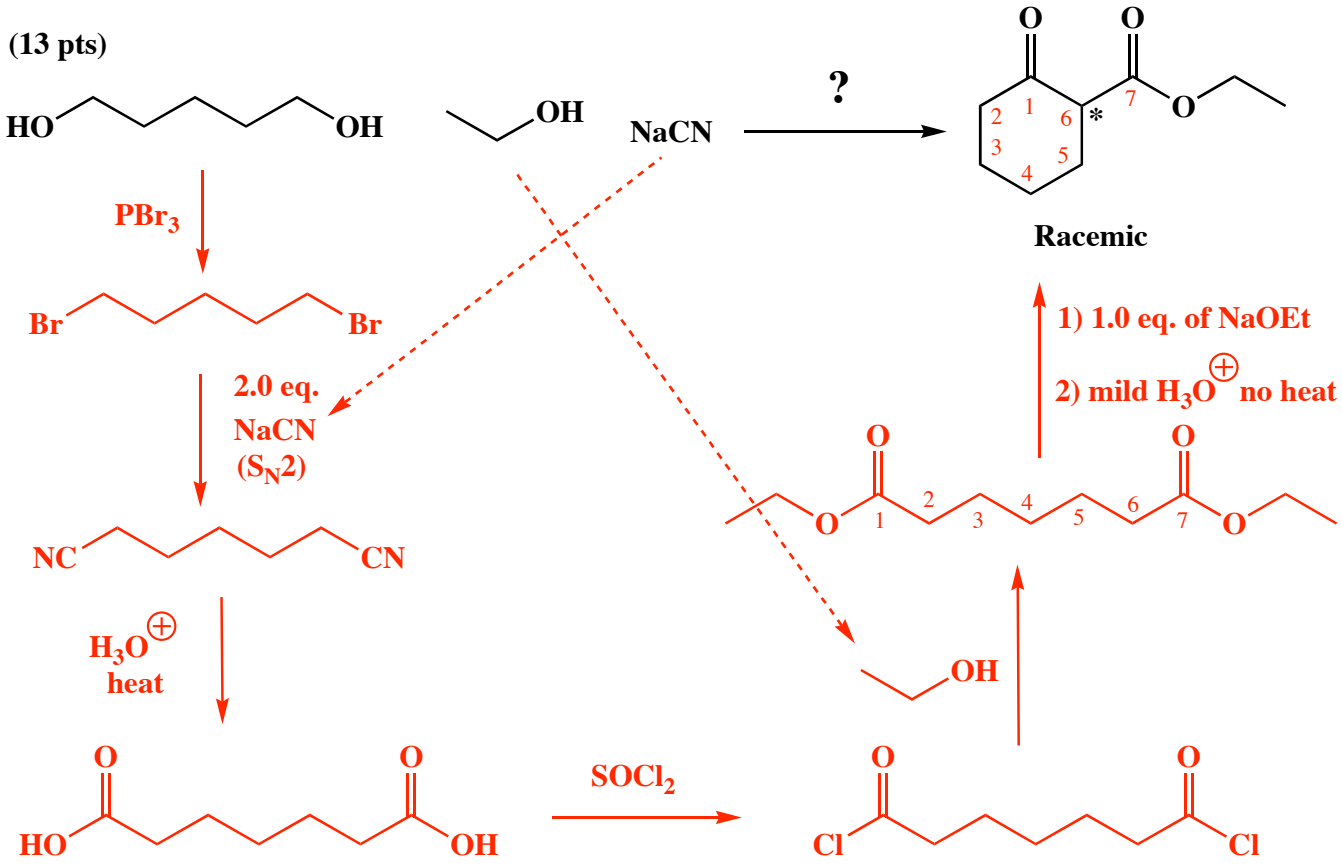
(16 pts)



Recognize that the OH groups must be derived from reaction of water with the corresponding double diazonium ion. **Recognize** further that the meta diol will direct an incoming Cl atom to the desired position, meaning there is only one isomer produced as stipulated in the directions. The meta isomer of the double diazonium species can be derived from the corresponding diamine after two sequential nitration reactions (which will give only the meta isomer) of the starting benzene.

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.**

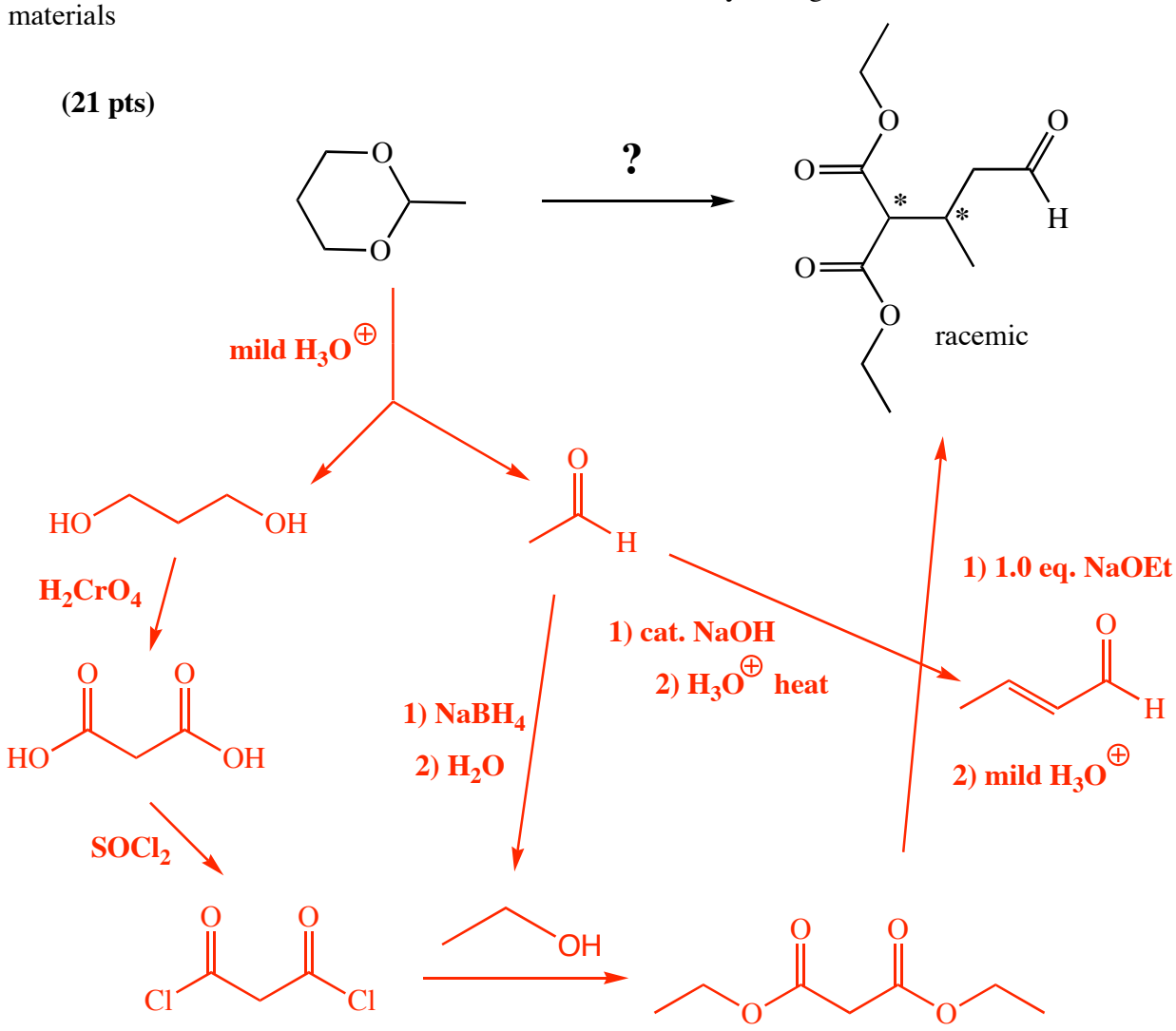
(13 pts)



Recognize the product as the KRE for the Dieckmann reaction of the diethyl ester of the seven carbon diacid (called pimelic acid). Diethyl pimelate can be created from the diacid chloride produced from reaction of thionyl chloride with pimelic acid. **Recognize** that pimelic acid can be derived from adding two carbon atoms to the 5 carbon diol starting material. **Recognize** further that a convenient way of adding carbons at either end to give the required diacid is by converting the diol to the dibromide, followed by a double S_N2 reaction to give the dinitrile, which, in turn, is hydrolyzed to give pimelic acid.

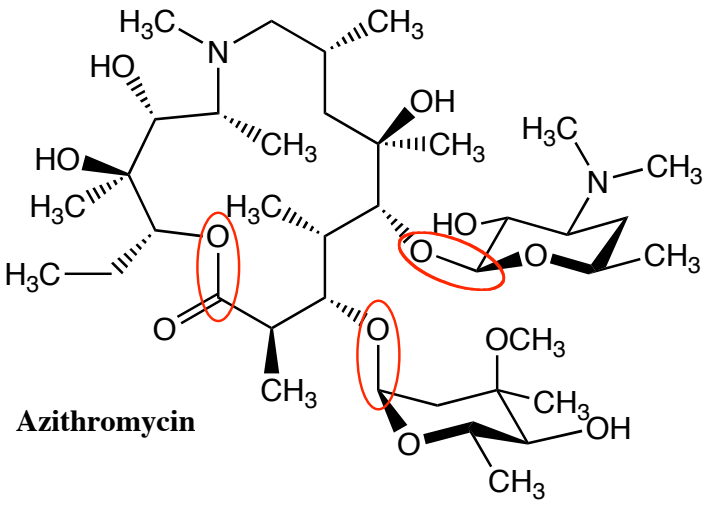
19. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule! Note, for these last two, you might not need to use all three starting materials

(21 pts)



Recognize that the product is the KRE for a Michael reaction between an α,β-unsaturated aldehyde and diethyl malonate. **Recognize** further that the required α,β-unsaturated aldehyde is the KRE for the aldol reaction of acetaldehyde. The difficult part of this question is **recognition** of the starting material as the cyclic acetal of acetaldehyde and 1,3-propanediol, both of which can be obtained up acidic hydrolysis. **Recognize** that diethyl malonated can be derived from oxidation of 1,3-propanediol with chromic acid to give malonic acid, followed by conversion to the acid chloride and treatment with ethanol. The ethanol could be made conveniently by reducing the acetaldehyde.

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 prevents 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.**

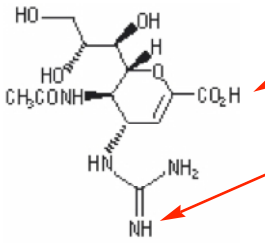


Azithromycin

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:



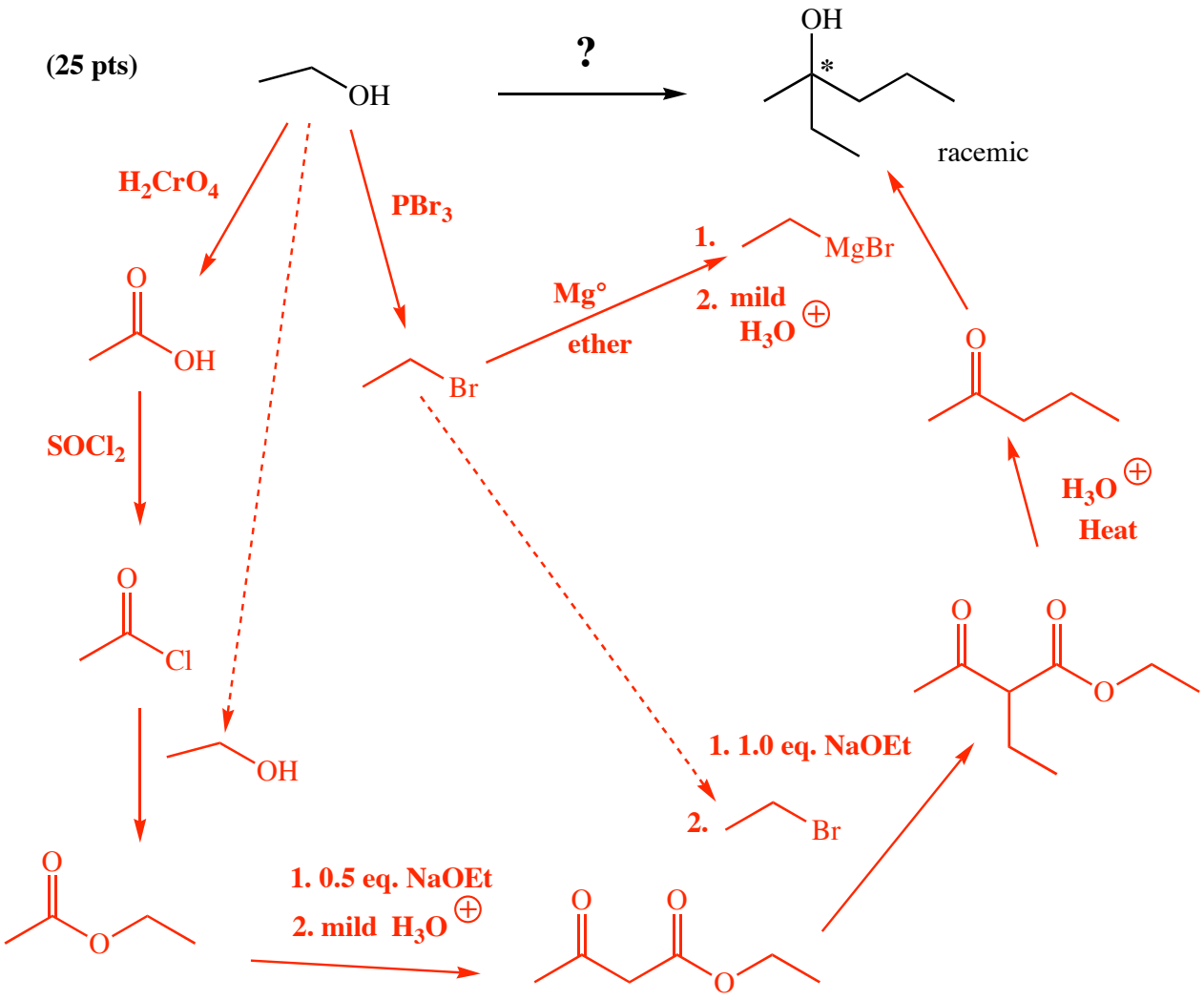
This is deprotonated above pH~3

This is protonated below pH ~12

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 structureof Relenza.

The guinidine group is extremely basic and the carboxylic acid group is very acidic, so **there is no pH range or any other condition in which the carboxylic acid group would be protonated, but not the guanidine group as is indicated in the structure.**

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!



Recognize the product is a tertiary alcohol, the KRE for a Grignard reaction. Although three are a couple of possible combinations of ketones and Grignard reagent possible for this step, the one that makes the most sense in using ethyl Grignard as shown. **Recognize** that this route requires using a methyl ketone, which is the KRE for the acetoester synthesis. **Recognize** that the required acetoester is the KRE of a Claisen reaction using ethylacetate. Ethylaceteate, in turn, can be synthesized from ethanol using the sequence of oxidation to acetic acid, conversion to an acid chloride withl. $SOCl_2$,then reaction with more ethanol.

Page	Points	
1		(36)
2		(20)
3		(14)
4		(16)
5		(24)
6		(15)
7		(13)
8		(32)
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