NAME (Print): _____

EID _____

SIGNATURE: _____

Chemistry 320N
Final Exam
May 1, 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 during your organic chemistry journey. 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!

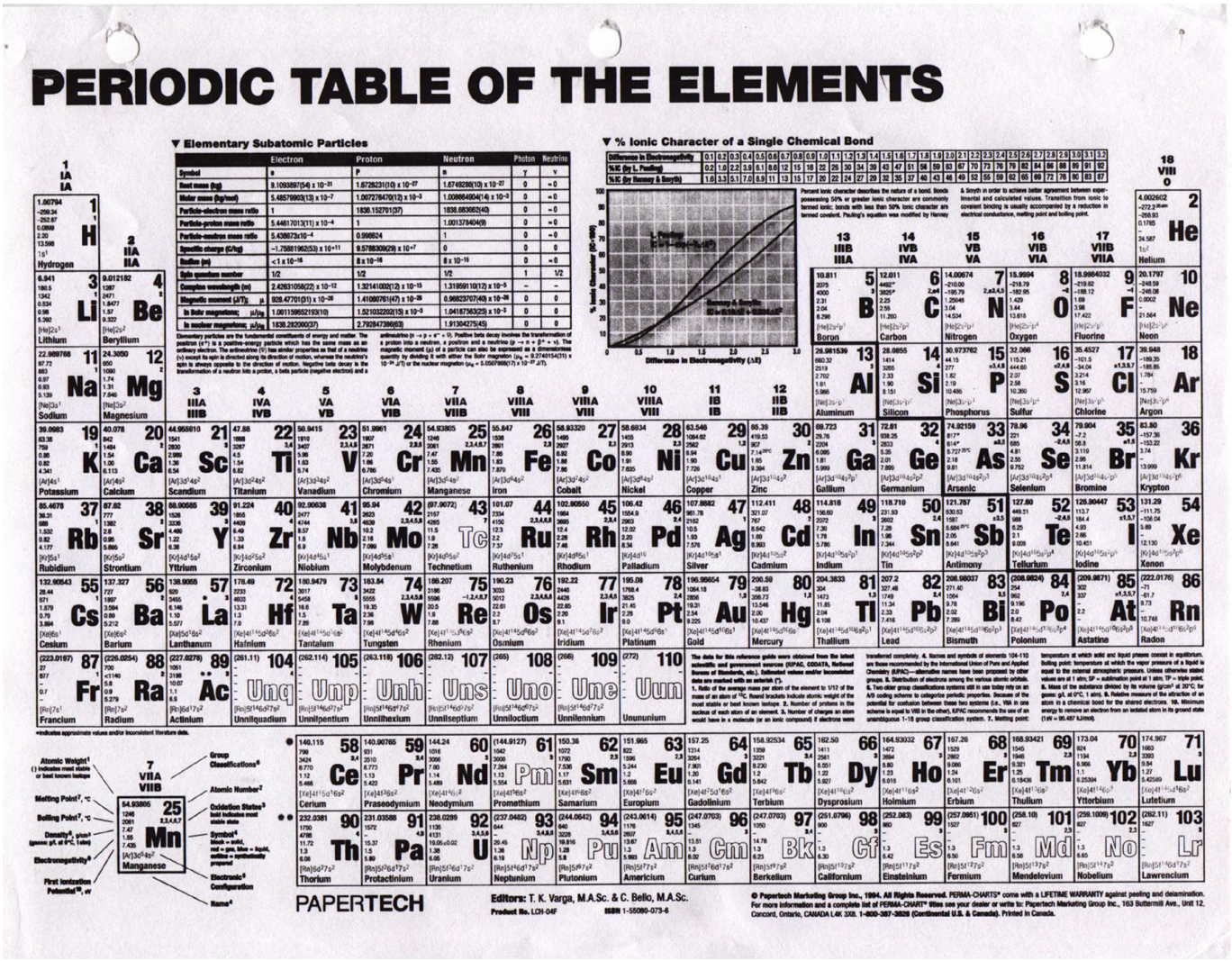
FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

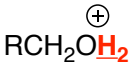
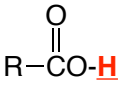
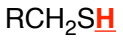
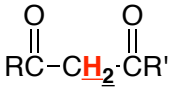
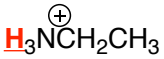
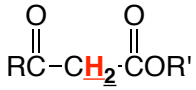
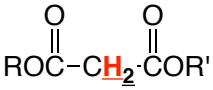
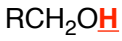
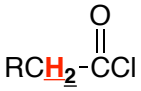
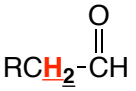
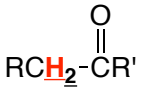
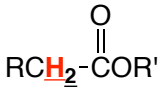
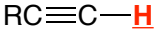
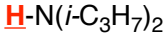
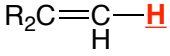
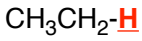
Student Honor Code

“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

Golden Rules of Chemistry for your reference

A. Predicting Structure and Bonding 1. In most stable molecules, all the atoms will have filled valence shells. 2. Five- and six-membered rings are the most stable. 3. There are two possible arrangements of four different groups around a tetrahedral atom. **B. Predicting Stability and Properties** 4. The most important question in organic chemistry is "Where are the electrons?" 5. Delocalization of charge over a larger area is stabilizing. 6. Delocalization of unpaired electron density over a larger area is stabilizing. 7. Delocalization of pi electron density over a larger area is stabilizing. **C. Predicting Reactions** 8. Reactions will occur if the products are more stable than the reactants and the energy barrier is low enough. 9. Functional groups react the same in different molecules. 10. A reaction mechanism describes the sequence of steps occurring during a reaction. 11. Most bond-making steps in reaction mechanisms involve nucleophiles reacting with electrophiles.

We have all been through a lot these past three years. But here we are, your final exam for second semester OChem. You have proven you are resilient and strong. I have really enjoyed getting to know all of you this past semester, and for many of you, the past two semesters. I no longer take for granted that we can be together in person, but we have been all year and I enjoyed every minute! And if you have gone through my previous finals you have seen this poem before, but I want you to read this on your own final exam. Here is my sincere wish for each of you, taken from the words of one of the great poets of the 20th Century, Bob Dylan.

"May your wishes all come true
May you always do for others
And let others do for you
May you build a ladder to the stars
And climb on every rung
May you stay forever young

May you always know the truth
And see the light surrounding you
May you always be courageous
Stand upright and be strong
May you stay forever young

May your hands always be busy
May your feet always be swift
May you have a strong foundation
When the winds of changes shift
May your heart always be joyful
May your song always be sung
And may you stay forever young"

And here are my own extra lines:

"Every chance you get,
You should go out for a run,
That is the very best way
For you to stay forever young."

Use this for scratch paper

Signature_____ Pg 1 _____(33)

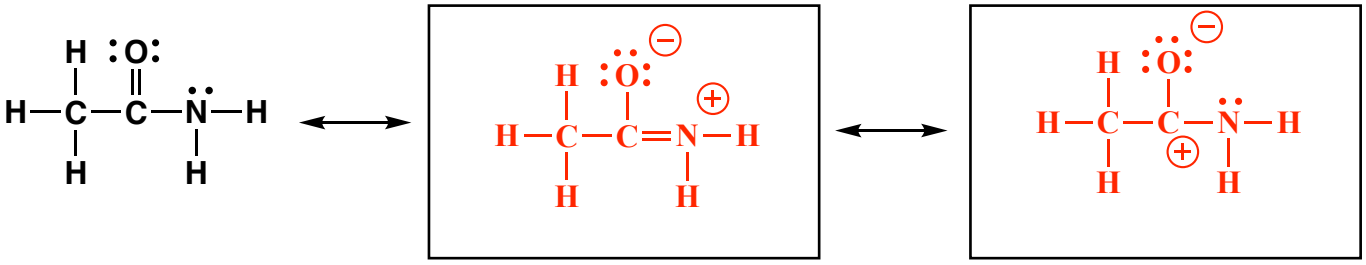
1. (5 pts) What is the most important question in organic chemistry?

Where are the electrons?

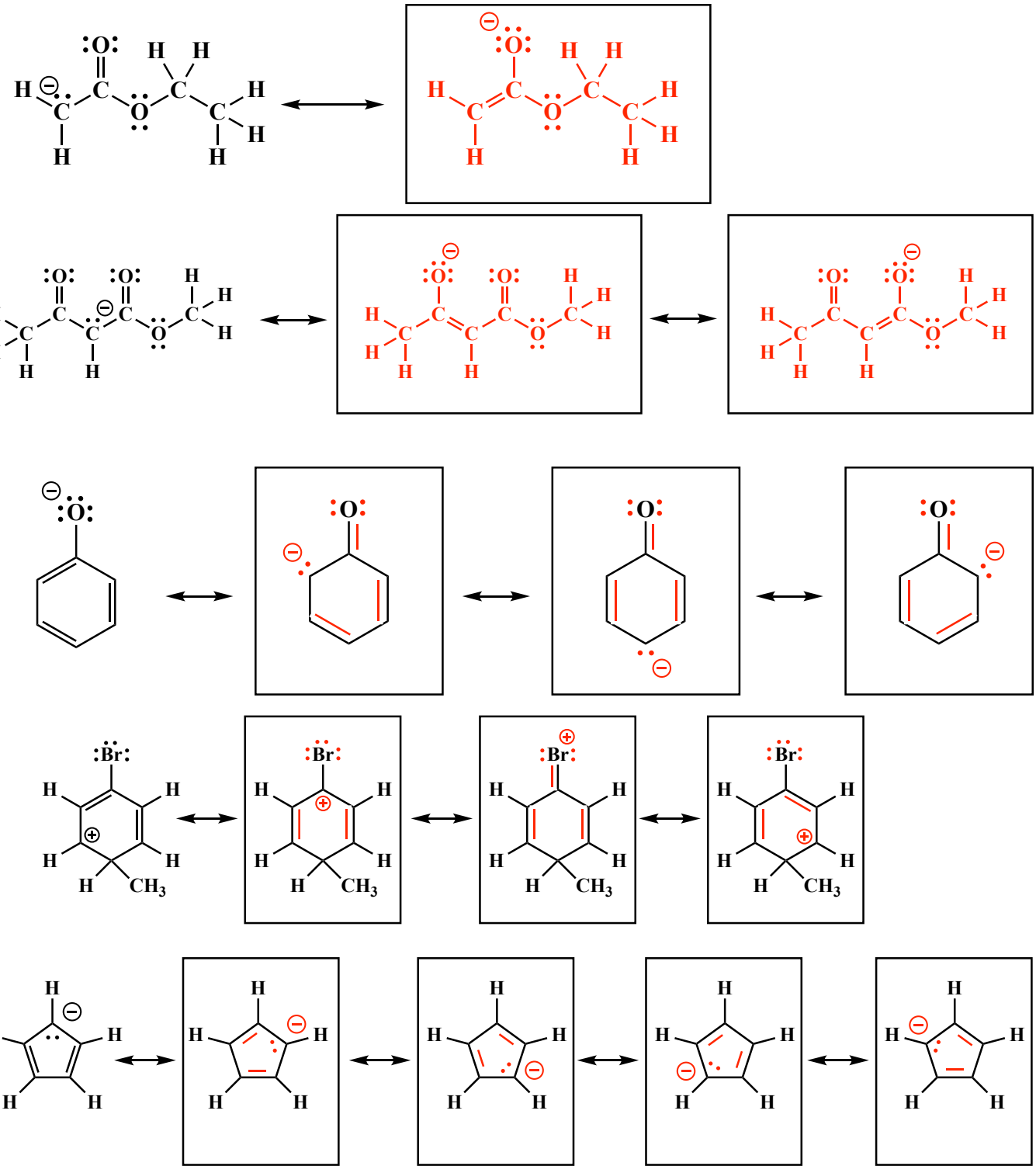
2. (1 pt each) Fill in each blank with the word that best completes the sentences. Yep, this is the MRI paragraph!

The popular 1. magnetic diagniostic technique of magnetic 2. resonance 3. imaging (MRI) is based on the same principles as 4. NMR, namely the 5. flipping (i.e. 6. resonance) of 7. nuclear spins of 8. H atoms by 9. radio frequency 10. irradiation when a patient is placed in a strong magnetic 11. field. Magnetic 12. field gradients are used to gain 13. imaging information, and 14. rotation of the 15. gradients 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 16. slices that when stacked make up the three-dimensional image of relative amounts of H atoms, especially the H atoms from 17. water and 18. fat, 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.

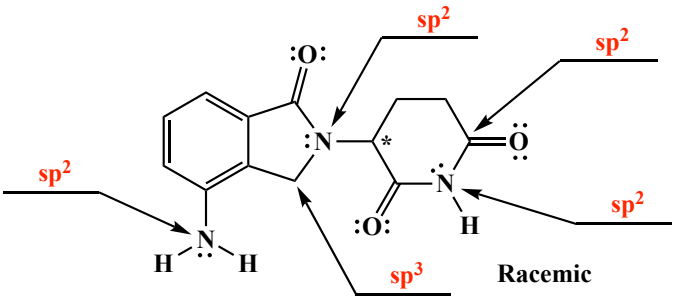


4. (2 pts each) Throughout the past two semesters, resonance contributing structures help you understand a variety of situations in which electron density and charges are delocalized. For the following molecules, draw the indicated number of important contributing structures. Make sure to indicate all lone pairs and formal charges. There is no need to draw arrows on any structures here. We added some ring templates at the bottom to save you time.

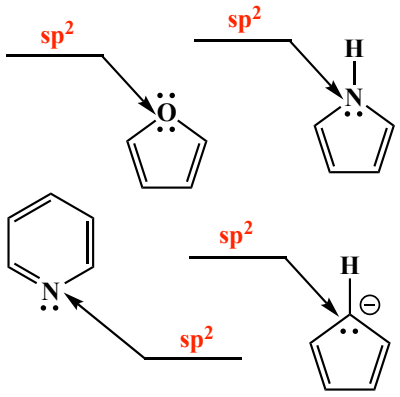


Signature_____ Pg 3_____(38)

5. (2 pts each) For each arrow, on the line provided write the hybridization state of the atom indicated. Appropriate asnwers might be sp, sp^2, or sp^3.

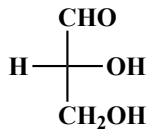


Lenalidomide
Used to treat cancer
$13 Billion in sales, 2021

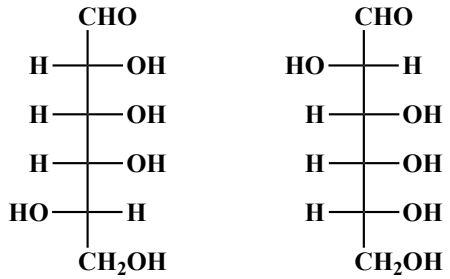


6. (2 pts each) For set of molecules, fill in the circles that correctly describe the situation.

A)



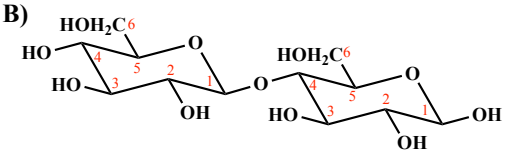
D-Glyceraldehyde



○ D-Carbohydrate
● Not a D-Carbohydrate

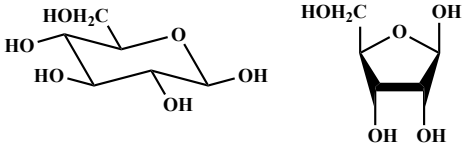
● D-Carbohydrate
○ Not a D-Carbohydrate

B)



○ β-1,3-Glycosidic Bond
● β-1,4-Glycosidic Bond
○ α-1,3-Glycosidic Bond
○ α-1,4-Glycosidic Bond

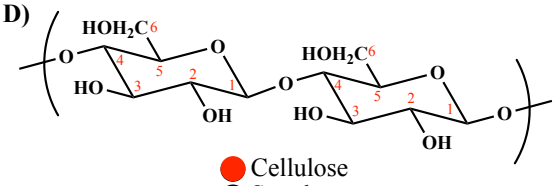
C)



○ Furanose
● Pyranose

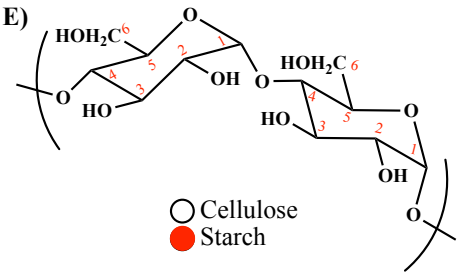
● Furanose
○ Pyranose

D)



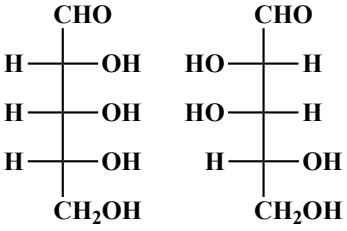
● Cellulose
○ Starch

E)



○ Cellulose
● Starch

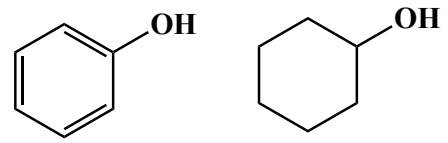
F)



○ Enantiomers
● Diastereomers

6 cont. (2 pts each) For each set of molecules, fill in all the circles that correctly describe the situation.

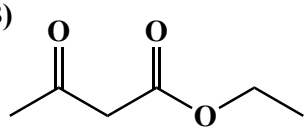
A)



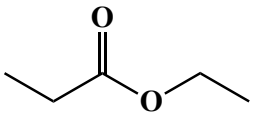
- ● Stronger acid
- ○ Weaker acid

- ○ Stronger acid
- ● Weaker acid

B)

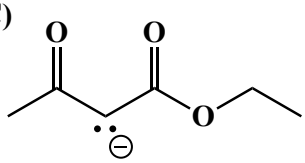


- ● Stronger acid
- ○ Weaker acid

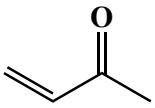


- ○ Stronger acid
- ● Weaker acid

C)

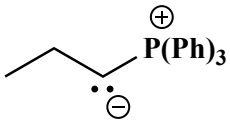


- ● Nucleophile
- ○ Electrophile

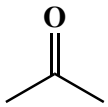


- ○ Nucleophile
- ● Electrophile

D)

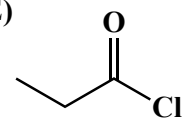


- ● Nucleophile
- ○ Electrophile

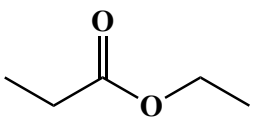


- ○ Nucleophile
- ● Electrophile

E)

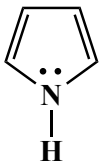


- ● More reactive with nucleophiles
- ○ Less reactive with nucleophiles

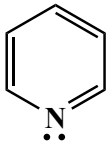


- ○ More reactive with nucleophiles
- ● Less reactive with nucleophiles

F)

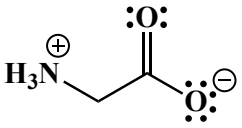


- ● Aromatic
- ○ Not aromatic

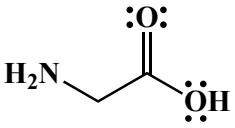


- ● Aromatic
- ○ Not aromatic

- ○ Aromatic
- ● Not aromatic

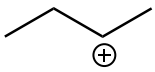


- ● The appropriate structure at pH = 7
- ○ Not the appropriate structure at pH = 7

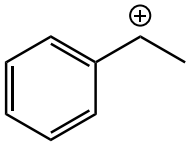


- ○ The appropriate structure at pH = 7
- ● Not the appropriate structure at pH = 7

F)

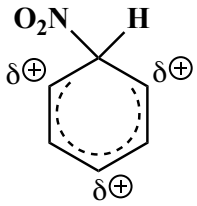


- ○ More stable
- ● Less stable

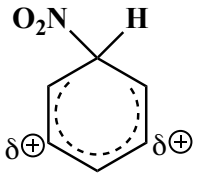


- ● More stable
- ○ Less stable

G)

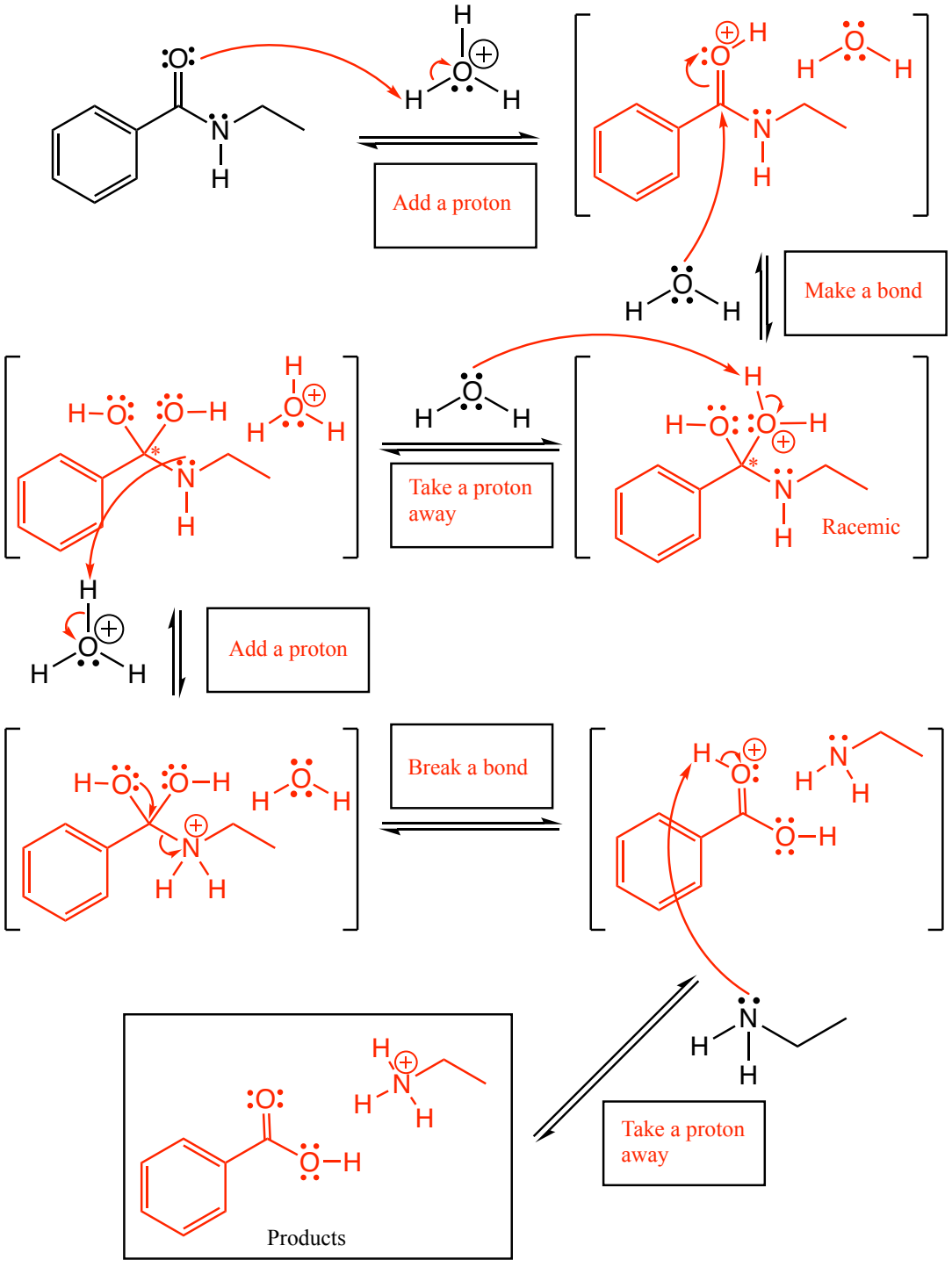


- ● Appropriate distribution of charge for an arenium ion intermediate
- ○ Not an appropriate distribution of charge for an arenium ion intermediate

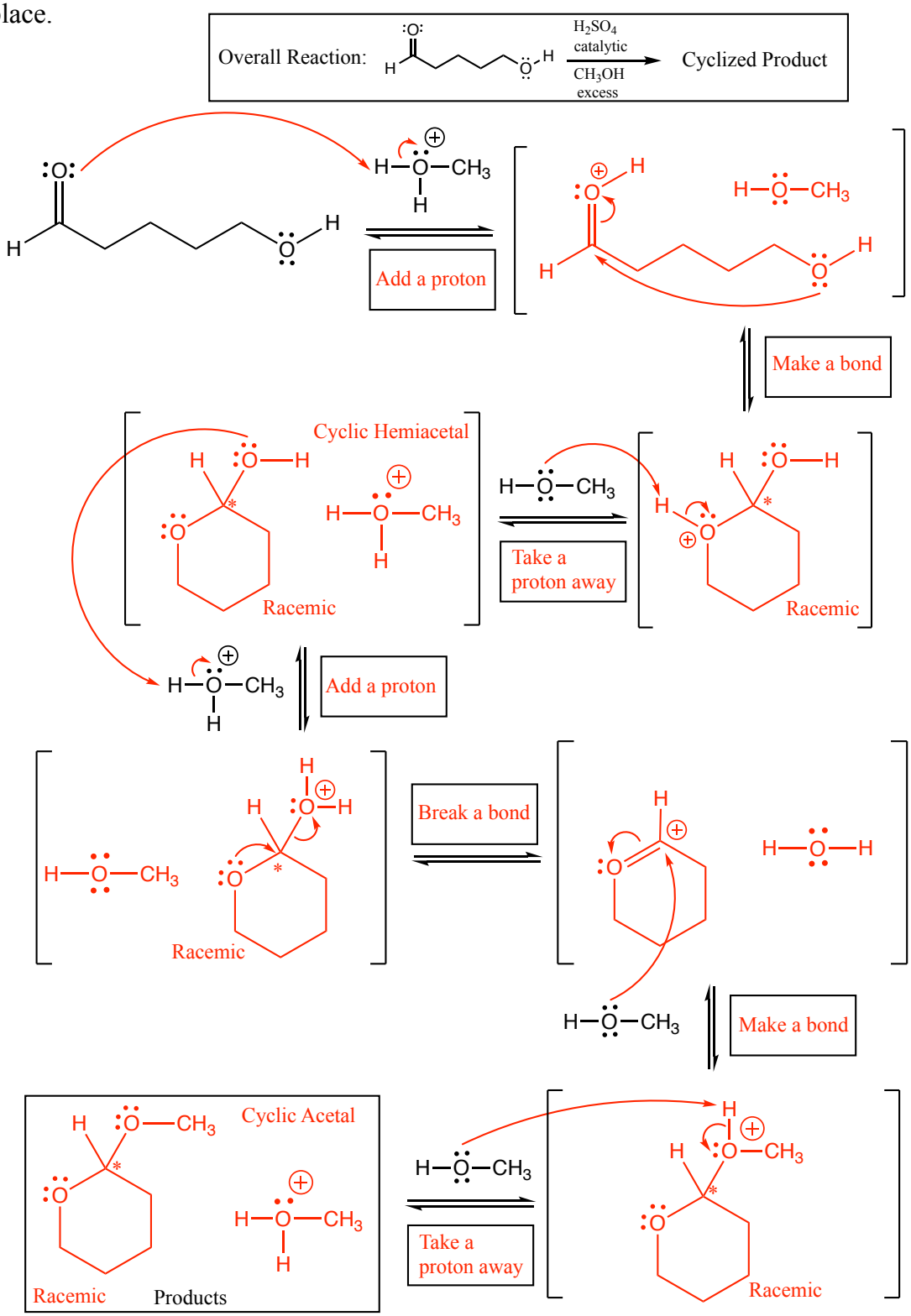


- ○ Appropriate distribution of charge for an arenium ion intermediate
- ● Not an appropriate distribution of charge for an arenium ion intermediate

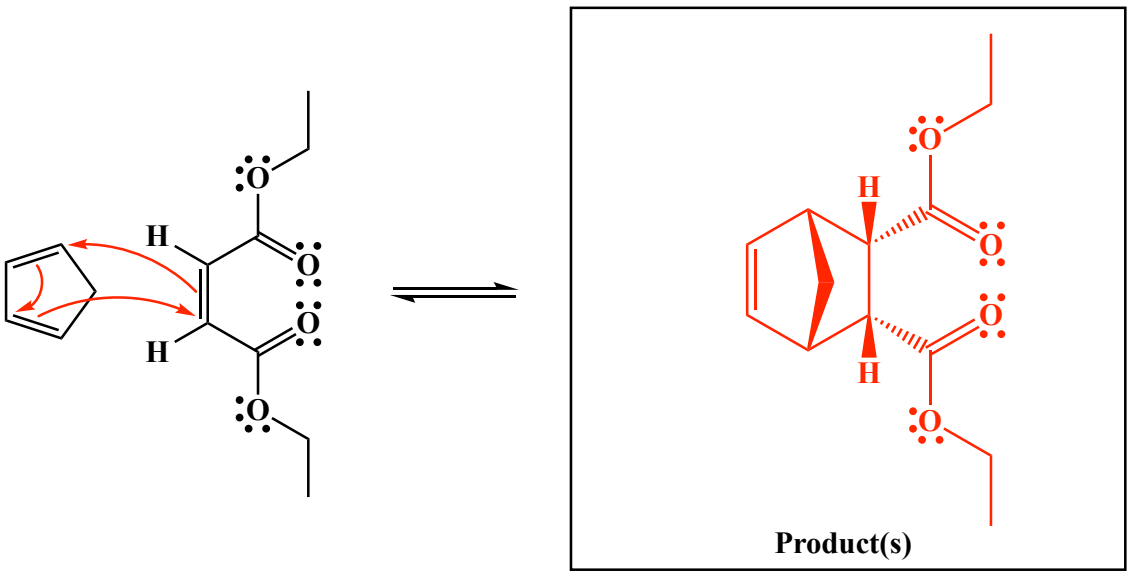
7. (34 pts) Complete the mechanism for the following acid-promoted amide hydrolysis reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS RACEMIC IF APPROPRIATE. In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.).

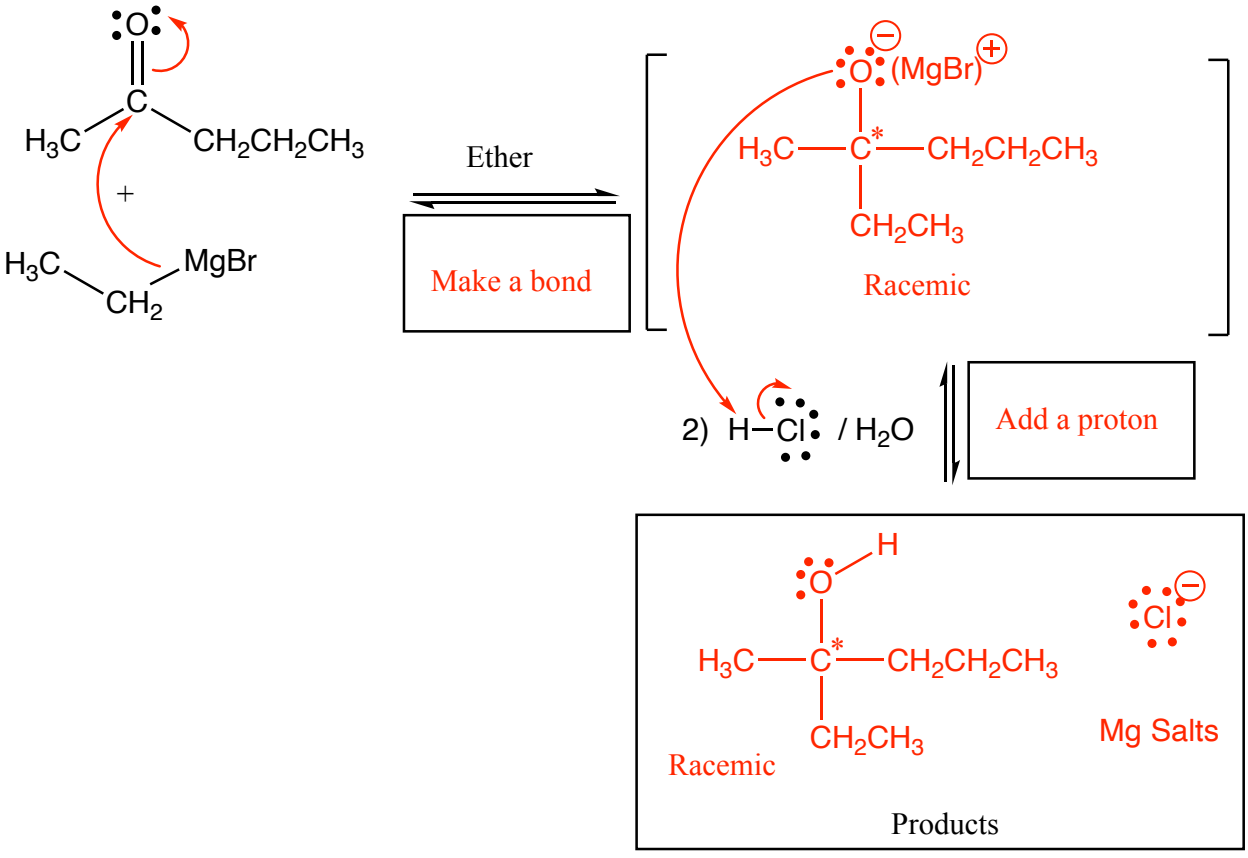


8. (44 pts) Complete this mechanism for the following acid-catalyzed acetal formation reaction. The directions are the same as for the mechanism on the previous page. To be clear, this reaction is run with methanol and the aldehyde-alcohol shown in the presense of catalytic H_2SO_4. Hint: Assume cyclization takes place.

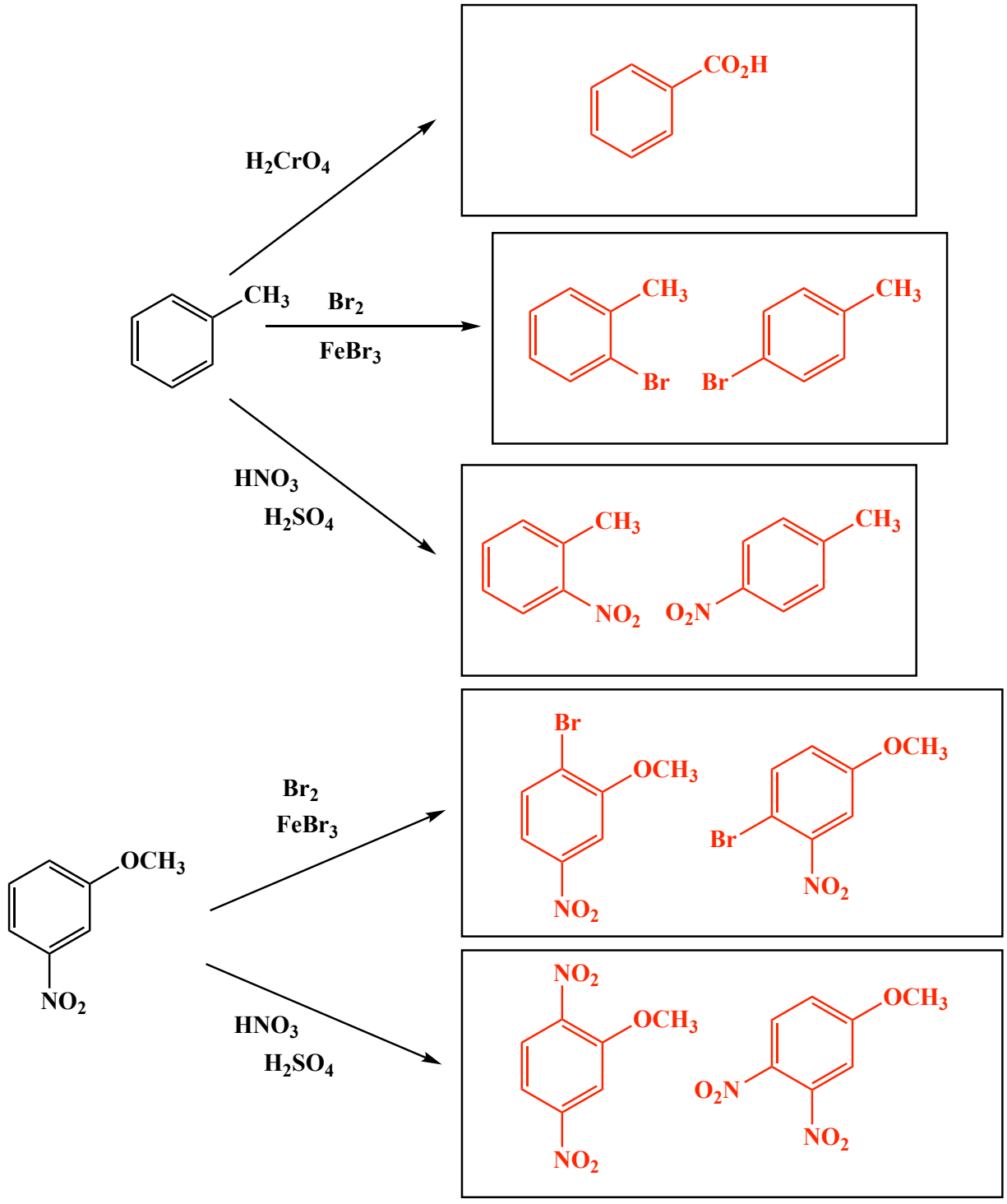


9. (17 pts) Complete the following two mechanisms. Use the same directions as for problem 7. The first one is from the last midterm. Make sure to add arrows to the starting materials of this Diels-Alder reaction!

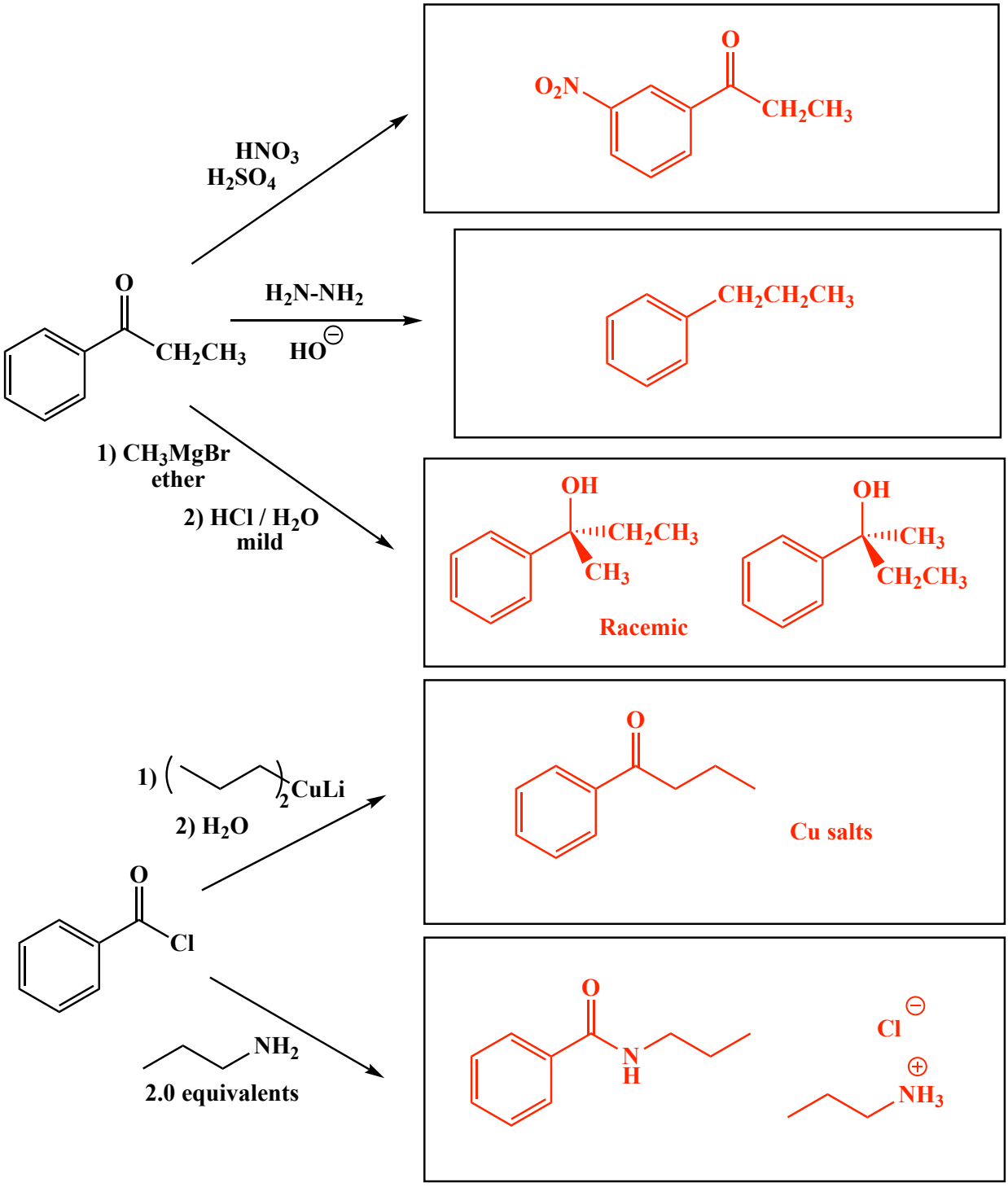




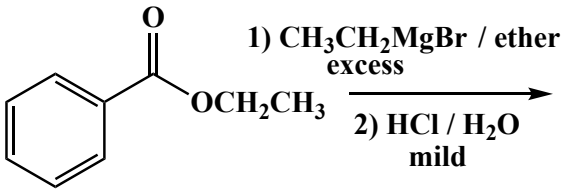
10. (3 or 5 pts.) Write the predominant product(s) that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. For these,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

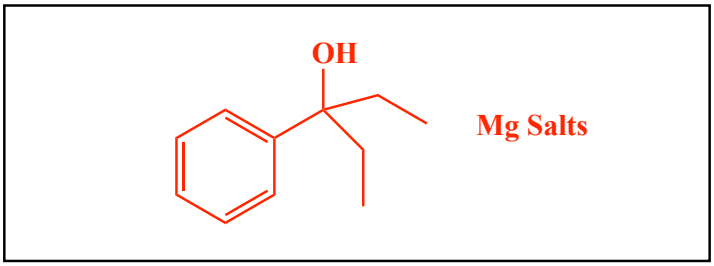


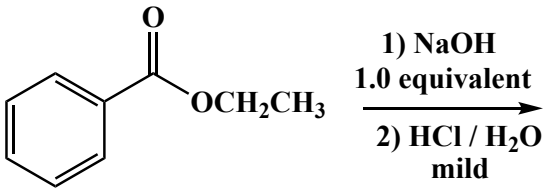
10 cont. (3 or 5 pts.) Write the predominant product(s) that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. For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

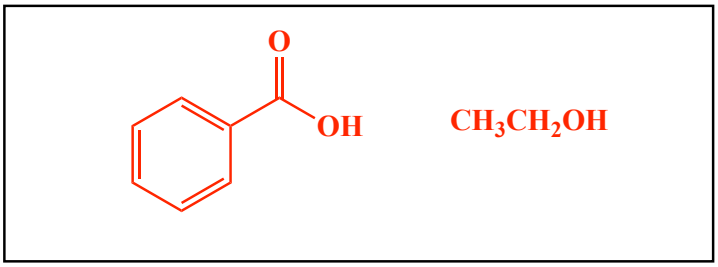


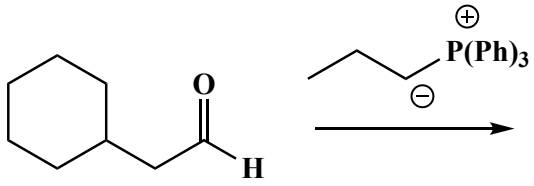
10 cont. (3 or 5 pts.) Write the predominant product(s) that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. For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

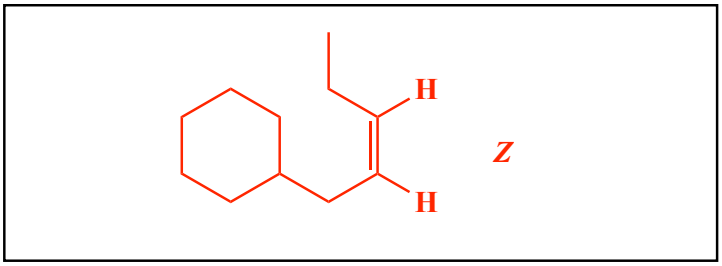


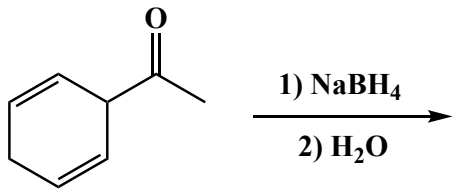


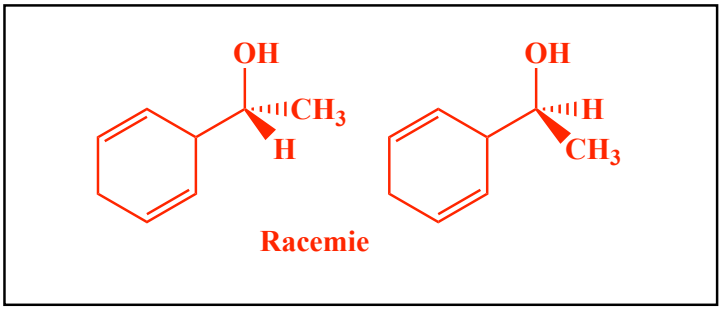


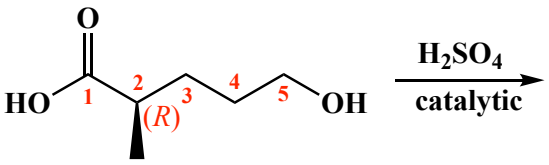


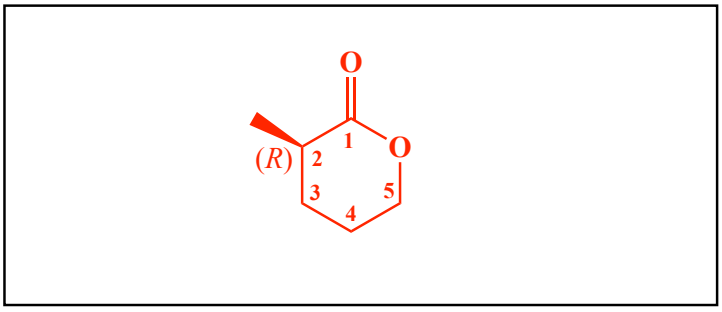




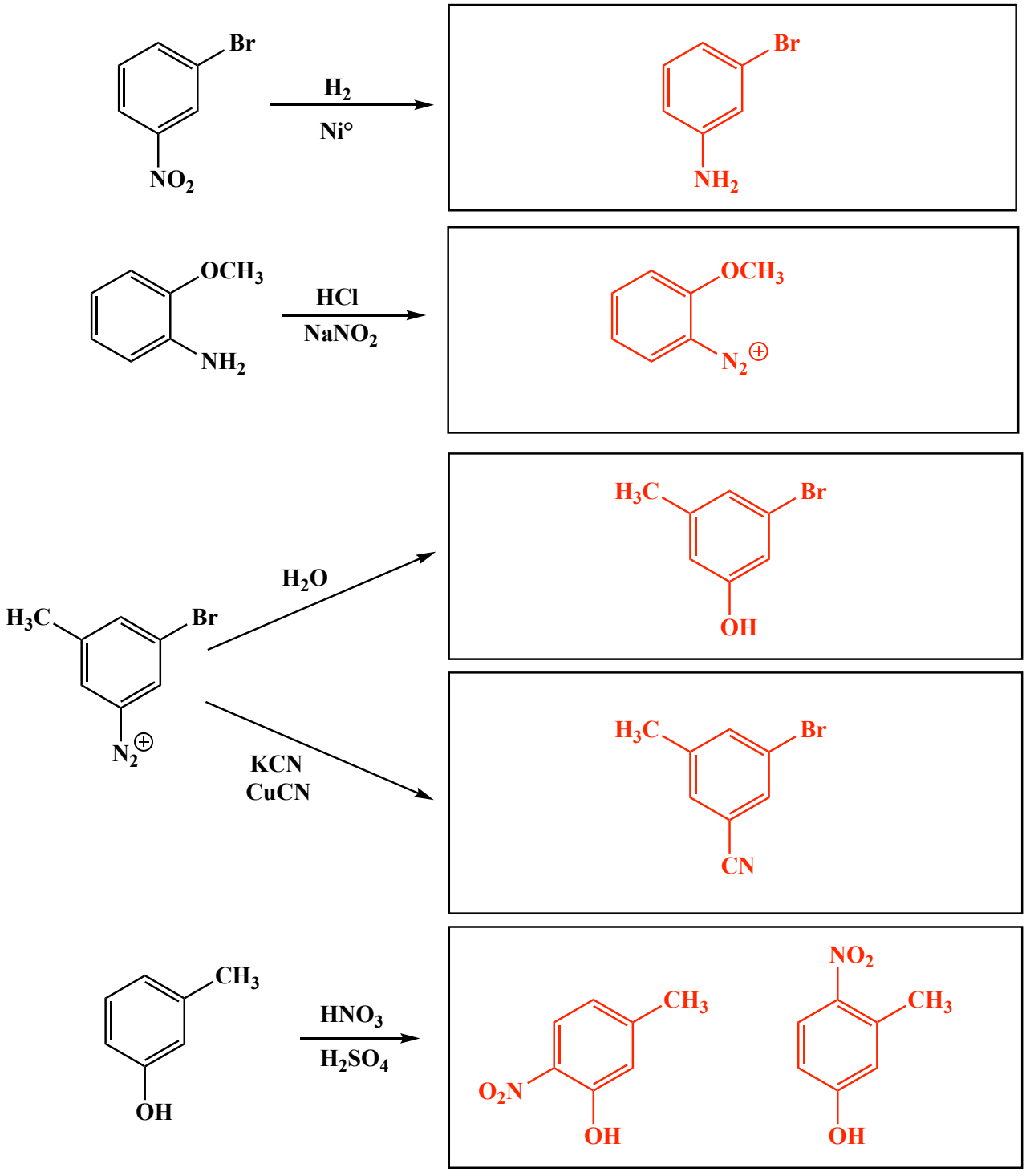




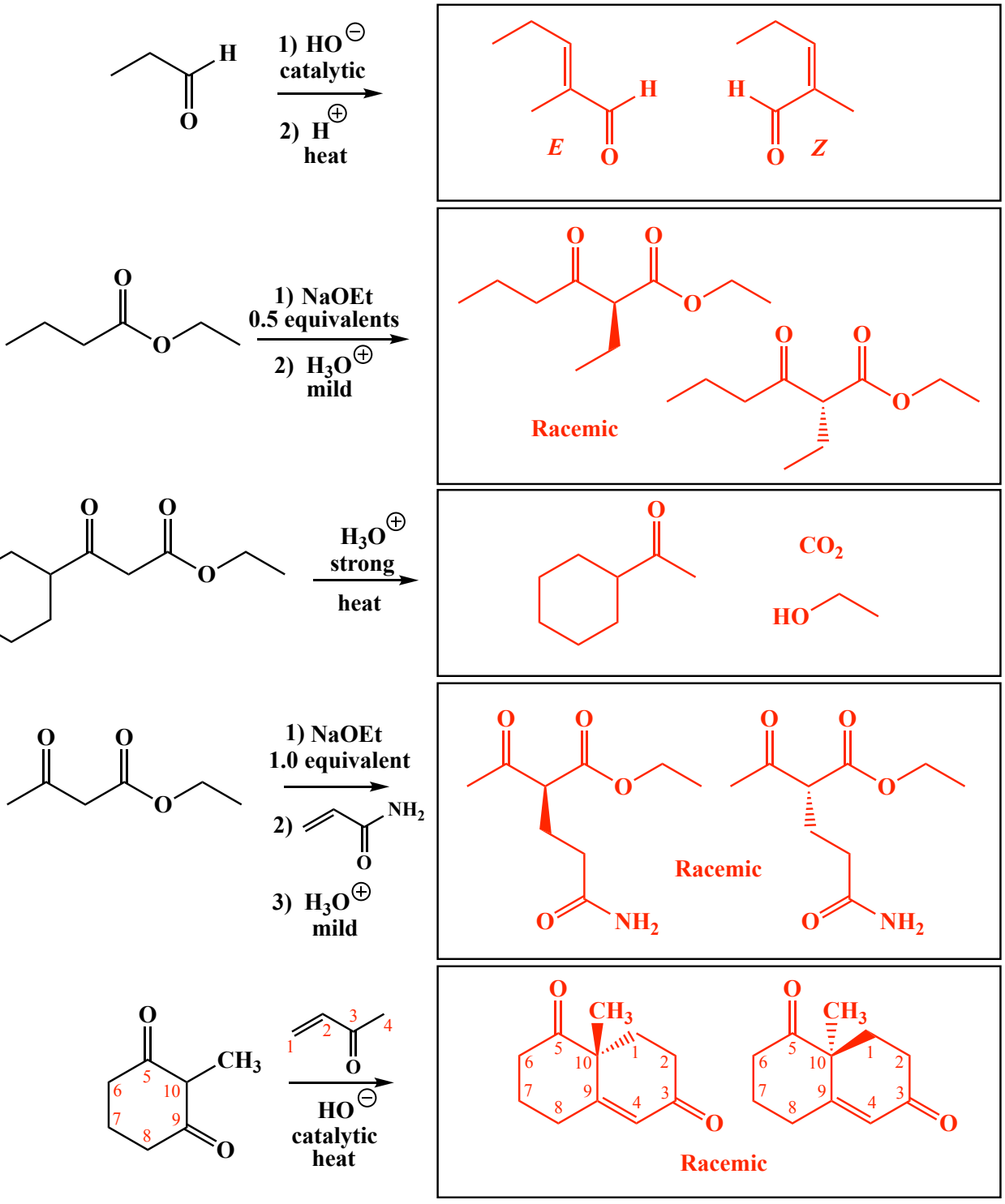




10 cont. (3 or 5 pts.) Write the predominant product(s) that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. For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

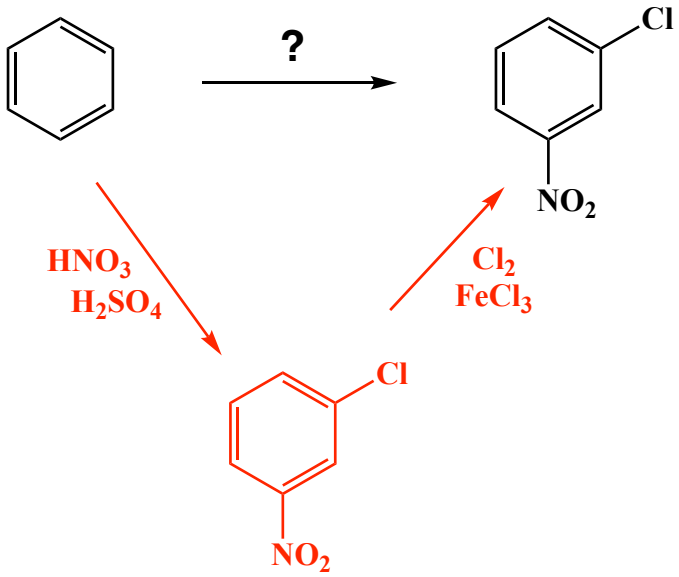


10 cont. (3 or 5 pts.) Write the predominant product(s) that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. For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



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.**

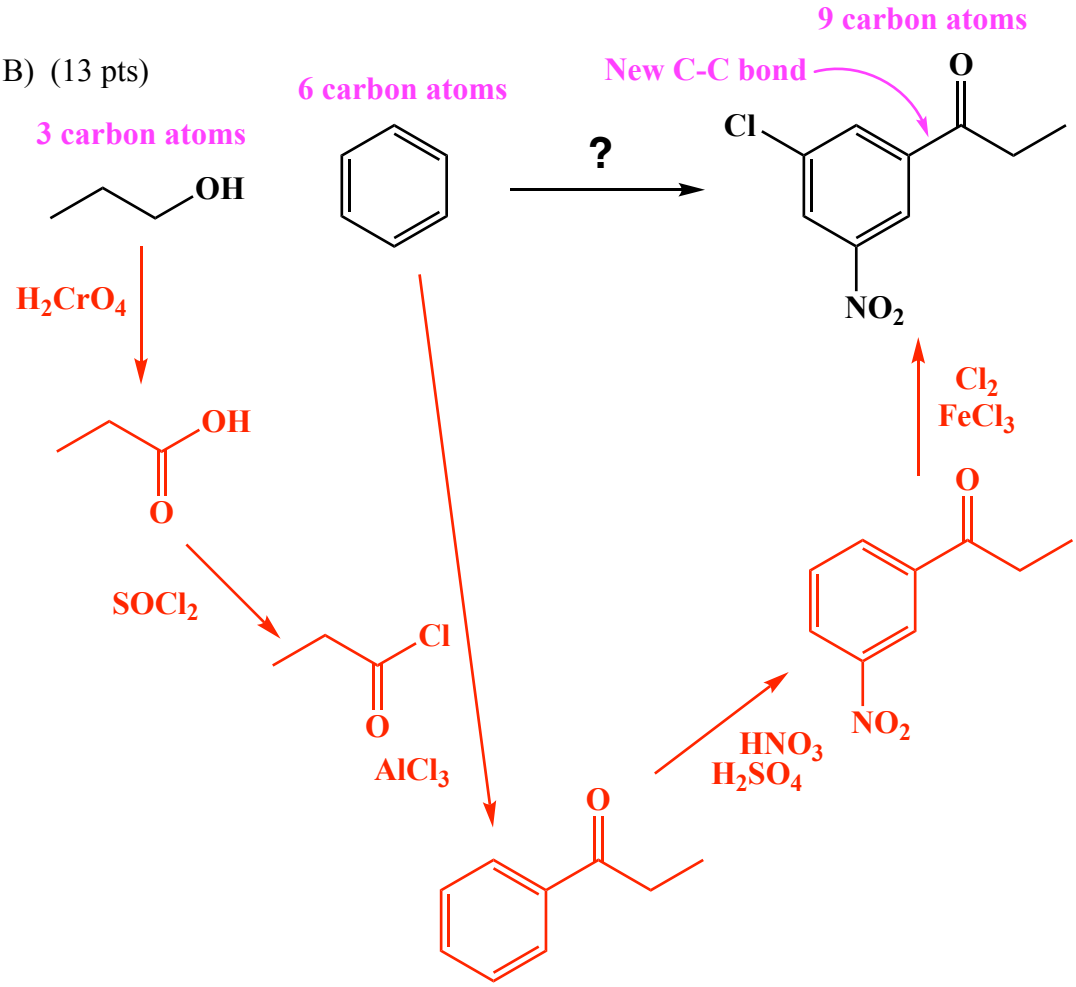
A) (4 pts)



Recognize that the product has the -Cl group meta to the nitro group. Therefore, add the nitro group (BAD) first as BAD groups are meta-directing. Cl groups are UGLY and therefore ortho,para directing.

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.**

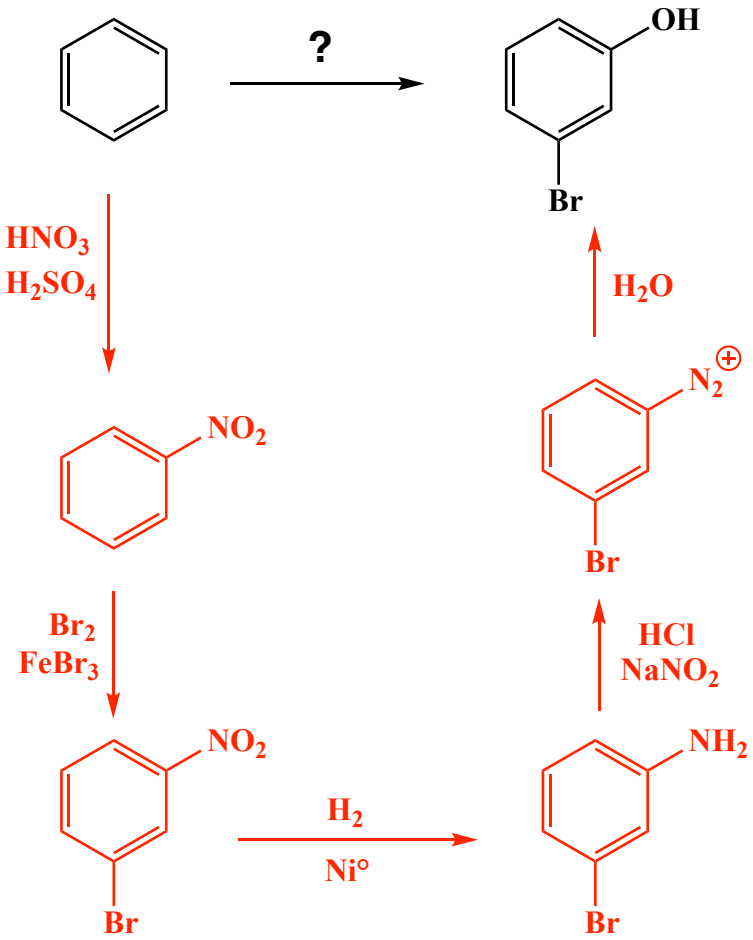
B) (13 pts)



Recognize that the product has 9 carbon atoms while the starting materials have 3 and 6 carbon atoms, so there must be a new carbon-carbon bond in the product as indicated. Because the product is an aryl ketone, assume a Friedel-Crafts reaction is the C-C bond-making step. **Recognize** further that all of the groups are meta to each other in the product, this will only occur if the only non-metadirecting group (-Cl group, UGLY) is added last. Recall that the Friedel-Crafts reaction cannot occur with a BAD group like the -NO_2 group already on the ring, so the Friedel-Crafts reaction must be first, followed by the nitration reaction, then finally, the halogenation reaction. No other oder of addition will work to make this product.

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.**

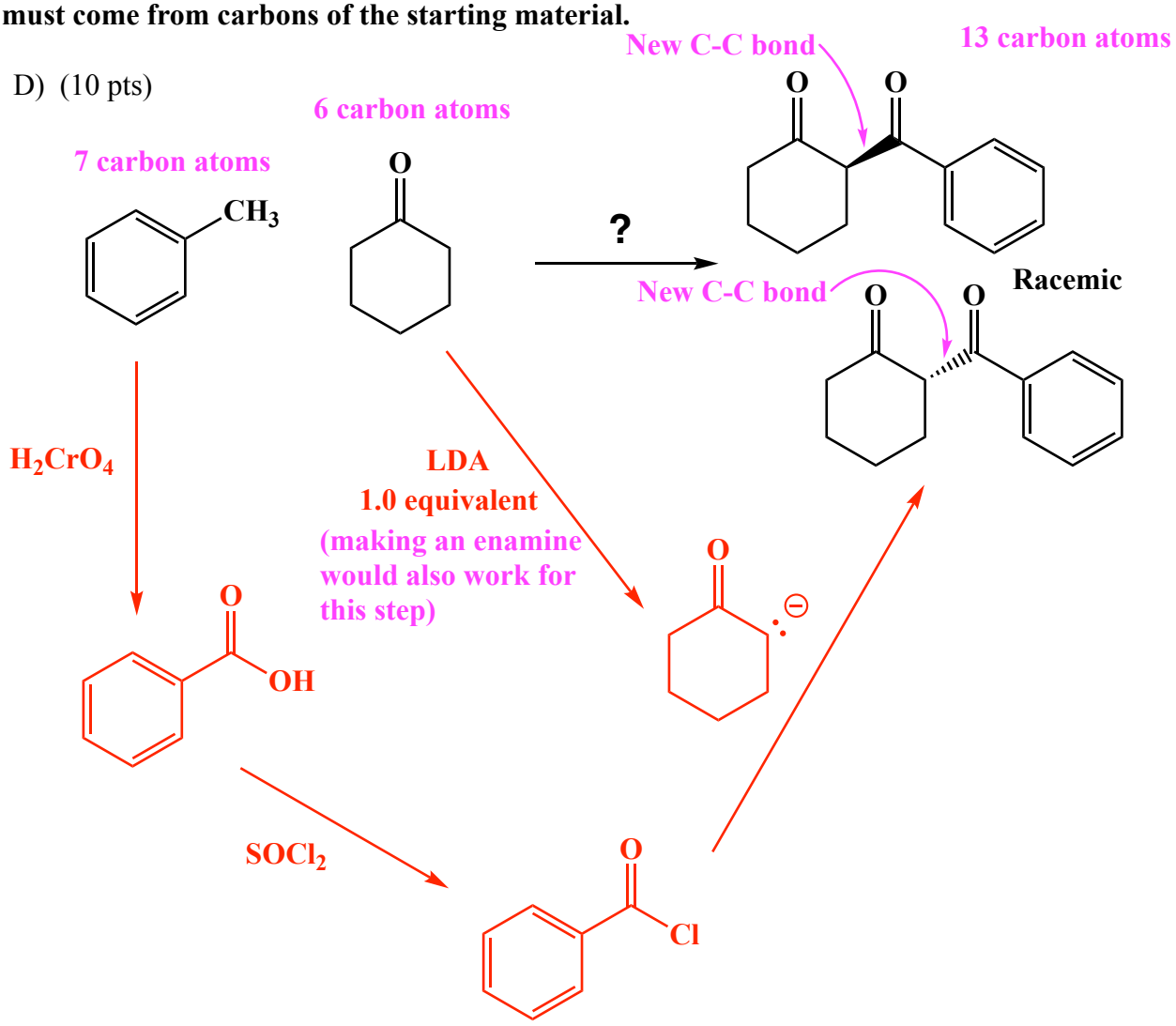
C) (13 pts)



Recognize that the product has two ortho,para directing groups, yet they are meta to each other: the -Br group (UGLY) and the -OH group (GOOD). **Recognize** further that there is an -OH group, and you only know how to add those to an aromatic ring using H_2O with a diazonium ion. Therefore, for both reasons, predict that a diazonium ion is involved in the synthesis of this product. **Recognize** that the only order of reactions that works is to start with a nitration reaction (HNO_3/H_2SO_4) to add the $-NO_2$ group (BAD, meta-directing), followed by bromination ($Br_2/FeBr_3$) to give the meta relationship, then reduction of the nitrogroup ($H_2/Ni°$) to an $-NH_2$ group, followed by creation of the diazonium ion from $-NH_2$ ($NaNO_2/HCl$) then reaction with H2O to give the final product.

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.**

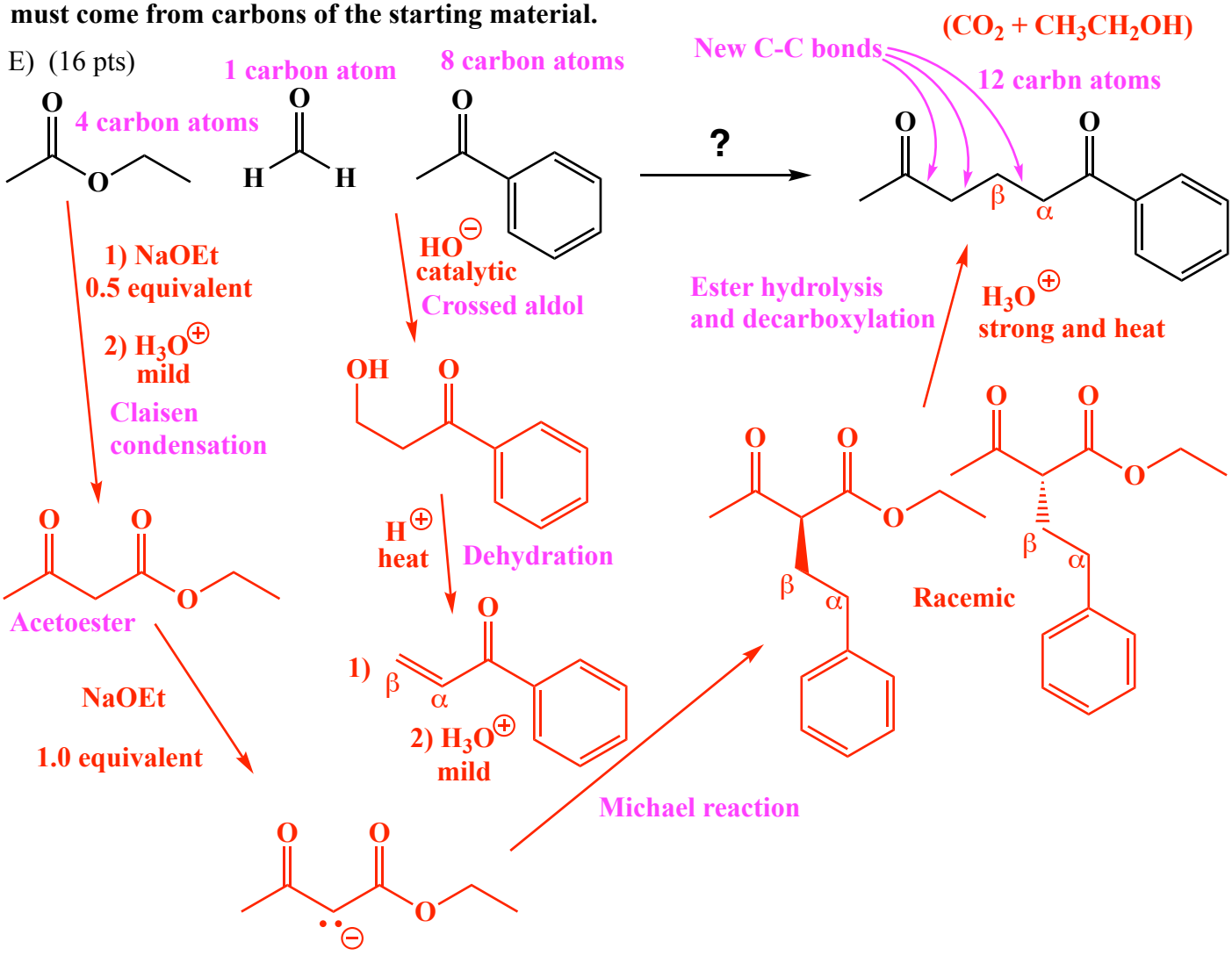
D) (10 pts)



Recognize that the starting materials have 7 and 6 carbon atoms, while the product has 13. **Recognize** also that the product is a β-diketone, the KRE of an enolate or enamine reacting with an acid chloride. Therefore predict that final reaction to be an acid chloride reacting with the enolate (or enamine) made from cyclohexanone using 1.0 equivalent of LDA (or a cyclic amine at pH 4.0). **Recognize** that you can make the required acid chloride from benzoic acid using $SOCl_2$. The benzoic acid can be made from toluene using chromic acid (H_2CrO_4) oxidation.

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.**

E) (16 pts)



Recognize that the product has 12 carbon atoms while the starting materials have 4, 1 and 8 carbon atoms. **Recognize** the product as a methy ketone, the KRE of an acetoester synthesis. Therefore the last step must be an ester hydrolysis, decarboxylation reaction in acid with heat, the last step of an acetoester synthesis. **Recognize** the required ester synthetic intermediate as having a nucleophile (the alpha carbon of acetoester) bonded with a new C-C bond to the β carbon atom of a ketone, the KRE of a Michael reaction. Therefore predict the key C-C bond-forming step is a Michael reaction between the α,β-unsaturated ketone shown with the enolate of acetoester. **Recognize** that acetoester is made from the starting ester (ethyl acetate) with a Claisen reaction as shown, and the required α,β-unsaturated ketone can be made from a crossed aldol reaction using formaldehyde and the methyl ketone starting mateials (acetophenone) using catalytic HO^- followed by dehydration in acid.