NAME (Print): _____

SIGNATURE: _____

Chemistry 320N
Dr. Brent Iverson
Final
May 7, 2014

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

Please Note: You will do your best if you are relaxed. Take a deep breath and close your eyes for a minute. Keep your mind clear and don't second guess yourself. **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.

You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK will be regraded.

Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.

FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENCTS 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!!!

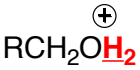
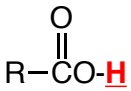
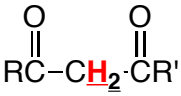
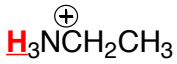
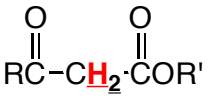
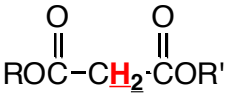
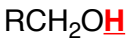
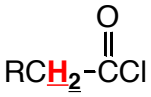
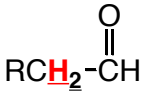
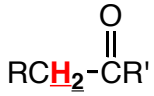
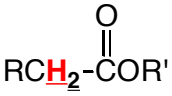
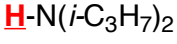
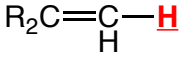
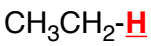
Page	Points	
1		(24)
2		(21)
3		(-)
4		(18)
5		(24)
6		(28)
7		(28)
8		(16)
9		(12)
10		(34)
11		(23)
12		(16)
13		(15)
14		(11)
15		(17)
16		(16)
17		(22)
18		(28)
19		(12)
20		(-)
Total		(365)

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
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

I have very much enjoyed getting to know you this semester. As long as I live I will not forget looking up at the beginning of class on April 7th to see all of those wonderful shirts in the audience. Thank you from the bottom of my heart! I am not sure if you knew, but April 7th is actually my birthday, so you officially gave me the best birthday gift ever. I mean best ever.

Success in your careers will be much more satisfying if you are healthy until you retire. Never sell yourself short. You are capable of amazing things, and an amazingly long and healthy life. You have to make your health your first priority. Do not take it for granted. Exercise every chance you get!

Brent Iverson

Signature_____ Pg 1 _____(24)

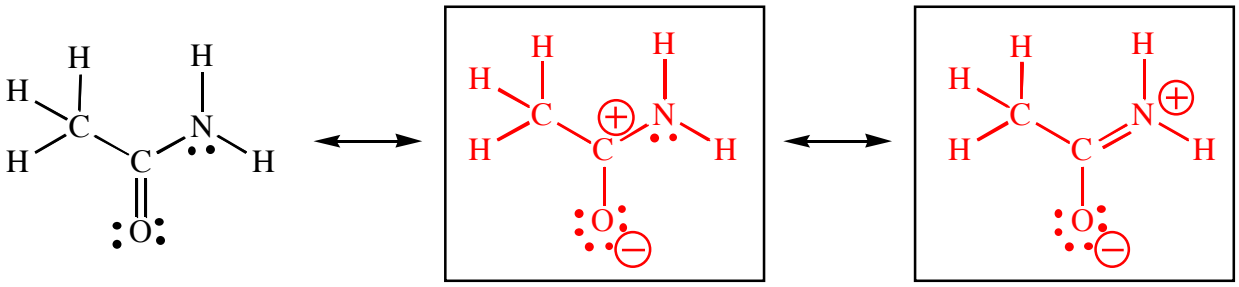
1. (2 pts) What is the most important question in chemistry?

Where are the electrons?

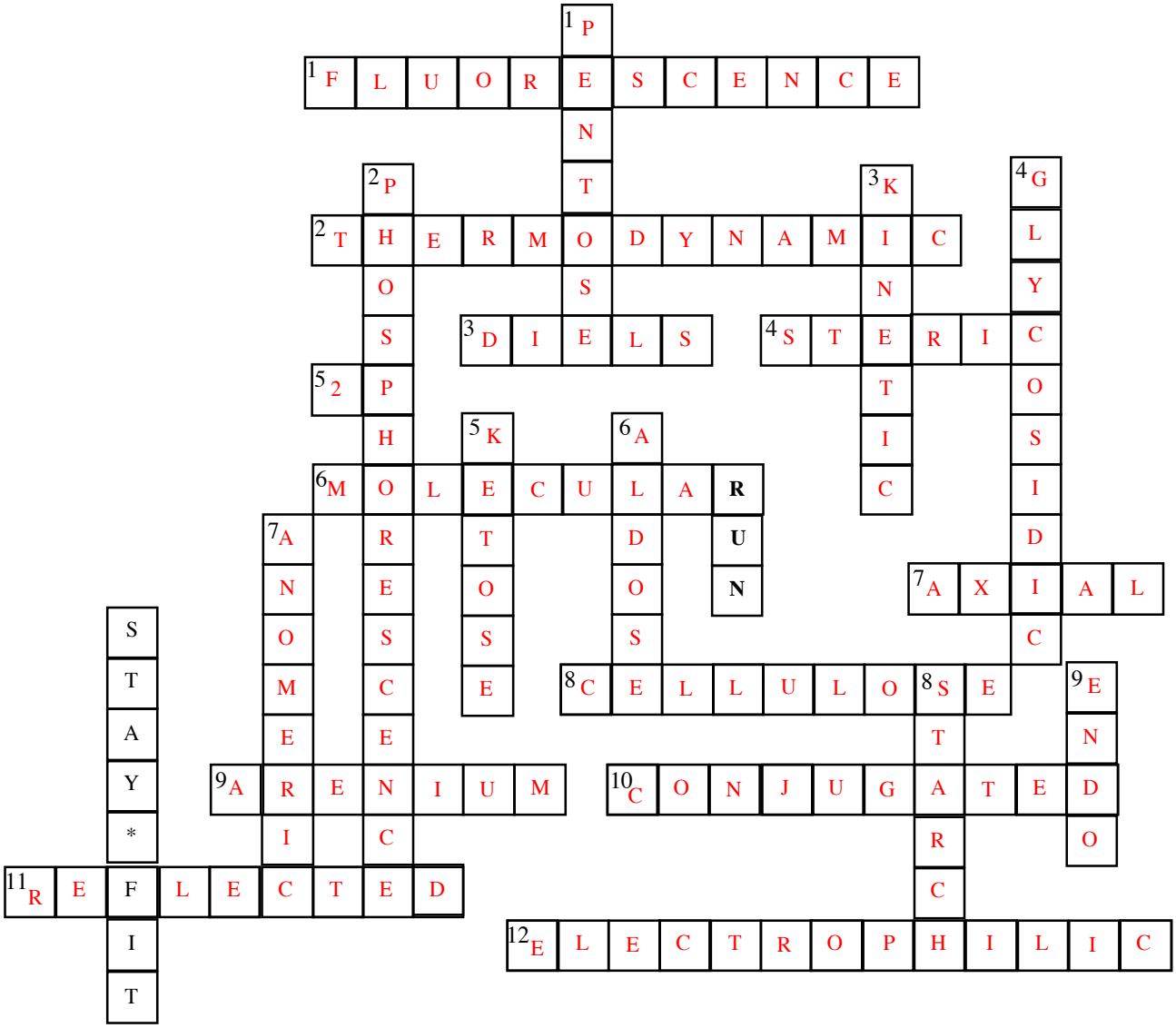
2. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

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 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



4. (21 pts total) Here is a crossword puzzle. Fill in the crossword spaces with the words that best complete the sentences listed in the clues. These are largely derived from "Rules of the Day", so they may seem familiar.



Across:

1: _____ occurs when there are not vibrations possible (a rigid molecule) so the photon is emited as the electron goes back to ground state.

2: At higher temperature, in which the products do equilibrate with each other, the more stable product predominates (called _____ control)

3: The _____-Alder reaction involves a diene reacting with a dienophile.

4: When large groups are present, some reactions cannot occur because the atoms crash into each other before a new bond can be made. Such interactions are referred to as _____ interactions.

5: The lone pair on the nitrogen atom of an amide is best described as being in a _____ orbital

6: Absorbance of a photon by a molecule corresponds to promotion of an electron from a filled _____ orbital to an unfilled _____ orbital.

7: When it comes to cyclic form of glucose, alpha is _____.

8: _____ has glucose monomers linked via beta linkages so it is flat and the chains can pack together nicely to create a highly rigid substance.

9: The _____ ion intermediate has partial positive charge located ortho and para to the position of the incoming electrophile, but not meta.

10: H-X and X_2 add to _____ dienes to give both 1,2 and 1,4 addition products, via a resonance stabilized allylic cation intermediate.

11: Molecules appear to our eye to be a combination of the wavelengths _____.

12: _____ aromatic substitution involves wicked strong electrophiles reacting with the aromatic pi system.

Down:

1: A carbohydrate with 5 carbon atoms is called a _____.

2: _____ (glow in the dark) happens when the excited electron must reflip its spin before entering the original filled orbital while emitting a photon.

3: At low temperature, in which the molecules cannot equilibrate, the more quickly forming product predominates (called _____ control).

4: Carbohydrate monomers can be linked together via acetal bonds, and this linkage can be alpha or beta. This type of acetal bond is called a _____ bond.

5: A _____ is a carbohydrate monomer that has a ketone carbonyl group.

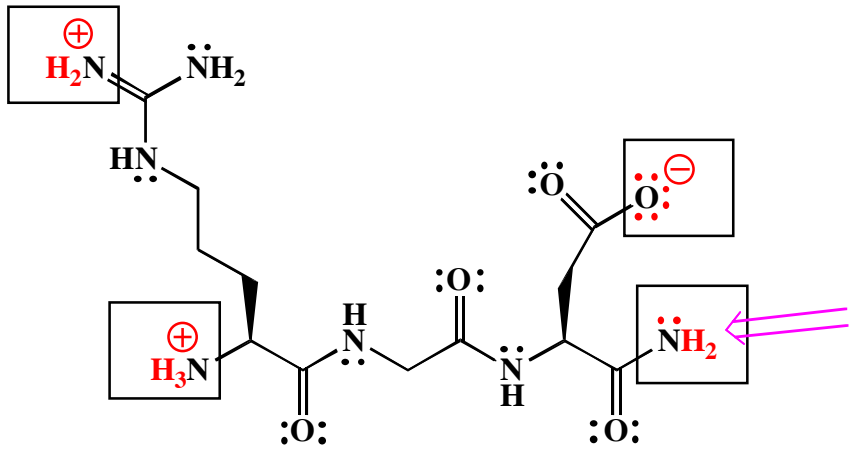
6: A _____ is a carbohydrate monomer that has an aldehyde carbonyl group.

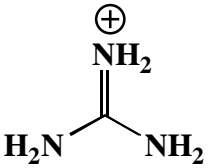
7: A new chiral center is created (at the _____ carbon) as the carbohydrate cyclizes.

8: _____ has glucose monomers linked via alpha linkages so it is bent and therefore not rigid.

9: Carbonyl groups on the dienophile react in the so-called _____ position "underneath" the double bonds of the diene.

5. (10 pts) The following tripeptide, referred to as RGD, binds to certain receptors in the integrin family involved with cell adhesion. **In each box, add the correct number of protons as well as lone pairs of electrons and draw any formal charges on the boxed atoms TO INDICATE THE APPROPRIATE PROTONATION STATES AT pH 7.0. Refer to pK_a values in the table at the beginning of the exam as well as the value for guanidinium listed below to the right:**



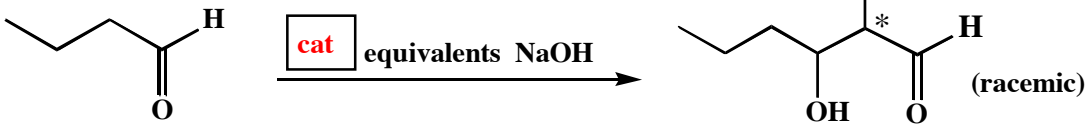


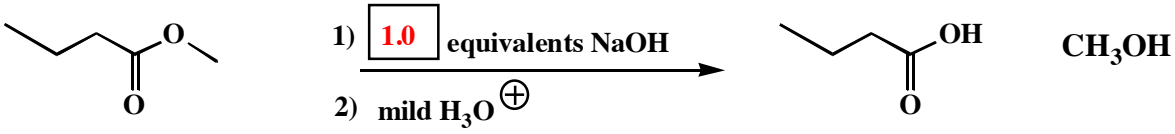
Guanidinium
pK_a = 13.6

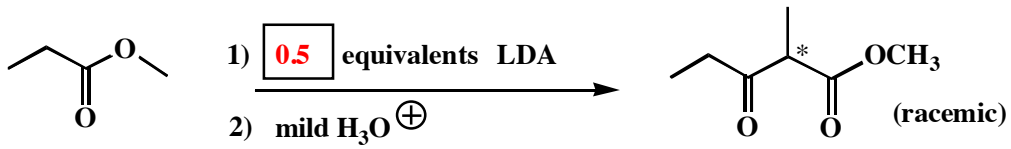
Recognize this as an amide that cannot be protonated near neutral pH because of the delocalized nature of the lone pair.

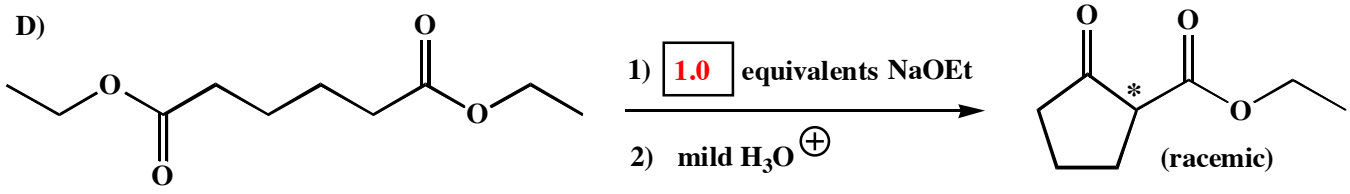
What is the overall charge on the RGD peptide at pH 7.0? **+ 1**

6. (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.**

A) 

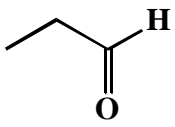
B) 

C) 

D) 

7 (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.



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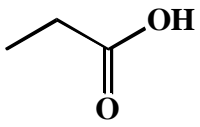

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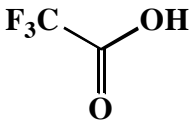

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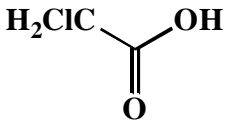
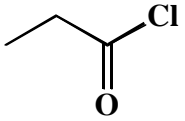


3

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



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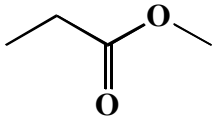

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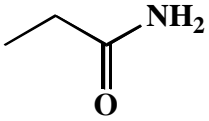
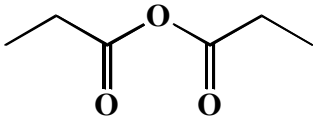


1



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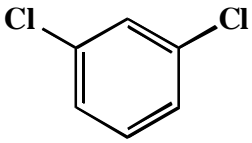
C. Rank from **least to most reactive with wicked strong electrophiles**, with a **1** under the least reactive and a **4** under the most reactive molecule.



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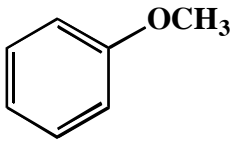

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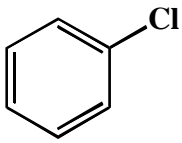
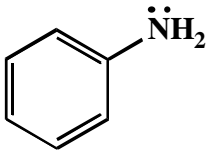


2

3

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



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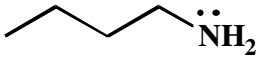

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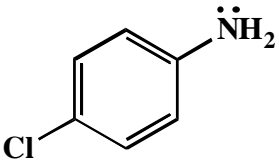

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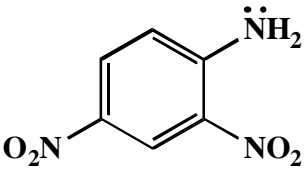
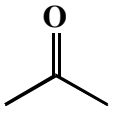


1

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



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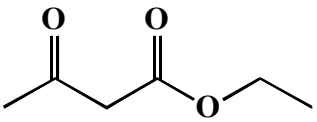

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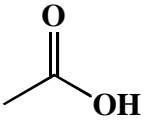

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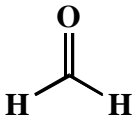
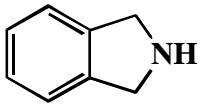


1

F. Think this through!! Rank from **least to most acidic**, with a **1** under the least acidic and a **4** under the most acidic molecule.



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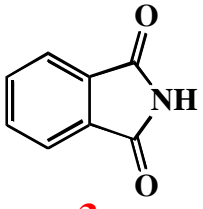

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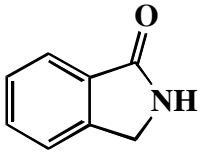

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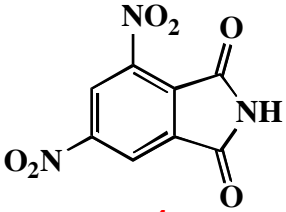
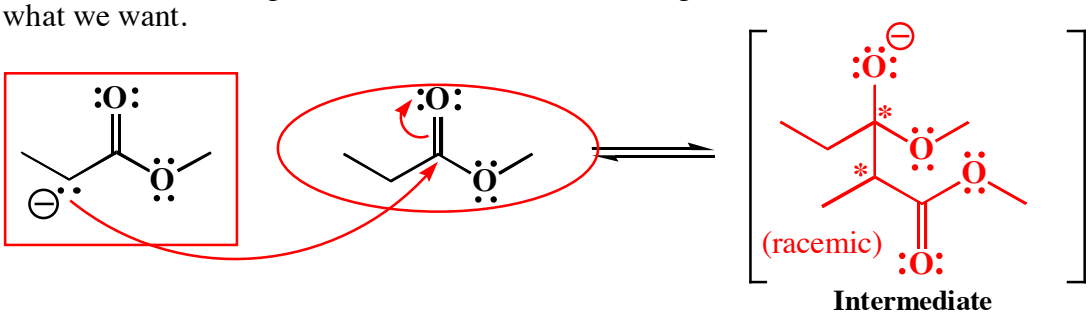


4

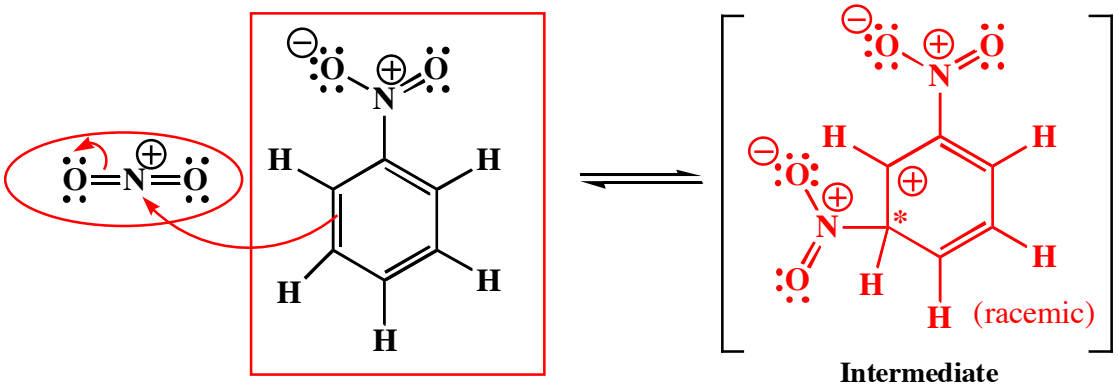
8. (28 points) Many of the reactions we have learned this semester involve steps with nucleophiles reacting with electrophiles. For the following examples of steps in mechanisms we have seen this semester, **1) Draw the intermediate that will be formed when the two molecules react. 2) Draw all formal 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 final products or any further steps of the mechanisms.** You do not have to worry about labeling chiral centers or writing "racemic" on this one. You might want to read these directions again so you know what we want.

A)



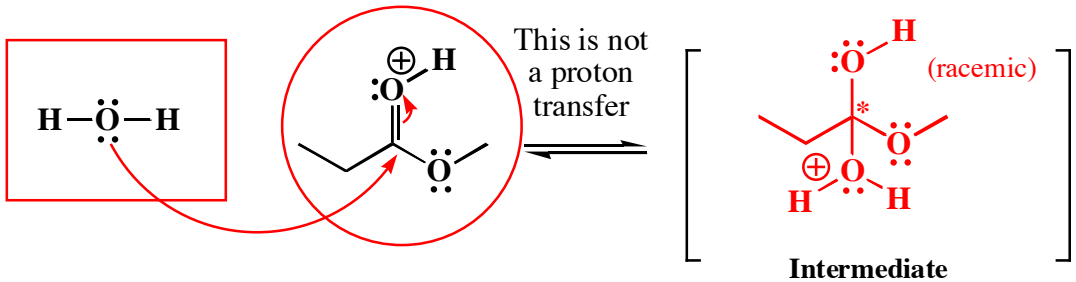
Intermediate

B)



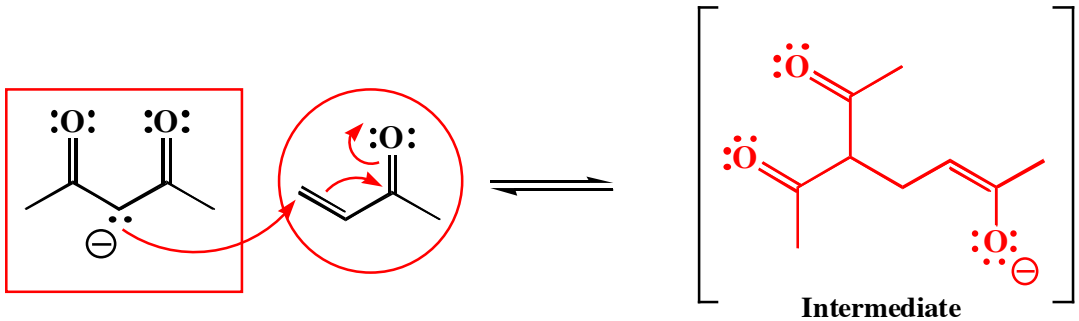
Intermediate

C)



Intermediate

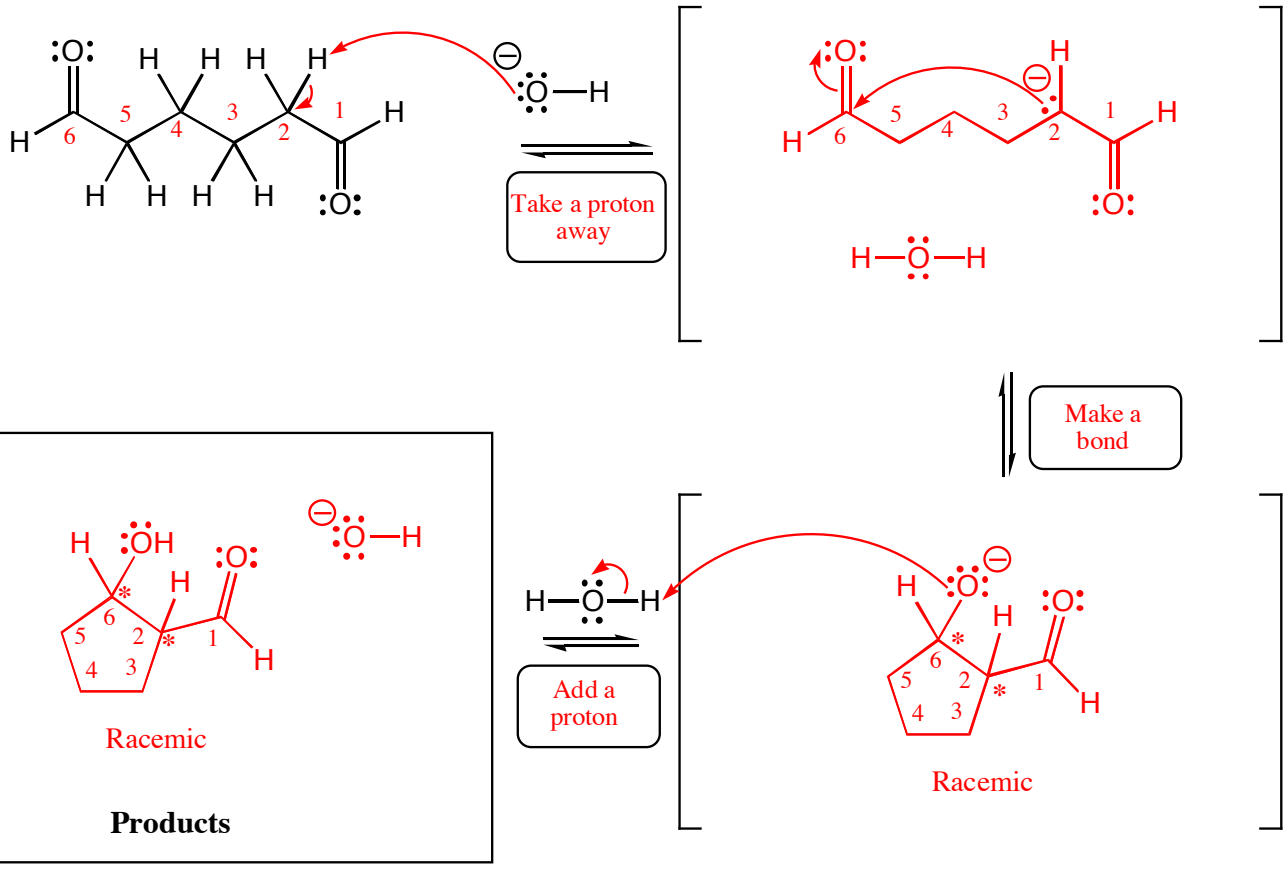
D)



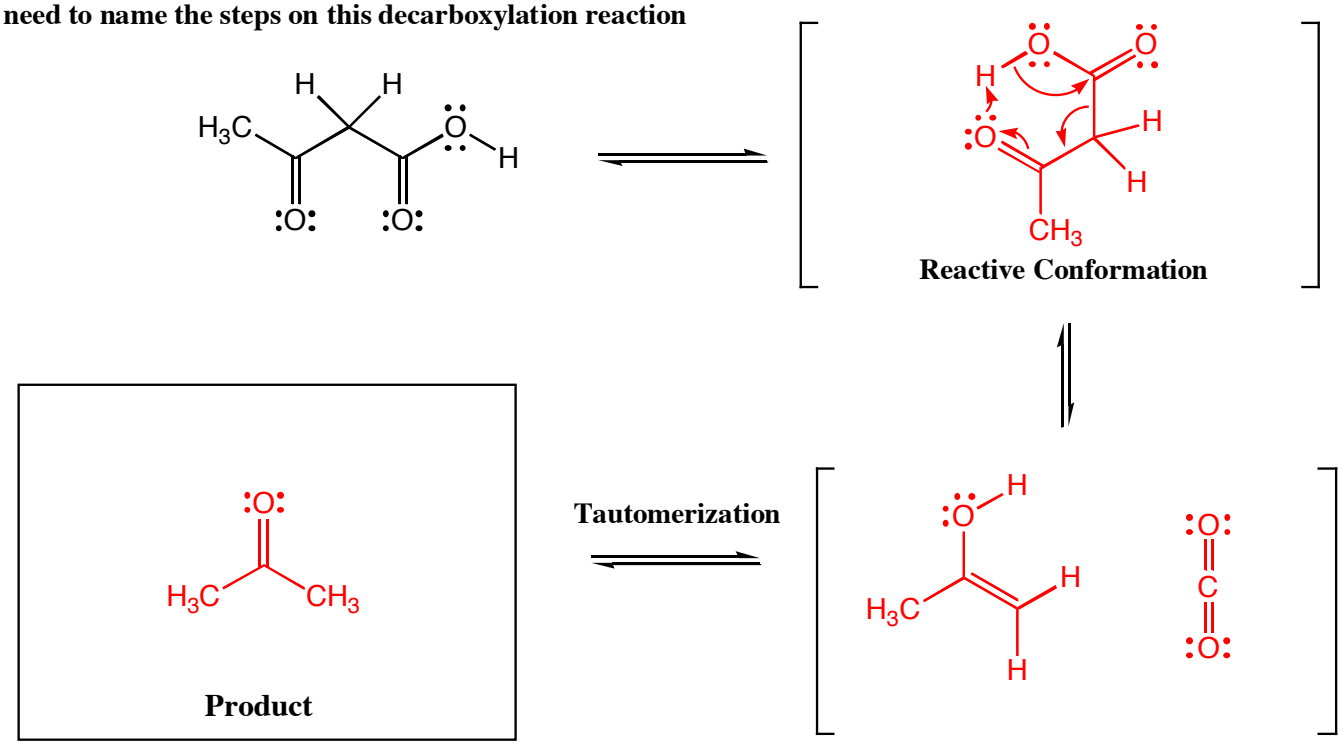
Intermediate

Did you remember to draw boxes and circles?

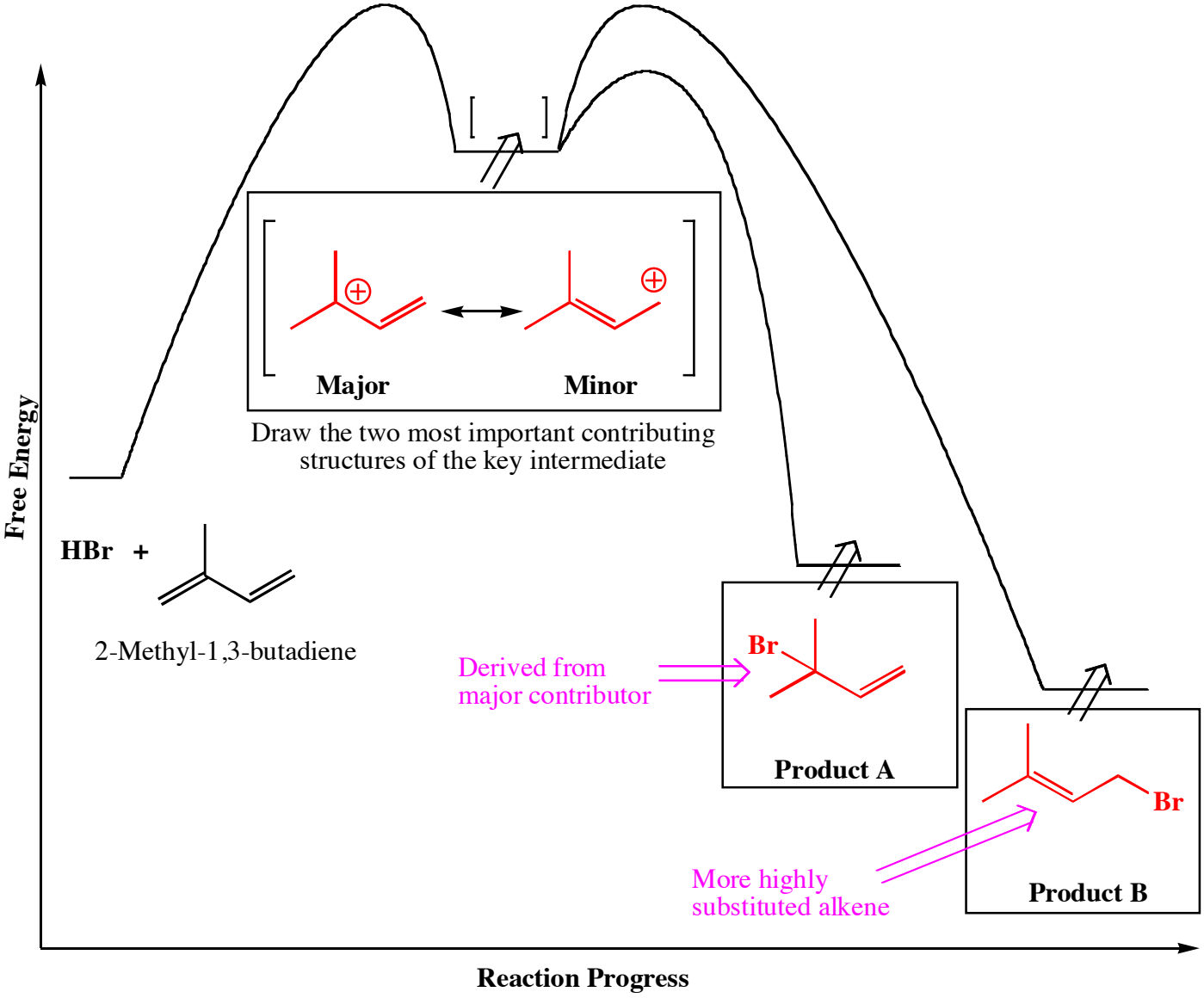
9. (28 pts total) Complete the mechanisms below for a cyclic aldol reaction and decarboxylation. DO NOT DEHYDRATE THE PRODUCT. Use arrows to show the movement of all electrons, and be sure to draw all lone pairs of electrons and all formal charges. Label all chiral centers with an asterisk (*) and write "racemic" if appropriate. ***Remember, you must show all products for each step.*** **Fill in the boxes below or beside each set of arrows to indicate which type of mechanistic element is involved, i.e. "add a proton", "break a bond", etc.**



No need to name the steps on this decarboxylation reaction



10. (16 pts total) This question is designed to probe your understanding of reaction mechanism, as well as the concepts surrounding kinetic vs. thermodynamic control of reactions. Below is the energy diagram for the addition of HBr to 2-methyl-1,3-butadiene. Fill in the boxes with appropriate structures.



(2 pts each) For the following four questions, circle the correct answer either "Product A" or "Product B"

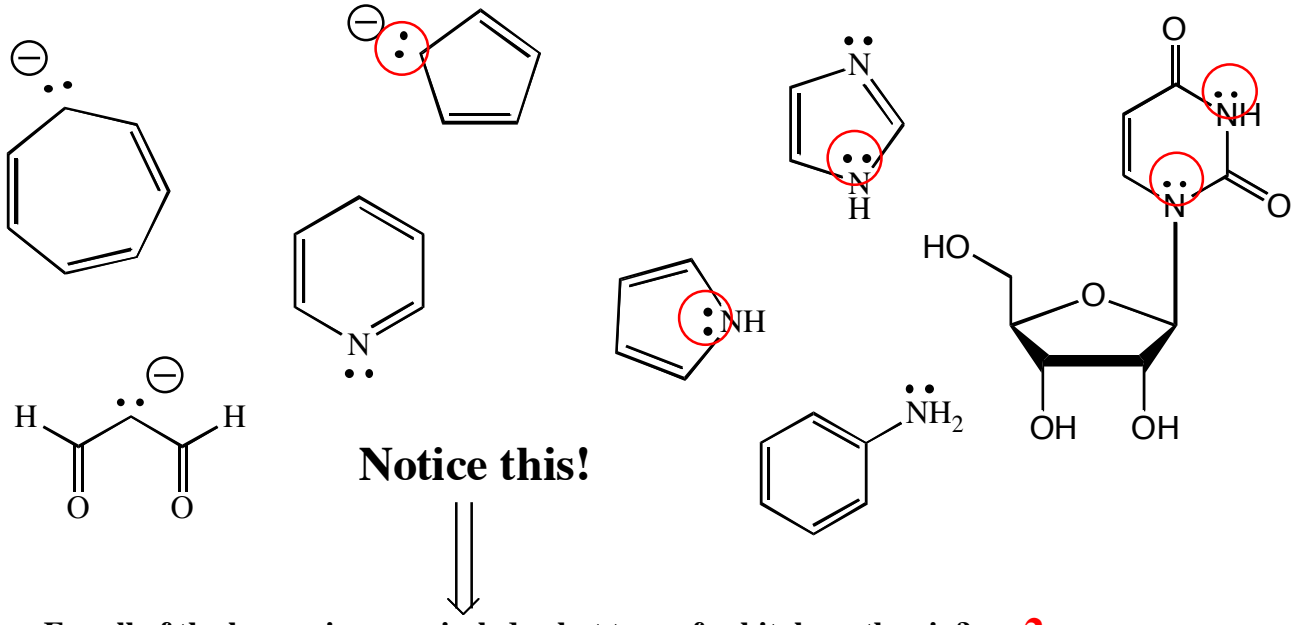
Which product will predominate a lower temperature? **Product A** **Product B**

Which product will predominate a higher temperature? **Product A** **Product B**

Which product will predominate under kinetic control? **Product A** **Product B**

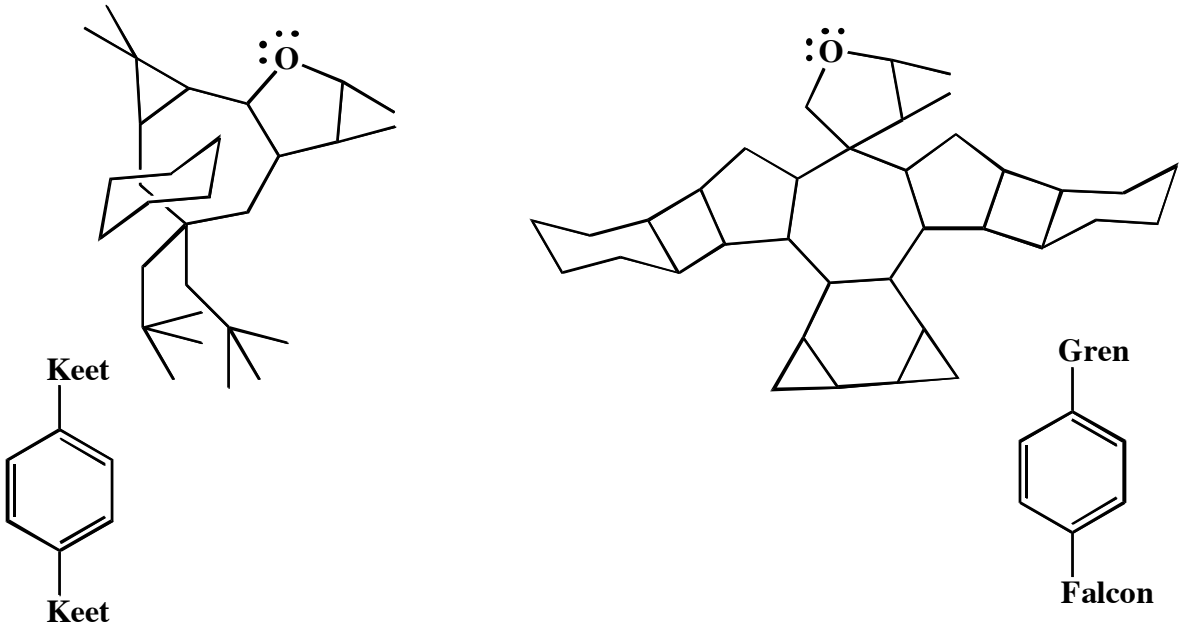
Which product will predominate under thermodynamic control? **Product A** **Product B**

11. (12 pts total) On the following molecules, circle all of the lone pairs that are part of the aromatic set of pi electrons. In other words, circle the lone pairs that are part of the 4N + 2 pi electrons according to Hückel. Note: you do not have to worry about the lone pairs we did not show on the structures below.

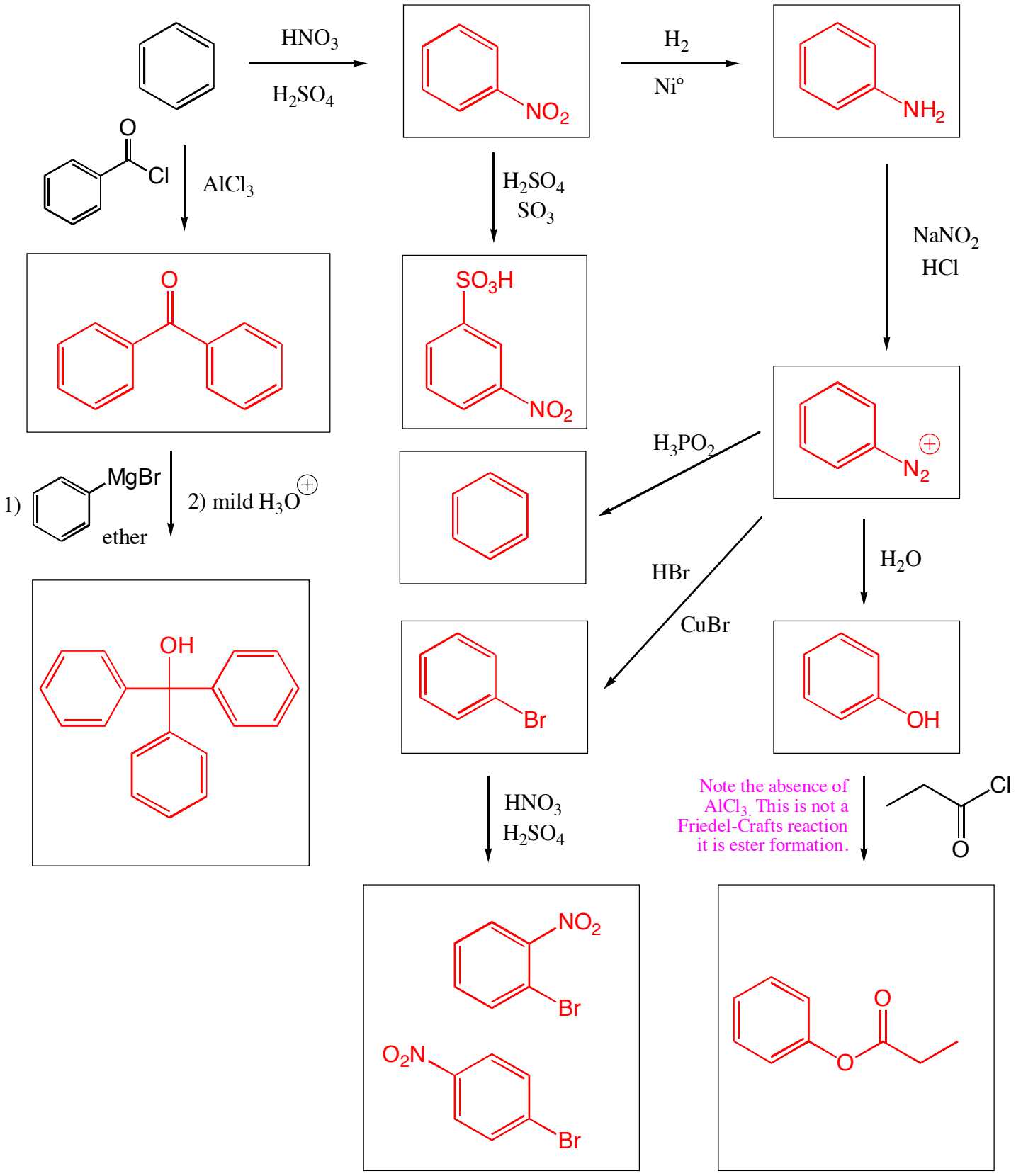


Notice this!

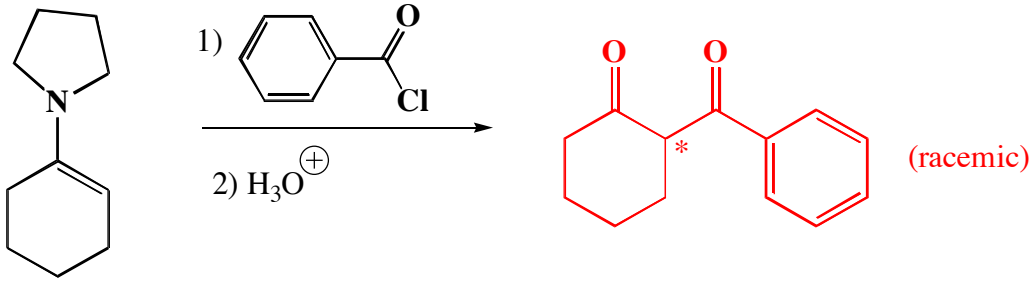
For all of the lone pairs you circled, what type of orbital are they in? **2p**

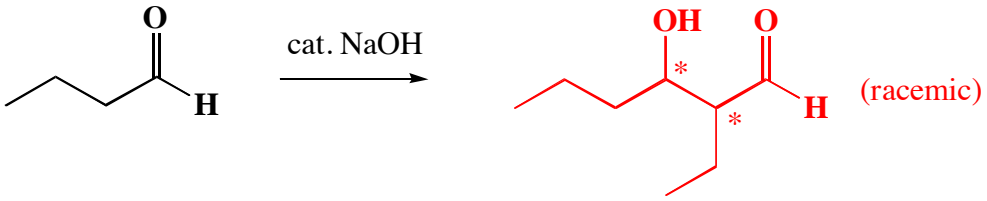


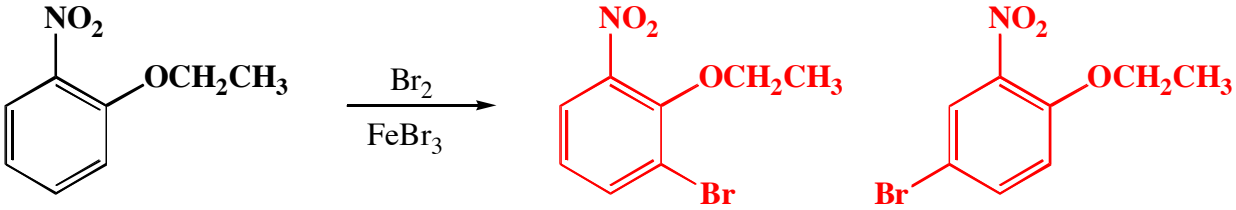
12. (34 pts.) Write the predominant product or products that will occur for each transformation. Assume each reagent only adds once to the ring. If predominantly ortho/para products are predicted, you must draw both.

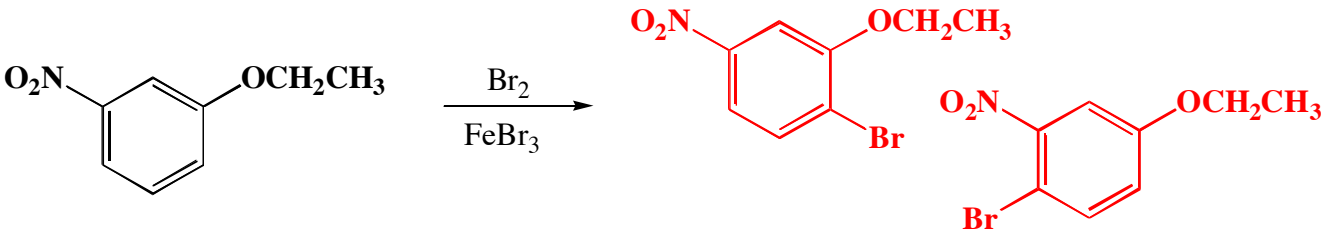


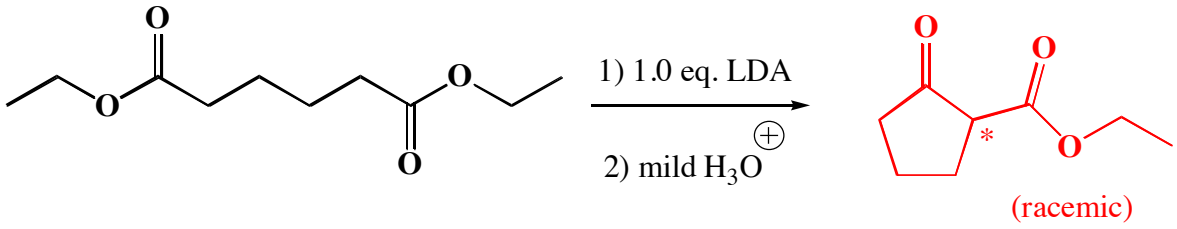
13. (23 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, mark the chiral center with an asterisk "*" and write "racemic" under the structure. If there is an aldol reaction, draw the product before any dehydration takes place. If an ortho/para mixture is predicted, you must write both.**



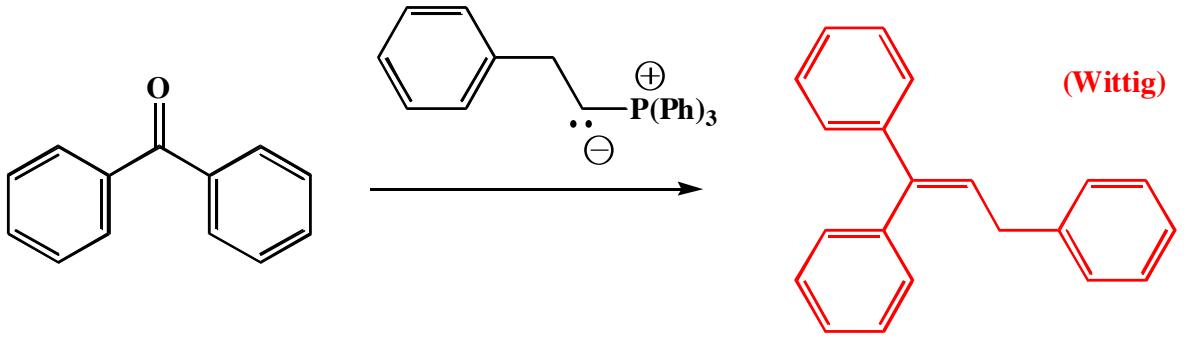




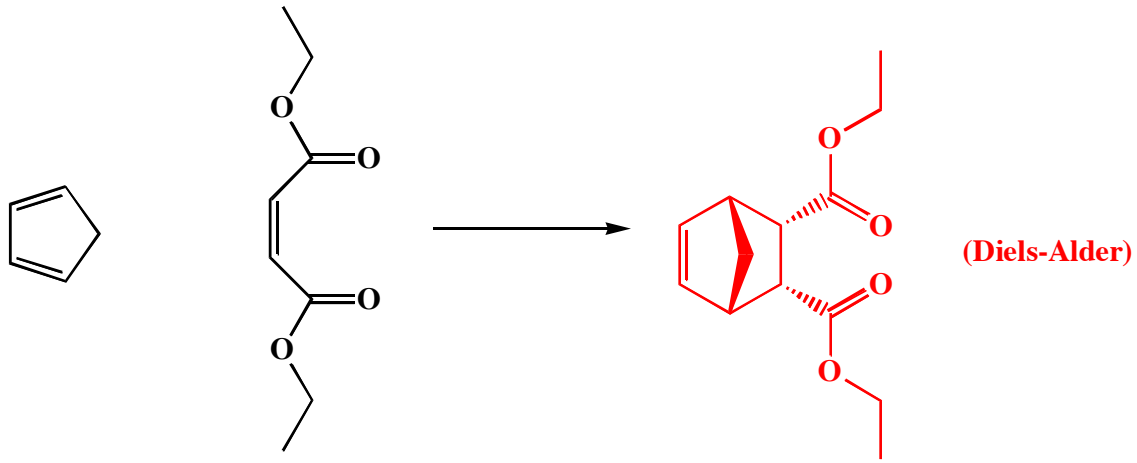




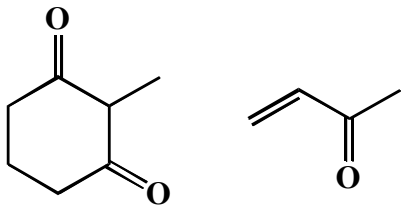
14. (16 pts.) You might find these are harder so take your time. Write the predominant product or products that will occur for each transformation. **If a new chrial center is created and a racemic mixture is formed, mark the chiral center with an asterisk "*" and write "racemic" under the structure. If ortho/para products are made, you must draw both. Note, for this problem, aldols can dehydrate if heated in dilute acid.**



(Wittig)

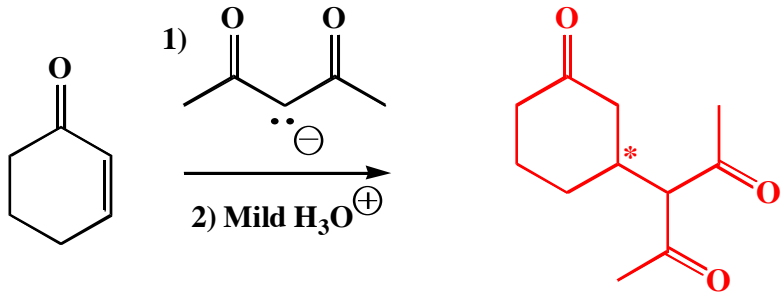


(Diels-Alder)



(Robinson)

(racemic)

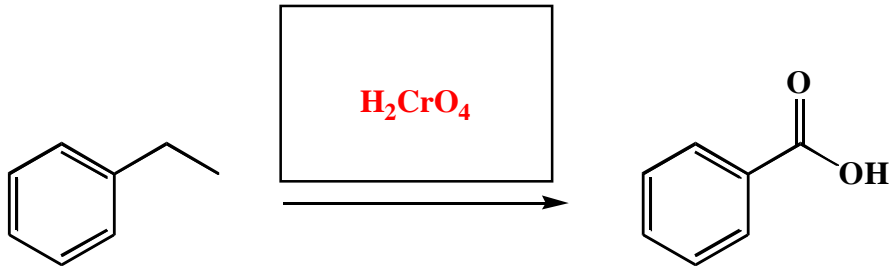


(Michael

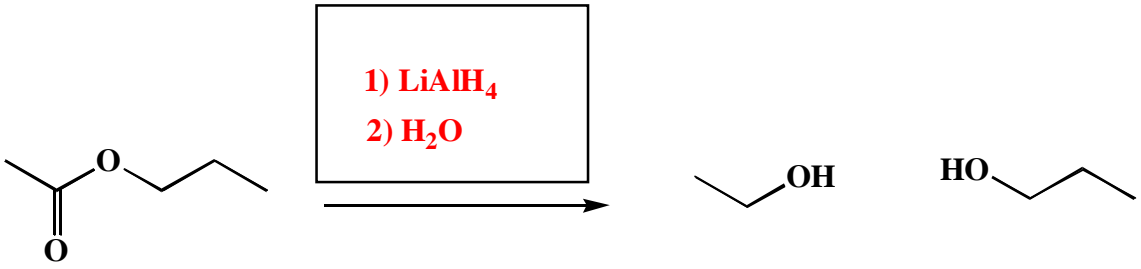
(racemic)

15.(3 pts each) Fill in each box with the reagents required to bring about the reactions indicated.

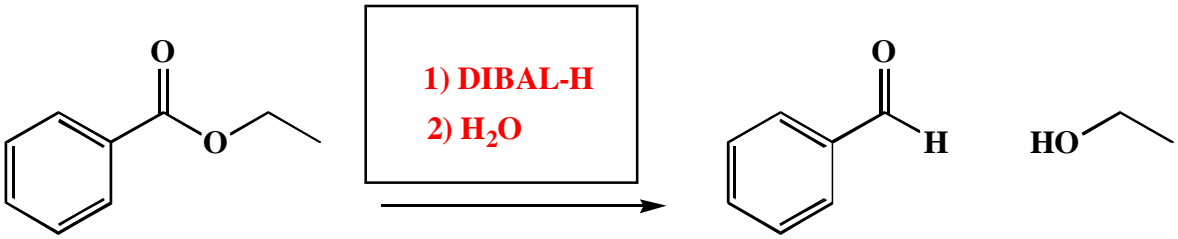
A.



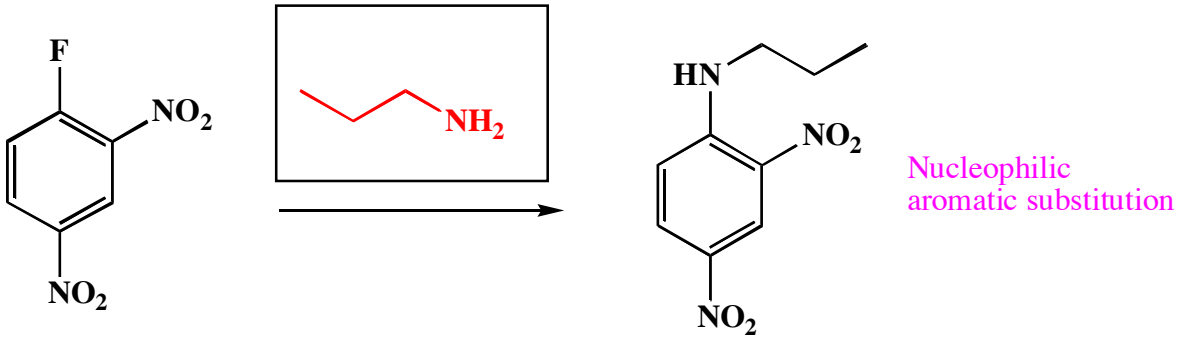
B.



C.

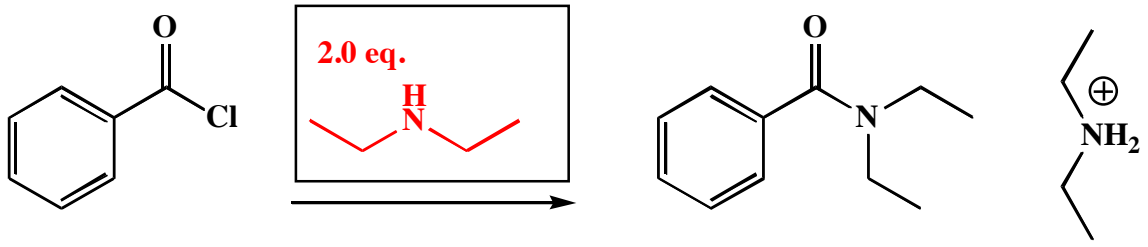


D.

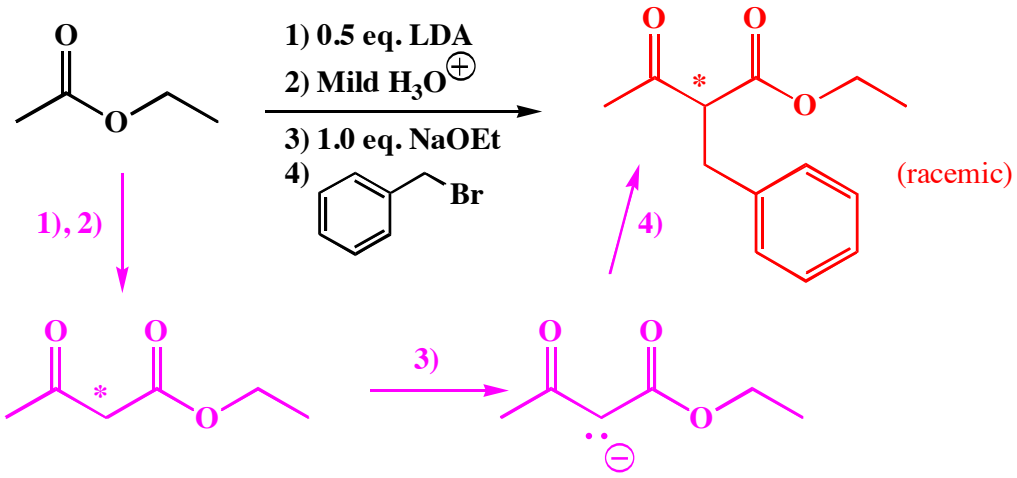


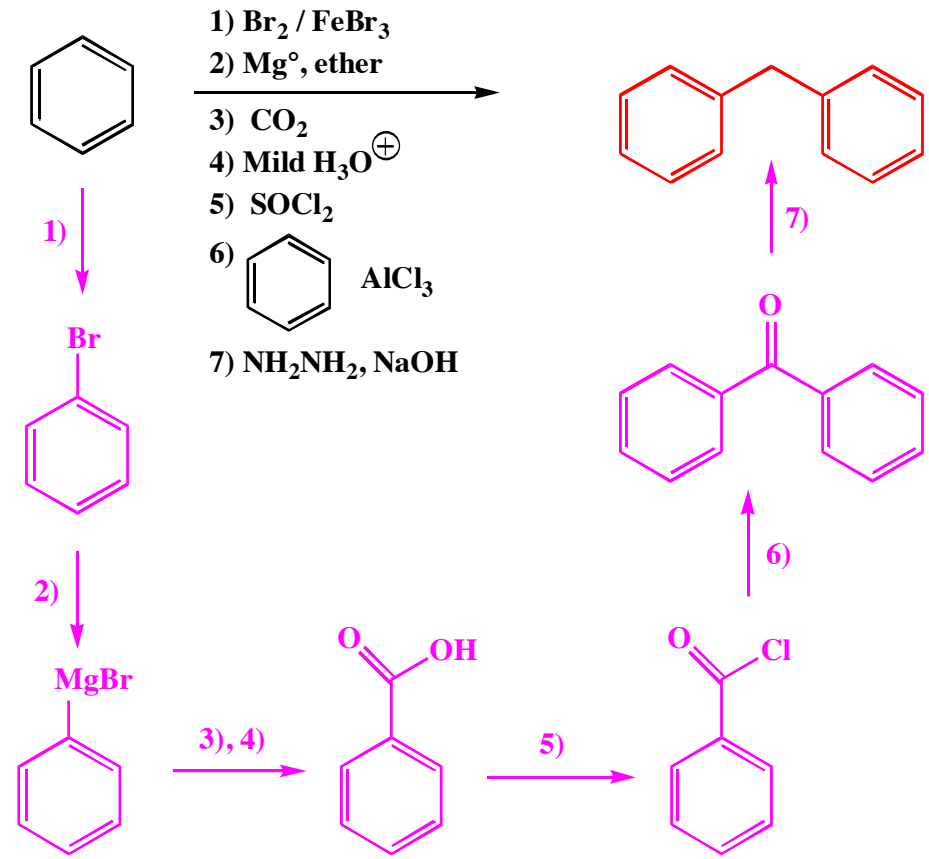
Nucleophilic aromatic substitution

E.



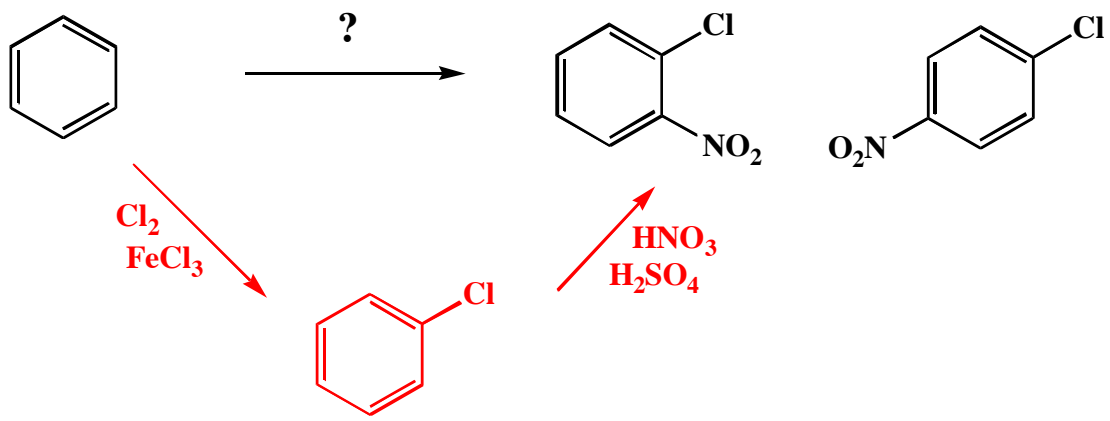
16. (11 pts.) For the following series of reactions, write the predominant product you would expect. You do NOT need to draw intermediates synthesized along the way, just the final product. You can use the back of the page as scratch paper if that will help. If a racemic mixture is produced, put an asterisk "*" next to any chiral centers and write "racemic".





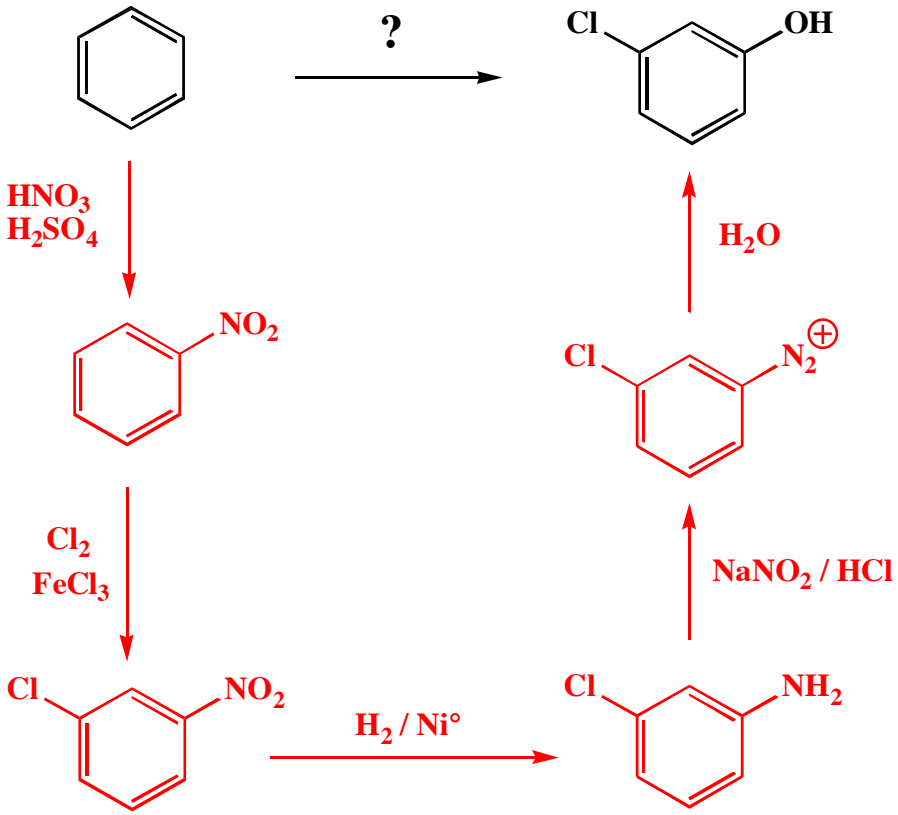
17. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

(4 pts)



This was just a warmup

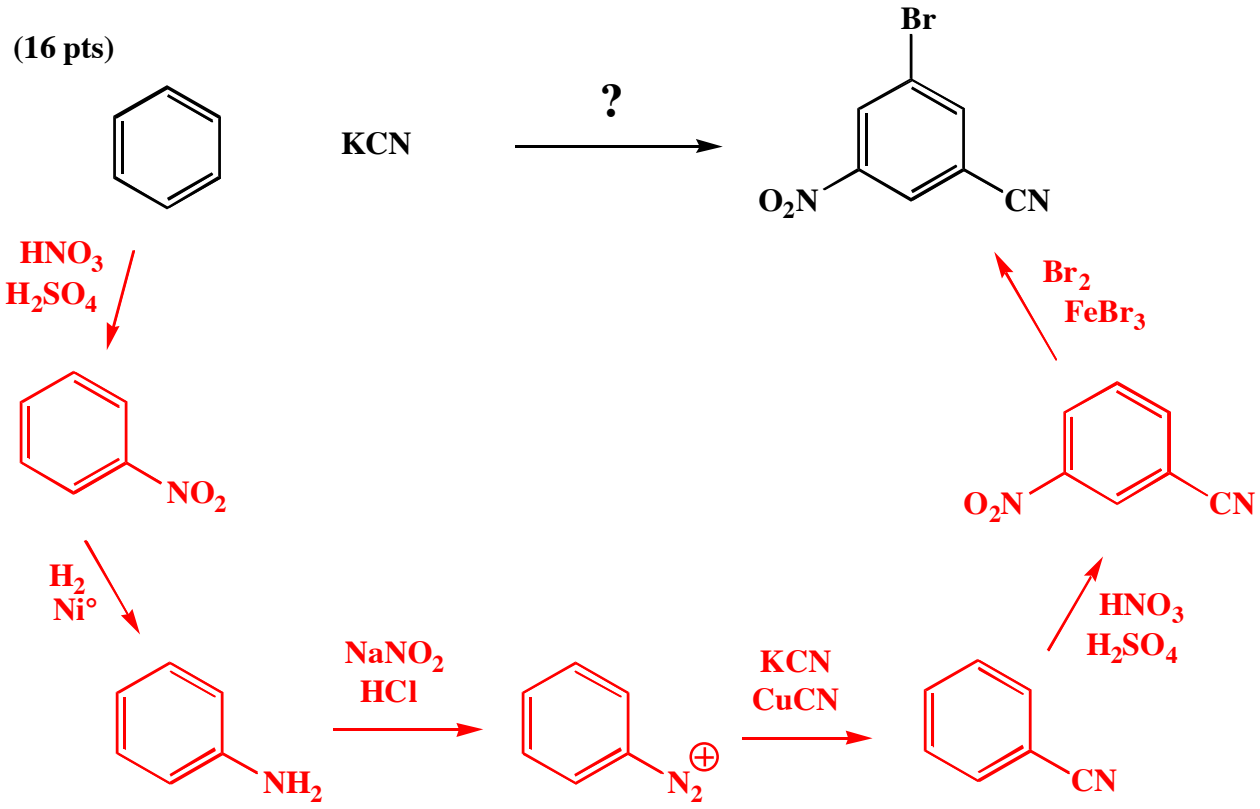
(13 pts)



Recognize that the product has the Cl atom and OH group in a meta orientation, meaning this could not be the major product from a simple sequence of reactions from benzene. **Recognize** further that the only way you know how to place an OH group on an aromatic ring is by adding water to a diazonium. Therefore, propose an initial nitration followed by chlorination to give the correct meta orientation. Reduction of the nitro group, reaction with HONO and finally addition of water gives the final product.

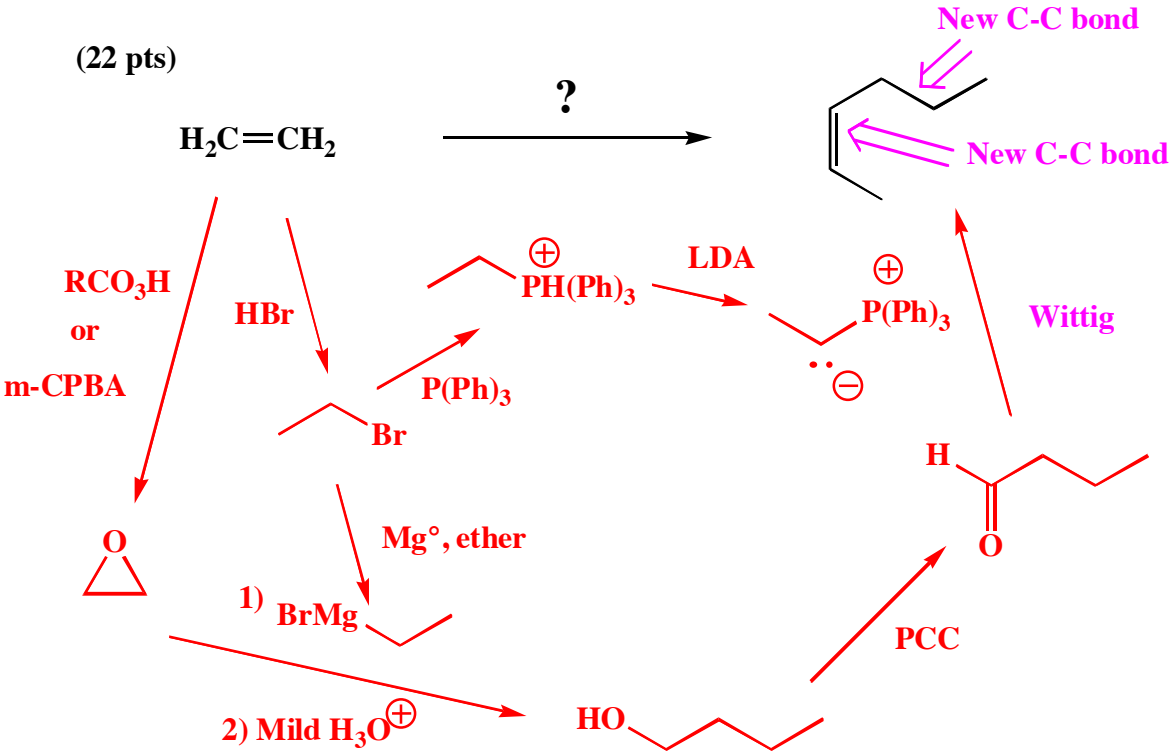
17.(cont.) Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

(16 pts)



Recognize that the product has two bad groups meta to the Br atom. Predict that the last step can be bromination. **Recognize** further that the cyano group would direct a nitro group meta, so predict nitration as the second to last step. That leaves cyanobenzene as a key intermediate to synthesize, and the only way you know to add a cyano group is through the sequence of nitration, reduction, HONO and the Sandmeyer reaction using KCN/CuCN.

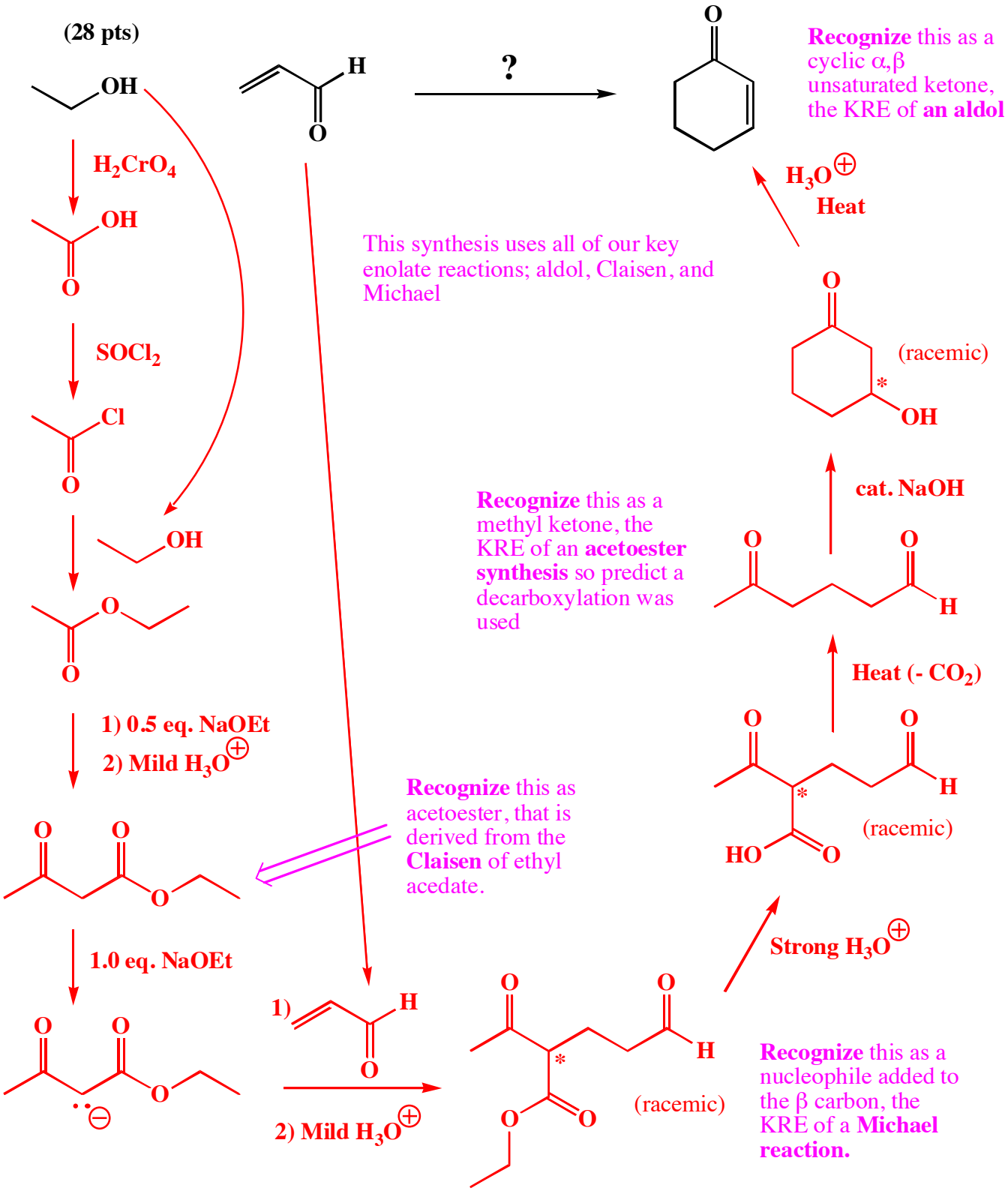
17.(cont.) Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!



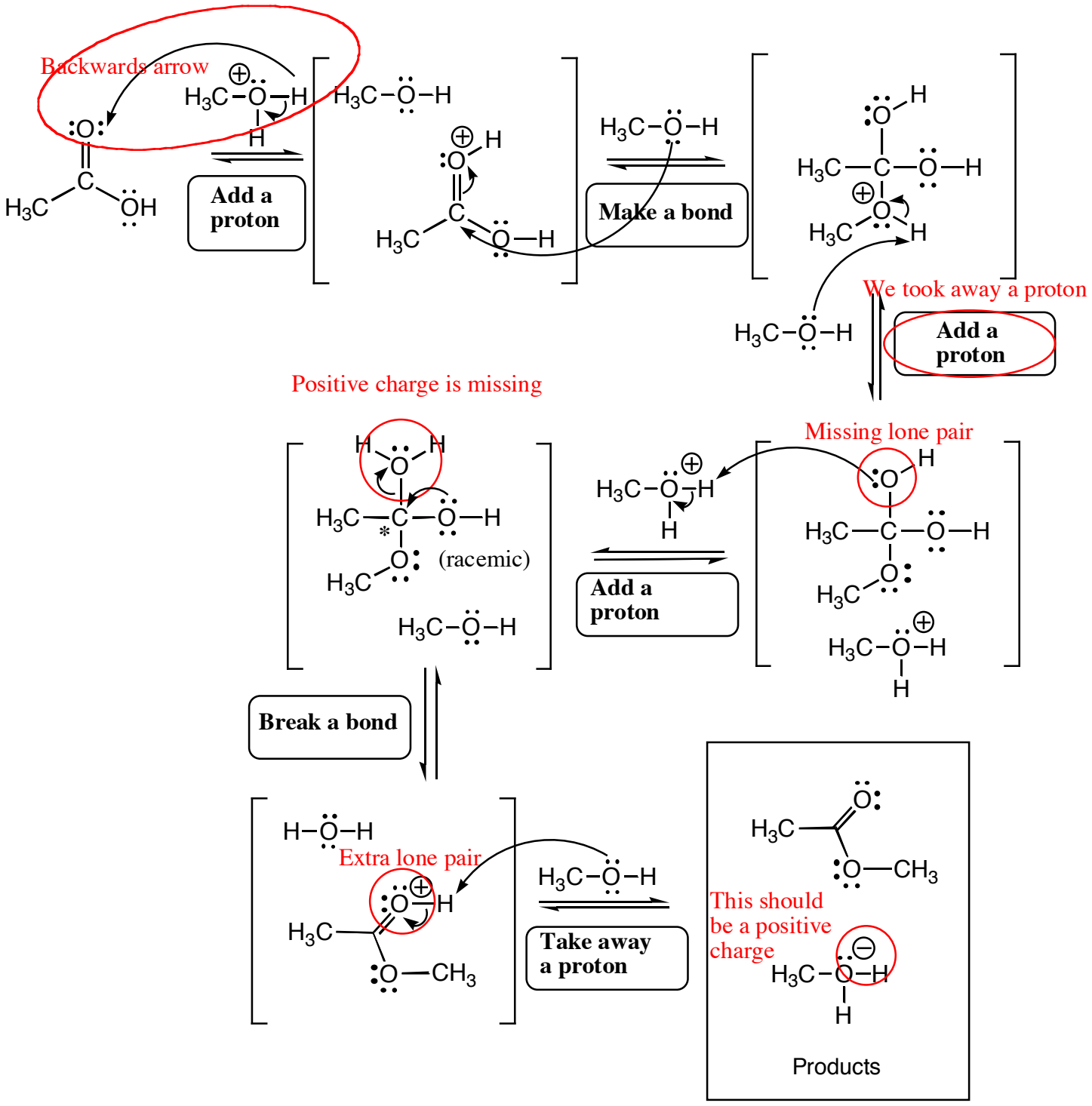
Recognize the product as a Z alkene, the KRE of a Wittig reaction. You could use two different combinations of aldehydeand Wittig reagent, I chose to illustrate the process using butanal and the ethyl Wittig reagent as the last step. **Recognize** that the ethyl Witting could be derived from bromoethane, that in turn can be made in one step from ethylene using HBr. **Recognize** that butanal could be made from the PCC oxidation of 1-butanol, which in turn can be derived from the reaction of ethyl Grignard with the epoxide made from ethylene using a peracid.

This reaction sequence illustrates how larger molecules can be built up readily from very small ones using the chemistry you have learned.

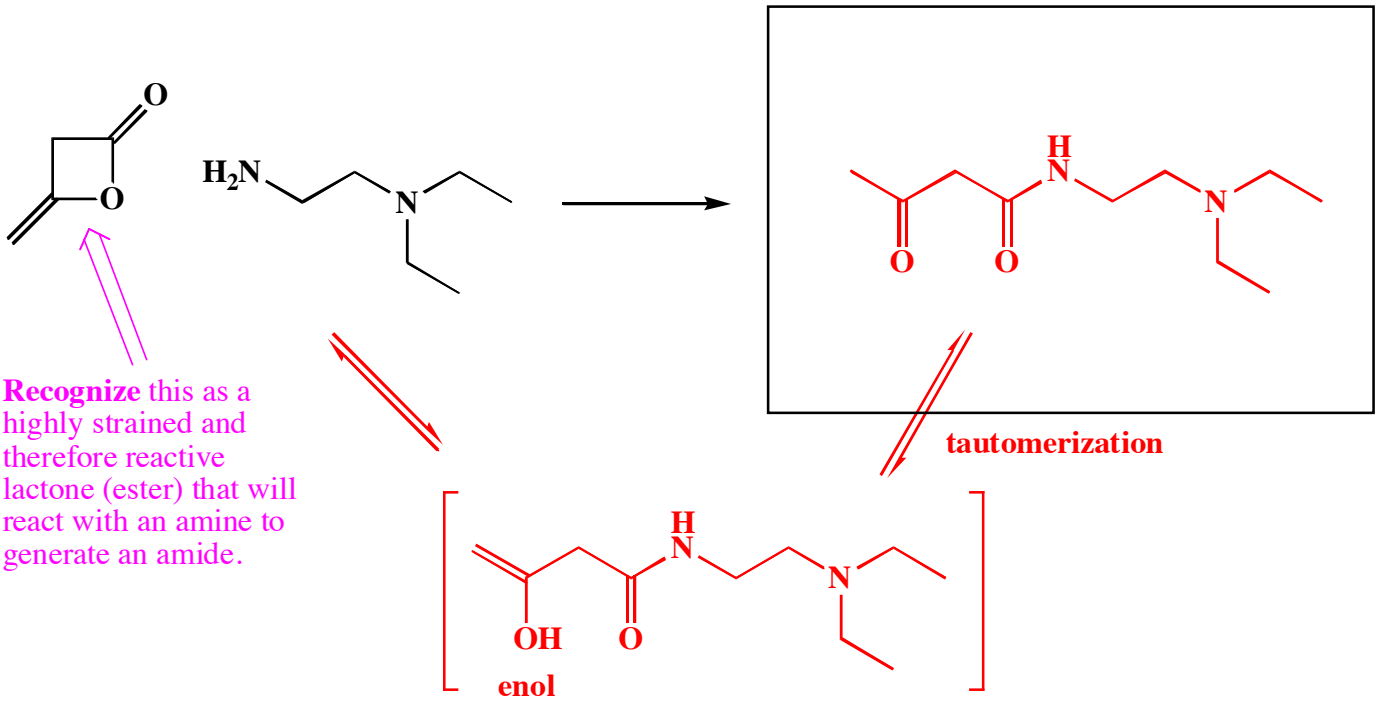
17.(cont.) Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!



18. (12 points) We decided to try something new. The following mechanism for Fischer esterification was on last year's final. One of the students in the course named Joe Bag O'Doughnuts made 6 mistakes. **Draw a circle around each of the 6 mistakes.** I suggest you just start from the beginning and pretend you were writing the mechanism, then look at each step to find the errors. You do not have to write what poor Joe did wrong, you only need to draw 6 circles.



19 (6 pts) Bonus question. This is part of the synthesis of the anticancer drug sunitinib. You have learned enough to predict the product if you recognize the key functional groups and work through the chemistry. In the box provided, write the structure of the final product of the following reaction.



Recognize this as a highly strained and therefore reactive lactone (ester) that will react with an amine to generate an amide.

Recognize this initial product as an enol, that will undergo tautomerization to give the ketone final product