NAME (Print): _____

SIGNATURE: _____

Chemistry 310N
Dr. Brent Iverson
Final Exam
May 14, 2010

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.

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		(28)
2		(11)
3		(20)
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8		(30)
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15		(12)
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17		(12)
18		(16)
19		(25)
20		(16)
Total		(400)
%		
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HW		
Total Grade		

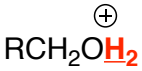
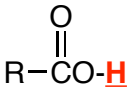
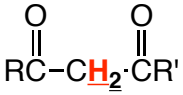
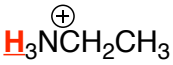
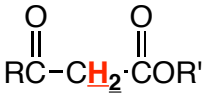
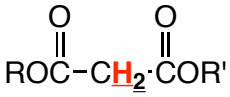
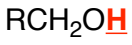
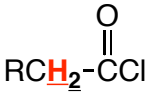
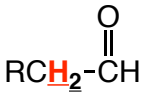
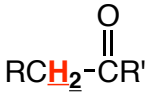
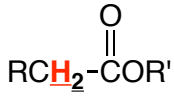
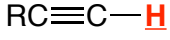
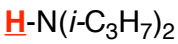
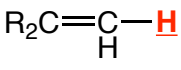
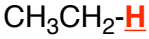
(HW score + Exam Grade) ⟹

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
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

Signature_____ Pg 1 _____(28)

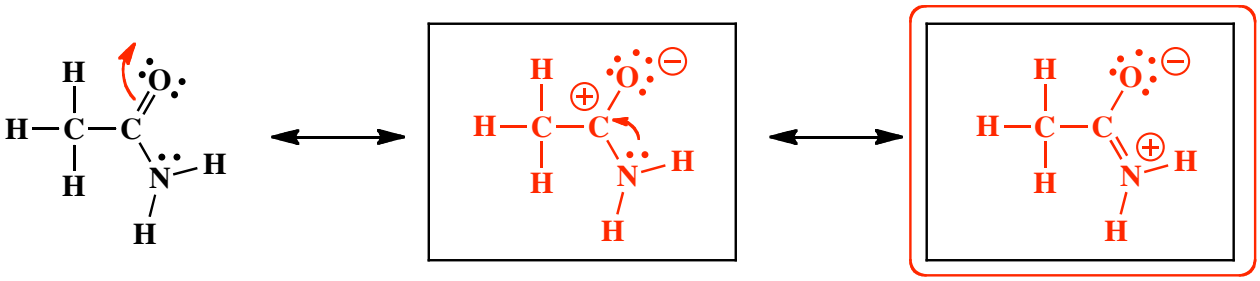
1. (16 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minumum of 7 key points here.

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**.

What is the most important question in chemistry? ⟸ **Notice This**

Where are the electrons?

2. (10 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. You do not need to draw arrows on the structures, but you can if it helps you.

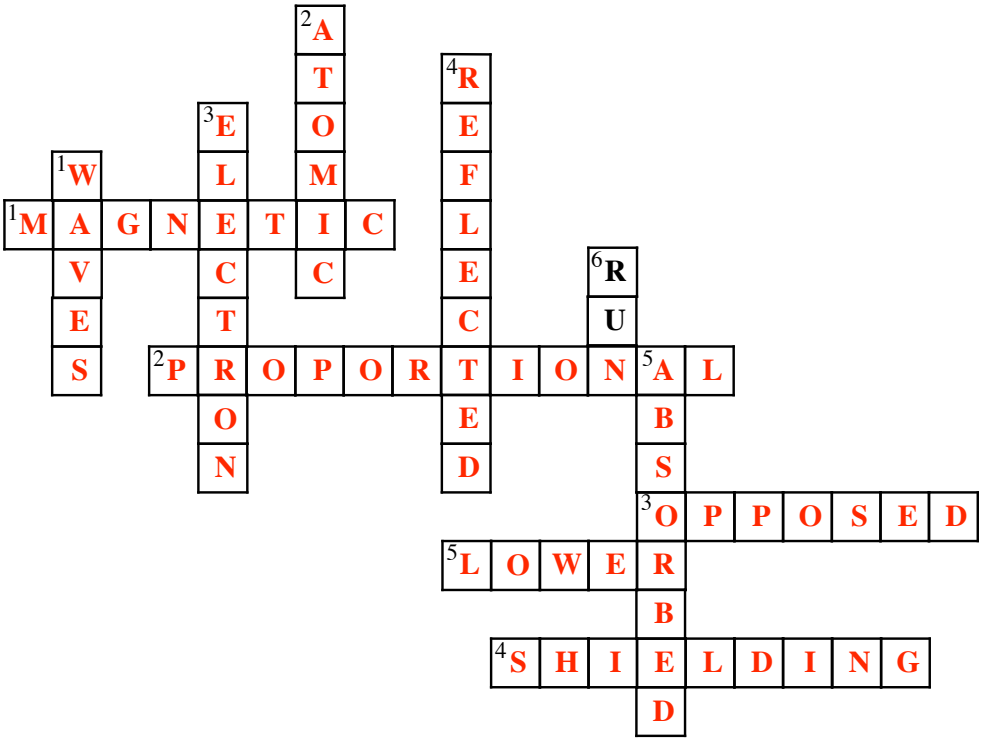


3. (2 pts) An important feature of an amide bond is that there is a partial double bond between the carbonyl carbon and nitrogen. For the contributing structures you drew in Problem **2.**, draw a circle around the one that predicts this partial double bond.

⇑ ⇑ ⇑

Notice This

4. (11 pts)Complete the following crossword puzzle



Across

The key to the NMR experiment is that in a strong external **1)** _____ field, the difference in energy between nuclear spin states is **2)** _____ to that field. Electron density is induced to move in a strong external magnetic field, and this movement induces a field that is **3)** _____ to the external magnetic field. This has the effect of **4)** _____ the underlying nuclei from the external magnetic field. The signal for an H atom with greater electron density around it will come at **5)** _____ ppm in an NMR spectrum compared to a similar H atom with less electron density.

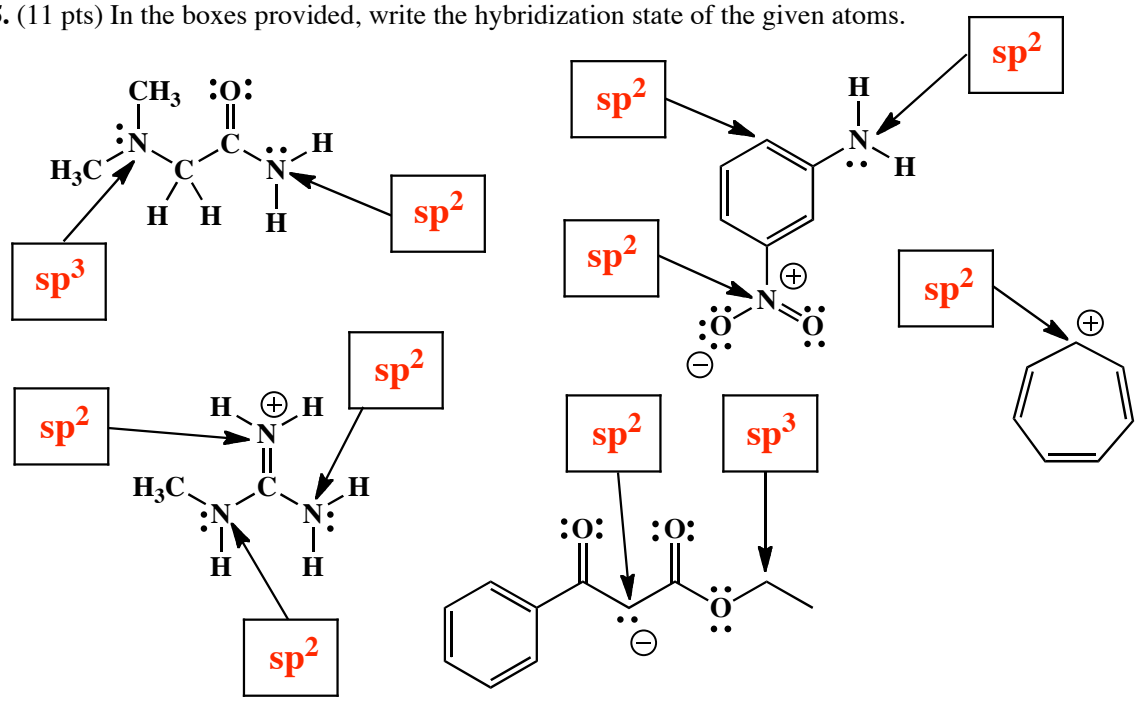
Down

Think of electron density as **1)** _____, in which you can get extra stability when they add constructively, and you lose stability when they cancel each other (add destructively). You generate as many new molecular orbitals as **2)** _____ orbitals used to create them.

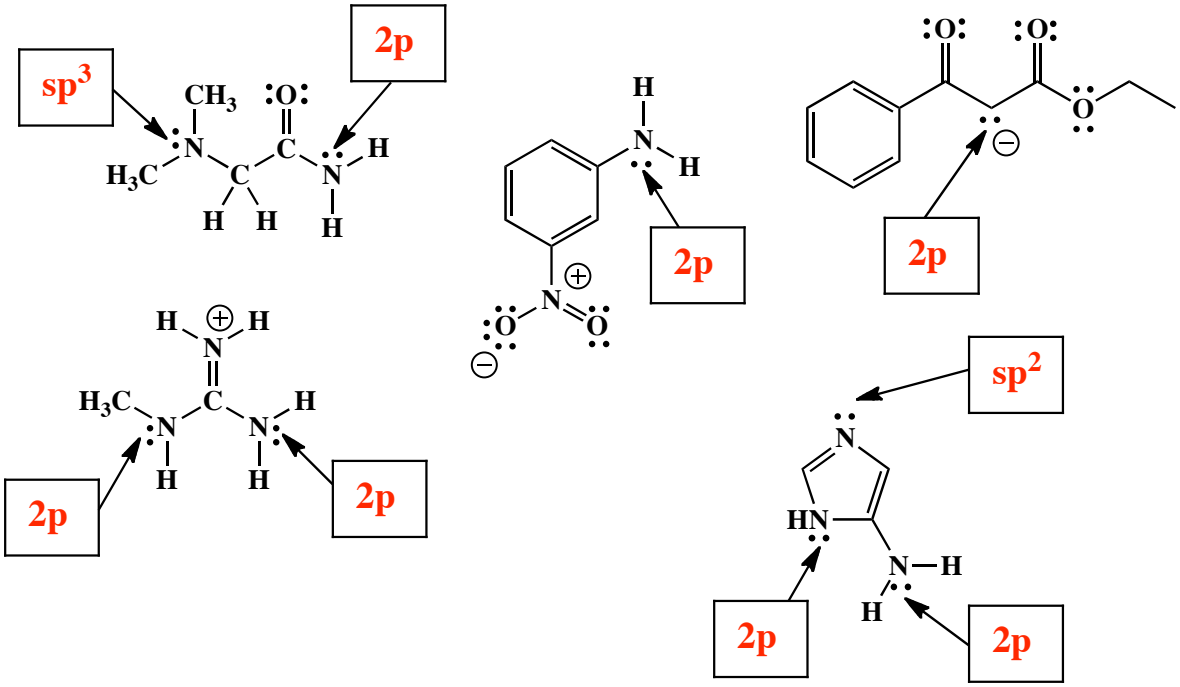
Absorbance of a photon by a molecule corresponds to promotion of a(n) **3)** _____ from a filled orbital to an unfilled orbital. Molecules appear to our eye to be a combination of the wavelengths **4)** _____ (not **5)** _____).

A great way to stay fit and healthy for the rest of your life is to 6)_____ every chance you get.

5. (11 pts) In the boxes provided, write the hybridization state of the given atoms.

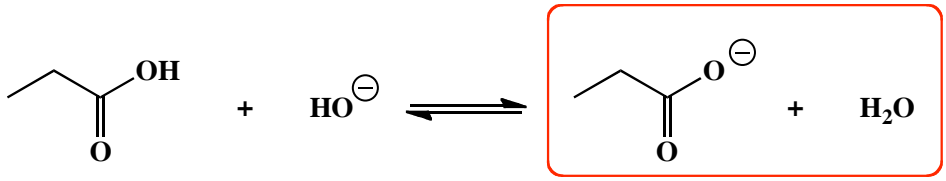


6. (9 pts) In the boxes provided, according to the valence bond approach, write the type of atomic orbital that contains the indicated lone pair of electrons..

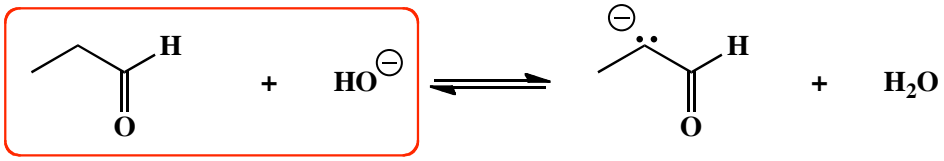


7. (2 pts each) For the following acid-base reactions, circle the side of the equation that is favored at equilibrium.

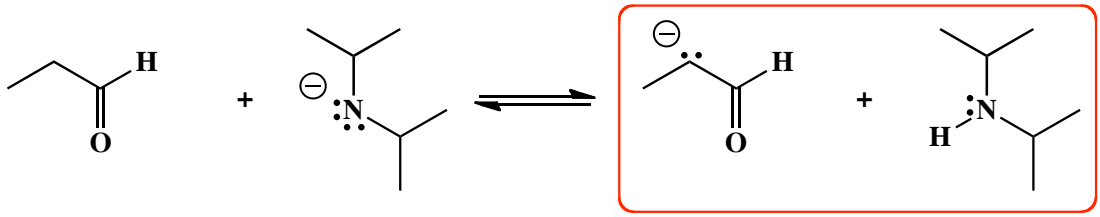
A)



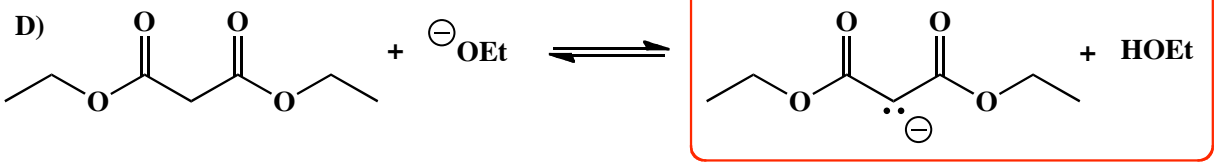
B)



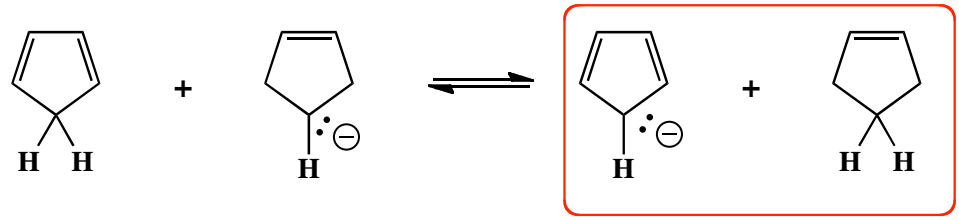
C)



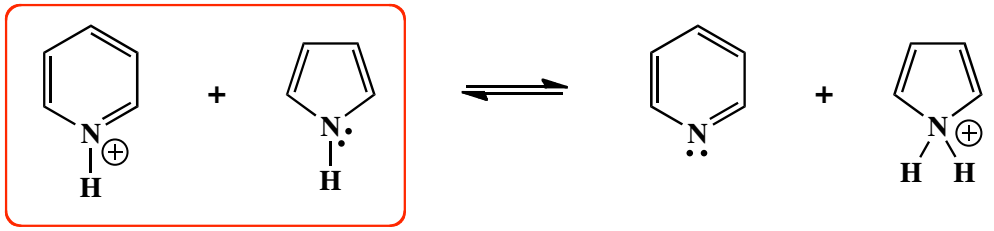
D)



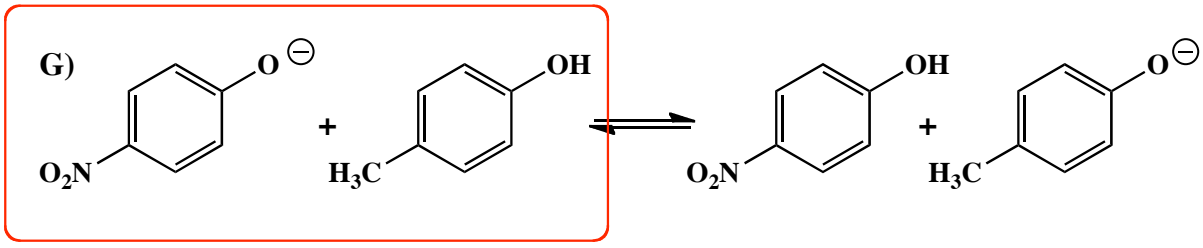
E)



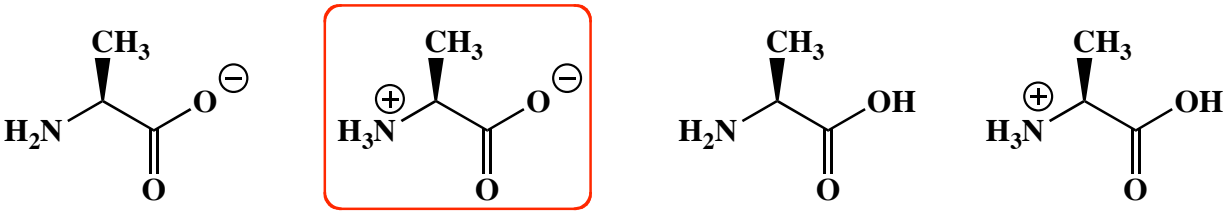
F)



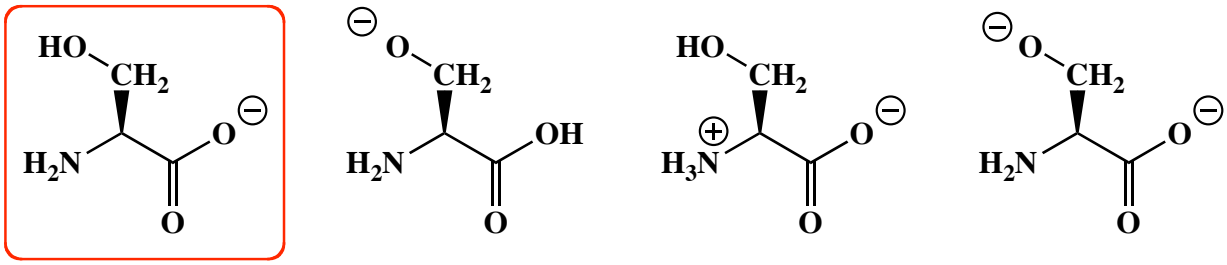
G)



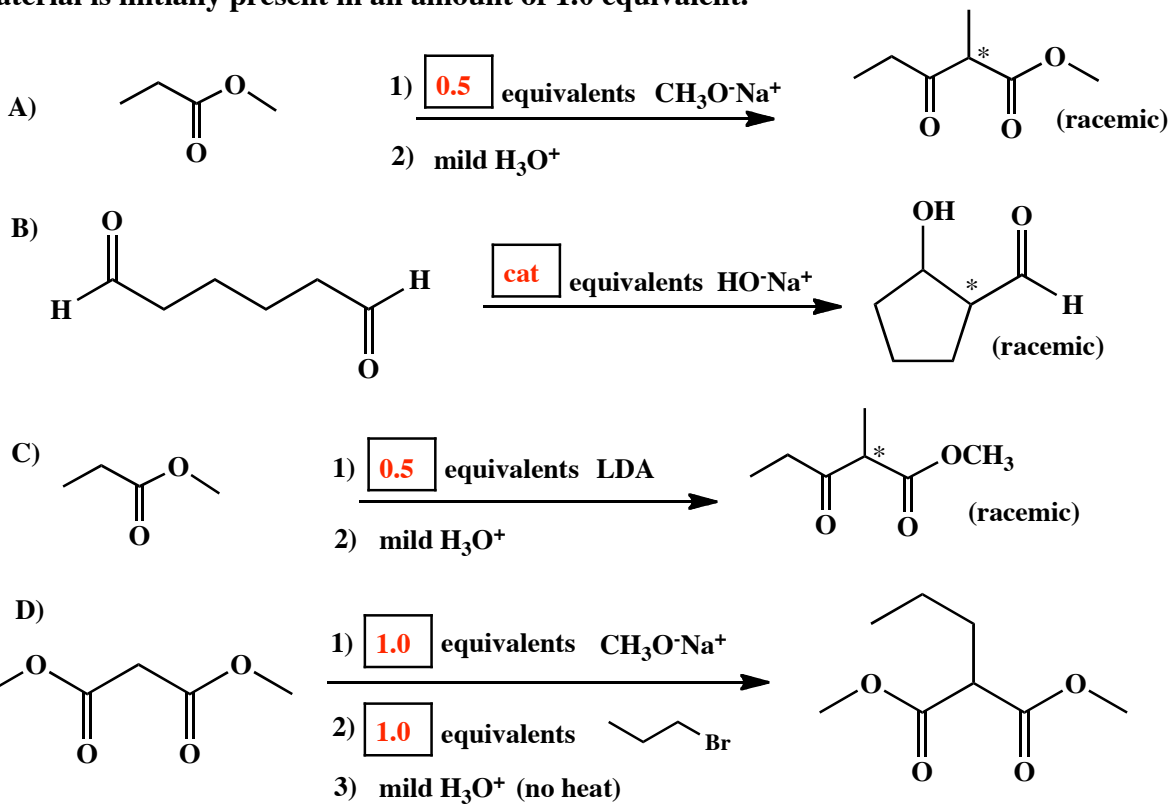
8. (8 pts) **A) Circle the predominant species presnt at pH 7.0**



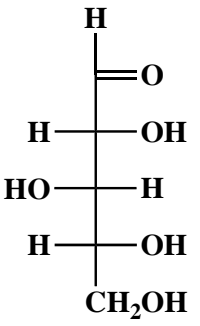
B) Circle the predominant species present at pH 11.0



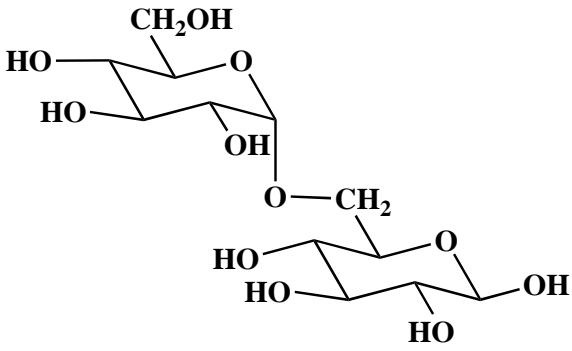
9. (2 pts each) In each of the boxes over an arrow, **write the minimum number of equivalents** of the specified reagent required to carry out the reaction shown **to completion**. If only a catalytic amount is needed, write **"CAT"**. Note: **You must assume the carbonyl compound starting material is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



10. (2 pts each) I know you were wondering how we were going to test the carbohydrate material. Here is what we came up with. Yes, it looks a lot like last year's test, but we changed the structures. **For the following structures, draw a circle around the terms that provide the most accurate description.**

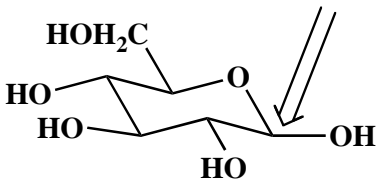


Aldohexose
Ketohexose
Aldopentose
Ketopentose
Pointy toes
Fred



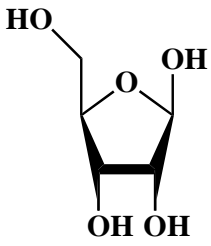
α-1,6-Glycosidic bond
β-1,6-Glycosidic bond
α-1,5-Glycosidic bond
β-1,5-Glycosidic bond
α-1,4-Glycosidic bond
β-1,4-Glycosidic bond
α-1,3-Glycosidic bond
β-1,3-Glycosidic bond
α-1,2-Glycosidic bond
β-1,2-Glycosidic bond
Fred

Monomeric carbon
Anomeric carbon
Polymeric carbon
Aldehyde carbon
Fred

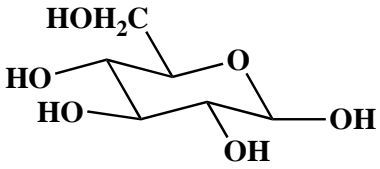


This structure is a:
Furanose
Pyranose
Comatose
Bloody nose
Fred

This molecule is a:
Aldohexose
Ketohexose
Aldopentose
Ketopentose
Pointy toes
Fred

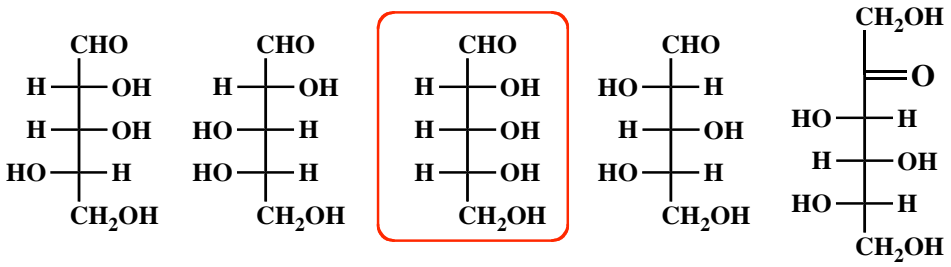


This structure is a:
Furanose
Pyranose
Comatose
Bloody nose
Fred



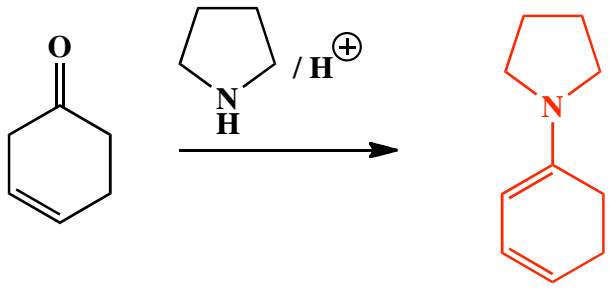
α-D-Glucose
β-D-Glucose
βββ-D-Glucose
ΔΓ-D-Glucose
Fred

11. (5 pts.) All of the following structures represent an L monosaccharide except one. Circle the single D monosaccharide.

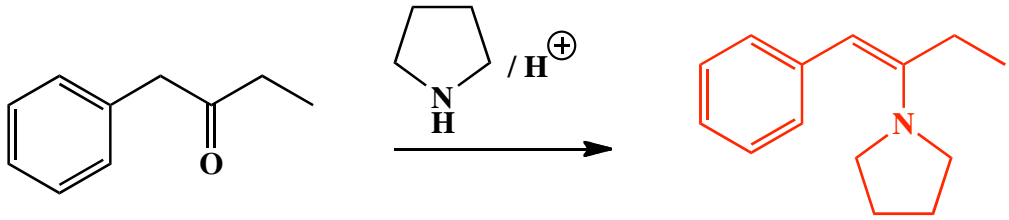


12. (12 pts) Here is an "apply what you know" problem. Given everything we have discussed in the last few weeks, draw the enamine that you predict will form as the predominant one when each unsymmetrical ketone is treated with pyrrolidine in mild acid and allowed to equilibrate.

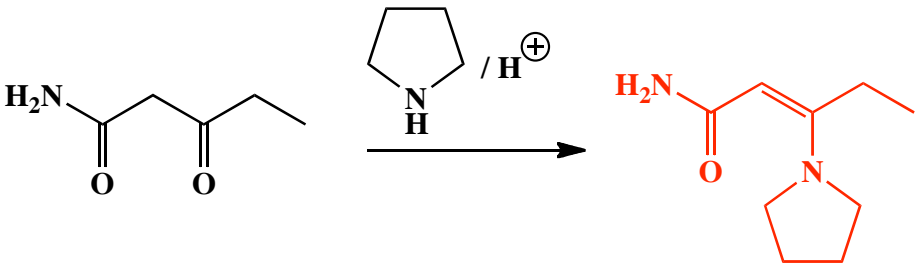
A.



B.



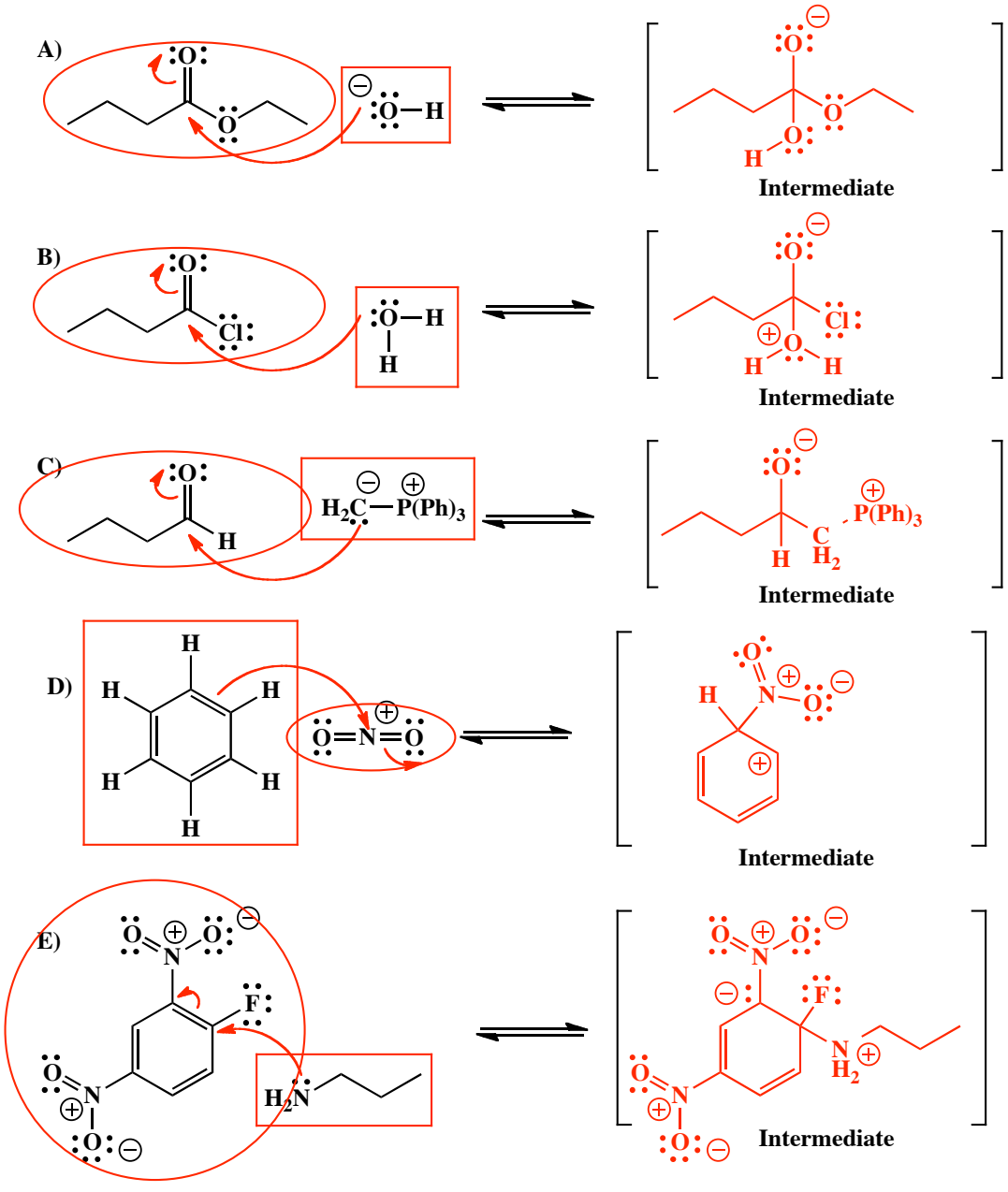
C.



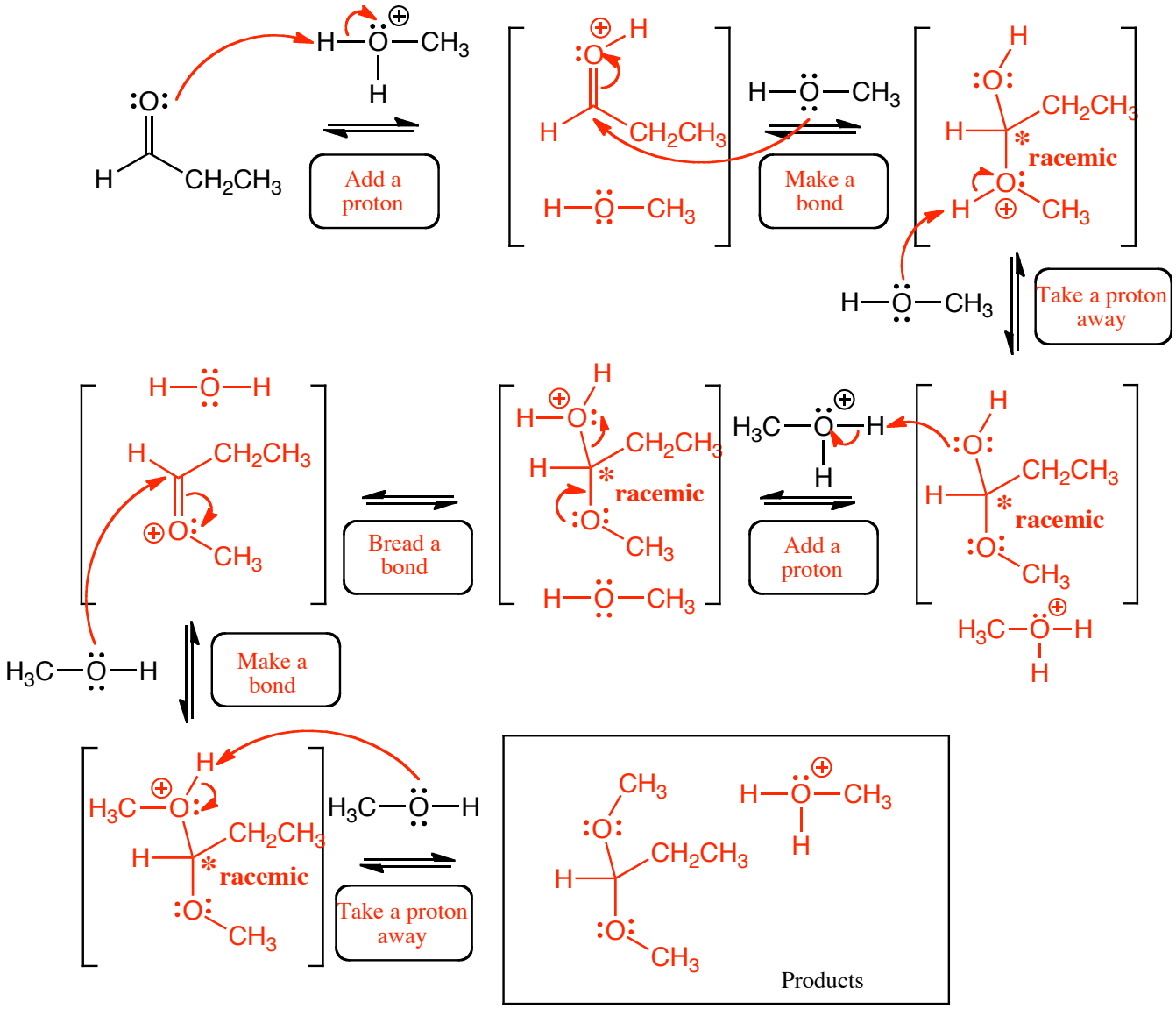
D. In one sentence, describe the common feature of each of the products you drew that make them the predominant ones.

In each case, the more stable enamine forms so that the new double bond is in conjugation with other pi bonds, increasing pi electron delocalization.

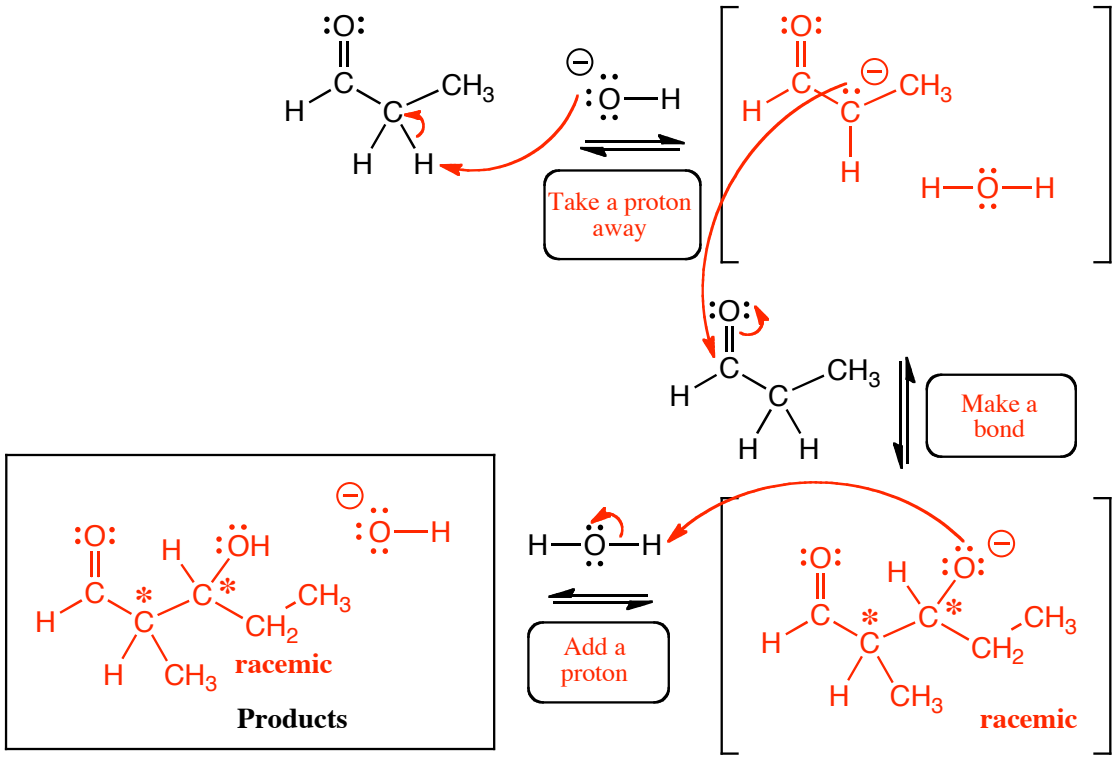
13. (30 points) Many of the reactions we have learned this semester involve steps with nuclephiles reacting with electrophiles. For the following examples of steps in mechanisms we have seen this semester, **1) Draw the intermediate that will be formed when the two molecules react. 2) Draw all formal 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.



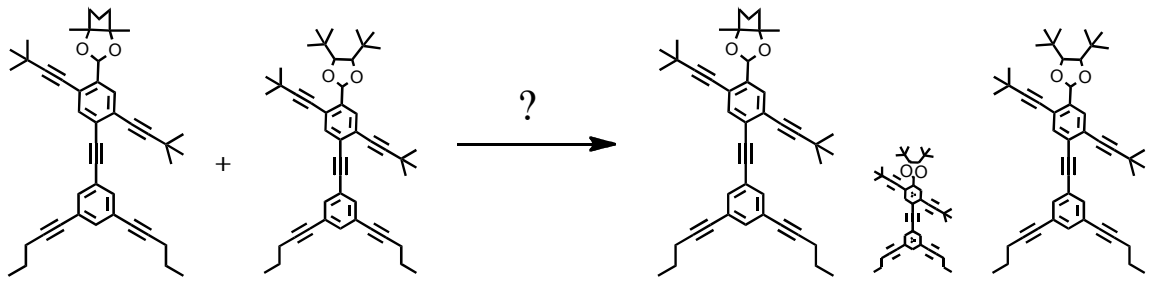
14. (36 pts total) Complete the following mechanism for acetal formation. Make sure to show all lone pairs, all formal charges and use arrows to indicate the flow of all electrons. You must draw all products that are made in each step. Fill in each box with the appropriate phrase such as "Make a bond", etc. This should look familiar, as it is identical to the mechanism sheet handed out in class. **Put an asterisk (*) next to any chiral center and write "racemic" wherever appropriate.**



15. (15 pts total) Complete the following mechanism for the following aldol reaction. Do not dehydrate the product. Make sure to show all lone pairs, all formal charges and use arrows to indicate the flow of all electrons. You must draw all products that are made in each step. Fill in each box with the appropriate phrase such as "Make a bond", etc. **Put an asterisk (*) next to any chiral center and write "racemic" wherever appropriate.**

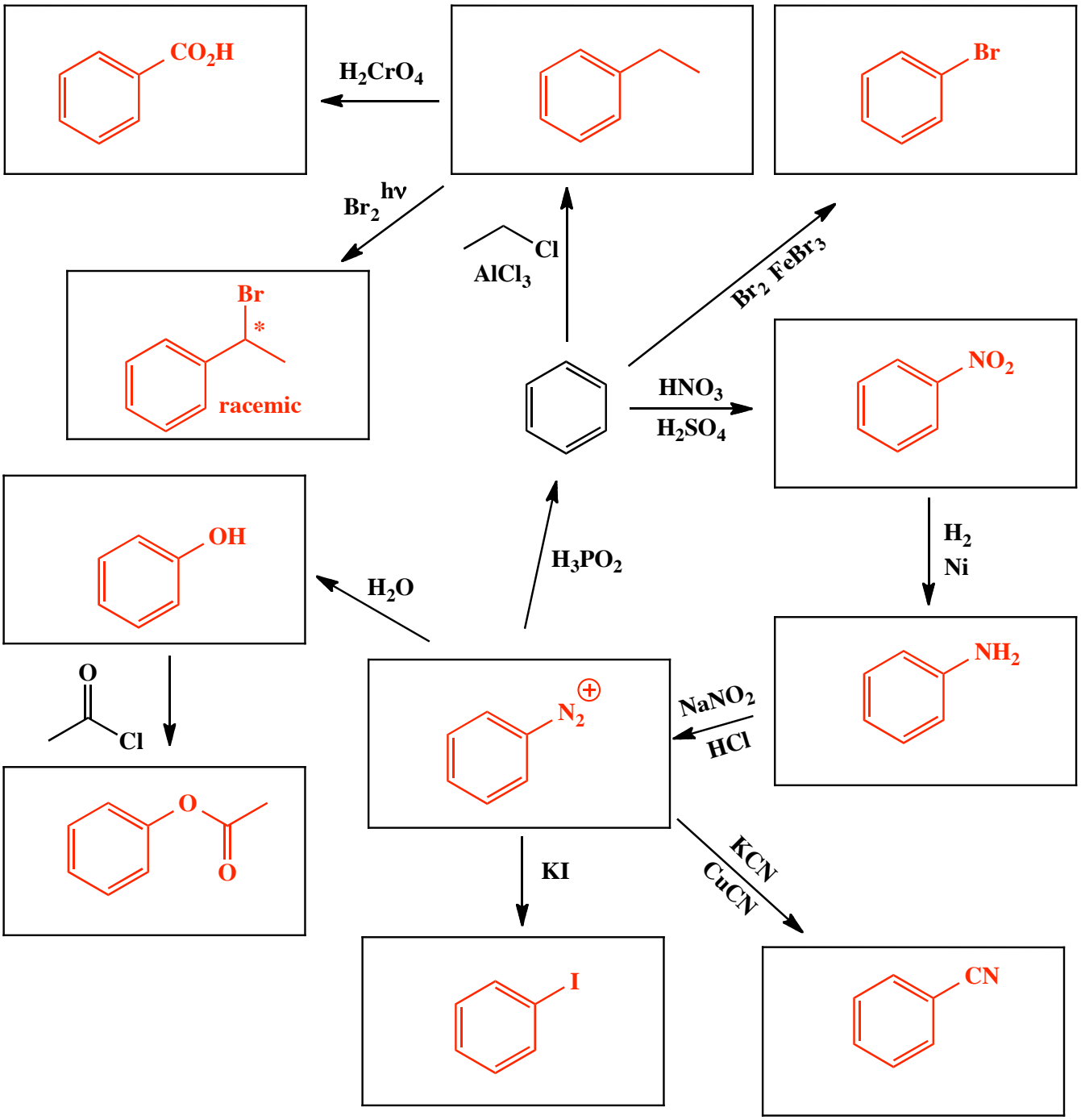


Synthesis Question for Chemistry Nerds

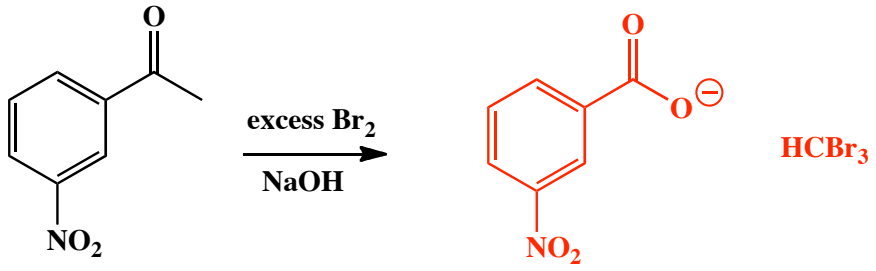


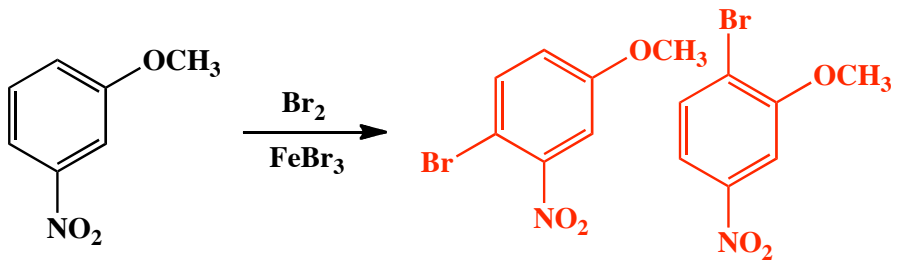
I realize it is a pretty nerdy form of humor, but what the heck, we are chemists.

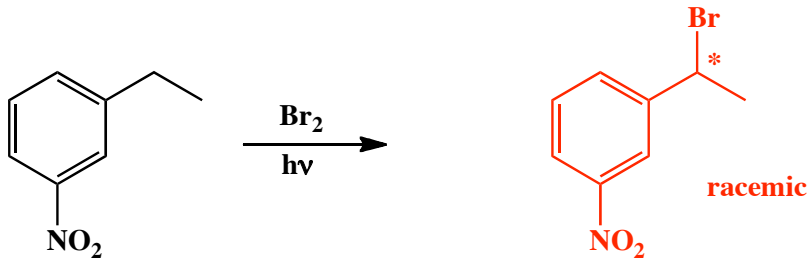
14. (3 or 5 points each) Fill in the boxes with the predominant product formed under the reaction conditions. If a new chiral center is formed in a racemic mixture, put an asterisk (*) next to it and write "racemic". If ortho/para products are created, you must draw both.

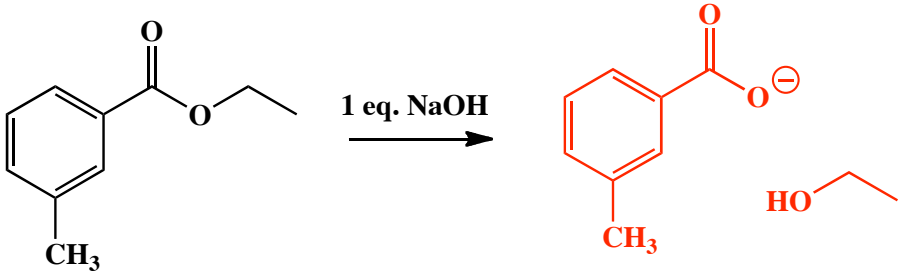


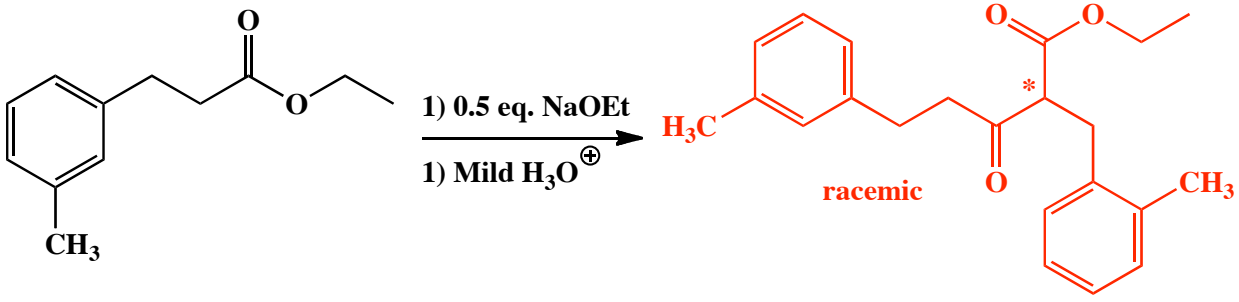
15. (3 or 5 points each) **DRAW ALL OF THE CARBON CONTAINING products formed under the reaction conditions.** If a new chiral center is formed in a racemic mixture, put an asterisk (*) next to it and write "racemic". If ortho/para products are created, you must draw both. NOTICE THESE DIRECTIONS ARE SLIGHTLY DIFFERENT THAN THE PREVIOUS PAGE!!!! (YOU MIGHT WANT TO READ THE FIRST SENTENCE AGAIN)



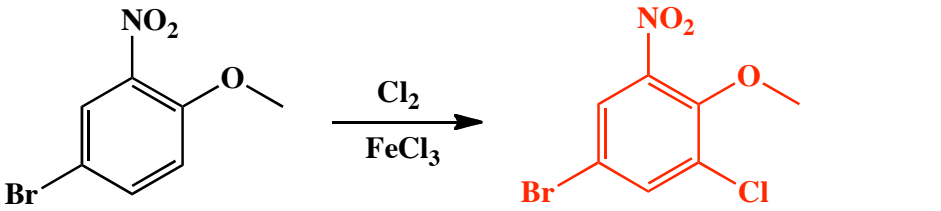


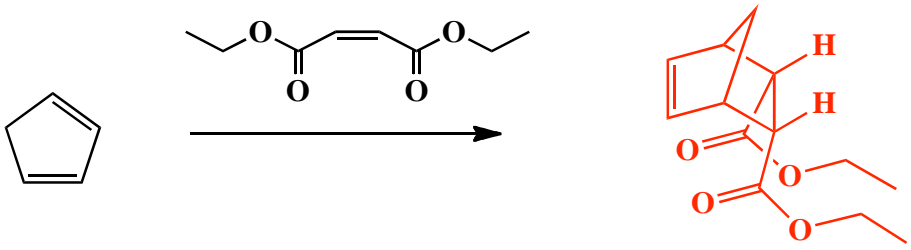




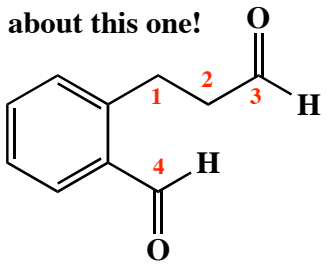


15. (3 or 5 points each) Fill in the boxes with the predominant product formed under the reaction conditions. If a new chiral center is formed in a racemic mixture, put an asterisk (*) next to it and write "racemic". If ortho/para products are created, you must draw both.





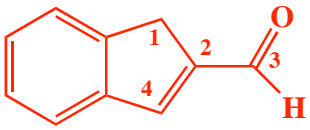
Think about this one!

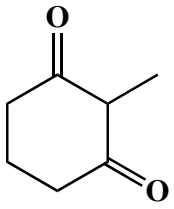


1) cat. NaOH

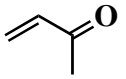
2) HCl / heat

(assume dehydration takes place)



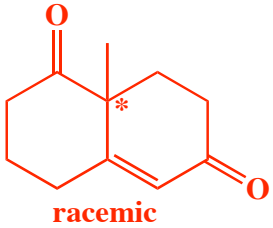


1) 1.0 eq. NaOEt

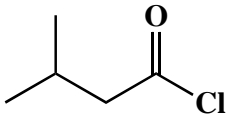
2) 

3) HCl / heat

(assume dehydration takes place)

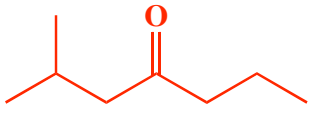


racemic

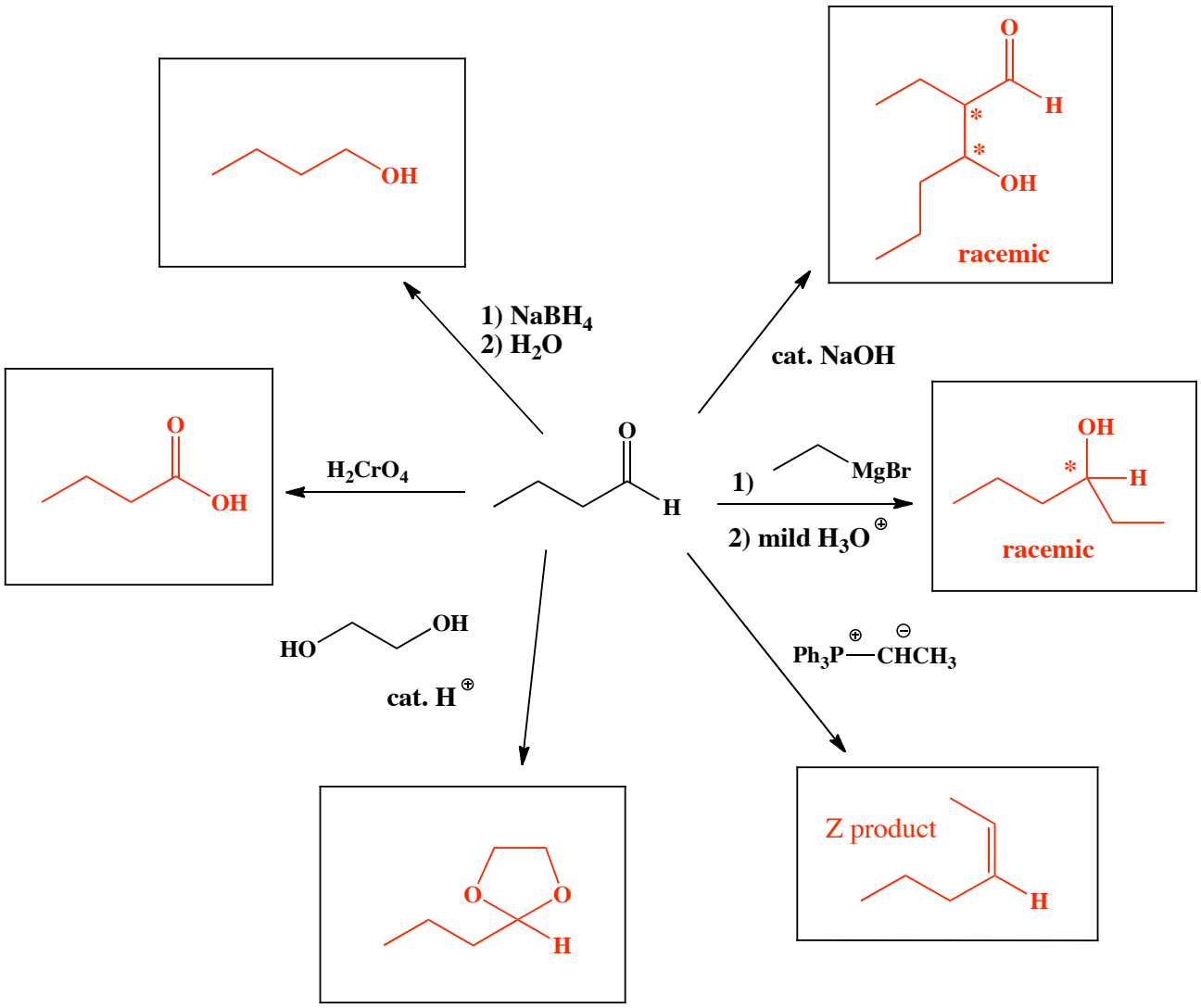


1) $(CH_3CH_2CH_2)_2CuLi$

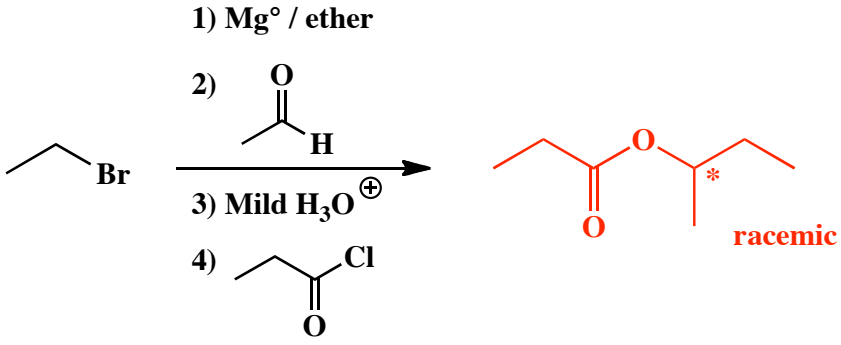
2) H_2O

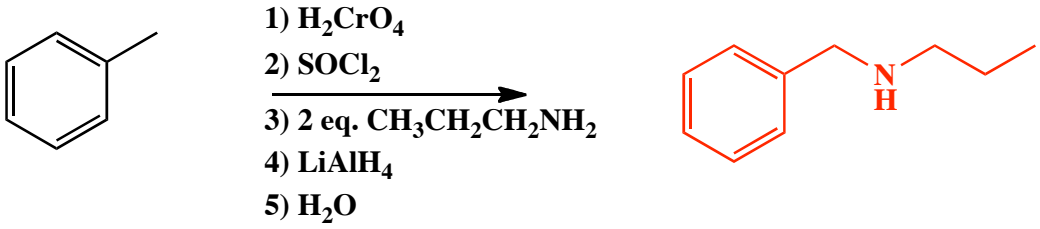


15. (3 or 5 points each) Fill in the boxes with the predominant product formed under the reaction conditions. If a new chiral center is formed in a racemic mixture, put an asterisk (*) next to it and write "racemic". If there is an aldol reaction on this page DO NOT DEHYDRATE IT!!!



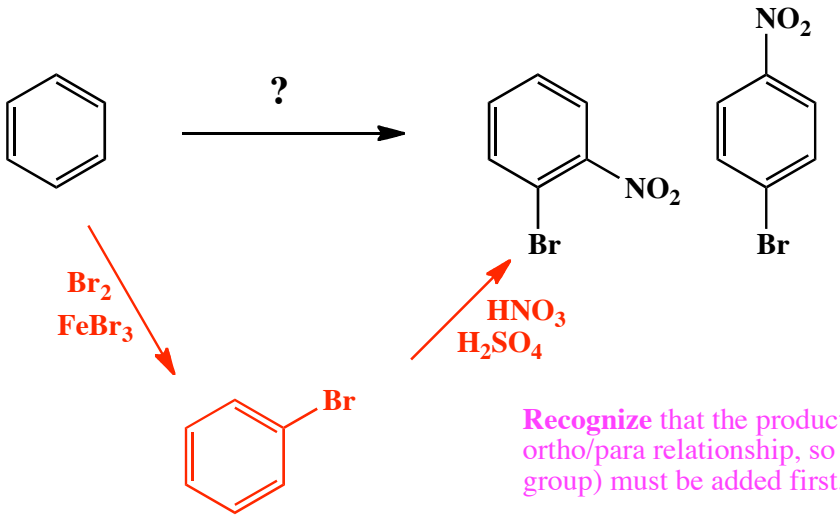
15. (5 or 7 points each) Fill in the boxes with the predominant product formed under the reaction conditions. If a new chiral center is formed in a racemic mixture, put an asterisk (*) next to it and write "racemic". If ortho/para products are created, you must draw both. These are worth a little more because they involve more than one step.





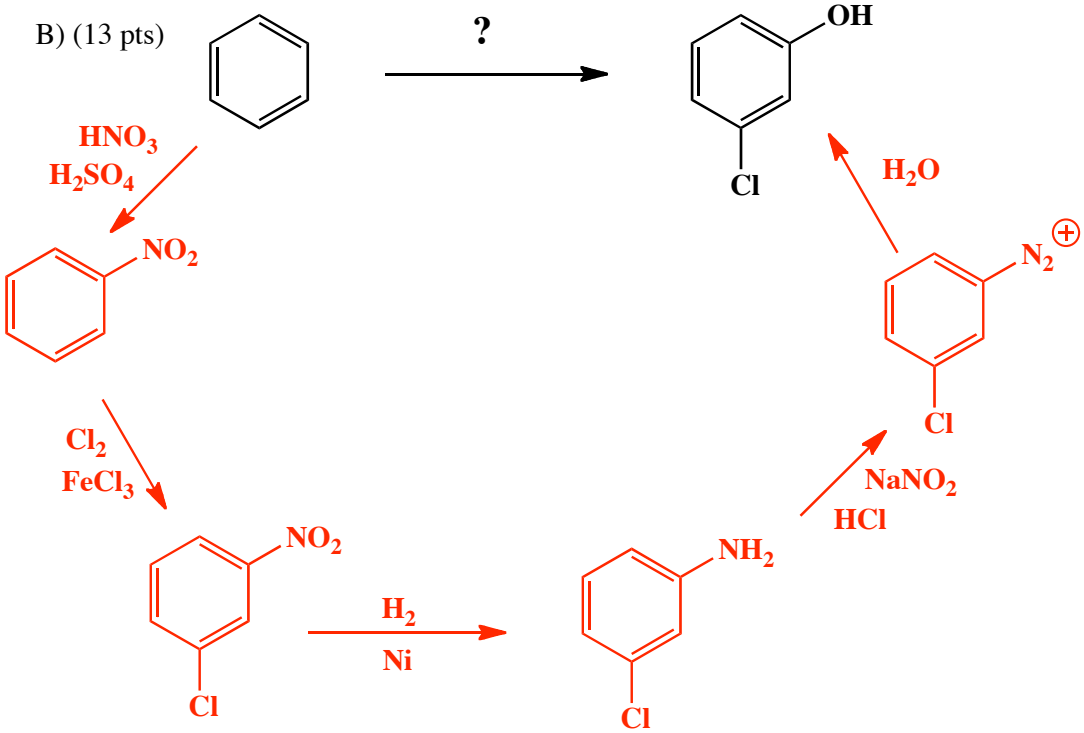
15. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

A) (4 pts)



Recognize that the product has an ortho/para relationship, so the Br ("bad" group) must be added first.

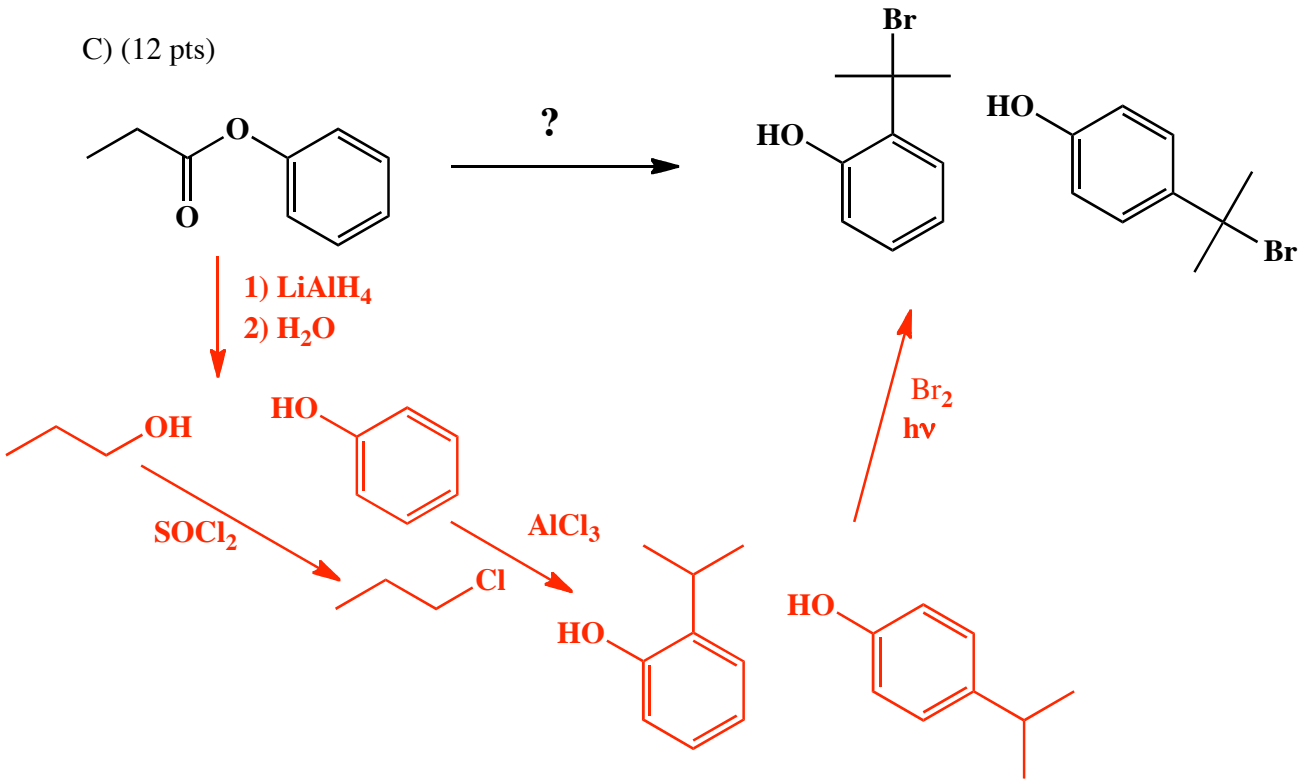
B) (13 pts)



Recognize that the two groups on the ring are ortho/para directors, yet have a meta relationship. Further **recognize** that the -OH group must come from an aryl diazonium ion. Putting these two pieces of information together, propose that you first add the nitro group ("bad" group) then the chlorine to give the meta relationship. Reduction then conversion to the diazonium and ultimately -OH completes the synthesis.

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

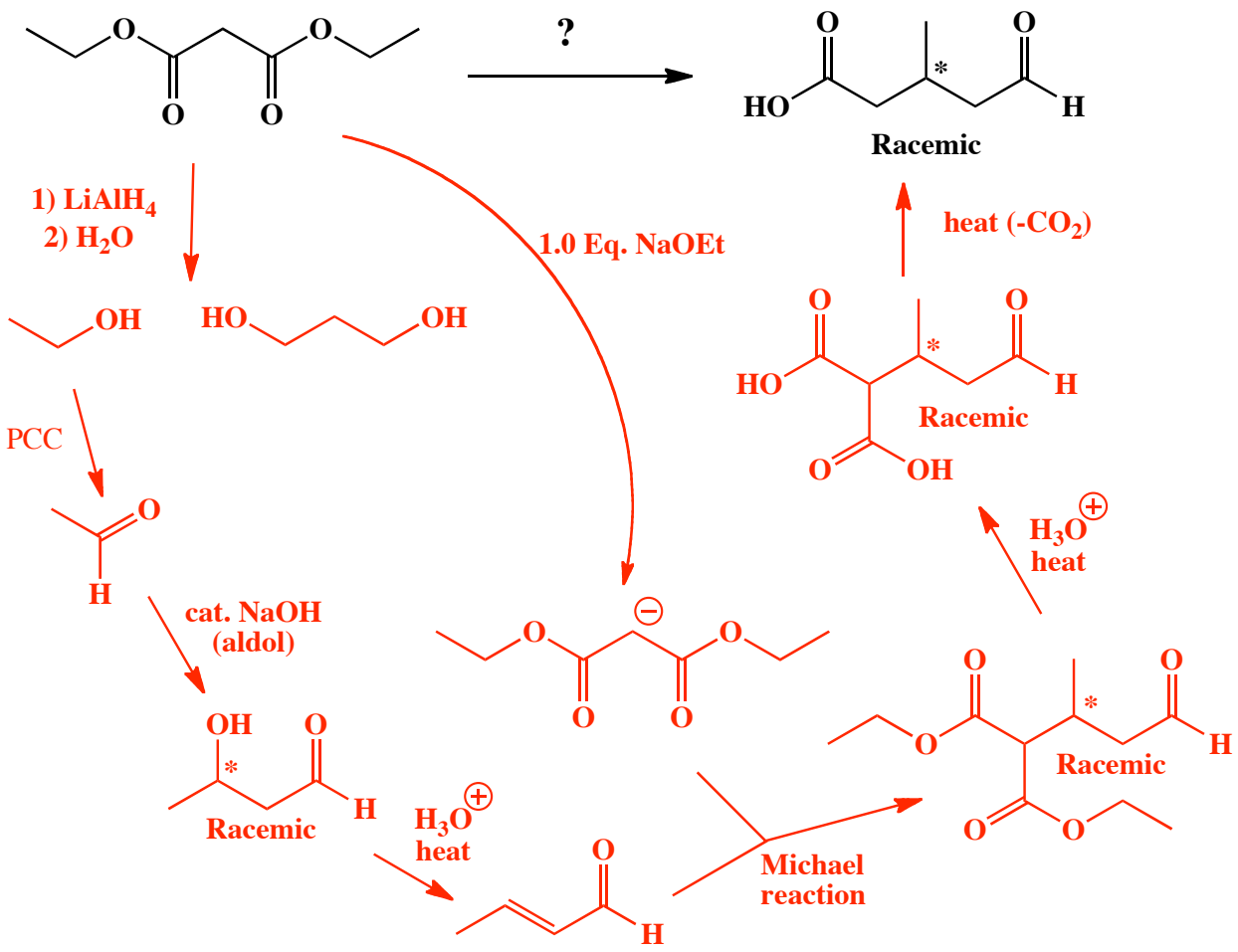
C) (12 pts)



Recognize that the product has bromine atoms at the benzylic position, so propose a free radical halogenation as the last step. **Recognize** further that the isopropyl group is added from a Friedel-Crafts alkylation that could use either 2-chloropropane or 1-chloropropane accompanied by a rearrangement (that always occurs for terminal haloalkanes under Friedel-Crafts conditions). Looking at the starting material, **recognize** that the starting ester can be converted to 1-propanol and phenol through reduction with $LiAlH_4$. Finish the synthesis by proposing $SOCl_2$ to convert 1-propanol to 1-chloropropane. Note that PBr_3 could also be used to produce 1-bromopropane, that is then used in a Friedel-Crafts alkylation with $AlBr_3$ as catalyst.

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

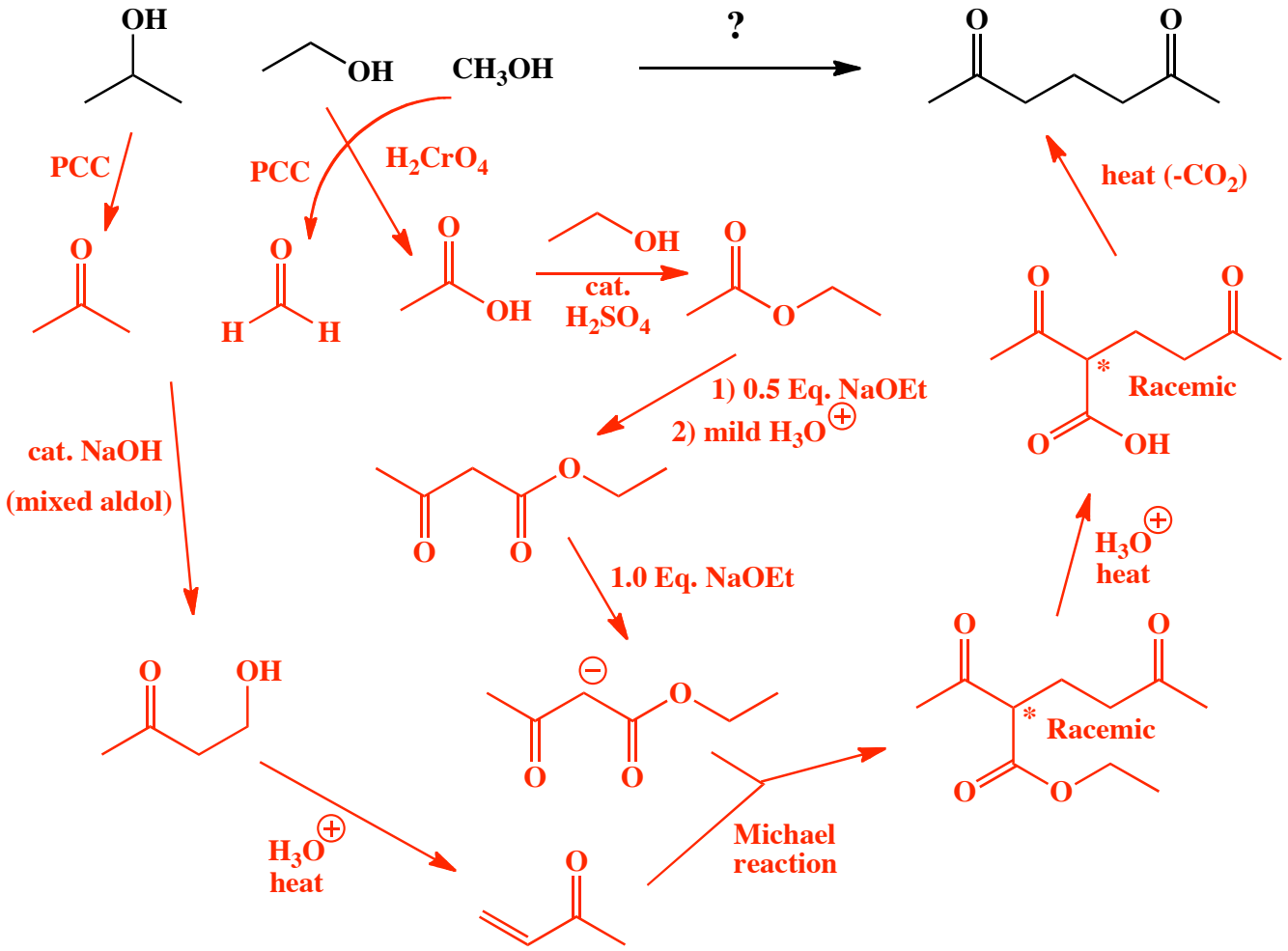
D) (16 pts)



Recognize that the product is a highly modified carboxylic acid derivative, so propose the last step is a decarboxylation from a malonic acid derivative. This is confirmed by the presence of diethyl malonate as the listed starting material. **Recognize** further that the malonic acid derivatives comes from the corresponding diethyl malonate derivative, which, in turn, is the product of the diethyl malonyl anion reacting as a nucleophile in a Michael reaction with the four carbon α,β-unsaturated aldhehyde shown. **Recognize** the α,β-unsaturated aldhehyde as being the product of the aldol reaction/dehydration of acetaldehyde, which can be derived from ethanol via PCC. The ethanol could be derived from the staring diethyl malonaed by ester hydrolysis or reduction using $LiAlH_4$.

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

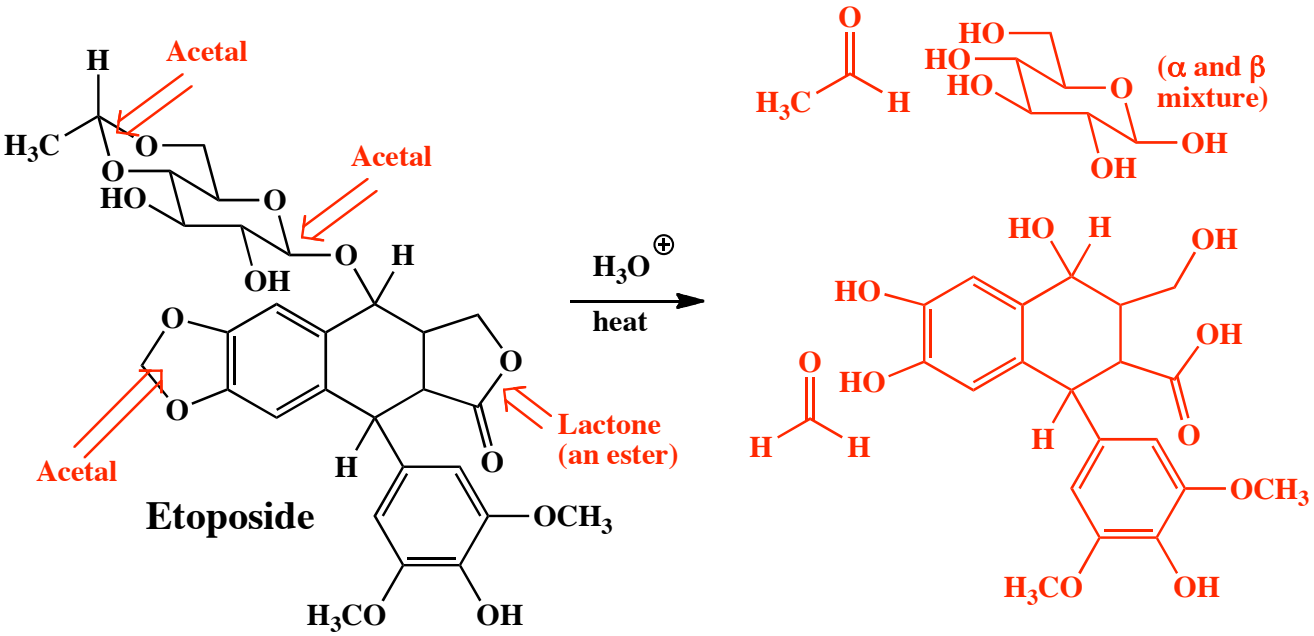
E) (25 pts)



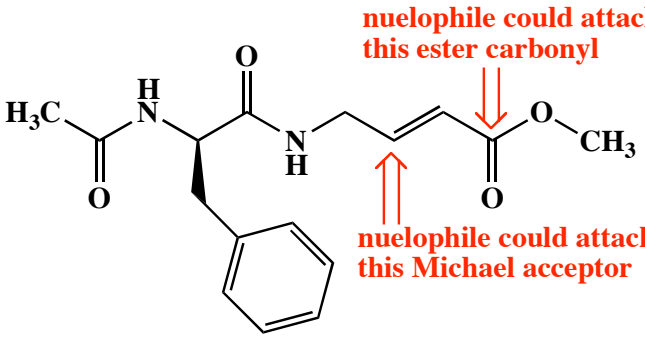
Recognize the product as a modified methyl ketone, so propose an acetoester synthesis. Therefore, propose the last step is a decarboxylation reaction. **Recognize** further that the required β-keto acid derives from the hydrolysis of the corresponding β-keto ester. **Recognize** further that the β-ketoester is the product of a Michael reaction between the ethyl acetoester enolate and the α,β-unsaturated methyl ketone shown. The key to this synthesis is realizing that the required α,β-unsaturated methyl ketone cannot be made by a straightforward aldol reaction/dehydration, but instead requires a mixed aldol between acetone and formaldehyde. **Recognize** that acetone and formaldehyde can be made from the PCC oxidation of the 2-propanol and methanol starting materials, respectively. Finally, **recognize** that the required aceto ester can be derived from the starting ethanol through the sequence of oxidation to aceetic acid, Fisher esterification with ethanol to give ethyl acetate and finally a Claisen reaction with ethyl acetate.

16. Here are two "apply what you" know questions based on complex molecules. A fundamental paradigm of Organic Chemistry is that functional groups behave the same in complex molecules as they do in simpler ones.

A. (10 pts.) The drug Etoposide is a chemotherapeutic agent that has been used against a number of cancers over the years. It operates by inhibiting an enzyme called topoisomerase that is required for DNA replication. Cancer cells need to replicate faster than normal cells, so drugs like Etoposide can be used to kill cancer selectively. **Look at Etoposide and determine what would happen if it is heated in aqueous acid. Draw all products formed and keep track of all bonds broken**.



B. (6 pts.) The following molecule reacts with certain important enzymes called proteases. You do not need to know anything about proteases to answer this question. By inspecting the structure below, **propose the two most likely ways in which a nucleophile could react with this inhibitor to make a new covalent bond.**



A strong nucleophile could react with either the ester carbonyl carbon according to mechanism B, or it could add to the alkene in a Michael reaction. the two amide bonds are too unreactive to propose any reaction at either of these. In the actual experiments, the Michael reaction is the one that was observed.