

NAME (Print): _____

Chemistry 310N
Dr. Brent Iverson
Final
May 11, 2006

SIGNATURE: _____

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

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

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

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

Page	Points	
1		(30)
2		(33)
3		(20)
4		(32)
5		(21)
6		(30)
7		(20)
8		(19)
9		(35)
10		(35)
11		(21)
12		(22)
13		(17)
14		(10)
15		(23)
16		(21)
Total		(389)
T Score		

Compound		pK _a
Hydrochloric acid	H-Cl	-7
Protonated alcohol	$\text{RCH}_2\text{OH}_2^{\oplus}$	-2
Hydronium ion	$\text{H}_3\text{O}^{\oplus}$	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-5
Ammonium ion	$\text{H}_4\text{N}^{\oplus}$	9.2
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CR}'$	10
β-Ketoesters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	11
β-Diesters	$\text{ROC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	16
Aldehydes	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	18-20
Ketones	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CR}'$	18-20
Esters	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\text{H}$	25
LDA	$\text{H}-\text{N}(\text{i}-\text{C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{H}$	44
Alkanes	$\text{CH}_3\text{CH}_2-\text{H}$	51

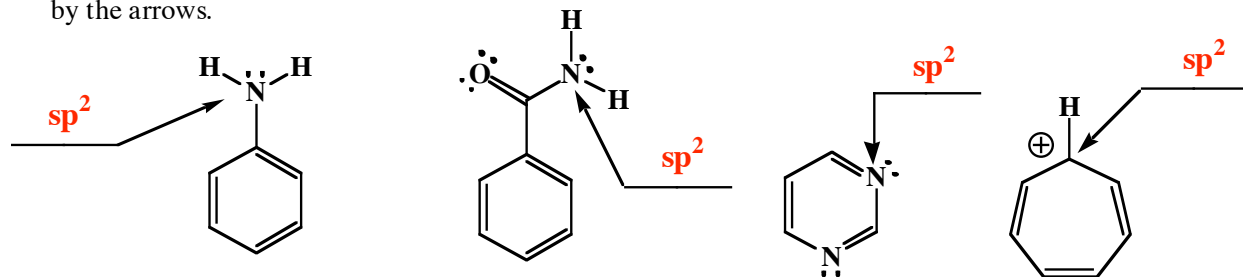
1. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

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**.

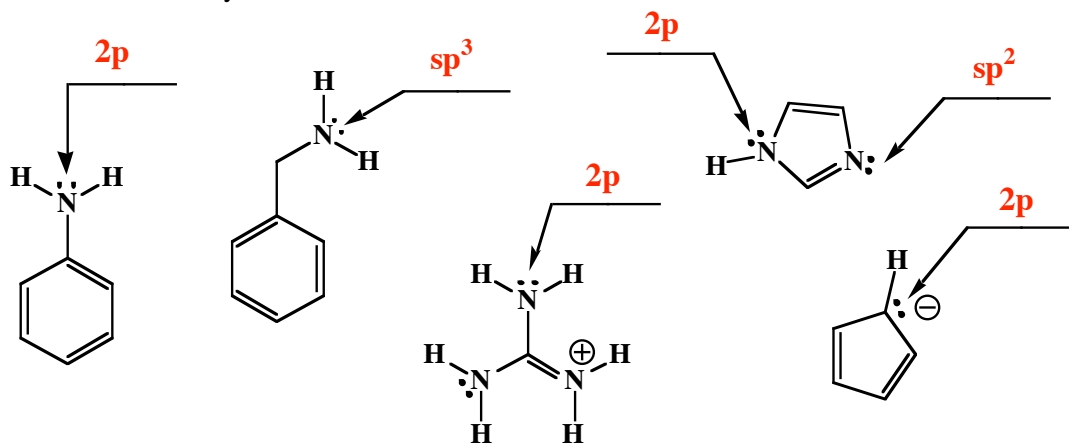
2. (2 pt. each) Here are a number of statements regarding general aspects of organic chemistry. Do not second guess yourself, this is not meant to be tricky! **Check the appropriate box to indicate whether the statement is true or false.**

	True	False
A. Resonance contributing structures generally involve moving lone pairs and pi bonds between atoms.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
B. Resonance contributing structures generally are used to describe pi electron delocalization.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
C. The exceptions to the VSEPR model we saw this semester involved pi electron delocalization.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
D. In $^1\text{H-NMR}$, signals for H atoms attached to more electronegative atoms appear closer to TMS than the signals for H atoms attached to less electronegative atoms.	<input type="checkbox"/>	<input checked="" type="checkbox"/>
E. A carbocation can be stabilized by either hyperconjugation or resonance.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
F. In $^1\text{H-NMR}$, spin-spin splitting is caused by induced electron density movement that in turn induces small magnetic fields.	<input type="checkbox"/>	<input checked="" type="checkbox"/>
G. Enolates are great electrophiles	<input type="checkbox"/>	<input checked="" type="checkbox"/>
H. When a reaction is under kinetic control, the more stable product is the predominant one (greater motive), while when a reaction is under thermodynamic control the product that forms faster (better opportunity) is the predominant one.	<input type="checkbox"/>	<input checked="" type="checkbox"/>

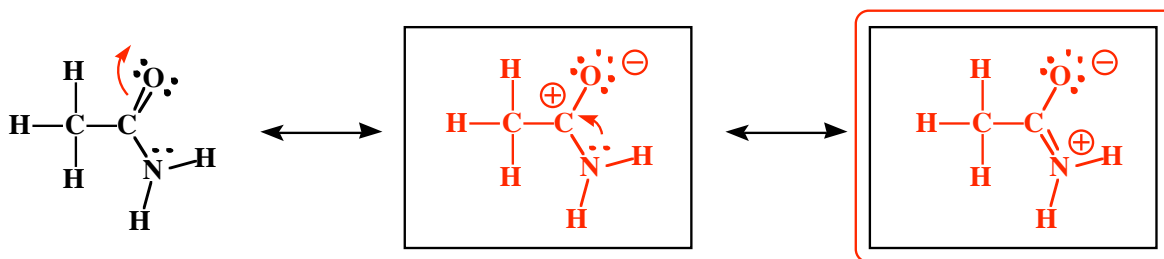
3. (8 points) For the following molecules, write the correct **hybridization state of the atoms** indicated by the arrows.



4. (12 points) For the following molecules, write the correct **type of orbital that contains the pair of electrons** indicated by the arrows.



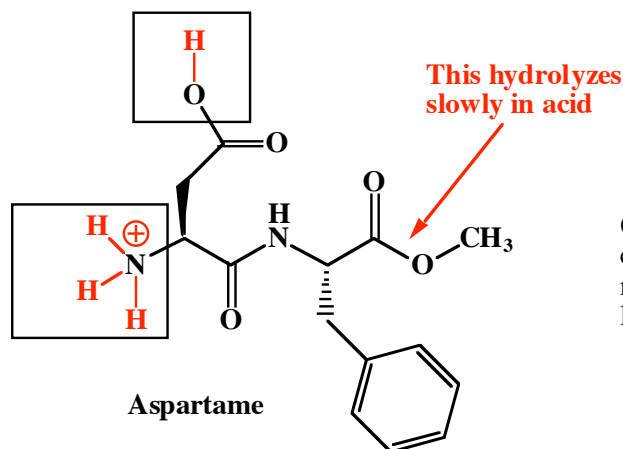
5. (10 pts) On the left is drawn the Lewis structure of a simple amide. Draw the two next most important contributing structures in the spaces provided. Be sure to show all lone pairs and formal charges. You do not need to draw arrows on the structures, but you can if it helps you.



6. (3 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

7. (10 points) A) This semester we have learned a great deal about both carboxylic acids and amines. Here is an apply what you know problem. Aspartame is the sweetener used in diet coke. Its structure is shown below. Because of carbonation and added phosphoric acid, the pH of diet coke is relatively acidic, near 2.0. Complete the following peptide structure by adding all appropriate hydrogen atoms and formal charges that will be present when this peptide is in diet coke at pH 2.0. Assume the pKa value for a protonated amine (RNH_3^+) is 9.2 and the pKa value for a carboxylic acid is 4.0.



B) What is the total charge on this peptide at pH 2.0? +1

C) Diet coke loses its sweetness over time, especially if heated. Can you suggest a likely reason for this based on the chemistry you have learned?

The methyl ester hydrolyzes

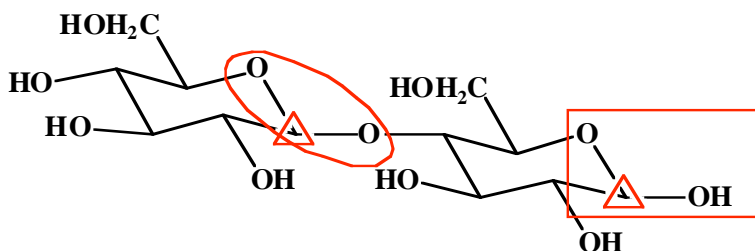
in the acidic pH and the free

acid is not sweet.

8. (10 points) A) On the following disaccharide, circle the O and C atoms of all acetals, and draw a box around the O and C atoms of all hemiacetals.

B) Next draw a triangle around each anomeric carbon atom.

C) Are the two sugars pyranosides or furanosides? Pyranosides

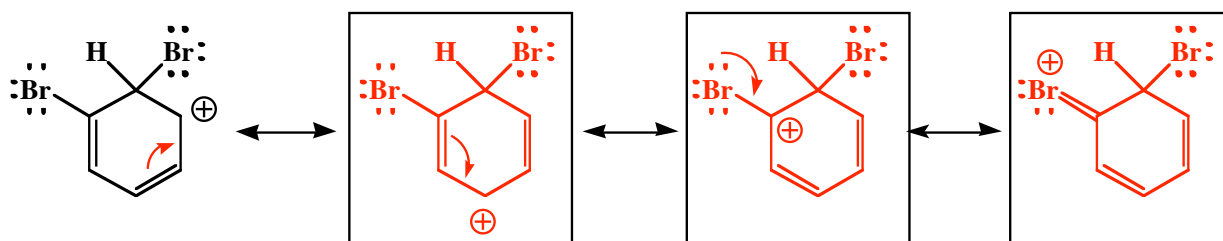
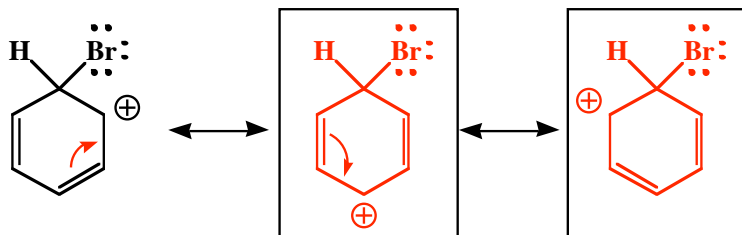
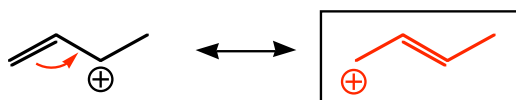
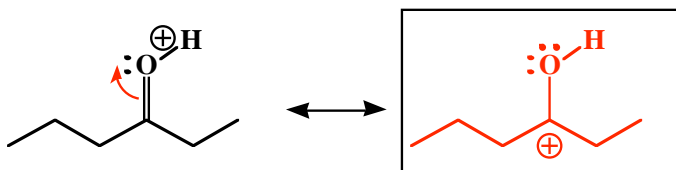


D) Are the two sugars of the α or β form? β

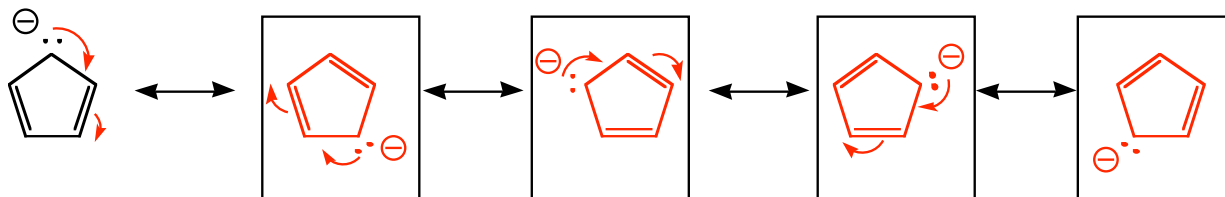
E) Is the glycosidic bond best described as $\alpha 1,4$; $\alpha 1,6$; $\beta 1,4$; or $\beta 1,6$? $\beta 1,4$

F) How many chiral centers does the molecule have? 10

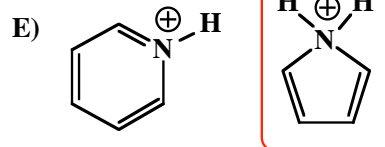
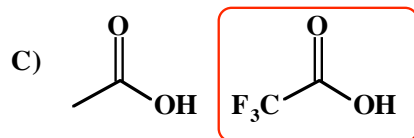
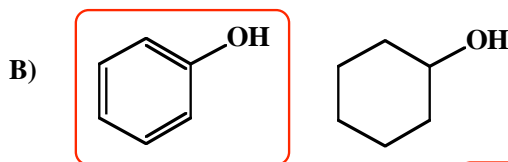
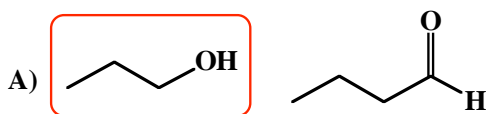
9. (22 points) A major theme of the course is that resonance can stabilize charged intermediates. For the following molecules, draw the indicated number of most important contributing structures. Show all formal charges and lone pairs. **Draw arrows on the structures to indicate the flow of electrons that produce the contributing structure immediately to the right.** In other words, only the structures farthest to the right will not have arrows on them.



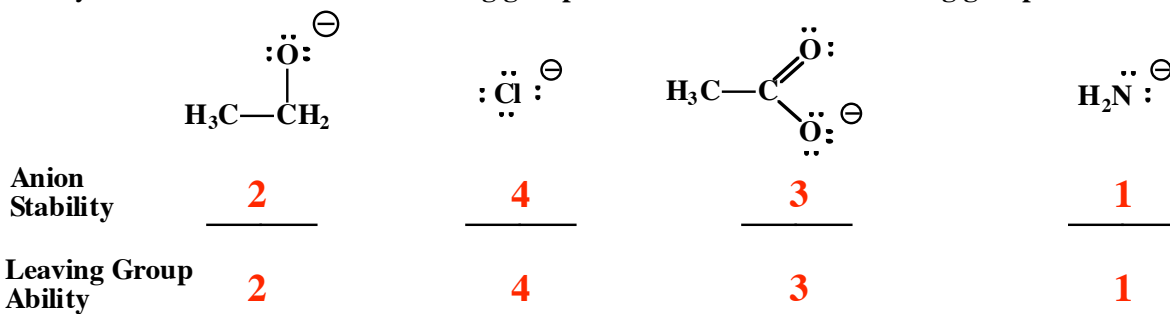
Think carefully about this next one



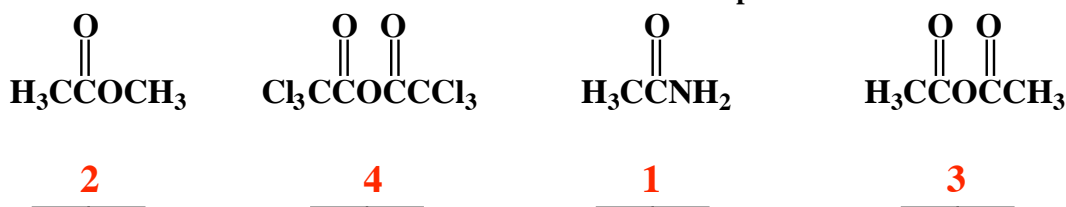
10. (10 points) For each pair of molecules, circle the more acidic molecule.



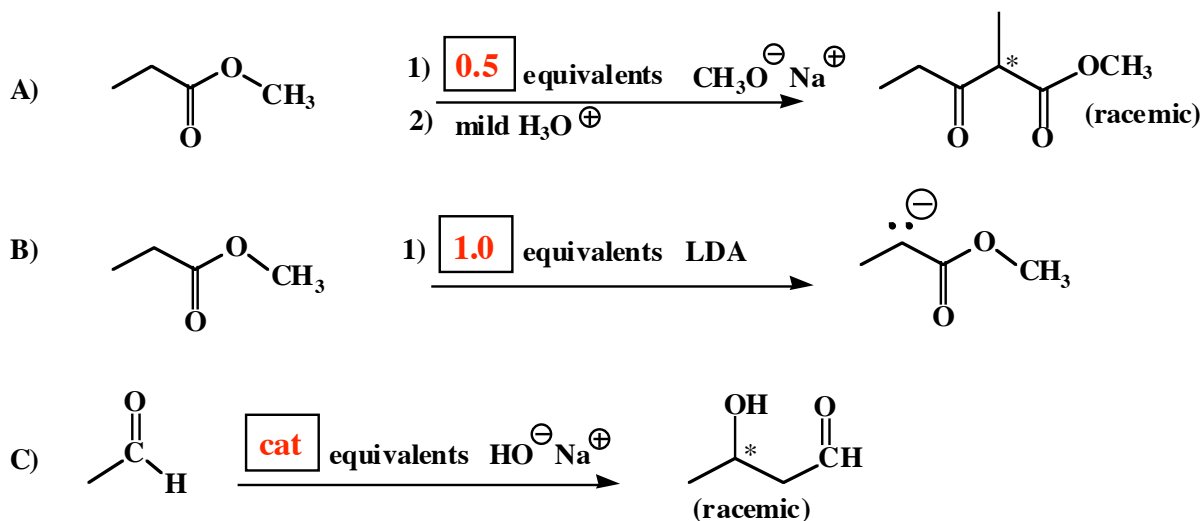
8. (8 pts) A) On the upper lines, rank the following with respect to relative anion stability, with a **1** under the least stable anion (i.e. most reactive with a proton) and a **4** under the most stable anion (i.e. least reactive with a proton). On the lower lines, rank the following with respect to leaving group ability, with a **1** under the worst leaving group, and a **4** under the best leaving group.



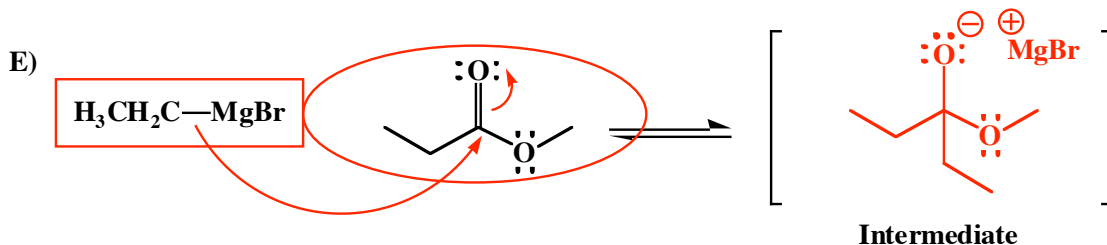
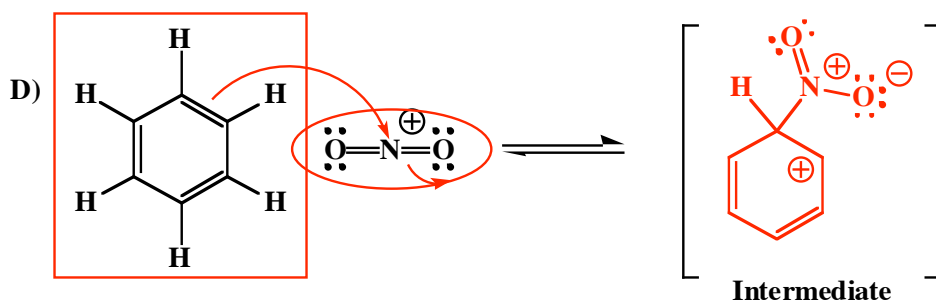
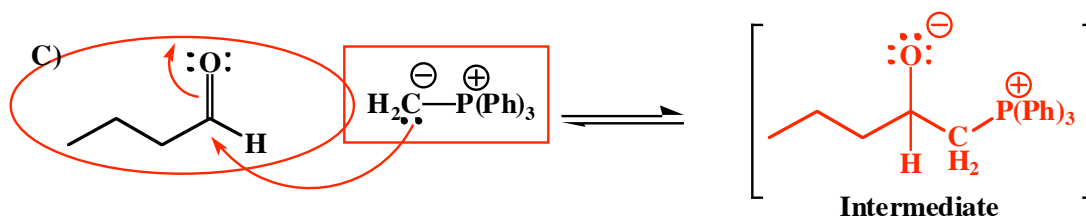
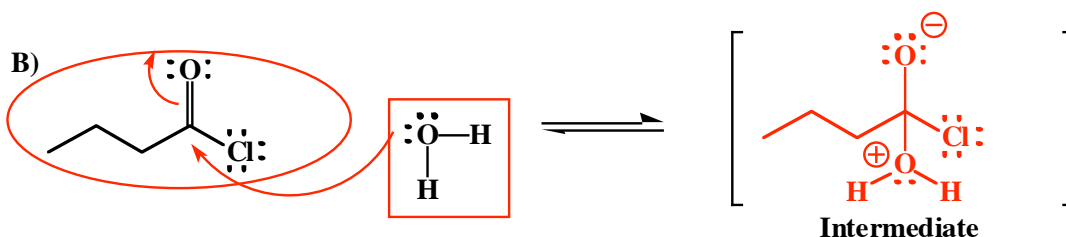
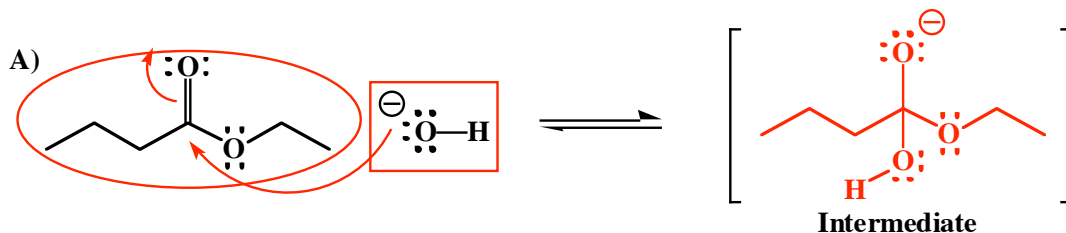
B) (4 pts) Rank the following in terms of relative reactivity with a nucleophile without acid catalysis. Place a **1** under the least reactive and a **4** under the most reactive species.



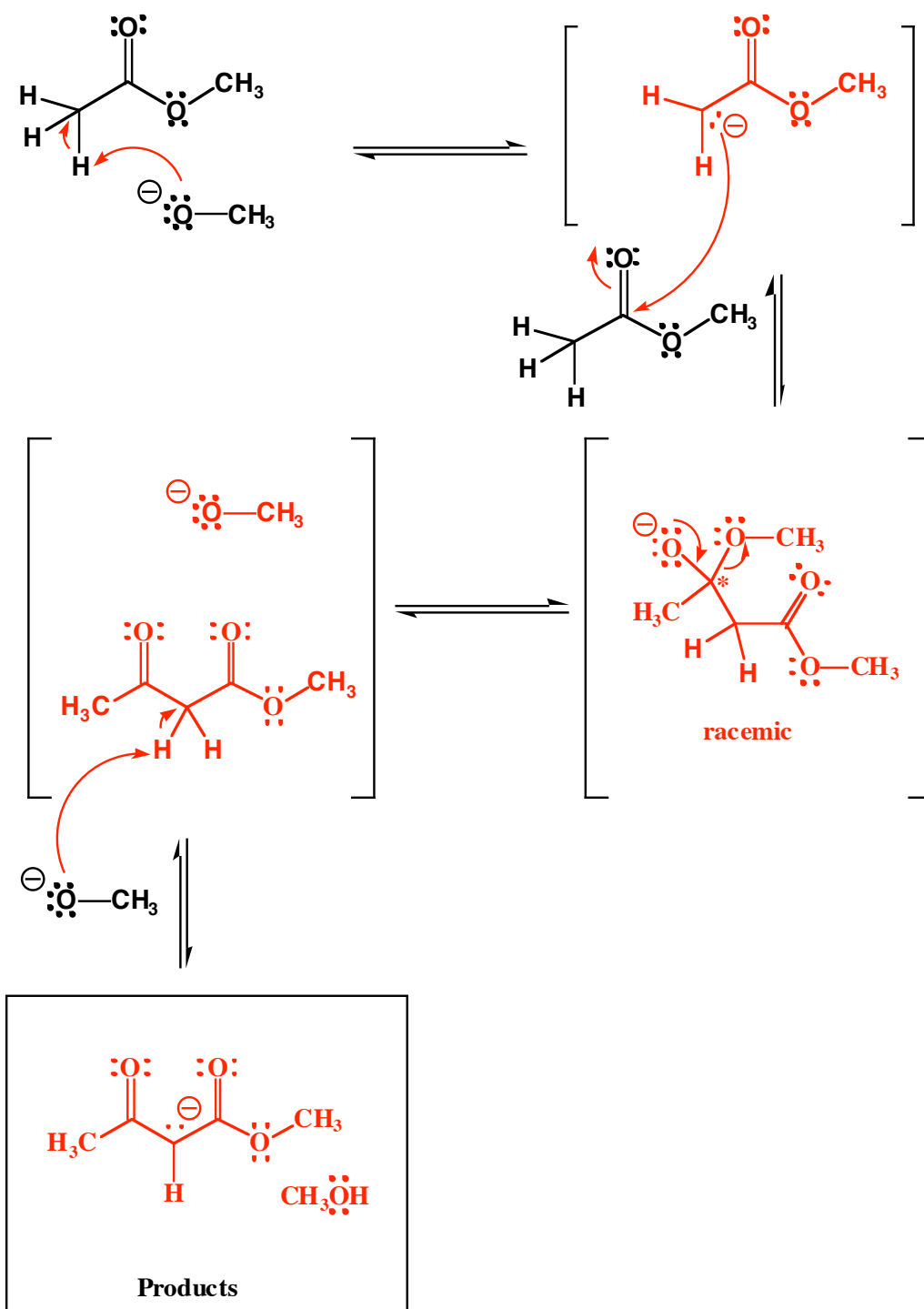
12. (3 pts each) In each of the boxes over an arrow, write the minimum number of equivalents of the specified reagent required to carry out the reaction shown to completion. If only a catalytic amount is needed, write "CAT". Note: You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent.



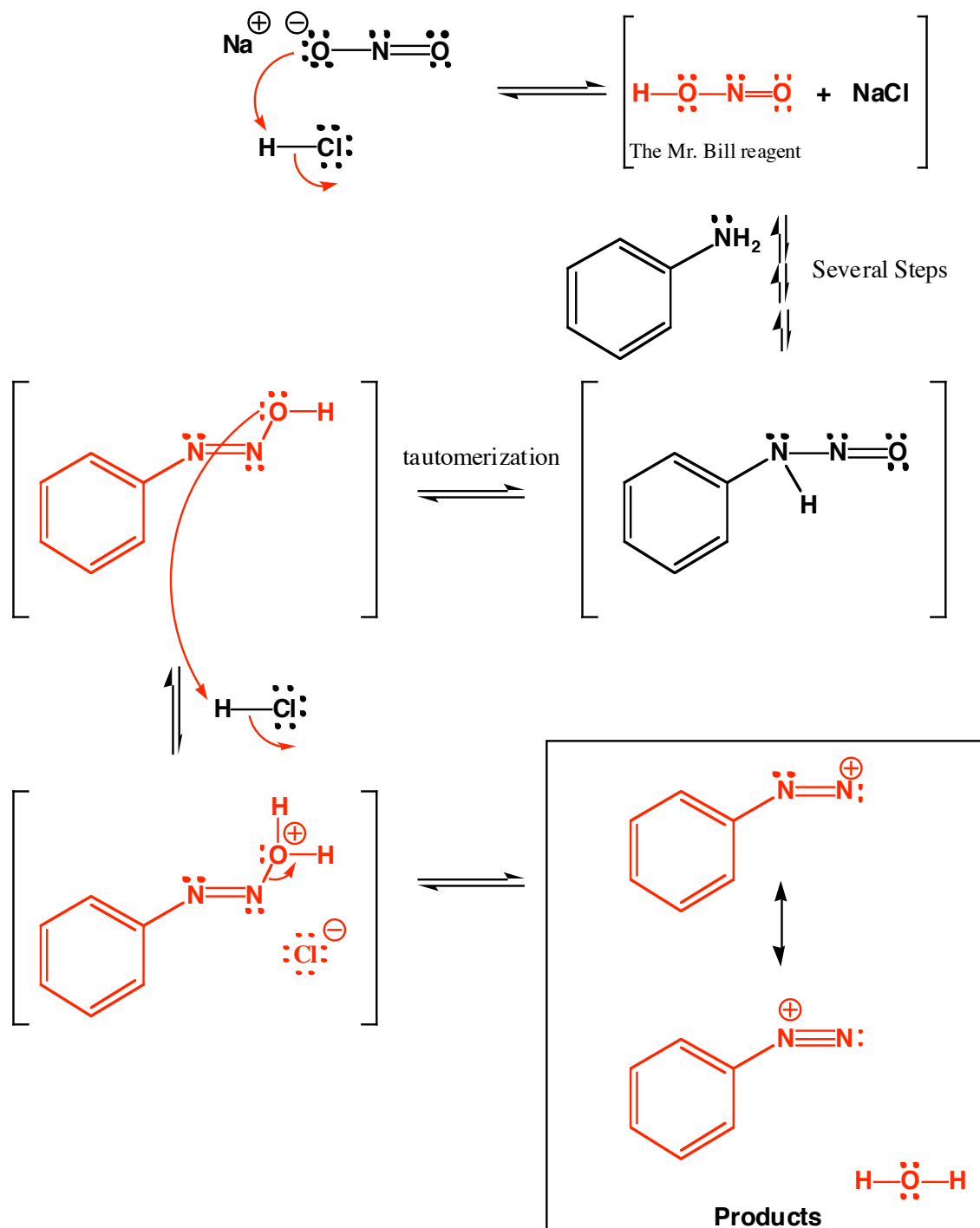
12. (30 points) Many of the reactions we have learned this semester involve steps with nucleophiles reacting with electrophiles. For the following examples of steps in mechanisms we have seen this semester, **1) Draw the intermediate that will be formed when the two molecules react. 2) Draw all formal charges and lone pairs on the intermediates. 3) Draw arrows on the starting materials to indicate the flow of electrons that leads to the intermediate. 4) Finally, draw a box around the nucleophile and a circle around the electrophile in each case. There is no need to draw products or any further steps of the mechanisms.** You might want to read these directions again so you know what we want.



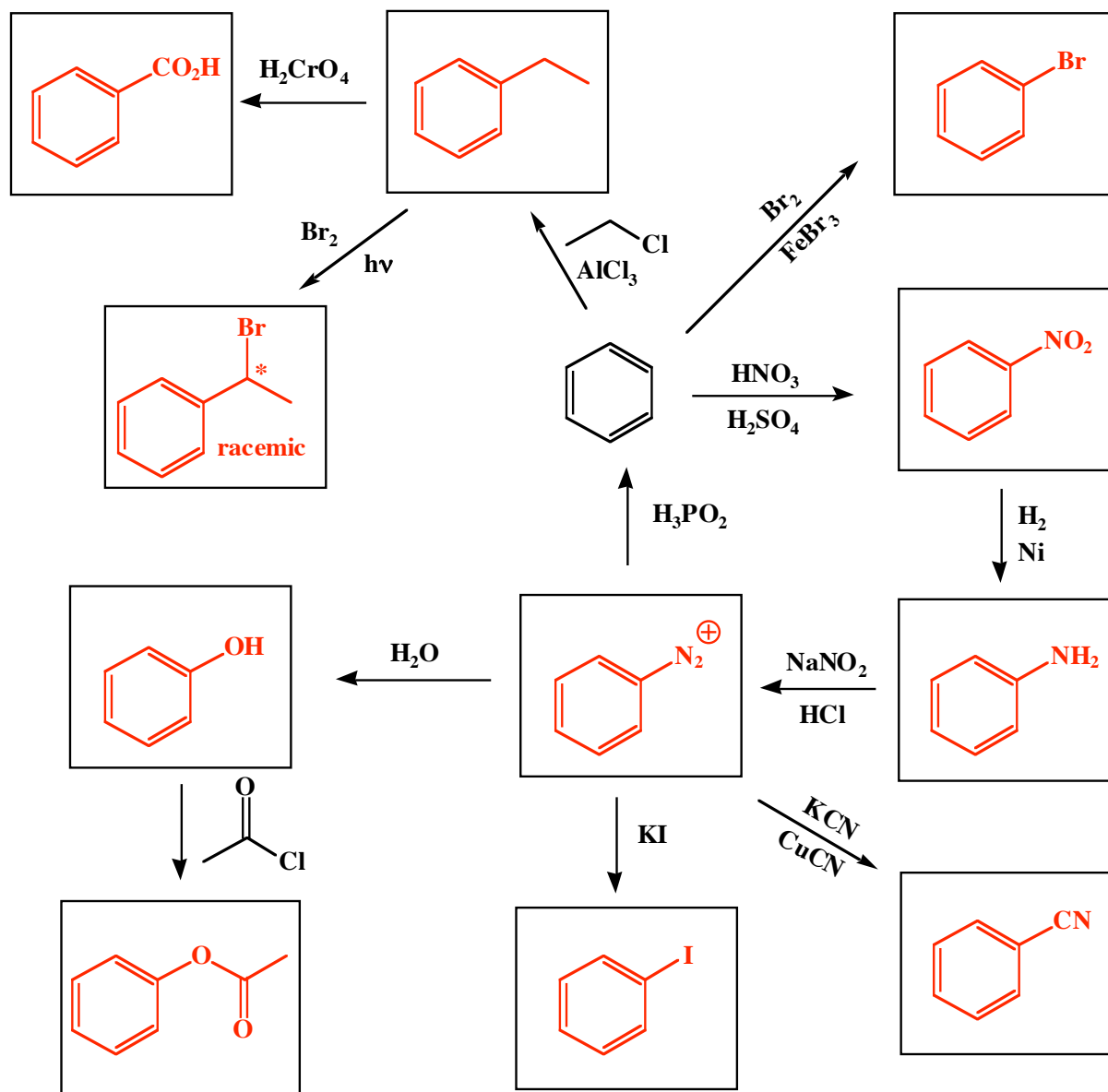
12. (20 points) Complete the following mechanism for the Claisen reaction. If chiral centers are present, just use an asterisk (*) to show where they are and write racemic as appropriate.



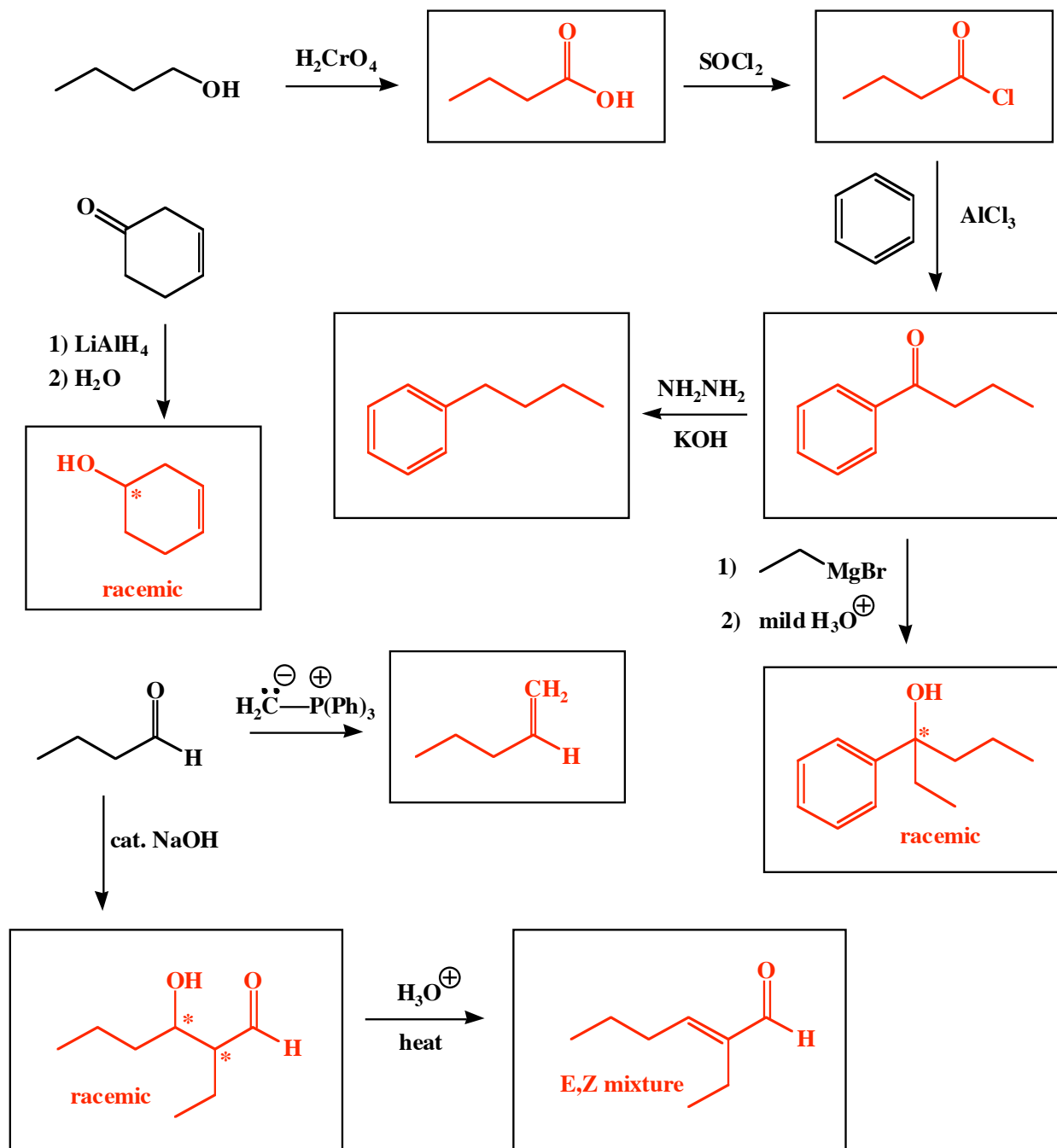
12. (19 points) Complete the following mechanism for the diazonium formation ("Mr. Bill") reaction. You need to draw the two major contributing structures of the aromatic product.



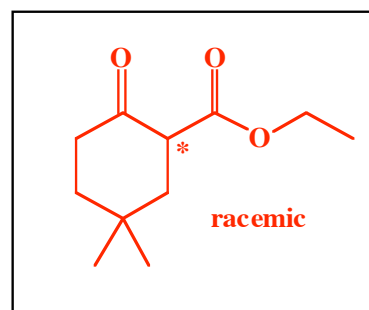
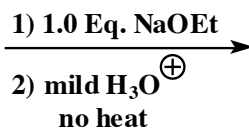
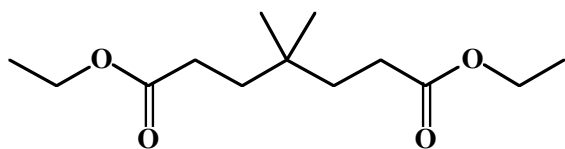
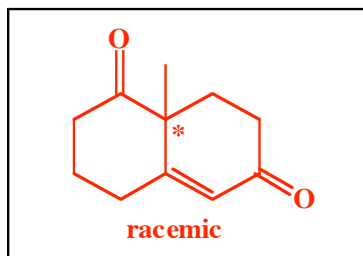
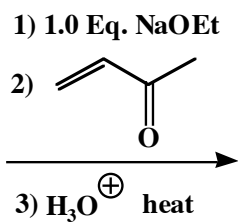
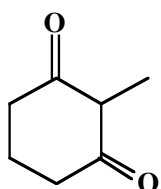
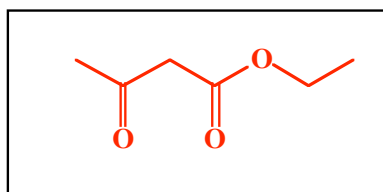
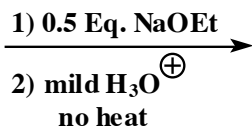
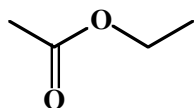
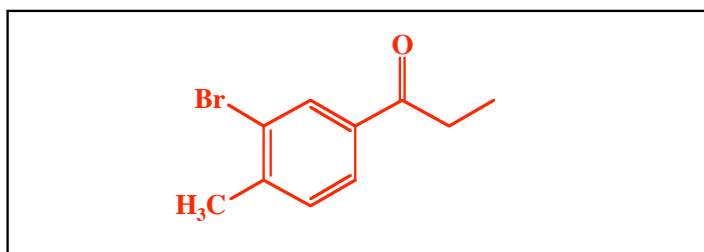
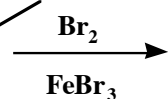
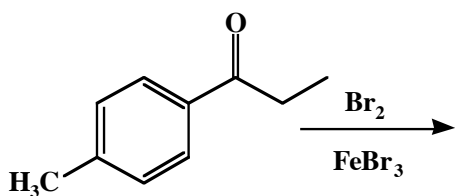
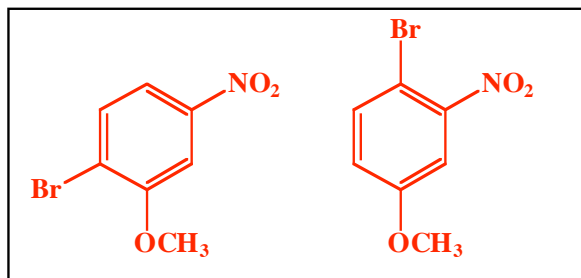
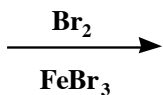
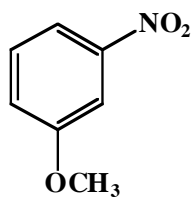
14. (3 or 5 points each) Fill in the boxes with the predominant product formed under the reaction conditions. If a new chiral center is formed in a racemic mixture, put an asterisk (*) next to it and write "racemic".



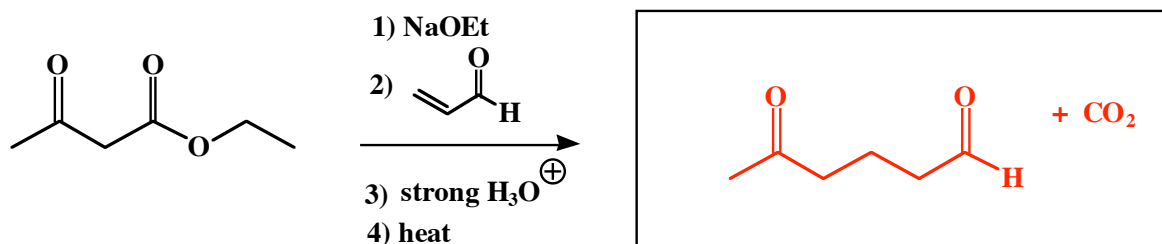
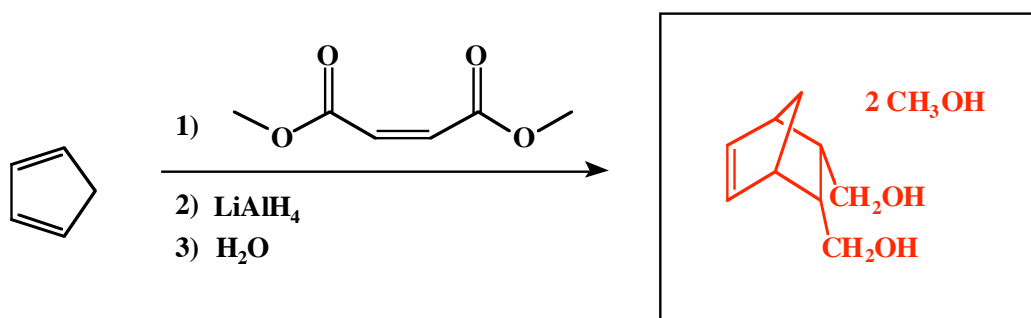
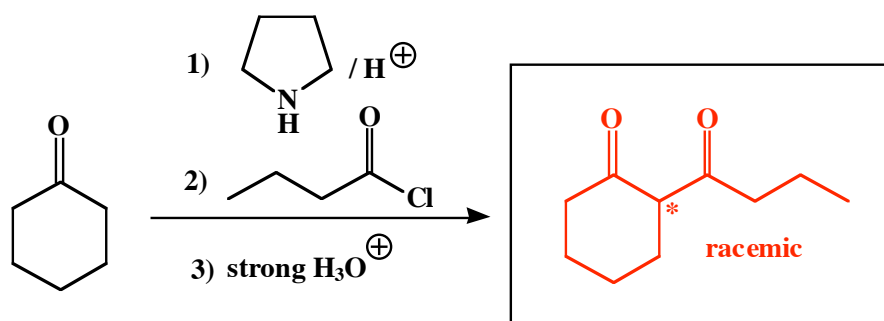
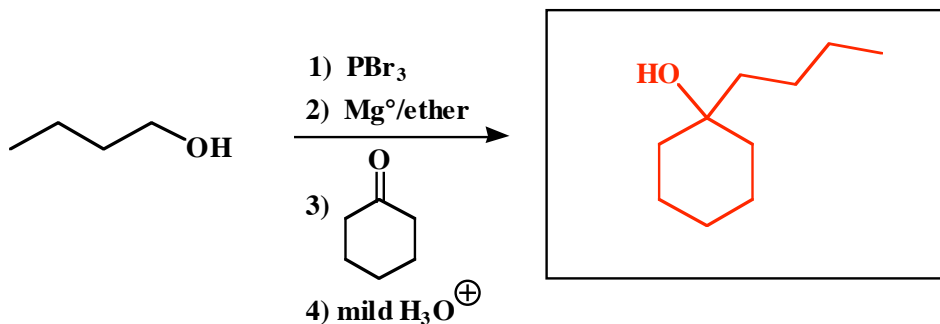
14. (3 or 5 points each) Fill in the boxes with the predominant product formed under the reaction conditions. If a new chiral center is formed in a racemic mixture, put an asterisk (*) next to it and write "racemic". If an E,Z mixture is produced, just draw one of the products and write E,Z mixture.



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 an E,Z mixture is produced, just draw one of the products and write E,Z mixture. If an ortho/para mixture is produced, draw both.

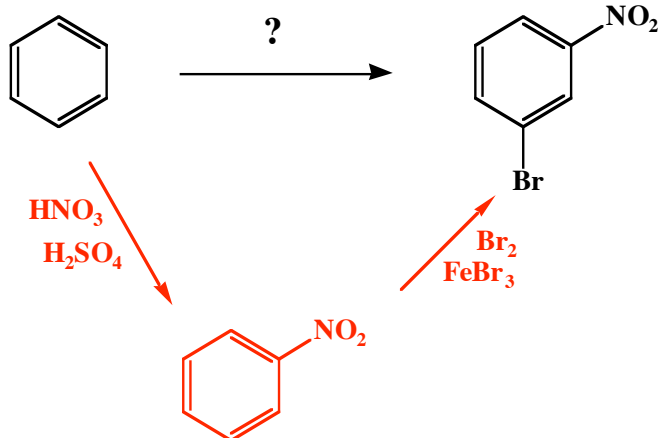


14. (5 or 7 points each) These involve multiple steps, so they are worth 5 or 7 points each. Fill in the boxes with the predominant product or products formed under the reaction conditions. If a new chiral center is formed in a racemic mixture, put an asterisk (*) next to it and write "racemic". If an E,Z mixture is produced, just draw one of the products and write E,Z mixture. If an ortho/para mixture is produced, draw both.

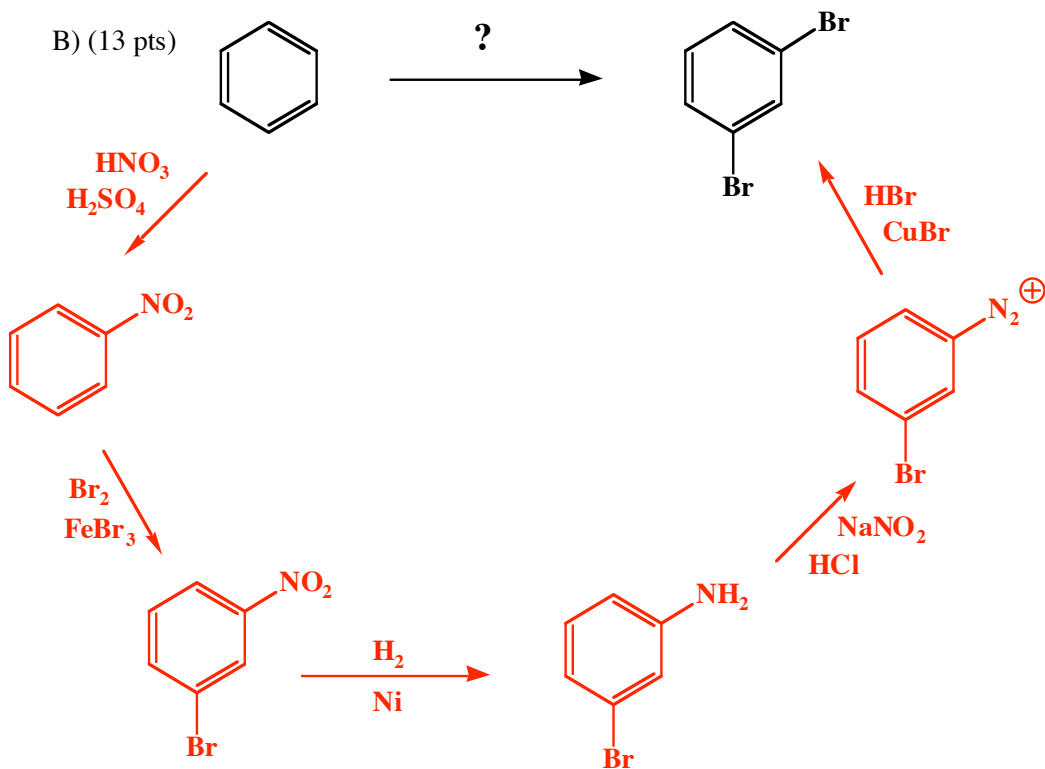


15. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

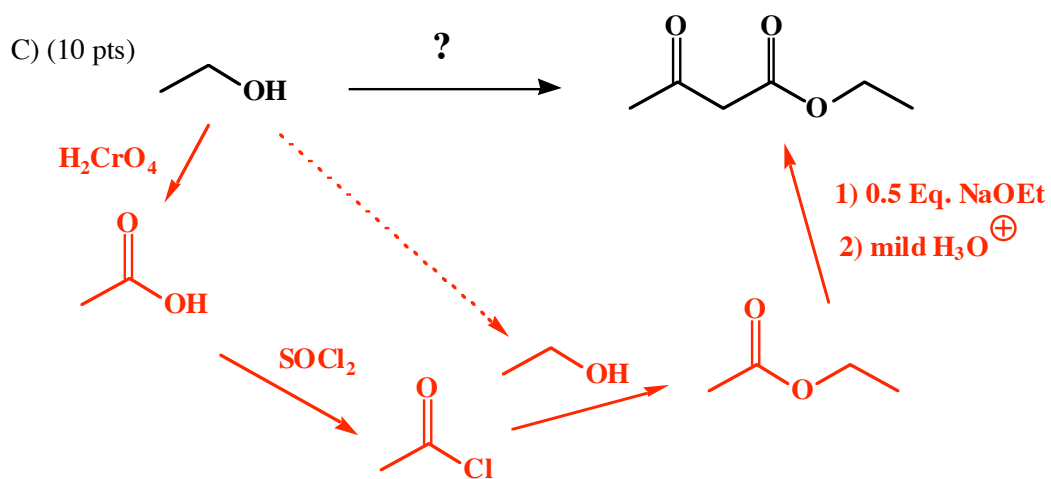
A) (4 pts)



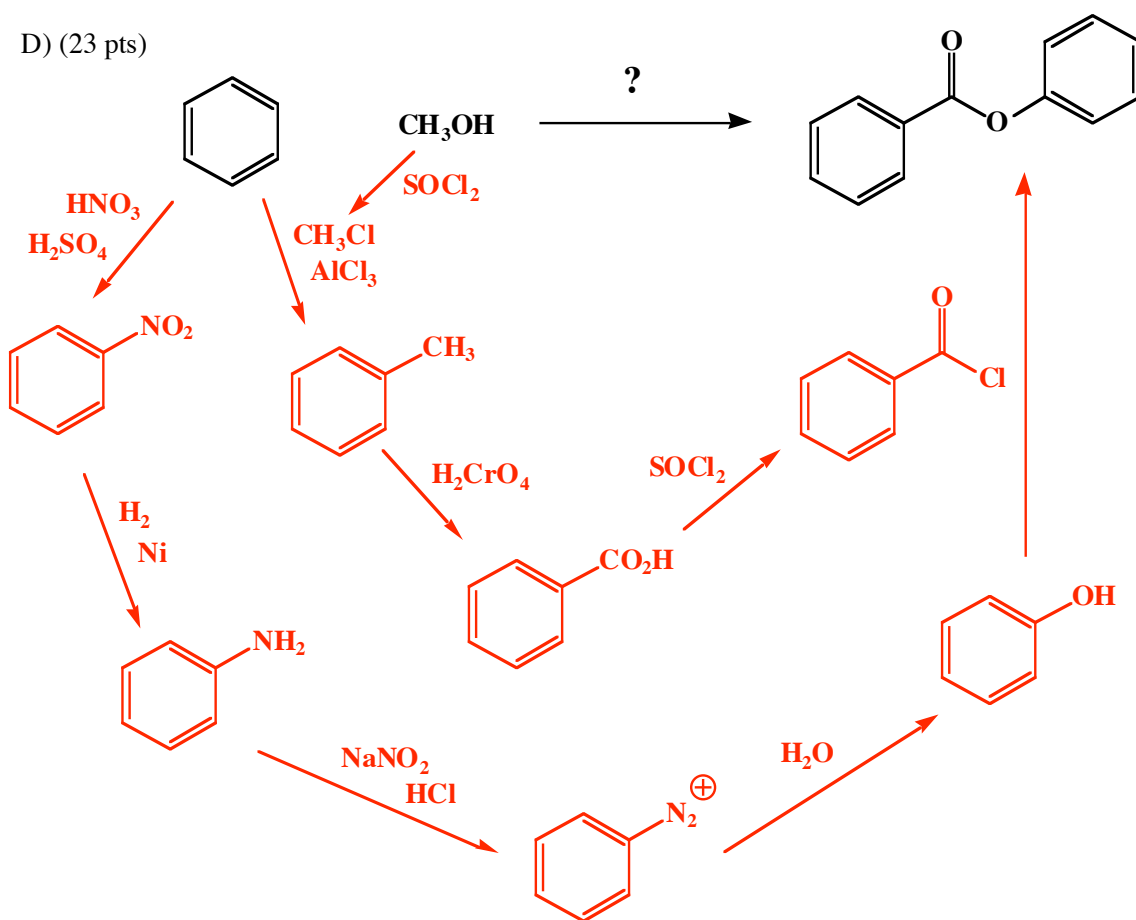
B) (13 pts)



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!



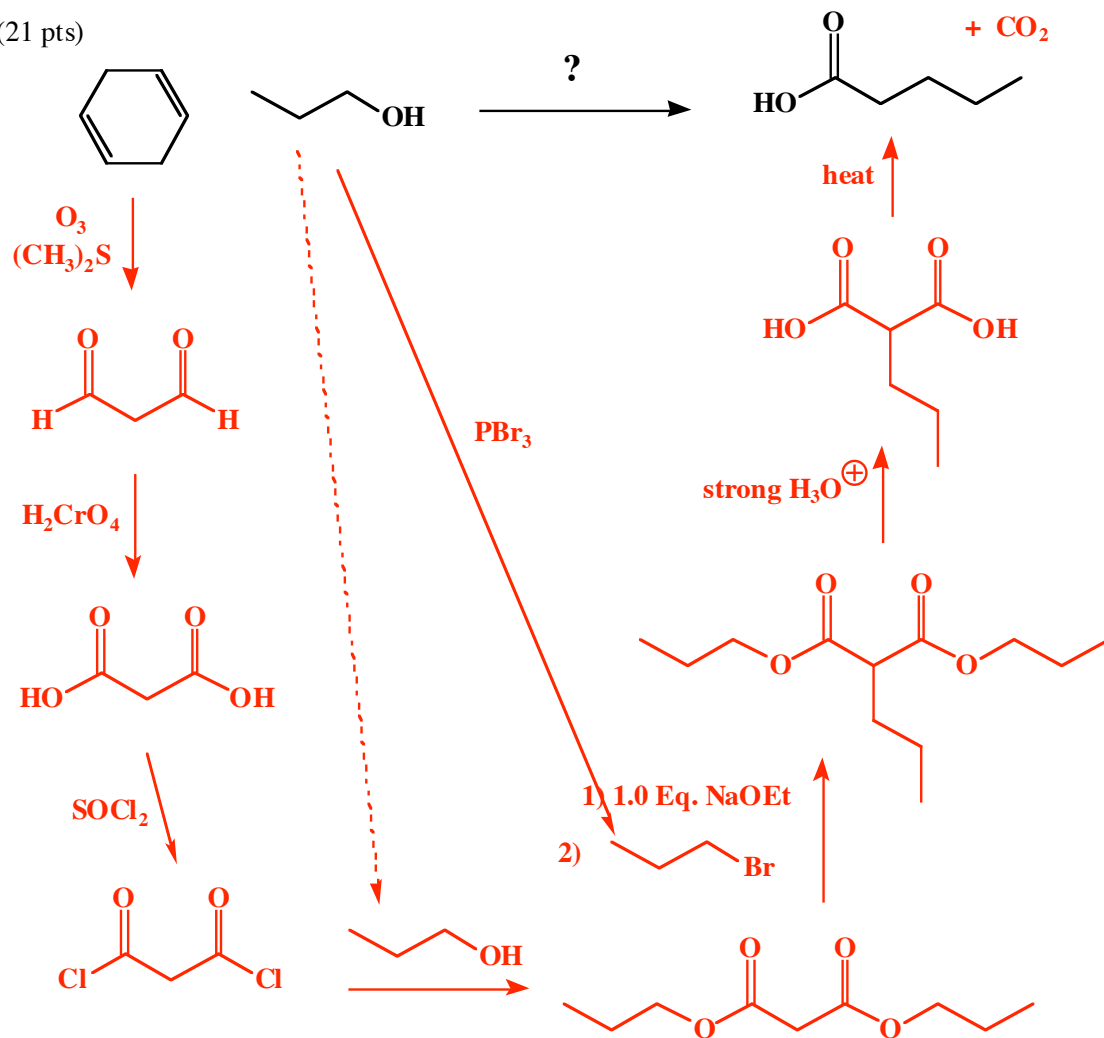
15. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!



Recognize the product as an ester, that must come from benzoyl chloride and phenol. Benzoyl chloride comes from benzoic acid, which is made from benzene via Jones oxidation of an alkyl benzene such as toluene. The phenol is derived from a diazonium species, which is made in the usual nitration reduction sequence of reactions.

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) (21 pts)



If you got this congratulations!!! Recognize the product as a substituted carboxylic acid that comes from the malonic synthesis. Notice that the three carbon piece can come from the propanol via reaction with PBr_3 to give the alkyl halide. Making a malonic ester is a little more challenging. The key is to recognize that ozonolysis of the starting 1,4-cyclohexadiene followed by Jones oxidation. Reaction with SOCl_2 followed by the starting propanol gives the required dialkylmalonate.

It has been a pleasure getting to know you this semester (and last). I was a little worried after the second midterm, but most of you came through on the third one. I hope that you found this final to be challenging, but fair.

It is the sincere wish of the TA's and myself that you look back on your organic chemistry courses with a sense of pride on how far you have come in two semesters. Wherever your careers take you, we hope you now have the intellectual tools to identify, analyze, and understand molecules.

Have a safe summer and remember to exercise every chance you get. If you stay in shape, you will thank yourself more than you can imagine in a few years!!!

Brent Iverson