

NAME (Print): \_\_\_\_\_

Chemistry 310N  
Dr. Brent Iverson  
Final  
May 12, 2007

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!!!!**

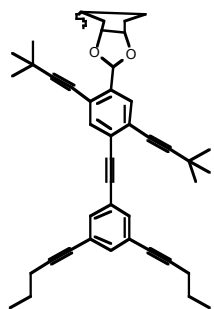
Page	Points
<b>1</b>	<b>(36)</b>
<b>2</b>	<b>(18)</b>
<b>3</b>	<b>(26)</b>
<b>4</b>	<b>(16)</b>
<b>5</b>	<b>(21)</b>
<b>6</b>	<b>(38)</b>
<b>7</b>	<b>(18)</b>
<b>8</b>	<b>(31)</b>
<b>9</b>	<b>(33)</b>
<b>10</b>	<b>(31)</b>
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<b>12</b>	<b>(25)</b>
<b>13</b>	<b>(21)</b>
<b>14</b>	<b>(29)</b>
<b>15</b>	<b>(14)</b>
<b>16</b>	<b>(16)</b>
<b>17</b>	<b>(10)</b>
<b>18</b>	<b>(16)</b>
<b>19</b>	<b>(34)</b>
<b>Total</b>	<b>(462)</b>
<b>HW</b>	
<b>T Score</b>	

## Honor Code

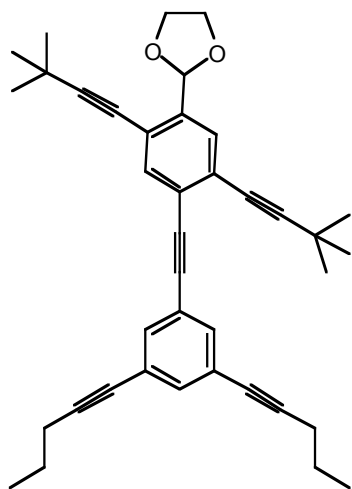
The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.

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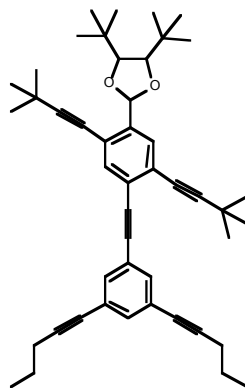
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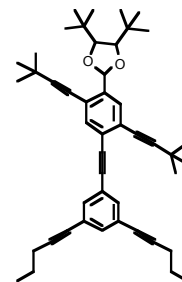
Dr. Iverson



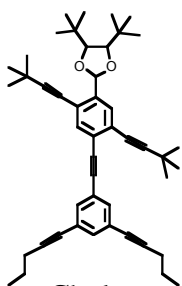
Dustin



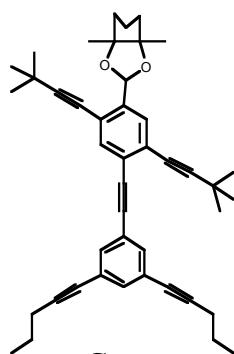
Valerie



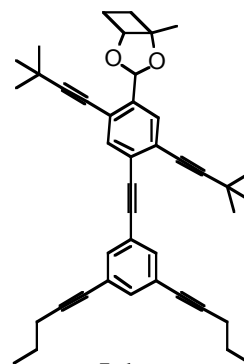
Natalie



Chelsea



Garen



John

It has been a pleasure getting to know you this semester. Based on your performance on the three midterms, we think you are clearly the best class we have ever had at the University of Texas. 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!!!*

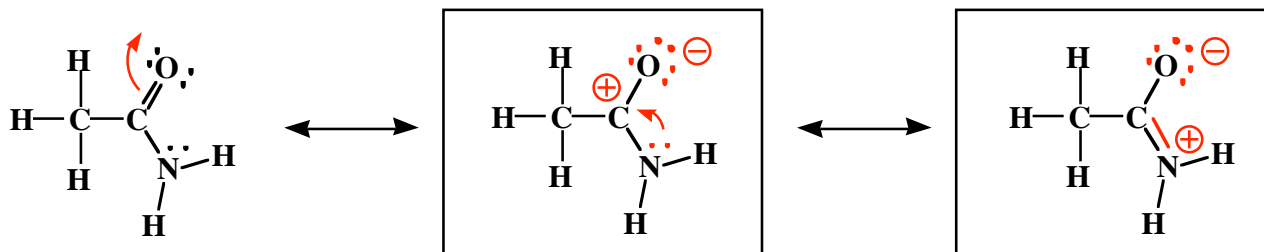
Brent Iverson

Compound		pK <sub>a</sub>
Hydrochloric acid	$\text{H-Cl}$	-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	$\text{HOH}$	15.7
Alcohols	$\text{RCH}_2\text{OH}$	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	$\text{H}-\text{N}(\text{i-C}_3\text{H}_7)_2$	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

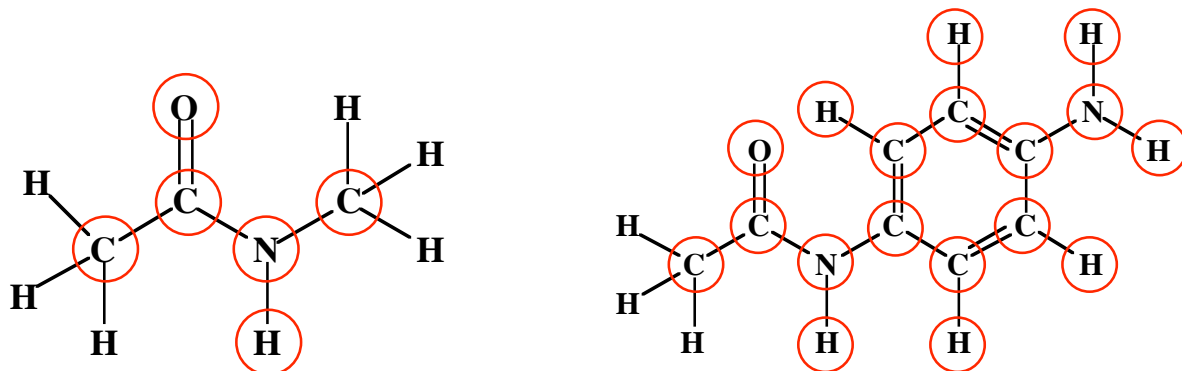
1. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

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.

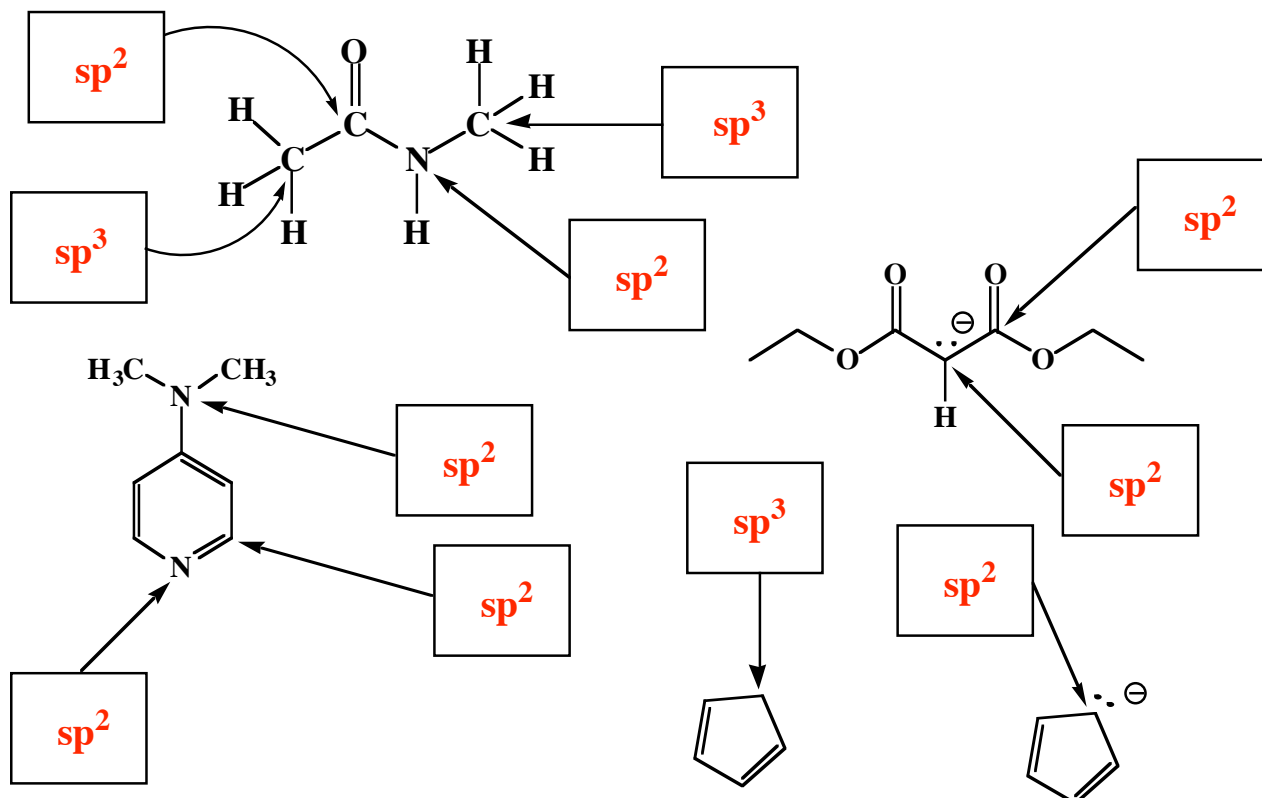
2. (10 pts) On the left is drawn the Lewis structure of a simple amide. Draw the two next most important contributing structures in the spaces provided. Be sure to show all lone pairs and formal charges.



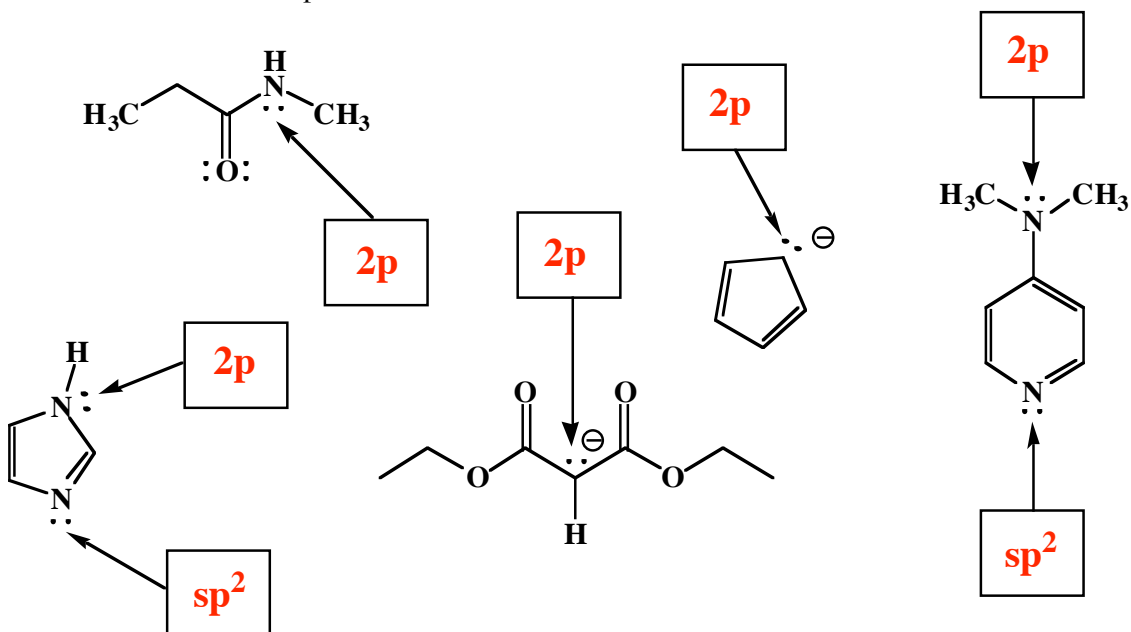
3. (12 pts) Because of pi delocalization, many of the atoms in the molecules below are predicted to be in the same plane. On the structures below, circle all the atoms that you believe will be located the same plane at all times. Do not circle atoms that are in the same plane only temporarily as bonds rotate freely at room temperature.



4. (11 pts) In the boxes provided, write the hybridization state of the given atoms.



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

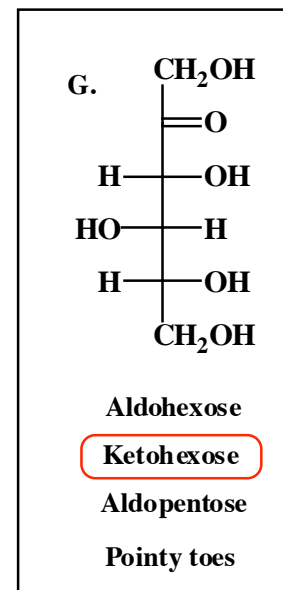
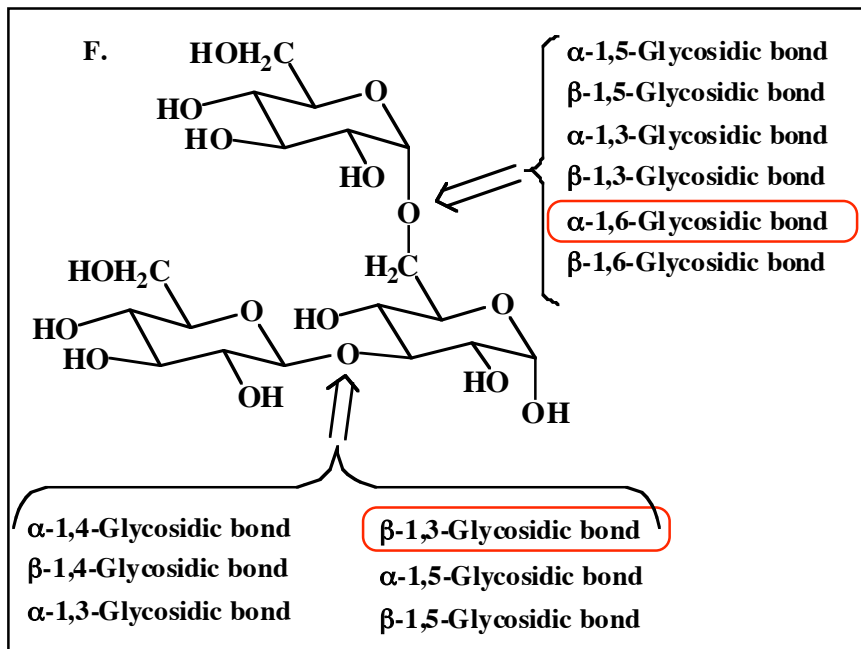
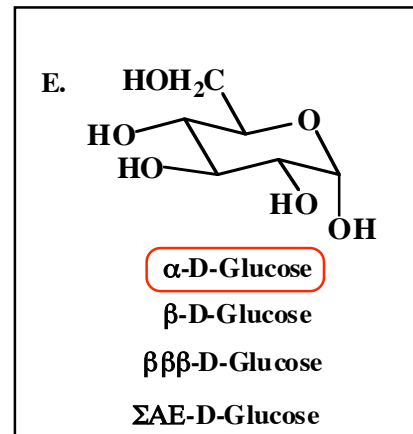
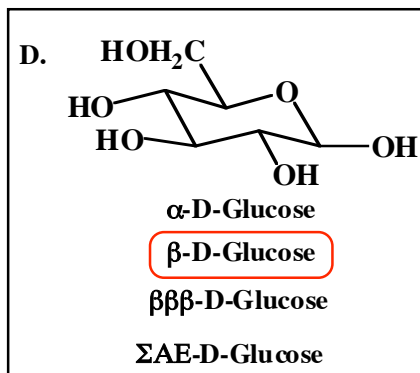
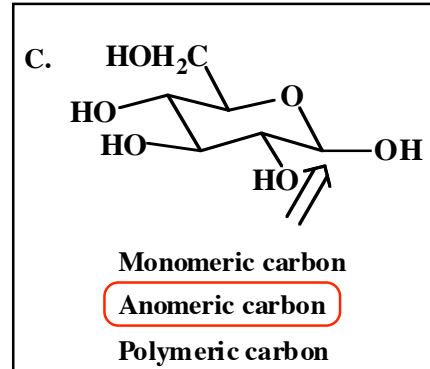
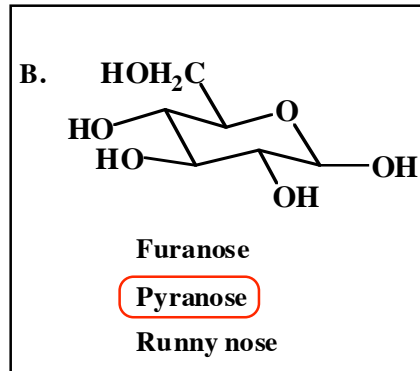
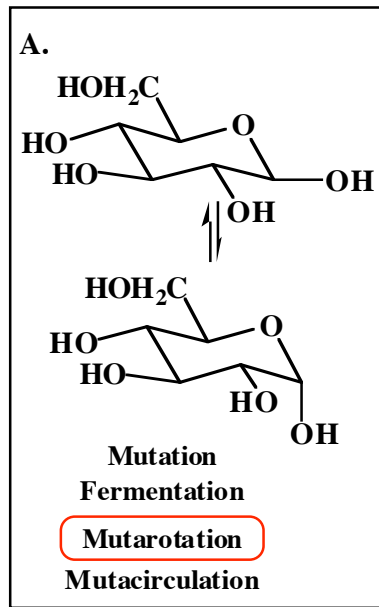


6. (2 pt. each) Here are a number of statements regarding general aspects of organic chemistry. Do not second guess yourself, this is not meant to be tricky! Check the appropriate box to indicate whether the statement is true or false.

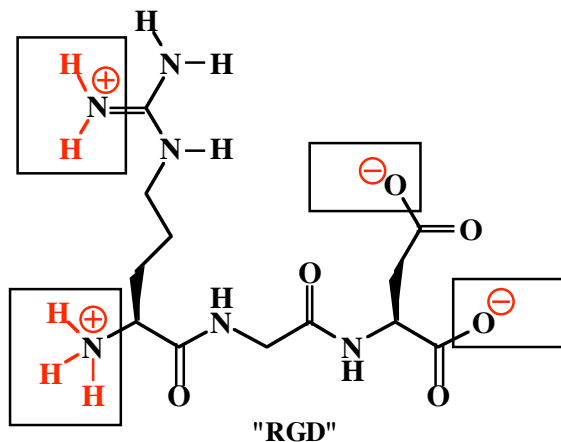
	True	False
A. In $^1\text{H}$ -NMR, a spectrum plots the energy (as frequency) necessary for the nuclei to be excited from the lower energy spin state to the higher energy spin state	<input checked="" type="checkbox"/>	<input type="checkbox"/>
B. Equivalent hydrogen atoms in a molecule have an identical relationship to all the other atoms in the molecule	<input checked="" type="checkbox"/>	<input type="checkbox"/>
C. Equivalent hydrogen atoms in a molecule give the same NMR signal.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
D. In $^1\text{H}$ -NMR, the peaks are plotted using "ppm" as the units, which stands for "proton peak measurement".	<input type="checkbox"/>	<input checked="" type="checkbox"/>
E. For alkyl groups with freely rotating bonds, complex splittings simplify because coupling constants ("J") are all about the same..	<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. An $\alpha,\beta$ -unsaturated aldehyde is a great nucleophile in a Michael reaction.	<input type="checkbox"/>	<input checked="" type="checkbox"/>
H. When a reaction is under thermodynamic control, only the relative energies of the products determines which one predominates.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
I. When a reaction is under kinetic control, only the relative energies of the products determines which one predominates.	<input type="checkbox"/>	<input checked="" type="checkbox"/>
J. The Diels-Alder reaction involves a two-step mechanism	<input type="checkbox"/>	<input checked="" type="checkbox"/>
K. The Diels-Alder reaction involves a concerted mechanism, with a transition state, but no intermediates.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
L. In the Diels-Alder reaction, the stereochemistry of the dienophile ( <i>cis</i> or <i>trans</i> ) is maintained in the product.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
M. In the Diels-Alder reaction, the diene must be in the <i>s-trans</i> geometry	<input type="checkbox"/>	<input checked="" type="checkbox"/>



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



8. (11 points) A) This semester we have learned a great deal about carboxylic acids, guanidine groups, and amines. Here is an apply what you know problem. The so-called RGD peptides bind to special receptors in the body, including adhesion receptors important for angiogenesis (production of blood vessels). Charge is a major factor that controls binding of RGD peptides to their receptors. Below is the tripeptide Arginine-Glycine-Aspartic acid (RGD). In the boxes provided, draw the correct protonation state of the carboxylic acid, amine, or guanidine group at neutral pH, 7.0. You must show all protons and formal charges that are present on the functional groups within the four boxes. For this problem, assume the  $pK_a$  values of the carboxylic acids are 4.0, the  $pK_a$  value for a protonated amine is 9.2, and the  $pK_a$  value for a protonated guanidine group is 13.2.

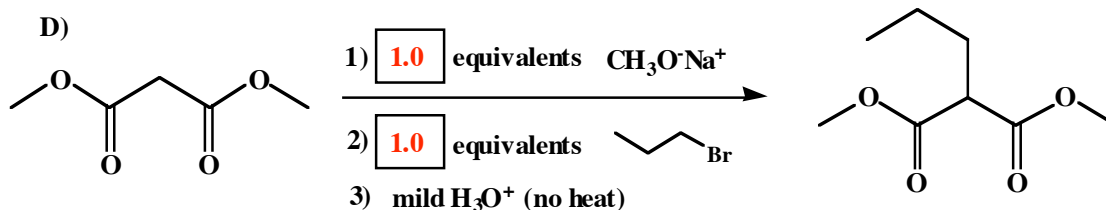
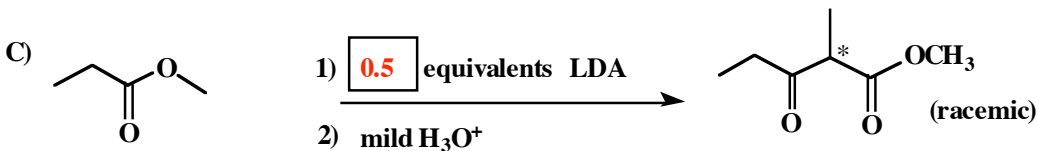
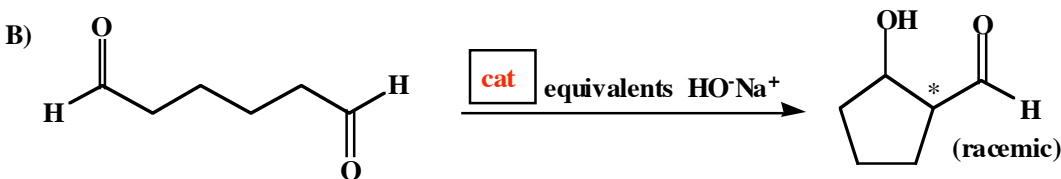
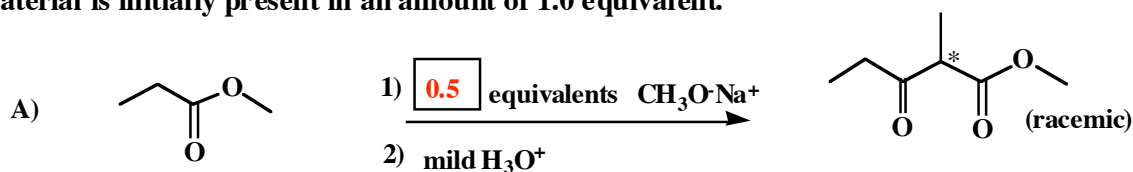


B) What is the total charge on this peptide at pH 7.0? 0

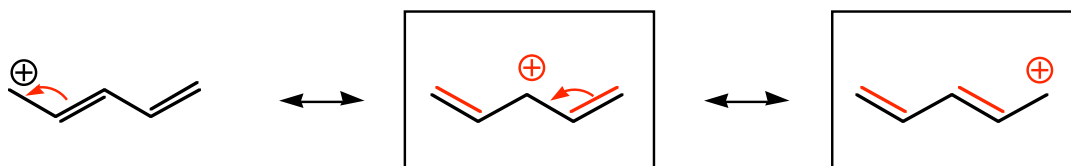
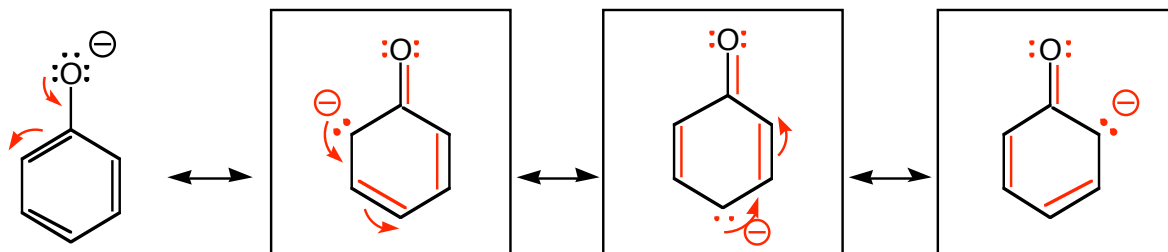
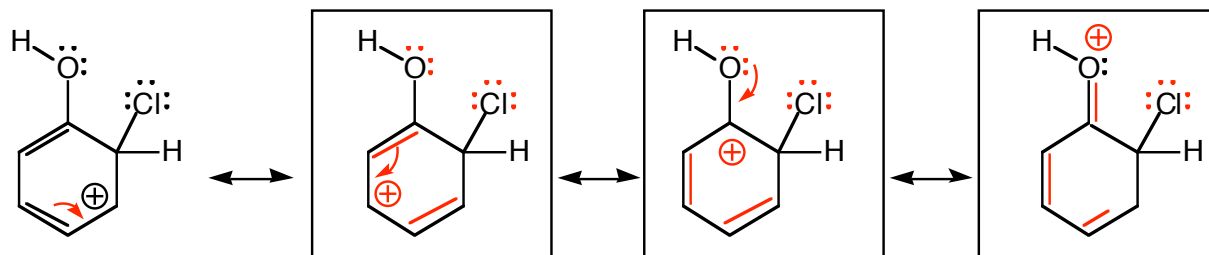
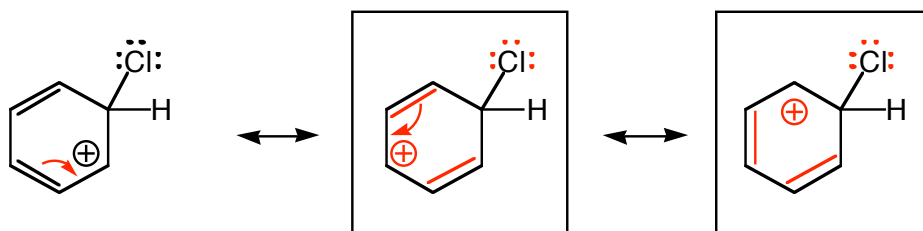
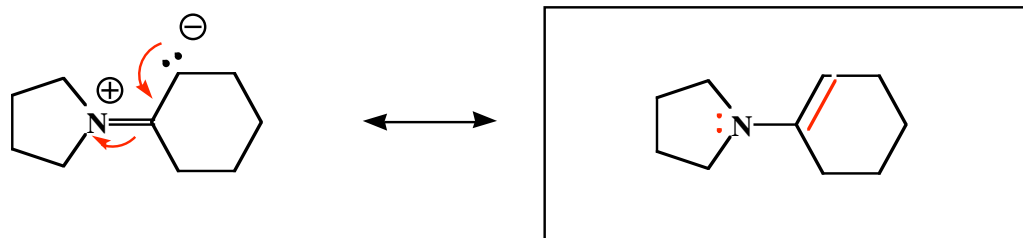
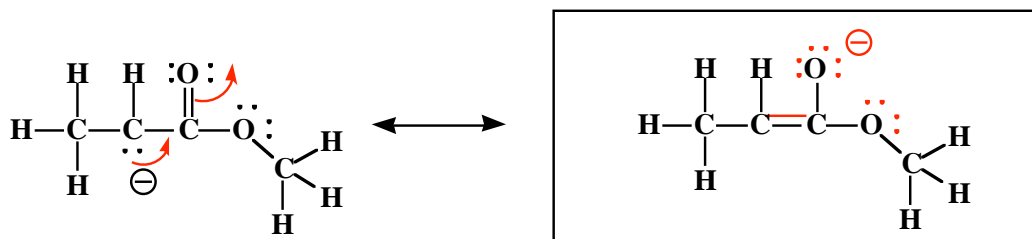
C) What is the total charge on this peptide at pH 2.0? +2

D) What is the total charge on this peptide at pH 11.2? -1

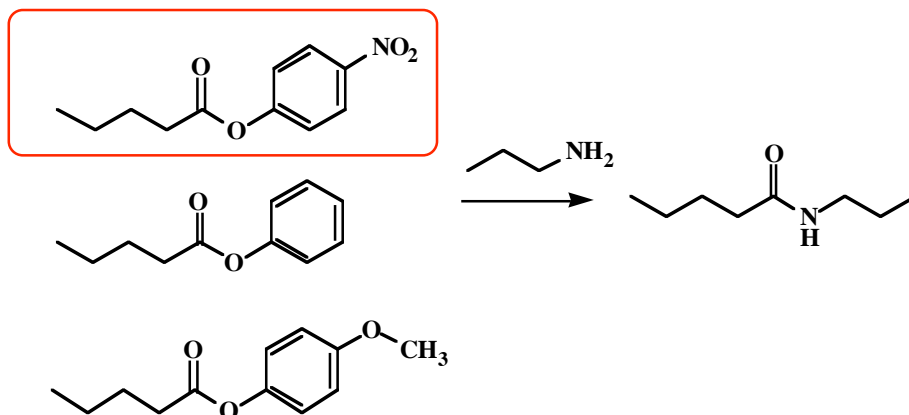
9. (2 pts each) In each of the boxes over an arrow, write the minimum number of equivalents of the specified reagent required to carry out the reaction shown to completion. If only a catalytic amount is needed, write "CAT". Note: You must assume the carbonyl compound starting material is initially present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



10. (38 pts total) For the following, draw the other important contributing structure or structures (resonance form(s)) we presented in class. You must draw arrows on the structure to the left to indicate the flow of electrons that leads to the contributing structure you draw to the right (All but the rightmost structure on each line has arrows on it). Be sure to show all lone pairs and formal charges on your structures. We have drawn template structures to save you time.



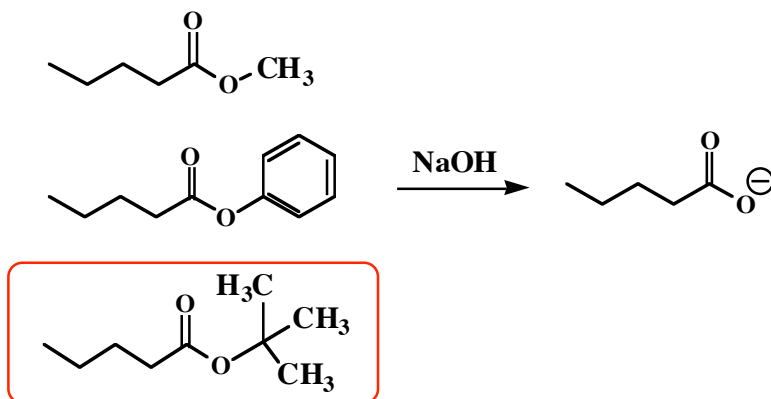
11. (9 pts) Here is an apply what you know problem. One of the following esters reacts with nucleophiles such as primary amines thousands of times faster than the others. Circle the ester that reacts faster, and in the space provided, in no more than two sentences explain why it reacts faster.



Explain your answer here (no more than two sentences):

Carboxylic acid derivatives react with nucleophiles according to leaving group ability, and the nitrophenoxide anion is the best leaving group. The nitro group is strongly electron withdrawing, so it stabilizes the negatively-charged phenoxide anion, and the most stable anion makes the best leaving group.

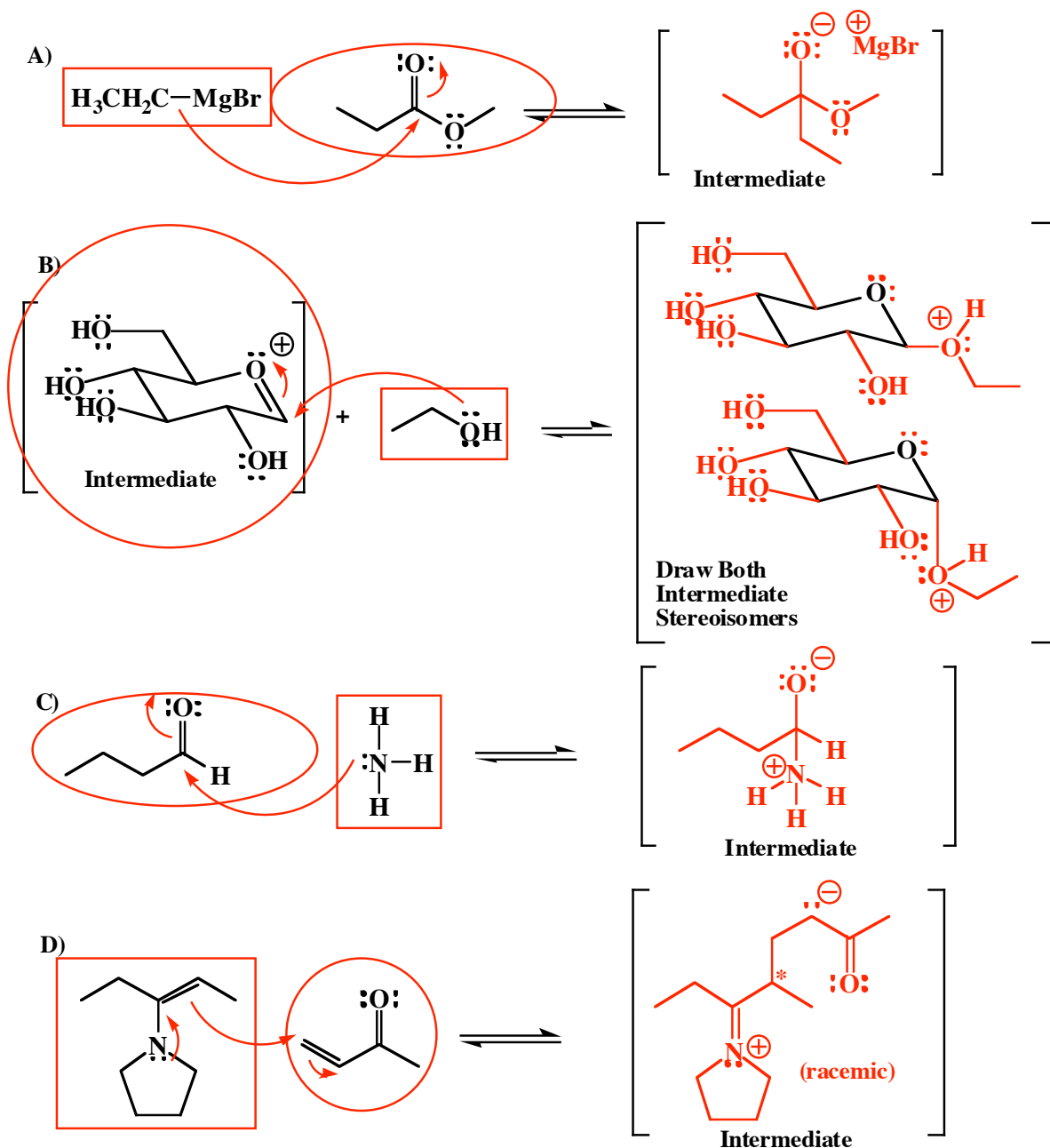
12. (9 pts) Here is another apply what you know problem. One of the following esters reacts MUCH MORE SLOWLY with NaOH. Circle the ester that does not react, and in the space provided, in no more than two sentences explain why it does not react.



Explain your answer here (no more than two sentences):

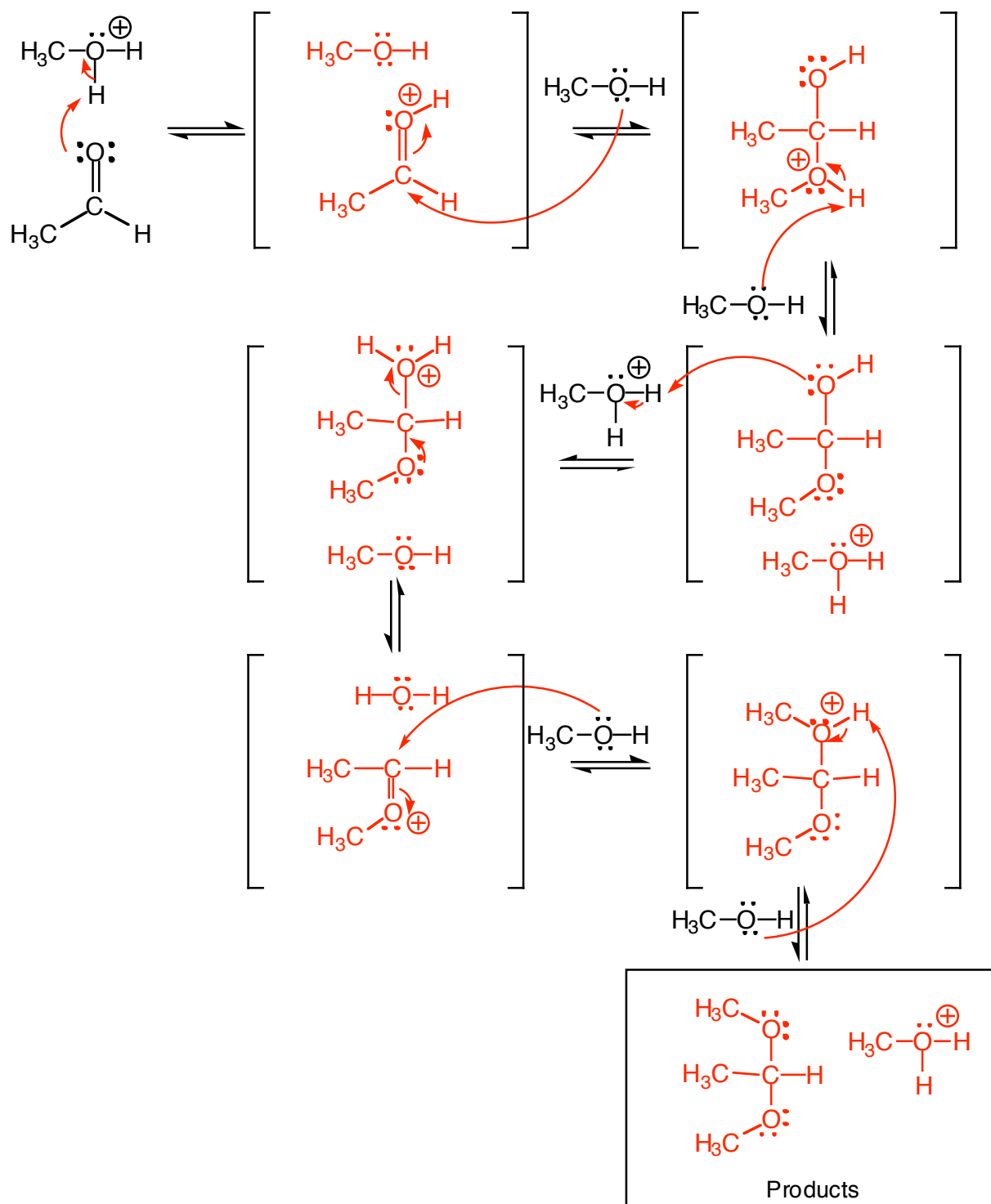
The steric hindrance provided by the *tert*-butyl group prevents nucleophilic attack of the carbonyl. The other two esters react fine, so we hoped you would pick the *tert*-butyl ester by process of elimination, then come to the conclusion that it must be steric.

13. (31 points) Many of the reactions we have learned this semester involve steps with nucleophiles reacting with electrophiles. For the following examples of steps in mechanisms we have seen this semester, 1) **Draw the intermediate that will be formed when the two molecules react.** 2) **Draw all formal charges and lone pairs on the intermediates.** 3) **Draw arrows on the starting materials to indicate the flow of electrons that leads to the intermediate.** 4) **Finally, draw a box around the nucleophile and a circle around the electrophile in each case.** There is no need to draw products or any further steps of the mechanisms. You might want to read these directions again so you know what we want.



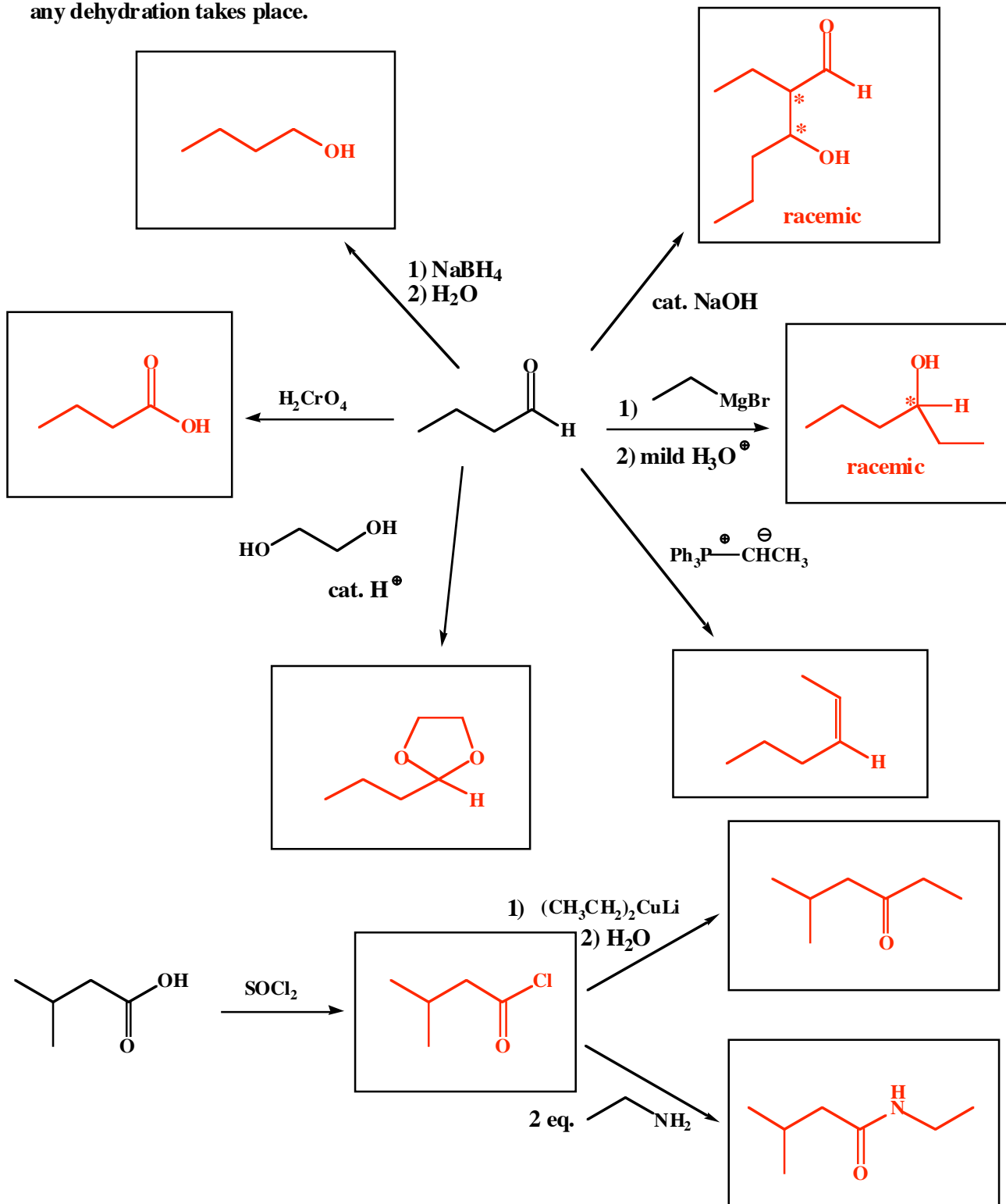
*Did you remember to draw boxes and circles?*

13. (33 points) Complete the mechanism below for acetal formation. Use arrows to show the movement of all electrons, and be sure to draw all lone pairs of electrons and all formal charges. You do not have to worry about labeling chiral centers on this one. **Remember, you must show all products for each step.**



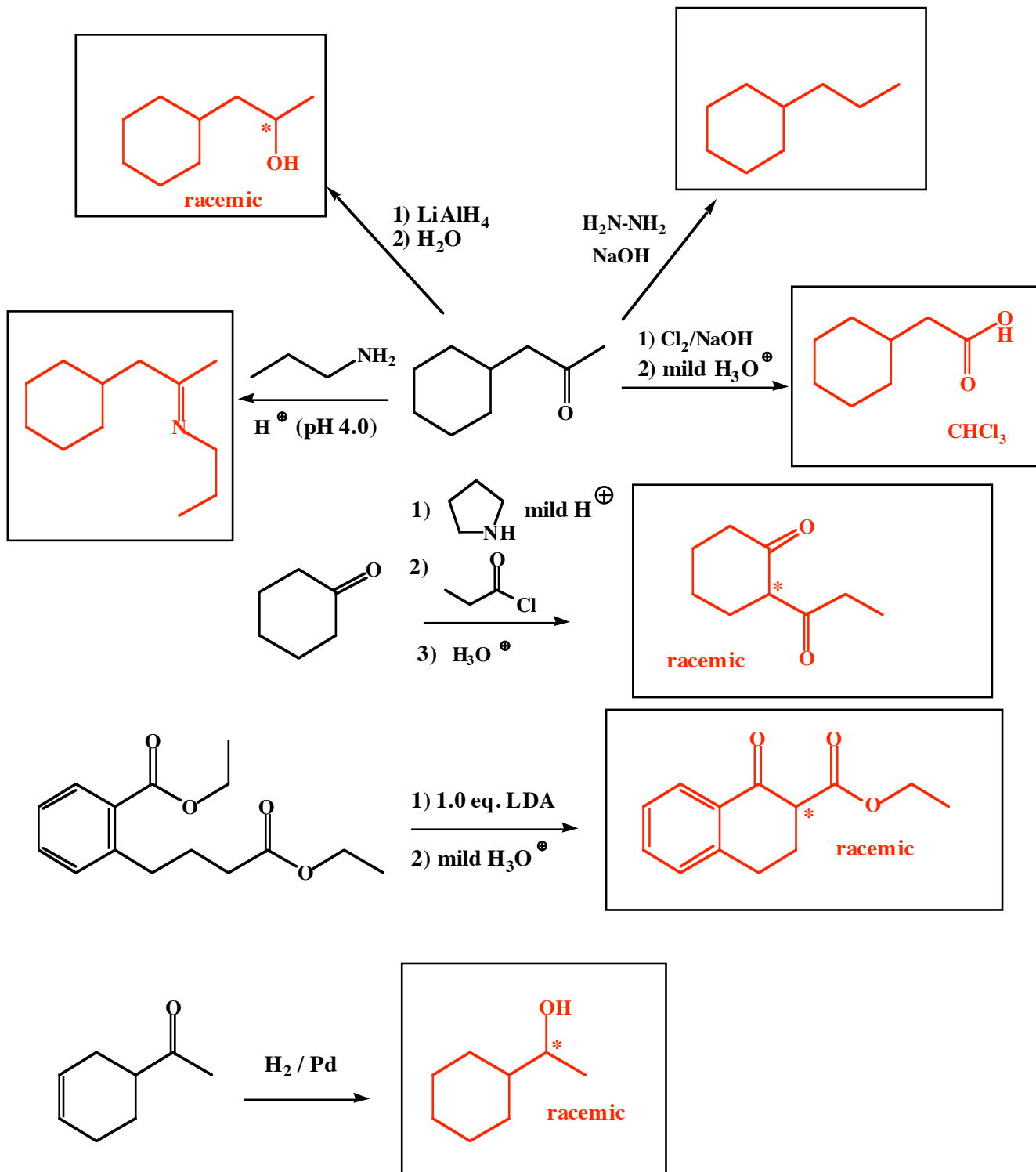
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14. (31 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, mark the chiral center with an asterisk "\*" and write "racemic" under the structure. If there is an aldol reaction, draw the product before any dehydration takes place.



Signature \_\_\_\_\_

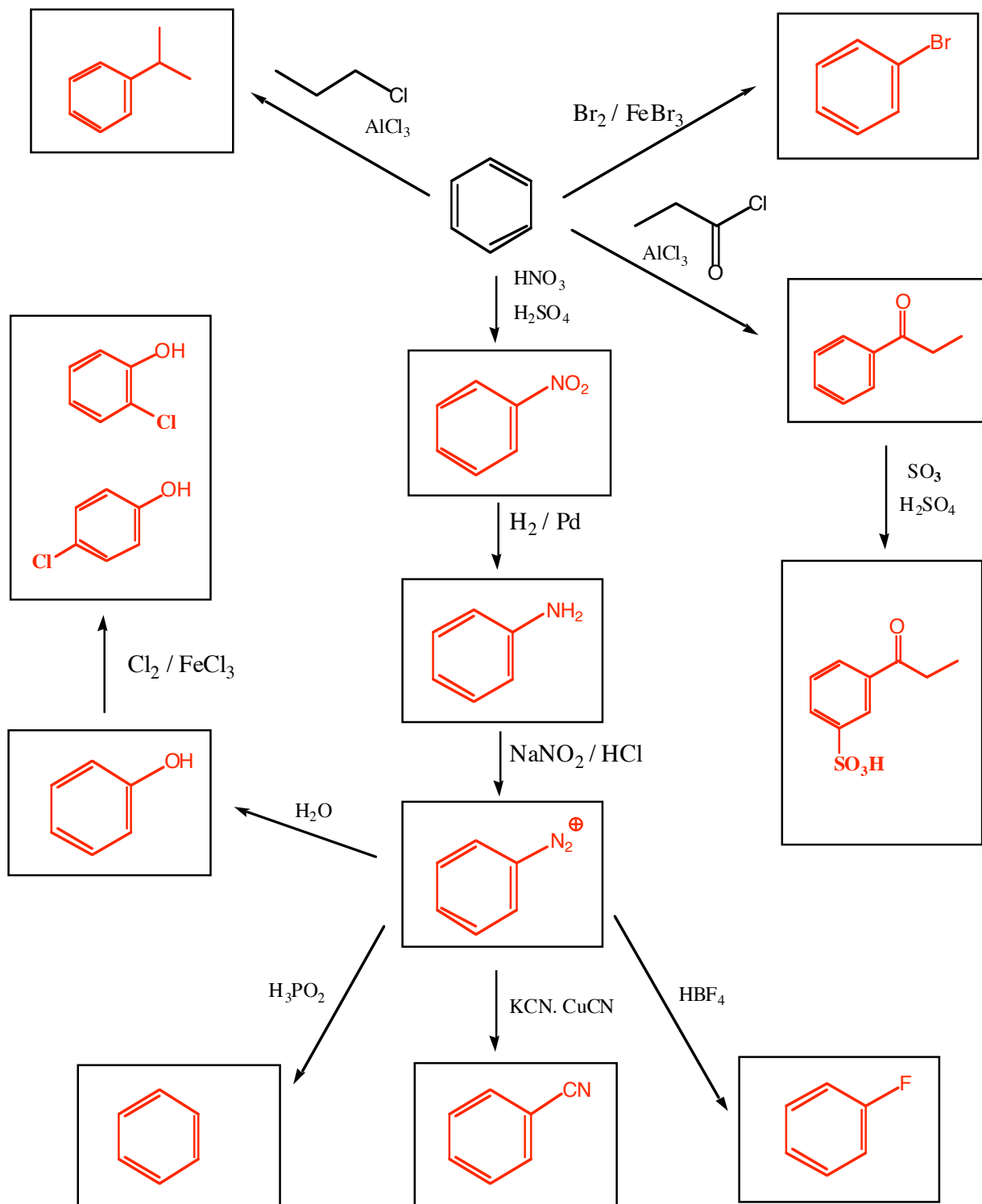
15. (29 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, mark the chiral center with an asterisk "\*" and write "racemic" under the structure. If there is an aldol reaction, draw the product before any dehydration takes place.



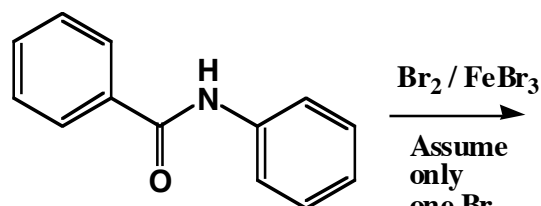
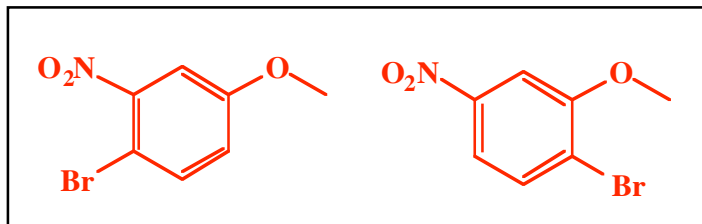
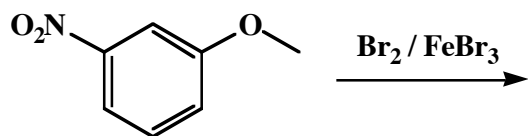


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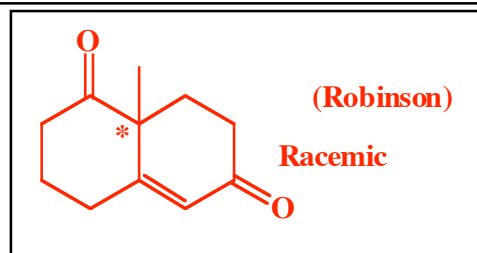
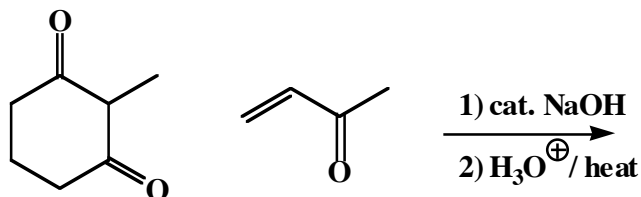
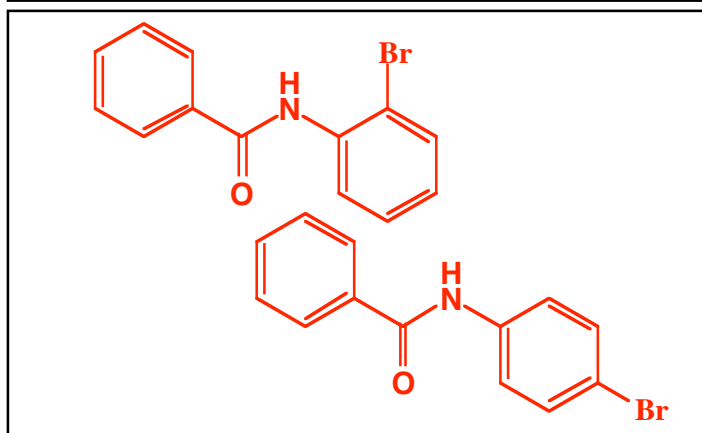
16. (25 pts.) Write the predominant product or products that will occur for each transformation. Assume each reagent only adds once to the ring. If predominantly ortho/para products are predicted, you must draw both.



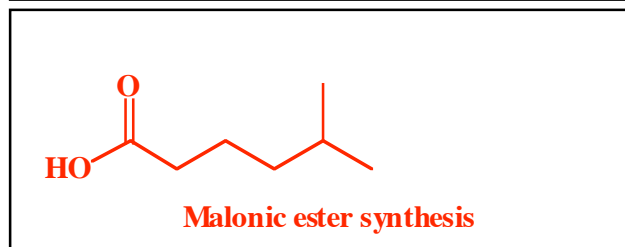
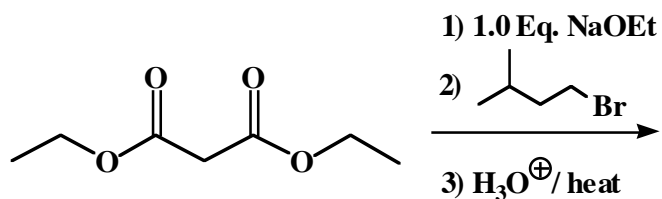
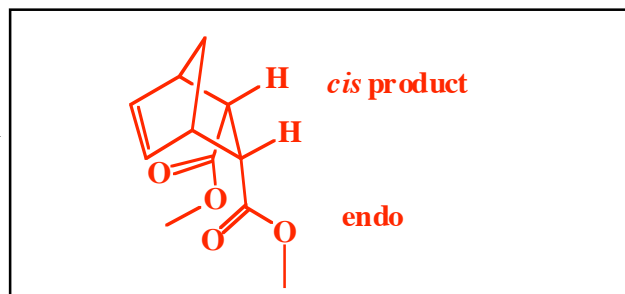
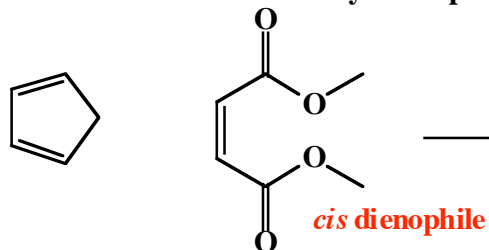
17. (21 pts.) You might find these are harder so take your time. Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, mark the chiral center with an asterisk "\*" and write "racemic" under the structure.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



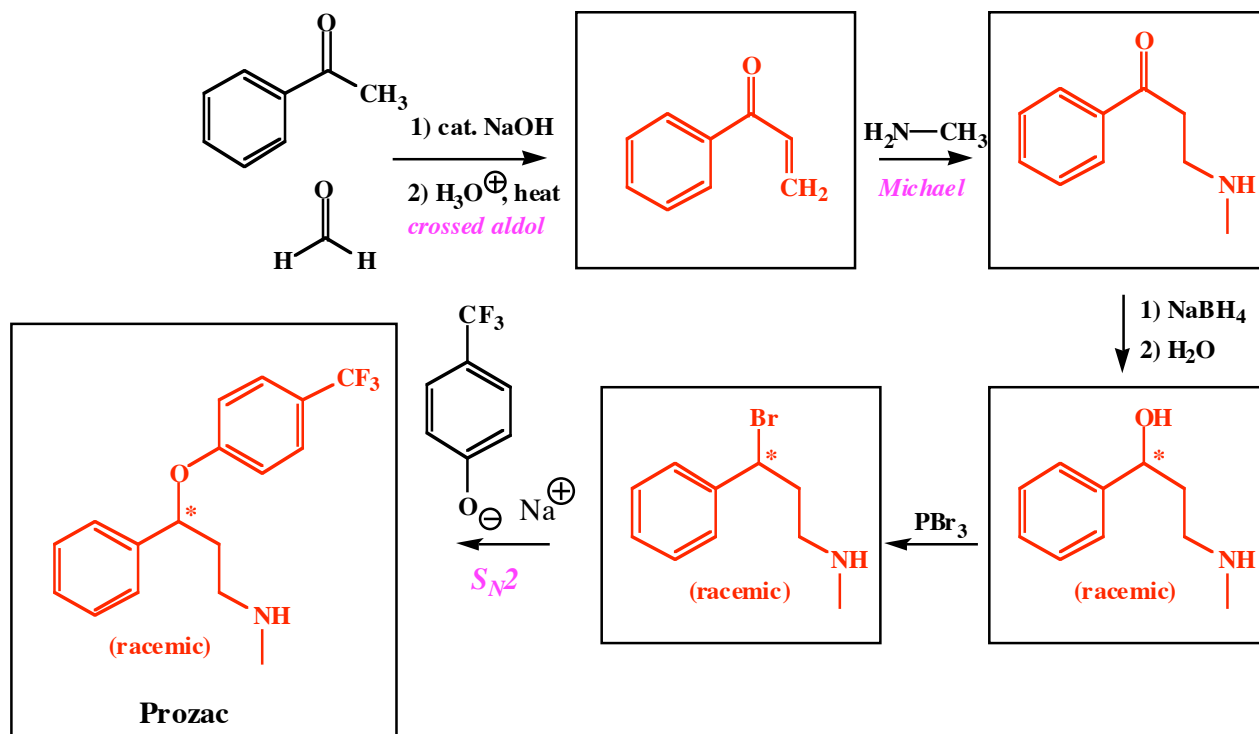
Assume only one Br atom adds



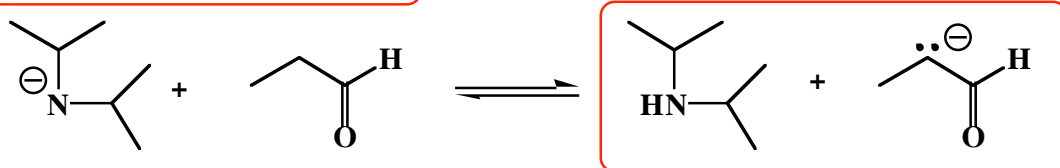
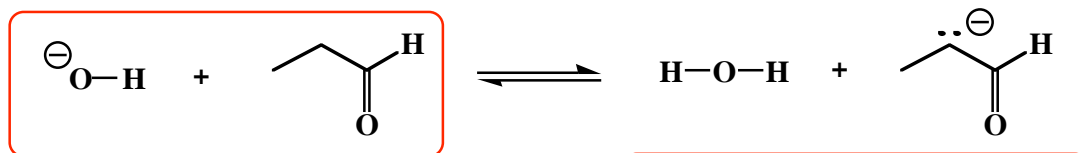
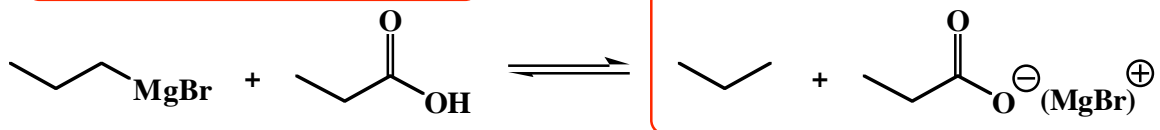
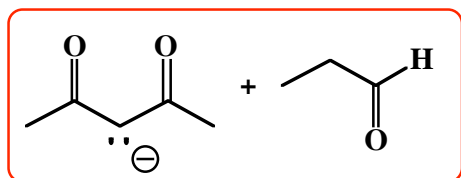
Be sure to indicate stereochemistry of the products on this next one.



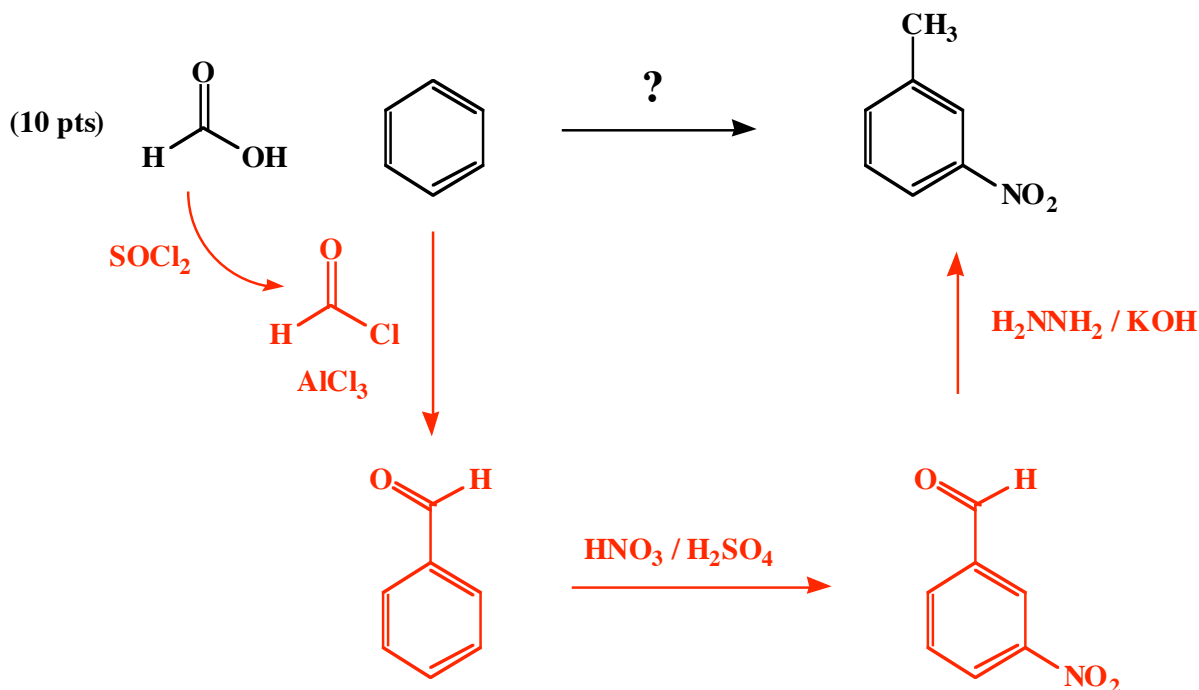
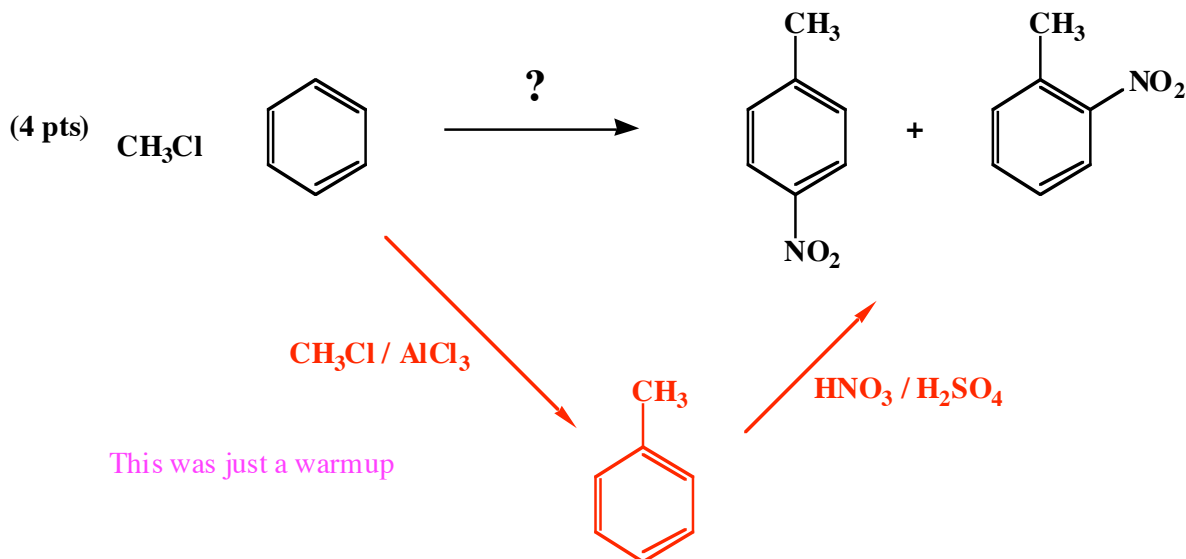
17. (21 pts.) Here is the synthesis of the important pharmaceutical Prozac. You are familiar with all of the chemistry, it just might take you a while to recognize the reactions. **Fill in the boxes with the appropriate structures, and remember to use an asterisk "\*" and write "racemic" to indicate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



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

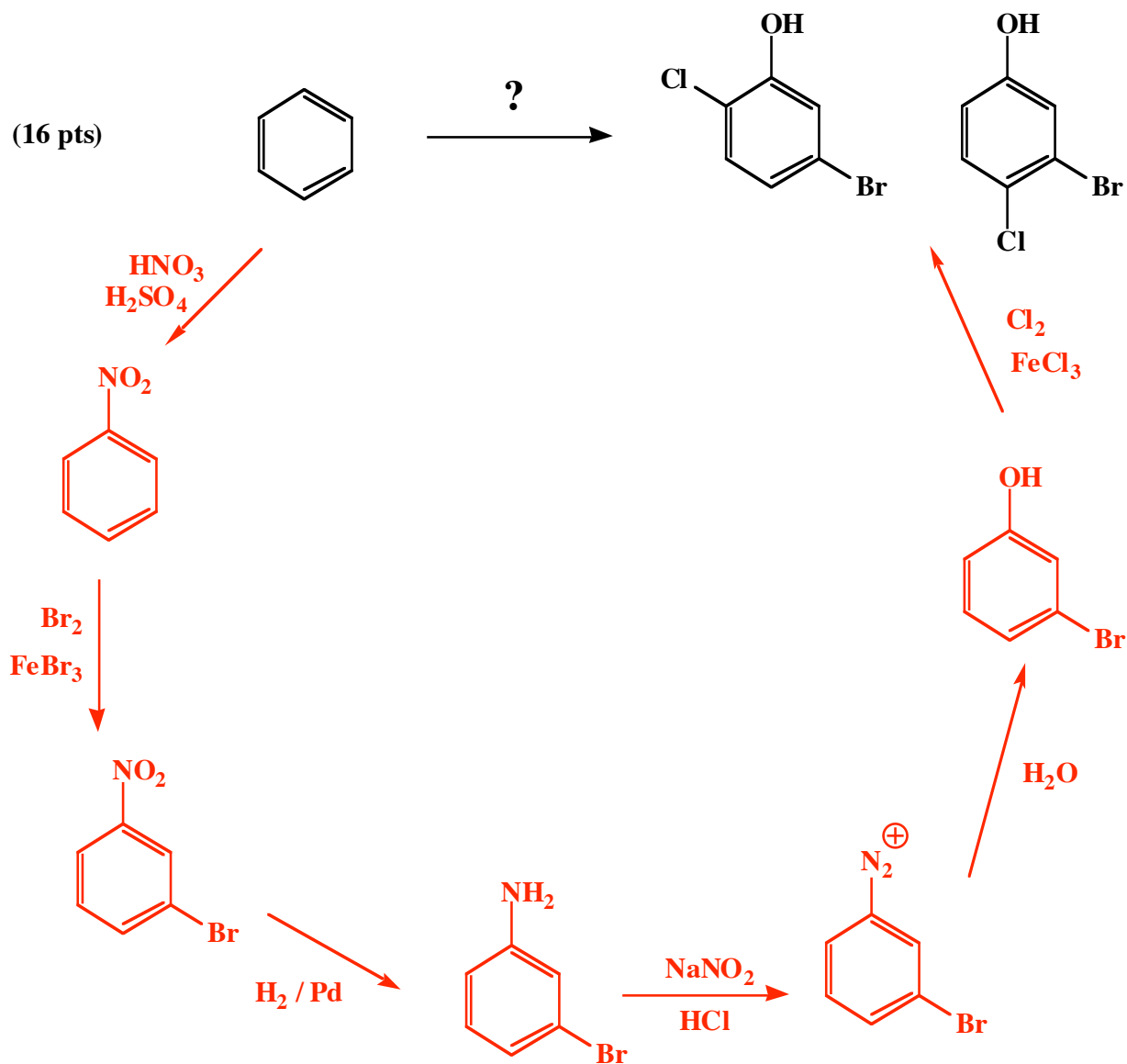


19. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule!



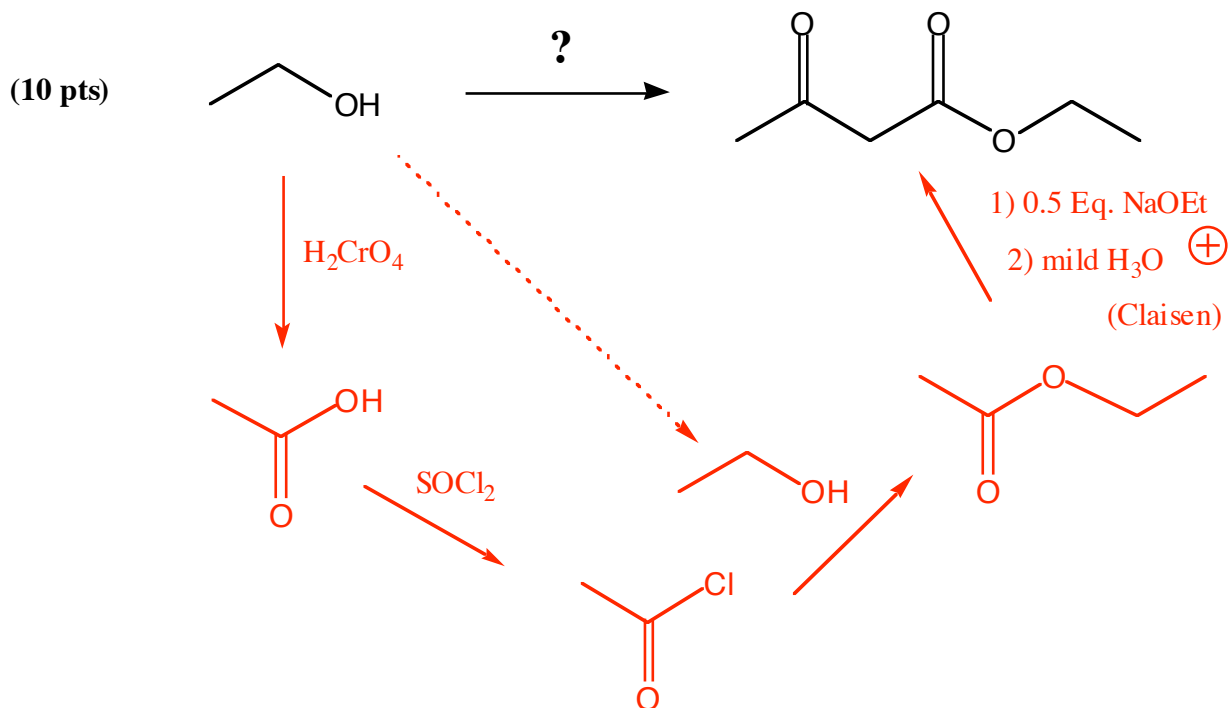
Recognize that this one is harder than it looks because the Friedel-Crafts reaction will not work on a ring with a bad group like the nitro group on it. Therefore, the methyl group has to be made using a Wolff-Kishner or Clemmensen reduction following nitration.

19. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule! **NOTE: For this one, you are not allowed to separate complex mixtures along the way and pull out just the isomers you want. In other words, the product isomers shown must be the only predominant isomers you make during your synthesis.**



**Recognize** that the last reaction had to be the chlorination reaction of the meta bromophenol. This is because we see both the ortho and para chlorination products. **Recognize** that both the OH and Br groups of meta bromophenol are ortho/para directors, so their meta relationship must derive from nitrobenzene, followed by the bromination reaction, followed by the Mr. Bill reaction and conversion to the phenol with  $\text{H}_2\text{O}$ .

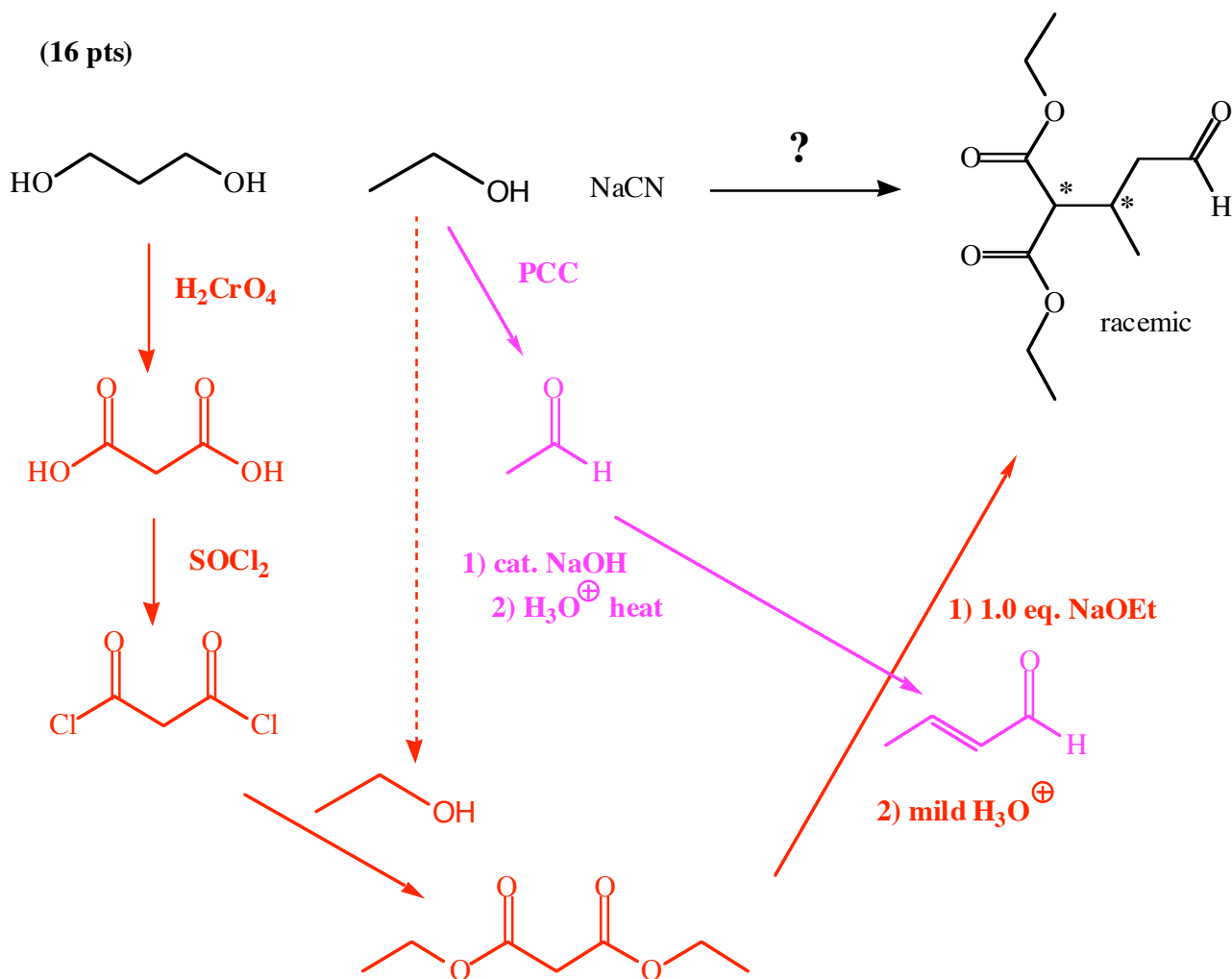
19. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule!



The key recognition element is the  $\beta$ -keto ester product indicating a Claisen as the last step.

Alternatively, the ethyl ester could have been made from a reaction of ethanol with sulfuric acid directly, avoiding the acid chloride intermediate.

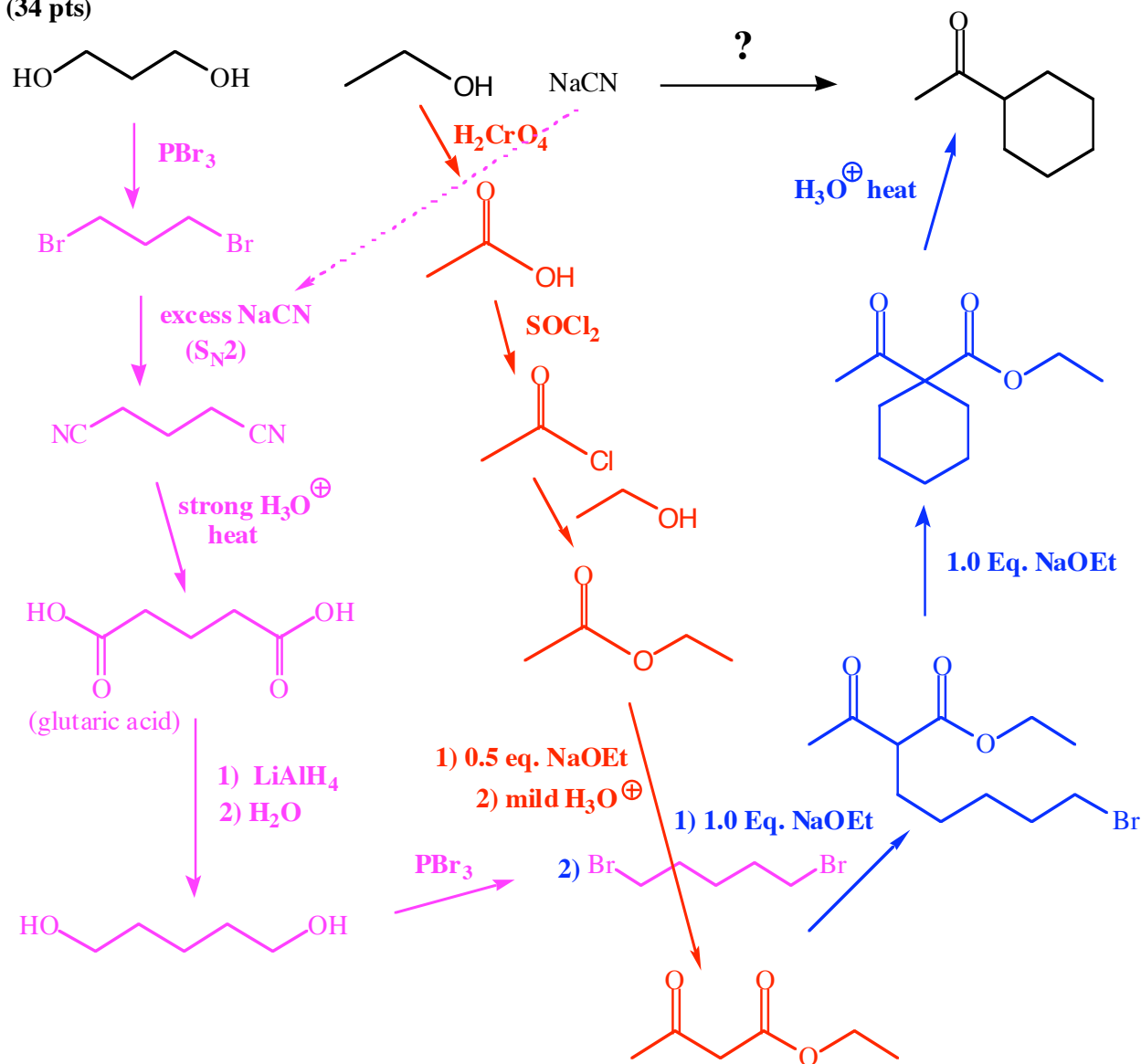
19. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Note, for these last two, you might not need to use all three starting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



**Recognize** the product as coming from a Michael reaction between an  $\alpha,\beta$ -unsaturated aldehyde and the enolate of diethyl malonate. **Recognize** the  $\alpha,\beta$ -unsaturated aldehyde as coming from an aldol reaction including dehydration using acetaldehyde. Acetaldehyde, in turn, is derived from the PCC oxidation of ethanol. **Recognize** that the malonic acid portion of diethyl malonate is available from the oxidation of the starting diol. Conversion to diethyl malonate can be accomplished using  $\text{SOCl}_2$  and ethanol, or a Fischer esterification. Note that the  $\text{NaCN}$  is not needed in this problem.

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

(34 pts)



**Recognize** the product as coming from an acetoester synthesis (methyl ketone is the KRE). The tricky part of this one is **recognizing** that the ring comes from alkylation of ethyl acetoacetate in two sequential steps by 1,5-dibromopentane. **Recognize** that the ethyl acetoacetate comes from the Claisen reaction of ethyl acetate which in turn comes from ethanol and acetic acid, the latter of which comes from chromic acid oxidation of ethanol. **Recognize** that the dibromopentane can be derived by converting the propane diol to the dibromide  $\text{S}_{\text{N}}2$  reaction with NaCN followed by hydrolysis to give glutaric acid, reduction to give 1,5 pentane diol, and finally conversion to the desired 1,5-dibromopentane using  $\text{PBr}_3$ .