

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

Chemistry 310N  
Dr. Brent Iverson  
3rd Midterm  
April 27, 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	(28)
2	(24)
3	(32)
4	(16)
5	(29)
6	(18)
7	(33)
8	(12)
9	(24)
10	(11)
11	(14)
12	(13)
13	(19)
Total	(273)
T Score	

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	$\text{H}-\text{N}(\text{i}-\text{C}_3\text{H}_7)_2$	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

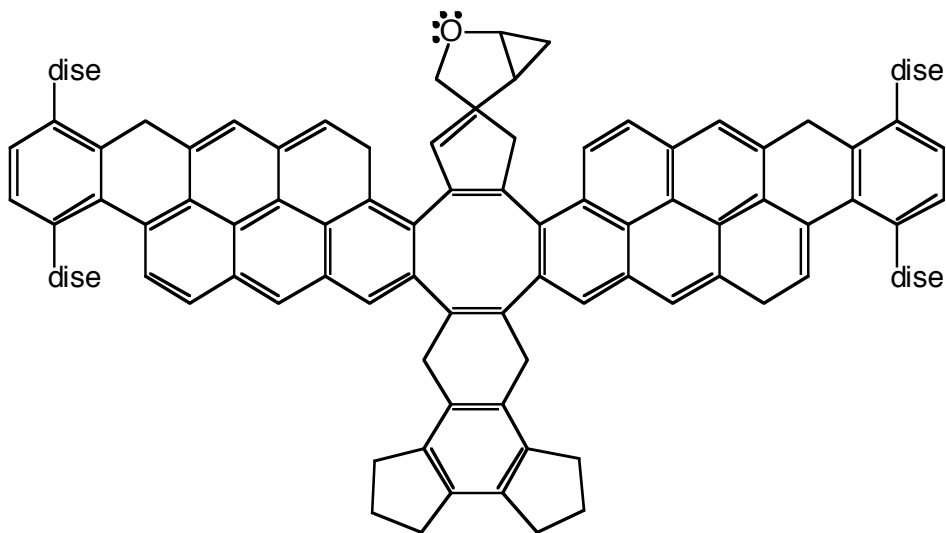
1. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

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**.

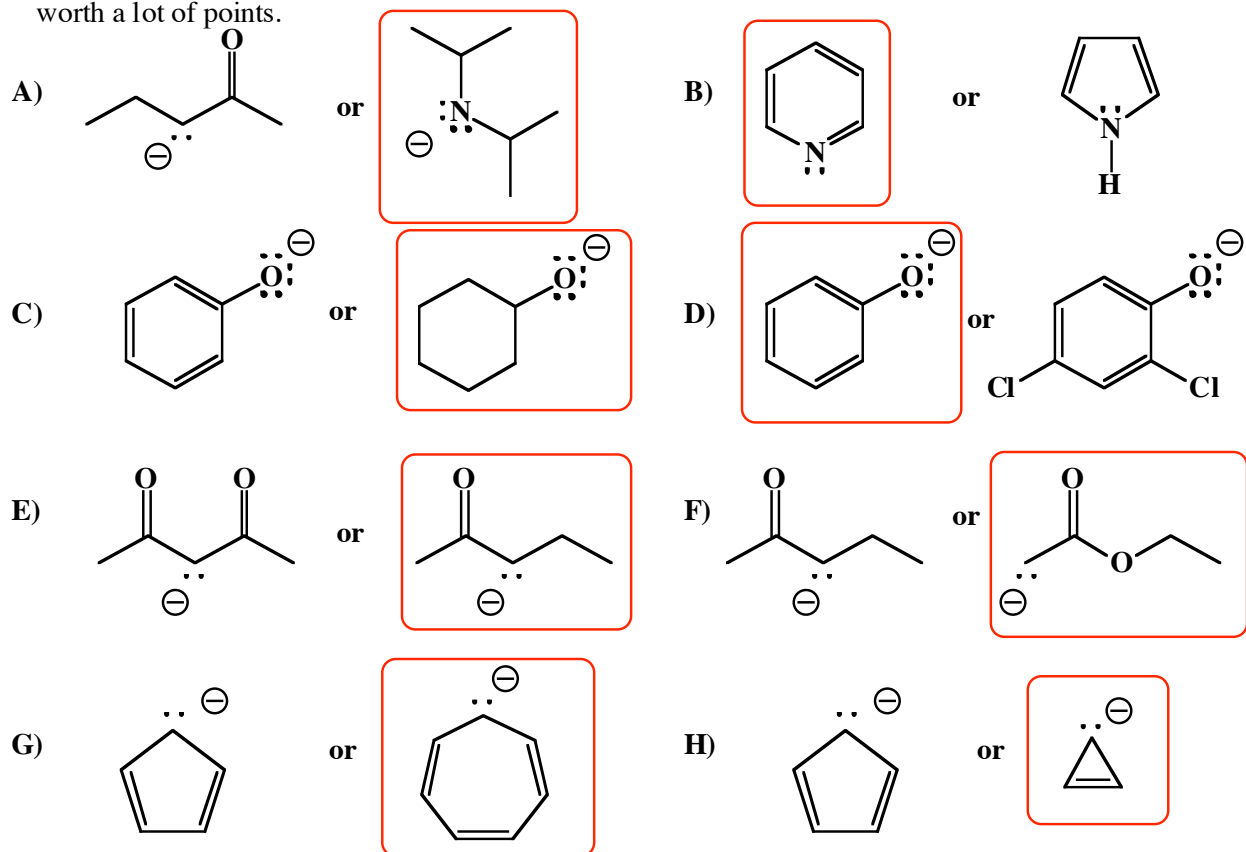
2. (2 pt. each) Here are a number of statements regarding aromaticity or other general aspects of organic chemistry. Do not second guess yourself, this is not meant to be tricky! **Check the appropriate box to indicate whether the statement is true or false.**

	True	False
A. When using molecular orbital theory, it is best to think of electron density as being like waves, since it is described mathematically using wave equations.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
B. According to Huckel's rule, aromatic molecules are flat, monocyclic, all ring atoms have a 2p orbital (no sp <sup>3</sup> ring atoms) and there are 4n + 2 pi electrons (i.e. 2, 6, 10, 14.....).	<input checked="" type="checkbox"/>	<input type="checkbox"/>
C. Most reactions you have learned in this class involve nucleophiles reacting with electrophiles.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
D. Electrophiles are areas in molecules with relatively high electron density.	<input type="checkbox"/>	<input checked="" type="checkbox"/>
E. Nucleophiles are areas in molecules with relatively low electron density.	<input type="checkbox"/>	<input checked="" type="checkbox"/>
F. When drawing mechanisms, arrows are used to indicate the flow of electrons from electrophiles to nucleophiles.	<input type="checkbox"/>	<input checked="" type="checkbox"/>
G. A strong resonance effect due to aromaticity can stabilize a positive charge, negative charge, or unpaired electron density on atoms attached to an aromatic ring.	<input checked="" type="checkbox"/>	<input type="checkbox"/>

## Molecule of the day: The rare central Texas bird of Paradise.



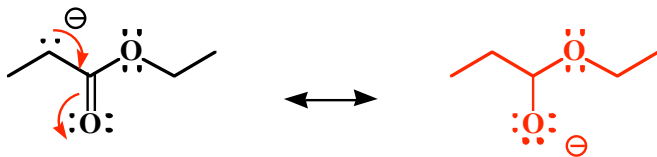
3. (3 pts each) For each pair, circle the molecule that is the **stronger base**. You may refer to the pKa table provided, or use any other chemical logic we have taught you to predict the answers. This is not meant to be tricky, but you might want to take your time here as there is much think about and this is worth a lot of points.



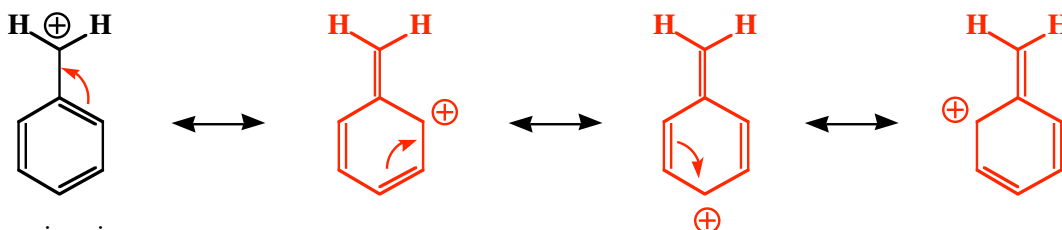
In each case, select the less stable anion, or when applicable, the anion derived from the weaker acid (higher pKa value).

4. (20 pts) Resonance contributing structures are important for both units covered by this exam, namely enolates and aromatic molecules. On the following, **draw the indicated number of most important resonance contributing structures. Show all lone pairs, pi bonds, and formal charges. Use arrows to indicate the redistribution of electrons on each molecule to the left, that leads to the contributing structure you draw immediately to its right.** (Only the structure on the farthest right on each line has no arrows on it). We drew template structures for you to save time.

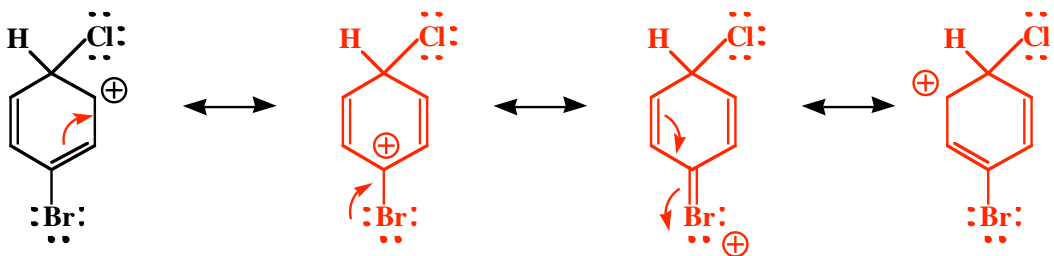
A. An enolate 2 pts each question to get arrows correct 2 pts per correct structure



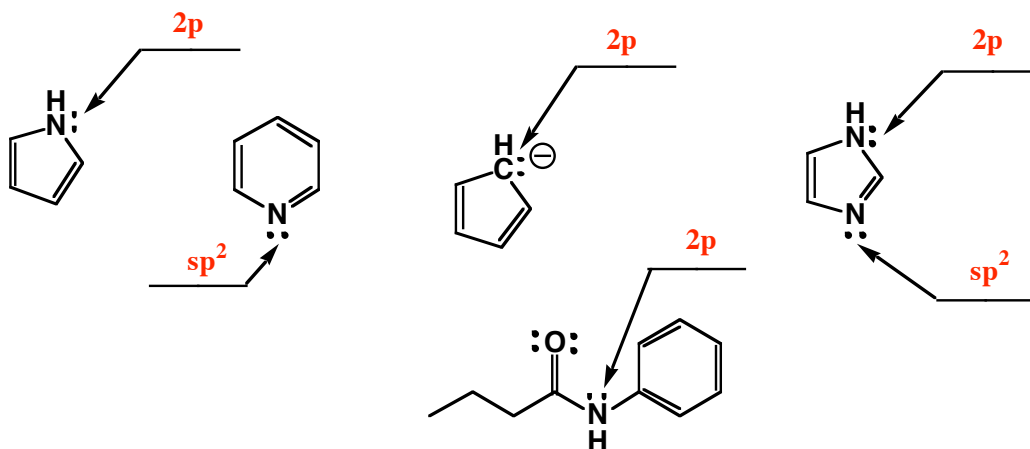
B. The benzyl cation




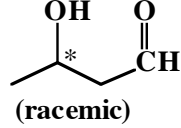
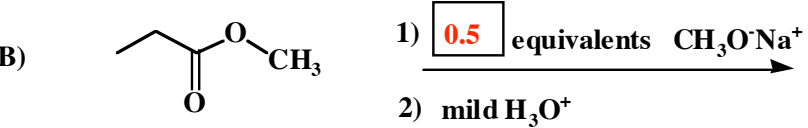
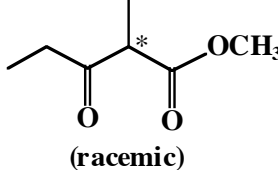
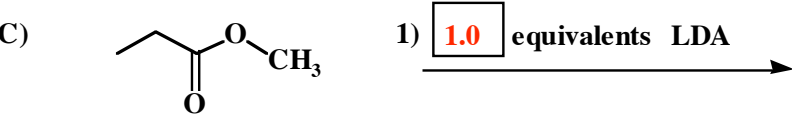
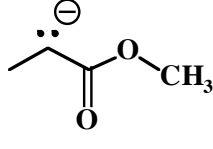
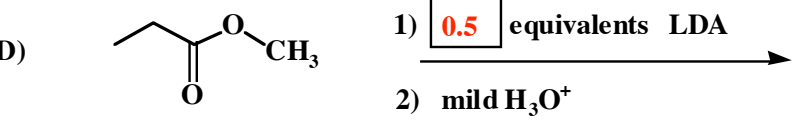
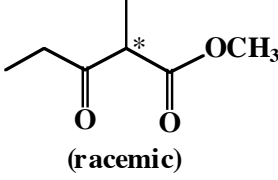
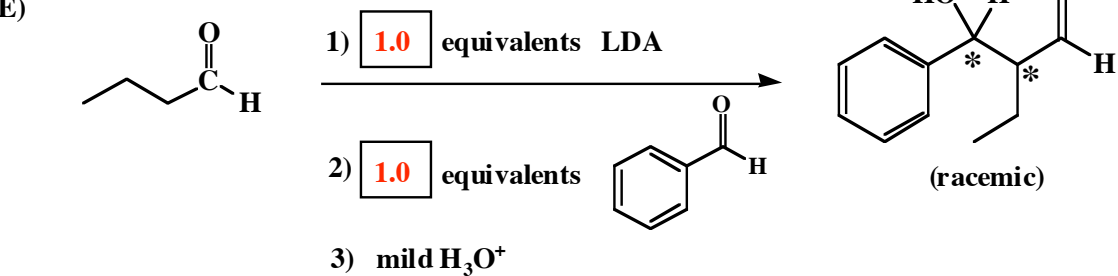
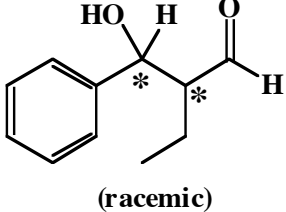
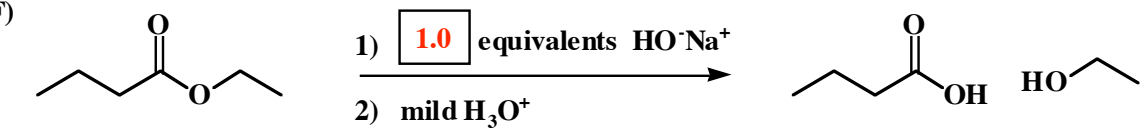
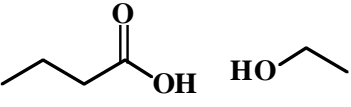
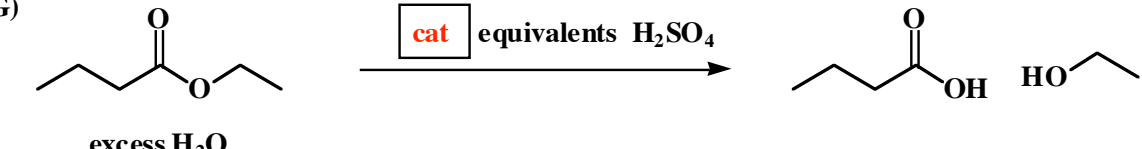
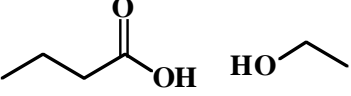
C. An arenium ion



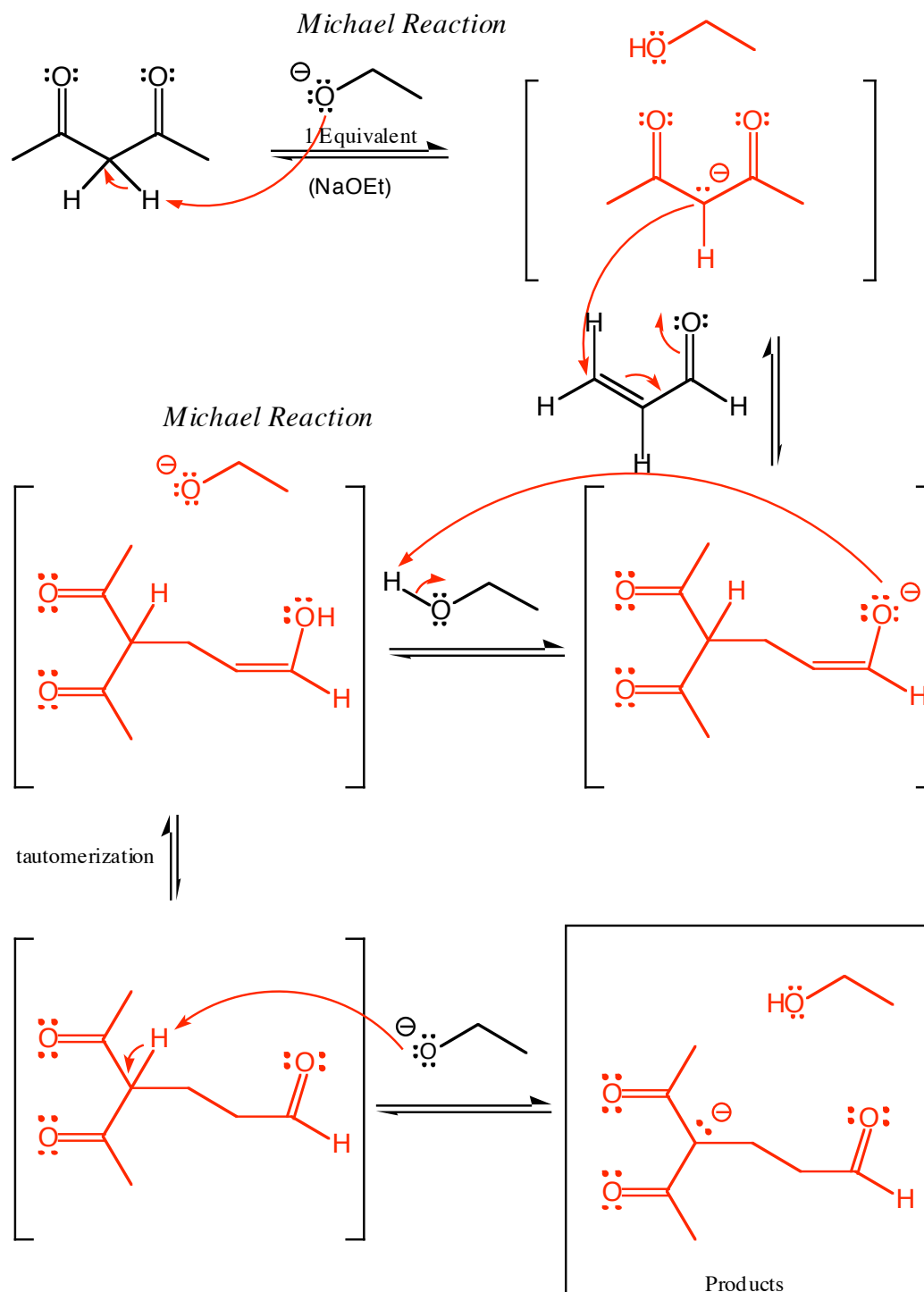
5. (2 pts each answer) Many important properties of molecules depend on the type of hybrid orbital that contains a lone pair. **On the line provided, write the type of orbital that contains the indicated lone pair of electrons.**



6. (2 pts each) In each of the boxes over an arrow, write the minimum number of equivalents of the specified reagent required to carry out the reaction shown **to completion**. If only a catalytic amount is needed, write "CAT". Note: You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent.

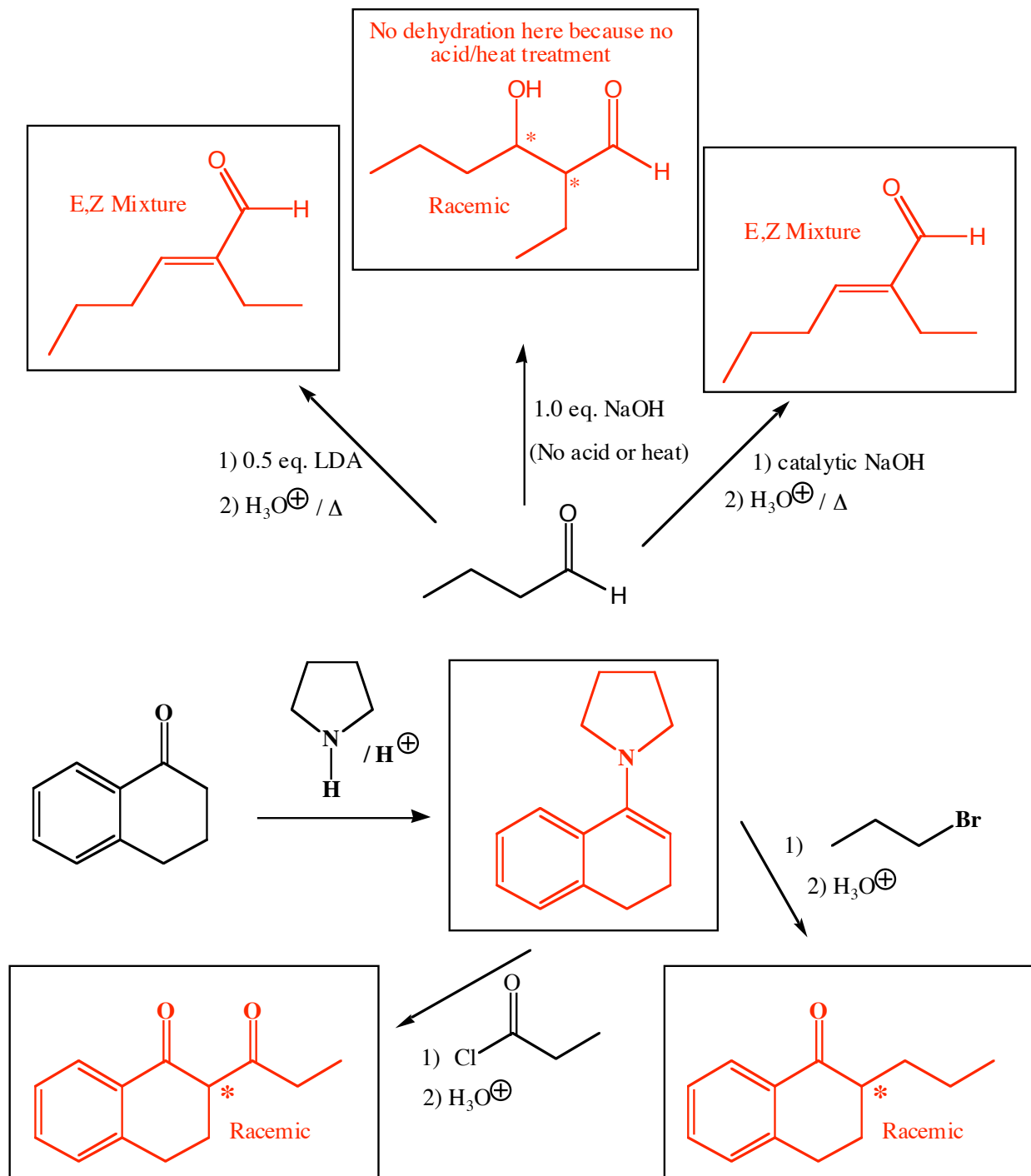
- A)   $\xrightarrow{\text{cat equivalents HO}^-\text{Na}^+}$   (racemic)
- B)   $\xrightarrow[2) \text{ mild H}_3\text{O}^+]{1) \text{ 0.5 equivalents CH}_3\text{O}^-\text{Na}^+}$   (racemic)
- C)   $\xrightarrow{1) \text{ 1.0 equivalents LDA}}$  
- D)   $\xrightarrow[2) \text{ mild H}_3\text{O}^+]{1) \text{ 0.5 equivalents LDA}}$   (racemic)
- E)   $\xrightarrow[3) \text{ mild H}_3\text{O}^+]{2) \text{ 1.0 equivalents C}_6\text{H}_5\text{CHO}}{1) \text{ 1.0 equivalents LDA}}$   (racemic)
- F)   $\xrightarrow[2) \text{ mild H}_3\text{O}^+]{1) \text{ 1.0 equivalents HO}^-\text{Na}^+}$  
- G)   $\xrightarrow{\text{cat equivalents H}_2\text{SO}_4}$     
 excess H<sub>2</sub>O

7. (3 pts each) Complete the following mechanism for the Michael reaction. 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. This should look familiar, as it is identical to the mechanism sheet handed out in class.

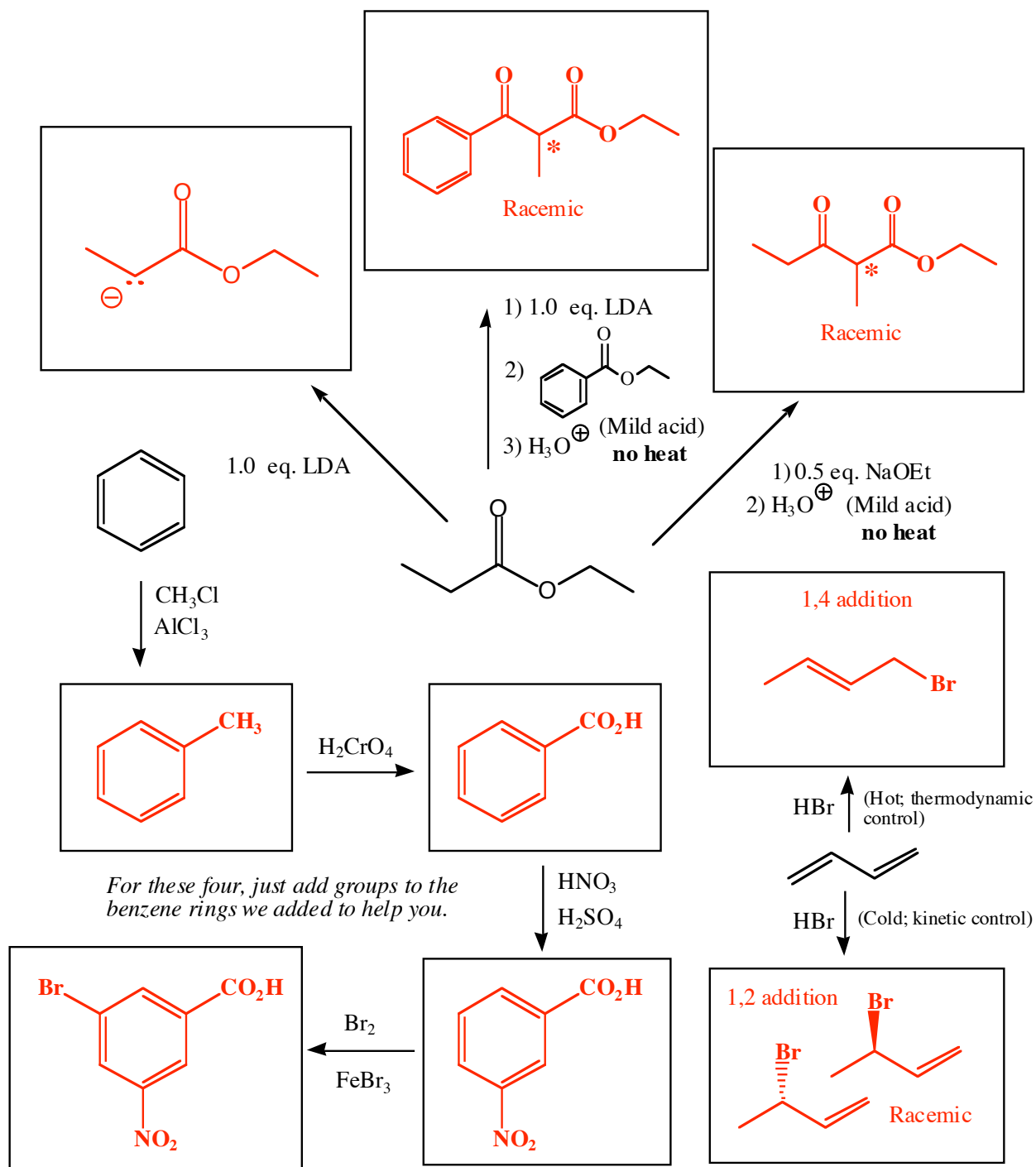




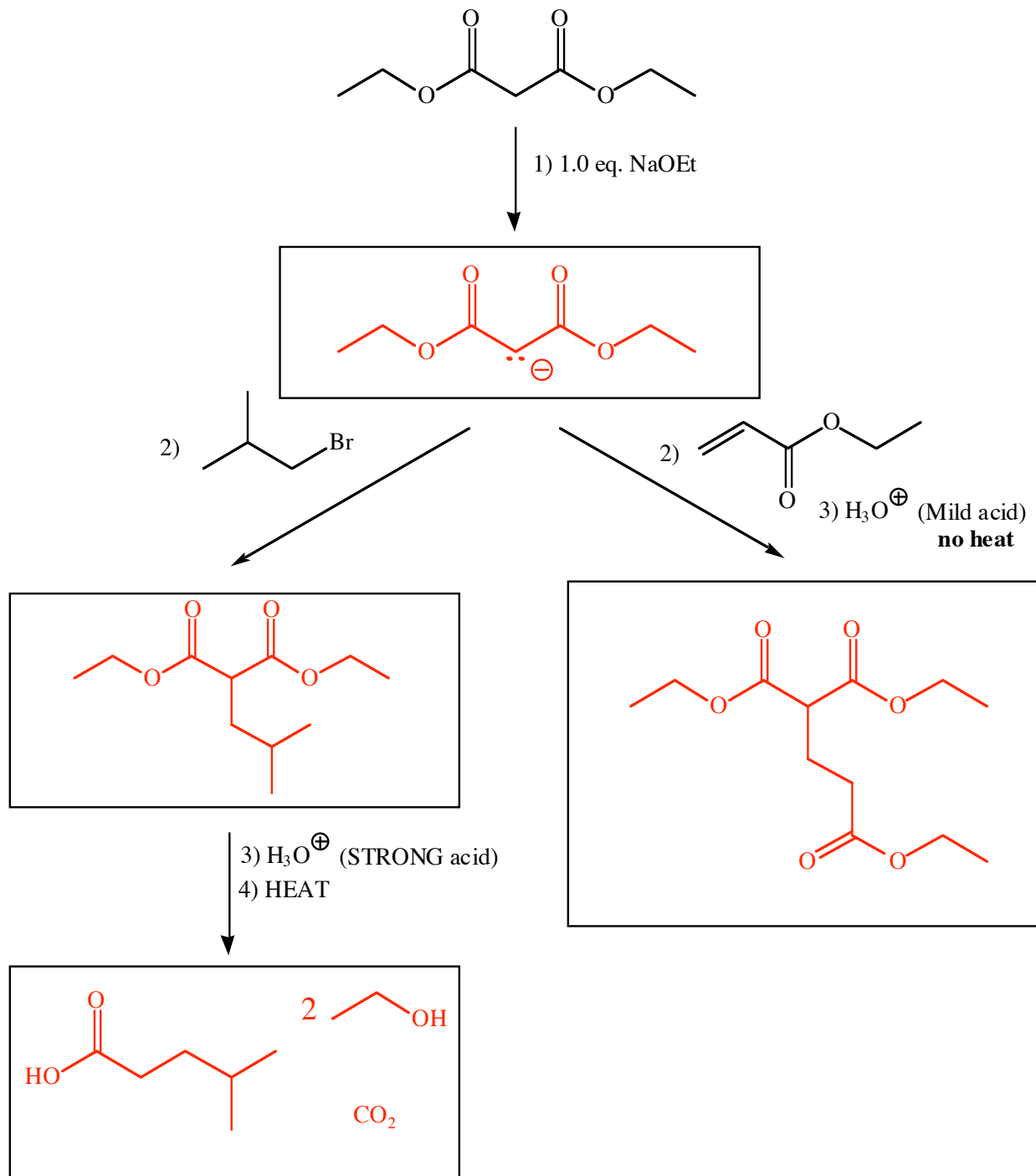
8. (3 or 5 pts each) For the following reactions, draw the predominant product or products. **When a new chiral center is created, mark it with an asterisk (\*) and if a racemic mixture is produced, you must write "racemic" under your structure. If an E,Z mixture is produced as the result of a dehydration step, write E,Z mixture, but you only have to draw one isomer, not both.** These directions are different than you may have seen before, and are intended to make it easier for you. You should read them again so you know what we want.



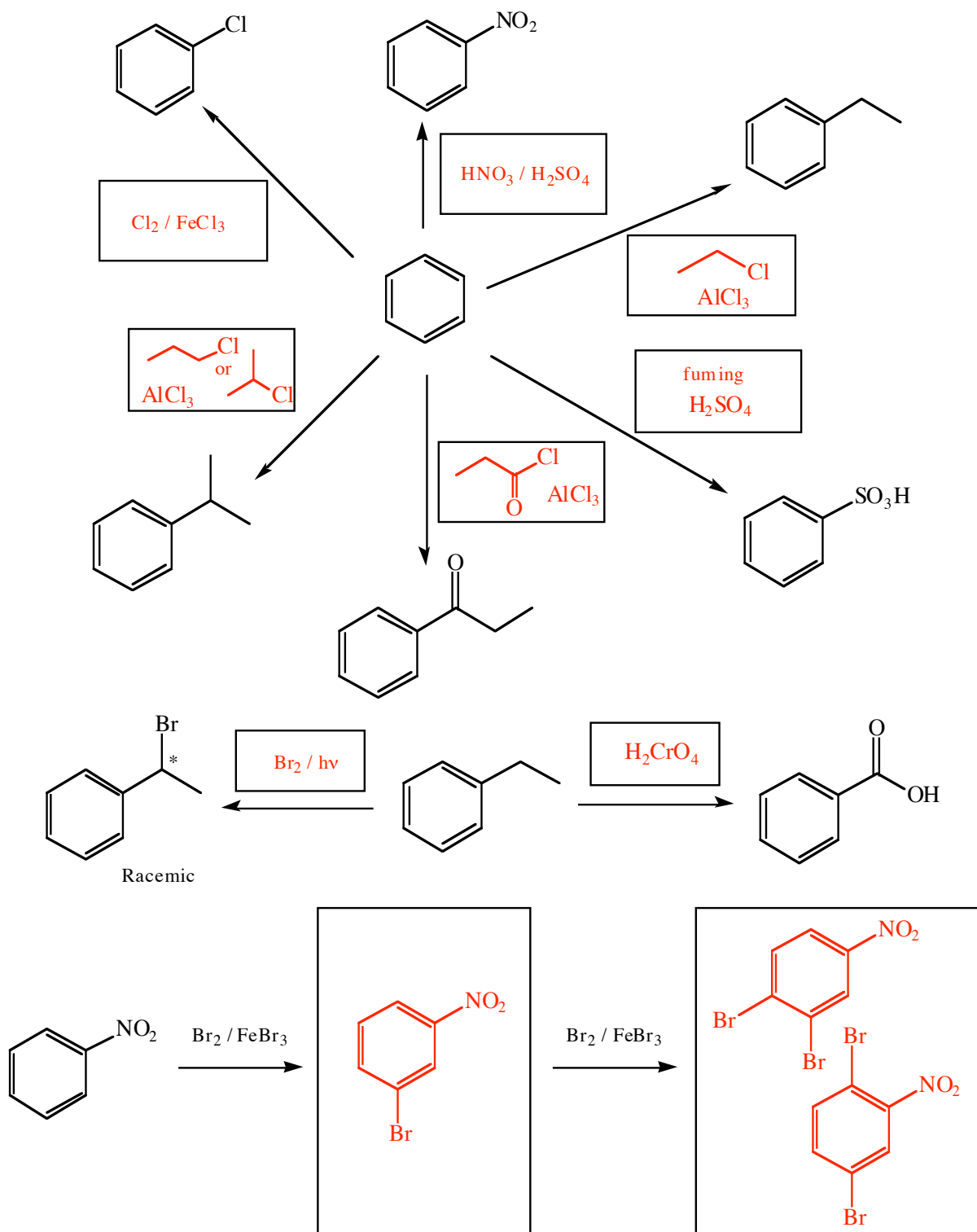
9. (3 or 5 pts each) For the following reactions, draw the predominant product or products. **When a new chiral center is created, mark it with an asterisk (\*) and if a racemic mixture is produced, you must write "racemic" under your structure. If an E,Z mixture is produced as the result of a dehydration step, write E,Z mixture, but you only have to draw one isomer, not both.** These directions are different than you may have seen before, and are intended to make it easier for you. You should read them again so you know what we want.



10. (3 or 5 pts each) For the following reactions, draw the predominant product or products. **When a new chiral center is created, mark it with an asterisk (\*) and if a racemic mixture is produced, you must write "racemic" under your structure. If an E,Z mixture is produced as the result of a dehydration step, write E,Z mixture, but you only have to draw one isomer, not both.** These directions are different than you may have seen before, and are intended to make it easier for you. You should read them again so you know what we want.

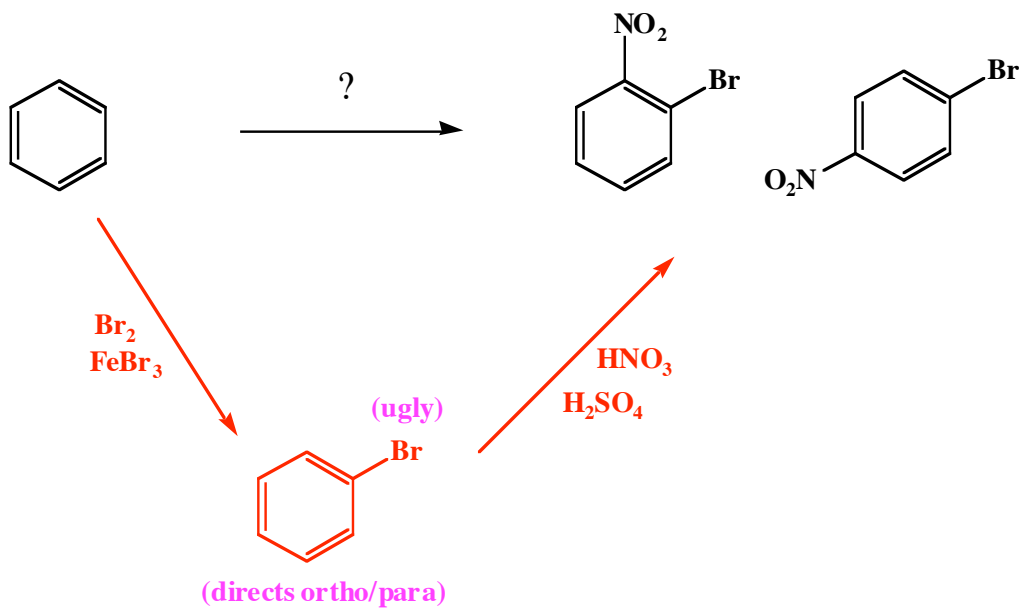


11. (2, 3, or 5 pts each) Fill in the boxes with reagents that will produce the products drawn. For the last one, fill in the products (draw both ortho and para products if that is appropriate).

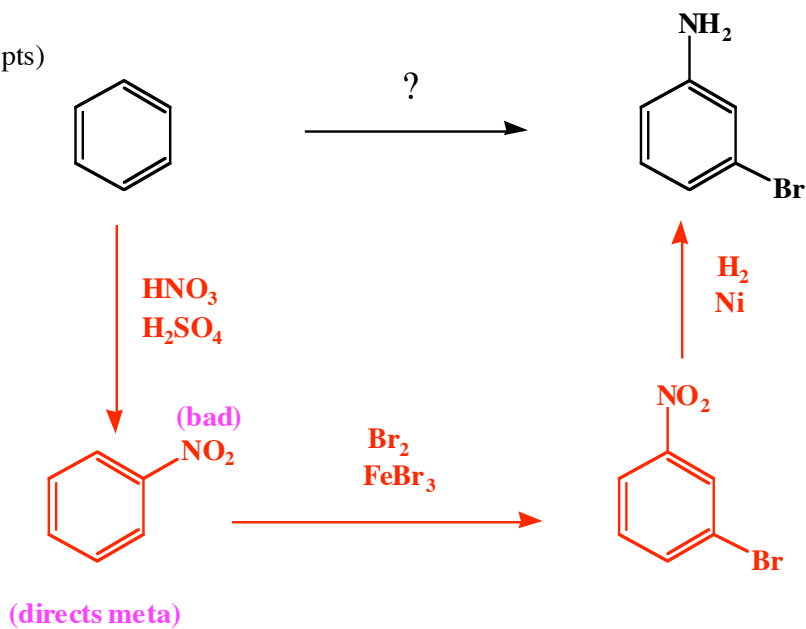


12. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

A) (4 pts)

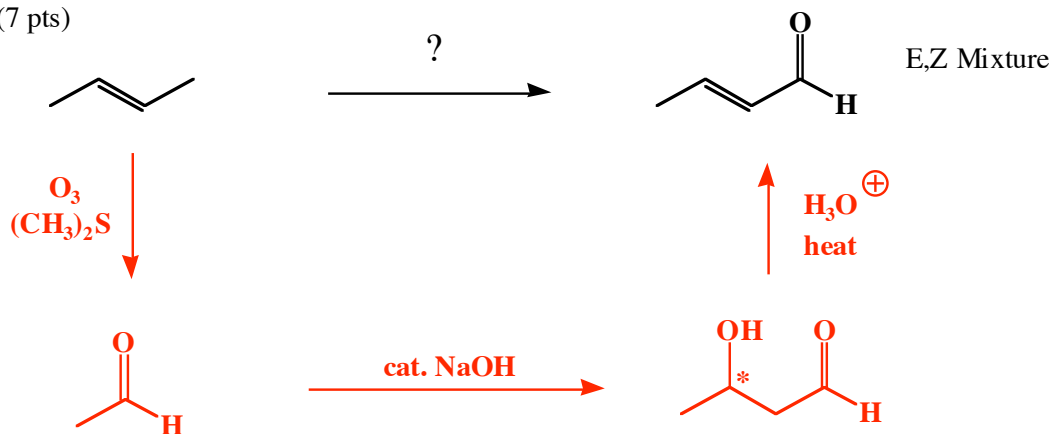


B) (7 pts)

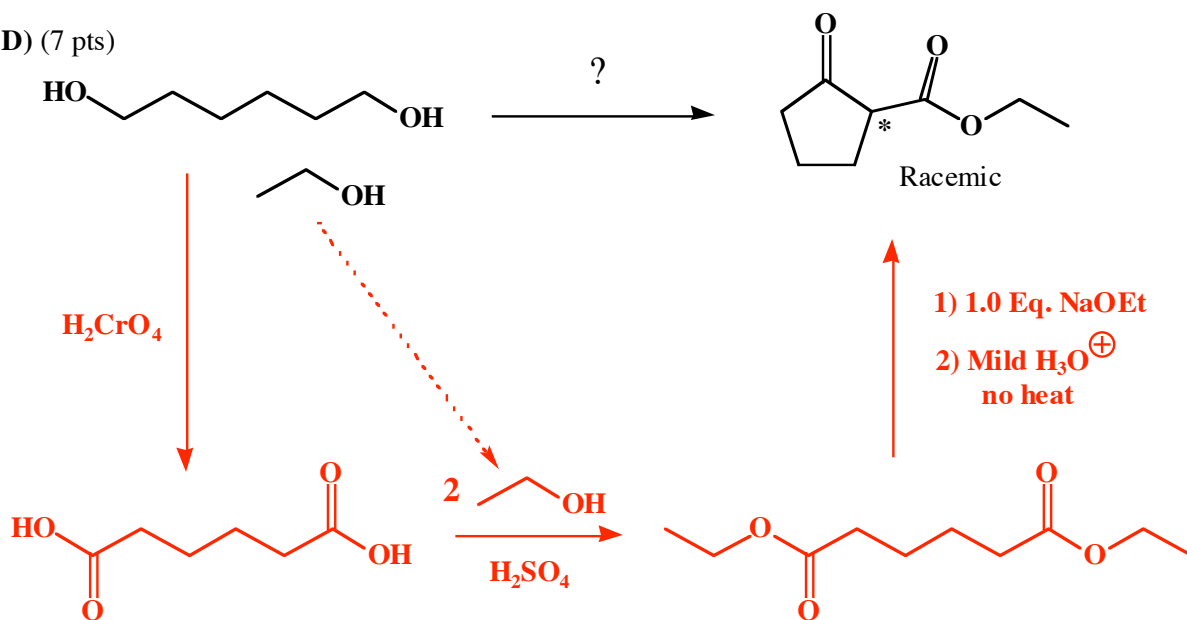


12. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule!

C) (7 pts)

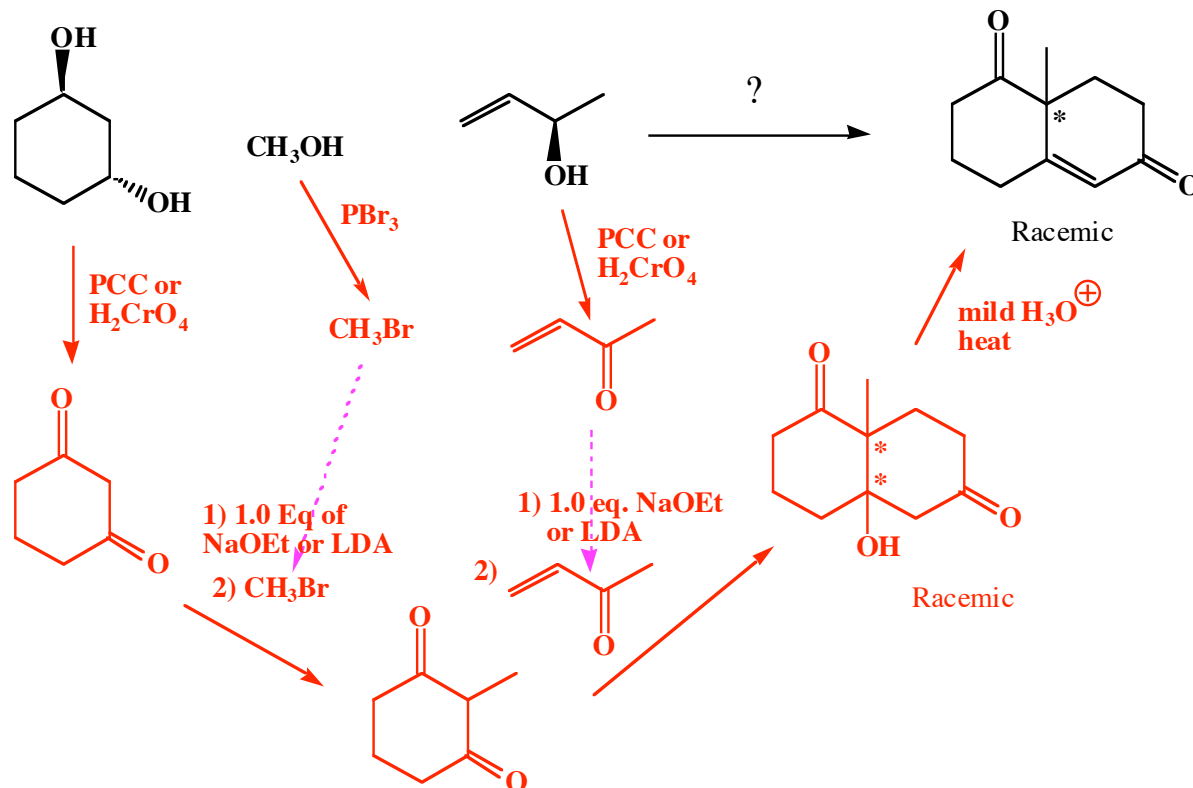


D) (7 pts)



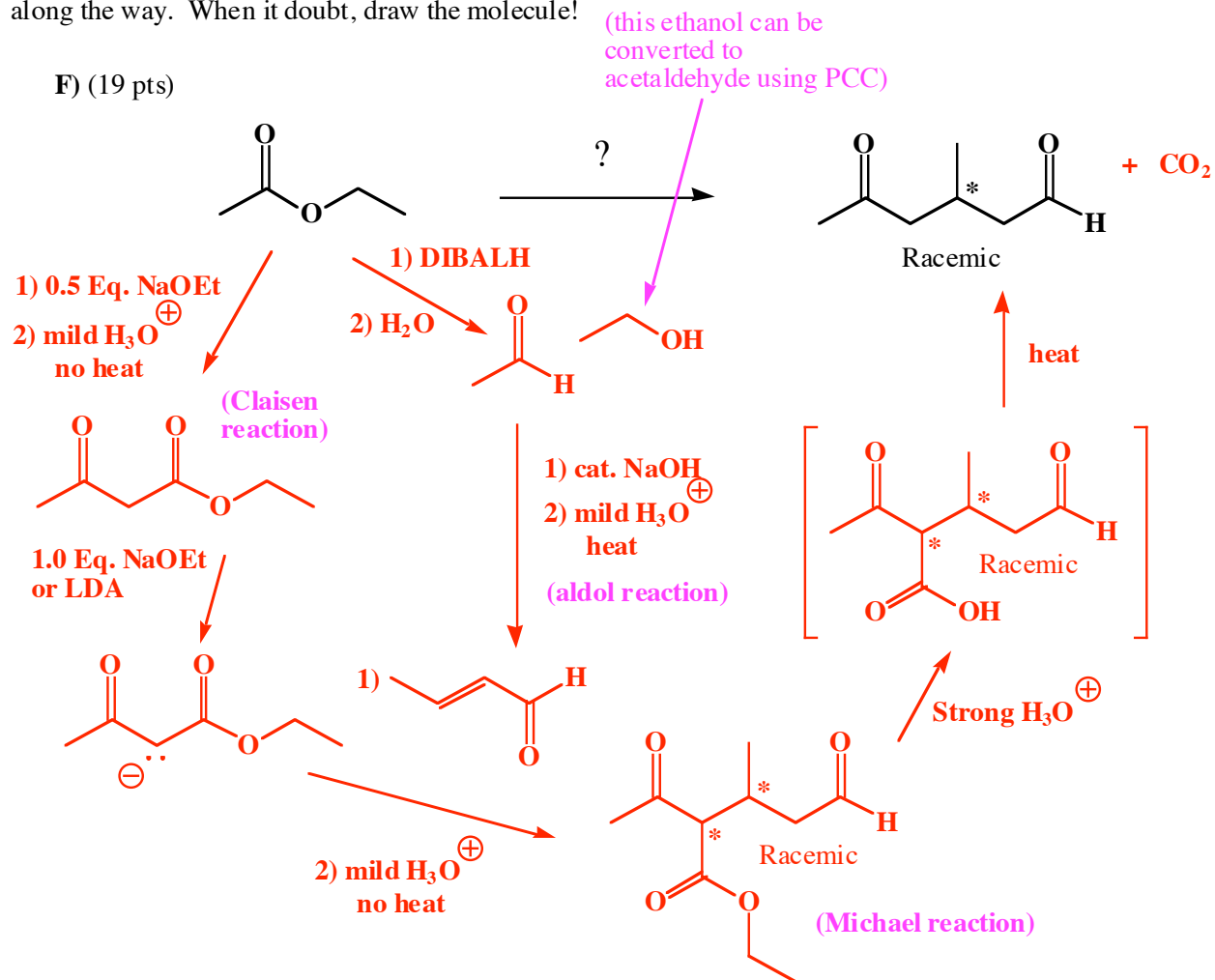
12. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When in doubt, draw the molecule!

E) (10 pts)



**Recognize** the product as coming from a Robinson annulation reaction. The pieces needed for the Robinson come from oxidation of the cyclic diol and alkene respectively. The last important piece is addition of the methyl group between the two ketone groups of 1,3 cyclohexanedione. The methylation is accomplished via the enolate after methanol is converted into the alkyl halide. (Note that  $\text{CH}_3\text{Cl}$  would have worked just as well, with  $\text{SOCl}_2$  being used to react with methanol.)

12. 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 in doubt, draw the molecule!



**Recognize** the product as coming from decarboxylation of a Michael product. This was clearly hard to spot, but becomes easier with practice. The Michael reaction requires a nucleophile that comes from a Claisen reaction of the starting ethyl acetate. The electrophile comes from the aldol reaction of acetaldehyde, which can be created from ethyl acetate using DIBALH. Perhaps a better way to make acetaldehyde from ethyl acetate is with  $\text{LiAlH}_4$  followed by PCC, since two molecules of acetaldehyde are made cleanly from each ethyl acetate molecule.

