

NAME (Print): _____

Chemistry 310N
Dr. Brent Iverson
3rd Midterm
April 22, 2010

SIGNATURE: _____

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 INCIDENTS 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		(21)
3		(15)
4		(18)
5		(16)
6		(26)
7		(28)
8		(30)
9		(24)
10		(17)
11		(7)
12		(19)
13		(19)
14		(19)
15		(17)
Total		(304)
%		
T Score		
HW		
(HW score + Exam Grade) \implies	Total 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	H-Cl	-7
Protonated alcohol	$\text{RCH}_2\text{O}^+\text{H}_2$	-2
Hydronium ion	H_3O^+	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-5
Ammonium ion	H_4N^+	9.2
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	10
β-Ketoesters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	11
β-Diesters	$\text{ROC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	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	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	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. (18 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**.

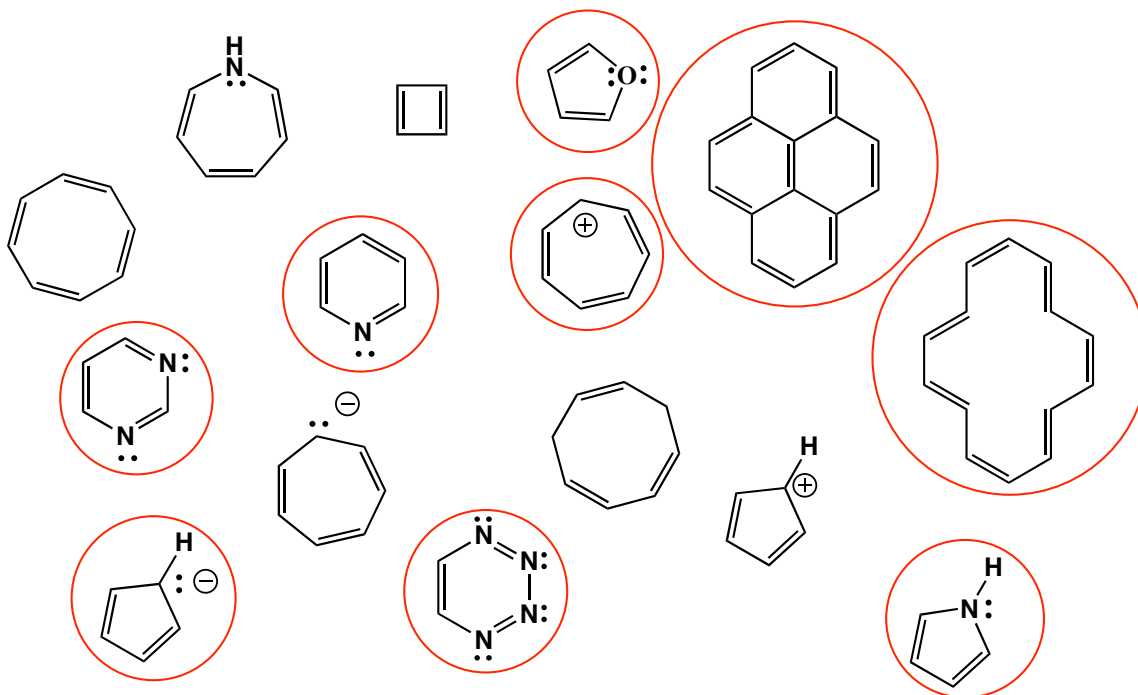
What is the most important question in chemistry?

Where are the electrons?

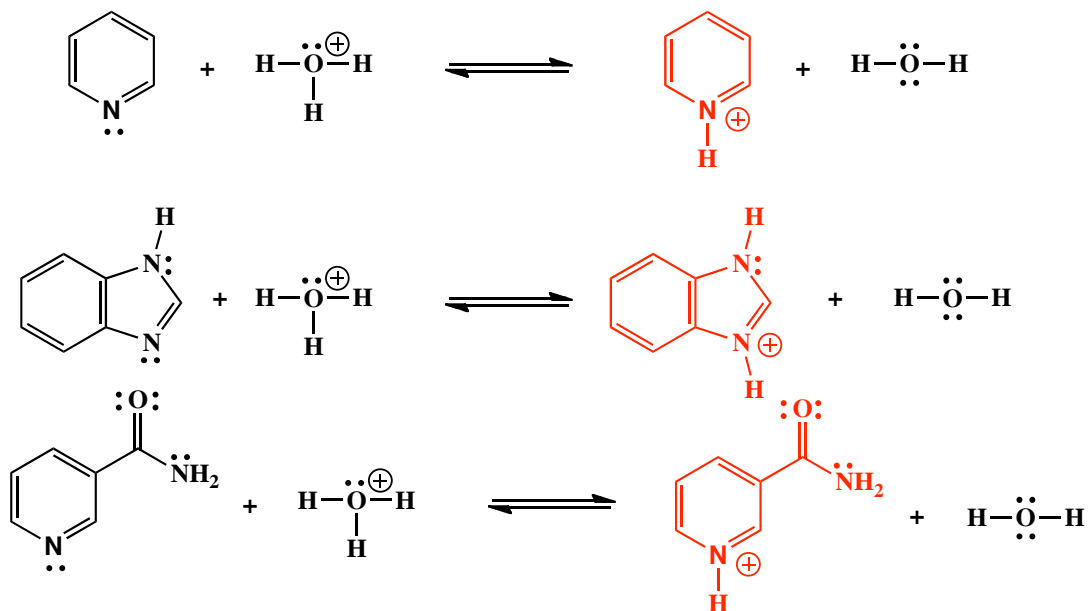
2. (1 pt. each) Here are a number of statements regarding aromaticity or other general aspects of organic chemistry. Do not second guess yourself, this is not meant to be tricky! **Check the appropriate box to indicate whether the statement is true or false.**

	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.	X	
B. According to Huckel's rule, aromatic molecules are flat, monocyclic, all ring atoms have a 2p orbital (no sp ³ ring atoms) and there are 4n + 2 pi electrons (i.e. 2, 6, 10, 14.....).	X	
C. Most reactions you have learned in this class involve nucleophiles reacting with electrophiles.	X	
D. Electrophiles are usually described as having relatively high electron density.		X
E. Nucleophiles are usually described as having relatively low electron density.		X
F. When drawing mechanisms, arrows are used to indicate the flow of electrons from electrophiles to nucleophiles.		X
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.	X	
H. Aromaticity makes pi electron density more reactive compared to simple alkenes		X
I. When molecules absorb light, electrons are excited into antibonding molecular orbitals.	X	
J. An object has the color of the wavelengths of light that are reflected, not absorbed, by the molecules on its surface.	X	

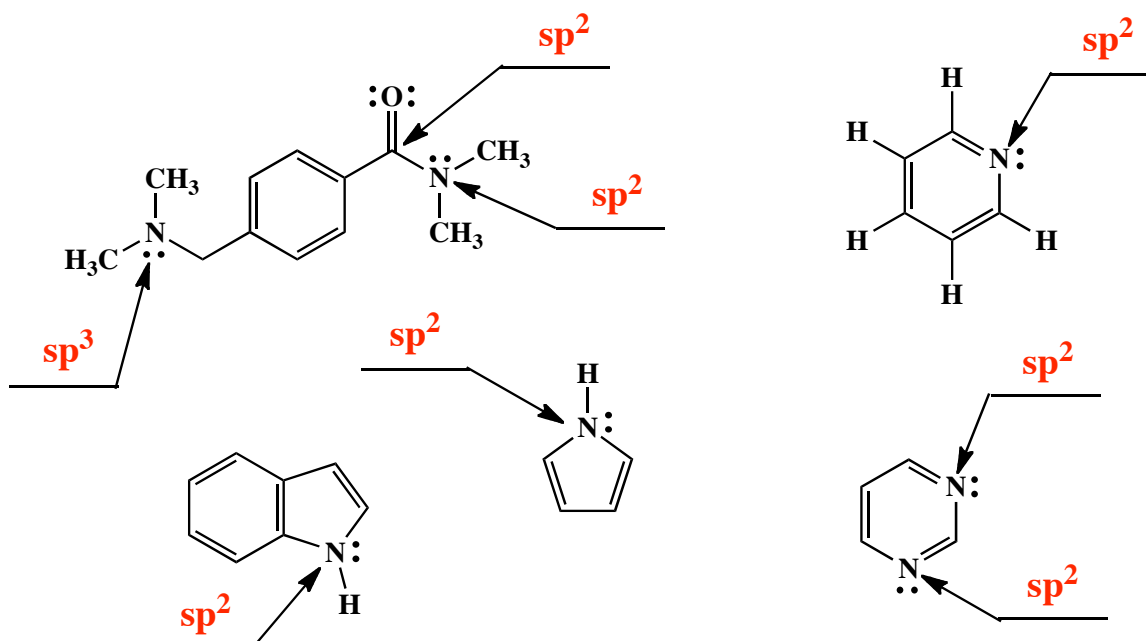
3. (15 points) Draw a circle around all of the molecules below that can be considered aromatic.



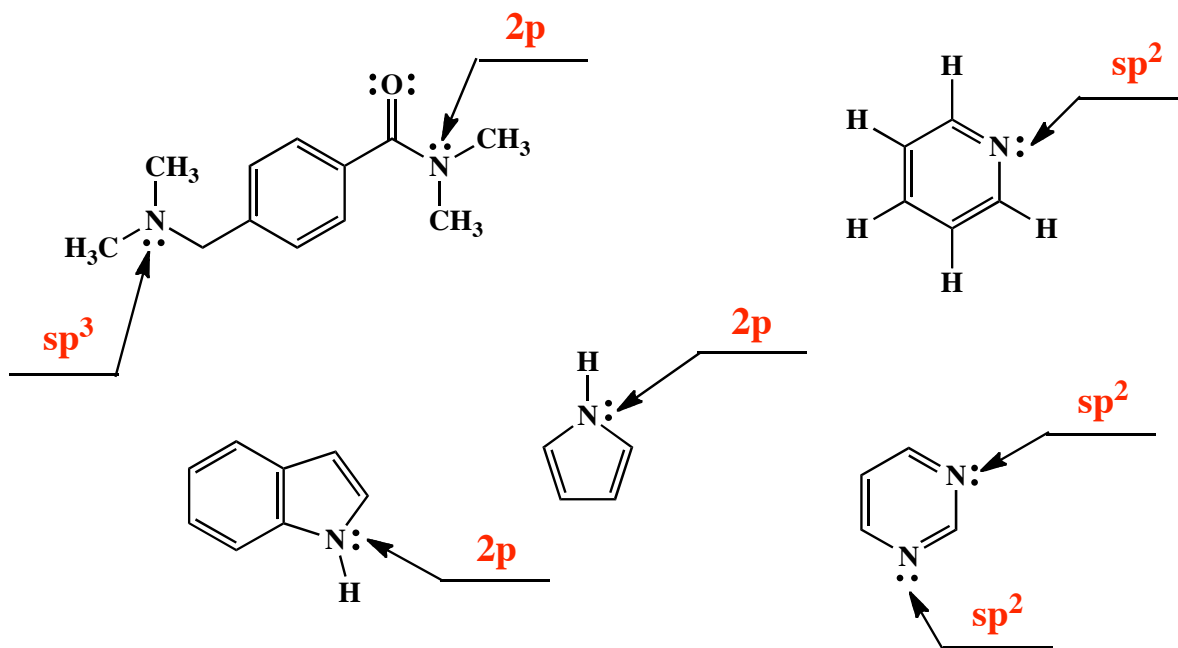
4. (6 points) In strong acid, the following molecules will become protonated. Draw the protonated form of each.



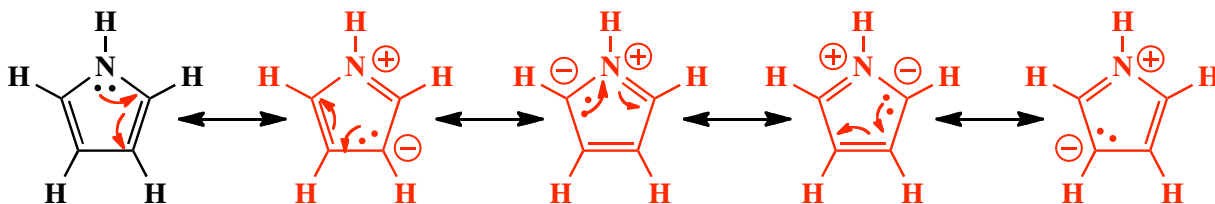
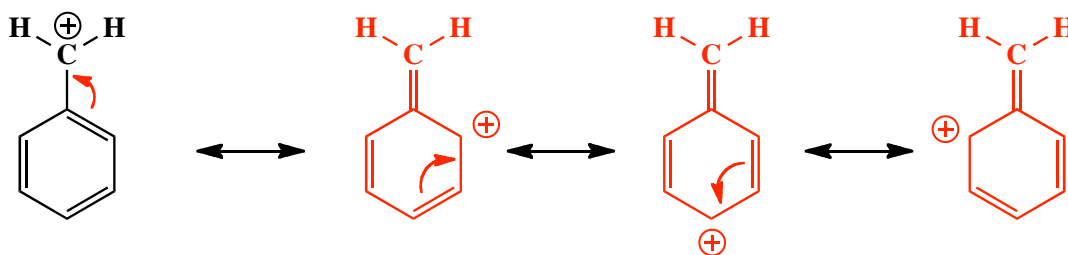
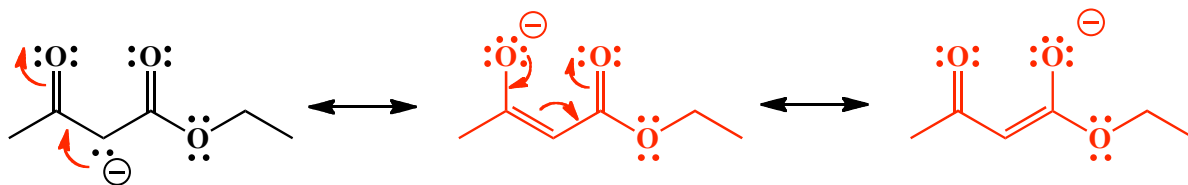
5. (8 pts) On the lines provided, state the **hybridization state of the atom** indicated by the arrow.



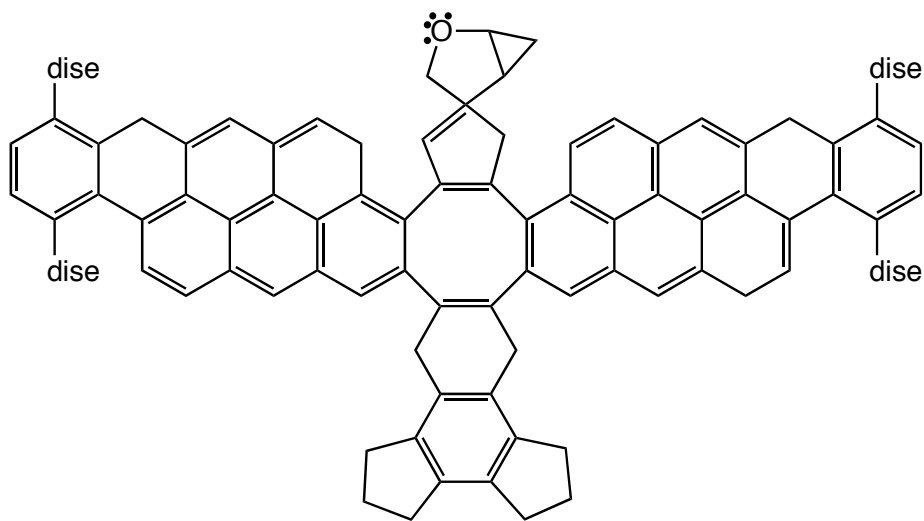
6. (7 pts) On the lines provided, state the **atomic orbital that contains the lone pair** of electrons indicated by the arrow.




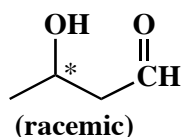
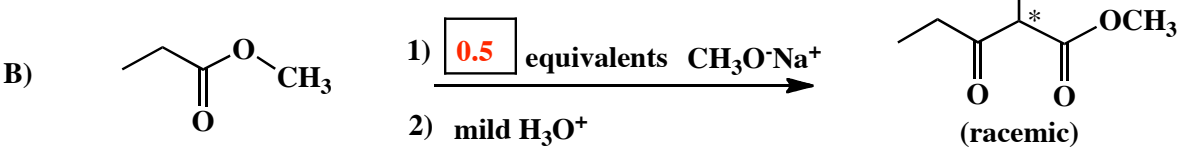
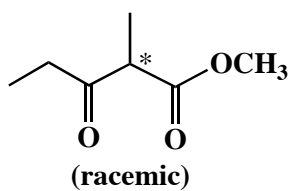
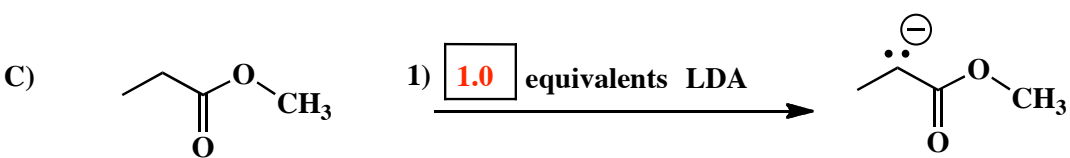
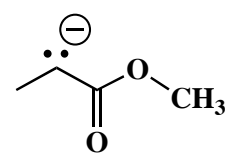
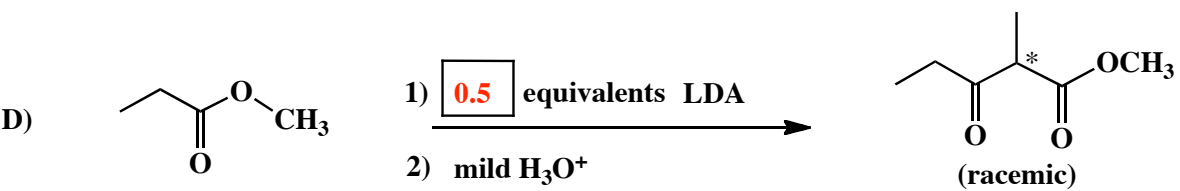
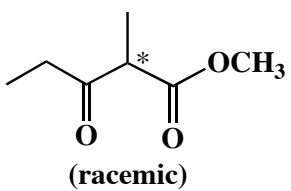
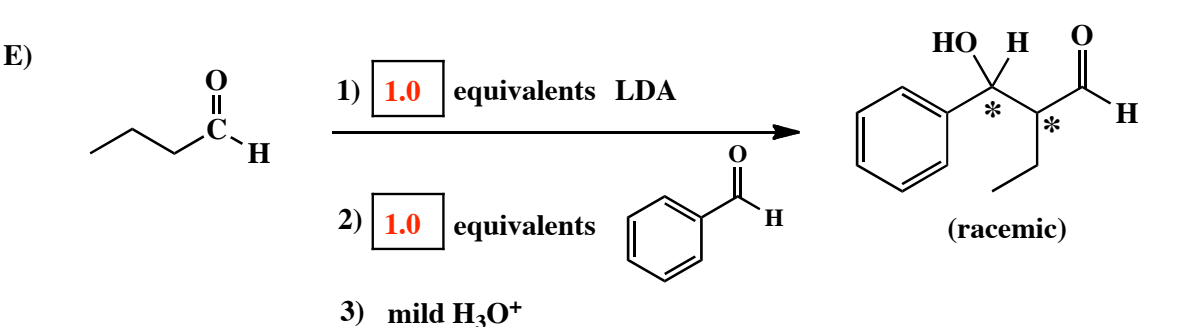
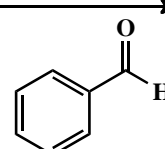
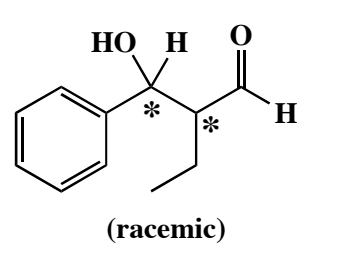
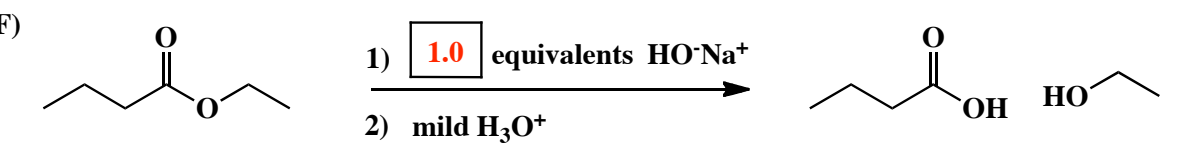
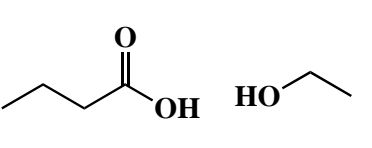
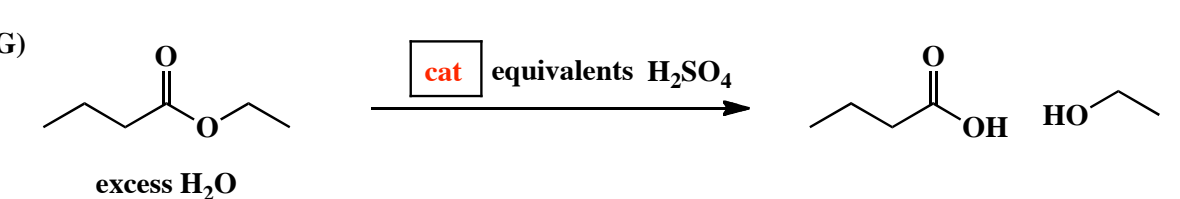
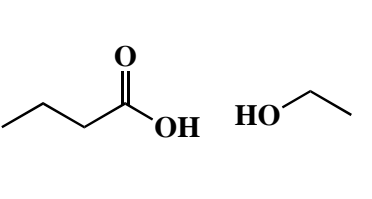
7. (18 points) In the spaces provided, draw all the important resonance contributing structures of the indicated species. We have provided template molecules to help you do this more quickly. You must draw all pi bonds, lone pairs of electrons and all formal charges on each of your structures. You DO NOT need to draw arrows to show electron movement.



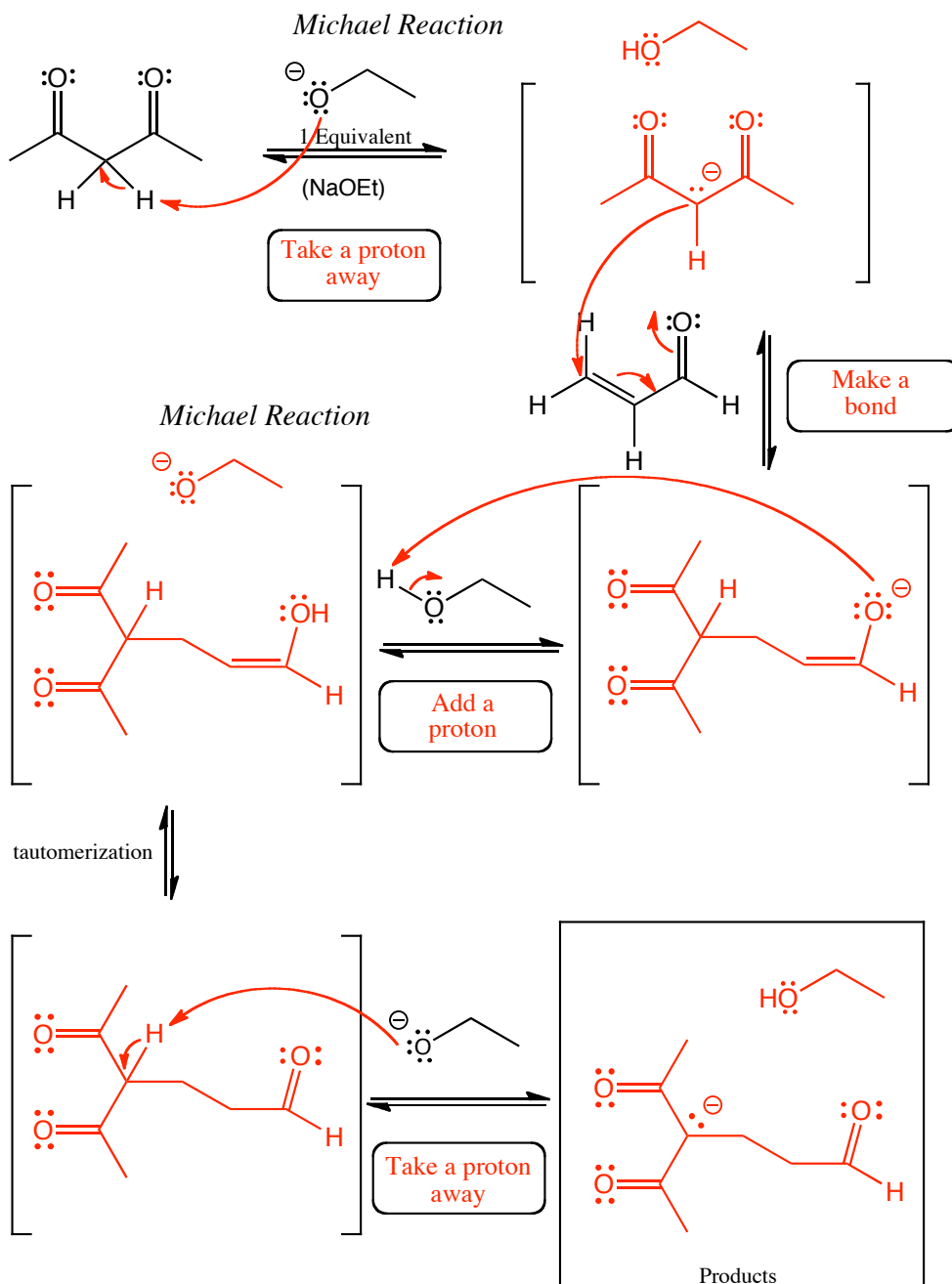
Molecule of the day: The rare central Texas bird of Paradise.



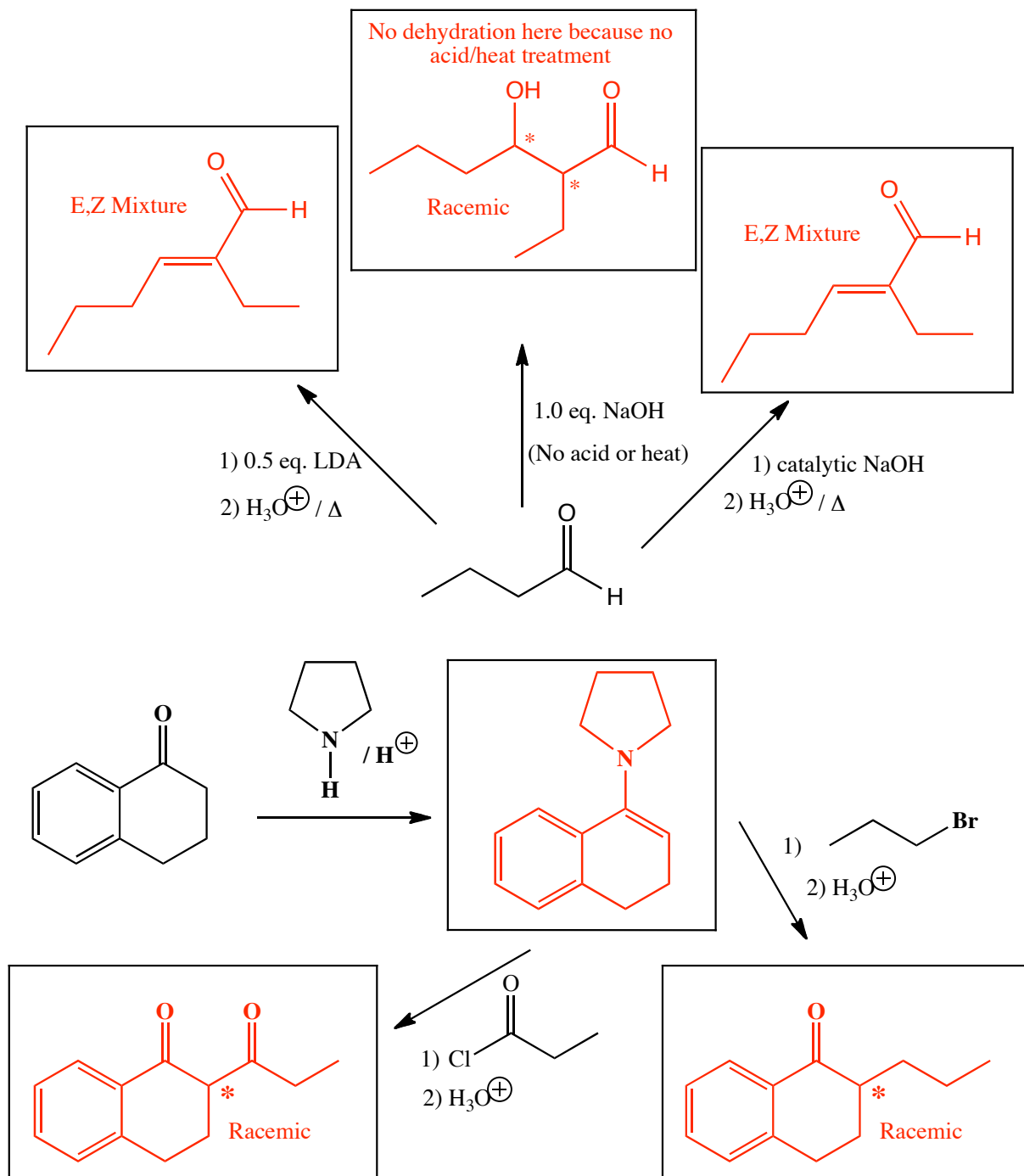
8. (2 pts each) In each of the boxes over an arrow, write the minimum number of equivalents of the specified reagent required to carry out the reaction shown **to completion**. If only a catalytic amount is needed, write "CAT". Note: You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent.

- A)  **cat** equivalents HO^-Na^+  (racemic)
- B)  1) **0.5** equivalents $\text{CH}_3\text{O}^-\text{Na}^+$
2) mild H_3O^+  (racemic)
- C)  1) **1.0** equivalents LDA 
- D)  1) **0.5** equivalents LDA
2) mild H_3O^+  (racemic)
- E)  1) **1.0** equivalents LDA
2) **1.0** equivalents 
3) mild H_3O^+  (racemic)
- F)  1) **1.0** equivalents HO^-Na^+
2) mild H_3O^+ 
- G)  **cat** equivalents H_2SO_4
excess H_2O 

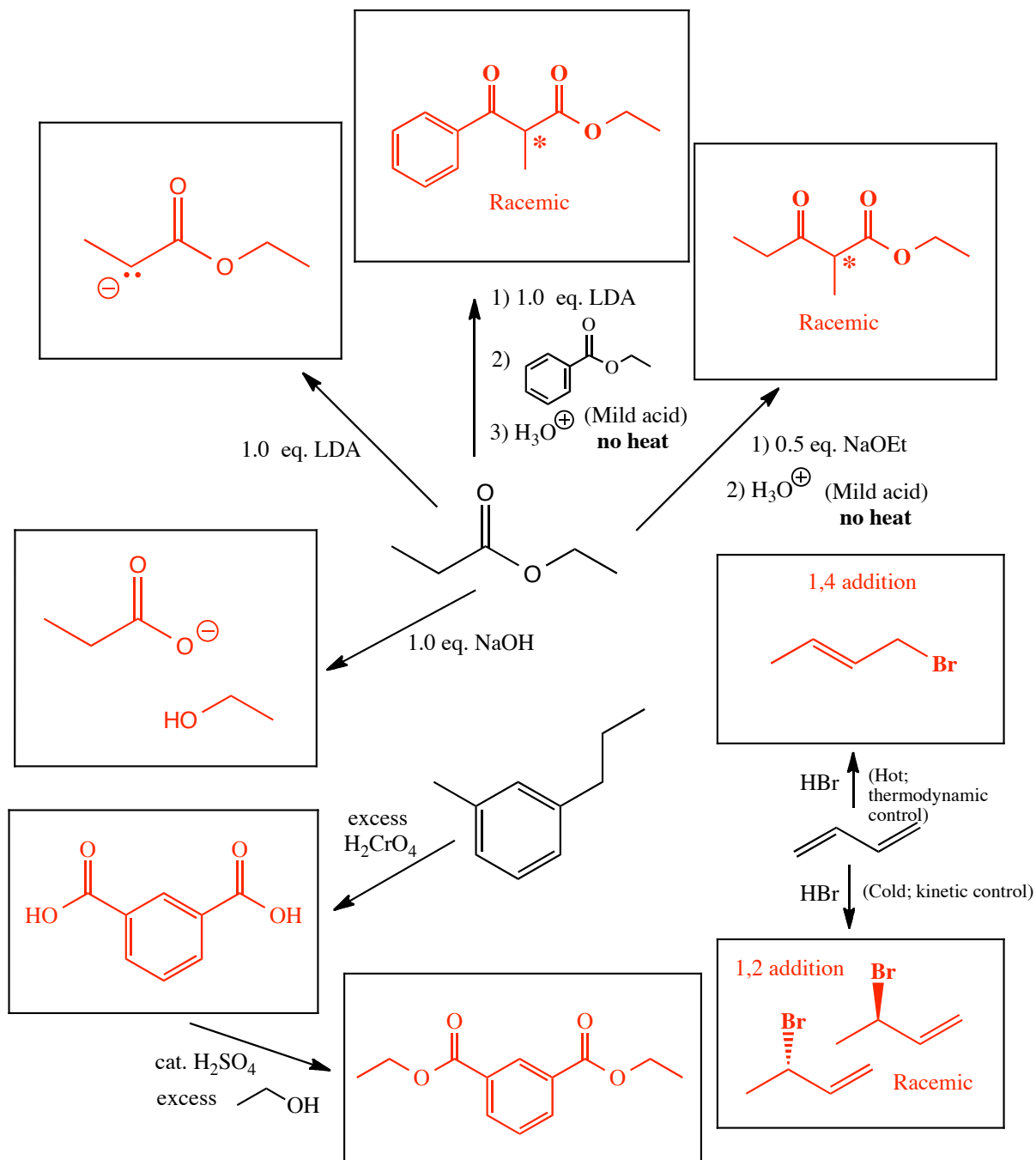
9. (22 pts total) Complete the following mechanism for the Michael reaction. Make sure to show all lone pairs, all formal charges and use arrows to indicate the flow of all electrons. You must draw all products that are made in each step. This should look familiar, as it is identical to the mechanism sheet handed out in class.



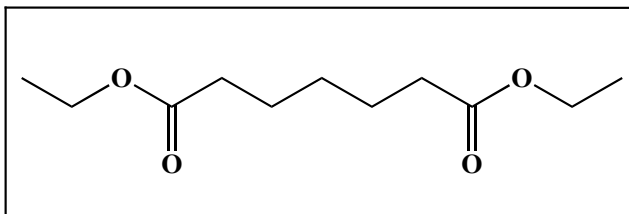
10. (3 or 5 pts each) For the following reactions, draw the predominant product or products. **When a new chiral center is created, mark it with an asterisk (*) and if a racemic mixture is produced, you must write "racemic" under your structure. If an E,Z mixture is produced as the result of a dehydration 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.



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.

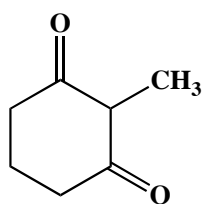
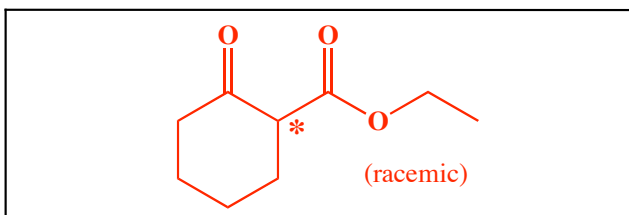
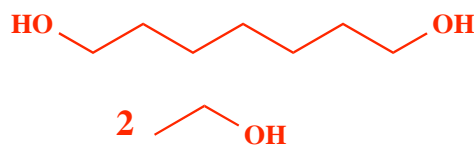


10. (3 or 5 pts each) For the following reactions, draw the predominant product or products. **When a new chiral center is created, mark it with an asterisk (*) and if a racemic mixture is produced, you must write "racemic" under your structure. If an E,Z mixture is produced as the result of a dehydration 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.

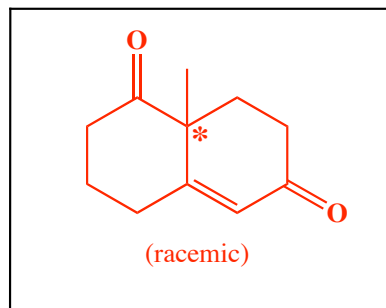


1) 1.0 eq. NaOEt
2) H_3O^+
(mild acid, no heat)

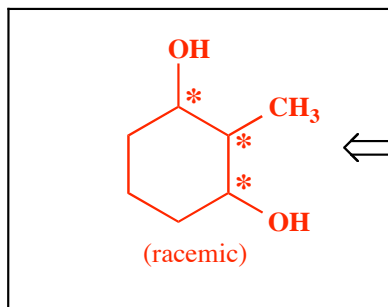
1) excess LiAlH_4
2) H_2O



1) 1.0 eq. NaOEt
2)
3) H_3O^+
(stronger acid, with heat)



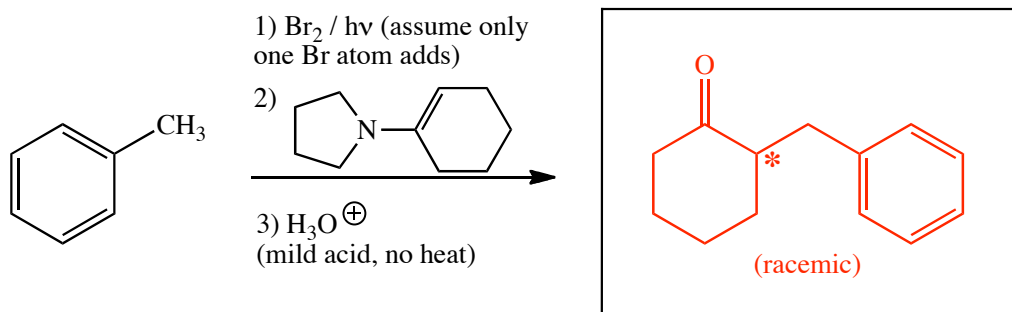
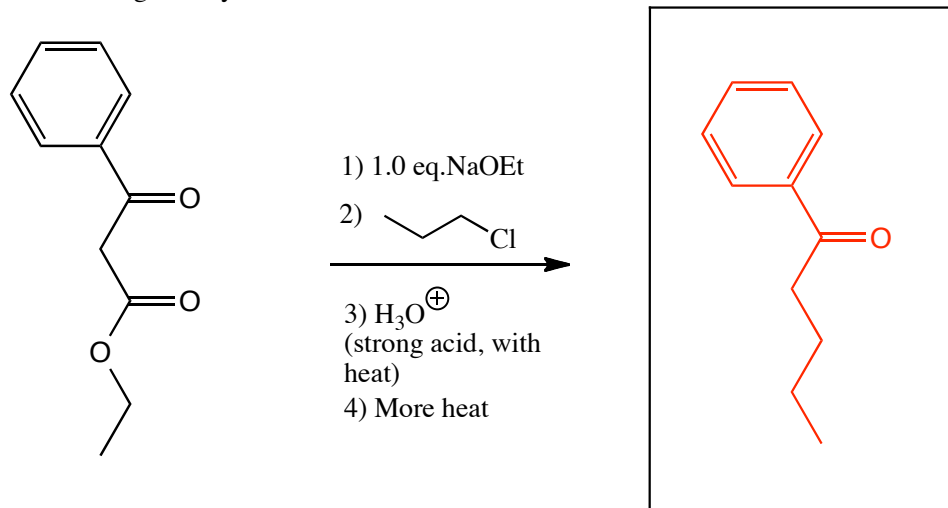
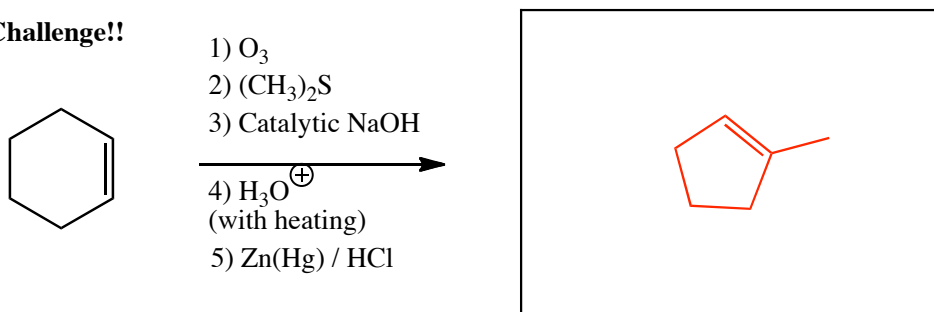
1) excess LiAlH_4
2) H_2O



Hardest problem on the test: How many different stereoisomers are created in this reaction? 6

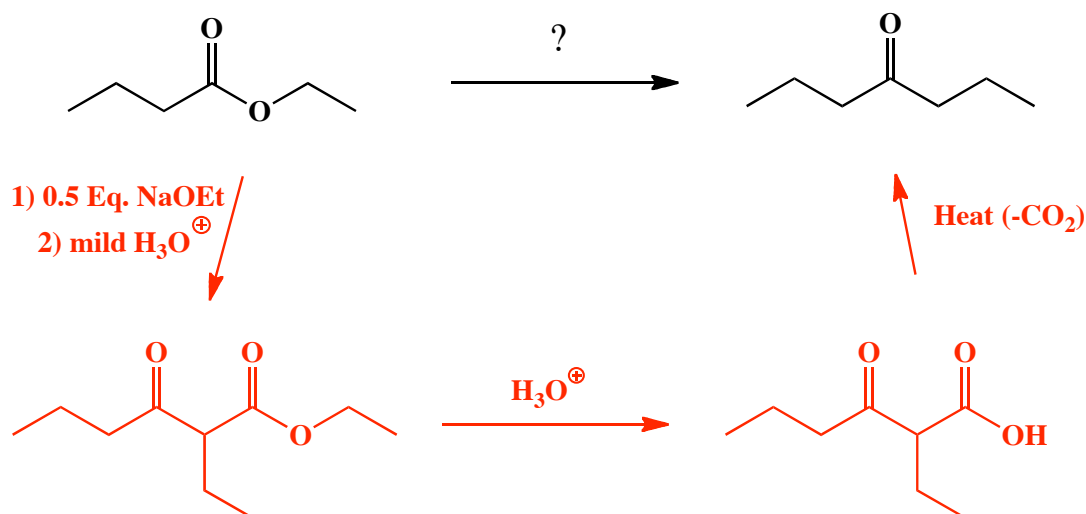
(There are two meso compounds)

11. (5 or 7 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.

**Challenge!!**

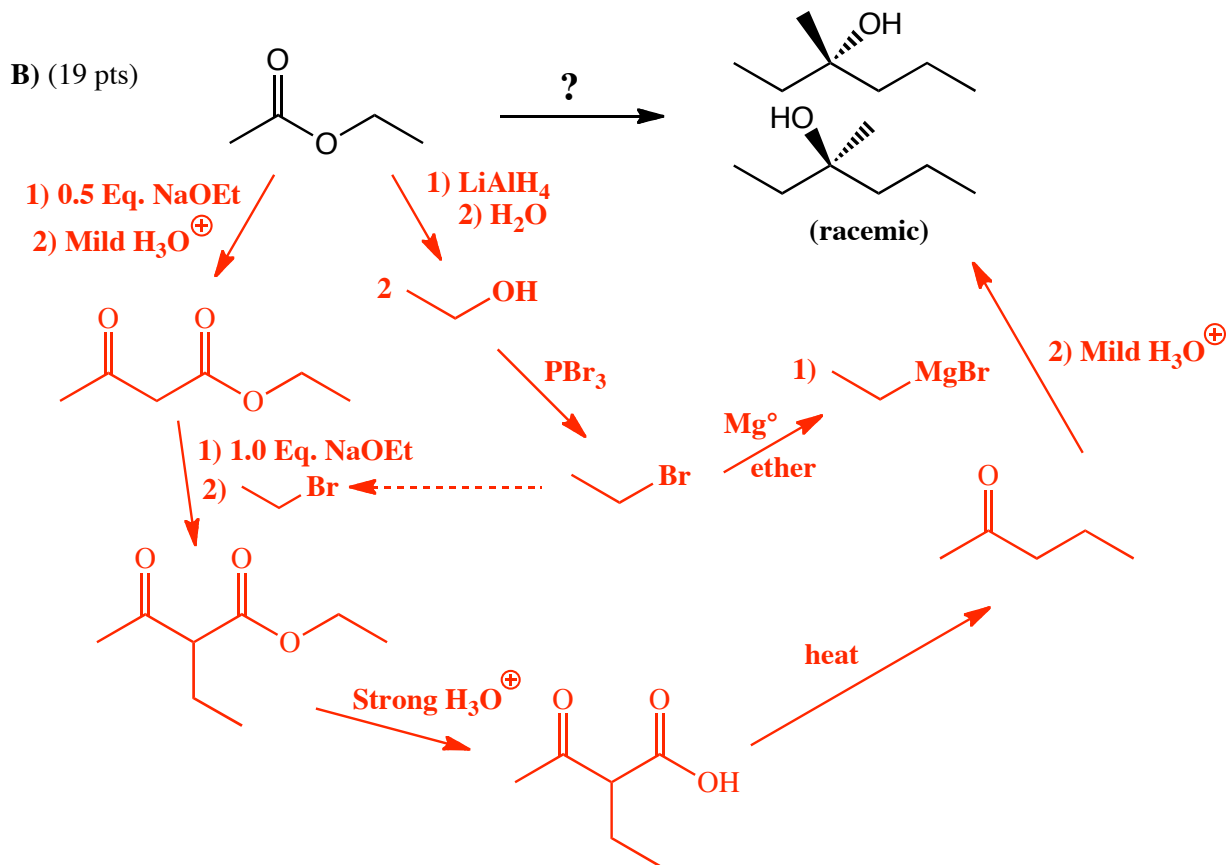
12. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

A) (7 pts)



This is a tricky one!! Recognize that the ketone product is not really a KRE of any particular reaction. However, the starting material is an ester, and with so few steps/points for this one, so recognize that the only reaction that uses esters to make carbon-carbon bonds is a Claisen reaction. Then the hard part is to recognize that the product is just the result of decarboxylation of the Claisen product you made in the first step.

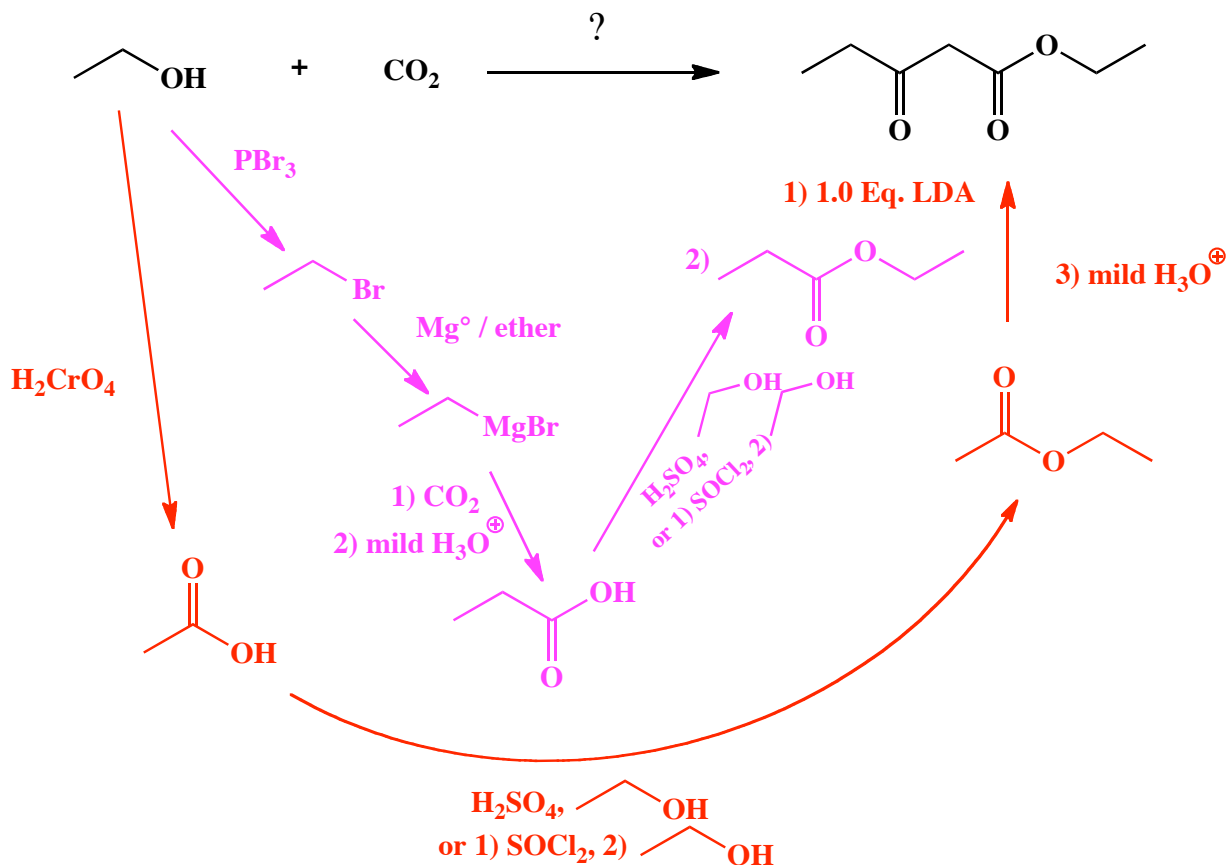
12. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!



Recognize this as a tertiary alcohol which is the KRE of a Grignard reaction with a ketone. **Recognize** that if you use an ethyl Grignard in this last step, you end up with a methyl ketone, that is the KRE of an acetoester synthesis. **Recognize** further that the acetoester synthesis can be accomplished by adding an ethyl group to ethyl acetoacetate. Both the ethyl bromide needed for the acetoester synthesis and the ethyl Grignard needed in the last step can be derived from ethanol, which is the reduction product of the ethyl acetate starting material. Finally, **recognize** that the ethyl acetoacetate can be derived from a Claisen reaction using the ethylacetate starting material.

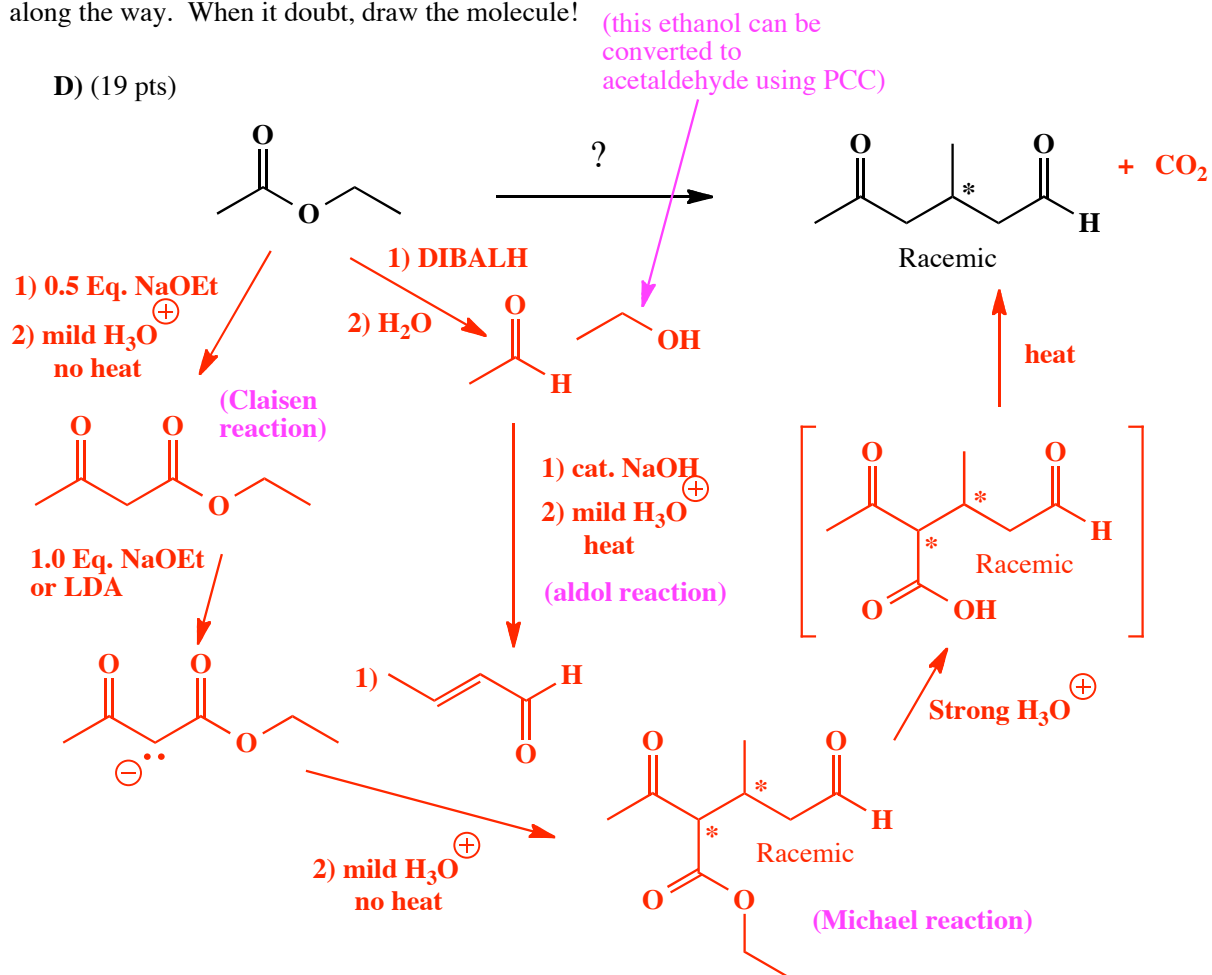
12. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!

C) (19 pts)

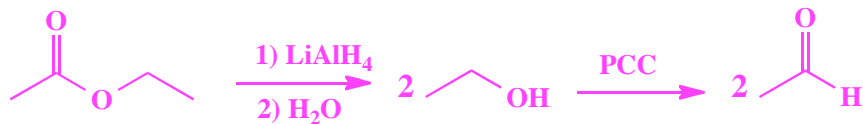


Recognize this as a β -keto ester, the KRE of a Claisen, but a non-symmetrical one. We must carry out a crossed Claisen here between esters with two and three carbons in their acid portions, respectively. The two carbon acid containing ester must be the enolate portion as shown. The three carbon acid building block can be made using the CO_2 in a Grignard reaction.

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!

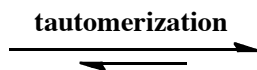
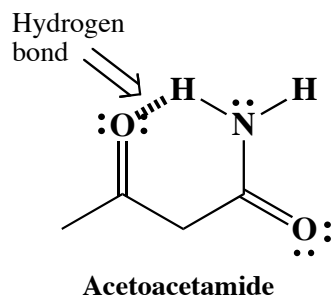


Recognize the product as coming from decarboxylation of a Michael product. This was clearly hard to spot, but becomes easier with practice. The Michael reaction requires a nucleophile that comes from a Claisen reaction of the starting ethyl acetate. The electrophile comes from the aldol reaction of acetaldehyde, which can be created from ethyl acetate using DIBALH. Perhaps a better way to make acetaldehyde from ethyl acetate is with LiAlH_4 followed by PCC, since two molecules of acetaldehyde are made cleanly from each ethyl acetate molecule.



13. Here is the first of two apply what you know problems. Acetoacetamide is a molecule with an interesting structure. The molecule is drawn as one tautomer, and in fact the less stable tautomer. Notice the hydrogen bond in the conformation shown. In the space provided, draw the more stable tautomer, and include a key hydrogen bond in the structure you draw.

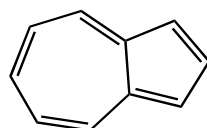
(6 pts)



(5 pts) In no more than two sentences, explain why the structure you drew is the more stable tautomer.

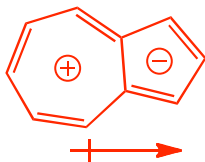
The more stable structure is the enol form, which is more stable due to the presence of conjugation with the amide carbonyl that more than compensates for having a weaker C=C (compared to a C=O of the keto form). The hydrogen bond between the enol H atom and the amide carbonyl is also stabilizing to the structure.

(6 pts) Here is the second apply what you know problem. Azulene is an amazing aromatic molecule with two notable features. It is blue and it has a very strong dipole moment of 0.8 D.



Azulene

Based on what you know about aromatic rings and the Hückel rules, explain the large dipole moment of azulene. You can draw a structure if you like to help describe your answer.



In order for both rings to have 6 π electrons, one electron is transferred from the seven membered ring to the five membered ring, analogous to the tropylium cation and cyclopentadiene anion we saw in class. Two former students of mine fell in love studying Organic chemistry together, and after graduation they were married. They put a large azulene molecule on their wedding cake. They said it symbolized the way that sharing their lives together made each one more complete (and therefore more stable one would guess). No, I did not make that up! As far as I know, they are still married.