NAME (Print): _____

EID _____

SIGNATURE: _____

Chemistry 320N
3rd Midterm Exam
April 13, 2023

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

Please Note: Please take your time. You have three hours to take this exam. Please do not rush, we want you to show us everything you have learned this semester so far! Making careless mistakes is not good for anyone! If you find yourself getting anxious because of a problem, skip it and come back. Please do not second guess yourself! Keep track of the questions worth a lot of points. (This does not mean they are hard, it just means we think they cover important material.)

One last thing: I recommend you close your eyes for a moment, then take some nice deep breaths before you begin. YOU GOT THIS!

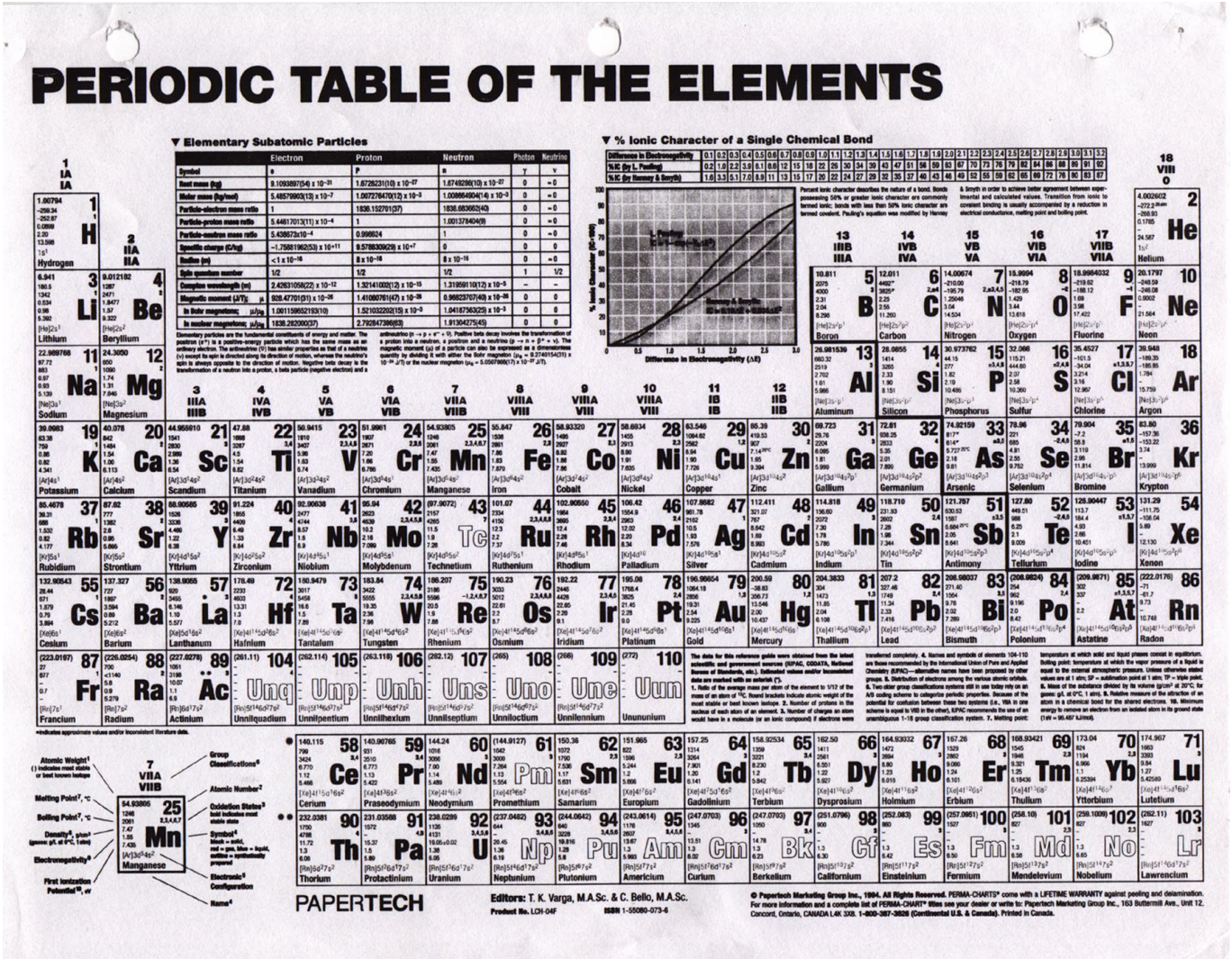
FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

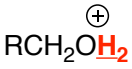
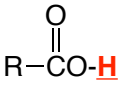
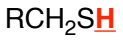
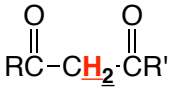
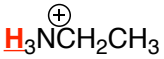
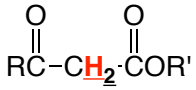
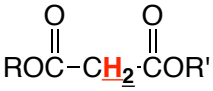
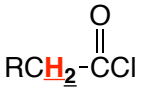
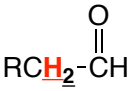
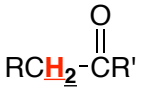
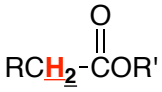
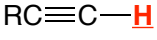
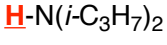
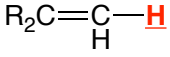
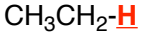
Student Honor Code

“As a student of The University of Texas at Austin, I shall abide by the core values of the University and uphold academic integrity.”

_____

(Your signature)



Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Carboxylic acids		3-5
Thiols		8-9
Ammonium ion		9.2
β-Dicarbonyls		10
Primary ammonium		10.5
β-Ketoesters		11
β-Diesters		13
Water		15.7
Alcohols		15-19
Acid chlorides		16
Aldehydes		18-20
Ketones		18-20
Esters		23-25
Terminal alkynes		25
LDA		40
Terminal alkenes		44
Alkanes		51

Signature_____ Pg 1 _____(32)

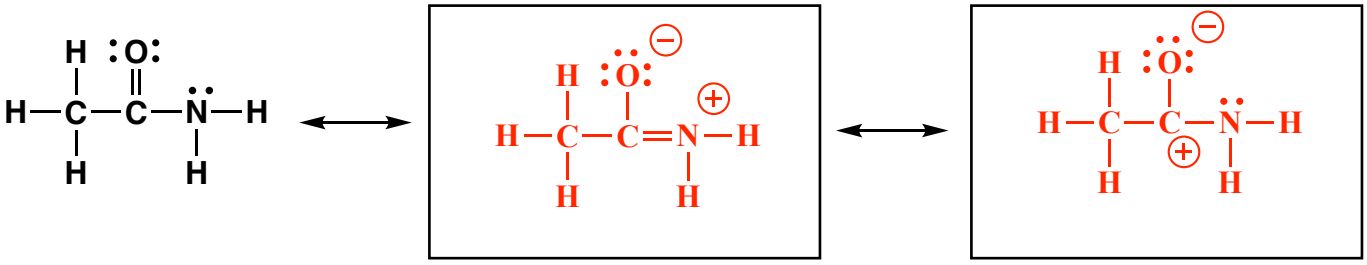
1. (5 pts) What is the most important question in organic chemistry?

Where are the electrons?

2. (1 pt each) Fill in each blank with the word that best completes the sentences. Yep, this is the MRI paragraph!

The popular medical 1. diagnostic technique of 2. magnetic 3. resonance imaging (MRI) is based on the same principles as 4. NMR, namely the 5. flipping (i.e. 6. resonance) of 7. nuclear spins of 8. H atoms by 9. radio frequency 10. irradiation when a patient is placed in a strong magnetic 11. field. Magnetic 12. field gradients are used to gain 13. imaging information, and rotation of the gradient around the 14. 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 15. stacked make up the three-dimensional image of relative amounts of 16. H atoms, especially the 17. H atoms from water and fat, in the different tissues.

3. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided.



4. (2 pts each) Indicate whether each statement is true or false by filling in the appropriate circle.

● **True**
○ **False**
A. According to Molecular Orbital theory, you generate as many new molecular orbitals as atomic orbitals used to create them. Half are bonding molecular orbitals (waves add constructively) and are filled with electron density, and half are antibonding molecular orbitals (waves add destructively) and are not filled with electron density.

○ **True**
● **False**
B. According to Molecular Orbital theory, you generate twice as many new molecular orbitals as atomic orbitals used to create them. Half are bonding molecular orbitals (waves add constructively) and are filled with electron density, and half are antibonding molecular orbitals (waves add destructively) and are not filled with electron density.

● **True**
○ **False**
C. Fluorescence occurs when there are not vibrations possible (a rigid molecule) so the photon is emited as the electron goes back to ground state.

○ **True**
● **False**
D. Phosphorescence occurs when there are not vibrations possible (a rigid molecule) so the photon is emited as the electron goes back to ground state.

● **True**
○ **False**
E. Chemiluminescence (firefly light, "light sticks") happens when a chemical reaction produces an excited electron in a rigid molecule

● **True**
○ **False**
F. For atoms attached directly to a benzene ring, the benzene ring stabilizes cations, anions and radicals

○ **True**
● **False**
G. The lower the number of pi bonds in conjugation, the smaller the energy difference between filled and unfilled orbitals, so the longer the wavelength of light that is absorbed.

● **True**
○ **False**
H. The greater the number of pi bonds in conjugation, the smaller the energy difference between filled and unfilled orbitals, so the longer the wavelength of light that is absorbed.

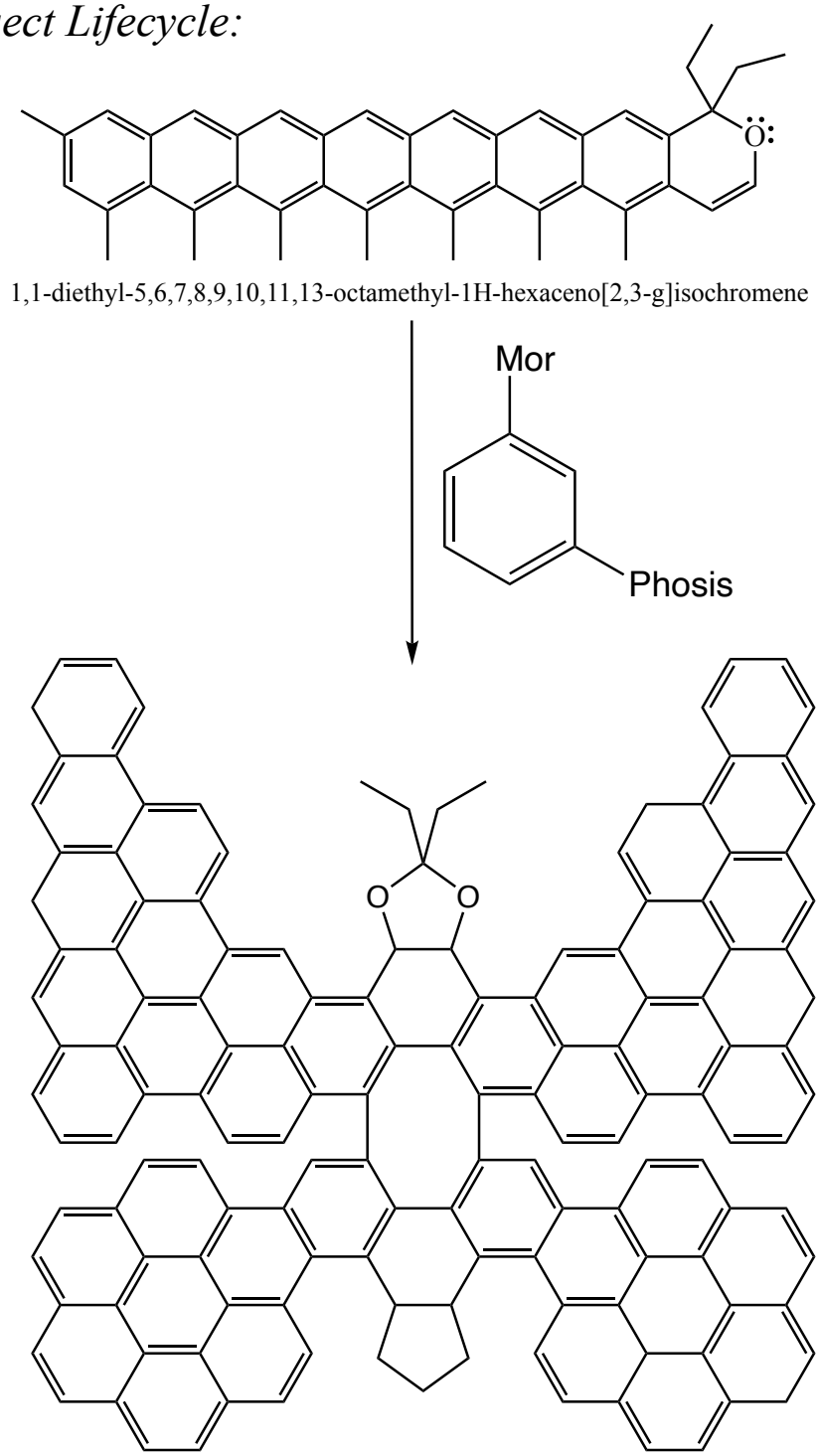
○ **True**
● **False**
I. Molecules appear to our eye to be a combination of the wavelengths absorbed (not reflected).

● **True**
○ **False**
J. When X_2 adds to 1,3-butadiene, the 1,2 addition is the kinetic product, that is, it forms faster (better opportunity since the reaction is occuring at the site of the positive charge in the major contributing structure).

○ **True**
● **False**
K. At low temperature, in which the molecules cannot equilibrate, the thermodynamic product predominates (called thermodynamic control).

This is where the nomenclature would have been!

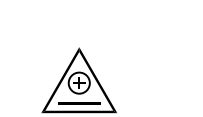
Aromatic Insect Lifecycle:



1,1-diethyl-5,6,7,8,9,10,11,13-octamethyl-1H-hexaceno[2,3-g]isochromene

I put this here to help you relax. You will do better on the exam in a relaxed frame of mind. (If the above equation made you laugh or even smile, you may be a chem nerd, but nobody has to find out.)

5. (1 pt each) Indicate whether each is aromatic or not aromatic by filling in the appropriate circle.

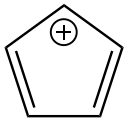


● Aromatic
○ Not aromatic

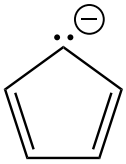
○ Aromatic
● Not aromatic

○ Aromatic
● Not aromatic

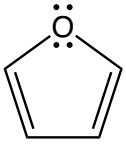
○ Aromatic
● Not aromatic



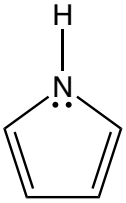
○ Aromatic
● Not aromatic



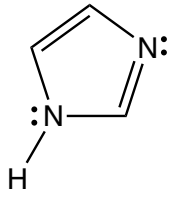
● Aromatic
○ Not aromatic



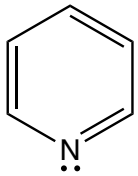
● Aromatic
○ Not aromatic



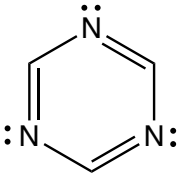
● Aromatic
○ Not aromatic



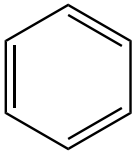
● Aromatic
○ Not aromatic



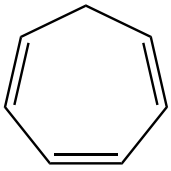
● Aromatic
○ Not aromatic



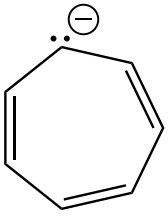
● Aromatic
○ Not aromatic



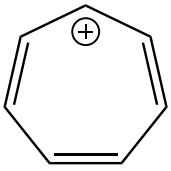
● Aromatic
○ Not aromatic



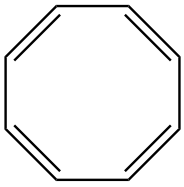
○ Aromatic
● Not aromatic



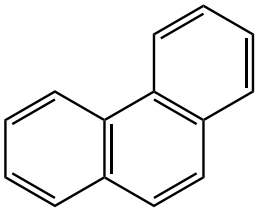
○ Aromatic
● Not aromatic



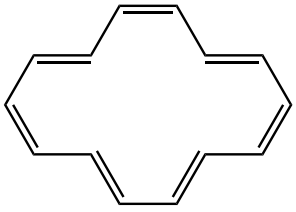
● Aromatic
○ Not aromatic



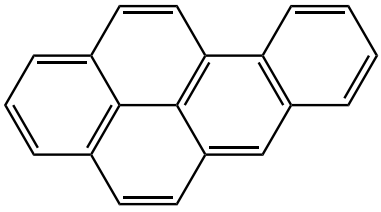
○ Aromatic
● Not aromatic



● Aromatic
○ Not aromatic



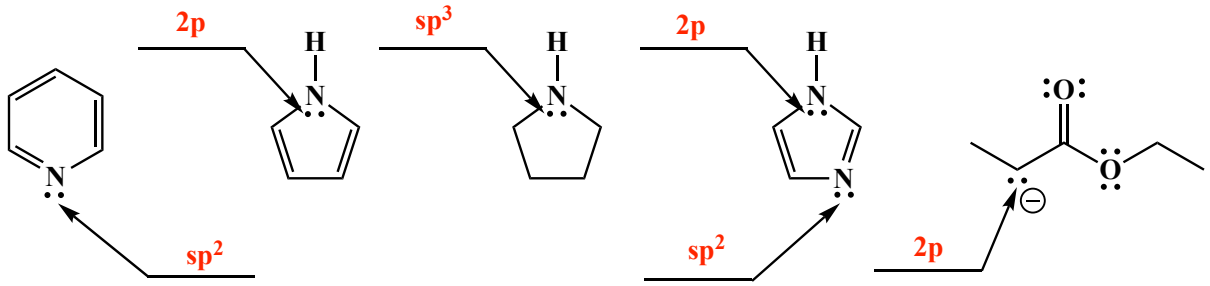
● Aromatic
○ Not aromatic



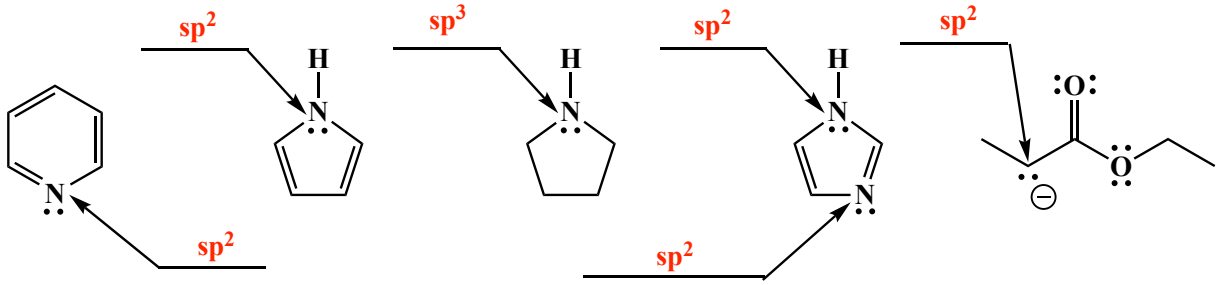
● Aromatic
○ Not aromatic

Signature_____ Pg 4_____(36)

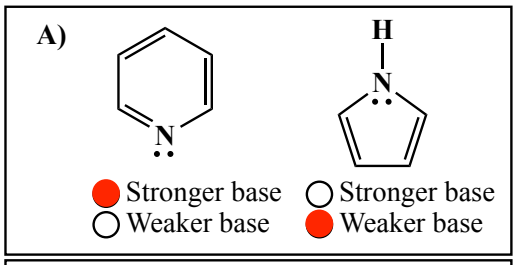
6. (2 pts each) For each arrow, on the line provided write the type of atomic orbital that contains the lone pair of electrons indicated. Appropriate asnwers might be sp, sp^2, sp^3 or 2p.

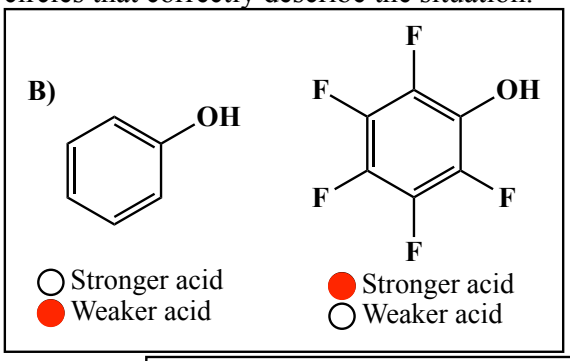


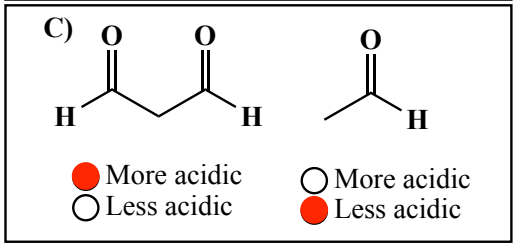
7. (2 pts each) For each arrow, on the line provided write the hybridization state of the atom indicated. Appropriate asnwers might be sp, sp^2, or sp^3.

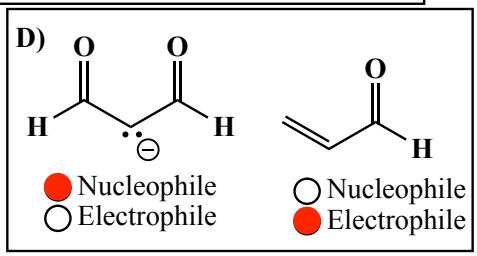


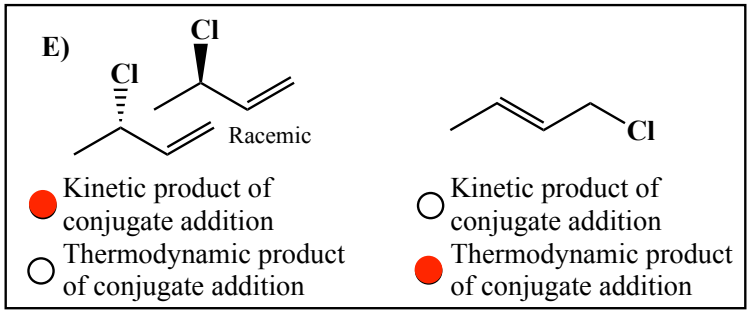
8. (2 pts each) For each pair of molecules, fill in all the circles that correctly describe the situation.

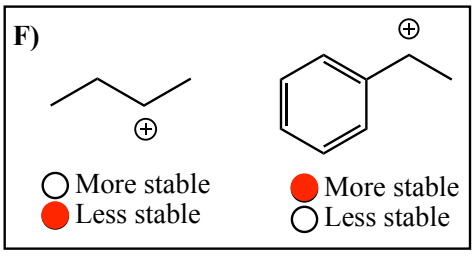




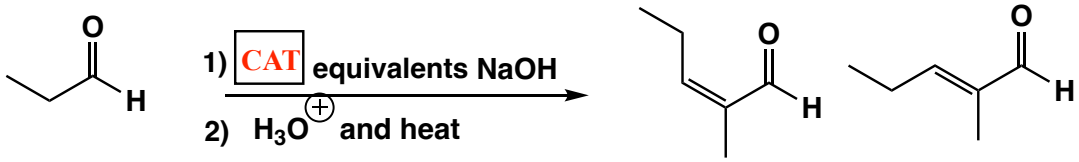






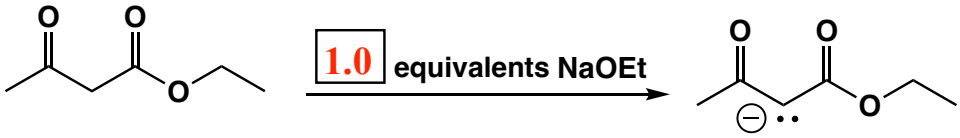


10. (24 pts) In each of the boxes over an arrow, write the minimum number of equivalents of the specified reagent required to carry out the reaction shown to completion. If only a catalytic amount is needed, write "CAT". **Note: You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent.**

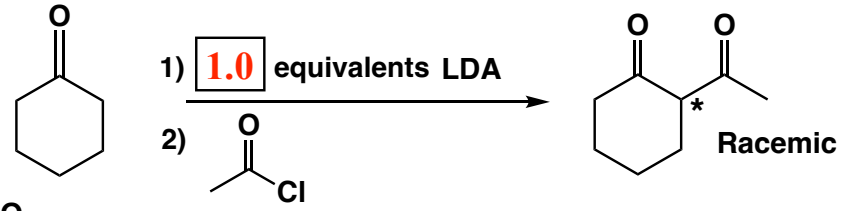
A) 

B) 

C) 

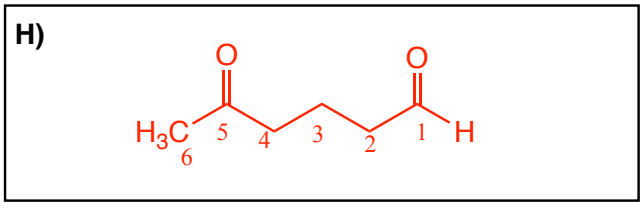
D) 

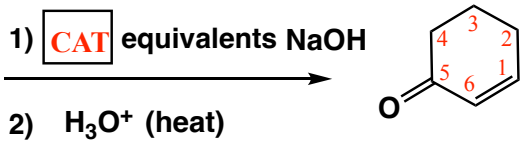
E) 

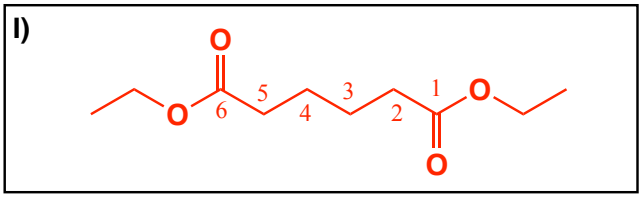
F) 

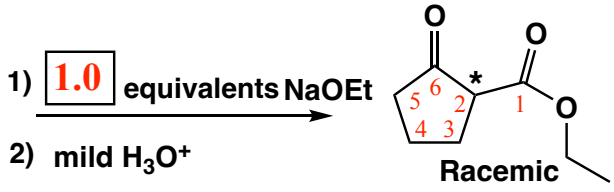
G) 

For these next two we have provided the product, you need to draw the starting material as well as fill in the number of equivalents.

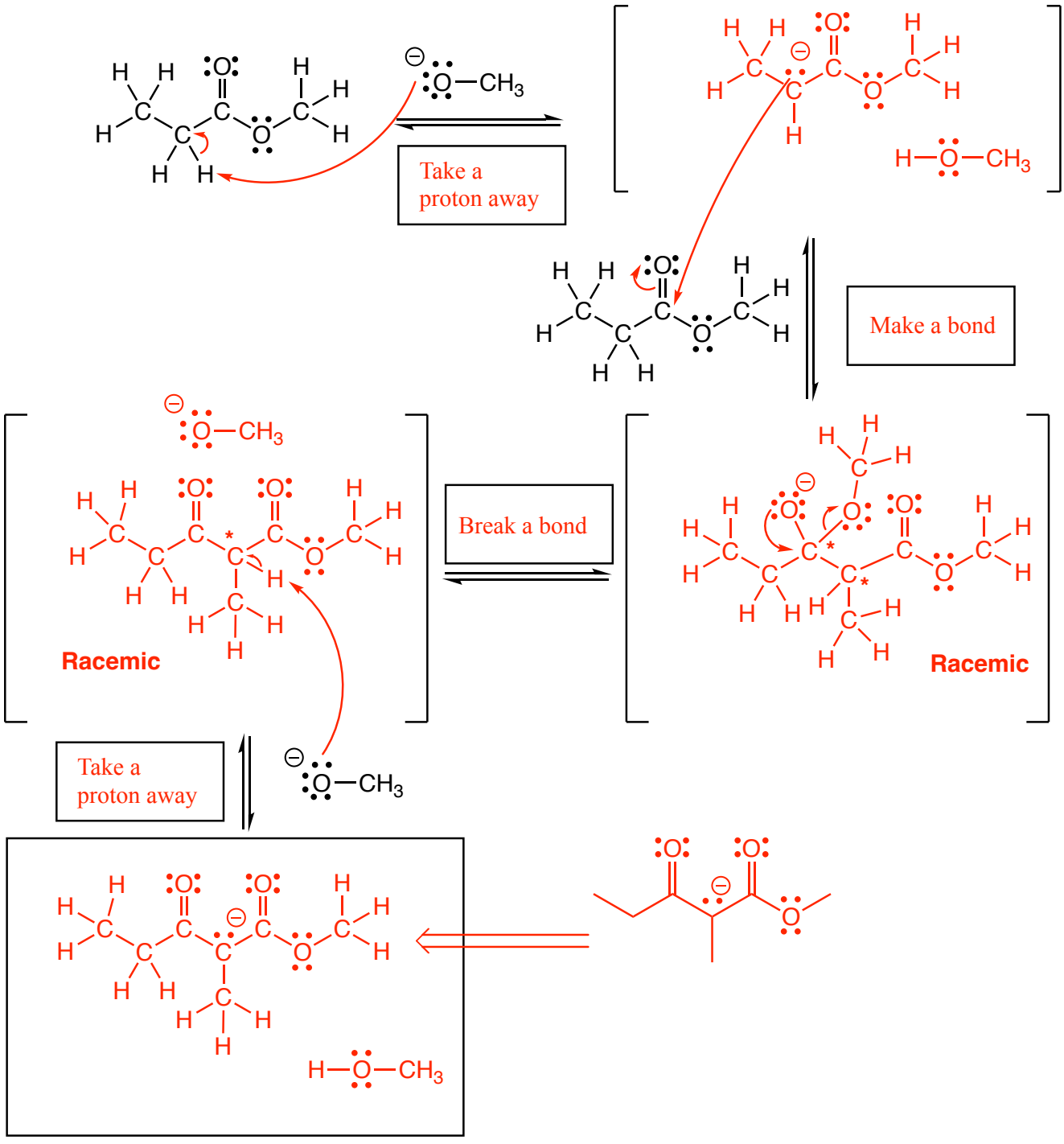
H) 



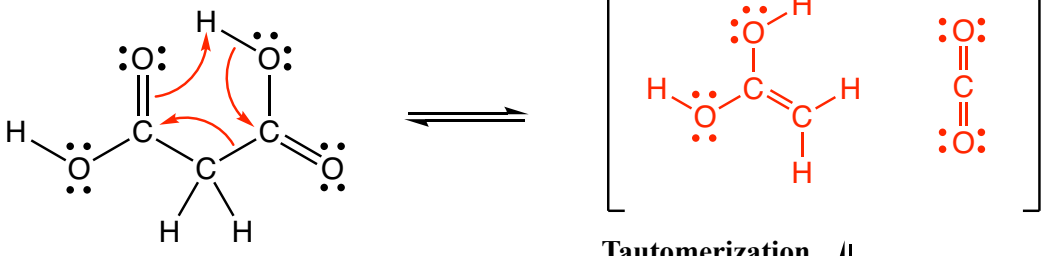
I) 



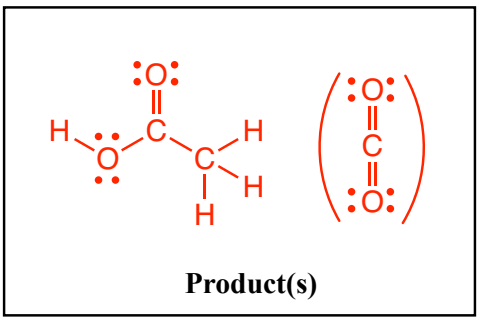
11. (23 pts) Complete the mechanism for the following Claisen condensation reaction. Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step. Remember, I said <u>all</u> the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS RACEMIC IF APPROPRIATE. In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.).



12. (16 pts) Complete the following two mechanisms. Be sure to show arrows to indicate movement of all electrons on both structures, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS RACEMIC IF APPROPRIATE.

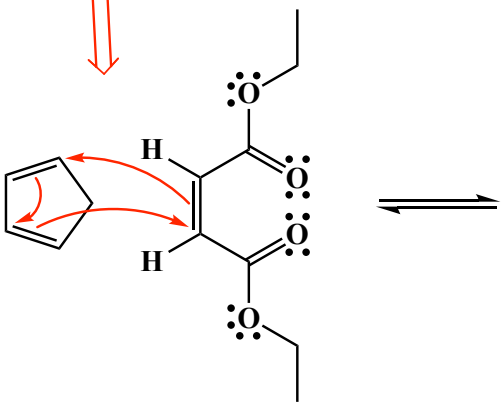


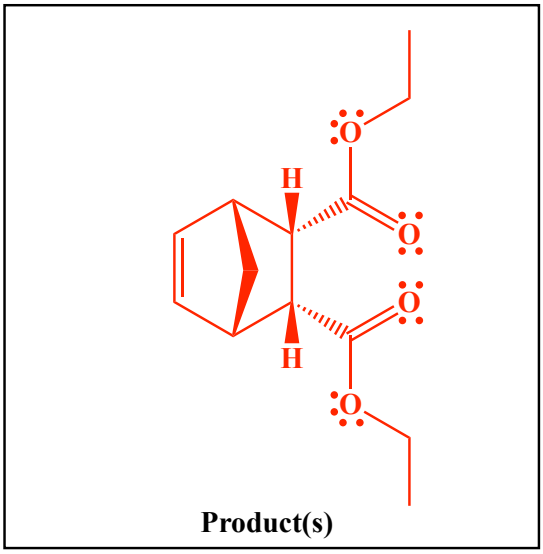
Tautomerization
(no need to draw arrows on the intermedidate structure above)



Product(s)

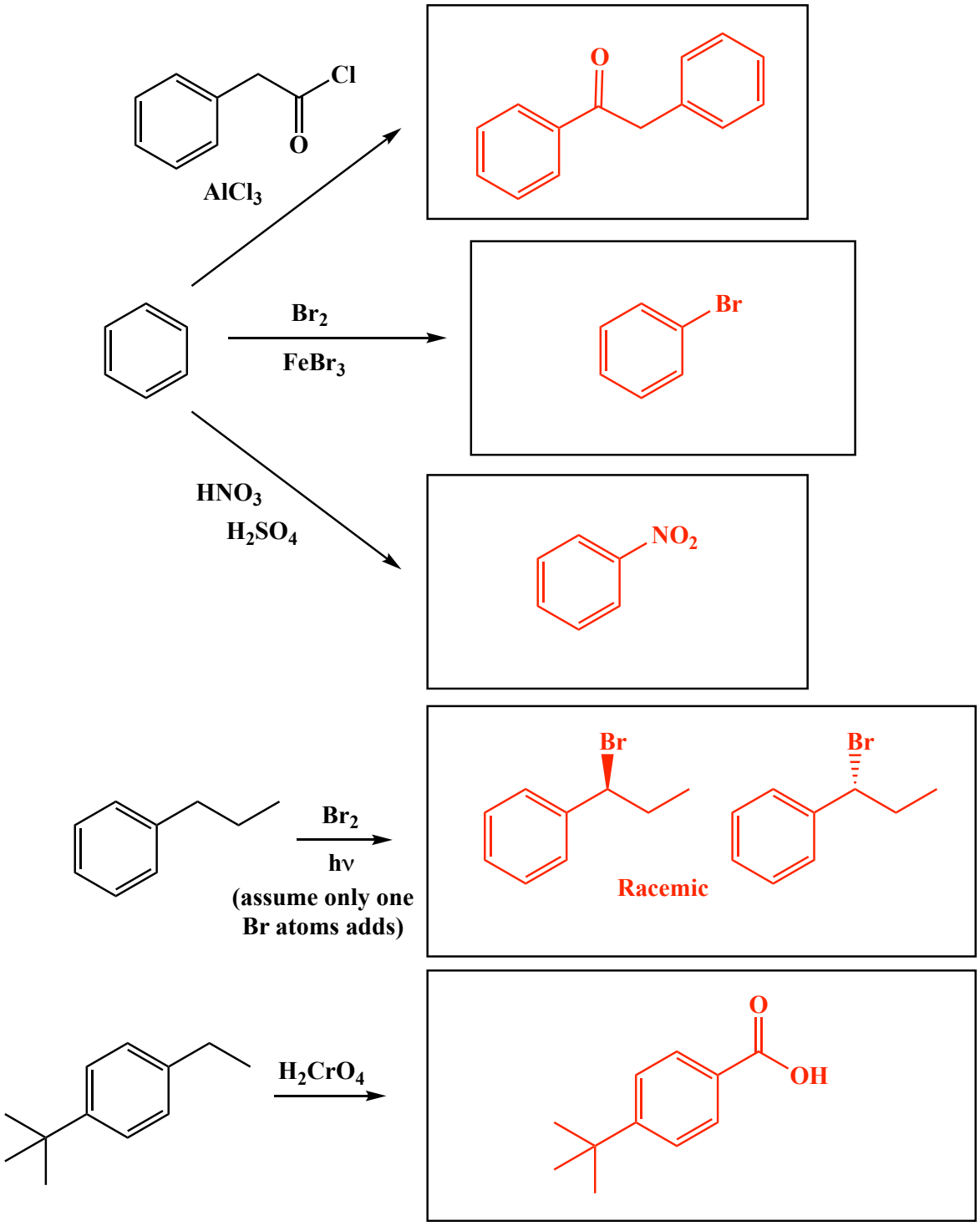
3 pi bonds (involving 6 pi electrons) are being made or broken in the transition state here. In other words, the transition state has aromatic character, explaining why this process has a reasonably small energy barrier and occuts with simple heating.





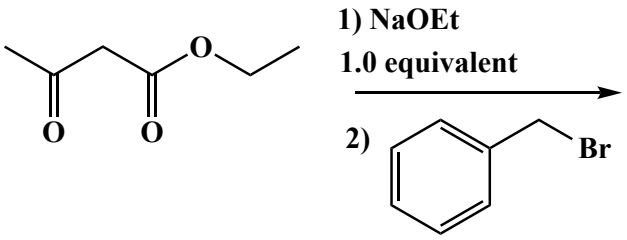
Product(s)

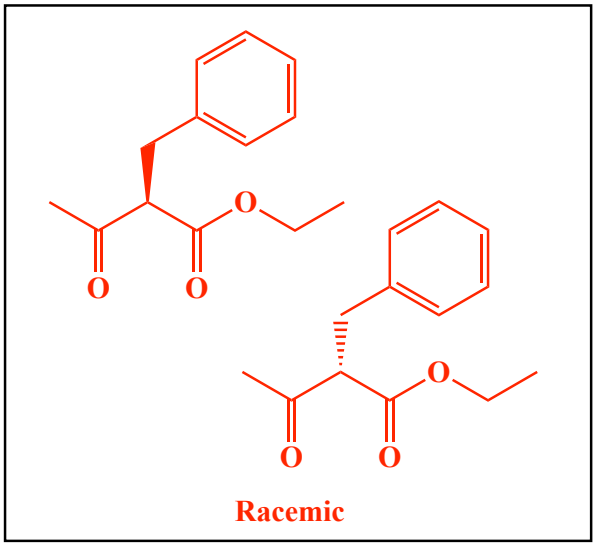
13. (3 or 5 pts.) Write the predominant product that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. For these, you do not have to worry about metal salts in the products. **For all aldol reactions, we only want you to draw the dehydrated products.**

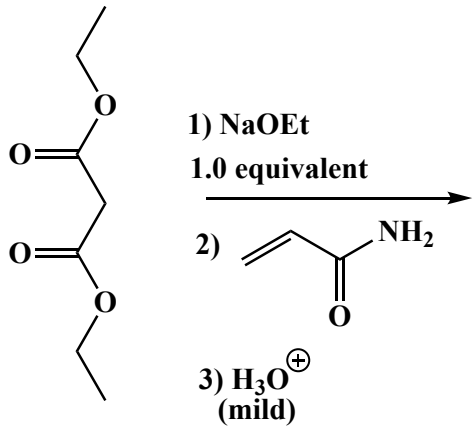


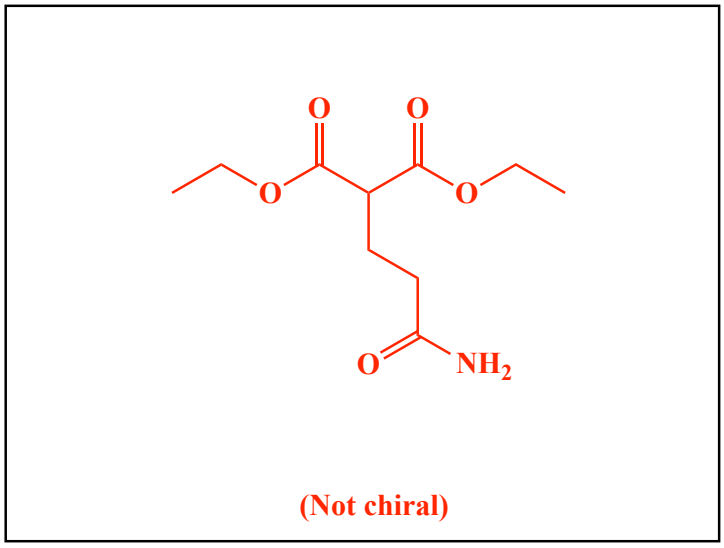
Signature_____ Pg 9 _____(13)

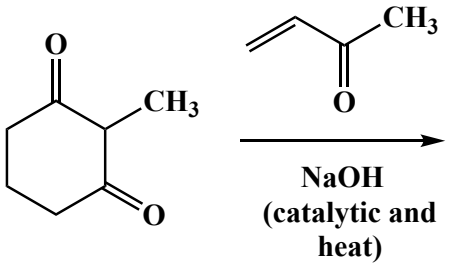
13. (3 or 5 pts.) Write the predominant product that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. For these, you do not have to worry about metal salts in the products. **For all aldol reactions, we only want you to draw the dehydrated products.**

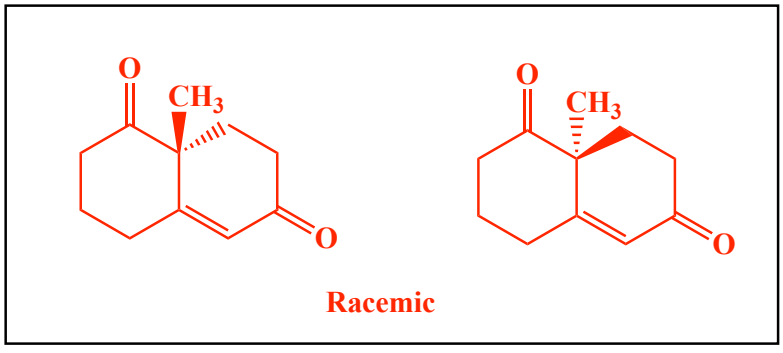






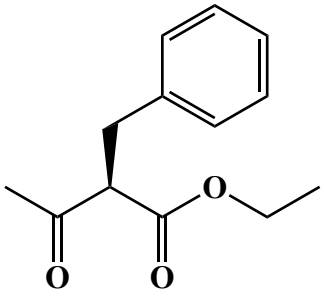




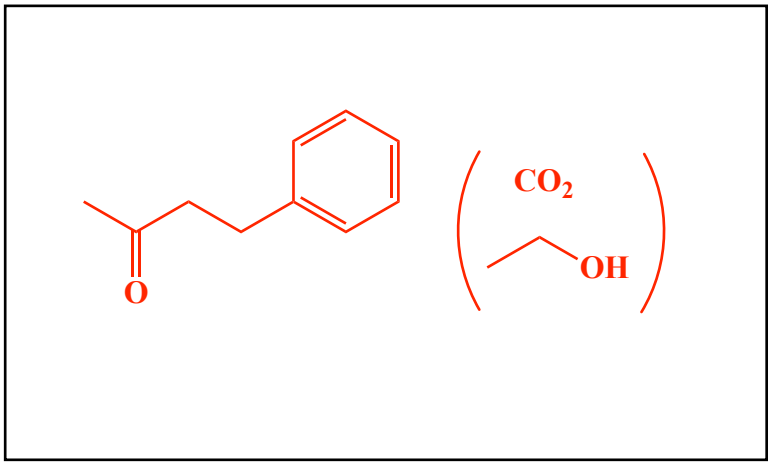


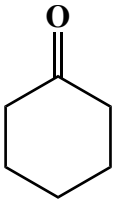
/

13. (3 or 5 pts.) Write the predominant product that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◀) and dashes (·····) to indicate stereochemistry. For these, you do not have to worry about metal salts in the products. **For all aldol reactions, we only want you to draw the dehydrated products.**

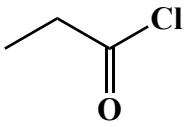


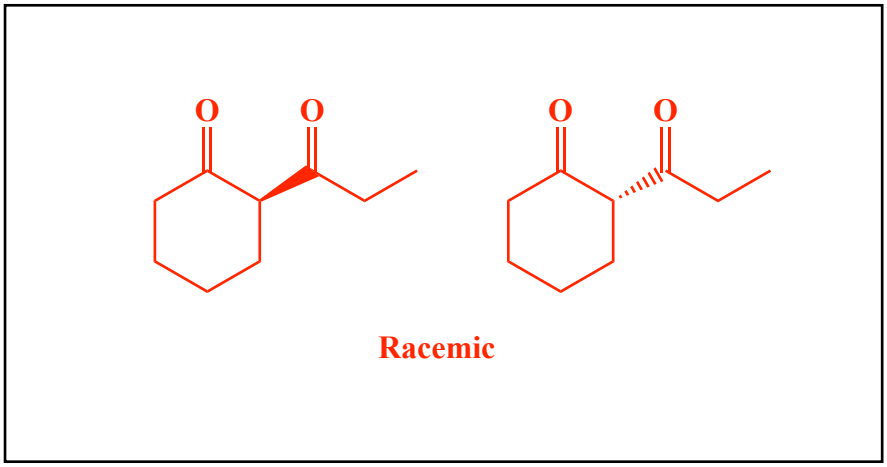
$H_3O^{\oplus}$
(strong acid and heat)

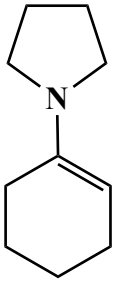




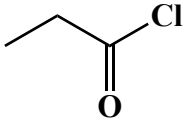
1) LDA
1.0 equivalent
2)



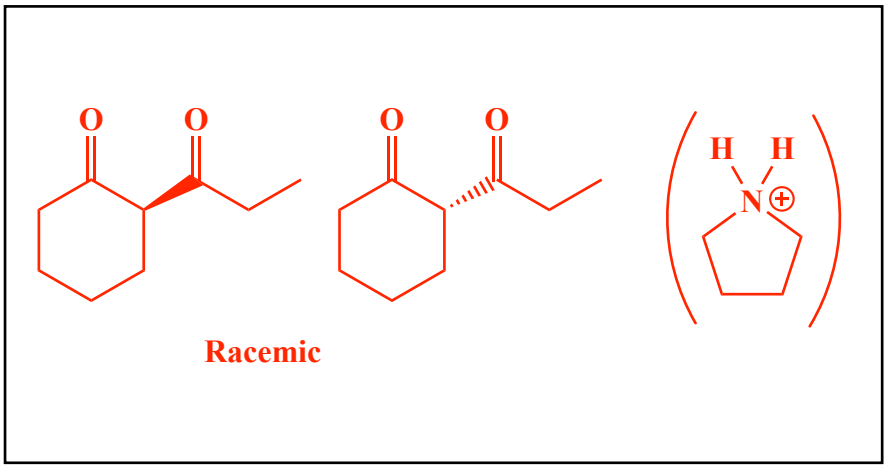




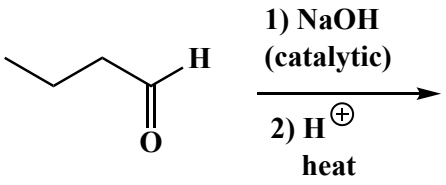
1)

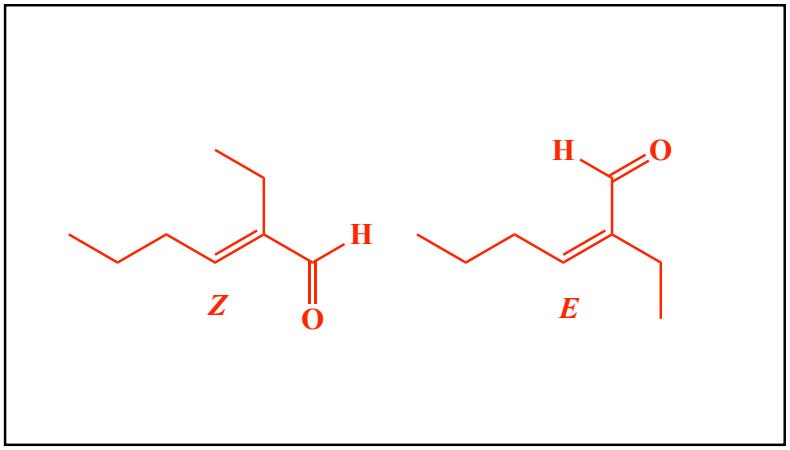


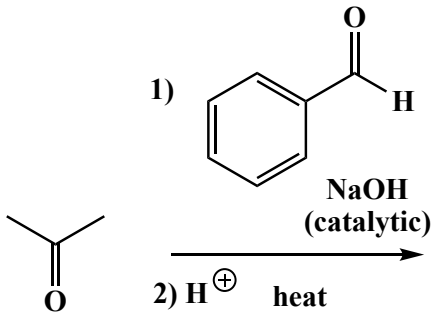
2) $H_3O^{\oplus}$

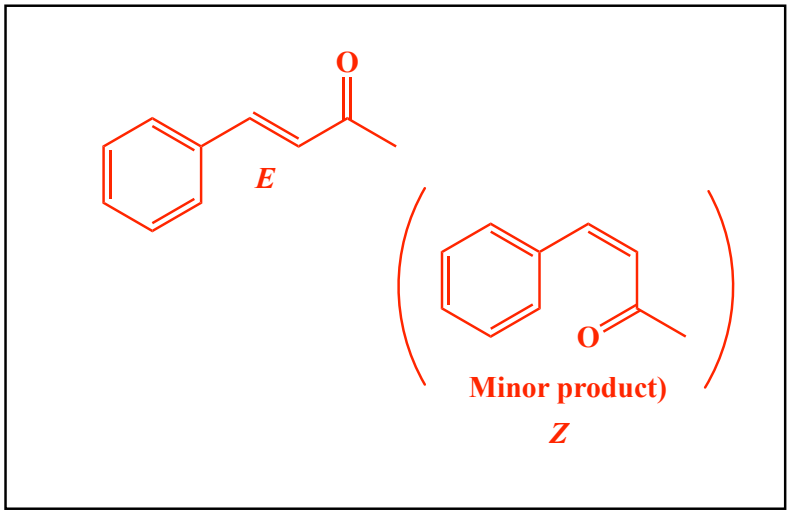


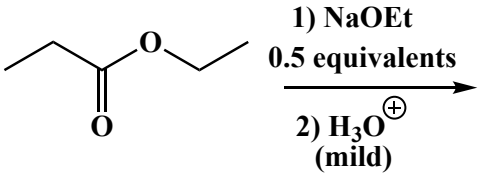
13. (3 or 5 pts.) Write the predominant product that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. For these, you do not have to worry about metal salts in the products. **For all aldol reactions, we only want you to draw the dehydrated products.**

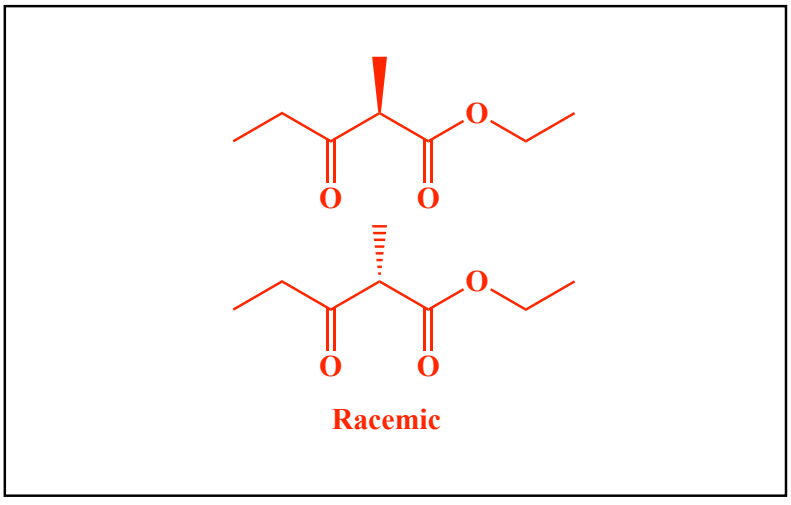






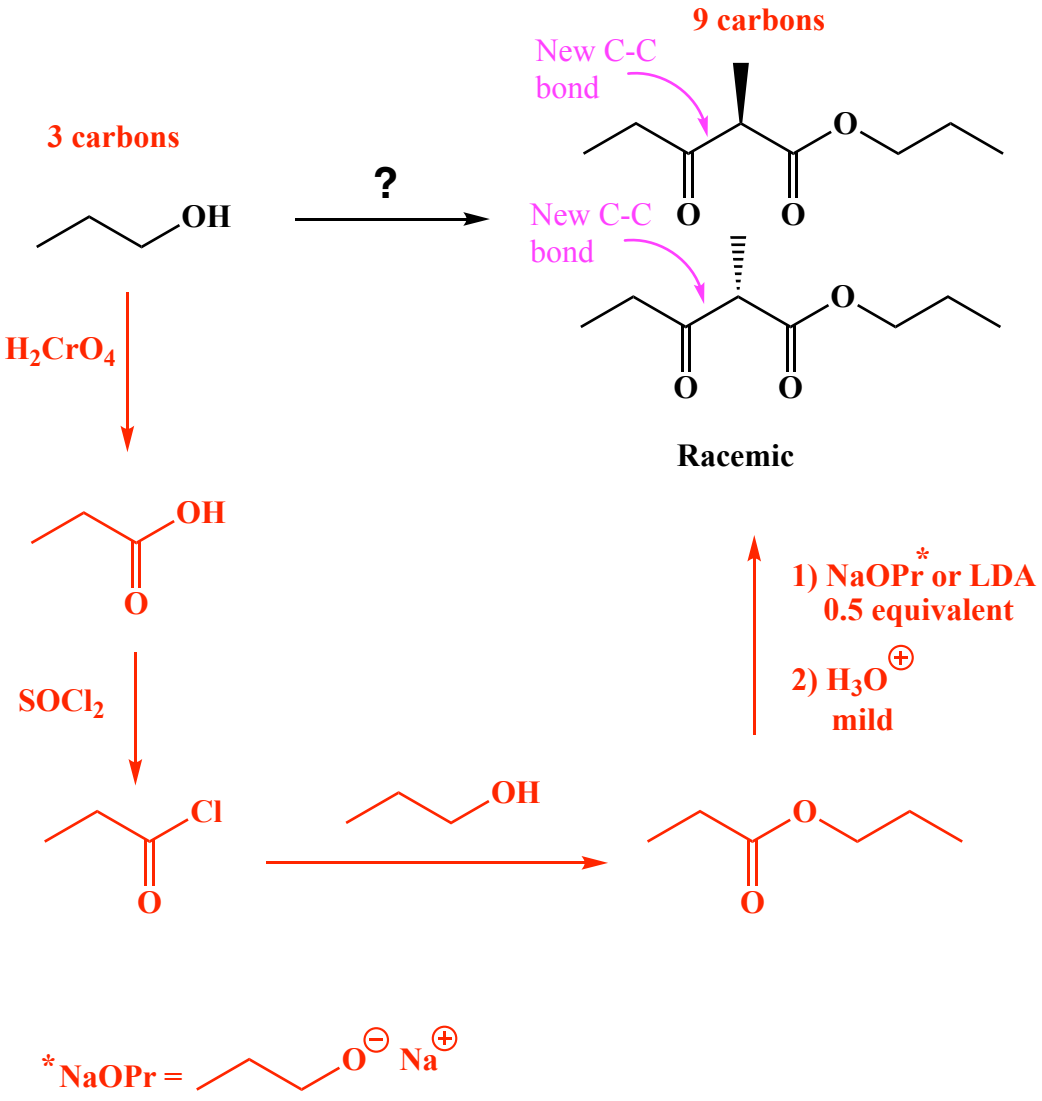






14. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

A) (10 pts)



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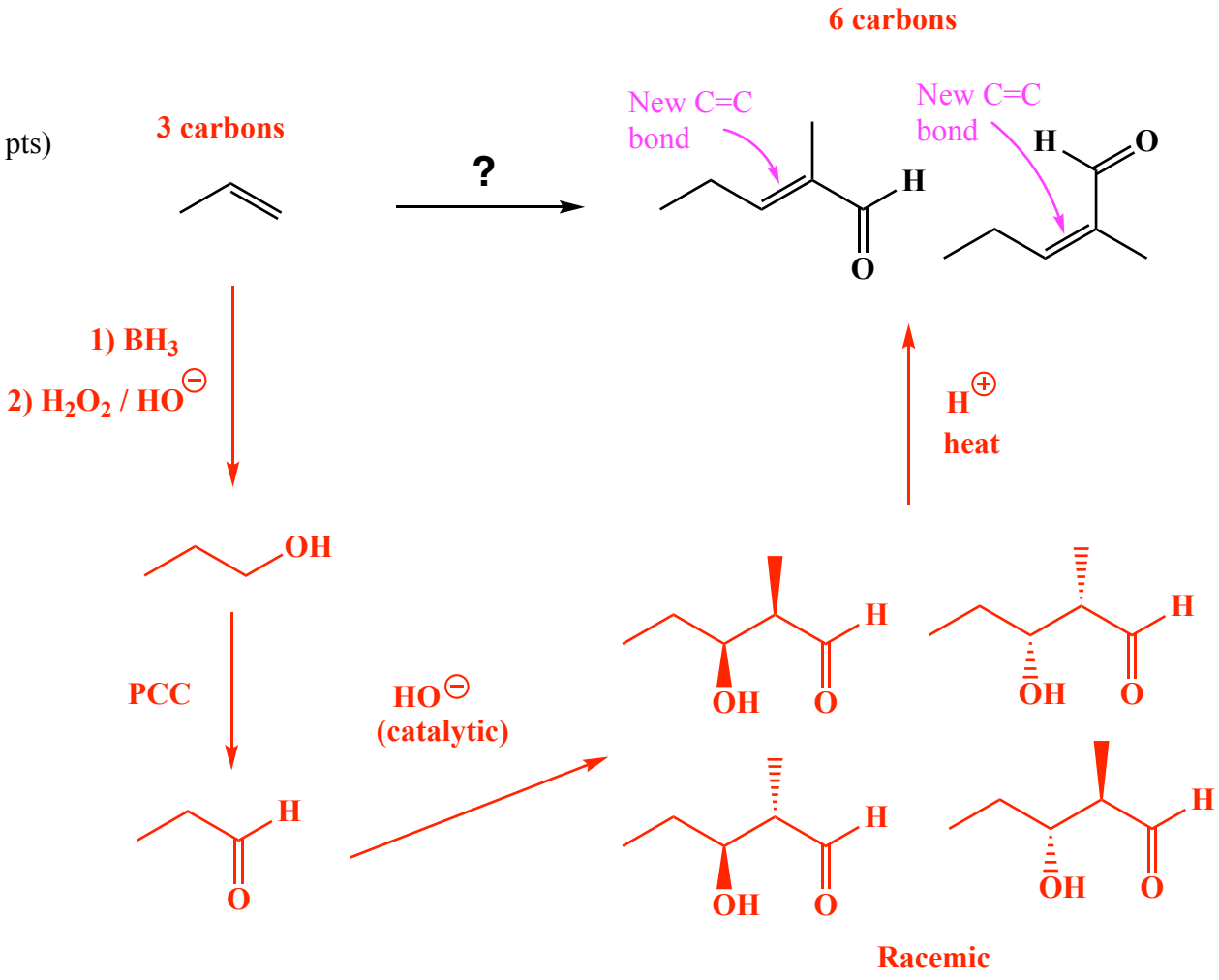
B) (10 pts)



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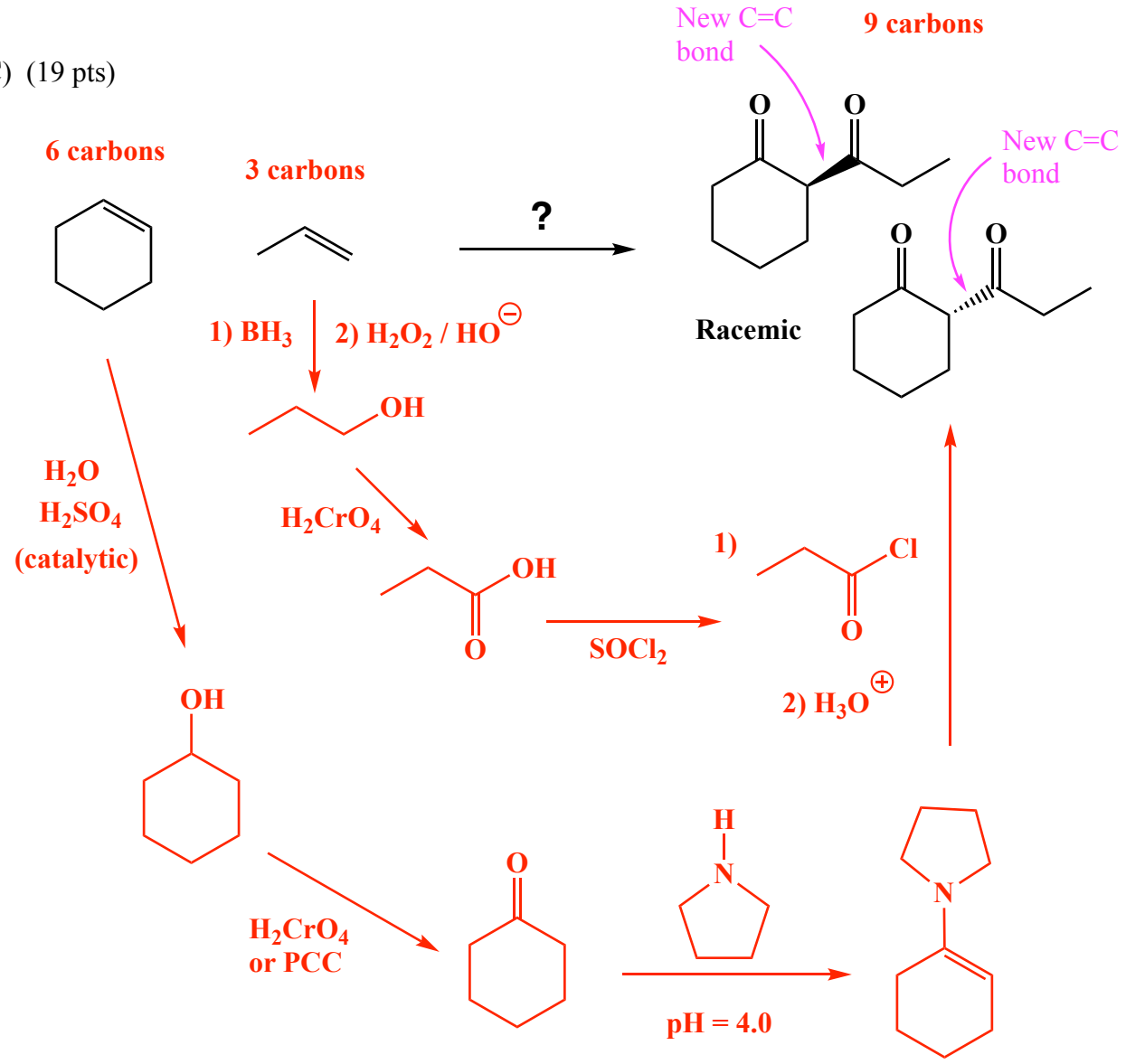
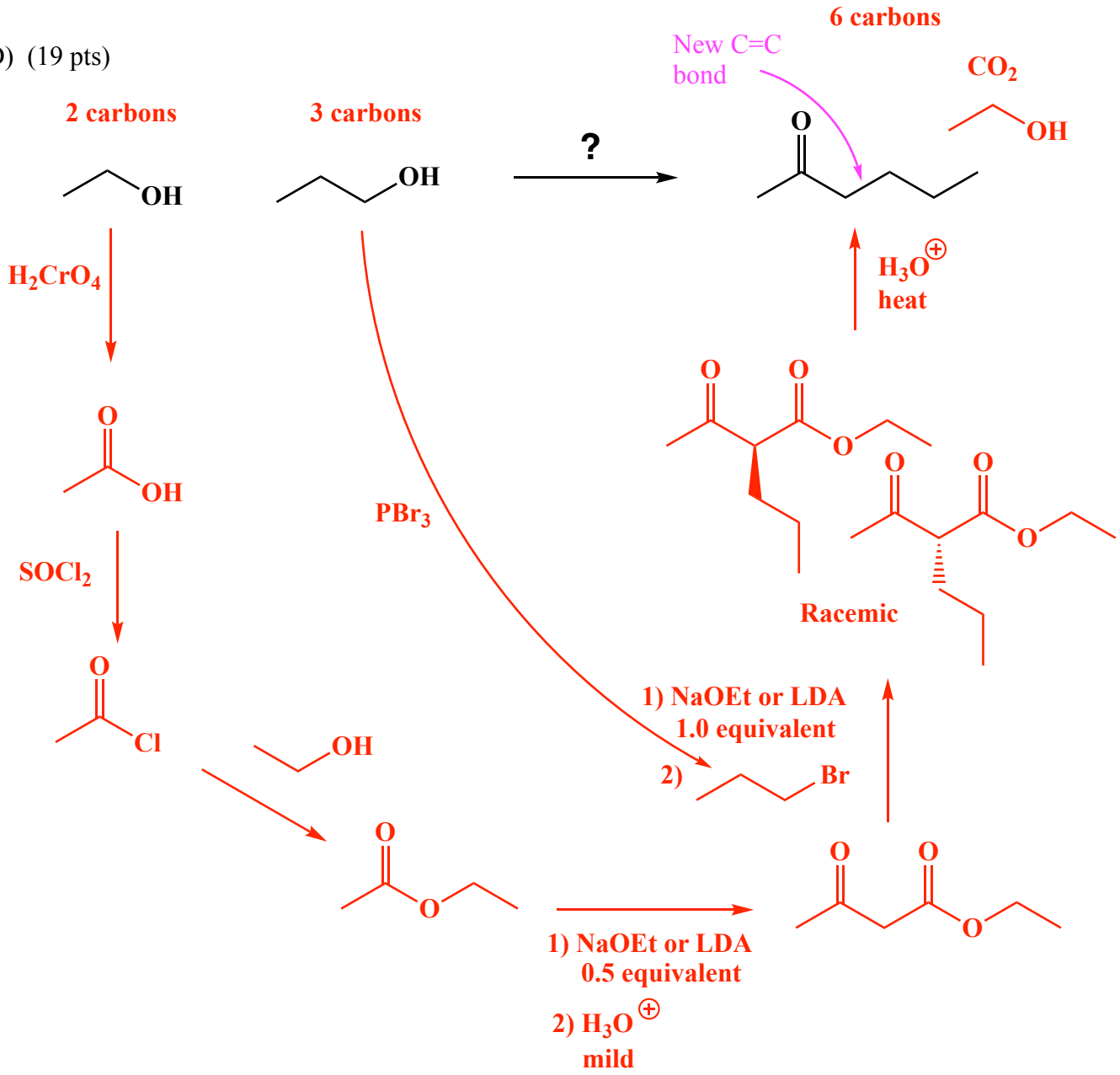
C) (19 pts)



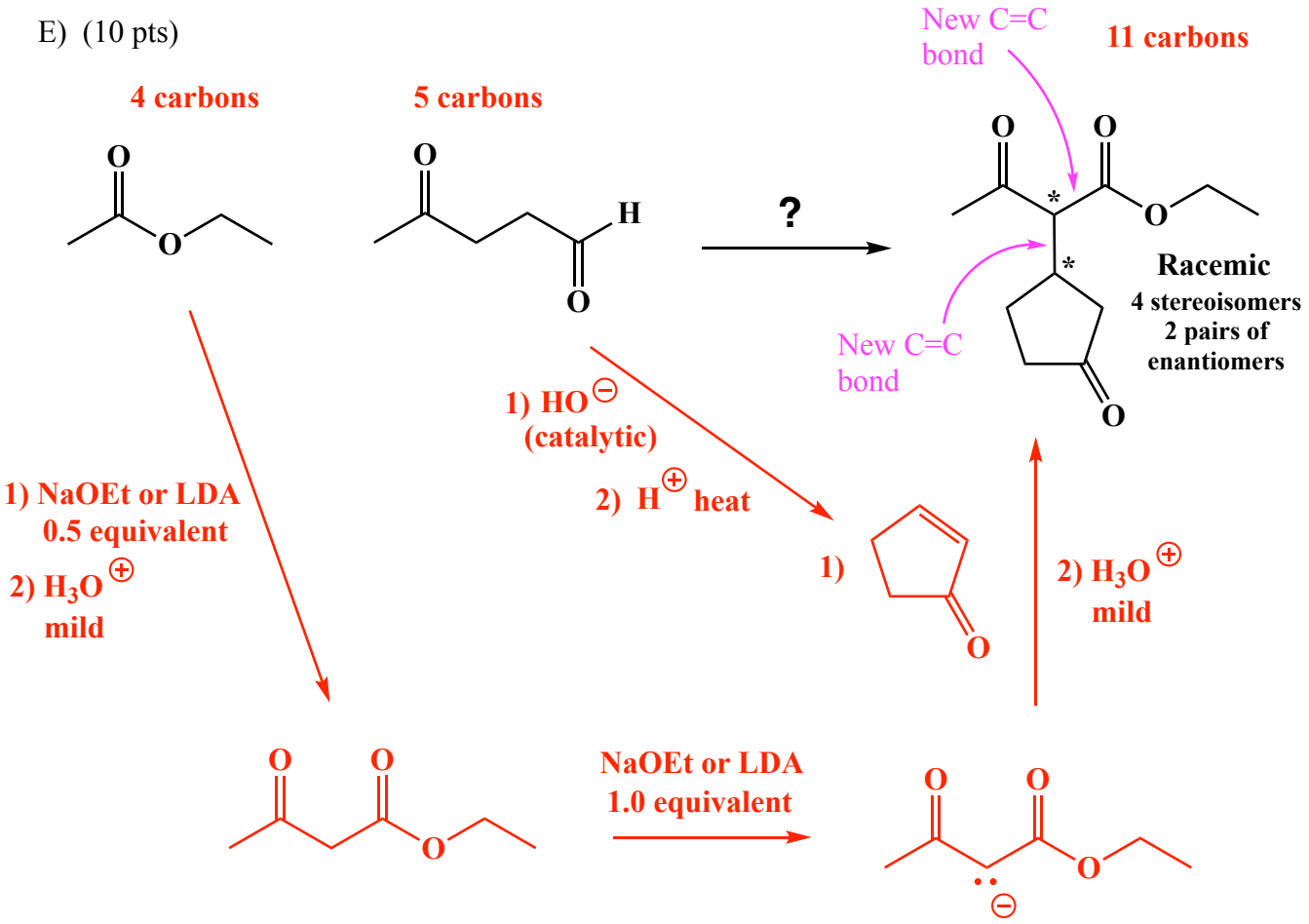
14. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

D) (19 pts)



14. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

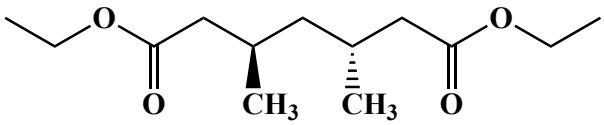
E) (10 pts)



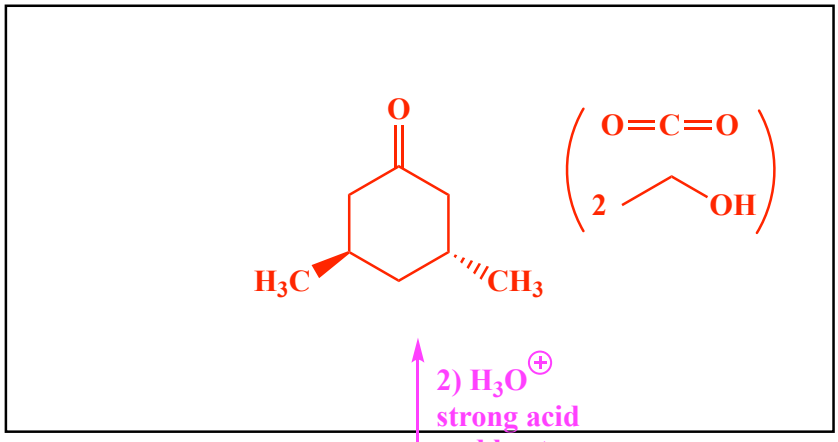
Signature_____ Pg 17 _____(8)

15. (8 pts.) Write the predominant product that will occur for this set of transformations. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. For these, you do not have to worry about metal salts in the products. **For all aldol reactions, we only want you to draw the dehydrated products.**

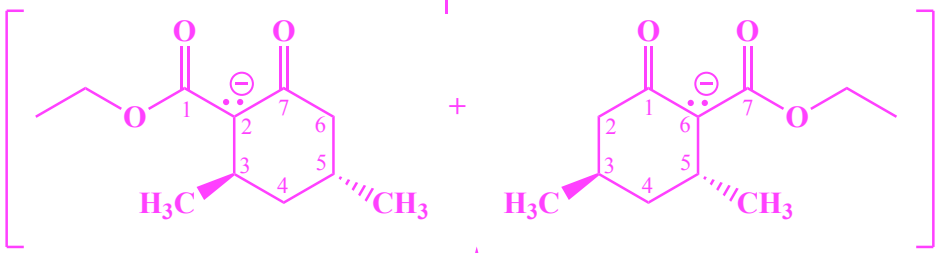
This is at the end because it will take you a while.



1) LDA 1.0 equivalent
2) $H_3O^{\oplus}$
strong acid
and heat



2) $H_3O^{\oplus}$
strong acid
and heat



1) LDA 1.0 equivalent