NAME (Print): ______________________________

EID _______________

SIGNATURE: ______________________________

Chemistry 320N
3rd Midterm Exam
April 11, 2024

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 for the University of Texas at Austin

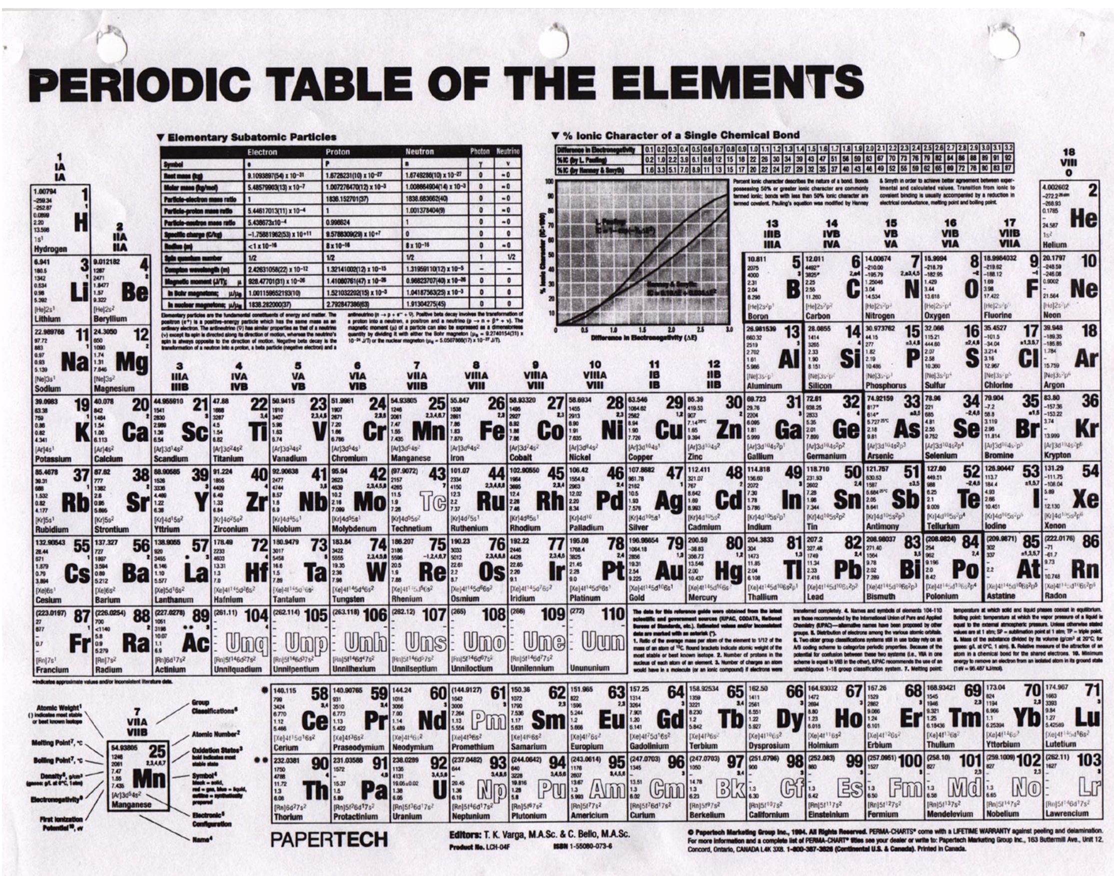
"I pledge, as a member of The University of Texas at Austin community, to do my work honestly, respectfully, and through the intentional pursuit of learning and scholarship."

Elaboration

1. I pledge to be honest about what I create and to acknowledge what I use that belongs to others.
2. I pledge to value the process of learning in addition to the outcome, while celebrating and learning from mistakes.
3. This code encompasses all of the academic and scholarly endeavors of the university community.

____

(Your signature)



Compound		pK_a
Hydrochloric acid	$H\text{-}Cl$	-7
Protonated alcohol	$RCH_2OH_2^{\oplus}$	-2
Hydronium ion	$H_3O^{\oplus}$	-1.7
Carboxylic acids	$R-C(=O)O\text{-}H$	3-5
Thiols	RCH_2SH	8-9
Ammonium ion	$H_4N^{\oplus}$	9.2
β-Dicarbonyls	$RC(=O)-CH_2\text{-}C(=O)R'$	10
Primary ammonium	$H_3\overset{\oplus}{N}CH_2CH_3$	10.5
β-Ketoesters	$RC(=O)-CH_2\text{-}C(=O)OR'$	11
β-Diesters	$ROC(=O)-CH_2\text{-}C(=O)OR'$	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides	$RCH_2\text{-}C(=O)Cl$	16
Aldehydes	$RCH_2\text{-}C(=O)H$	18-20
Ketones	$RCH_2\text{-}C(=O)R'$	18-20
Esters	$RCH_2\text{-}C(=O)OR'$	23-25
Terminal alkynes	$RC\equiv C-H$	25
LDA	$H\text{-}N(i\text{-}C_3H_7)_2$	40
Terminal alkenes	$R_2C=C(H)-H$	44
Alkanes	$CH_3CH_2\text{-}H$	51

=[-p[]\’

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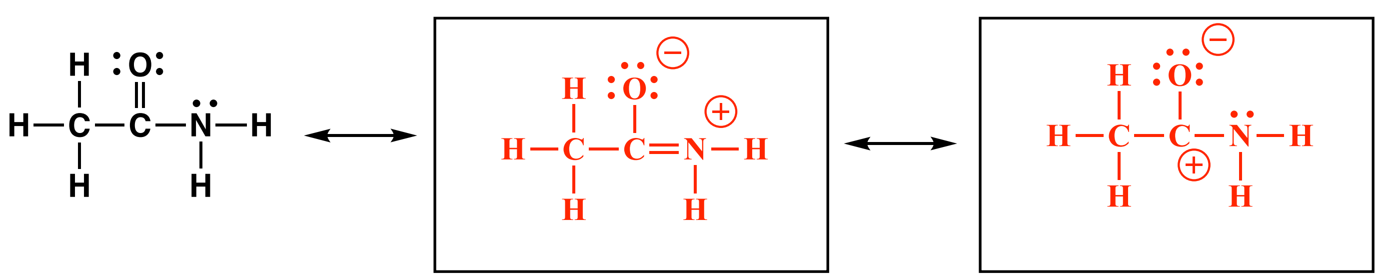
1. (5 pts) What is the most important question in organic chemistry?

Where are the electrons?

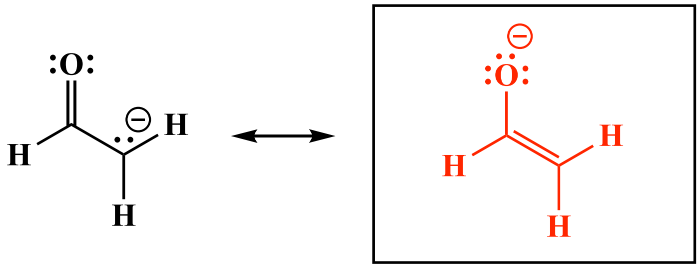
2. (1 pt each) Fill in each blank with the word that best completes the sentences. Yep, this is the MRI paragraph!

The popular 1.______medical______ diagnostic technique of 2.______magnetic______ 3.______resonance______ 4.______imaging______ (_5.__MRI__) is based on the same principles as NMR, namely the 6.______flipping______ (i.e. resonance) of 7.______nuclear______ spins of 8. ___H___ atoms by radio 9.______frequency______ 10.______irradiation______. 11. ______Magnetic______ 12.______field______ gradients are used to gain imaging information, and 13. ______rotation______ of the 14. ______gradients______ around the 15. ______center______ of the object gives imaging in an entire plane (i.e. slice inside 16.______patient______). In an MRI image, you are looking at individual 17.______slices______ that when 18.______stacked______ make up the three-dimensional image of relative amounts of 19. ______H______ atoms, especially the 20.______H______ atoms from 21.______water______ and 22.______fat______, in the different 23.______tissues______.

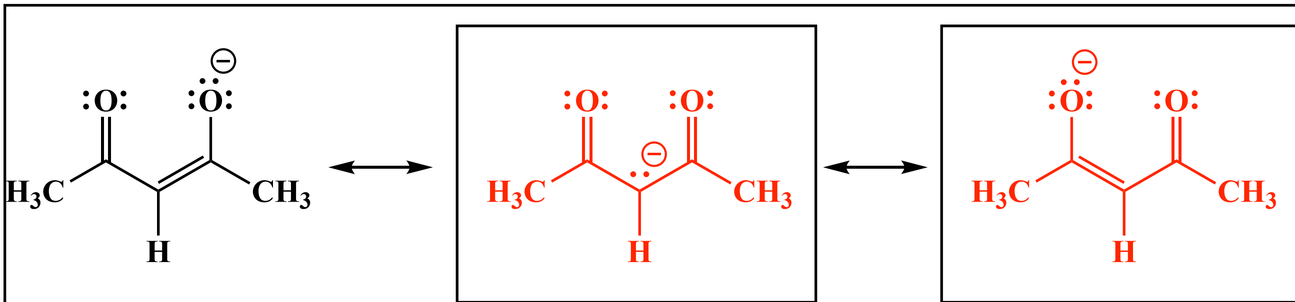
3. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided. (No need to draw any arrows for this.)



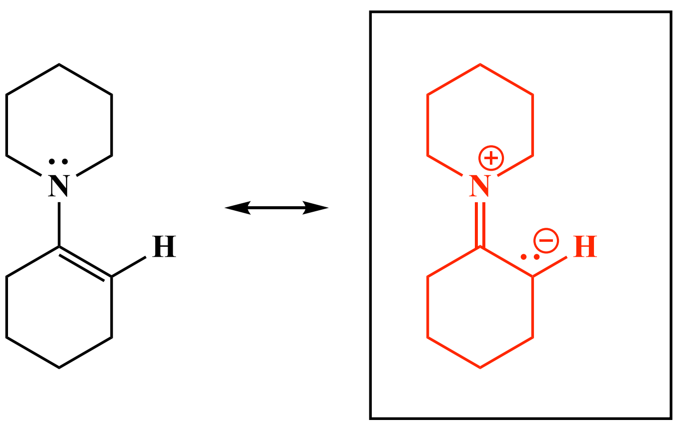
4. (23 pts) The following molecules are all ones we have seen in mechanisms recently. Please draw all of the important conttributing structures. Include all formal charges and lone pairs. There is no need to draw arrows on any of these structures.



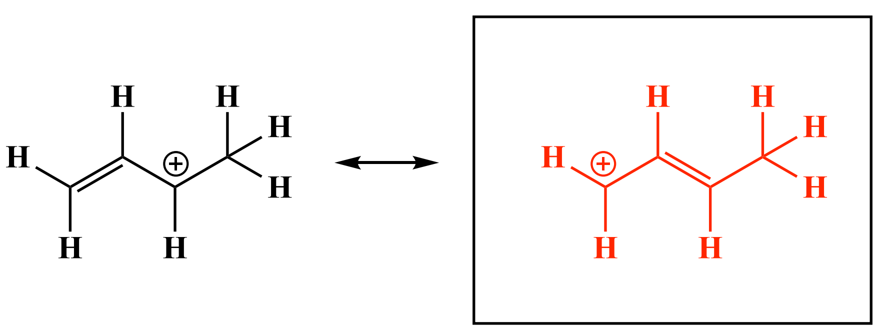
The "π-way" in this molecule covers __3__ atoms



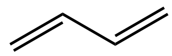
The "π-way" in this molecule covers __5__ atoms



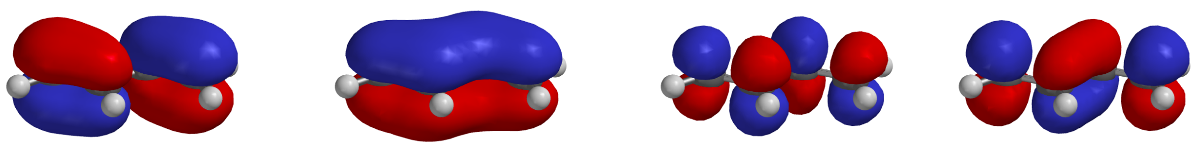
The "π-way" in this molecule covers __3__ atoms



5. (16 pts) The following are the pi molecular orbitals for 1,3-butadiene. Under each one place a number corresponding to energy, with a "1" under the lowest energy (most stable) molecular orbital, a "4" under the highest energy (least stable) molecular orbital and a "2" and a "3" as appropriate.



1,3-Butadiene



2	1	4	3

B) On the lines below, write "bonding" or "antiboding" as appropriate to describe the orbitals above:

Bonding	Bonding	Antibonding	Antibonding

C) On the lines below, write how many electrons are in each orbital BEFORE a photon is absorbed:

2	2	0	0

D) On the lines below, write how many electrons are in each orbital immediately AFTER a photon is absorbed (before the energy is lost as heat):

1	2	0	1

6. (9 pts) When thinking of the Robinson Annulation reaction, it is helpful to think of the mechanism as being composed of three different parts. From the following, select the correct three reactions involved with a Robinson Annulation.

Part 1:	**Part 2:**	**Part 3:**
○ **Aldol Reaction**	● **Aldol Reaction**	○ **Aldol Reaction**
● **Michael Reaction**	○ **Michael Reaction**	○ **Michael Reaction**
○ **Claisen Reaction**	○ **Claisen Reaction**	○ **Claisen Reaction**
○ **Gilman Reaction**	○ **Gilman Reaction**	○ **Gilman Reaction**
○ **Iverson Reaction**	○ **Iverson Reaction**	○ **Iverson Reaction**
○ **Hydration**	○ **Hydration**	○ **Hydration**
○ **Dehydration**	○ **Dehydration**	● **Dehydration**
○ **Dehalogenation**	○ **Dehalogenation**	○ **Dehalogenation**

Signature___________________________ Pg 4____________(24)

7. (2 pts each) Indicate whether each statement is true or false by filling in the appropriate circle.

○ **True**
● **False**
A. When considering orbitals and bonding in chemistry, it is best to think of electrons as particles.

● **True**
○ **False**
B. When considering orbitals and bonding in chemistry, it is best to think of electrons as waves.

● **True**
○ **False**
C. When the energy of a photon is absorbed by a molecule, an electron in a filled molecular orbital is transferred to a higher energy unfilled orbital.

● **True**
○ **False**
D. The <u>more</u> 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**
E. Fluorescence occurs when an electron flips its spin as a photon is absorbed, so it must flip back before emitting a photon as it goes back to the ground state.

● **True**
○ **False**
F. Phosphorescence ("glow in the dark") occurs when an electron flips its spin as a photon is absorbed, so it must flip back before emitting a photon as it goes back to the ground state.

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

○ **True**
● **False**
H. An object sitting in sunshine that appears red to our eyes absorbs light in the red region of the visible light spectrum.

○ **True**
● **False**
I. A pericyclic reaction such as the Diels-Alder reaction produces an aromatic product, so that is why the reaction has a relatively low energy barrier.

● **True**
○ **False**
J. A pericyclic reaction such as the Diels-Alder reaction has a transition state that has aromatic character, so that is why the reaction has a relatively low energy barrier.

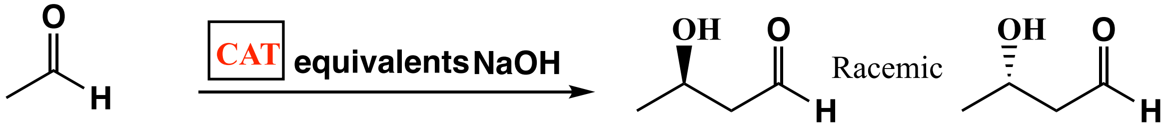
● **True**
○ **False**
K. In the Michael reaction, the first intermediate is an enolate.

○ **True**
● **False**
L. In a Michael reaction, the thermodynamic reason that conjugate addition of a nucleophile is favored over reaction at the carbonyl carbon atom is because a C=C in a product is a stronger bond than a C=O in a product.

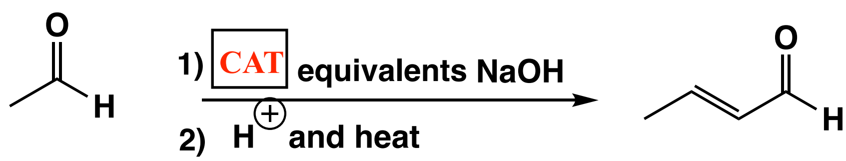
8. (20 pts) In each of the boxes over an arrow, write the minimum number of equivalents of the specified reagent required to carry out the reaction shown to completion. If only a catalytic amount is needed, write "CAT". **Note: You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent.**

A)

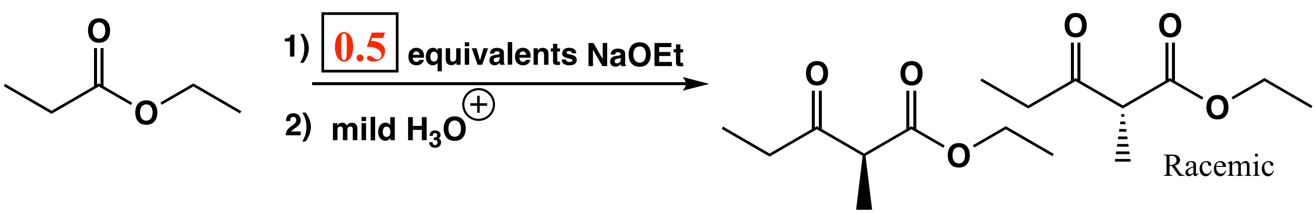
B)



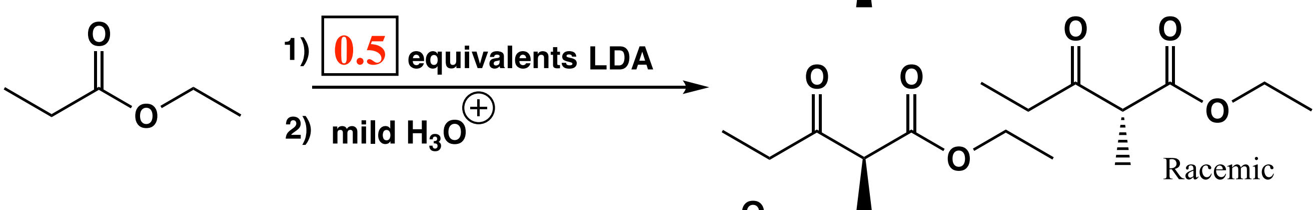
C)



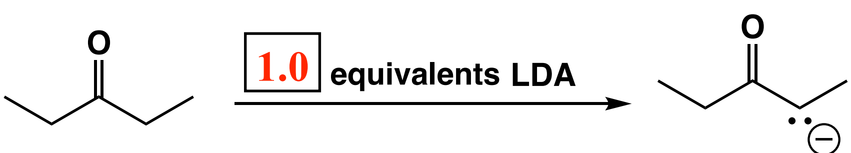
D)



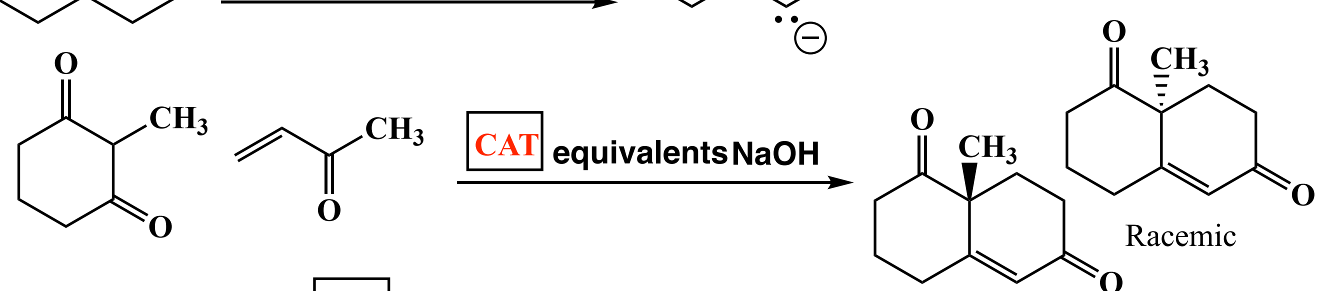
E)



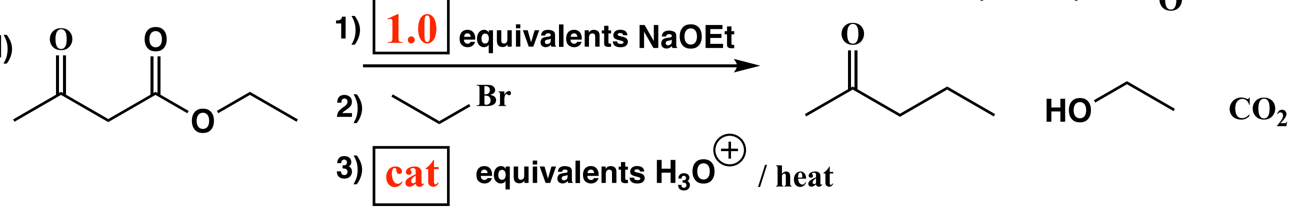
F)



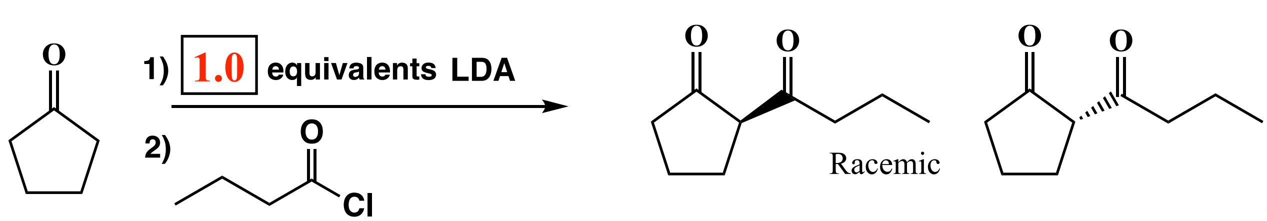
G)



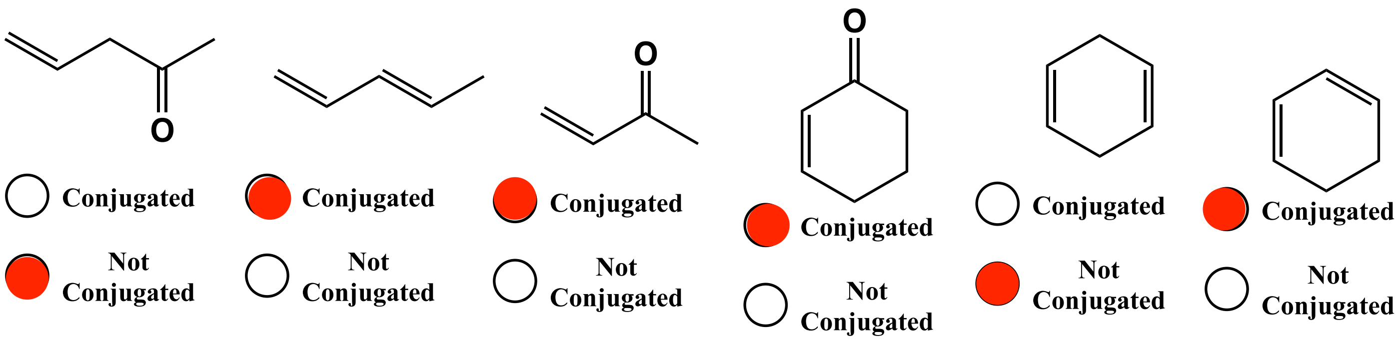
H)



I)

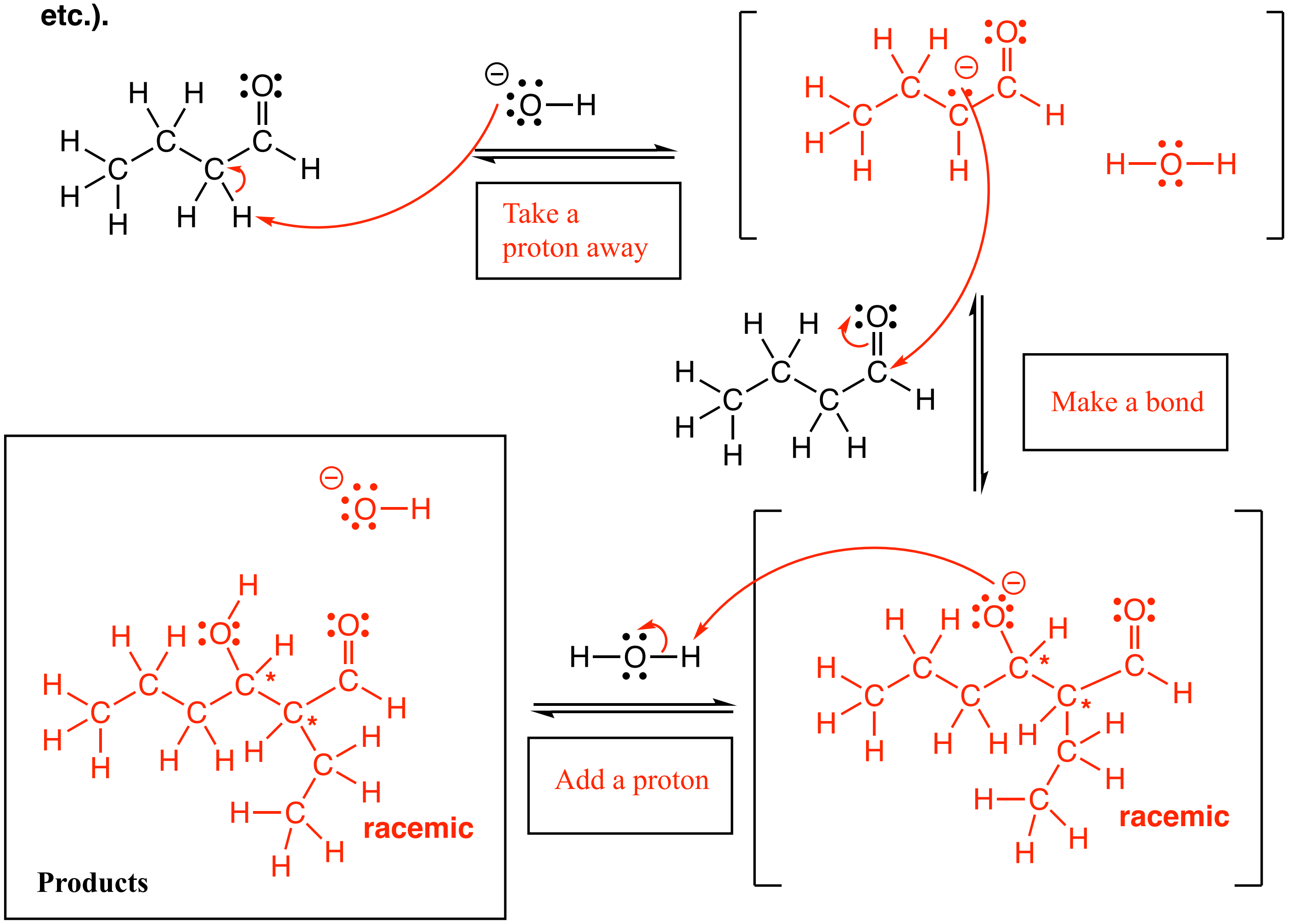


9. (12 pts) Indicate whether each of the following molecules is conjugated or not conjugated.

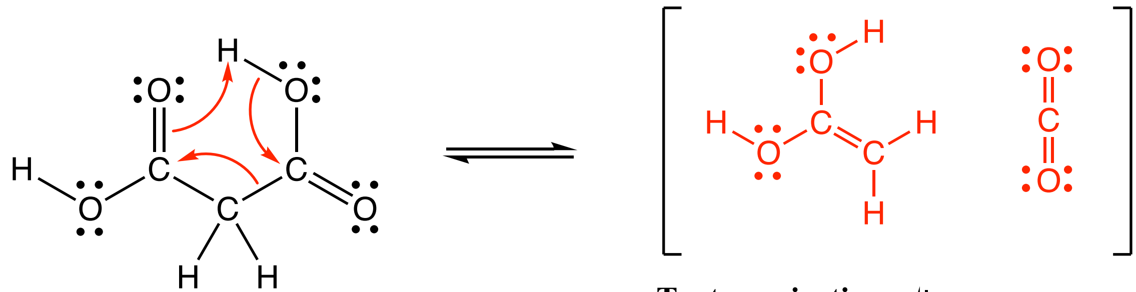


This would have been the nomenclature section. Because I am positive that more than half of you will participate in the 3.1 mile challenge, there is no nomenclature here!

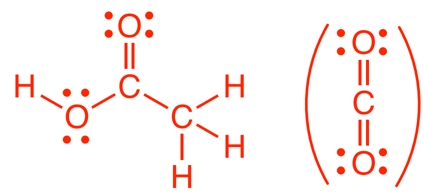
10. (22 pts) Complete the mechanism for the following aldol reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS RACEMIC IF APPROPRIATE. In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.).**



11. (16 pts) Complete the following two mechanisms. Be sure to show arrows to indicate movement of <u>all</u> electrons on both structures, 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.

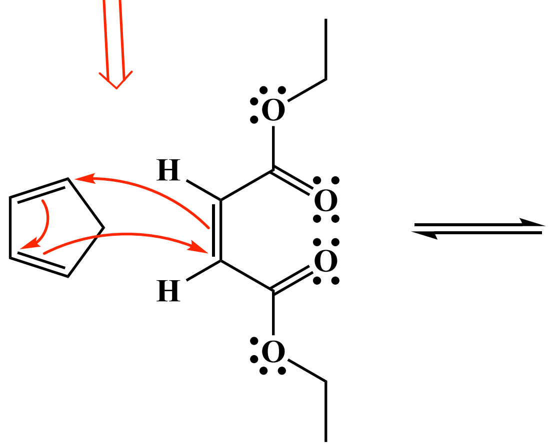


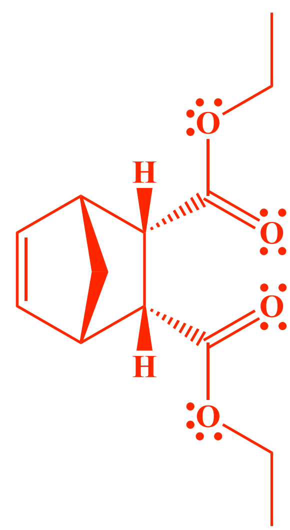
Tautomerization
(no need to draw arrows on the intermedidate structure above)



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.

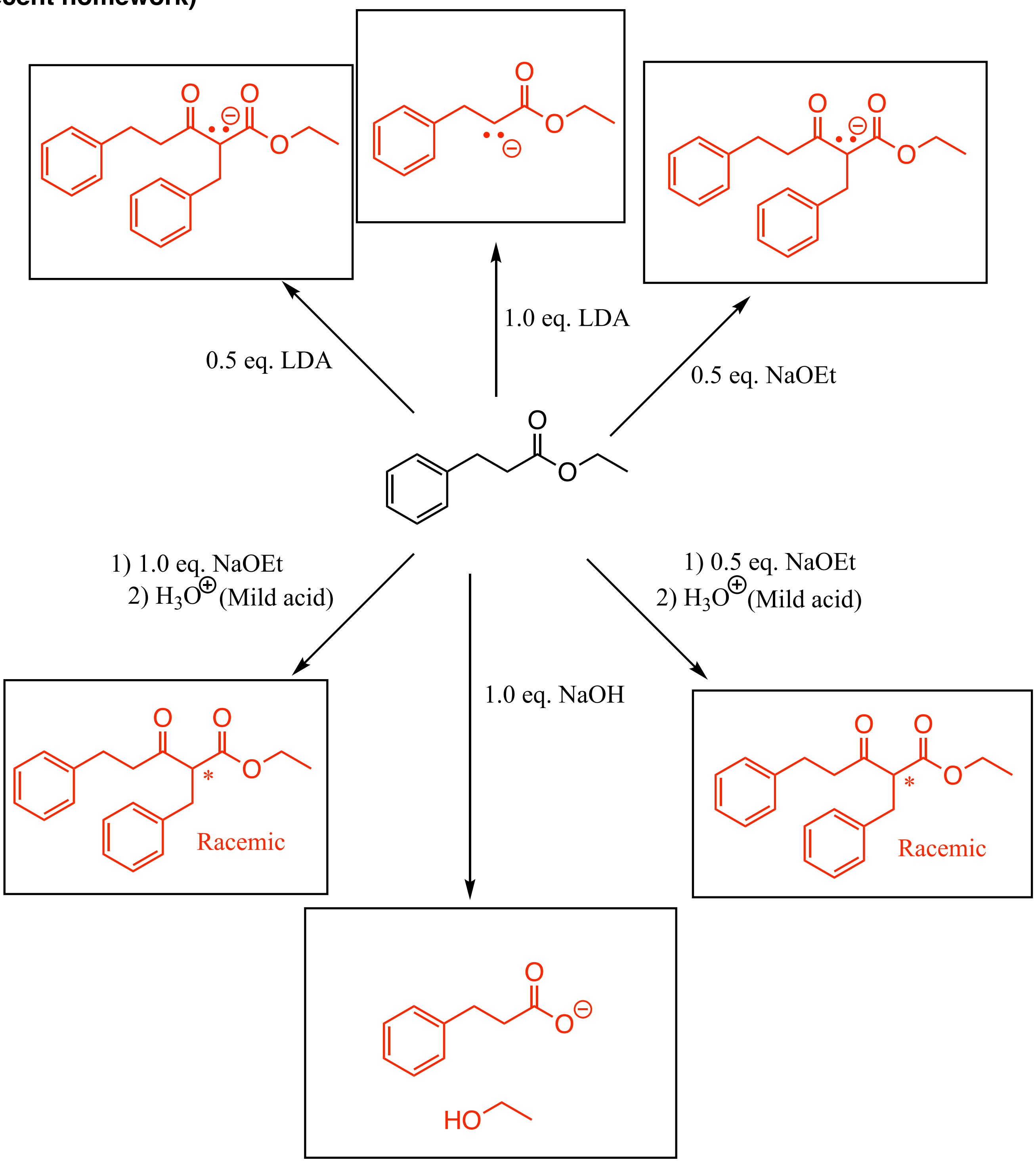




Product(s)

Signature____________________________ Pg 8 _____________(20)

12. (3, 4,5 or 7 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are multiple carbon containing products, WRITE ALL OF THEM. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and write racemic. If an E,Z mixture is created as the products, YOU NEED TO DRAW BOTH THE E AND Z PRODUCT. No need for wedges and dashes. Also, do not worry about balancing these equations, but you do need to show us ALL of the major carbon-containing products of these transformations. (You should recognize this page from a recent homework)**



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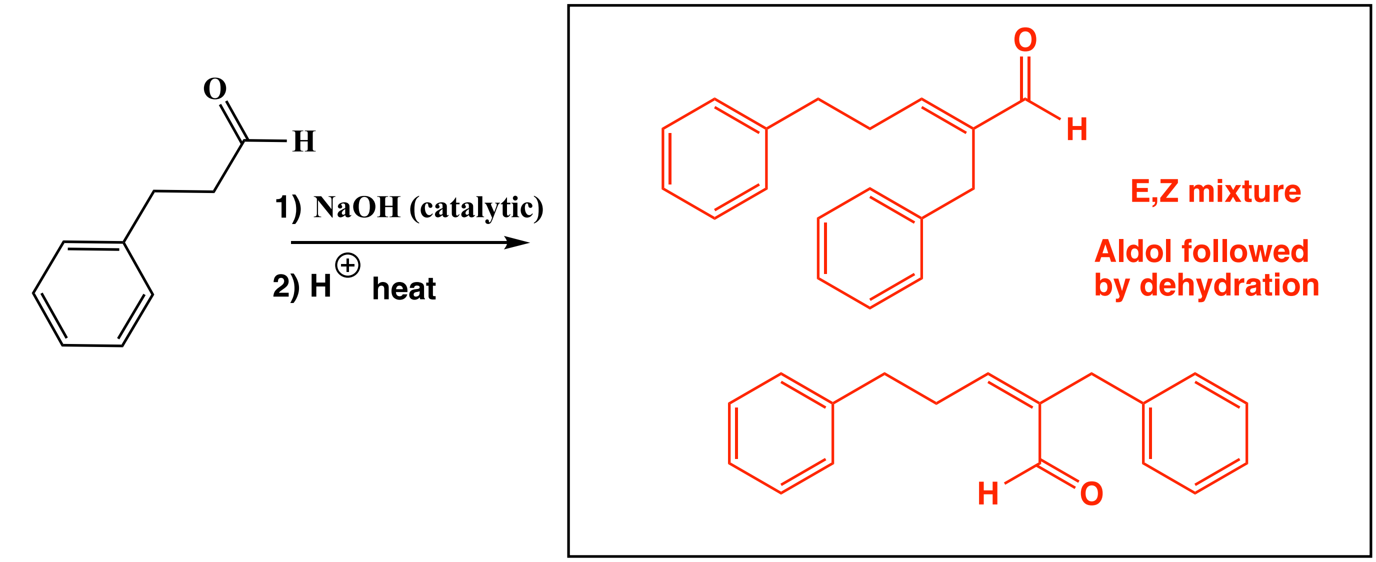
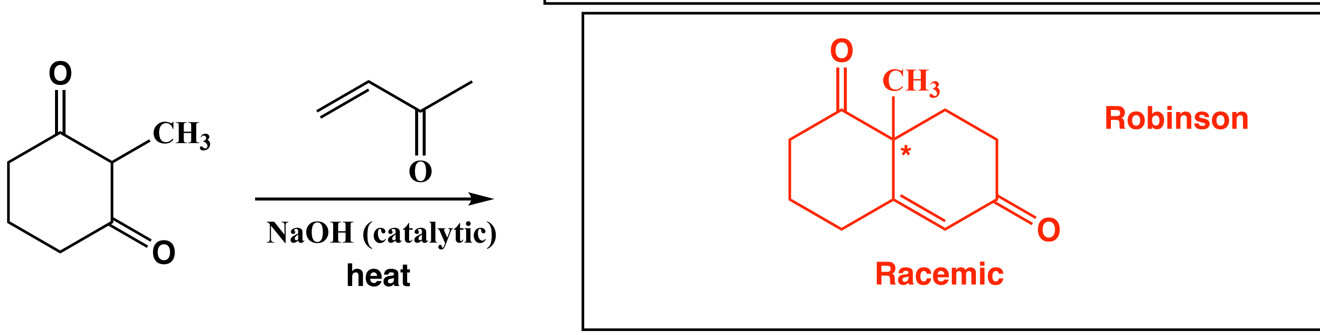
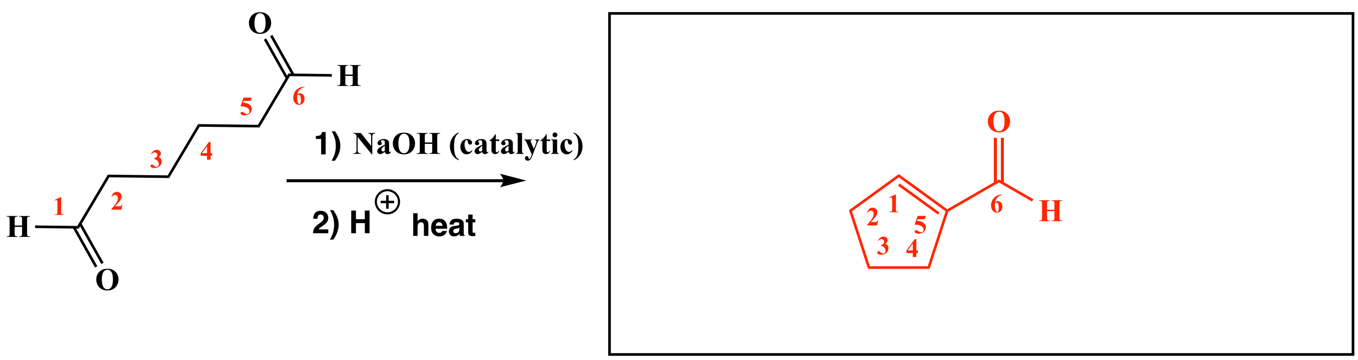
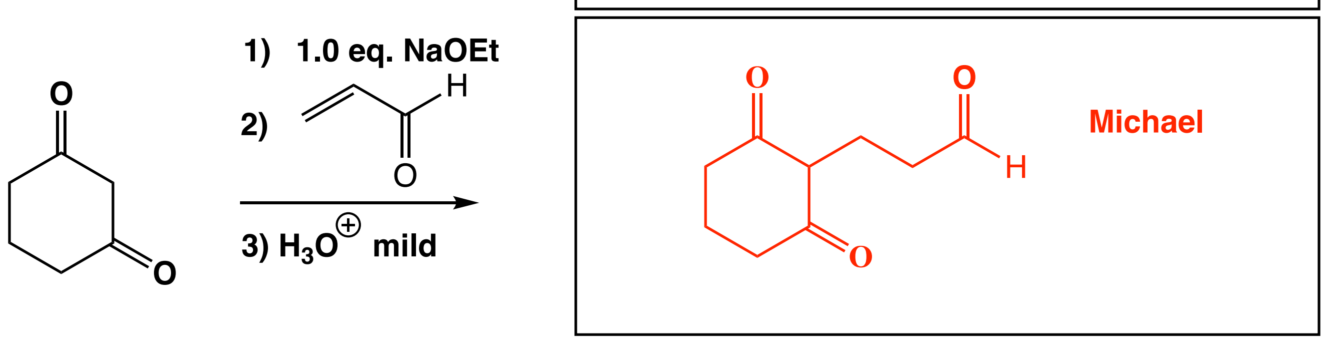
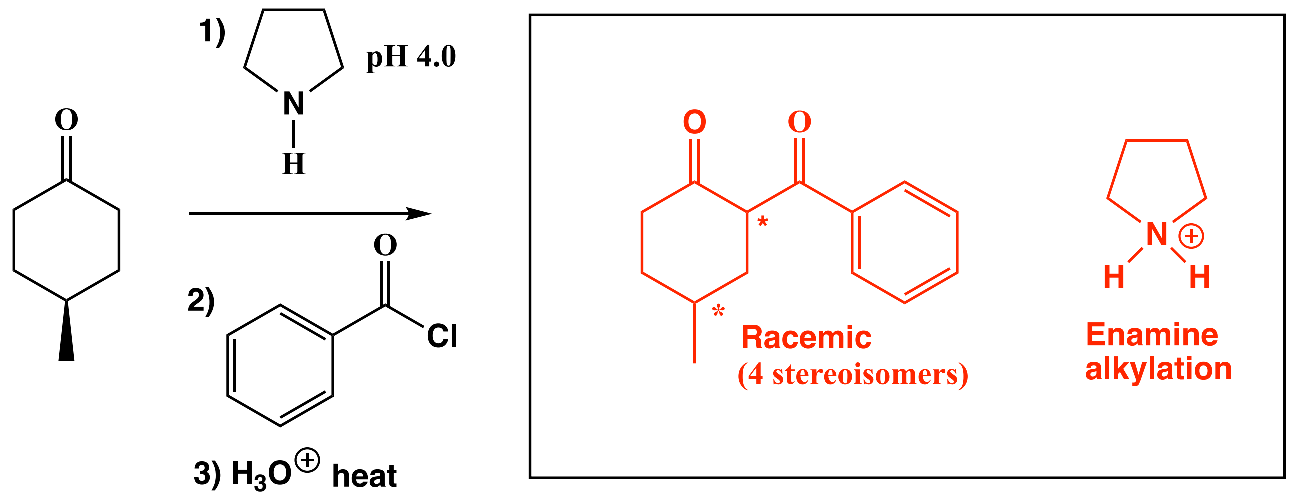




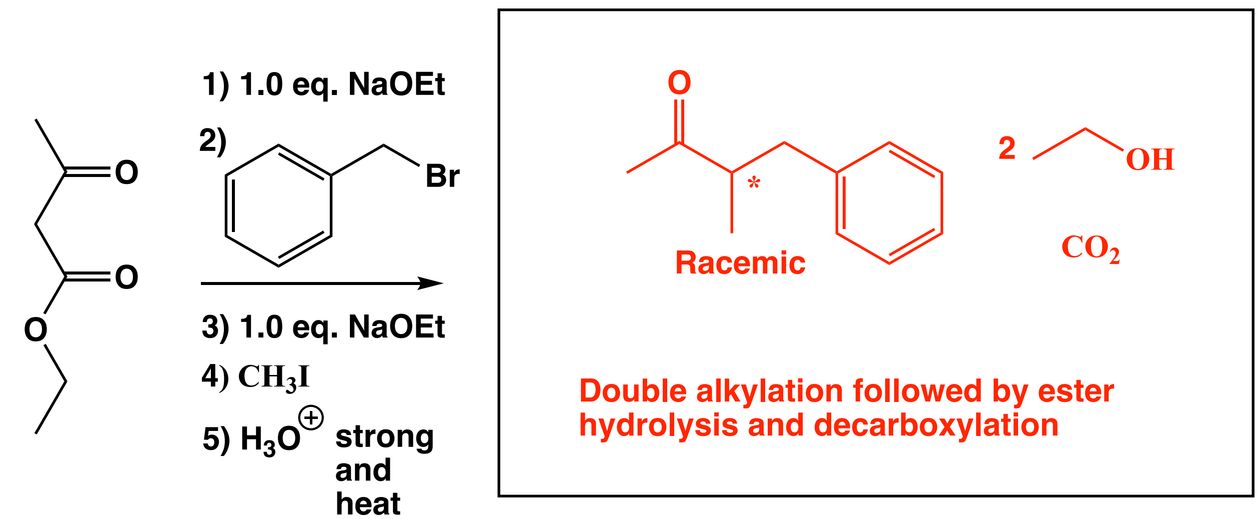


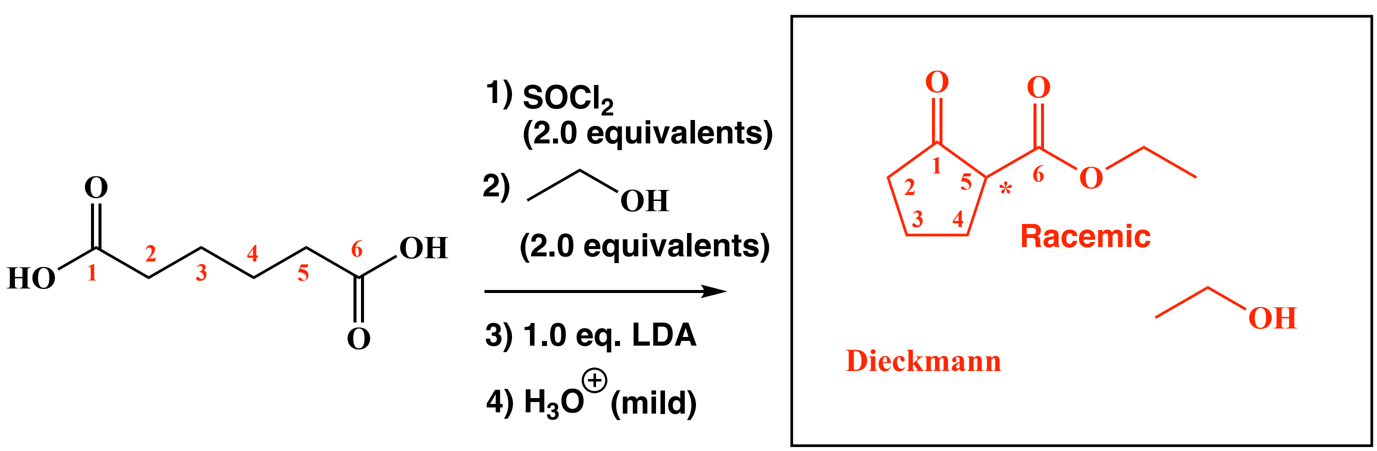


14. (3, 4,5 or 7 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are multiple carbon containing products, WRITE ALL OF THEM. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and write racemic. If an E,Z mixture is created as the products, YOU NEED TO DRAW BOTH THE E AND Z PRODUCT. No need for wedges and dashes. Also, do not worry about balancing these equations, but you do need to show us ALL of the major carbon-containing products of these transformations.**



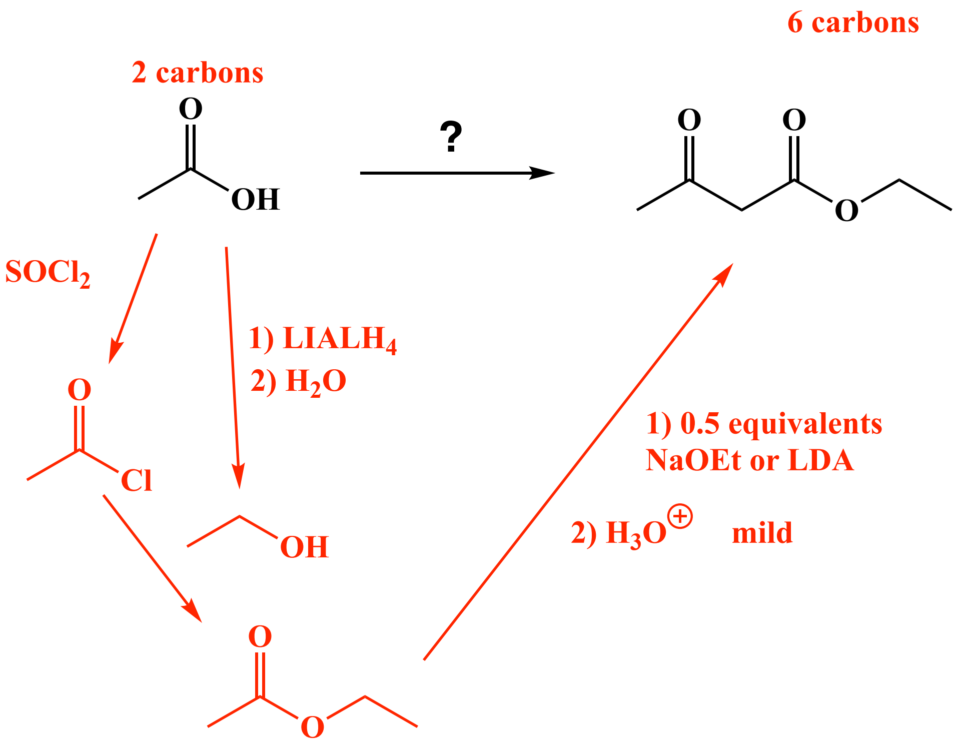
Be sure to write down all the carbon-containing products.





15. 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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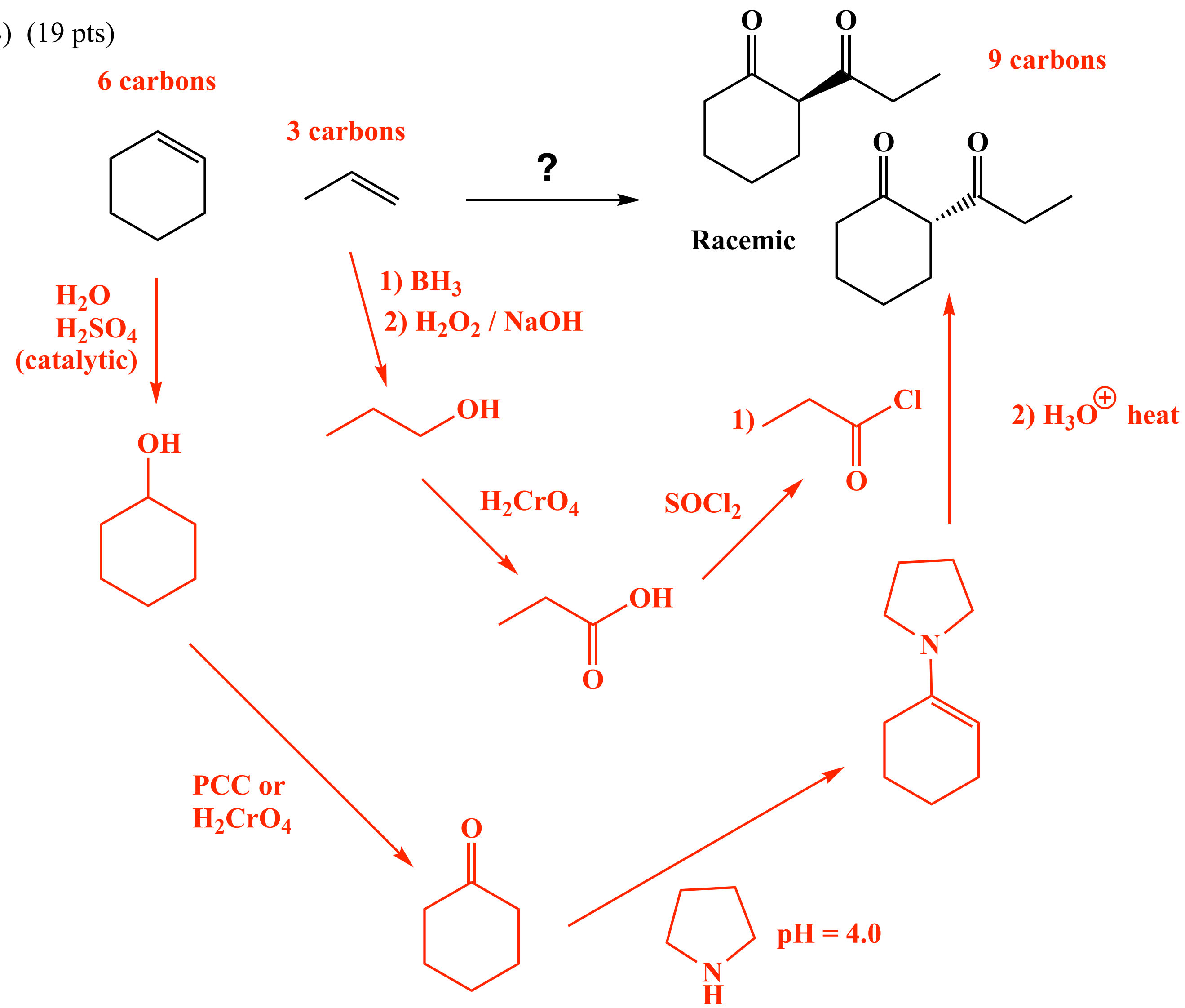
B) (19 pts)



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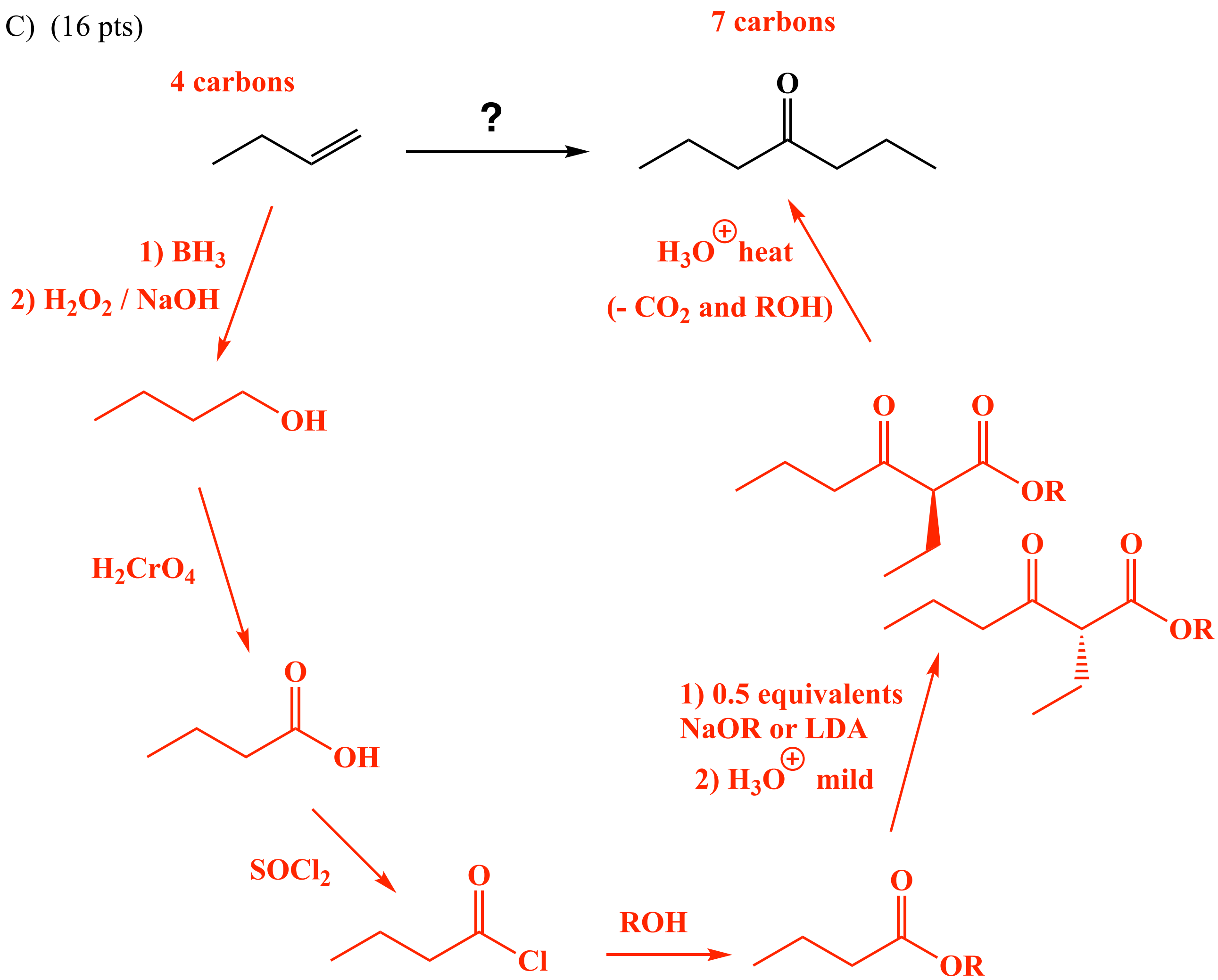
C) (16 pts)



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D) (22 pts)