

NAME (Print): _____

Chemistry 320N
3rd Midterm Exam
April 11, 2024

EID _____

SIGNATURE: _____

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

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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!!!

Compound		pK _a
Hydrochloric acid	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
Thiols	RCH_2SH	8-9
Ammonium ion	$\text{H}_4\text{N}^{\oplus}$	9.2
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	10
Primary ammonium	$\text{H}_3\text{N}^{\oplus}\text{CH}_2\text{CH}_3$	10.5
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	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

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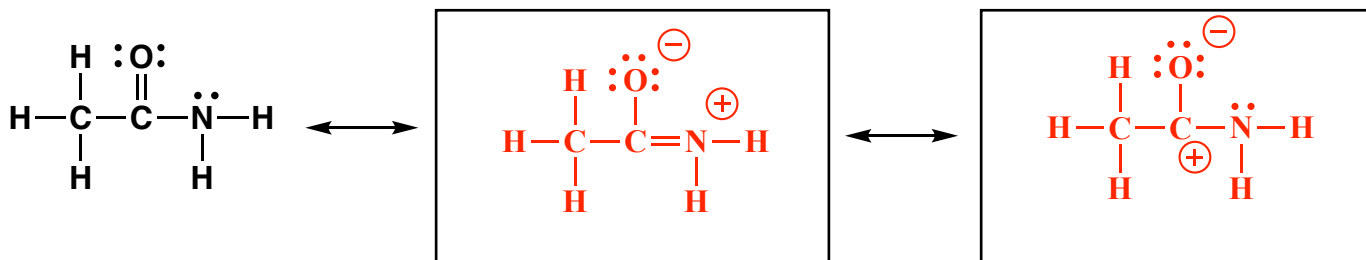
1. (5 pts) What is the most important question in organic chemistry?

Where are the electrons?

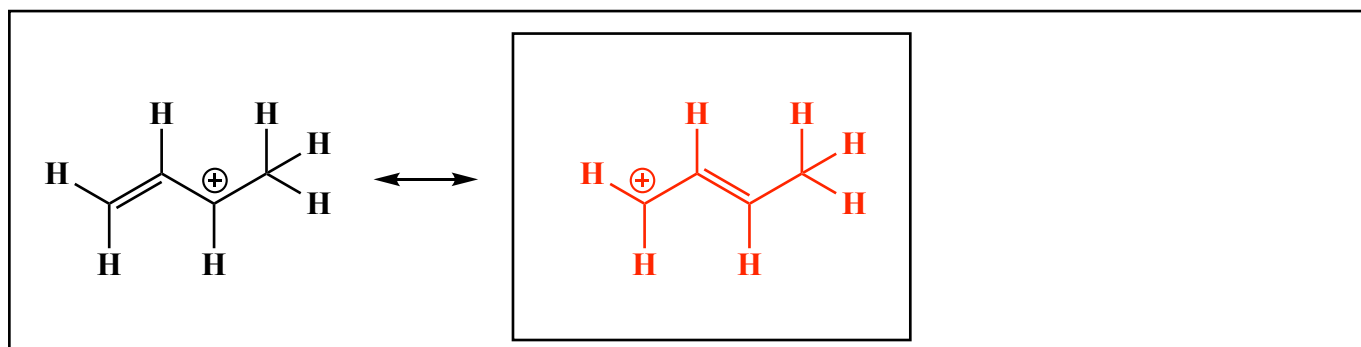
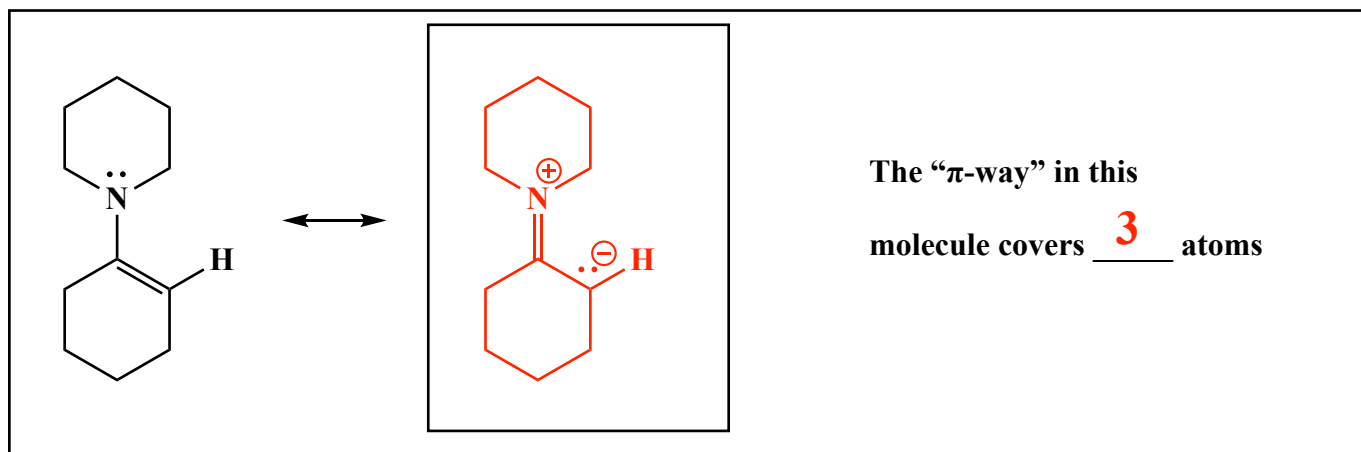
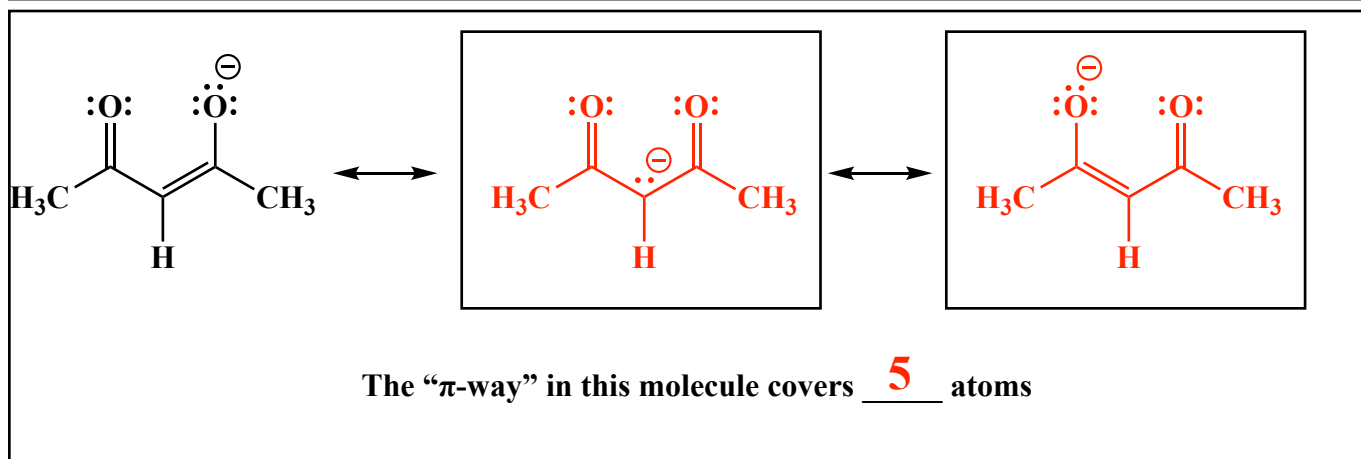
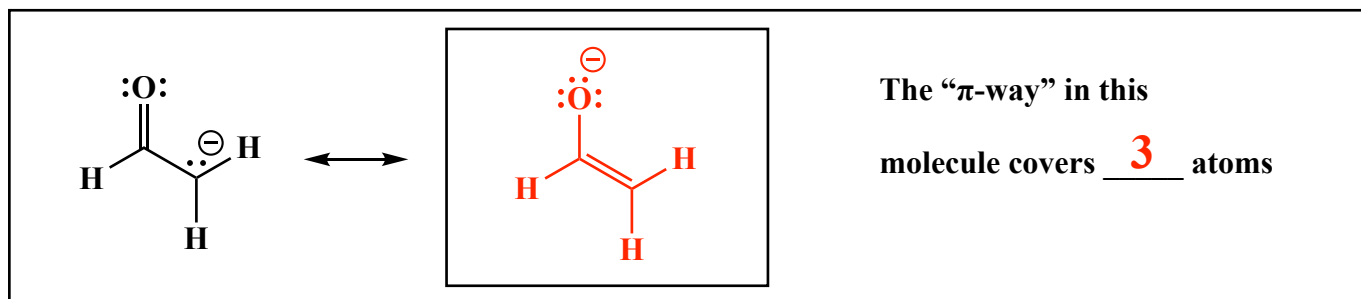
2. (1 pt each) Fill in each blank with the word that best completes the sentences. Yep, this is the MRI paragraph!

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**.

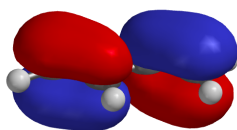
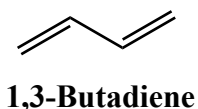
3. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided. (No need to draw any arrows for this.)



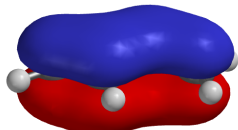
4. (23 pts) The following molecules are all ones we have seen in mechanisms recently. Please draw all of the important contributing structures. Include all formal charges and lone pairs. There is no need to draw arrows on any of these structures.



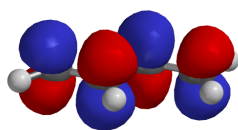
5. (16 pts) The following are the pi molecular orbitals for 1,3-butadiene. Under each one place a number corresponding to energy, with a "1" under the lowest energy (most stable) molecular orbital, a "4" under the highest energy (least stable) molecular orbital and a "2" and a "3" as appropriate.



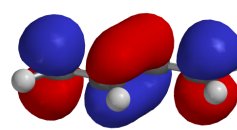
2



1



4



3

B) On the lines below, write "bonding" or "antibonding" 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: Aldol Reaction
 Michael Reaction
 Claisen Reaction
 Gilman Reaction
 Iverson Reaction
 Hydration
 Dehydration
 Dehalogenation


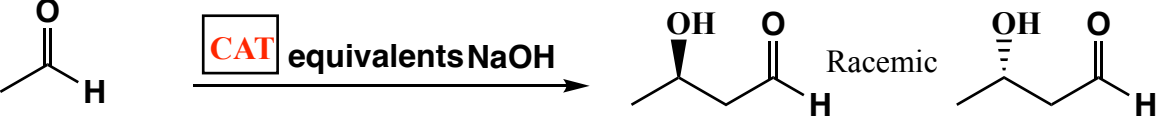

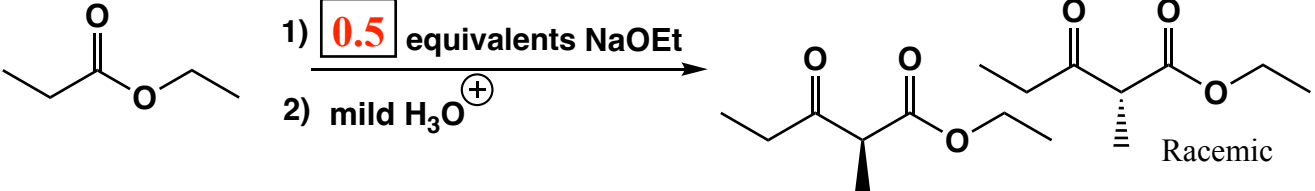
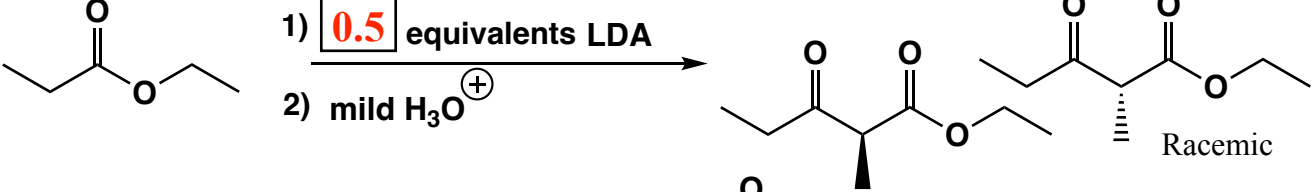
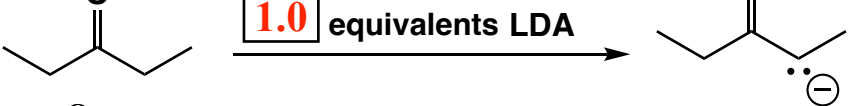
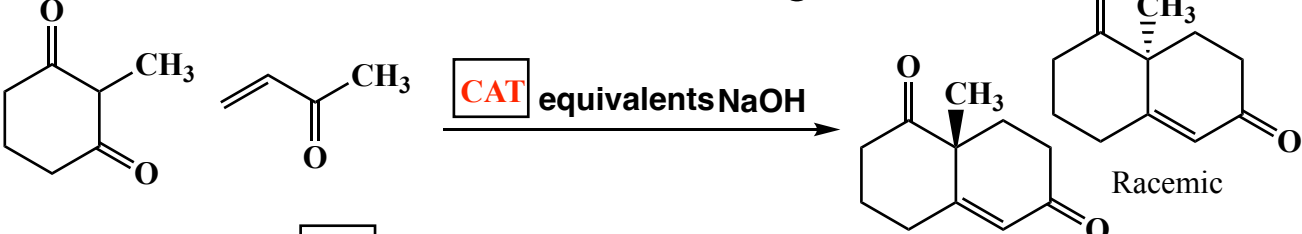
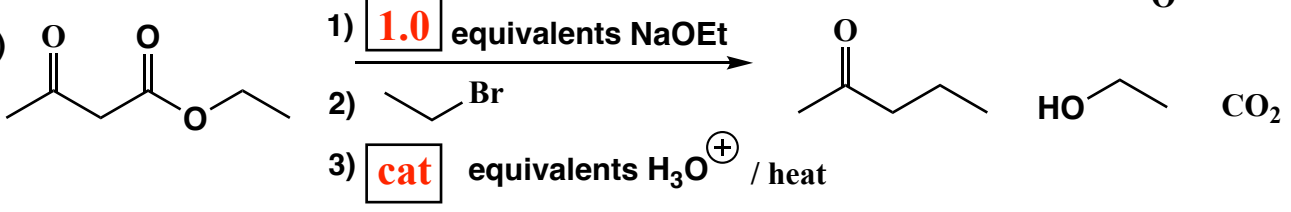
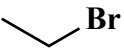
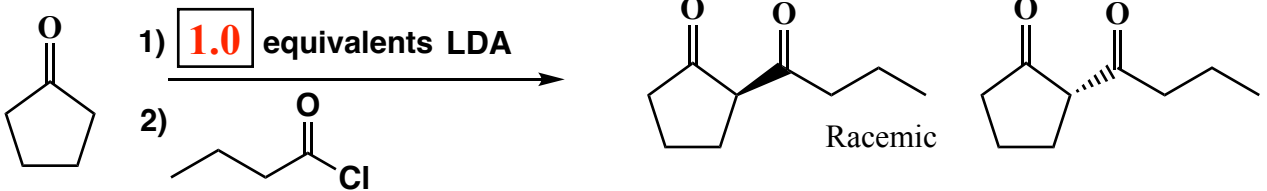
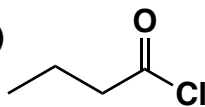
- Part 2: Aldol Reaction
 Michael Reaction
 Claisen Reaction
 Gilman Reaction
 Iverson Reaction
 Hydration
 Dehydration
 Dehalogenation

- Part 3: Aldol Reaction
 Michael Reaction
 Claisen Reaction
 Gilman Reaction
 Iverson Reaction
 Hydration
 Dehydration
 Dehalogenation

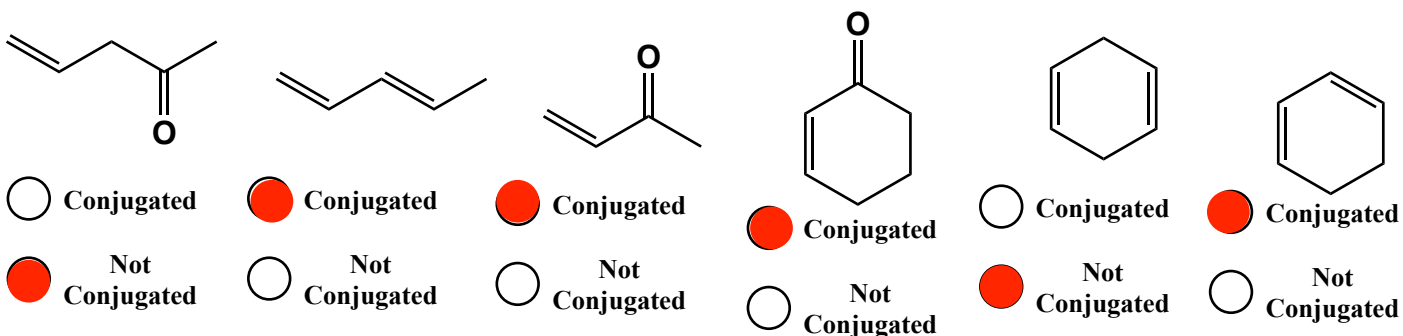
7. (2 pts each) Indicate whether each statement is true or false by filling in the appropriate circle.

- True A. When considering orbitals and bonding in chemistry, it is best to think of
 False electrons as particles.
- True B. When considering orbitals and bonding in chemistry, it is best to think of electrons
 False as waves.
- True C. When the energy of a photon is absorbed by a molecule, an electron in a filled
 False molecular orbital is transferred to a higher energy unfilled orbital.
- True D. The more pi bonds in conjugation, the smaller the energy difference between
 False filled and unfilled orbitals, so the longer the wavelength of light that is absorbed.
- True E. Fluorescence occurs when an electron flips its spin as a photon is absorbed, so it
 False must flip back before emitting a photon as it goes back to the ground state.
- True F. Phosphorescence (“glow in the dark”) occurs when an electron flips its spin as a
 False photon is absorbed, so it must flip back before emitting a photon as it goes back to
the ground state.
- True G. Chemiluminescence (firefly light, "light sticks") happens when a chemical
 False reaction produces an excited electron in a rigid molecule
- True H. An object sitting in sunshine that appears red to our eyes absorbs light in the red
 False region of the visible light spectrum.
- True I. A pericyclic reaction such as the Diels-Alder reaction produces an aromatic
 False product, so that is why the reaction has a relatively low energy barrier.
- True J. A pericyclic reaction such as the Diels-Alder reaction has a transition state that has
 False aromatic character, so that is why the reaction has a relatively low energy barrier.
- True K. In the Michael reaction, the first intermediate is an enolate.
 False
- True L. In a Michael reaction, the thermodynamic reason that conjugate addition of a
 False 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.

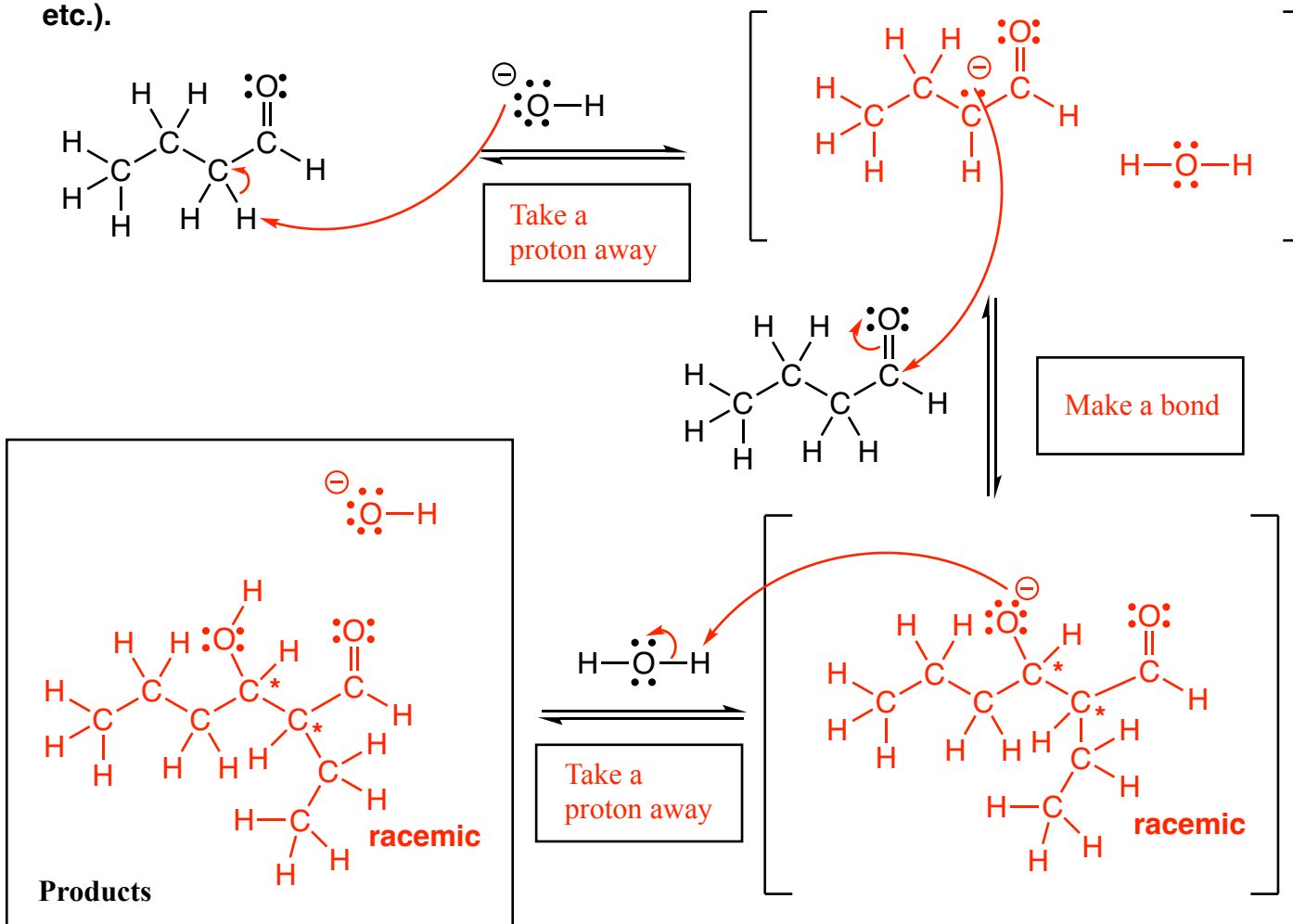
- A)  **CAT** equivalents H_2SO_4
- B)  **CAT** equivalents NaOH Racemic
- C)  1) **CAT** equivalents NaOH
2) H^+ and heat
- D)  1) **0.5** equivalents NaOEt
2) mild H_3O^+ Racemic
- E)  1) **0.5** equivalents LDA
2) mild H_3O^+ Racemic
- F)  **1.0** equivalents LDA
- G)  **CAT** equivalents NaOH Racemic
- H)  1) **1.0** equivalents NaOEt
2)  Br
3) **cat** equivalents H_3O^+ / heat
- I)  1) **1.0** equivalents LDA
2)  Cl Racemic

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

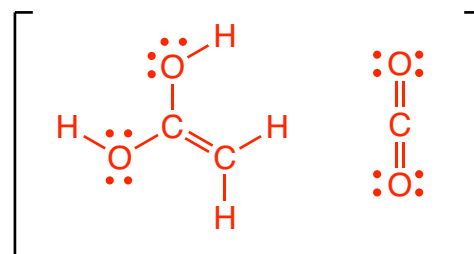
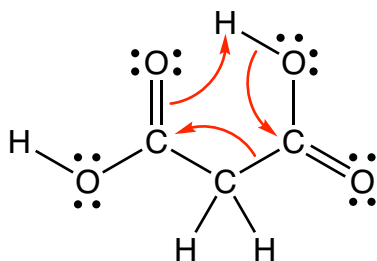


This would have been the nomenclature section. Because I am positive that more than half of you will participate in the 3.1 mile challenge, there is no nomenclature here!

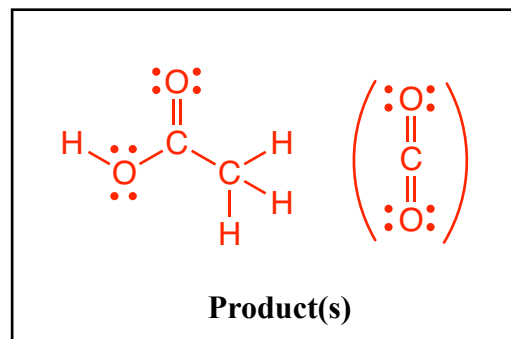
10. (22 pts) Complete the mechanism for the following aldol reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN 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.).



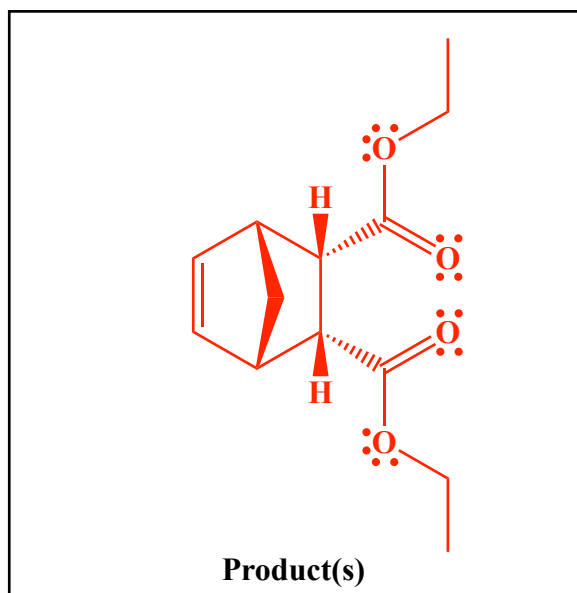
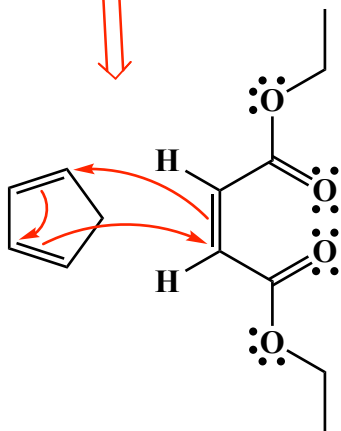
11. (16 pts) Complete the following two mechanisms. Be sure to show arrows to indicate movement of all electrons on both structures, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS RACEMIC IF APPROPRIATE.



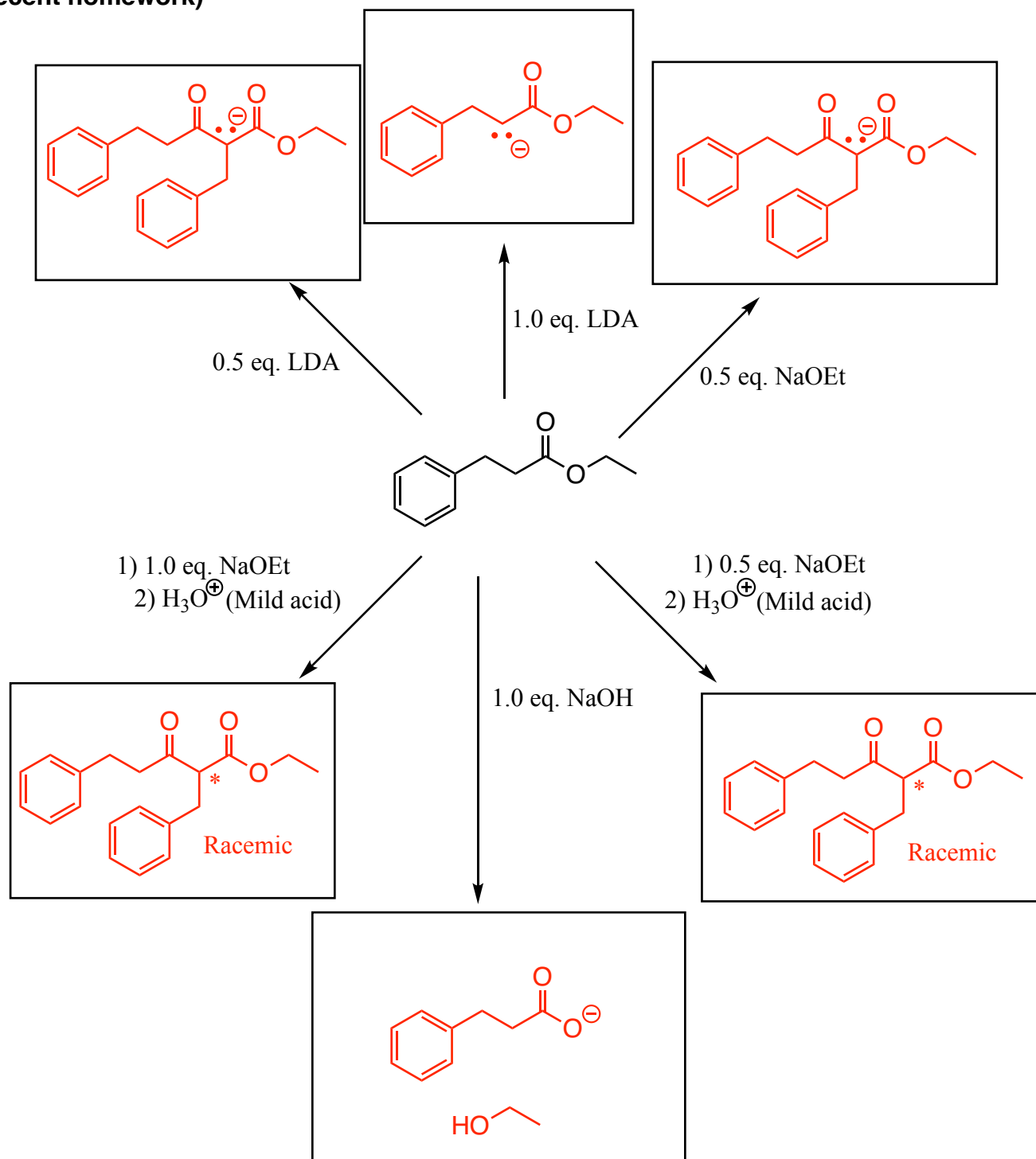
Tautomerization
(no need to draw arrows on the intermediate structure above)



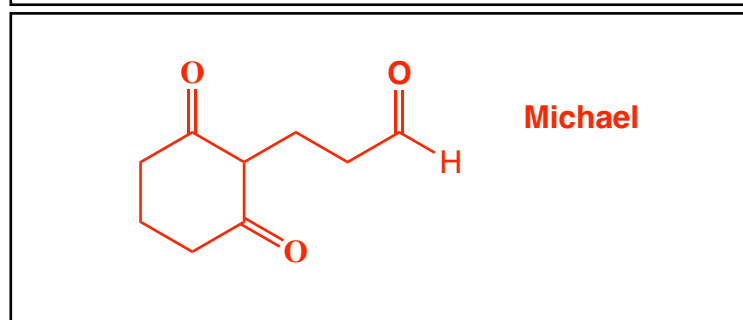
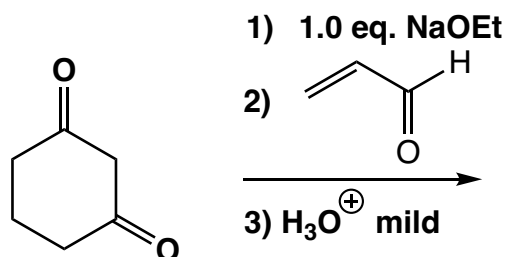
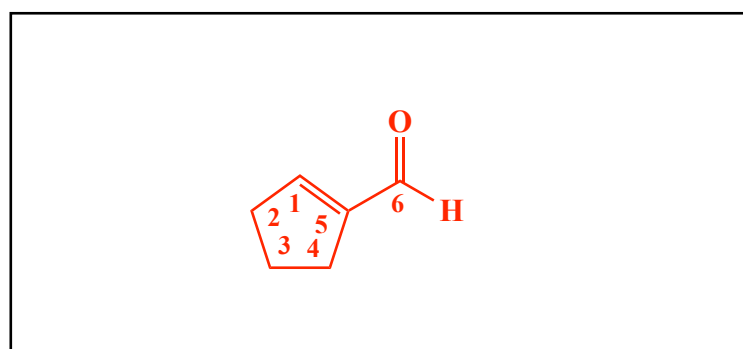
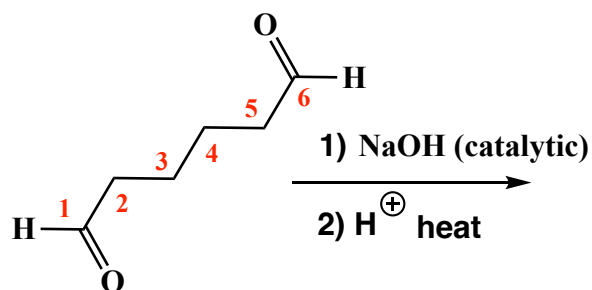
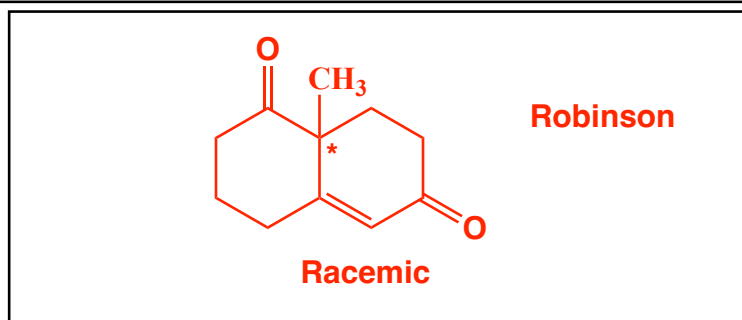
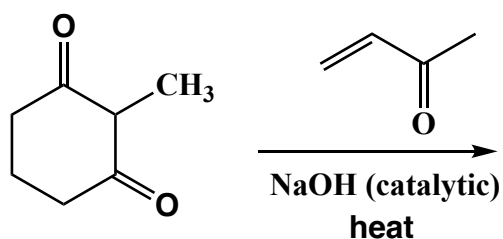
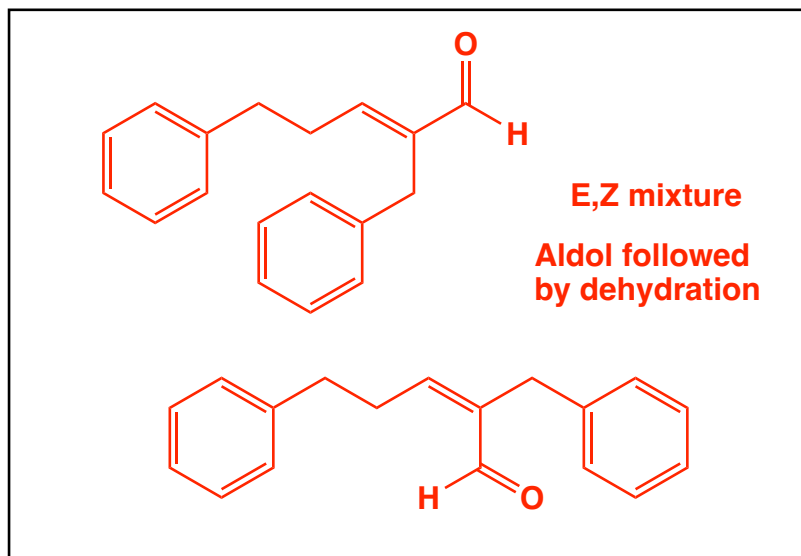
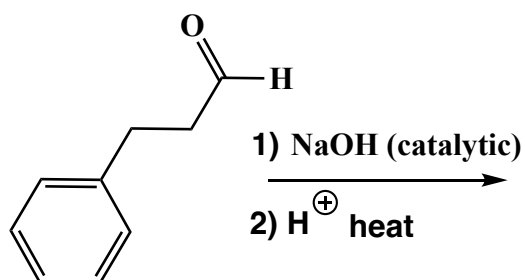
3 pi bonds (involving 6 pi electrons) are being made or broken in the transition state here. In other words, the transition state has aromatic character, explaining why this process has a reasonably small energy barrier and occurs with simple heating.



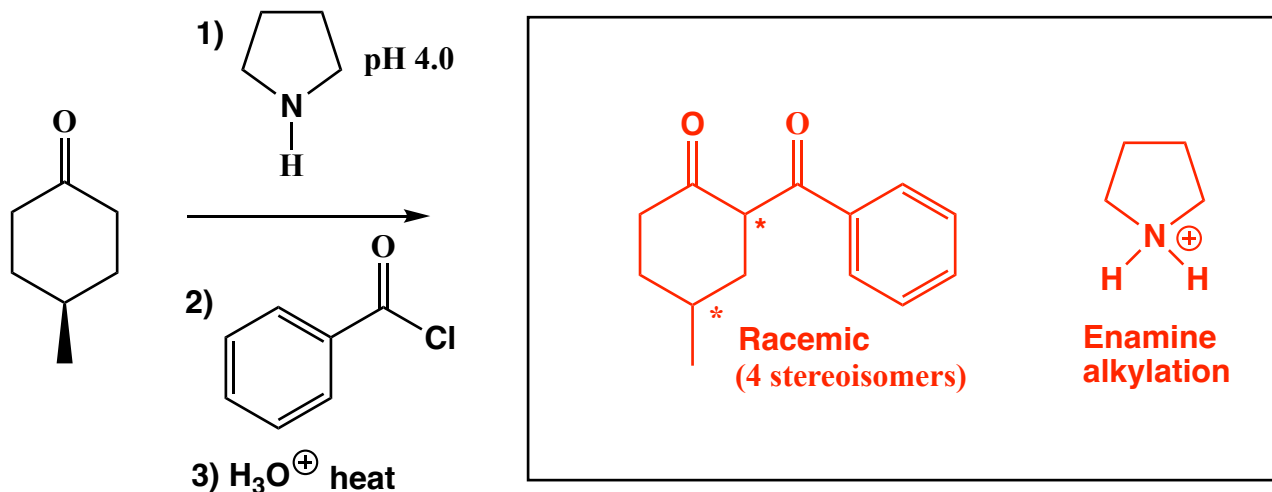
12. (3, 4,5 or 7 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are multiple carbon containing products, WRITE ALL OF THEM. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) 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)**



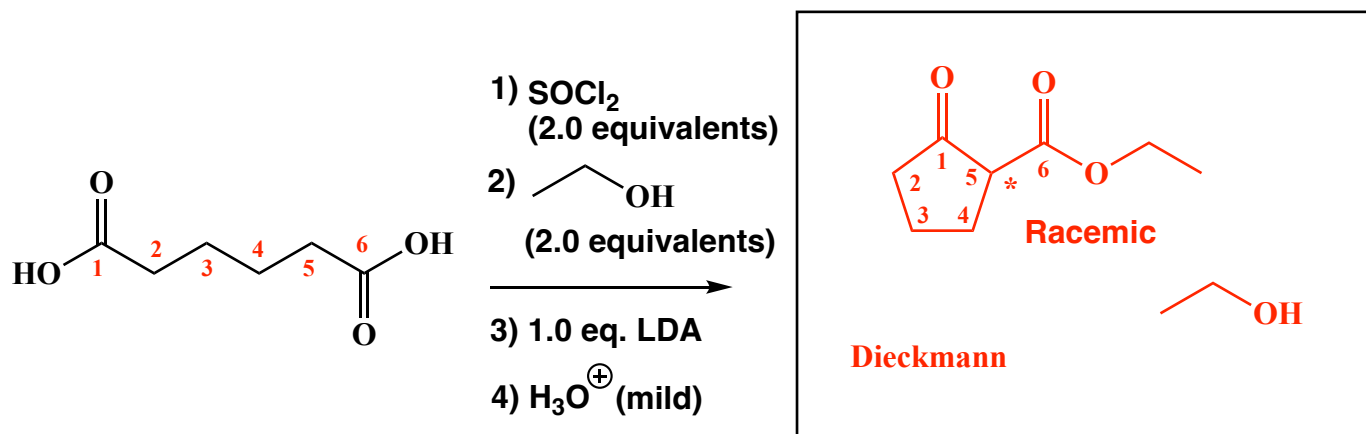
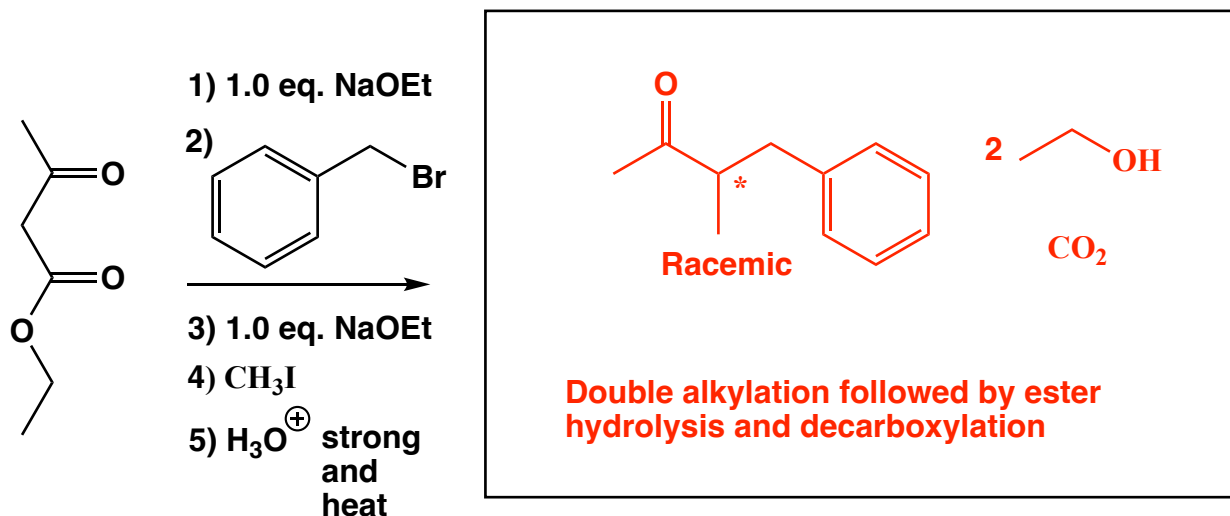
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14. (3, 4,5 or 7 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are multiple carbon containing products, WRITE ALL OF THEM.** If a new chiral center is created and a racemic 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.



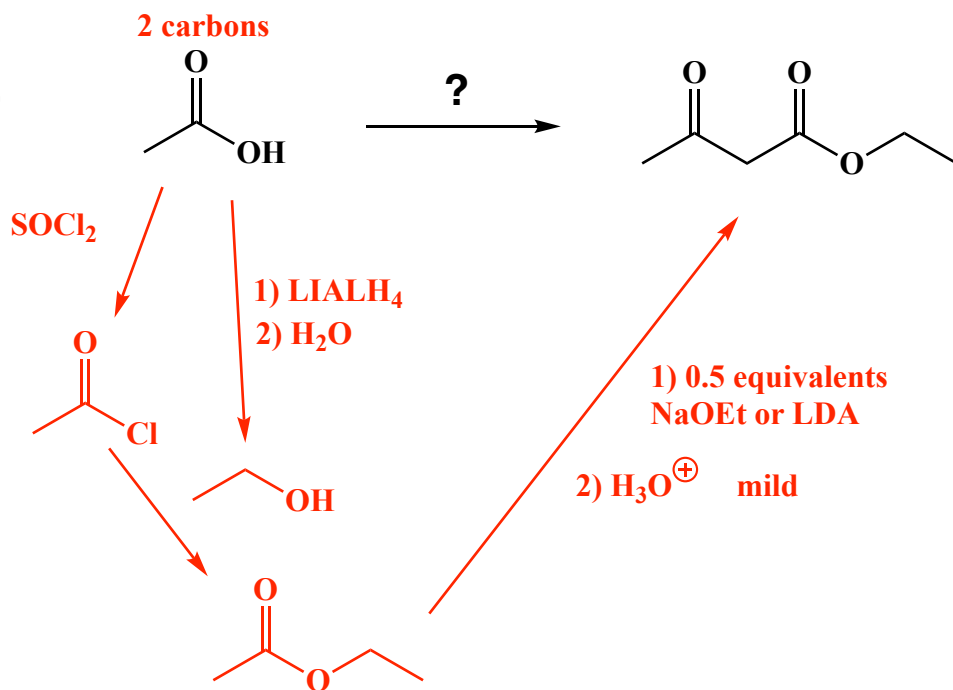
Be sure to write down all the carbon-containing products.



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.**

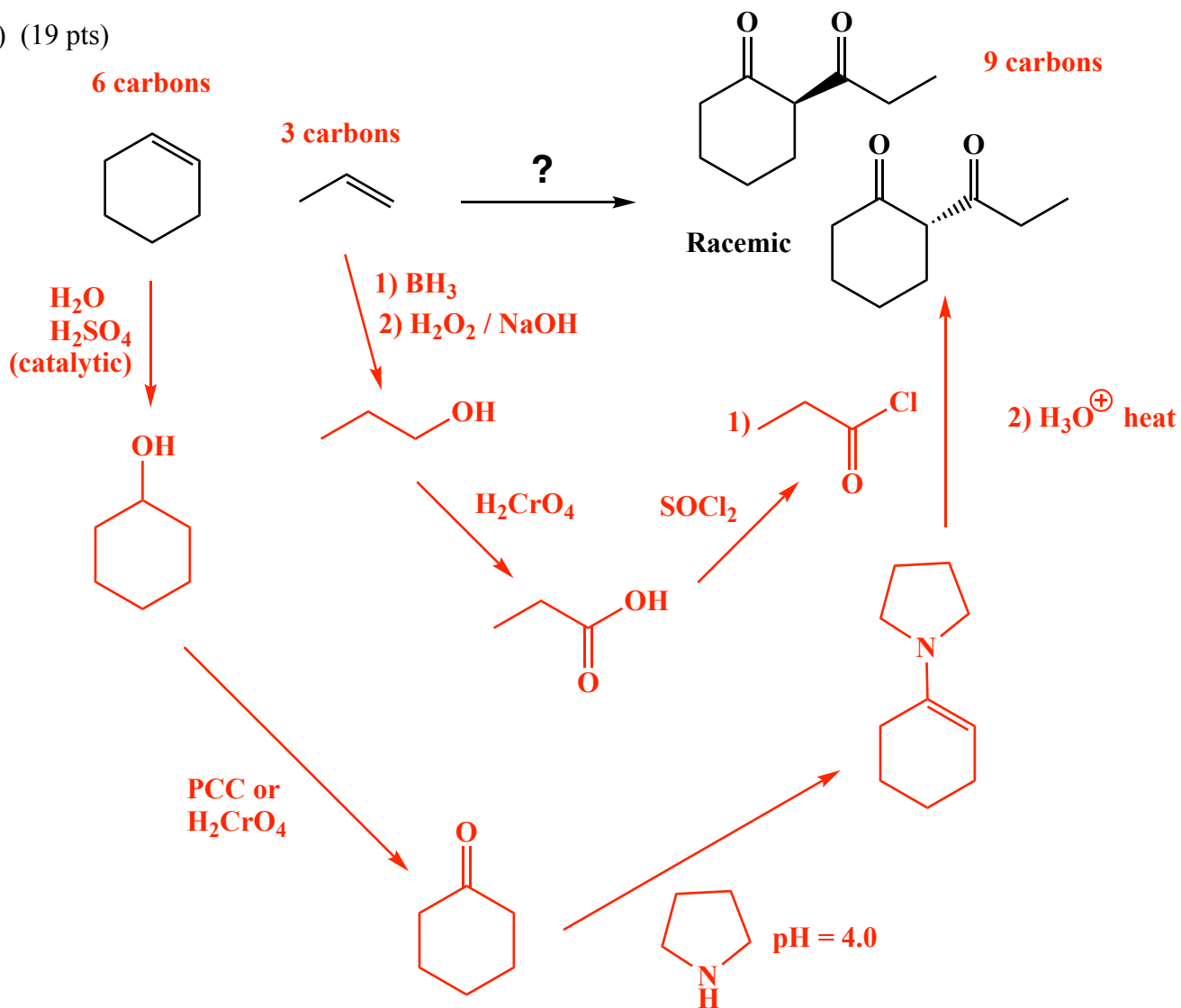
6 carbons

A) (10 pts)



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.**

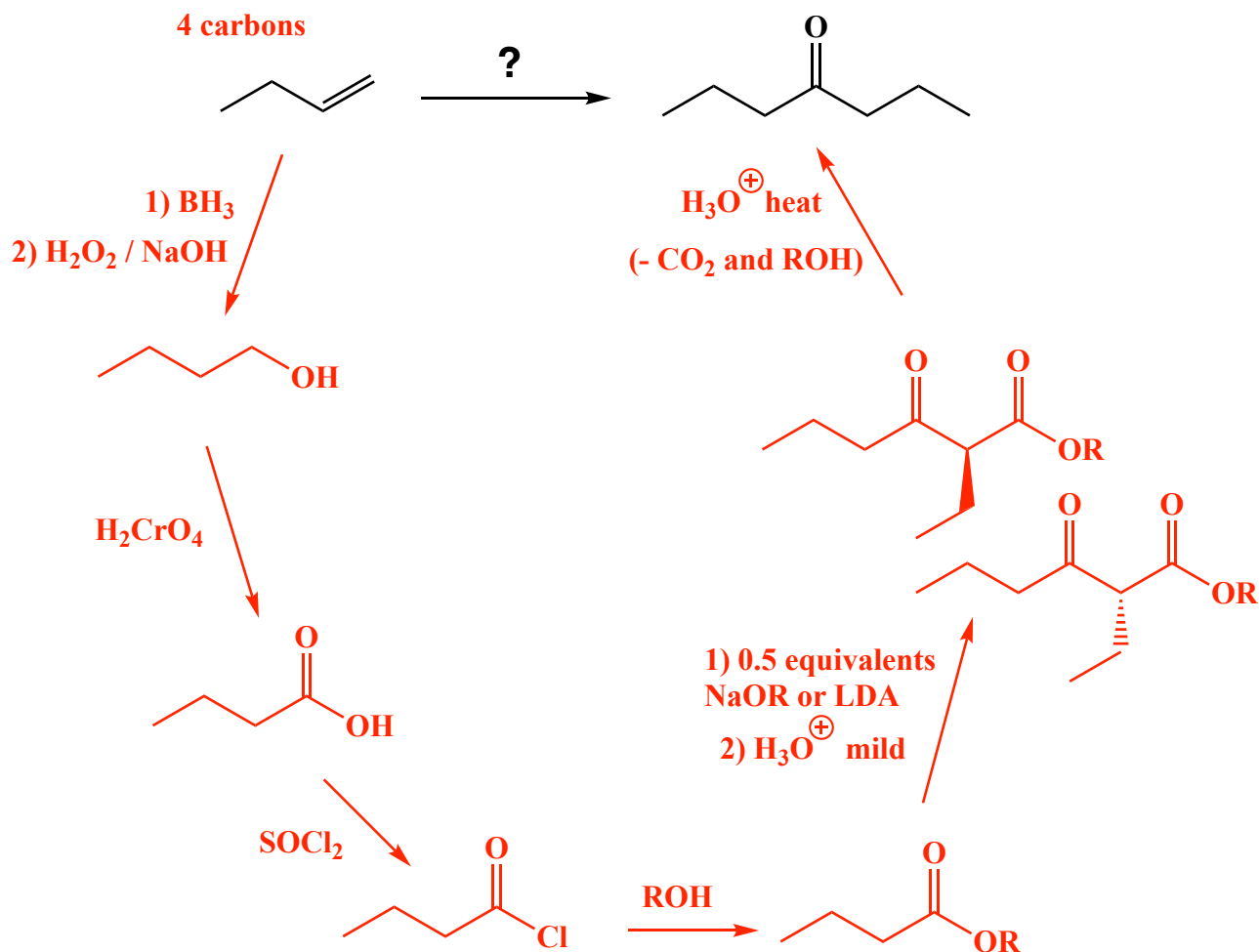
B) (19 pts)



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.**

C) (16 pts)

7 carbons



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.**

D) (22 pts)

