

NAME (Print): _____

Chemistry 320N
Dr. Brent Iverson
3rd Midterm
April 20, 2017

SIGNATURE: _____

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

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Please Note: This test may be a bit long, but there is a reason. I would like to give you a lot of little questions, so you can find ones you can answer and show me what you know, rather than just a few questions that may be testing the one thing you forgot. **I recommend you look the exam over and answer the questions you are sure of first**, then go back and try to figure out the rest. Also make sure to **look at the point totals** on the questions as a guide to help budget your time.

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	(49)
5	(24)
6	(20)
7	(23)
8	(26)
9	(18)
10	(25)
11	(19)
12	(14)
13	(10)
14	(19)
15	(19)
16	(16)
17	(19)
Total	(301)

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	$\text{H}-\text{Cl}$	-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	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CR}'$	10
Primary ammonium	$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_3$	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	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	16
Aldehydes	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	18-20
Ketones	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CR}'$	18-20
Esters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\text{H}$	25
LDA	$\text{H}-\text{N}(\text{i}-\text{C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{H}$	44
Alkanes	$\text{CH}_3\text{CH}_2-\text{H}$	51

DO NOT TEAR OUT THIS PAGE!!

We are trying something new to improve grading accuracy. You must write the answers for the questions on the next three pages on this single sheet.

Question 1, page 2 (13 pts) True false questions.
As appropriate, circle True or False in each space corresponding to the statements on page 2.

- | | | | |
|-----------|-------|-----------|-------|
| 1.1 True | False | 1.2 True | False |
| 1.3 True | False | 1.4 True | False |
| 1.5 True | False | 1.6 True | False |
| 1.7 True | False | 1.8 True | False |
| 1.9 True | False | 1.10 True | False |
| 1.11 True | False | 1.12 True | False |
| 1.13 True | False | | |

Question 2, page 3 (16 pts) Write the word that best completes the sentences.

- 2.1 _____
- 2.2 _____
- 2.3 _____
- 2.4 _____
- 2.5 _____
- 2.6 _____
- 2.7 _____
- 2.8 _____
- 2.9 _____
- 2.10 _____
- 2.11 _____
- 2.12 _____
- 2.13 _____
- 2.14 _____
- 2.15 _____
- 2.16 _____

Question 3, page 3 (8 pts) For each molecule, write "Conjugated" or "Not Conjugated"

- | | |
|-----------|-----------|
| 3.1 _____ | 3.2 _____ |
| 3.3 _____ | 3.4 _____ |
| 3.5 _____ | 3.6 _____ |
| 3.7 _____ | 3.8 _____ |

Question 4, page 4 (4 pts) Rank by relative acidity with a 1 under the most acidic and a 4 under the least acidic.

- | | | | |
|-----------|-----------|-----------|-----------|
| 4.1 _____ | 4.2 _____ | 4.3 _____ | 4.4 _____ |
|-----------|-----------|-----------|-----------|

Question 5, page 4 (4 pts) Rank by relative acidity with a 1 under the most acidic and a 4 under the least acidic.

- | | | | |
|-----------|-----------|-----------|-----------|
| 5.1 _____ | 5.2 _____ | 5.3 _____ | 5.4 _____ |
|-----------|-----------|-----------|-----------|

Question 6, page 4 (4 pts) Write the correct statement. Wait, I will give you these four points!

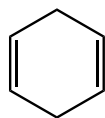
d. all of the above (of course)

Write your answers to these questions on the answer sheet on page 1

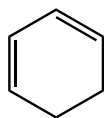
1. (13 pts). On page 1, circle True or False to indicate whether each of the following statements is true or false.
 - 1.1 “Kinetic control” in a chemical reaction refers to situations at low temperature in which the predominant product is the one that forms the fastest.
 - 1.2 “Kinetic control” in a chemical reaction refers to situations at low temperature in which the predominant product is the one that is more stable (lower in energy).
 - 1.3 “Thermodynamic control” in a chemical reaction refers to situations at low temperature in which the predominant product is the one that is more stable (lower in energy).
 - 1.4 “Thermodynamic control” in a chemical reaction refers to situations at high temperature in which the predominant product is the one that is more stable (lower in energy).
 - 1.5 “Thermodynamic control” in a chemical reaction refers to situations at high temperature in which the predominant product is the one that forms the fastest.
 - 1.6 In the first step of a Claisen condensation with ethyl acetate using NaOEt as the base, equilibrium favors formation of the enolate.
 - 1.7 In the first step of a Claisen condensation with ethyl acetate using LDA as the base, equilibrium favors the starting ethyl acetate.
 - 1.8 In the first step of a Claisen condensation with ethyl acetate using LDA as the base, equilibrium favors the enolate.
 - 1.9 According to molecular orbital theory, you generate as many new molecular orbitals as atomic orbitals used to create them.
 - 1.10 Conjugation refers to the situation in which 2p orbitals on more than two adjacent atoms in the same molecule overlap, allowing the pi electron density to delocalize into all the adjacent 2p orbitals to provide for extra stability.
 - 1.11 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 (wavelength is inversely proportional to energy of light).
 - 1.12 The greater the number of pi bonds in conjugation, the larger the energy difference between filled and unfilled orbitals, so the shorter the wavelength of light that is absorbed (wavelength is inversely proportional to energy of light).
 - 1.13 H-X adds to conjugated dienes to give both 1,2 and 1,4 addition products, via a resonance stabilized allylic cation intermediate.

Write your answers to these questions on the answer sheet on page 1

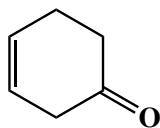
2. (16 pts). On page 1, fill in each blank with the **one word** that best completes the following sentences.
- A. In a _____ (2.1) condensation reaction, two esters react to create a β -ketoester product.
 - B. In the _____ (2.2) reaction, two aldehyde molecules react to create initially a β -_____ (2.3) aldehyde product, that can dehydrate in the presence of acid and heating to give a conjugated α,β -unsaturated _____ (2.4).
 - C. In one example of the _____ (2.5) reaction, a _____ (2.6) such as an enolate or enamine reacts with an electrophile such as an α,β -unsaturated ketone to give a new carbon-carbon bond at the _____ (2.7) carbon atom of the ketone.
 - D. The Robinson annulation reaction involves a _____ (2.8) reaction followed by an _____ (2.9) reaction then dehydration to make a six-membered ring.
 - E. _____ (2.10) occurs when there are not vibrations possible (a rigid molecule) so the photon is emitted as the electron goes back to ground state.
 - F. _____ (2.11) (glow in the dark) happens when the excited electron has a flipped spin, and must reflip back before entering the original filled orbital while emitting a photon.
 - G. _____ (2.12) (firefly light, "light sticks") happens when a chemical reaction produces an excited electron in a rigid molecule that then emits a photon as it transitions back to a ground state.
 - H. When illuminated with normal white light, a substance appears to our eyes to be the combination of the wavelengths _____ (2.13) minus the wavelengths _____ (2.14).
 - I. When light of the proper frequency is absorbed by a molecule, an electron in a(n) _____ (filled/unfilled) (2.15) orbital will be excited to a(n) _____ (filled/unfilled) (2.16) orbital.
3. (8 pts). On page 1, for the following list of molecules, write "conjugated" or "not conjugated" to indicate whether or not the given molecule contains a conjugated pi system.



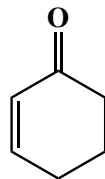
3.1



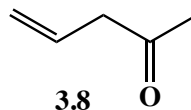
3.2



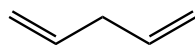
3.3



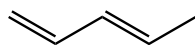
3.4



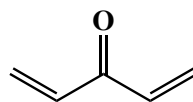
3.8



3.5



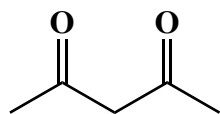
3.6



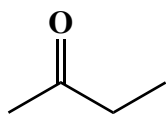
3.7

Write your answers to these questions on the answer sheet on page 1

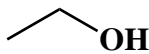
4. (4 pts). On page 1, **rank the following from most to least acidic**, with a 1 corresponding to the number of the molecule that is most acidic and 4 next the number of the molecule that is least acidic and 2 and 3 for the molecules with those relative acidities.



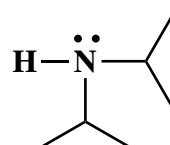
4.1



4.2



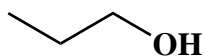
4.3



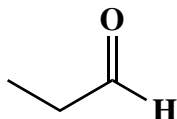
H-LDA

4.4

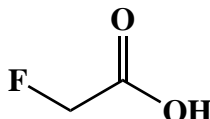
5. (4 pts). On page 1, **rank the following from most to least acidic**, with a 1 corresponding to the number of the molecule that is most acidic and 4 next the number of the molecule that is least acidic and 2 and 3 for the molecules with those relative acidities.



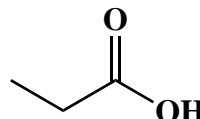
5.1



5.2



5.3



5.4

6. (4 pts). On page 1, write down the correct statement.
- An average adult burns about 100 calories for every mile they run.
 - After about age 25 you will need to *actively* take care of your body to remain healthy, and running should be part of your exercise routine.
 - A very recent study, correcting for all other factors, has offered evidence that running is the best form of exercise for staying healthy, and that running for one hour adds an average of seven hours to your life.
 - All of the above!

This would have been the nomenclature section. Because your class **KILLED** the Longhorn run with 164 runners there is none. Great job!

Signature _____

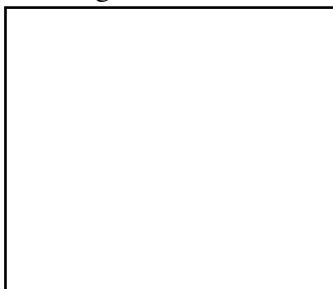
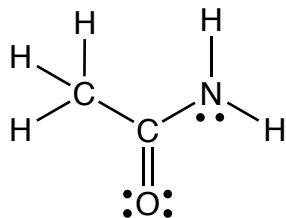
Pg 5 _____(24)

7. (2 pts) What is the most important question in chemistry?

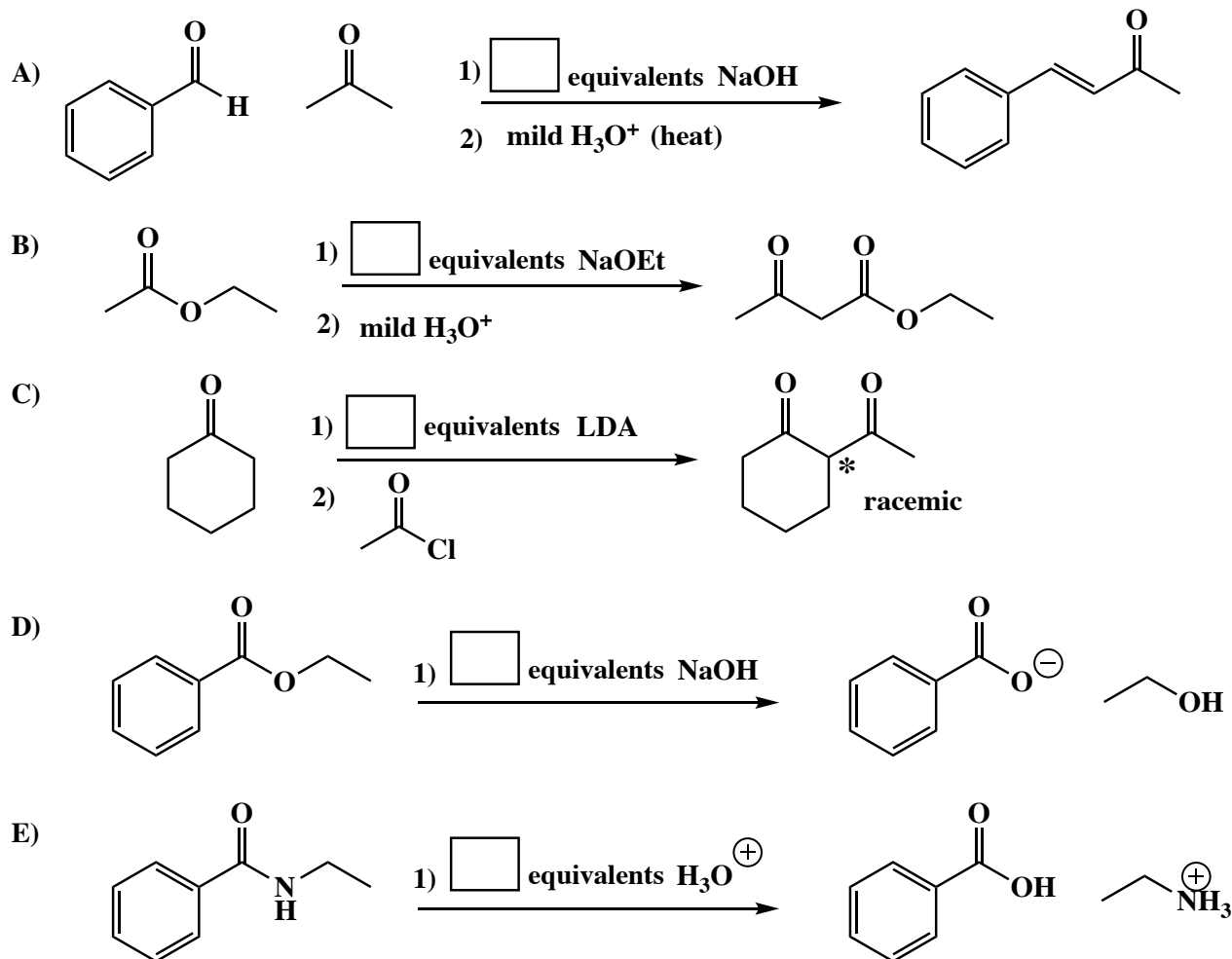
?

8. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

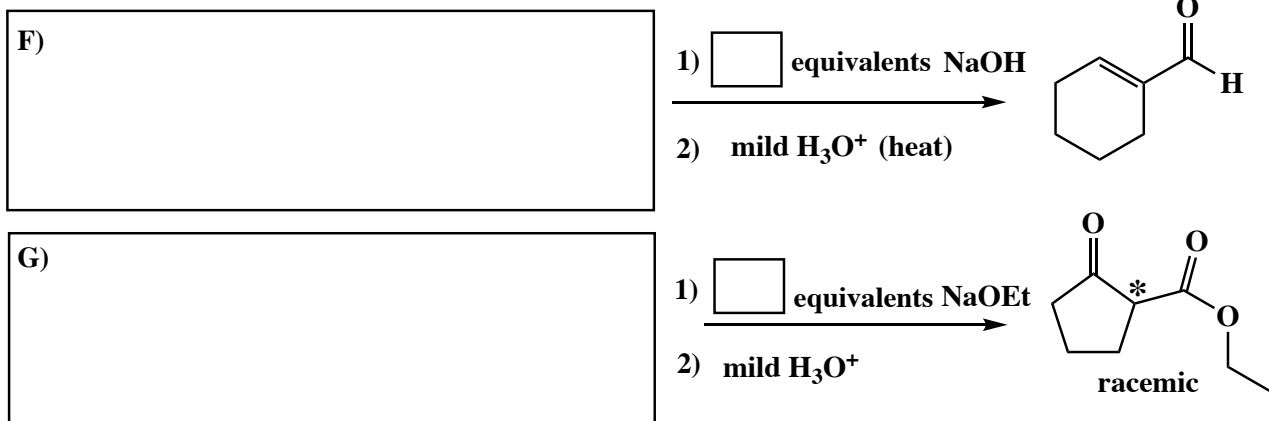
9. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



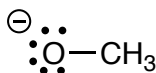
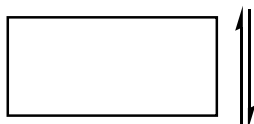
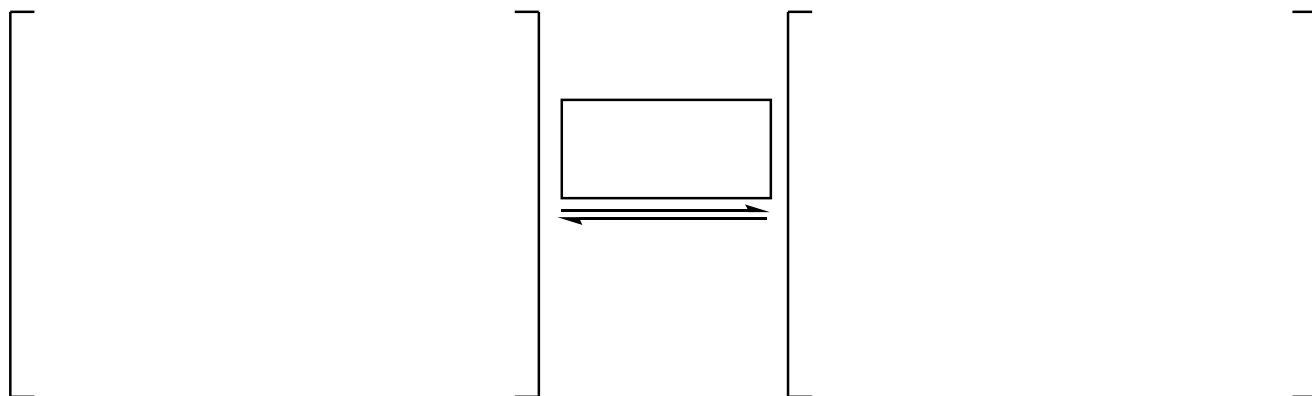
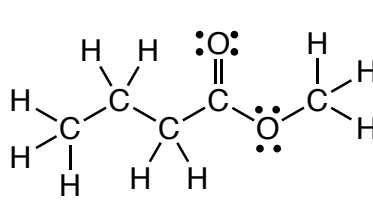
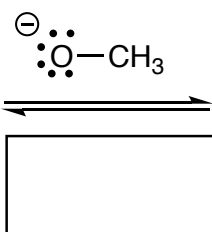
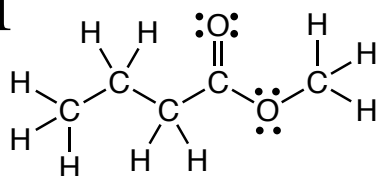
10. (20 pts) In each of the boxes over an arrow, write the minimum number of equivalents of the specified reagent required to carry out the reaction shown to completion. If only a catalytic amount is needed, write "CAT". Note: You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent.



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.



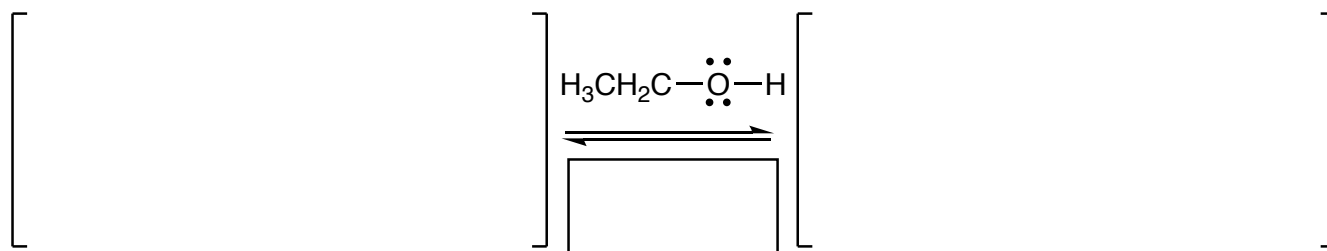
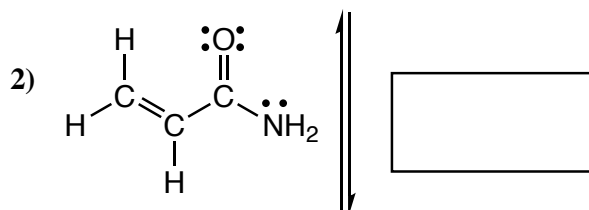
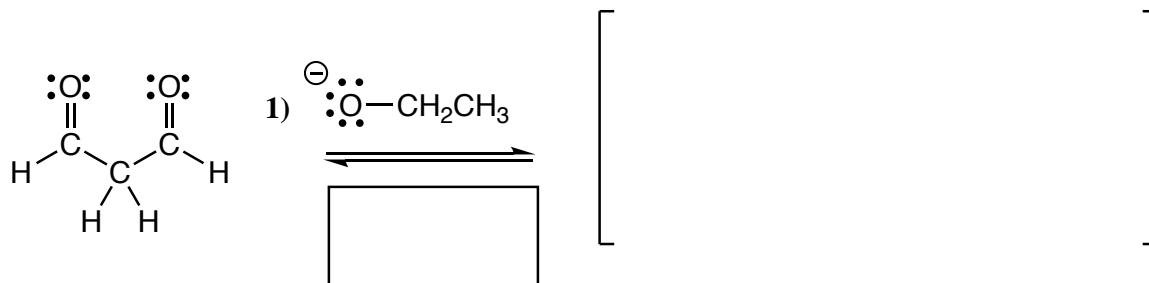
11. (23 pts) Complete the mechanism for the following Claisen condensation reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER 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.).

1

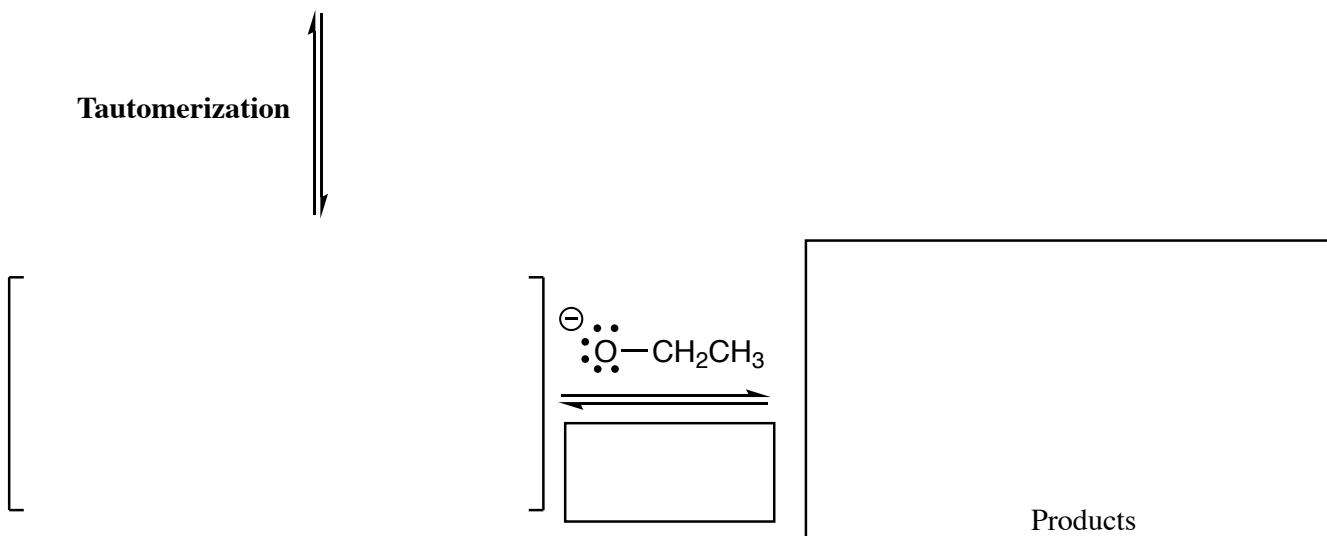
Note you will have to write a balanced equation for this mechanism on PAGE 9

12. (26 pts) Complete the mechanism for the following Michael 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.).

2



Tautomerization



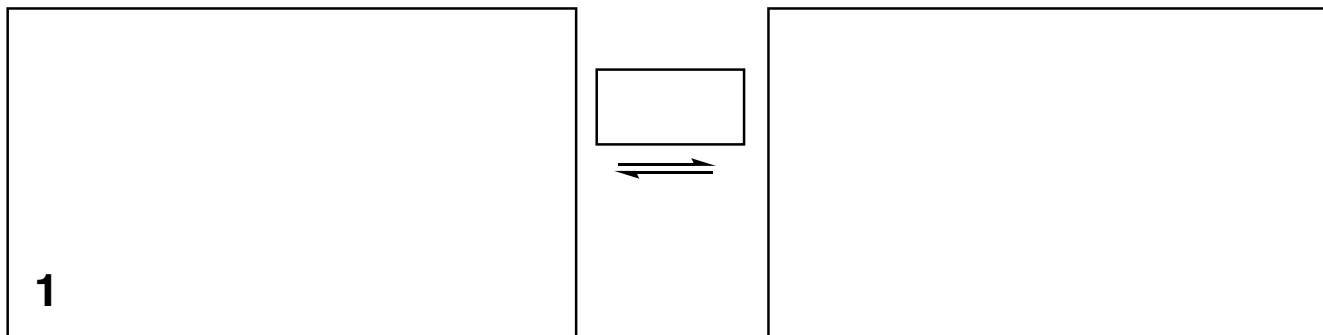
Note you will have to write a balanced equation for the above mechanism on PAGE 9

Signature _____

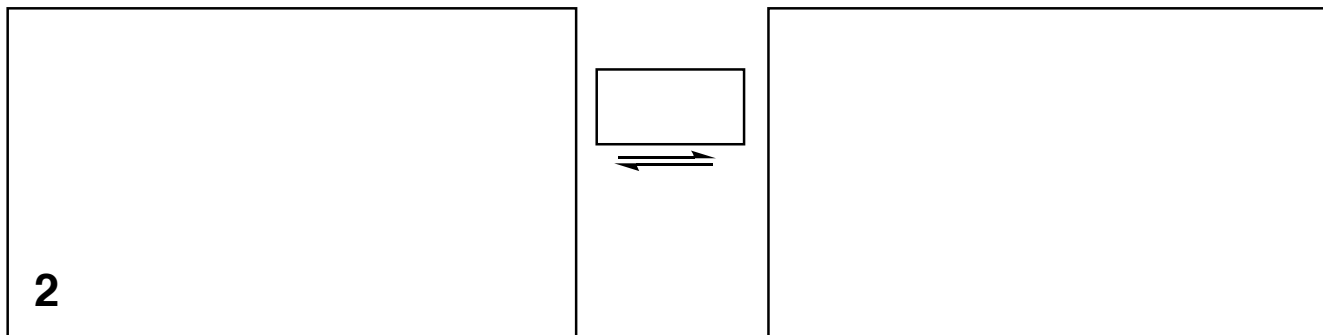
Pg 9 _____(18)

13. (18 pts) Write BALANCED equations for all three of the mechanisms that you drew on the last two pages. Note that because we want balanced equations **you will need to specify the amount of each of the reagents you start with as well as the equivalents of each of the products made**. Any reagent used in a catalytic amount should be placed in the box over the arrow (not all of the boxes over the arrows will necessarily have anything in them).

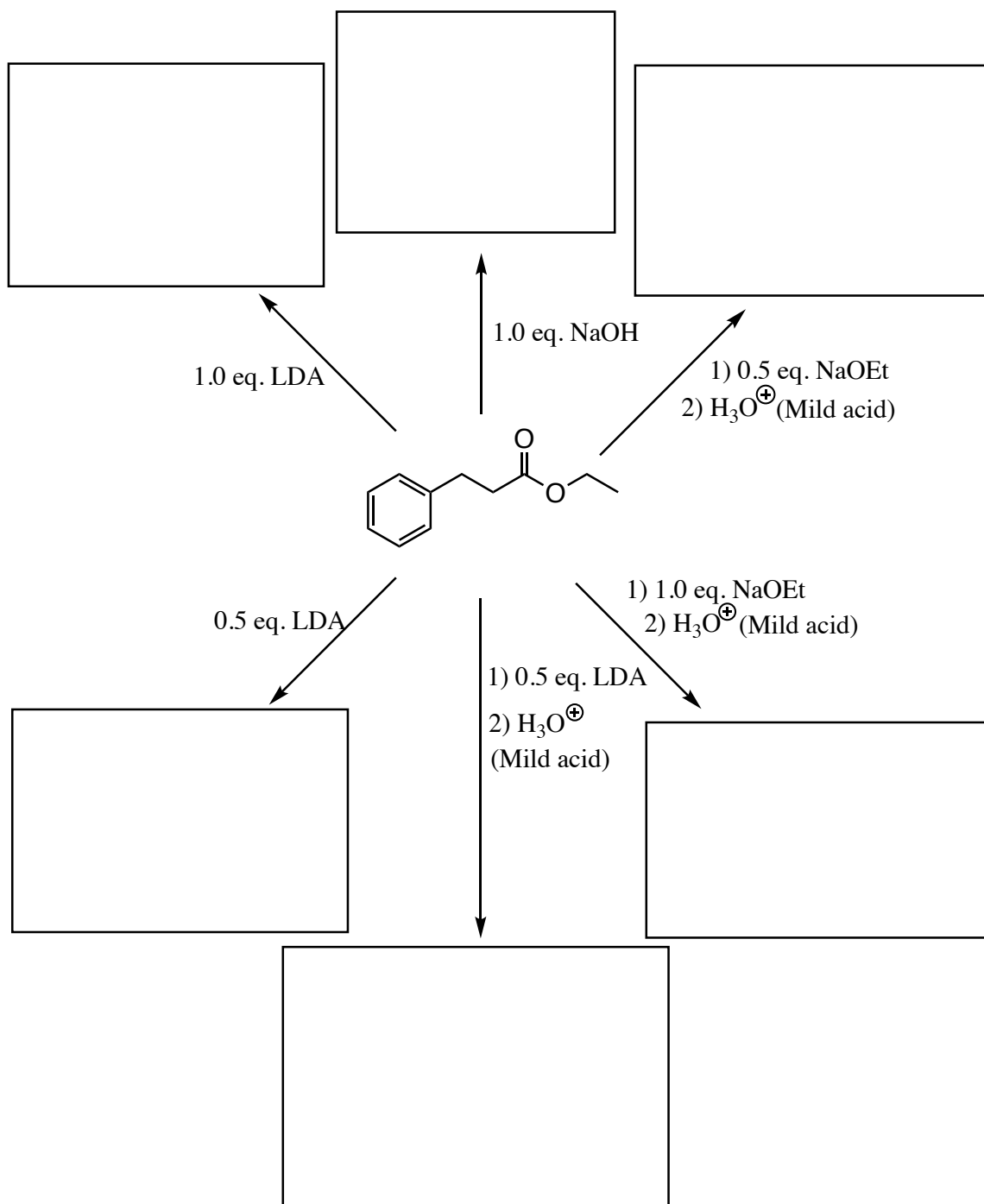
Write a balanced equation for the overall process described by mechanism 1 from page 7



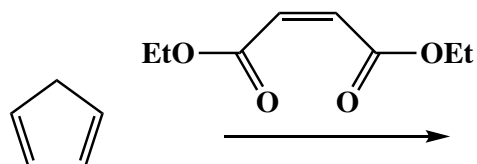
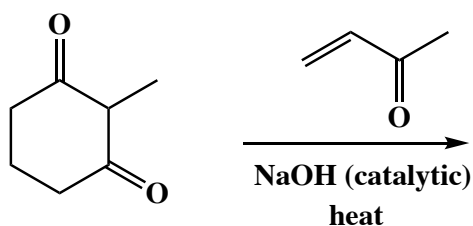
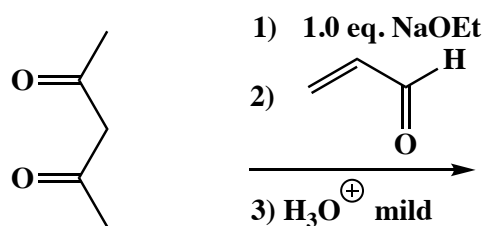
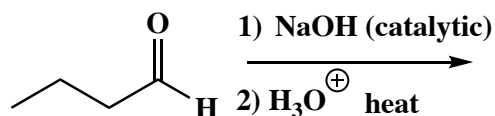
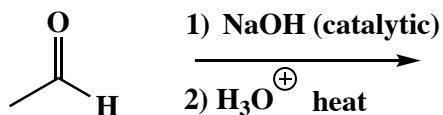
Write a balanced equation for the overall process described by mechanism 2 from page 8



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. (You should recognize this page from a recent homework)



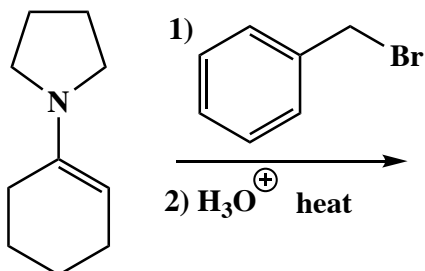
14. (3, 4, 5 or 7 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are multiple carbon containing products, WRITE ALL OF THEM. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk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



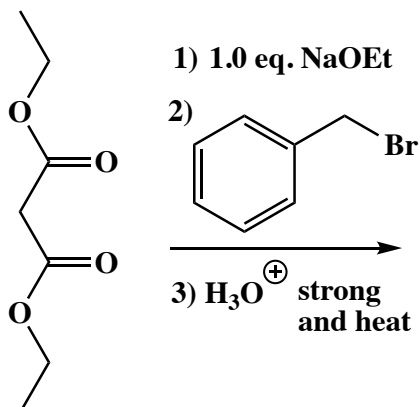
Signature _____

Pg 12 _____(14)

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.

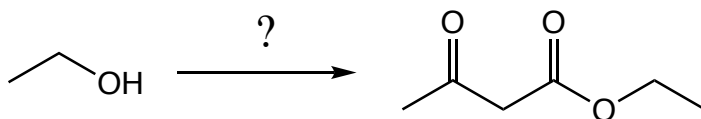


15. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to write "Racemic" where appropriate. You will notice a theme in these problems in that you will be starting with very simple structures and making more complex products.

Remember, all of the carbons of the product must come from the given starting material.

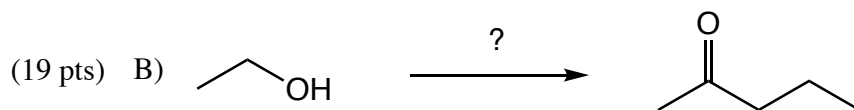
(10 pts)

A)



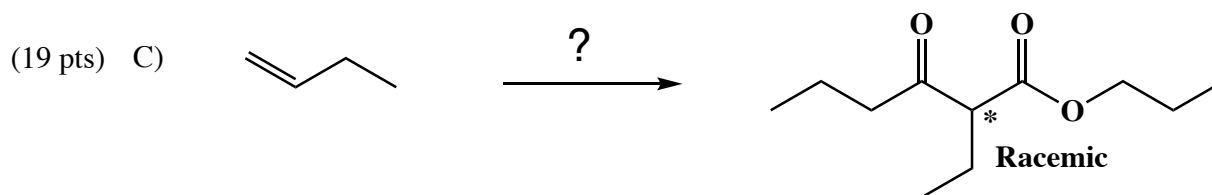
15. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to write "Racemic" where appropriate. You will notice a theme in these problems in that you will be starting with very simple structures and making more complex products.

Remember, all of the carbons of the product must come from the given starting material.



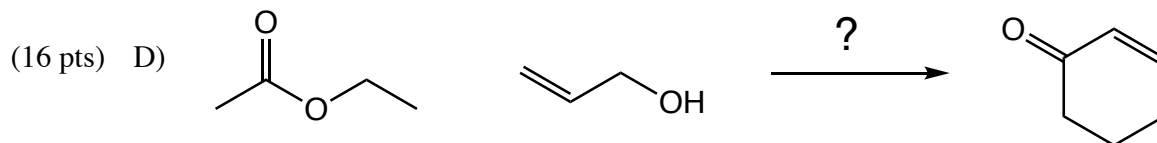
15. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to write "Racemic" where appropriate. You will notice a theme in these problems in that you will be starting with very simple structures and making more complex products.

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Remember, all of the carbons of the product must come from the given starting material. This one is much harder because there is no real KRE in the product. Save it until last and be creative! The chemistry is not hard to understand once you are on the right track.

(19 pts) E)

