NAME (Print): _____

SIGNATURE: _____

Chemistry 320N
Dr. Brent Iverson
3rd Midterm
April 21, 2016

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

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

You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK will be regraded.

Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.

FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENCTS 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!!!

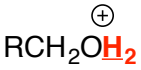
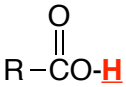
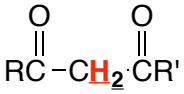
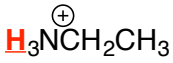
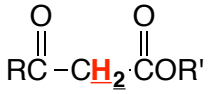
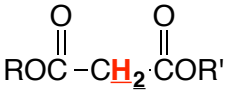
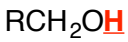
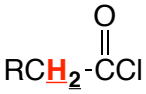
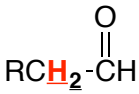
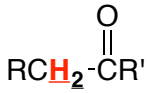
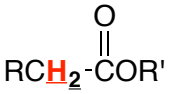
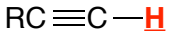
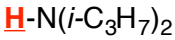
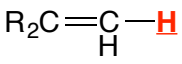
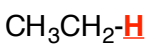
Page	Points	
1		**(53)**
5		**(24)**
6		**(18)**
7		**(23)**
8		**(10)**
9		**(20)**
10		**(18)**
11		**(10)**
12		**(19)**
13		**(23)**
14		**(16)**
15		**(15)**
16		**(8)**
Total		**(257)**

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
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 _____(53)

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 (16 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	1.14 True False
1.15 True False	1.16 True False

Question 2, page 3 (4 pts) Write the word that best completes the sentences.

2.1 _____

2.2 _____

2.3 _____

2.4 _____

Question 3, page 3 (4 pts) Write the word or symbol that best completes the sentences.

3.1 _____

3.2 _____

3.3 _____

3.4 _____

Question 4, page 3 (6 pts) Write the letter (A or B) of the more acidic molecule.

4.1 ____ 4.2 ____ 4.3 ____

4.4 ____ 4.5 ____ 4.6 ____

Question 5, page 4 (17 pts) For each molecule, write "Aromatic" or "Not Aromatic"

5.1 _____ 5.2 _____

5.3 _____ 5.4 _____

5.5 _____ 5.6 _____

5.7 _____ 5.8 _____

5.9 _____ 5.10 _____

5.11 _____ 5.12 _____

5.13 _____ 5.14 _____

5.15 _____ 5.16 _____

5.17 _____

Question 6, page 4 (6 pts) State the hybridization state of the atom indicated by the arrow.

6.1 ____ 6.2 ____ 6.3 ____

6.4 ____ 6.5 ____ 6.6 ____

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

1. (16 pts). On page 1, circle True or False to indicate whether each of the following statements is true or false.

1.1 Photons in the visible region are absorbed by organic molecules when an electron in a filled molecular orbital is excited to an unfilled, antibonding molecular orbital.

1.2 Photons in the visible region are absorbed by organic molecule when an electron in a lower atomic orbital on a single atom such as a 1*s* orbital is excited to a higher orbital such as a 2*s* or 2*p* orbital.

1.3 A material appears to our eyes to be the combination of wavelengths absorbed minus the wavelengths reflected.

1.4 A material appears to our eyes to be the combination of wavelengths reflected minus the wavelengths absorbed.

1.5 In calculating the number of molecular orbitals, you get as many new molecular orbitals as the number of atomic orbitals used to construct them.

1.6 Pi electron density delocalization occurs through overlapping 2*p* orbitals, so to take part in pi electron density delocalization atoms must be sp^2 or *sp* hybridized and reside in the same plane.

1.7 Pi electron density cannot delocalize onto or through sp^3 hybridized atoms because an sp^3 atom has no 2*p* orbital.

1.8 An enolate reacts at carbon because a product with a C=C bond is lower in energy.

1.9 An enolate reacts at oxygen because a product with a C=O bond is lower in energy.

1.10 An enolate reacts at carbon because the carbon has greater negative charge.

1.11 An enolate reacts at oxygen because the oxygen has greater negative charge.

1.12 H-X adds to conjugated dienes to give both 1,2 and 1,4 addition products, via a resonance stabilized allylic cation intermediate.

1.13 Conjugated dienes equilibrate between the *s-cis* and *s-trans* geometry, referring to the conformation of the single bond between the double bonds. The *s-cis* geometry predominates.

1.14 Conjugated dienes equilibrate between the *s-cis* and *s-trans* geometry, referring to the conformation of the single bond between the double bonds. The *s-trans* geometry predominates.

1.15 For Diels-Alder reactions, the diene must be in the *s-cis* geometry to react with a dienophile.

1.16 For Diels-Alder reactions, the diene must be in the *s-trans* geometry to react with a dienophile.

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

2. (4 pts). On page 1, fill in each blank with the word that best completes the following sentences.

A. Using _____ (alkoxide/LDA) (2.1) as the base creates only a small amount of enolate from a starting ester at equilibrium.

B. Using _____ (alkoxide/LDA) (2.2) as the base creates essentially a quantitative amount of enolate from a starting ester at equilibrium.

C. The Robinson annulation involves a(n) _____ (2.3) reaction followed by a(n) _____ (2.4) reaction to make a six-membered ring.

3. (4 pts). On page 1, fill in each blank with the word or symbol that best completes the following sentences.

According to the four Hückel's rules, for a molecule to be aromatic:

A. All of the ring atoms must have a _____(3.1) orbital.

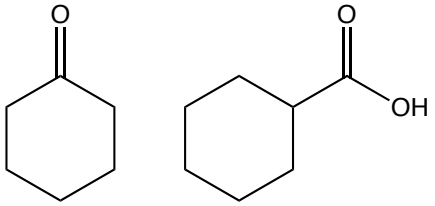
B. The molecule must be _____(3.2).

C. The molecule must be _____ (3.3).

D. There are 4n + 2 _____(3.4) electrons.

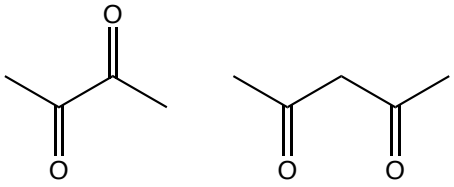
4. (6 pts). On page 1, for each pair of molecules, **write the letter (A or B)** corresponding to the MORE ACIDIC molecule.

4.1



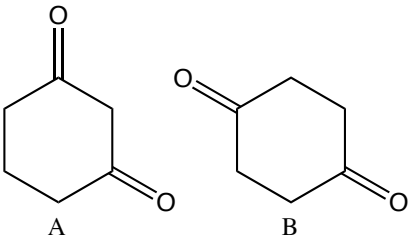
A B

4.2



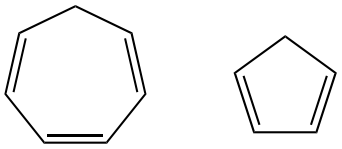
A B

4.3



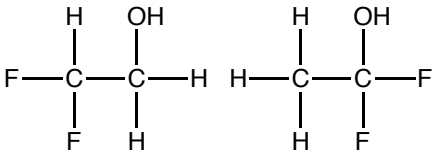
A B

4.4



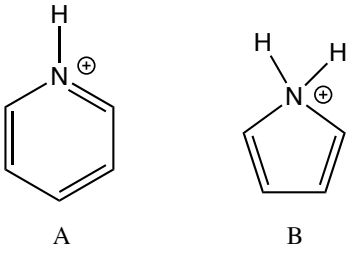
A B

4.5



A B

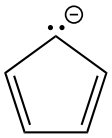
4.6

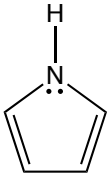
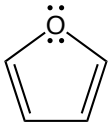
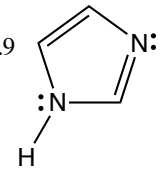


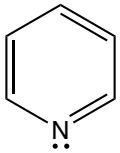
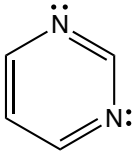
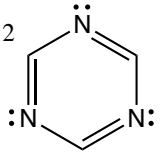
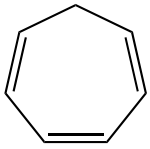
A B

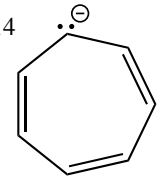
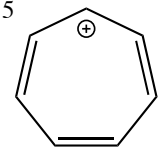
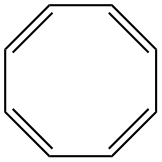
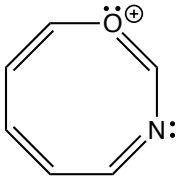
Write your answers to these questions on the answer sheet on page 1

5. (17 pts). On page 1, for each molecule, in the spaces provided write "AROMATIC" if the molecule is aromatic according to the Hückel definition, write "NOT AROMATIC" if the molecule is not aromatic.

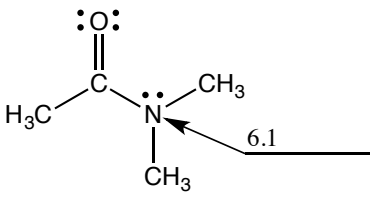
5.1 
5.2 
5.3 
5.4 
5.5 

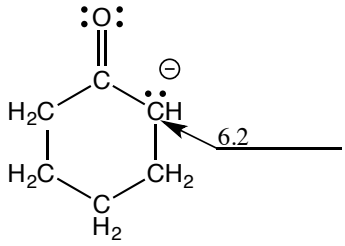
5.6 
5.7 
5.8 
5.9 

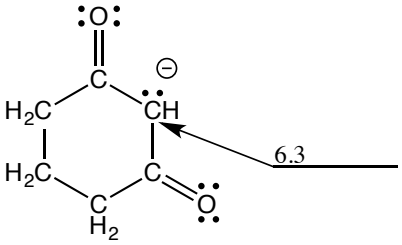
5.10 
5.11 
5.12 
5.13 

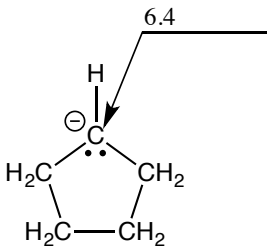
5.14 
5.15 
5.16 
5.17 

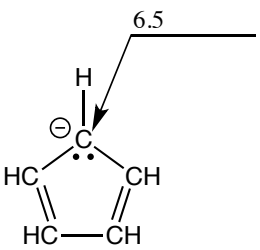
6. (6 pts). On page 1, in the spaces provided write the hybridization state of the atom indicated by the arrow.

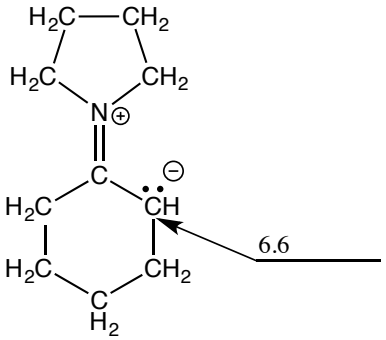




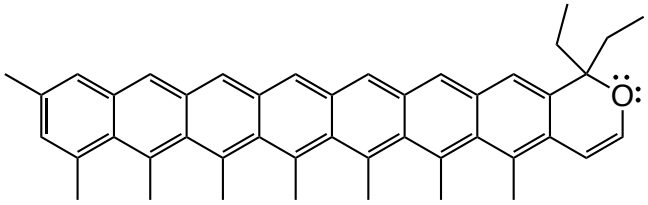




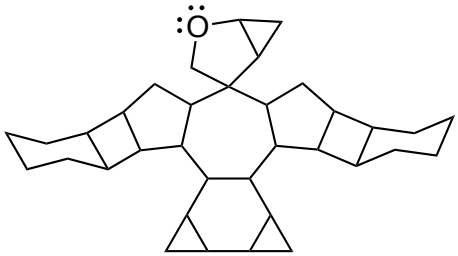




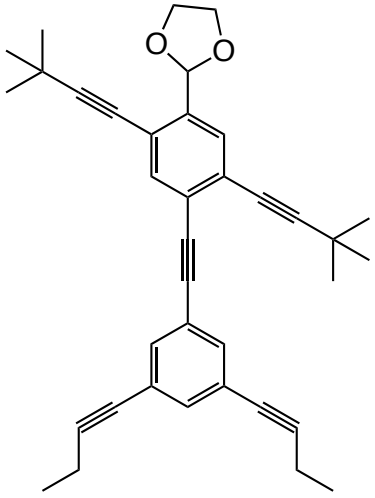
This would have been the nomenclature question page. Because your class ROCKED the Longhorn run with 161 runners, I have simply drawn a few of my favorite molecular creatures, complete with their official IUPAC name. No kidding, these are their real IUPAC names.



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



(1e*R*,5a*S*,8b*R*,12a*S*)-triacontahydro-4'-oxaspiro[benzo[3',4']cyclobuta[1',2':3,4]cyclopenta[1,2-*f*]benzo[3,4]cyclobuta[1,2-*a*]dicyclopropa[3,4:5,6]benzo[1,2-*h*]azulene-7,2'-bicyclo[3.1.0]hexane]



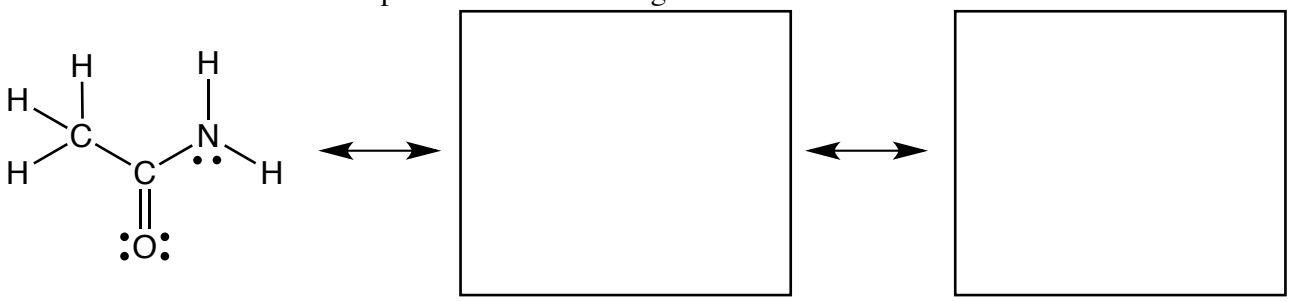
2-(4-((3,5-di(but-1-yn-1-yl)phenyl)ethynyl)-2,5-bis(3,3-dimethylbut-1-yn-1-yl)phenyl)-1,3-dioxolane

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

_____ **?**

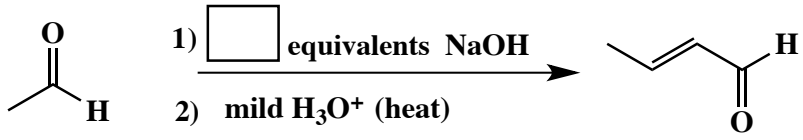
8. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We wil be looking for a minumum of 7 key points here.

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.

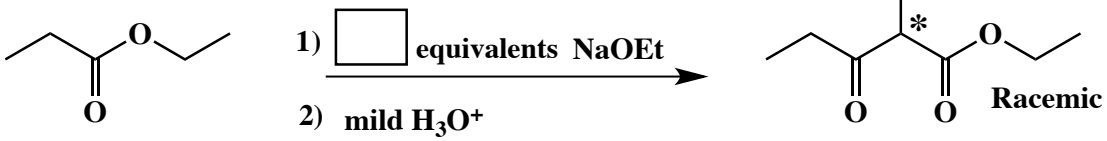


10. (18 pts) In each of the boxes over an arrow, **write the minimum number of equivalents** of the specified reagent required to carry out the reaction shown **to completion**. If only a catalytic amount is needed, write **"CAT"**. Note: **You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent.**

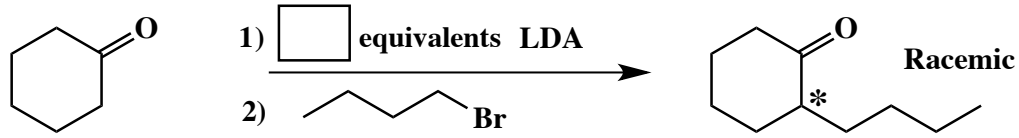
A)



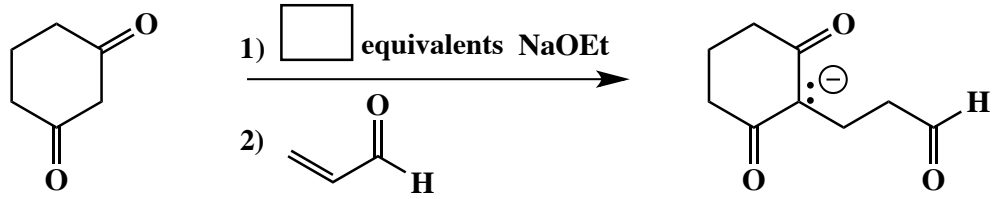
B)



C)

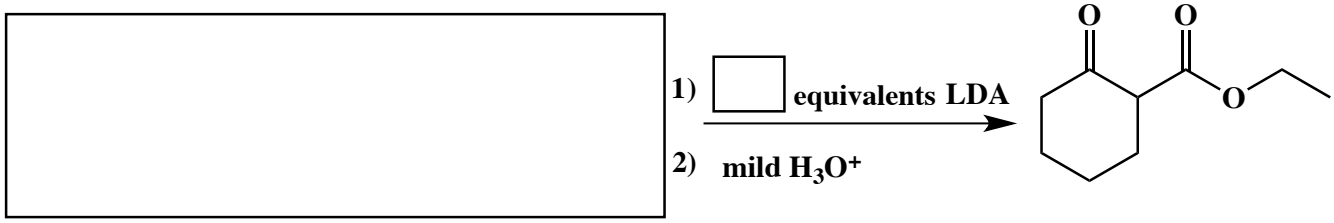


D)

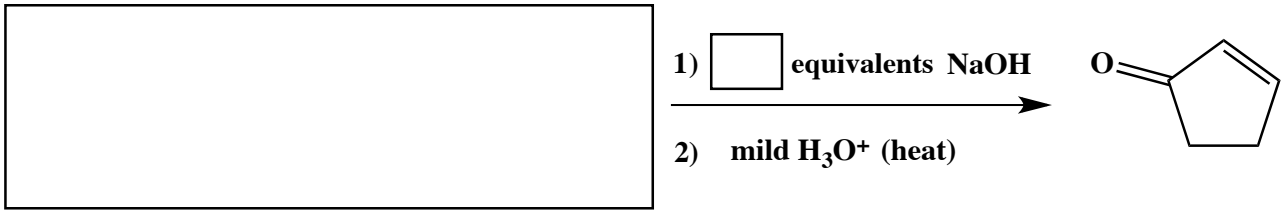


For these next two we have provided the product, you need to draw the starting material as well as fill in the number of equivalents.

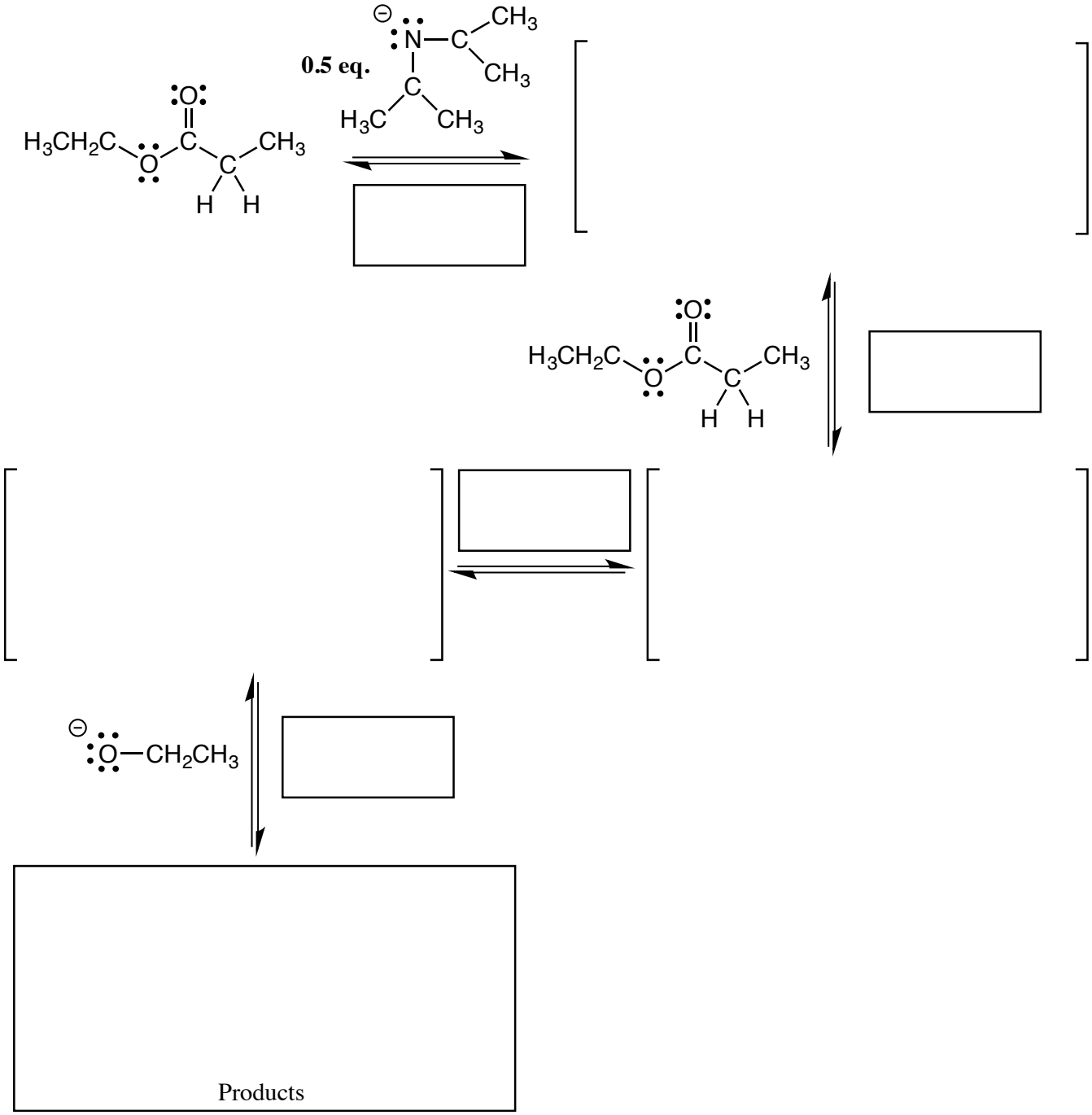
E)



F) This one might take you a while so you might want to save it until the end.



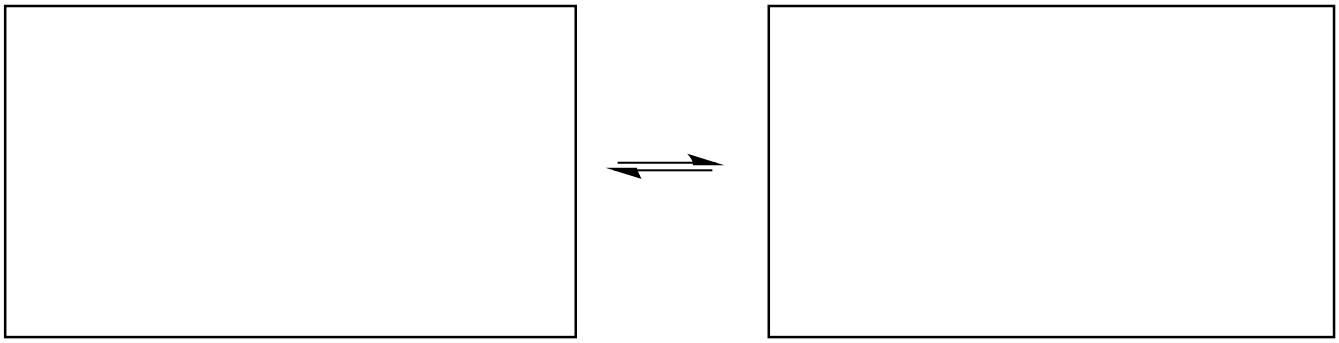
11. (23 pts) Complete the mechanism for the following Claisen reaction using LDA. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each 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.).**



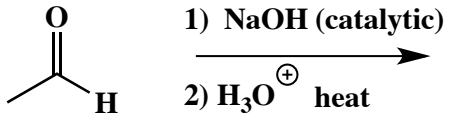
Note you will have to write a balanced equation for the above mechanism on PAGE 8

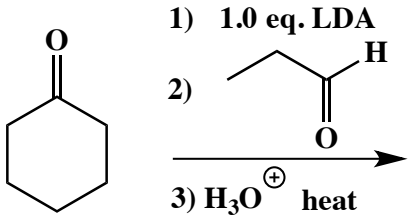
12. (10 pts) Write a BALANCED equation for the mechanism that you drew on page 7. Note that because we want balanced equations **you will need to specify the amount of <u>each</u> of the reagents you start with as well as the equivalents of <u>each</u> of the products made**.

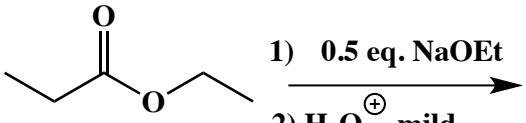
Write a balanced equation for the overall process described by the mechanism from page 7

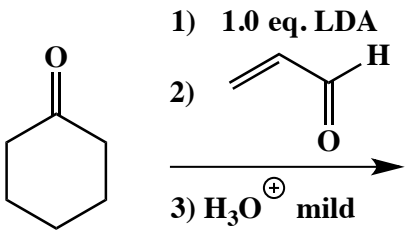


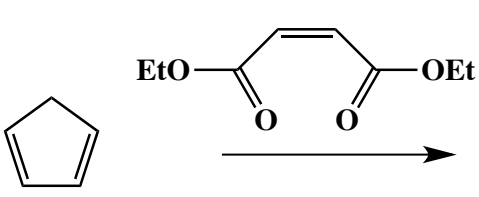
13. (3, 4, 5 or 7 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are multiple carbon containing products, WRITE ALL OF THEM. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and write racemic. No need for wedges and dashes. If an E,Z mixture is formed you must draw both. Also, do not worry about balancing these equations, you just need to show us the major carbon-containing products of these transformations.**



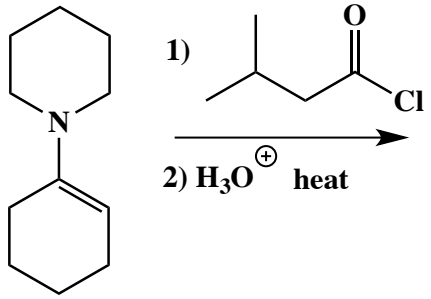




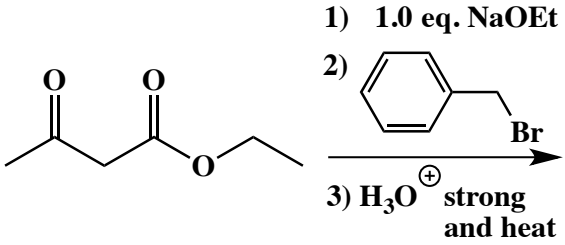


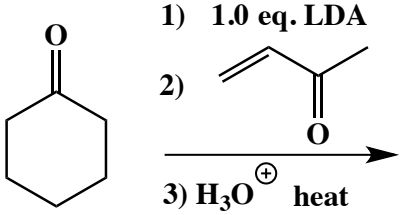


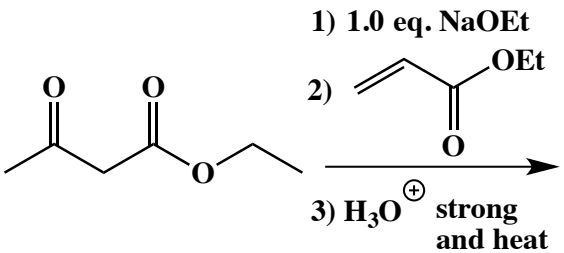
13. (3, 4, 5 or 7 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are multiple carbon containing products, WRITE ALL OF THEM. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and write racemic. No need for wedges and dashes. If an E,Z mixture is formed you must draw both. Also, do not worry about balancing these equations, you just need to show us the major carbon-containing products of these transformations.**



These next two are a little more complicated, they might take a bit more time. Be sure to write down all the carbon containing products.





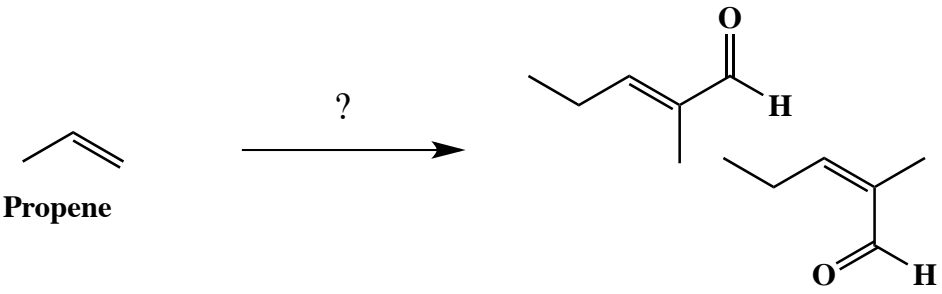


14. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" 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)



Propene

14. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe 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 right "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.
(19 pts)

B)

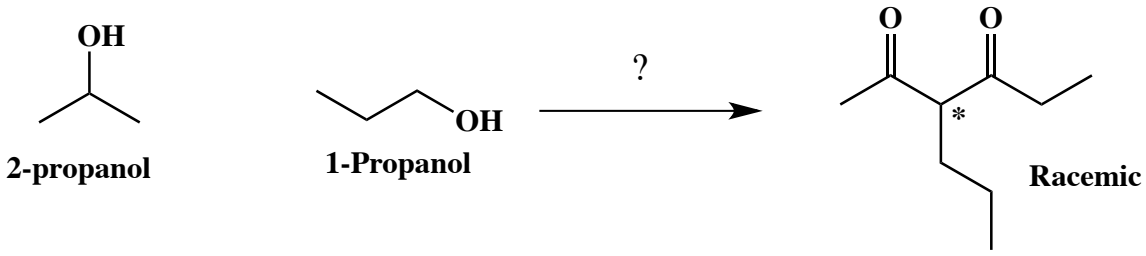
Propylene glycol **1-Propanol** **Pentanoic acid**

14. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe 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 right "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.

(21 pts)

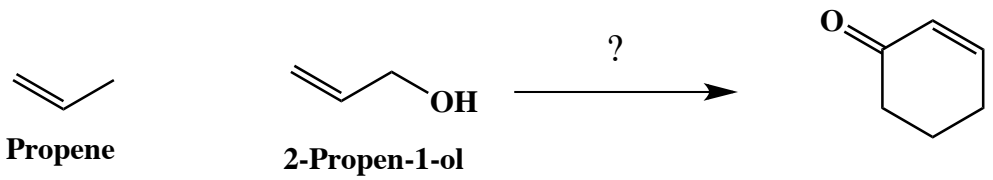
C)



14. Using any reagents turn the starting material into the indicated product. All carbon atoms inthe 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 right "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.

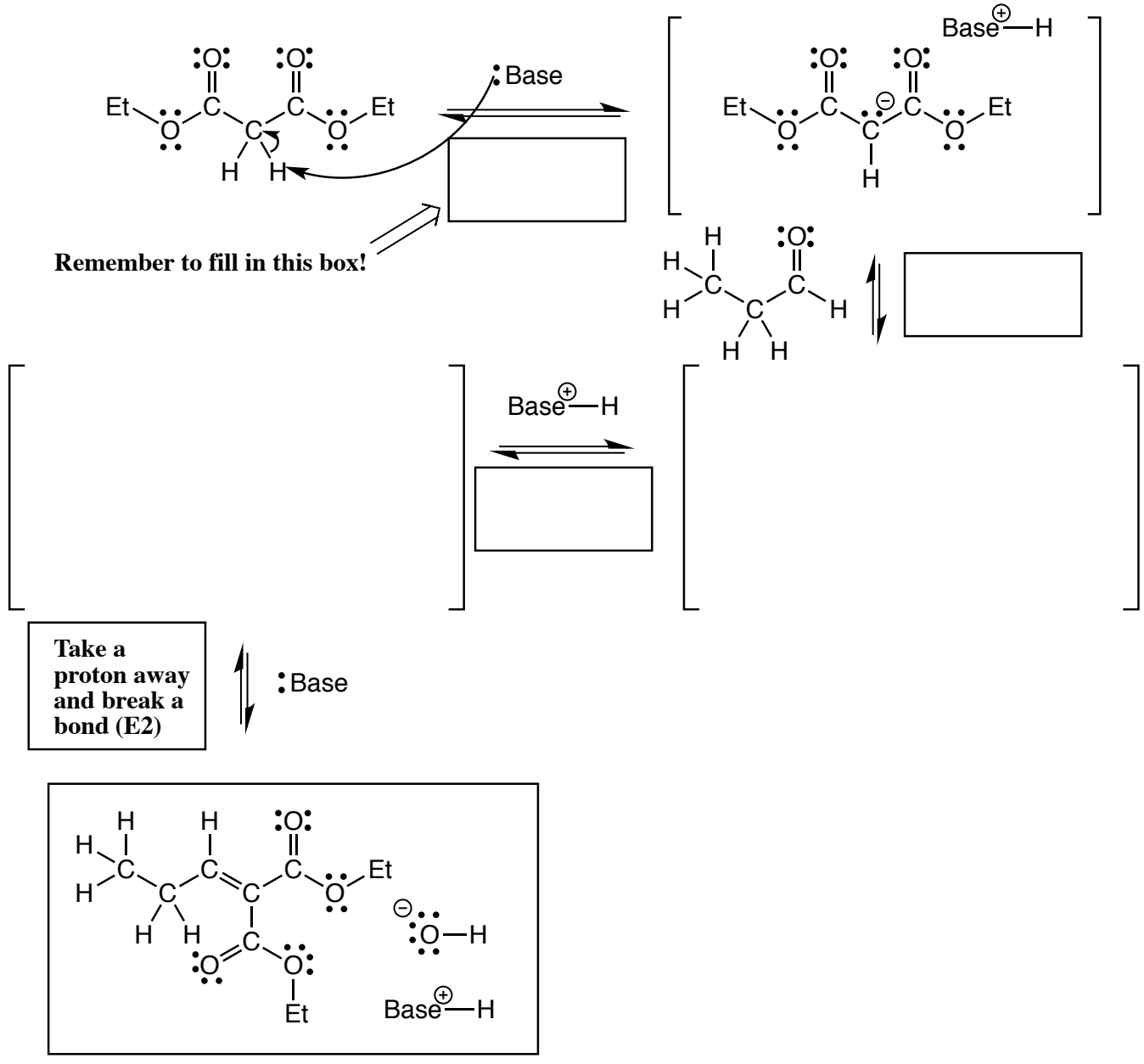
Remember, all of the carbons of the product must come from the given starting material.
(16 pts)

D)



Propene **2-Propen-1-ol**

15. (15 pts) Here is an "apply what you know" problem. An interesting reaction we did not study is the Knoevenagel Condensation reaction. It involves the reaction of β-dicarbonyl species with aldehydes to give new C=C bonds (cue the trumpet!) in base. The Knoevenagel Condensation provides a rapid way to make very complex molecules from simple starting materials. Use what you know about the reactions we have been studying to fill in the parts of the Knoevenagel condensation reaction mechanism. For the following mechanism, **fill in all the missing arrows, draw the missing intermediates (all charges and lone pairs) and fill in all of the blank boxes with the type of mechanistic element involved ("make a bond", "add a proton"). Remember to use asterisks (*) to indicate any chiral centers and write "racemic" if appropriate.**



16. (8 pts) You might be surprised to learn that the based used often in the Knoevenagel Condenation is pyridine. Fill in the boxes with the structures that correspond to product of the following Knoevenagel Condensation, followed by what happens when this initial product is heated in strong, aqueous acid. For the following, you one have to draw the main product derived from the starting materials.