

NAME (Print): _____

Chemistry 320N
Dr. Brent Iverson
3rd Midterm
April 23, 2015

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	(44)
5	(24)
6	(18)
7	(23)
8	(26)
9	(11)
10	(22)
11	(10)
12	(13)
13	(19)
14	(13)
15	(18)
16	(8)
Total	(249)

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	H-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	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	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	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	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

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 (12 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 |

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

- 2.1 _____
2.2 _____
2.3 _____ (Red or Green)
2.4 _____ (Red or Green)

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

- 3.1 _____
3.2 _____
3.3 _____

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 (12 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 _____

Question 6, page 4 (7 pts) State the type of orbital containing the lone pair of electrons indicated by the arrow.

- 6.1 _____ 6.2 _____ 6.3 _____
6.4 _____ 6.5 _____ 6.6 _____
6.7 _____

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

1. (12 pts). On page 1, circle True or False to indicate whether each of the following statements is true or false.
 - 1.1 When **HBr** adds to conjugated dienes, the 1,4 addition product is the product that predominates when the reaction is considered to be under kinetic control.
 - 1.2 When **HBr** adds to conjugated dienes, the 1,4 addition product is the product that predominates when the reaction is considered to be under thermodynamic control.
 - 1.3 When **HBr** adds to conjugated dienes, thermodynamic control of the reaction will occur at higher temperatures and kinetic control will occur at lower temperatures.
 - 1.4 When **HBr** adds to conjugated dienes, thermodynamic control of the reaction will occur at lower temperatures and kinetic control will occur at higher temperatures.
 - 1.5 When trying to understand molecular orbitals in aromatic molecules it is best to think of electrons as waves.
 - 1.6 In molecular orbital theory, the number of molecular orbitals generated equals the number of atomic orbitals used to construct them. For example, six 2p orbitals will combine to give six new pi molecular orbitals.
 - 1.7 Fluorescence occurs when an electron is excited to an unfilled orbital upon absorption of a photon, then a new photon is emitted as the electron immediately returns to the orbital from where it originated (ground state).
 - 1.8 Chemiluminescence occurs when the product of a reaction happens to be generated in an electronically excited state, and a photon is emitted as the electron returns to the ground state orbital.
 - 1.9 Chemiluminescence occurs when an electron is excited to an unfilled orbital upon absorption of a photon, then the electron is trapped in this excited state for a while. After a time, a new photon is emitted as the electron returns to the orbital from where it originated (ground state).
 - 1.10 Phosphorescence occurs when the product of a reaction happens to be generated in an electronically excited state, and a photon is emitted as the electron returns to the ground state orbital.
 - 1.11 The greater the number of atoms taking part in conjugation (larger “pi-way”), the larger the energy gap between the highest energy filled pi molecular orbital and the lowest energy unfilled pi molecular orbital.
 - 1.12 The greater the number of atoms taking part in conjugation (larger “pi-way”), the smaller the energy gap between the highest energy filled pi molecular orbital and the lowest energy unfilled pi molecular orbital.

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.

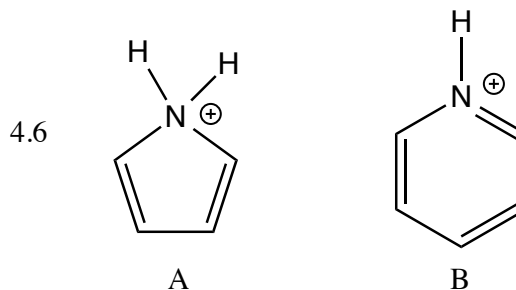
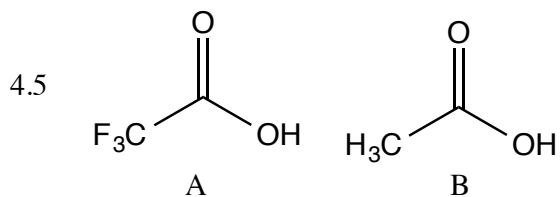
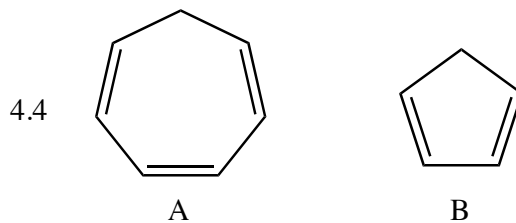
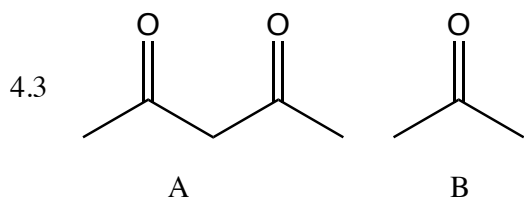
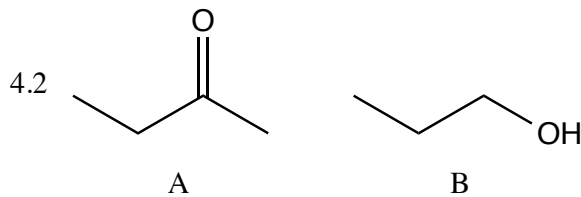
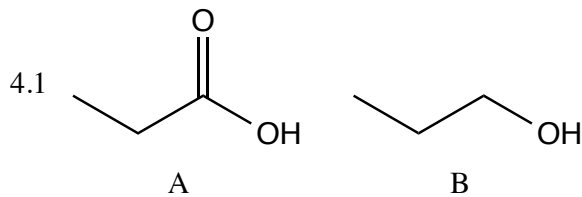
The color we see for an object is determined by the combination of wavelengths of light that are _____(2.1) minus the wavelengths of light that are _____(2.2) This is precisely why the _____(2.3) (red or green) laser was able to shine through my finger while the _____(2.4) (red or green) laser was completely absorbed by hemoglobin, the main colored pigment in our tissues.

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

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

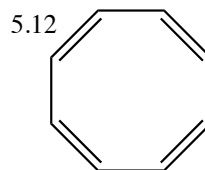
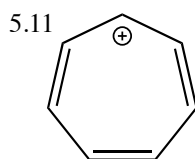
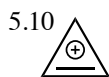
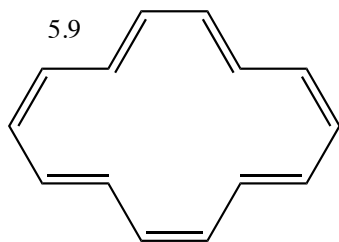
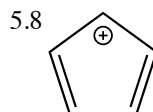
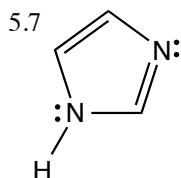
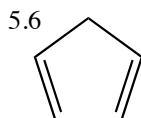
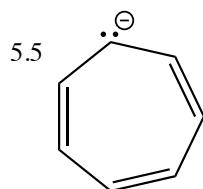
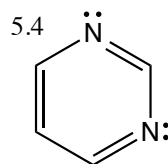
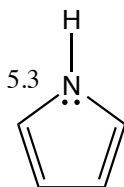
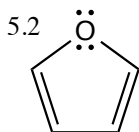
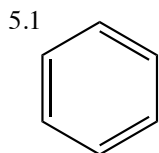
- A. The ring must be _____(3.1).
B. All of the ring atoms have a _____(3.2) orbital.
C. There are $4n + 2$ _____(3.3) electrons.

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

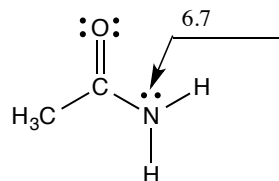
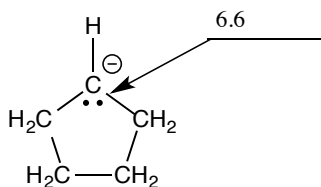
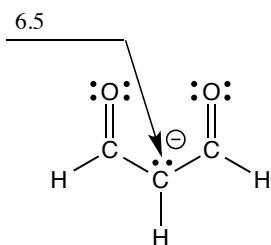
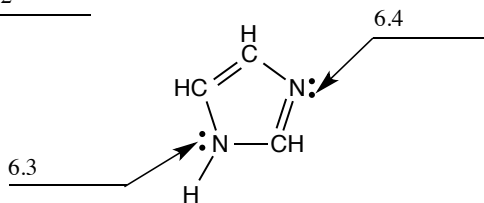
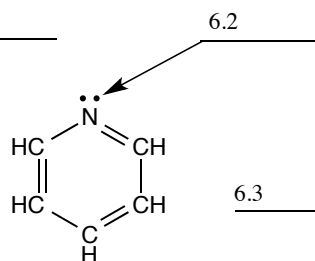
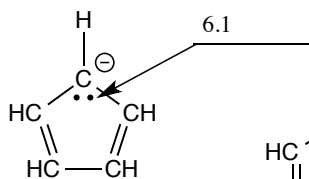


Write your answers to these questions on the answer sheet on page 1

5. (12 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.



6. (7 pts). On page 1, in the spaces provided write the type of atomic orbital (sp^3 , $2p$, etc.) that contains the electron pair indicated by the arrow.



Signature _____

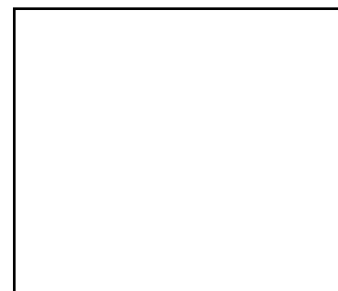
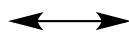
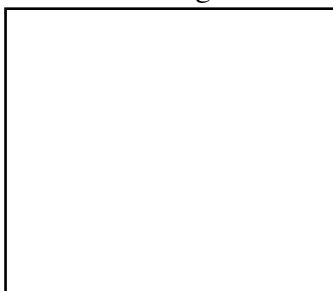
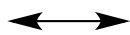
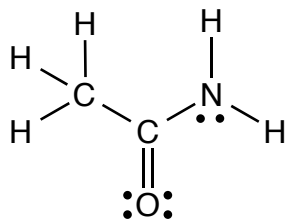
Pg 5 _____(24)

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

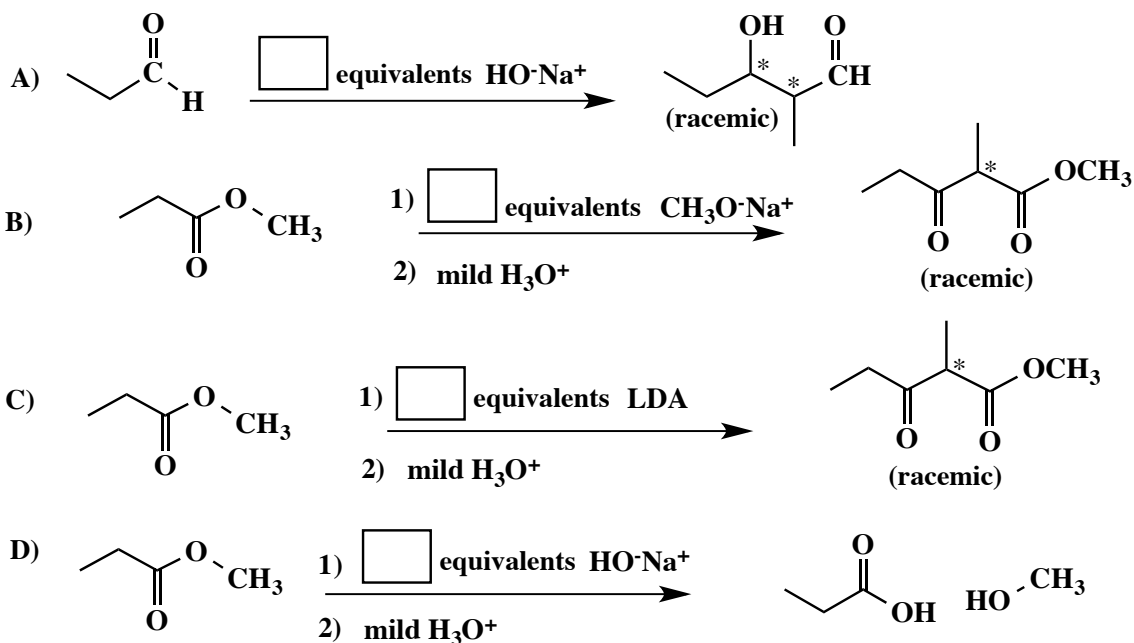
?

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.

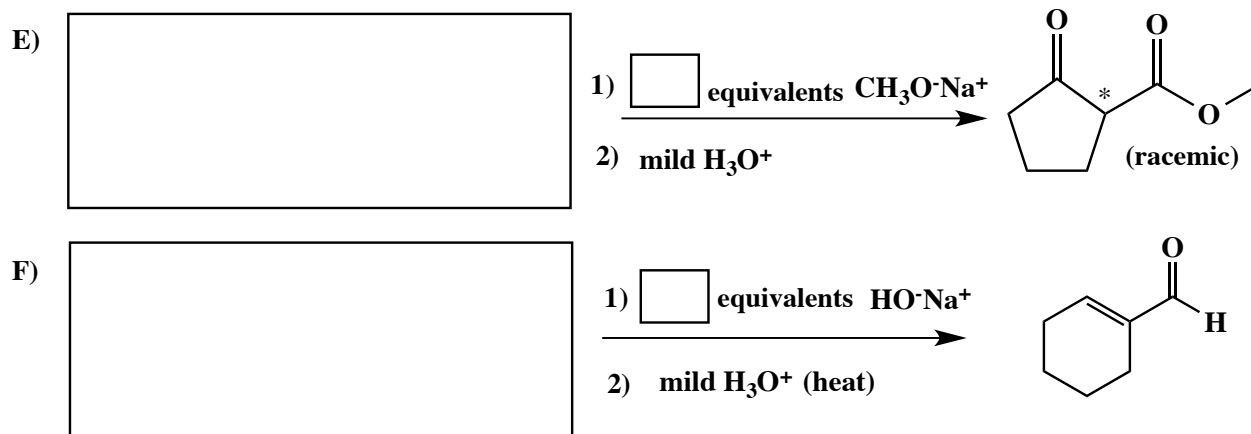
9. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



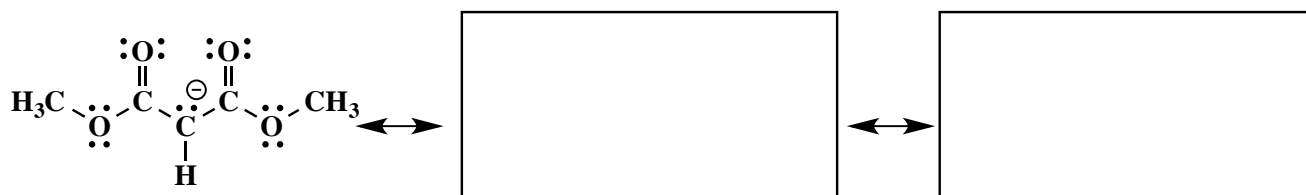
10. (10 pts) In each of the boxes over an arrow, write the minimum number of equivalents of the specified reagent required to carry out the reaction shown **to completion**. If only a catalytic amount is needed, write "CAT". Note: You must assume the carbonyl compound starting material is initially present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

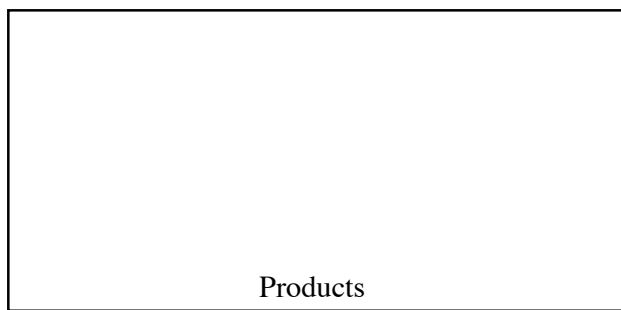
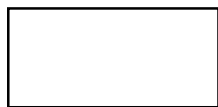
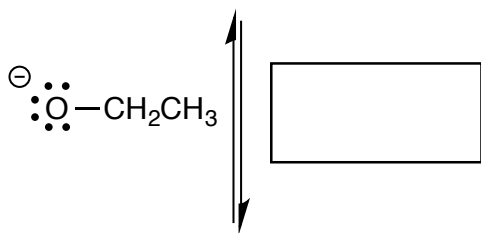
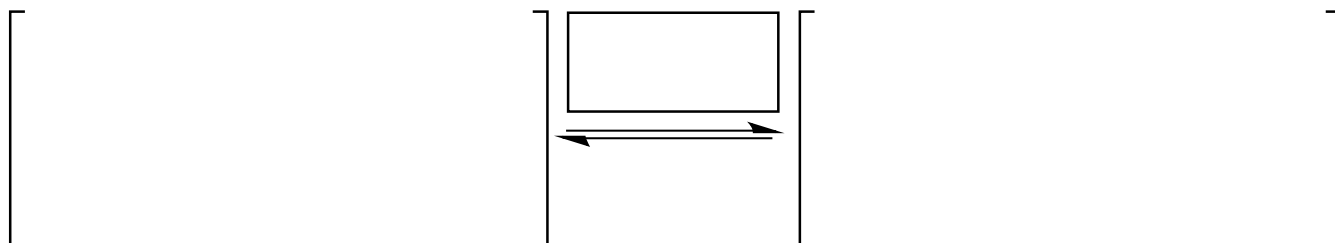
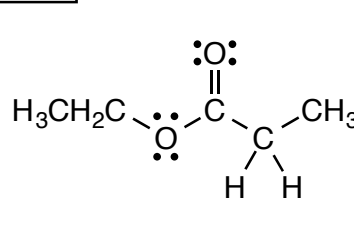
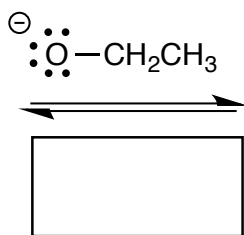
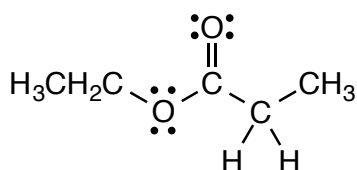


11. (8 pts) For the following enolate, draw the two other most important contributing structures. You do not need to draw arrows here, but be sure to show all lone pairs and formal charges.



12. (23 pts) Complete the mechanism for the following Claisen 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.).

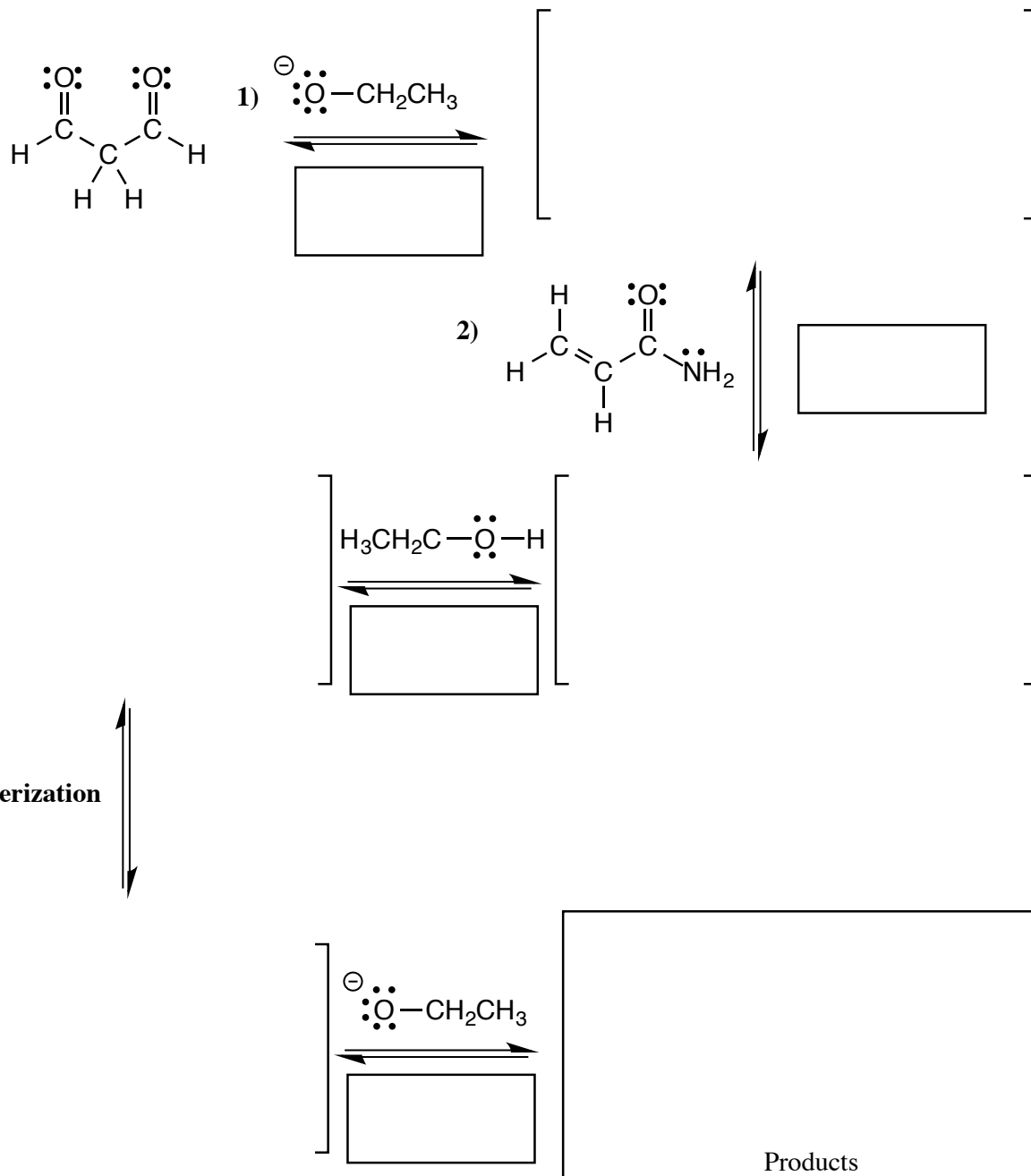
1



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

13. (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



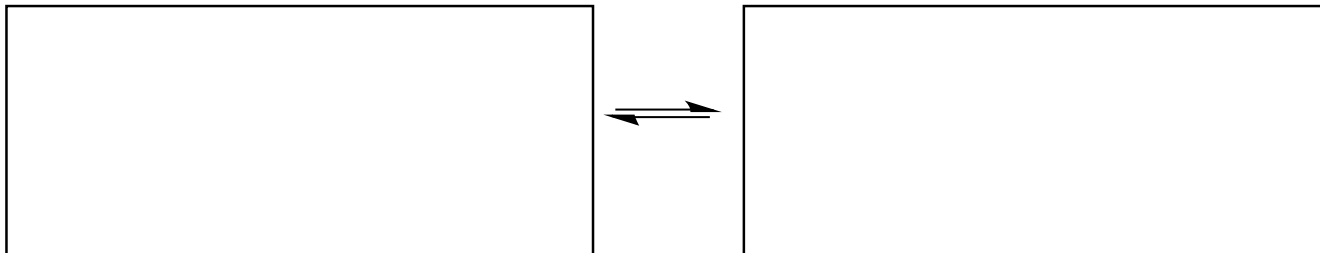
Note you will have to write a balanced equation for the above mechanism on PAGE 9

Signature _____

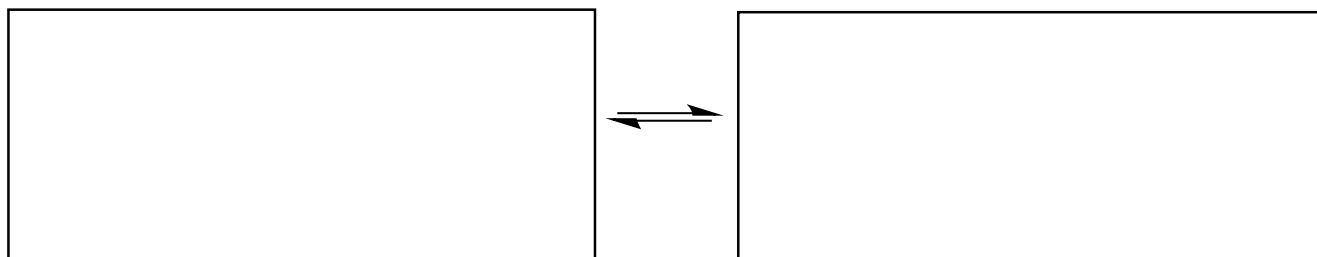
Pg 9 _____(11)

14. (11 pts) Write BALANCED equations for both mechanisms that you drew on the last two pages. Note that because we want balanced equations **you will need to specify the equivalents of each of the reagents you start with as well as the equivalents of each of the products made.** PLEASE READ THIS CAREFULLY, WE ARE NOT TRYING TO TRICK YOU SO MAKE SURE YOU READ THE WORD EACH IN THE LAST SENTENCE!!

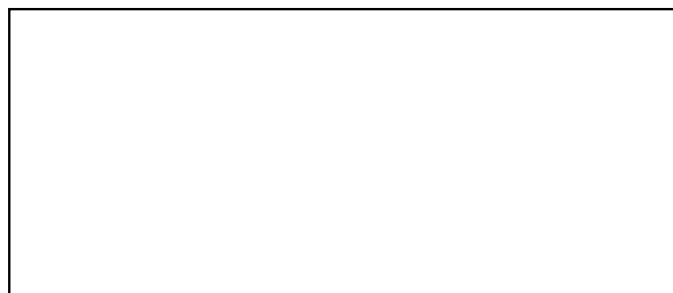
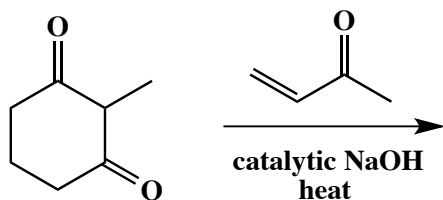
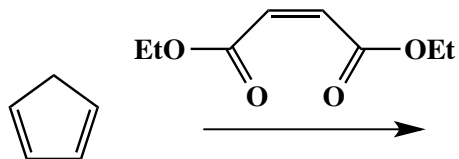
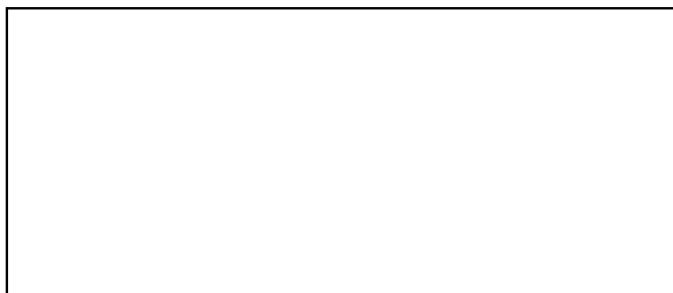
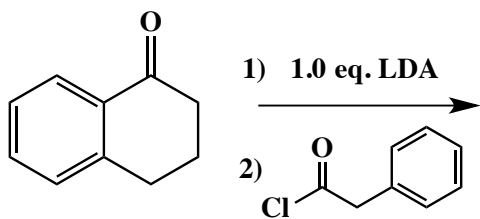
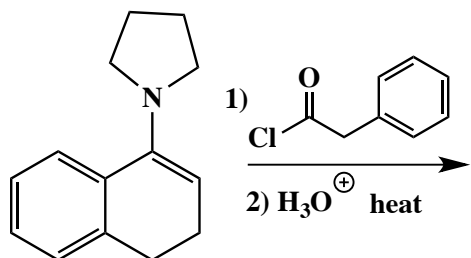
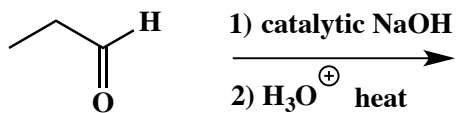
Write a balanced equation for the overall process described by mechanism 1 from page 7



Write a balanced equation for the overall process (including adding both reagents) described by mechanism 2 from page 8



15. (3, 4 or 5 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH. 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. Also, do not worry about balancing these equations, you just need to show us the major carbon-containing products of these transformations.



Signature _____

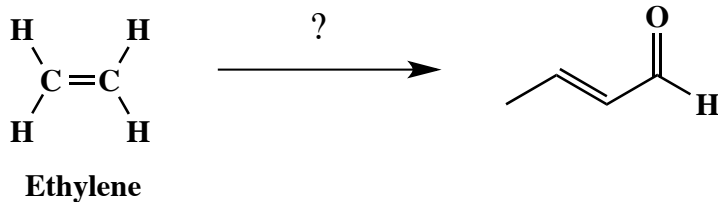
Pg 11 _____(10)

16. 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 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)

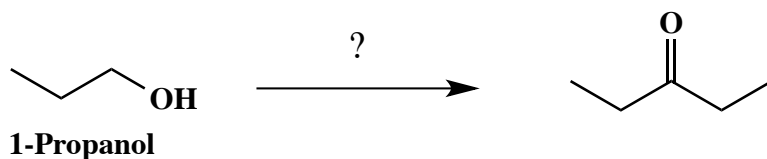


16. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic"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

(13 pts)

B)

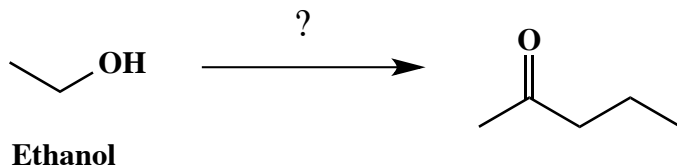


16. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic"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

C)

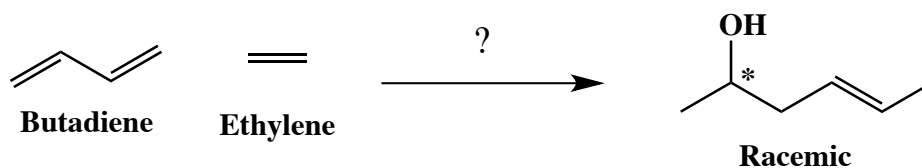


16. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic"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

(13 pts)

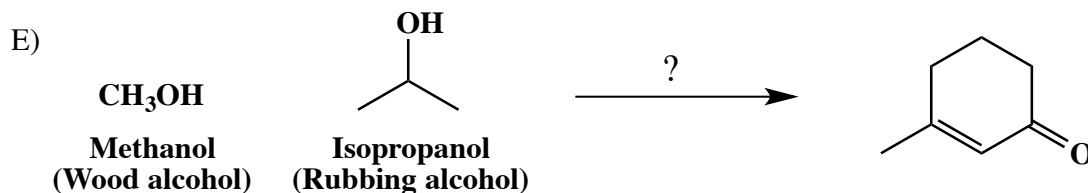
D)



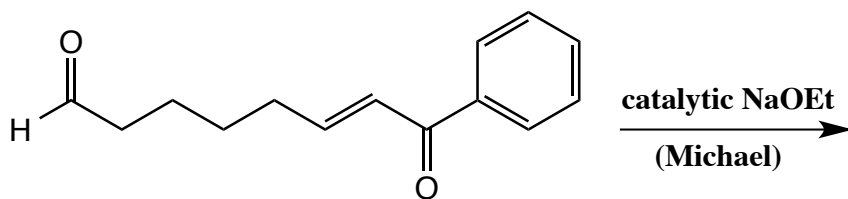
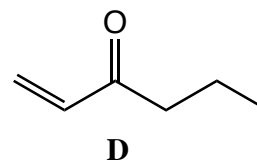
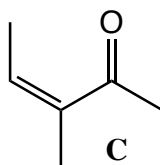
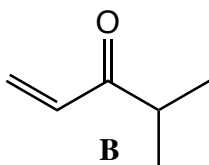
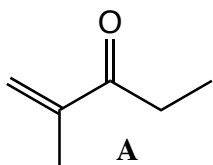
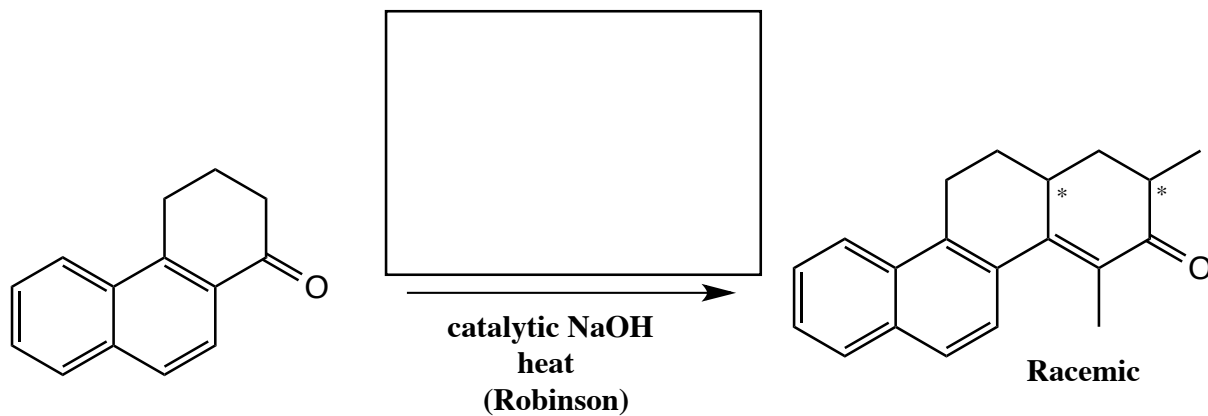
16. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic"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

(13 pts) **You will get 5 bonus points for getting this one entirely correct!**



16. (8 pts) The reactions we have learned now are powerful enough to make some very sophisticated molecules. Using the reactions you know, draw the missing reagent or product in the box. In both cases, one of the four molecules listed (A-D) is the correct answer.



I stongly recommend you number the atoms on this one!

