

X

NAME (Print): _____

Chemistry 320N
Dr. Brent Iverson
Final Exam
May 14, 2016

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 cannot use a red pen to take the exam. 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	(90)
8	(24)
9	(31)
10	(26)
11	(35)
12	(20)
13	(21)
14	(15)
15	(37)
16	(19)
17	(16)
18	(25)
19	(16)
20	(8)
21	(12)
22	(10) extra credit
Total	(390)

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

Scratch Paper

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.

DO NOT TEAR OUT THIS PAGE!!

Question 1, page 2 (24 pts) Write the word or symbol that best completes the sentences.

1.1 _____

1.2 _____

1.3 _____

1.4 _____

1.5 _____

1.6 _____

1.7 _____

1.8 _____

1.9 _____

1.10 _____

1.11 _____

1.12 _____

Question 2, page 2 (2 pts) Write the letter (A, B, C, or D) corresponding to the correct rank (most to least acidic)

2 _____

Question 3, page 3 (2 pts) Write the letter (A, B, C, or D) corresponding to the correct rank (most to least reactive with a wicked strong electrophile)

3 _____

Question 4, page 3 (2 pts) Write the letter (A, B, C, or D) corresponding to the correct rank (most to least basic)

4 _____

Question 5, page 3 (2 pts) Write the letter (A, B, C, or D) corresponding to the correct rank (most to least reactive with a nucleophile like water)

5 _____

Question 6, page 4 (14 pts) Write the hybridization state of the indicated N atom

6.1 _____ 6.2 _____ 6.3 _____ 6.4 _____

6.5 _____ 6.6 _____ 6.7 _____

Question 7, page 4 (2 pts) Most reactive with a nucleophile

7 _____

Question 8, page 4 (2 pts) Most reactive with a nucleophile

8 _____

Question 9, page 5 (4 pts) Write the pH (2.0, 5.0, 8.0, 11.0) corresponding to the protonation state of the molecule

9 _____

Question 10, page 5 (6 pts) Write the type of glycosidic bond indicated by the arrow. Answers might be α -1,4 or β -1,2, etc.

10.1 _____ 10.2 _____ 10.3 _____

Question 11, page 6 (14 pts) Label the nucleophile and electrophile with A and B as appropriate for each pair of reagents.

11.1 Nucleophile: _____ Electrophile _____

11.2 Nucleophile: _____ Electrophile _____

11.3 Nucleophile: _____ Electrophile _____

11.4 Nucleophile: _____ Electrophile _____

11.5 Nucleophile: _____ Electrophile _____

11.6 Nucleophile: _____ Electrophile _____

11.7 Nucleophile: _____ Electrophile _____

Question 12, page 7 (6 pts)

12.1 _____ 12.2 _____ 12.3 _____

Question 13, page 7 (6 pts) Write the word or symbol that best completes the sentences.

13.1 _____

13.2 _____

13.3 _____

Question 14, page 7 (4 pts) Write the word or symbol that best completes the sentences.

14.1 _____

14.2 _____

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

1. (24 pts) On page 1, fill in each blank with the word or words that best complete(s) the following sentences.

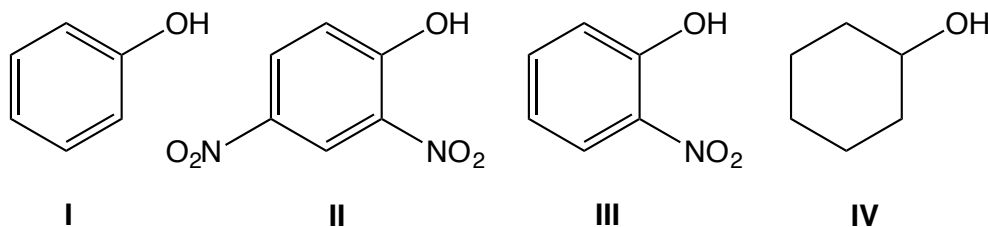
NMR spectra record the energy (plotted as frequency) necessary for hydrogen _____ (1.1) to be excited from the lower energy spin state to the higher energy spin state in the presence of a strong external _____ (1.2) field.

The greater the electron density around a nucleus, the (more shielded or less shielded) _____ (1.3) it is, and the (lower or higher) _____ (1.4) the energy of electromagnetic radiation required to flip its nuclear _____ (1.5).

A five-membered ring formed by a carbohydrate is called a _____ (1.6) while a six-membered ring formed by a carbohydrate is called a _____ (1.7). In both cases, the ring is formed by an -OH group reacting with a carbonyl to give a cyclic _____ (1.8). When looking at a Fischer projection, groups that are horizontal are oriented (toward or away from) _____ (1.9) you, while groups that are vertical are oriented (toward or away from) _____ (1.10) you.

Both starch and cellulose are polymers of glucose, but starch has (alpha or beta) _____ (1.11) glucose linkages, so it is bent and therefore not rigid (potatoes). Cellulose has the glucose monomers linked via (alpha or beta) _____ (1.12) glucose linkages so it is flat and the chains can pack together nicely to create rigid cellulose (wood).

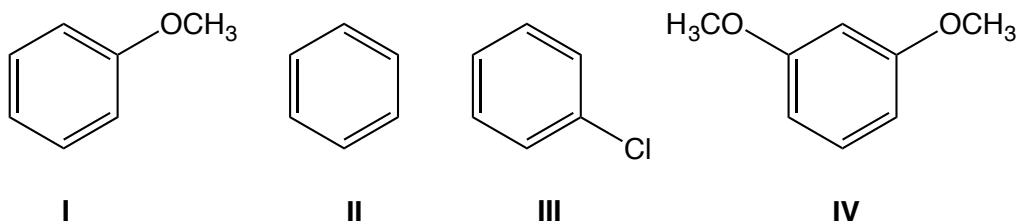
2. (2 pts) On page 1, write the letter (A, B, C, or D) corresponding to the order of acidity of the following molecules. Rank them starting with the strongest acid and ending with the weakest acid.



- A: IV > I > III > II**
B: II > III > I > IV
C: IV > II > III > I
D: I > IV > III > II

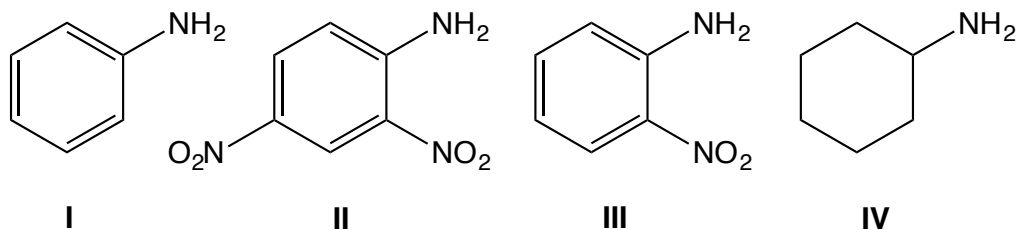
Write your answers to these questions on the answer sheet on page 1

3. (2 pts). On page 1, write the letter (A, B, C, or D) corresponding to the order of reactivity of the following molecules reacting with a wicked strong electrophile. Rank them starting with the most reactive (reacts the fastest) and ending with the least reactive (reacts the slowest).



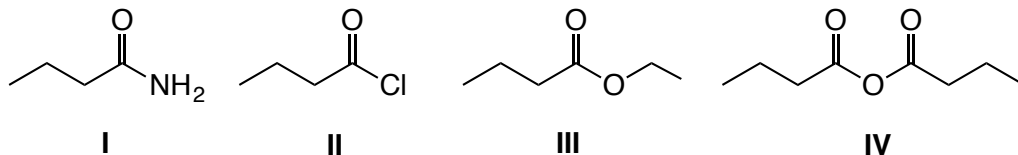
- A: IV > I > II > III
 B: IV > I > III > II
 C: III > II > I > IV
 D: III > II > IV > I

4. (2 pts) On page 1, write the letter (A, B, C, or D) corresponding to the order of base strength of the following molecules. Rank them starting with the strongest base and ending with the weakest base.



- A: IV > I > III > II
 B: II > III > I > IV
 C: IV > II > III > I
 D: II > III > IV > I

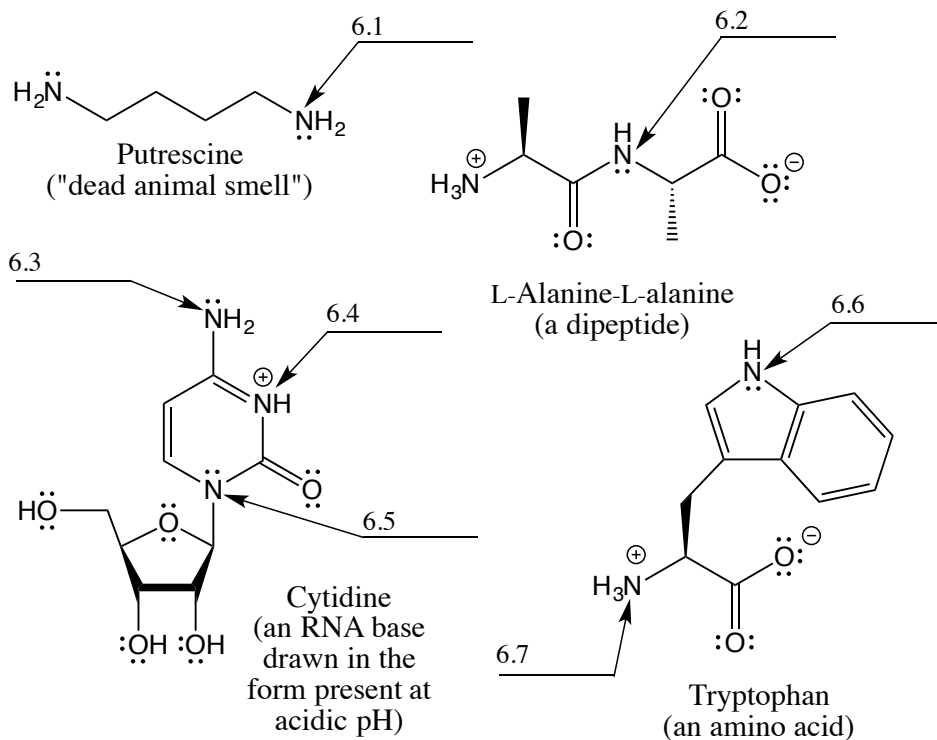
5. (2 pts). On page 1, write the letter (A, B, C, or D) corresponding to the order of reactivity of the following molecules reacting with a nucleophile such as water. Rank them starting with the most reactive (reacts the fastest) and ending with the least reactive (reacts the slowest).



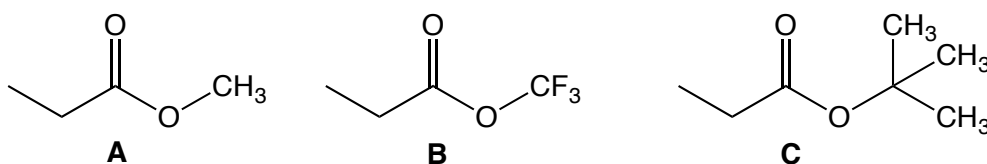
- A: I > II > III > IV
 B: II > IV > I > III
 C: III > II > IV > I
 D: II > IV > III > I

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

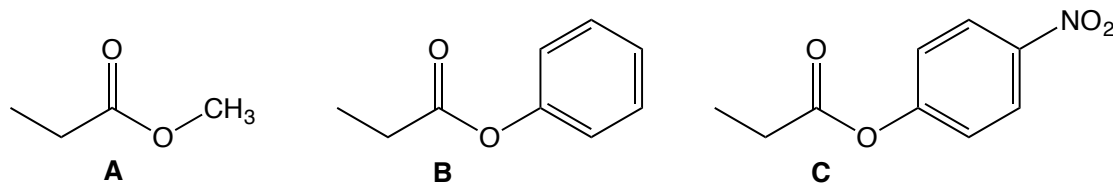
6. (14 pts). Following are several biological molecules with nitrogen atoms. On page 1, write the hybridization state of each nitrogen atom indicated by an arrow.



7. (2 pts). On page 1, write the letter (A, B or C) corresponding to the molecule that is most reactive (reacts fastest) with a nucleophile.

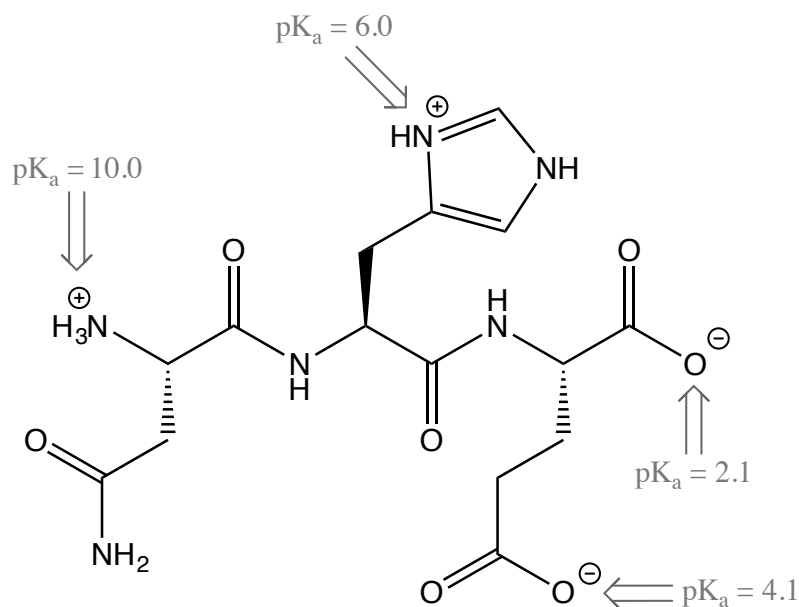


8. (2 pts). On page 1, write the letter (A, B or C) corresponding to the molecule that is most reactive (reacts fastest) with a nucleophile.

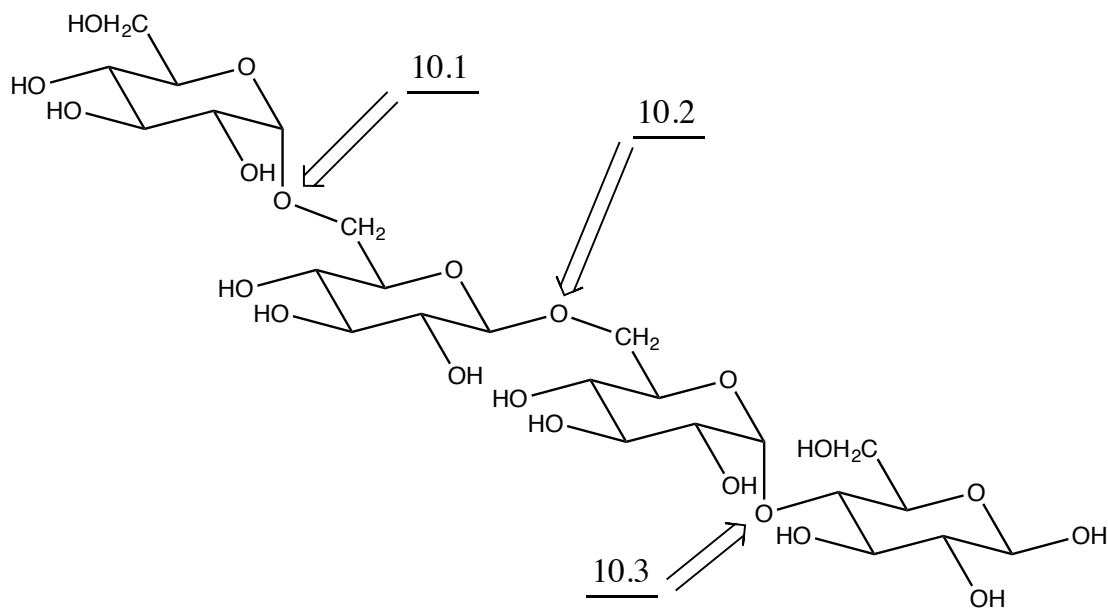


Write your answers to these questions on the answer sheet on page 1

9. (4 pts). For the following peptide, the relevant pK_a values are provided. Based on the protonation states of the different functional groups, is the pH of the solution 2.0, 5.0, 8.0 or 11.0?

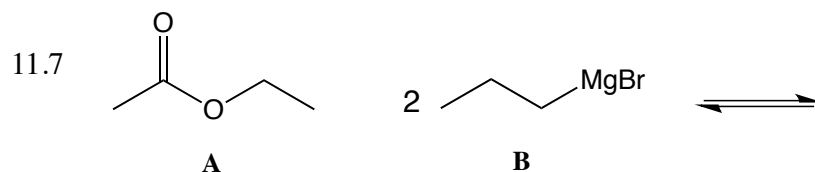
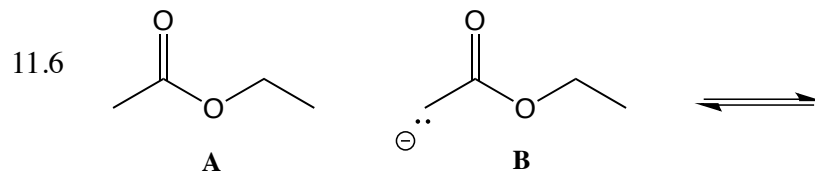
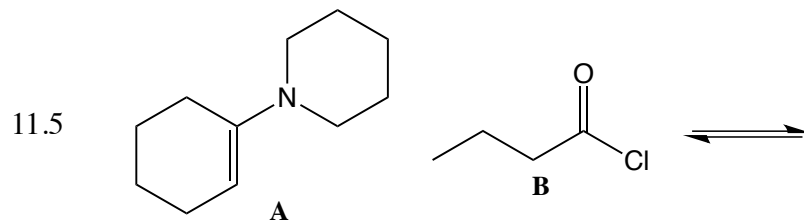
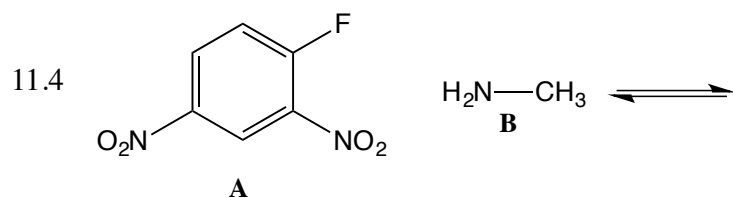
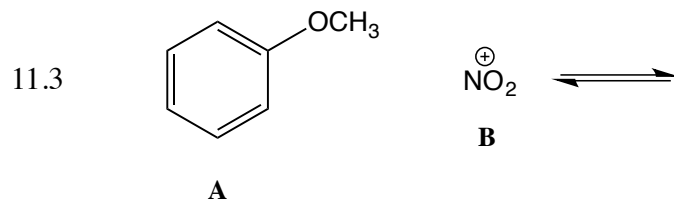
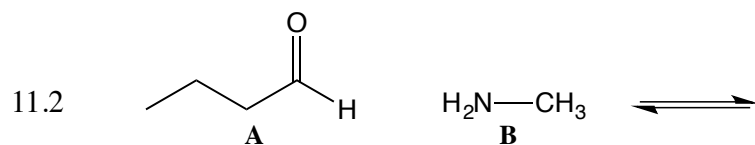
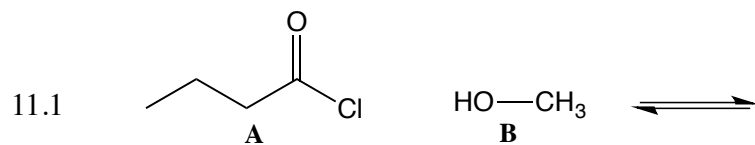


10. (6 pts). On page 1, for the following tetrasaccharide, write the type of glycosidic bond indicated by the arrows. Answers should be in the form α -1,4 or β -1,2, etc.



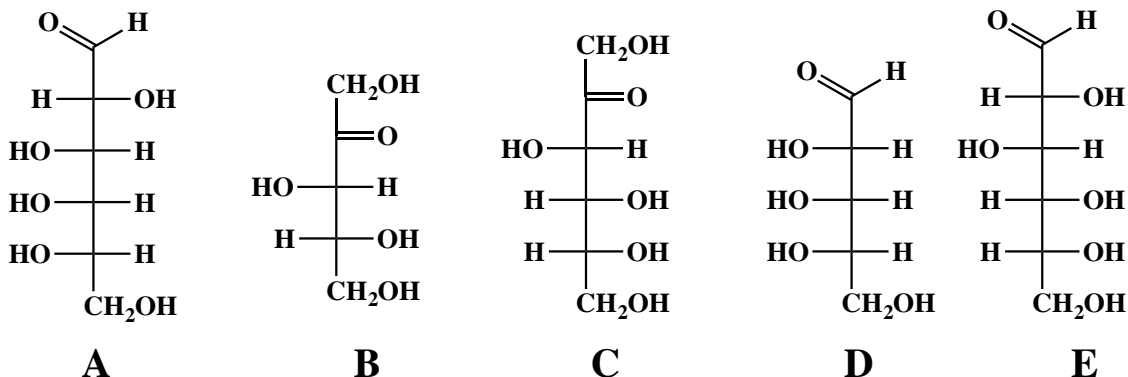
Write your answers to these questions on the answer sheet on page 1

11. (2 pts each). On Page 1, for the following sets of reagents write the correct letter A or B to identify which is the nucleophile and which is the electrophile.



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

12. (6 pts). Consider the following five carbohydrates A-E, drawn as Fischer projections.



12.1 On page 1, write the letter (A-E) corresponding to which of the five carbohydrates is a D-ketopentose

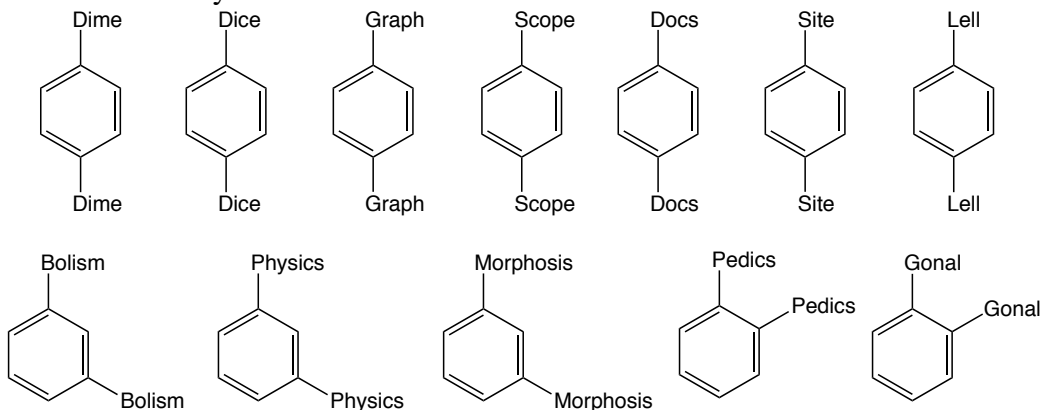
12.2 On page 1, write the letter (A-E) corresponding to which of the five carbohydrates is an L-aldohexose?

12.3 How many of the five carbohydrates are D?

13. (6 pts) According to the Golden Rules of Chemistry numbers 5-7, delocalization of three different things “over a larger area is stabilizing”. On page 1, write those three things that are stabilized when delocalized over a larger area.

14. (4 pts) According to the Golden Rule of Chemistry number 8, “Reactions will occur if the (14.1) _____ are more stable than the reactants and the (14.2) _____ barrier is low enough.” On page 1, fill in the two words that complete the Golden Rule of Chemistry number 8.

These are here to make you smile:



Signature _____

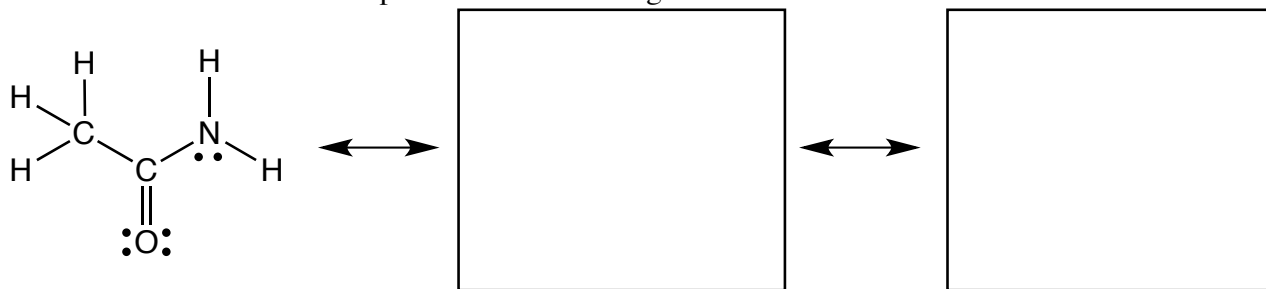
Pg 8 _____ (24)

15. (2 pts) What is the most important question in chemistry?

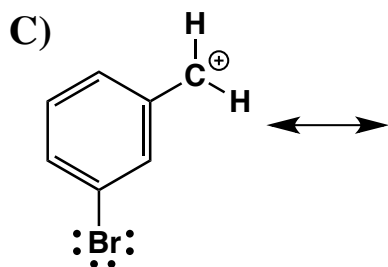
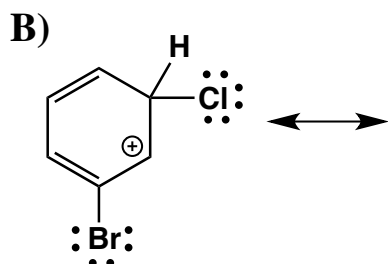
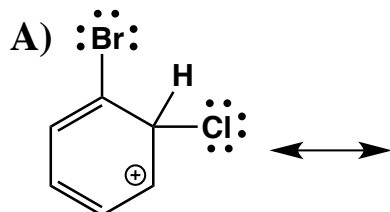
?

16. (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.

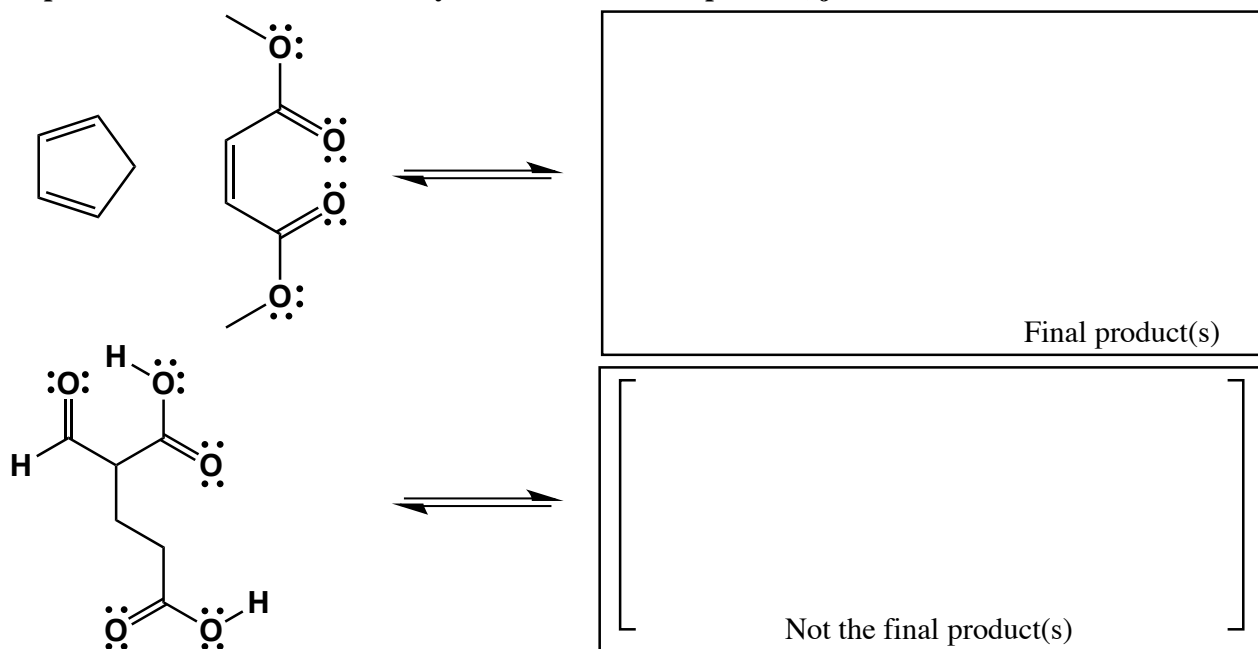
17. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



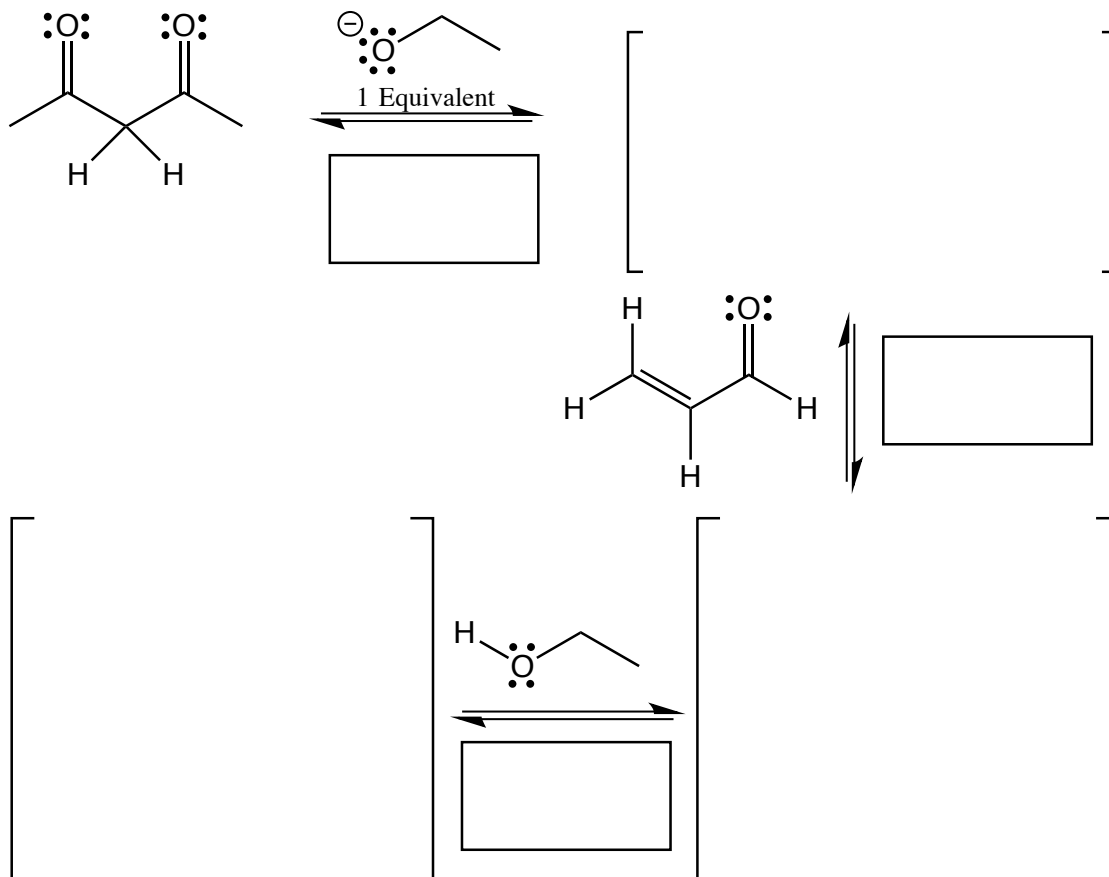
18. (16 pts) Draw all of the important contributing structures for the following ions. You do NOT need to draw arrows for this one. Draw all charges and lone pairs. Note: you will have to decide how many contributing structures are important, and that number will vary. Also, you only need to draw the H atoms shown below. You do not have to draw any of the others if you do not want to draw them.



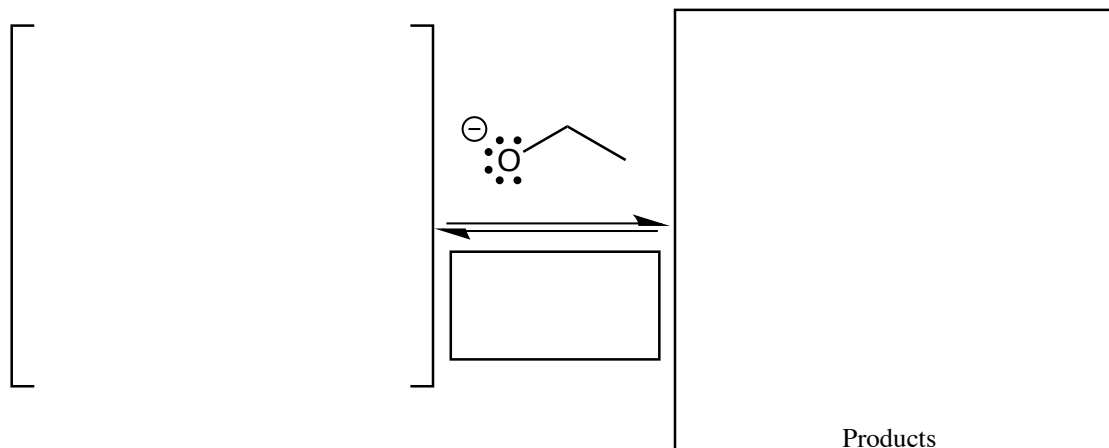
19. (15 pts) Draw arrows on the following molecules then the product(s) you expect to be formed in these reactions. Notice, in the second reaction you will actually be drawing an intermediate, not a final product. There is not need for you to draw the final product, just the intermediate.



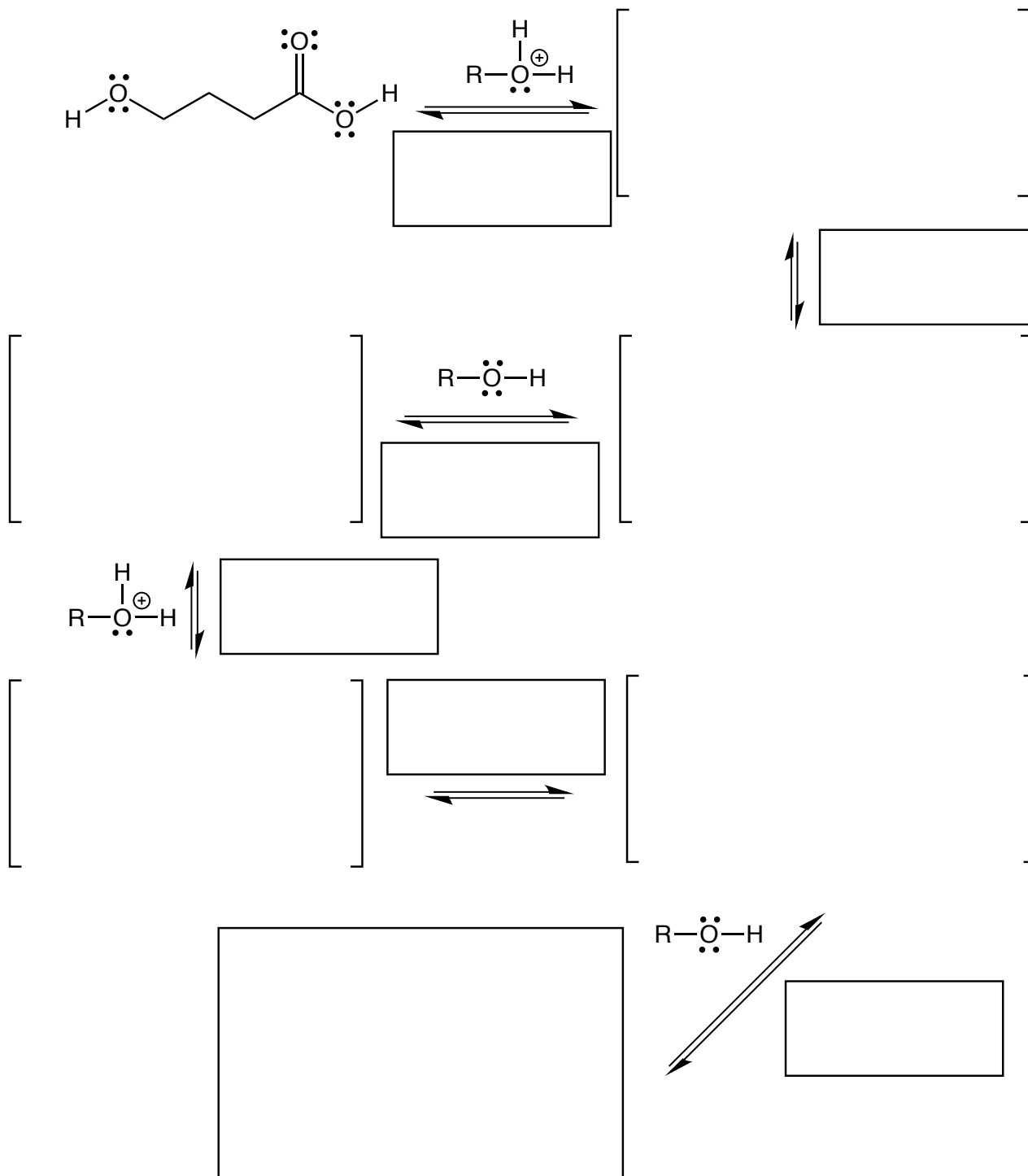
20. (26 pts) Complete the mechanism for the following Michael reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN 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.).



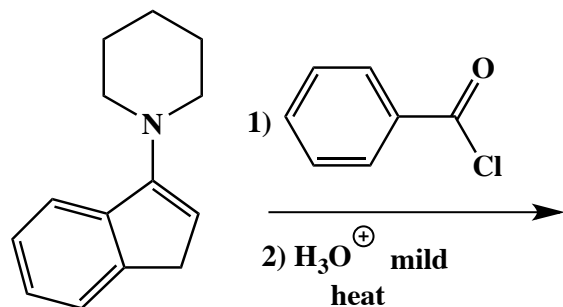
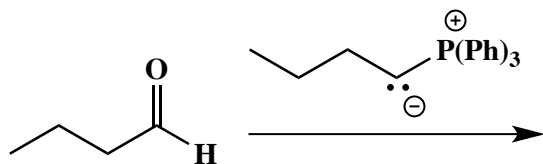
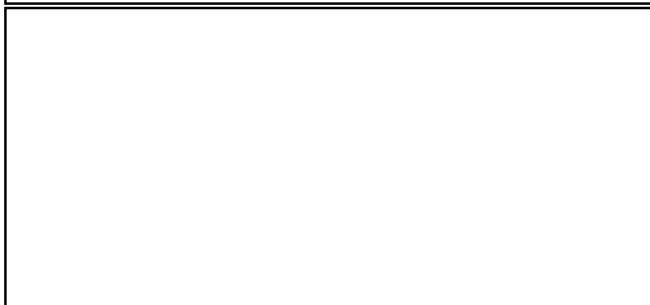
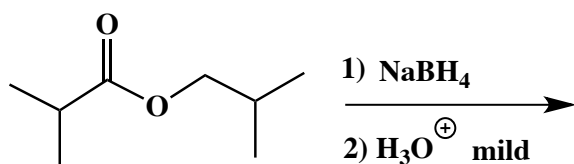
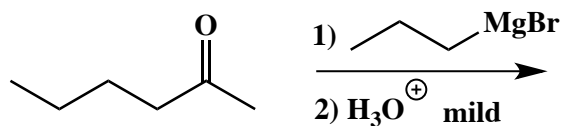
Tautomerization



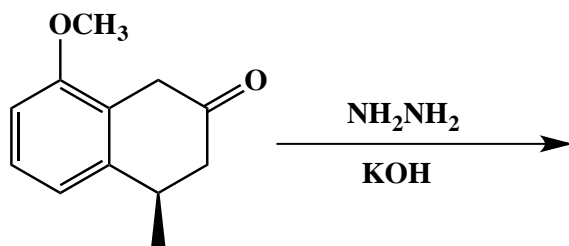
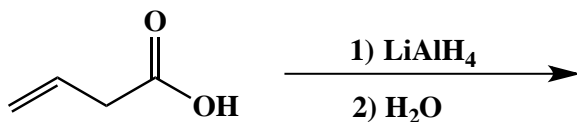
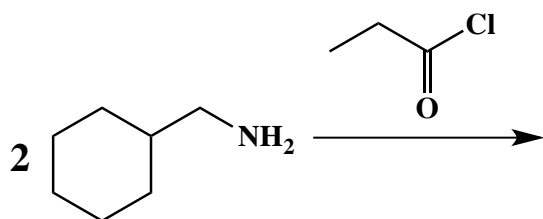
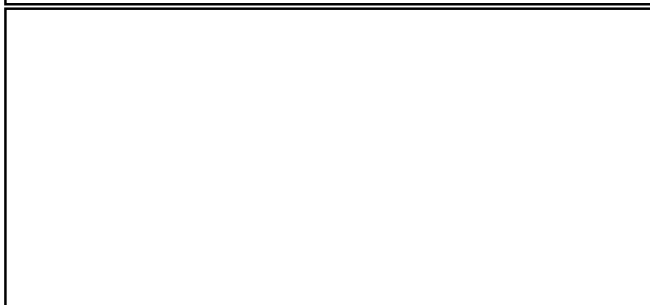
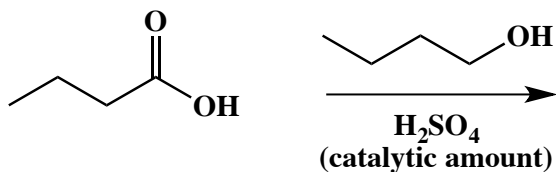
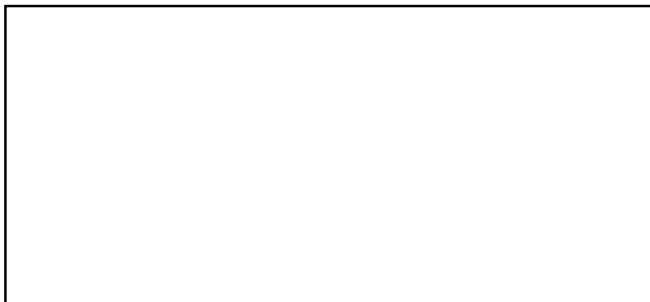
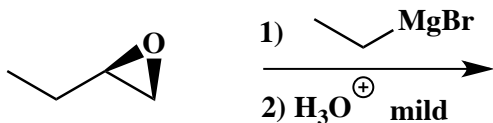
21. (35 pts) Complete the mechanism for the following lactone formation reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS 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.).



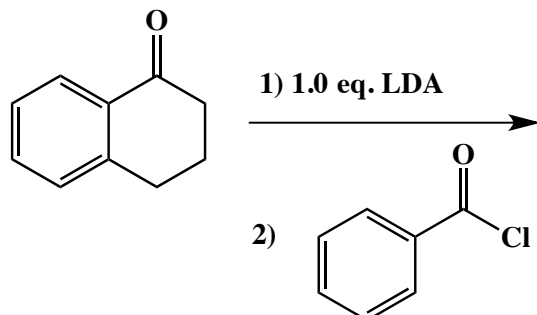
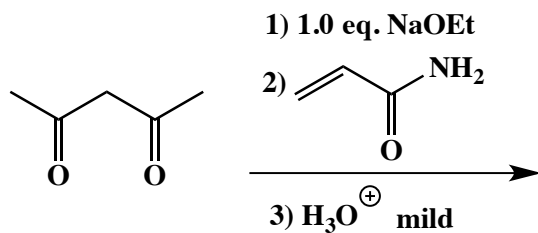
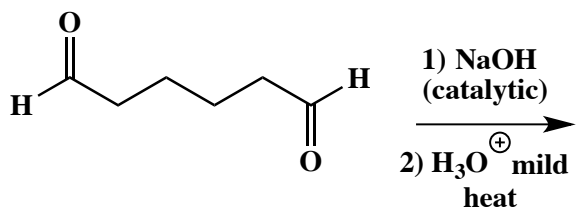
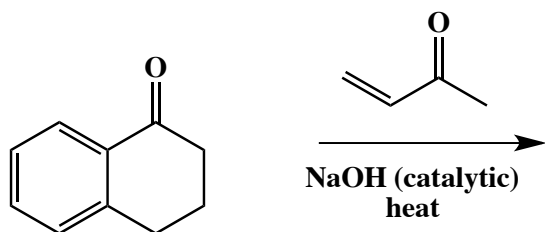
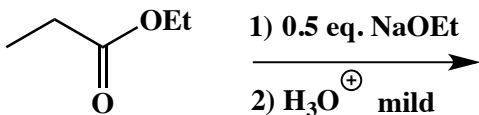
22. (3, 4, 5 or 6 pts.) Write the predominant carbon containing product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH.** If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and write racemic. **If a new chiral center is created but the products DO NOT REPRESENT A RACEMIC MIXTURE then you MUST USE WEDGES AND DASHES TO INDICATE STEREOCHEMISTRY.** Also, do not worry about balancing these equations, you just need to show us the all of the major carbon-containing products of these transformations.



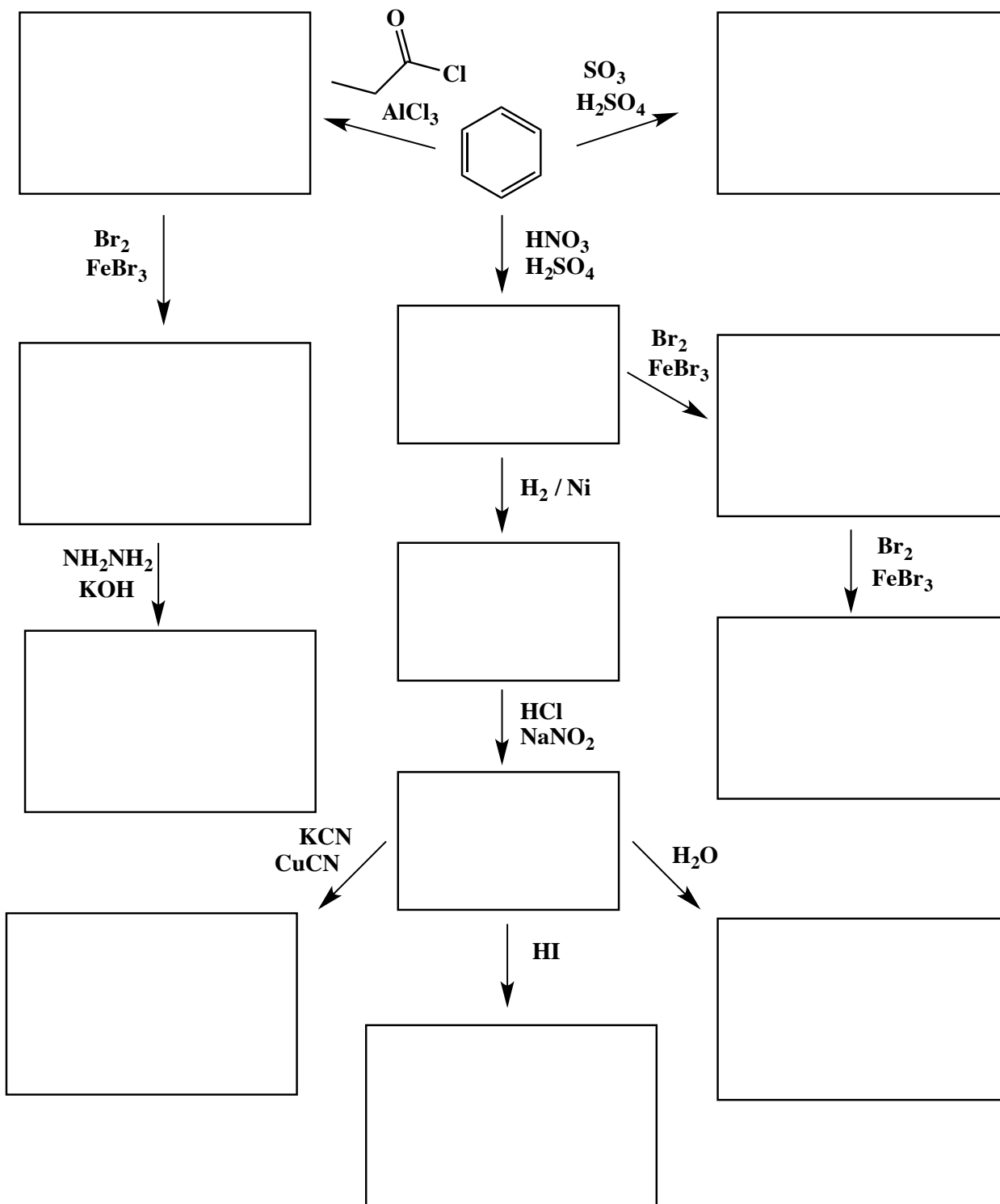
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22. (3, 4 or 5 pts.) Write the predominant carbon containing product or products that will occur for each transformation. If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, 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.

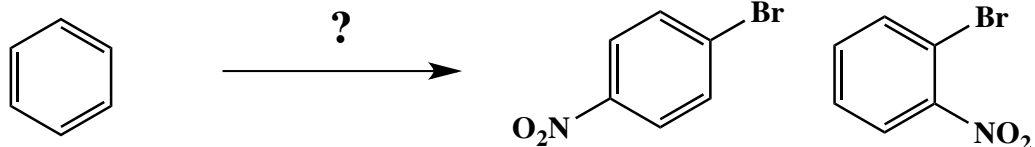


23. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic"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

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

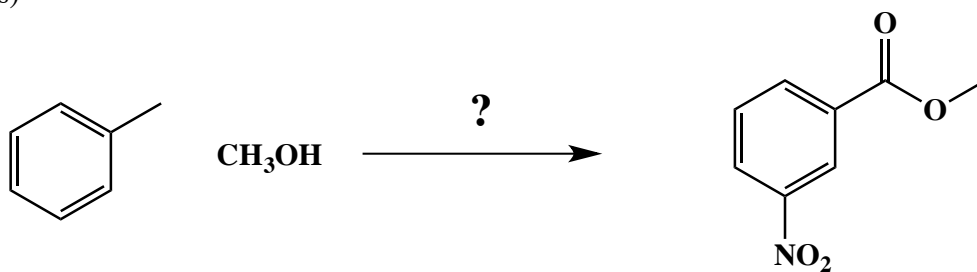
(4 pts)

A)



(10 pts)

B)

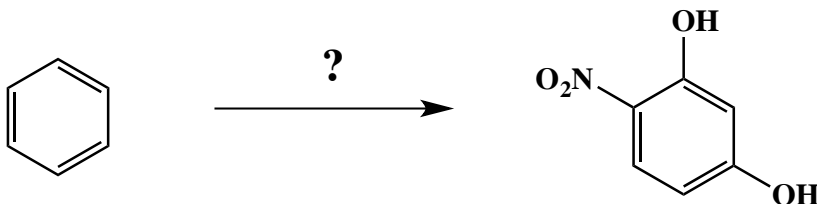


23. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic"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

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

(16 pts)

C)

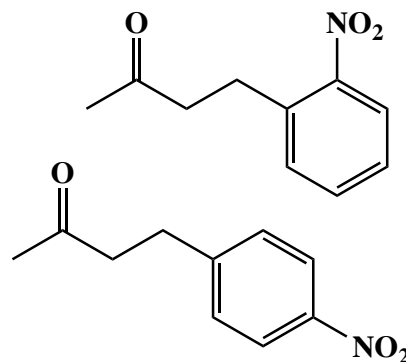
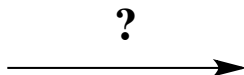
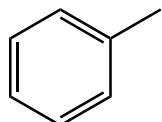
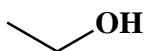


23. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic"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

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

(25 pts)

D)



Signature _____

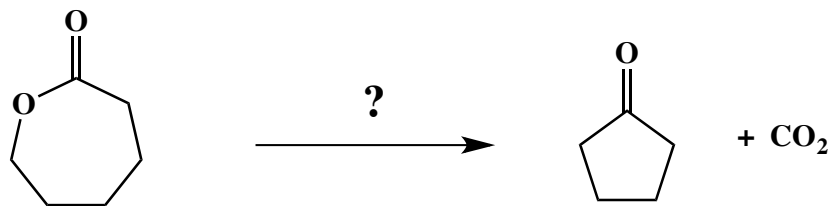
Pg 19 _____(16)

23. 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.

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

(16 pts)

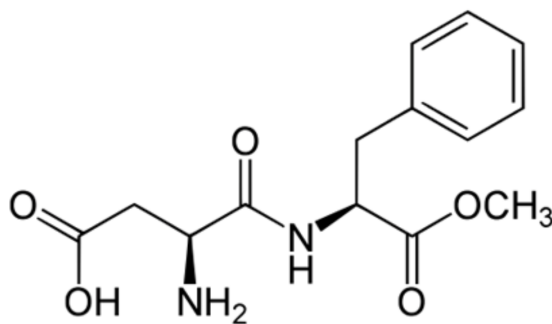
E)



24. (12 pts total). Here is an apply what you know problem. The ingredient label for diet coke reads:

Carbonated water, caramel color, aspartame, **phosphoric acid**, potassium benzoate (to protect taste), natural flavors, citric acid, caffeine.

Phosphoric acid is added to soft drinks to provide for a tangy taste as well as stabilize the carbonic acid present (i.e. carbonation). An unintended consequence of having phosphoric acid in diet soda is that the pH is relatively acidic. **For example, the pH of diet coke is about 3.** The unintended consequence of this is that aspartame, the artificial sweetener in diet coke, is chemically modified when diet coke is heated (left in the sun for example). The absence of sweetness indicates the can or bottle was left out in the sun or other source of heat for too long. The following is the structure of aspartame that I copied from a website:



The structure of the artificial sweetener copied from a website
(<http://www.foodengineeringmag.com/articles/89664-another-look-at-aspartame>)

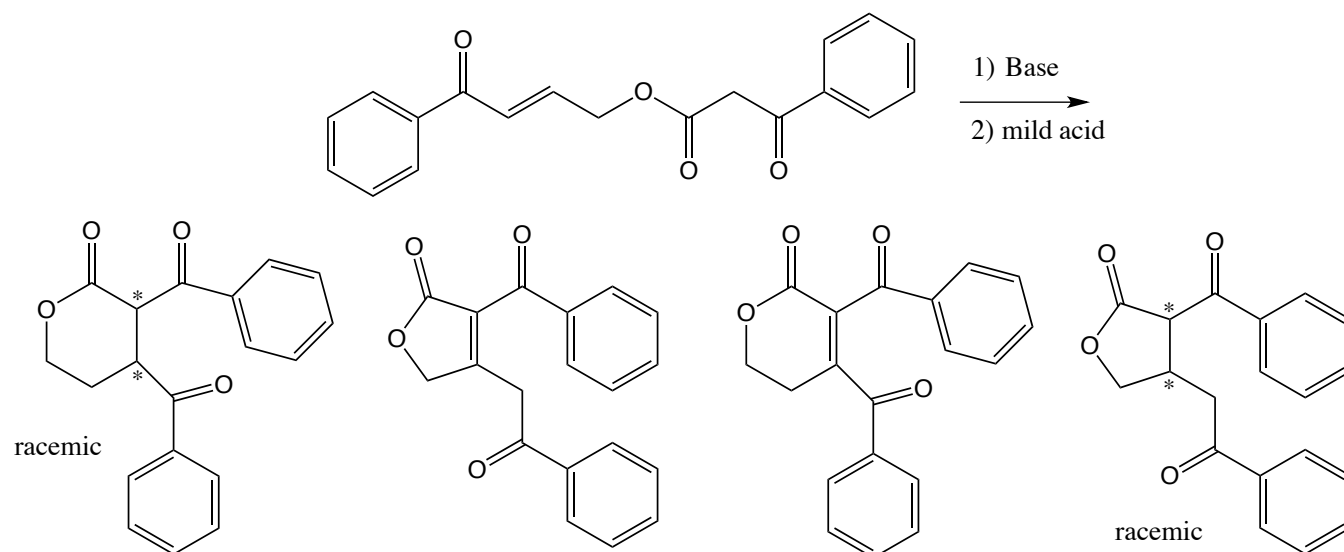
24.1 (4 pts) Based on the structure of aspartame shown above, in one or two sentences total, explain why diet coke loses its sweetness when left out in the sun.

24.2 (4 pts) There is a problem with the above structure I copied from a website. In one or two sentences total, explain what is wrong with the structure.

24.3 (2 pts) Aspartame is a chiral molecule, present as the single enantiomer shown. How many chiral centers are in aspartame?

24.4 (2 pts) How many different stereoisomers are possible for aspartame?

25 (8 pts) The following intramolecular Michael reaction is used to prepare important classes of molecules. From the following list, circle the product of the reaction shown:



Signature _____

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22. This one is extra credit. 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.

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

(10 pts)



I very much enjoyed getting to know you this semester. Second semester O Chem is a difficult but rewarding journey. We started with NMR, ended with aromatic chemistry, and saw plenty of new C-C bonds along the way. I hope that all of you have gained a new understanding and appreciation for the molecules that surround us and make modern life possible. I also hope you now have a very strong molecular foundation upon which to build your understanding of biology and medicine. Have a safe and wonderful summer and remember to run every chance you get. And when you see me on campus or running around town lake, please remember to say “Where are the electrons?”