x

NAME (Print): _____

SIGNATURE: _____

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

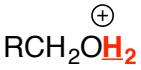
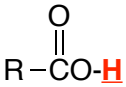
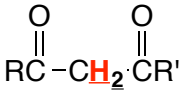
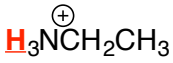
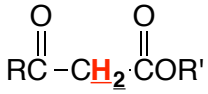
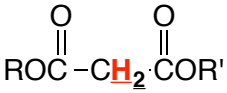
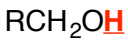
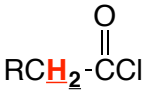
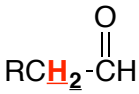
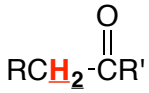
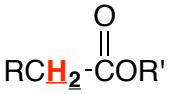
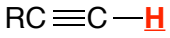
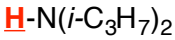
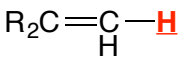
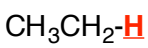
Page	Points	
1		(90)
8		(24)
9		(31)
10		(26)
11		(35)
12		(20)
13		(21)
14		(15)
15		(37)
16		(19)
17		(16)
18		(25)
19		(16)
20		(8)
21		(12)
22		(10) extra credit
Total		(390)

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		-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 _____(90)

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 nuclei

1.2 magnetic

1.3 more shielded

1.4 lower

1.5 spin

1.6 furanose

1.7 pyranose

1.8 hemiacetal

1.9 toward

1.10 away from

1.11 alpha (α)

1.12 beta (β)

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

2 B

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 A

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

4 A

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 D

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

6.1 sp^3 6.2 sp^2 6.3 sp^2 6.4 sp^2

6.5 sp^2 6.6 sp^2 6.7 sp^3

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

7 B

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

8 C

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 5.0

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

10.1 α-1,6 10.2 β-1,6 10.3 α-1,4

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: B Electrophile A

11.2 Nucleophile: B Electrophile A

11.3 Nucleophile: A Electrophile B

11.4 Nucleophile: B Electrophile A

11.5 Nucleophile: A Electrophile B

11.6 Nucleophile: B Electrophile A

11.7 Nucleophile: B Electrophile A

Question 12, page 7 (6 pts)

12.1 B 12.2 A 12.3 3

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

13.1 charges

13.2 unpaired electron density (any order)

13.3 pi electrons

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

14.1 products

14.2 energy

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.**

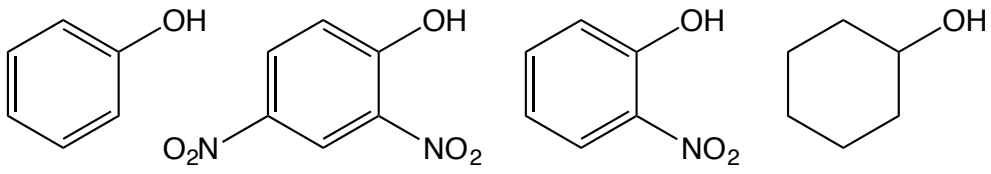
NMR spectra record the energy (plotted as frequency) necessary for hydrogen _____ (1.1) to be excited from the lower energy spin state to the higher energy spin state in the presence of a strong external _____(1.2) field.

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.**

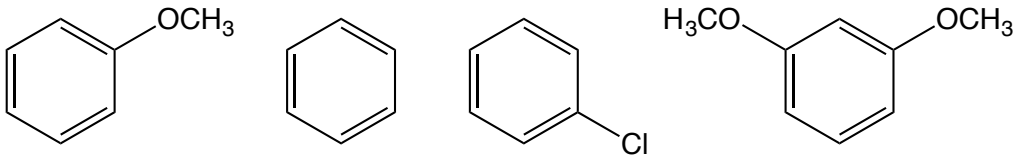


I **II** **III** **IV**

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

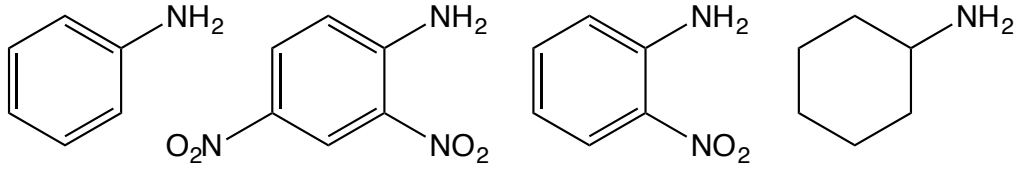
3. (2 pts). **On page 1, write the letter (A, B, C, or D) corresponding to the order of reactivity of the following molecules reacting with a wicked strong electrophile. Rank them starting with the most reactive (reacts the fastest) and ending with the least reactive (reacts the slowest).**



I **II** **III** **IV**

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

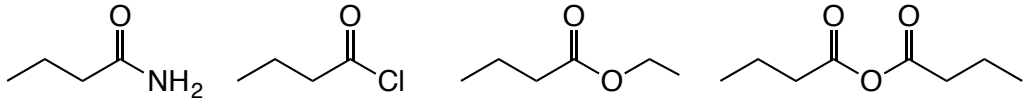
4. (2 pts) **On page 1, write the letter (A, B, C, or D) corresponding to the order of base strength of the following molecules. Rank them starting with the strongest base and ending with the weakest base.**



I **II** **III** **IV**

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).**

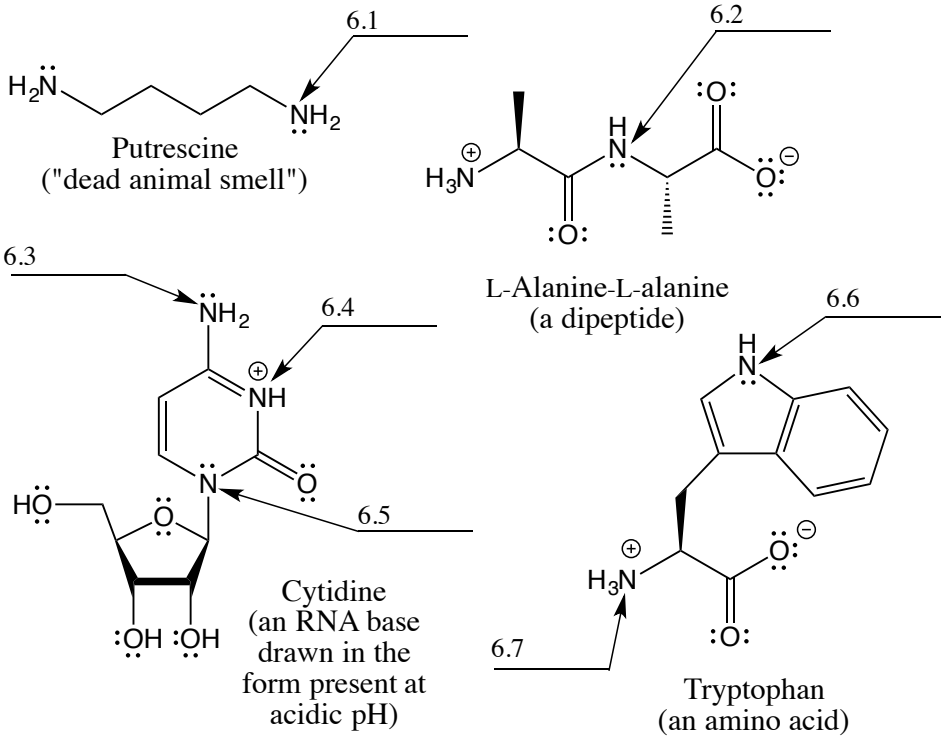


I **II** **III** **IV**

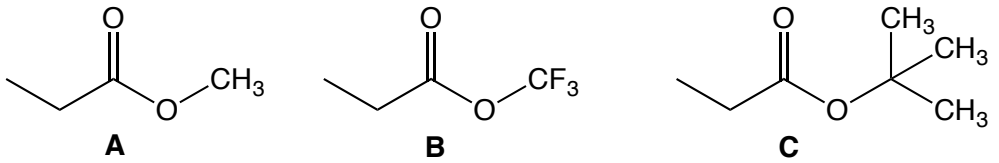
A: I > II > III > IV
B: II > IV > I > III
C: III > II > IV > I
D: II > IV > III > I

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

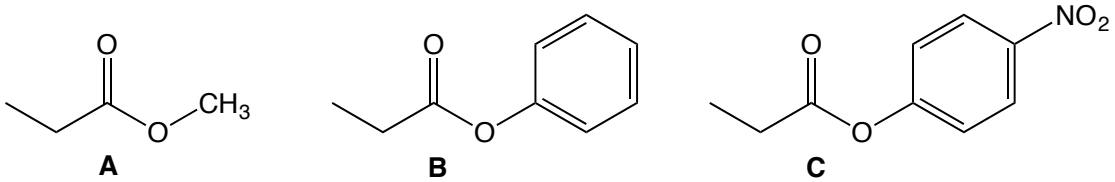
6. (14 pts). **Following are several biological molecules with nitrogen atoms. On page 1, write the hybridization state of each nitrogen atom indicated by an arrow.**



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**.

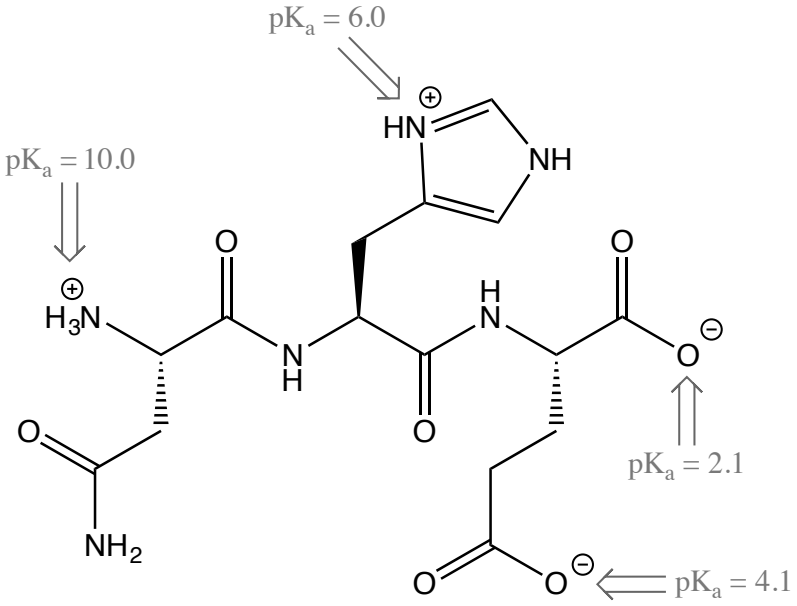


8. (2 pts). **On page 1, write the letter (A, B or C) corresponding to the molecule that is most reactive (reacts fastest) with a nucleophile**.

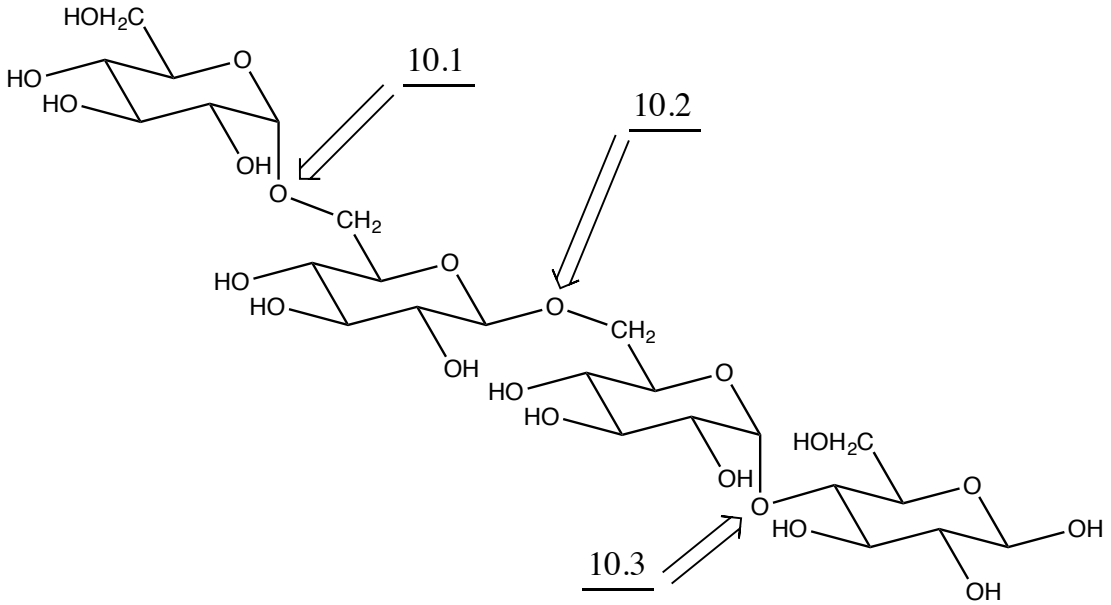


Write your answers to these questions on the answer sheet on page 1

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?**

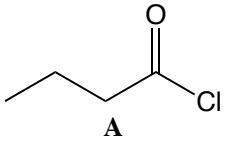


10. (6 pts). **On page 1, for the following tetrasaccharide, write the type of glycosidic bond indicated by the arrows. Answers should be in the form α-1,4 or β-1,2, etc.**

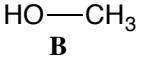


Write your answers to these questions on the answer sheet on page 1

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.

11.1 

A



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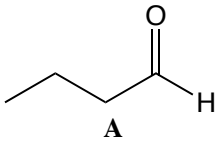
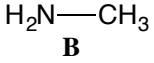
11.2 

A



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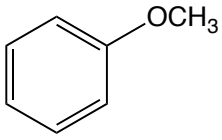
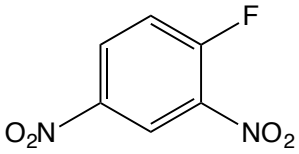
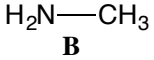
11.3 

A

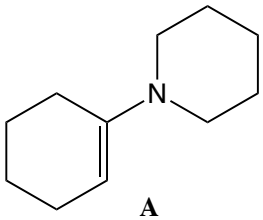
B

11.4 

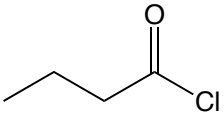
A



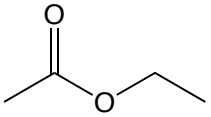
B

11.5 

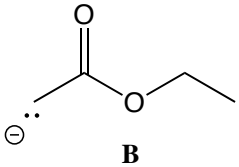
A



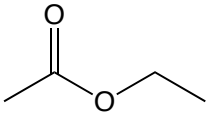
B

11.6 

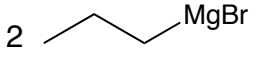
A



B

11.7 

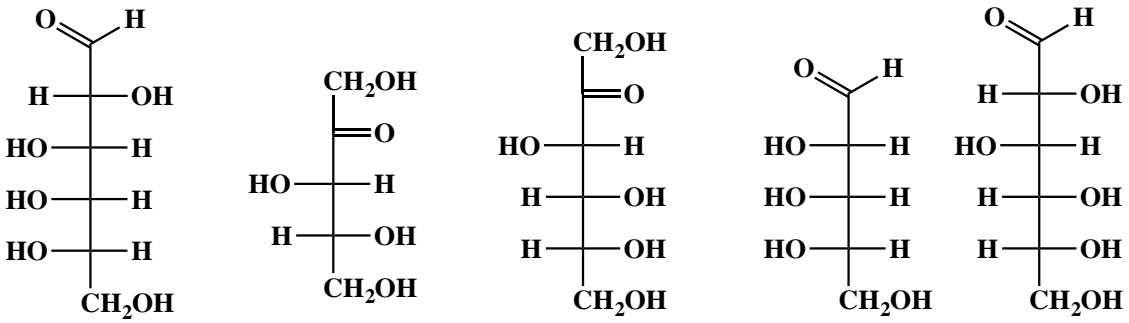
A



B

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

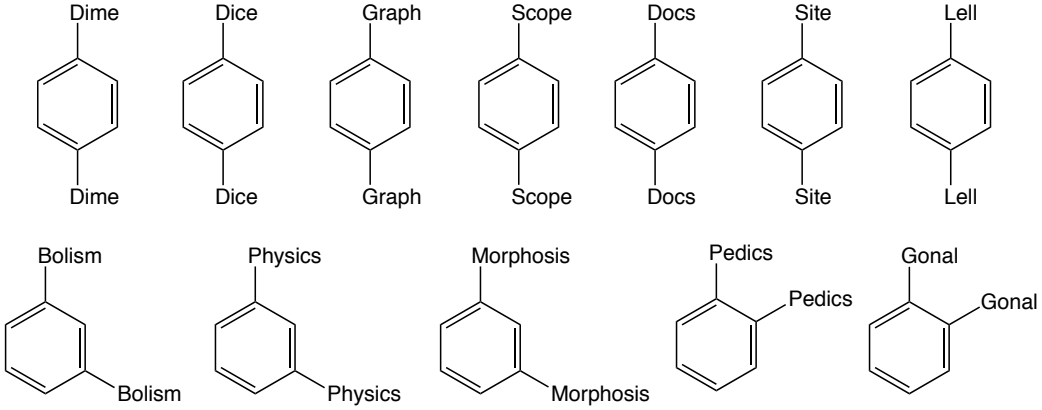
12.2 On page 1, write the letter (A-E) corresponding to which of the five carbohydrates is an L-aldohexose?

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:



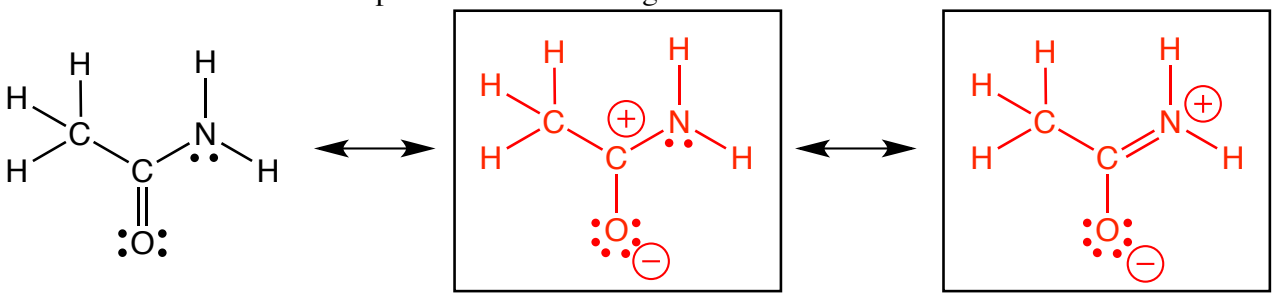
15. (2 pts) What is the most important question in chemistry?

Where are the electrons ?

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 wil be looking for a minimum of 7 key points here.

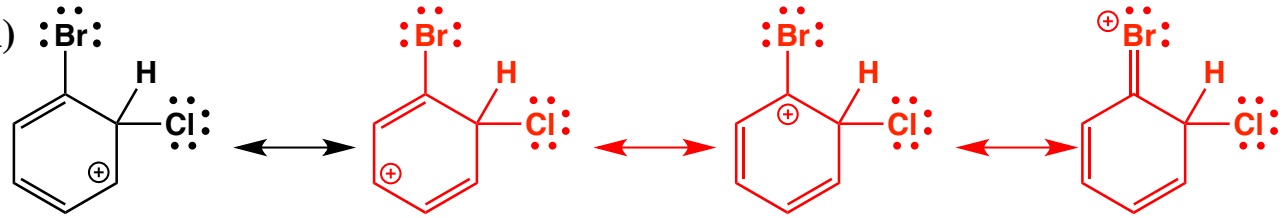
The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on the **same principles as NMR**, namely the **flipping (i.e. resonance) of nuclear spins of protons** by **radio frequency irradiation** when a patient is placed in a **strong magnetic field**. **Magnetic field gradients** are used to gain imaging information, and **rotation of the gradient around the center of the object** gives imaging in an entire plane **(i.e. slice inside patient)**. In an MRI image, you are looking at **individual slices** that **when stacked make up the three-dimensional image** of **relative amounts of protons, especially the protons from water and fat, in the different tissues**.

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.

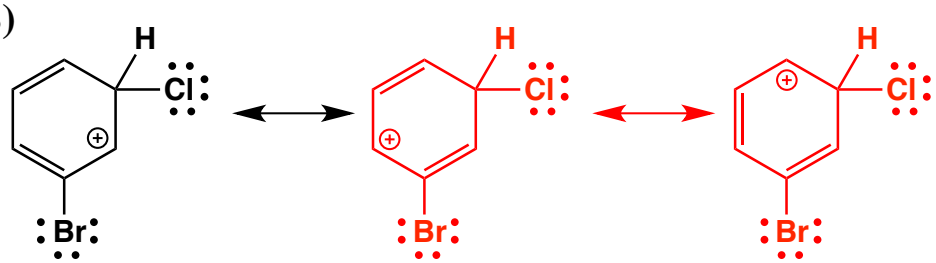


18. (16 pts) **Draw all of the <u>important</u> contributing structures for the following ions. You do NOT need to draw arrows for this one. Draw all charges and lone pairs. Note: you will have to decide how many contributing structures are important, and that number will vary. Also, you only need to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

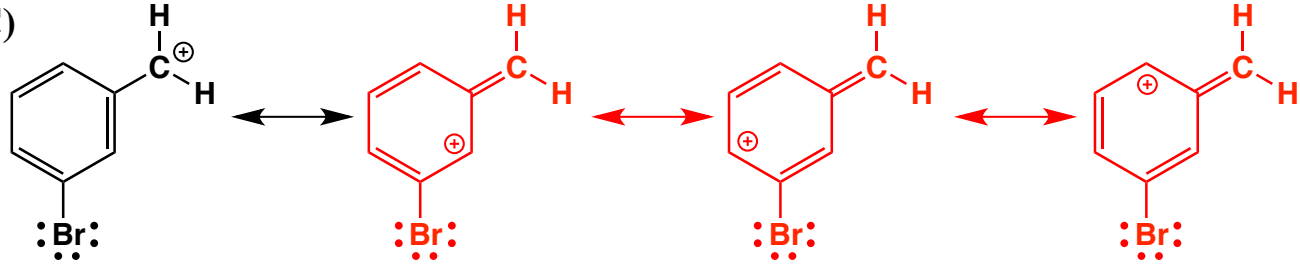
A)



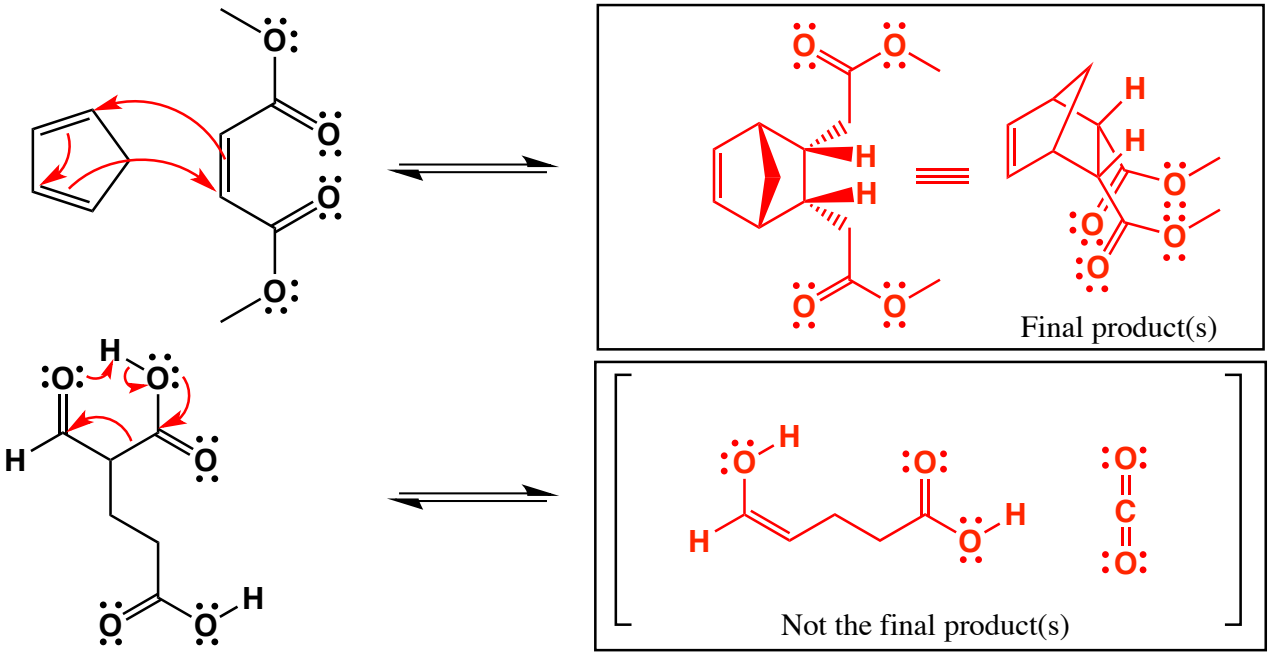
B)



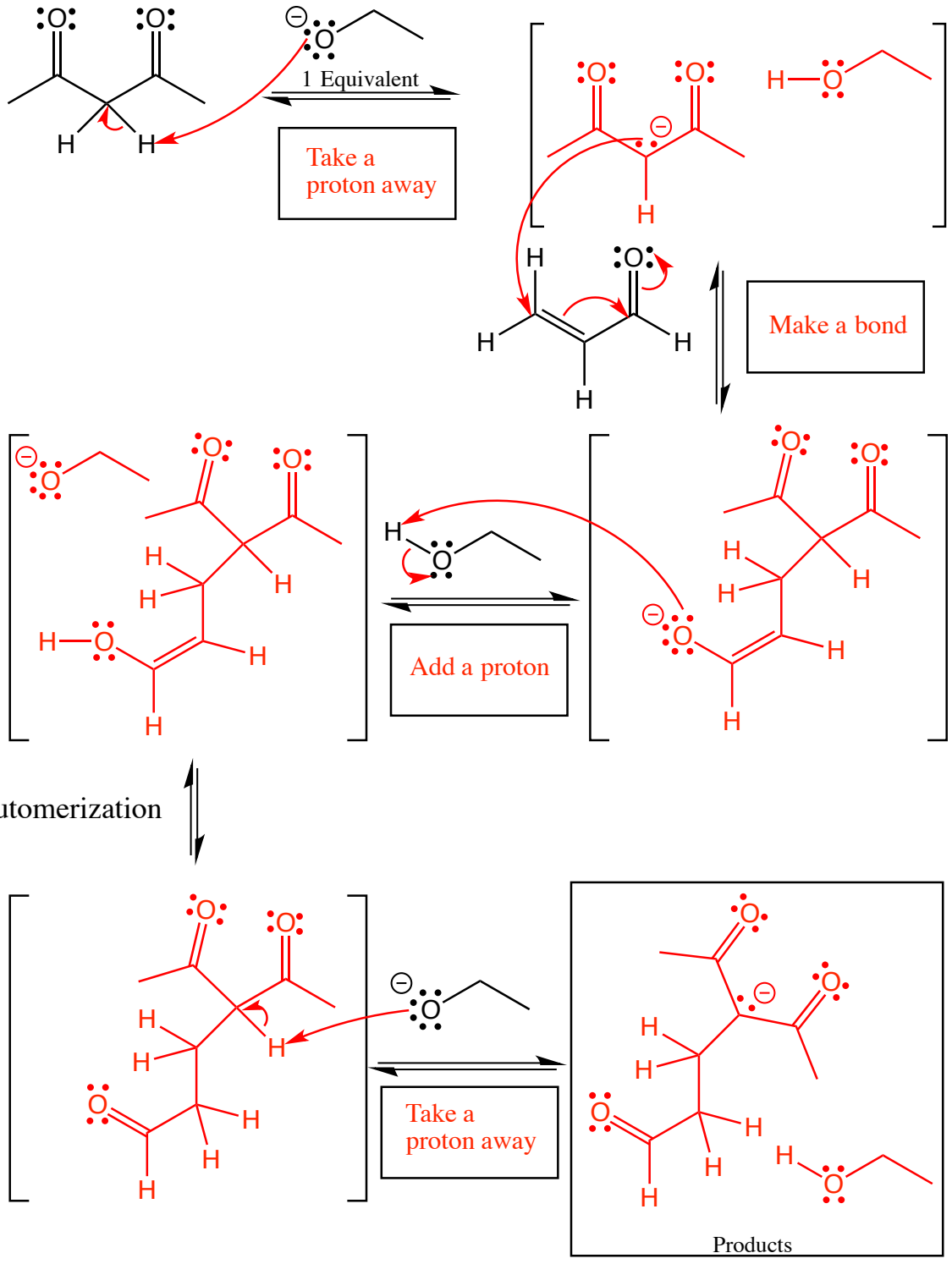
C)



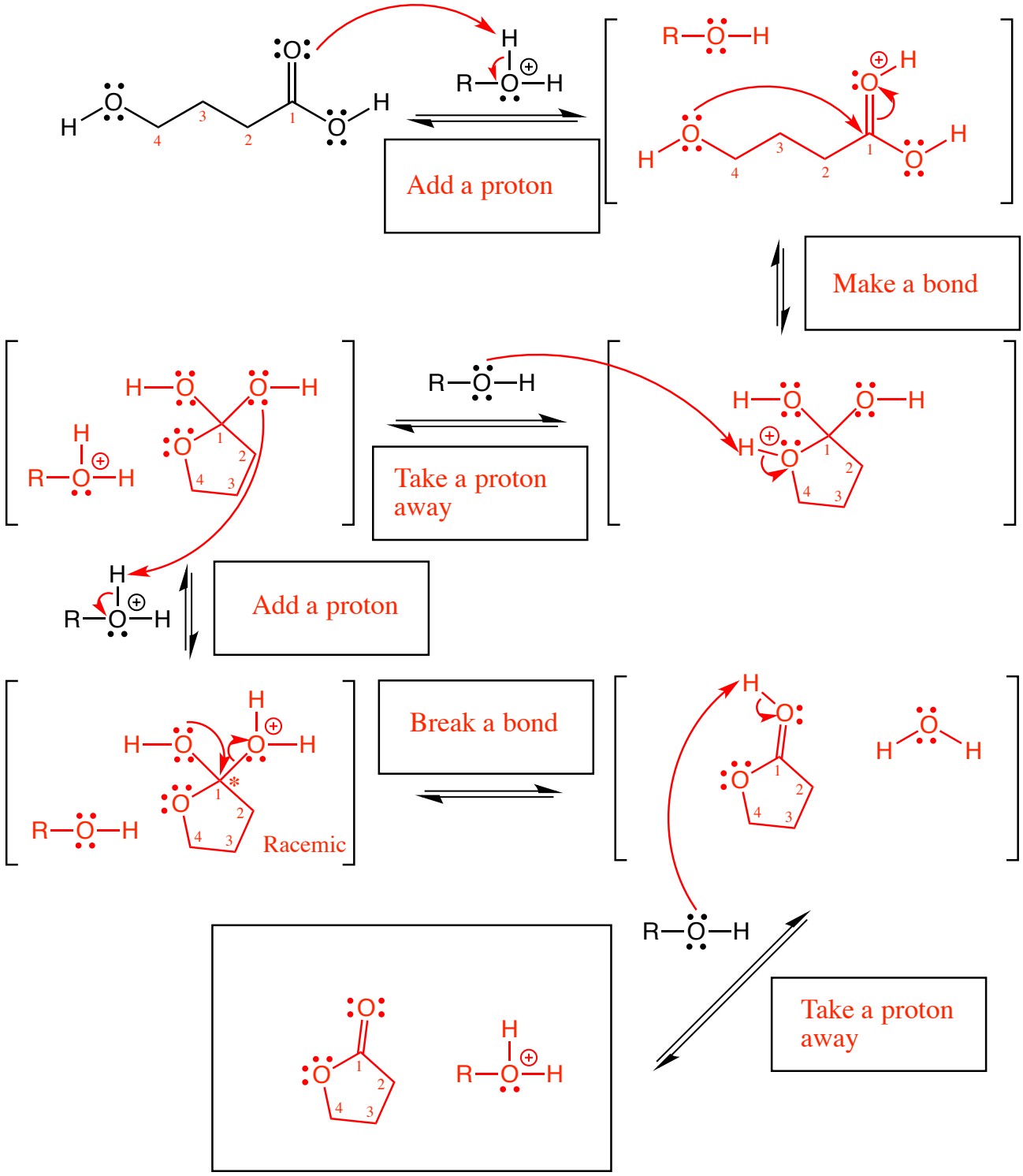
19. (15 pts) **Draw arrows on the following molecules then the product(s) you expect to be formed in these reactions. Notice, in the second reaction you will actually be drawing an intermediate, not a final product. There is not need for you to draw the final product, just the intermediate.**



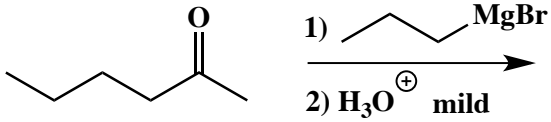
20. (26 pts) Complete the mechanism for the following Michael reaction. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **IF 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.).**

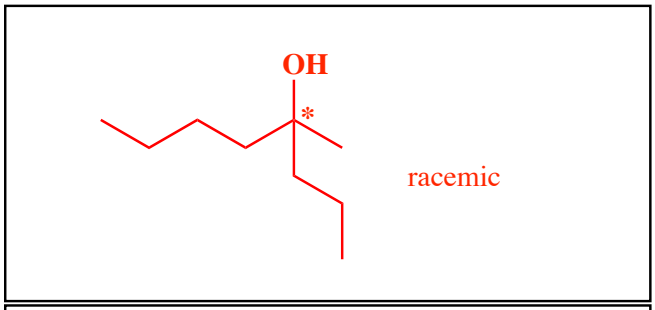


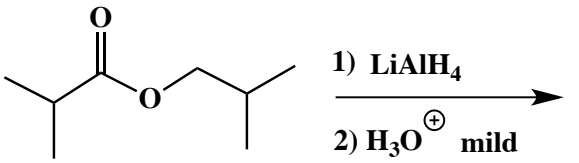
21. (35 pts) Complete the mechanism for the following lactone formation reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS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

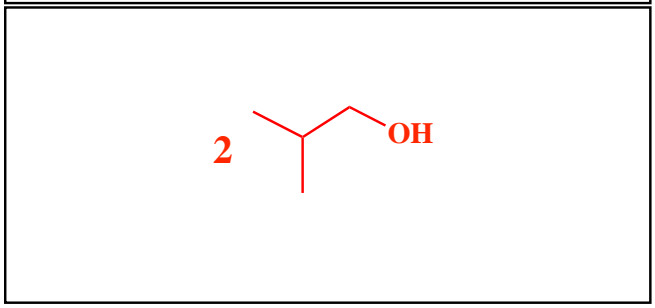


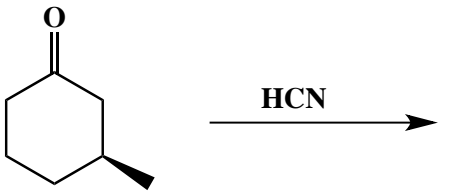
22. (3, 4, 5 or 6 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH.** If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) 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.

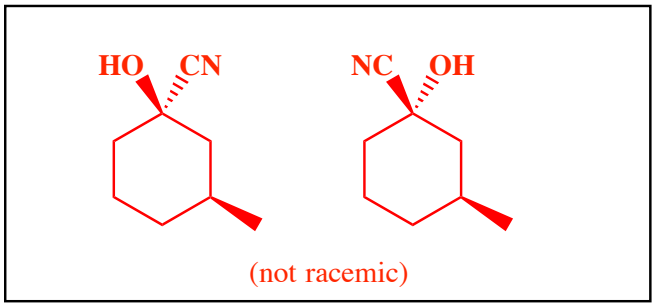


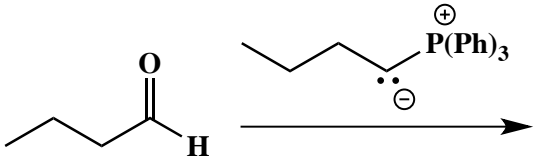


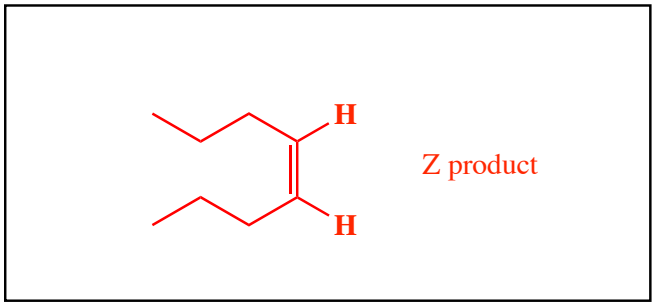


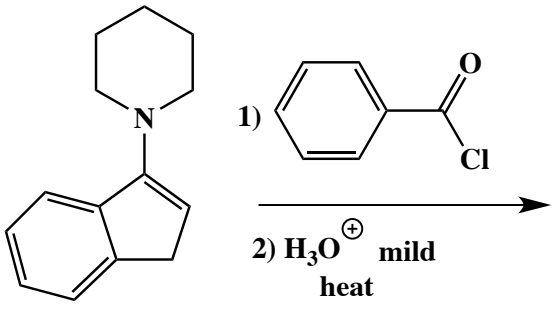


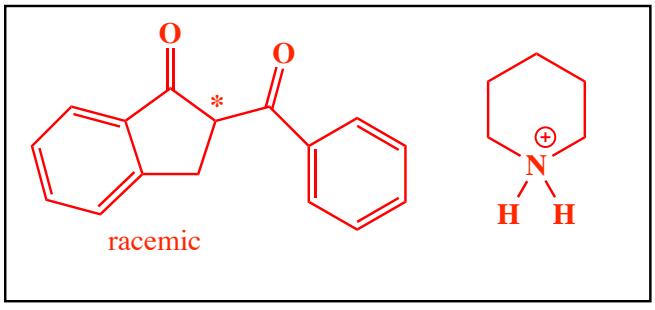




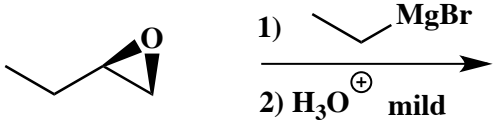


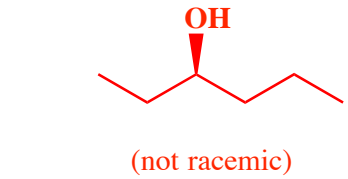




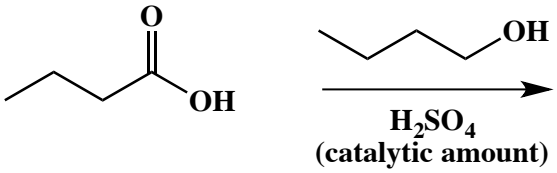


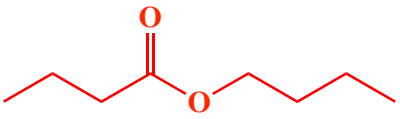
22. (3, 4, 5 or 6 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH.** If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) 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.

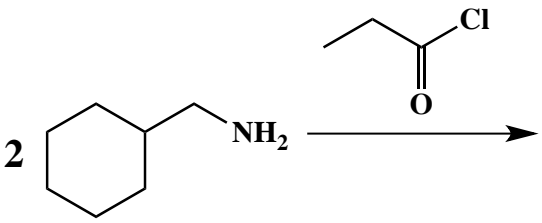


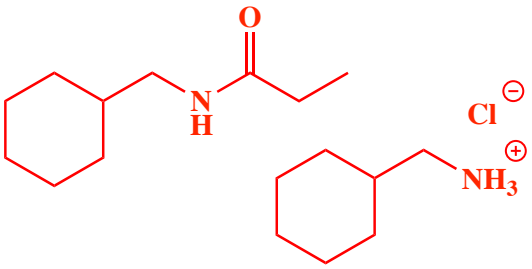


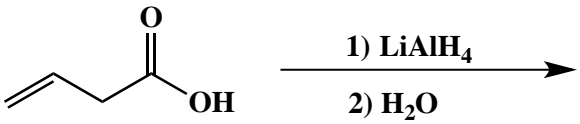
(not racemic)

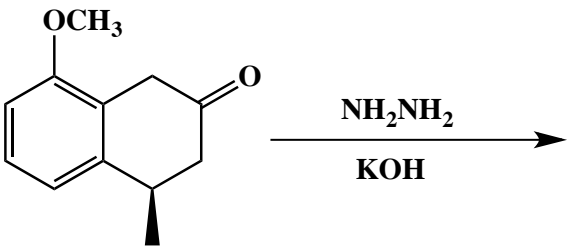


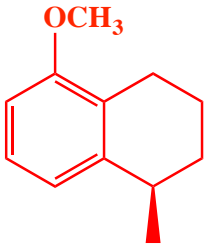






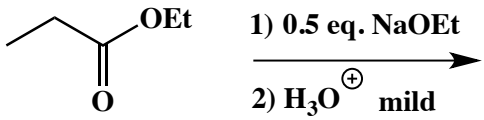


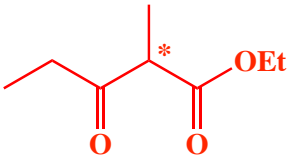




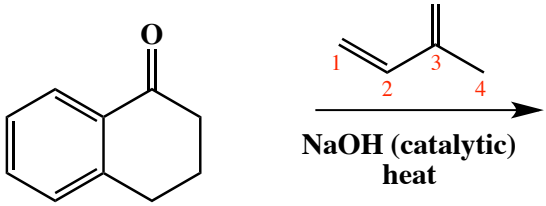
(not racemic)

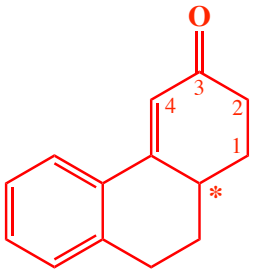
22. (3, 4, 5 or 6 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH.** If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) 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.



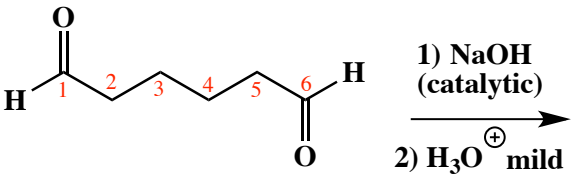


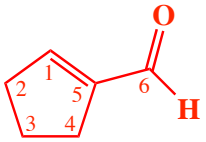
racemic

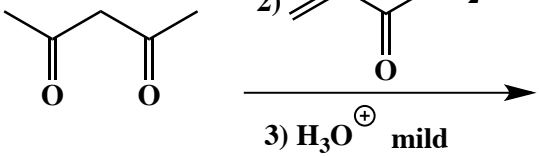


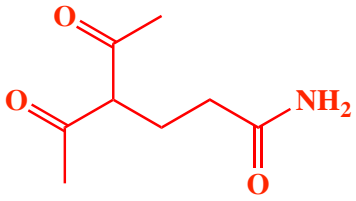


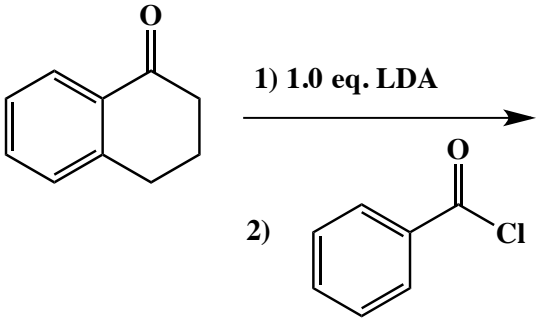
racemic

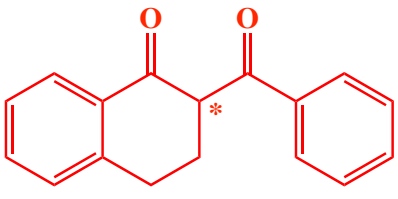






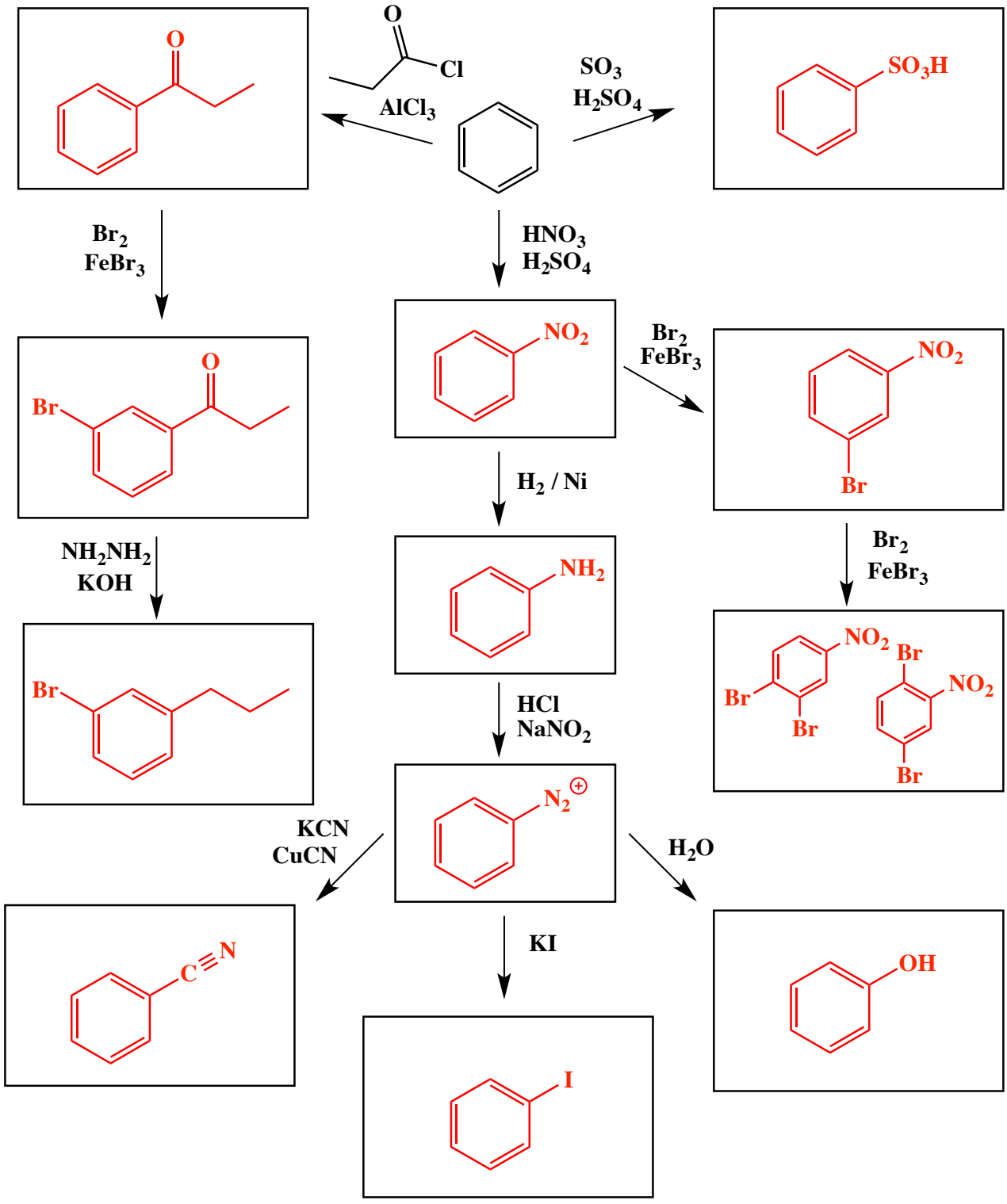






racemic

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.**

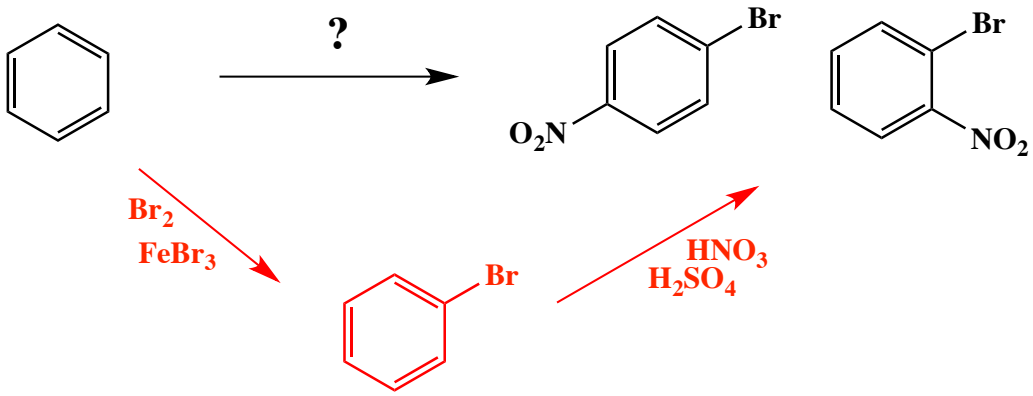


23. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic"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

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

(4 pts)

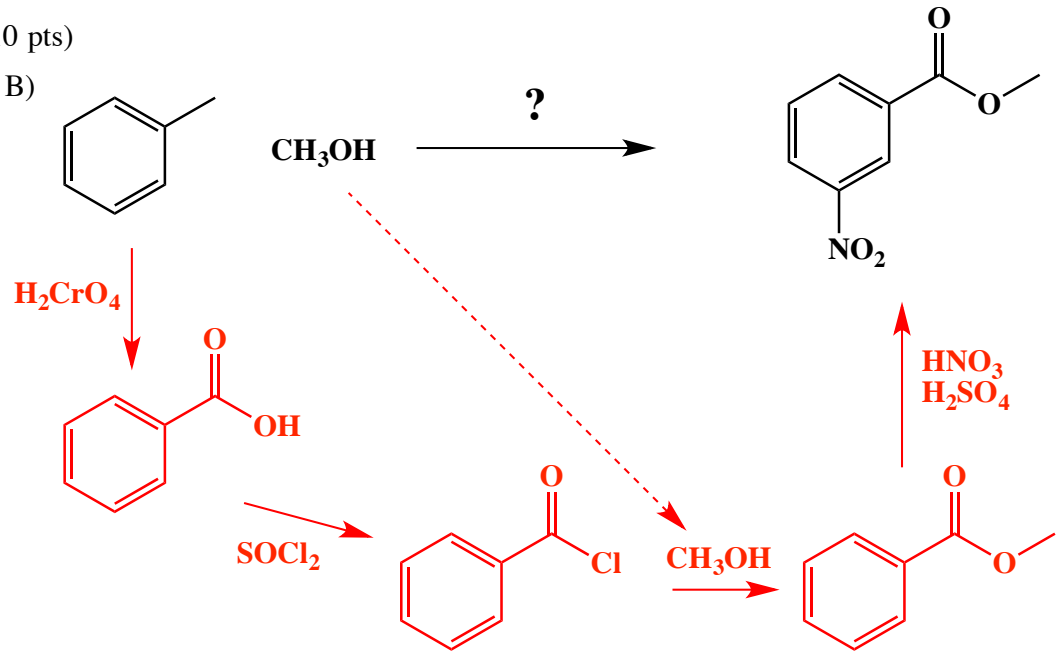
A)



Recognize that because of the ortho-para products, the Br (o,p directing) must be added first.

(10 pts)

B)



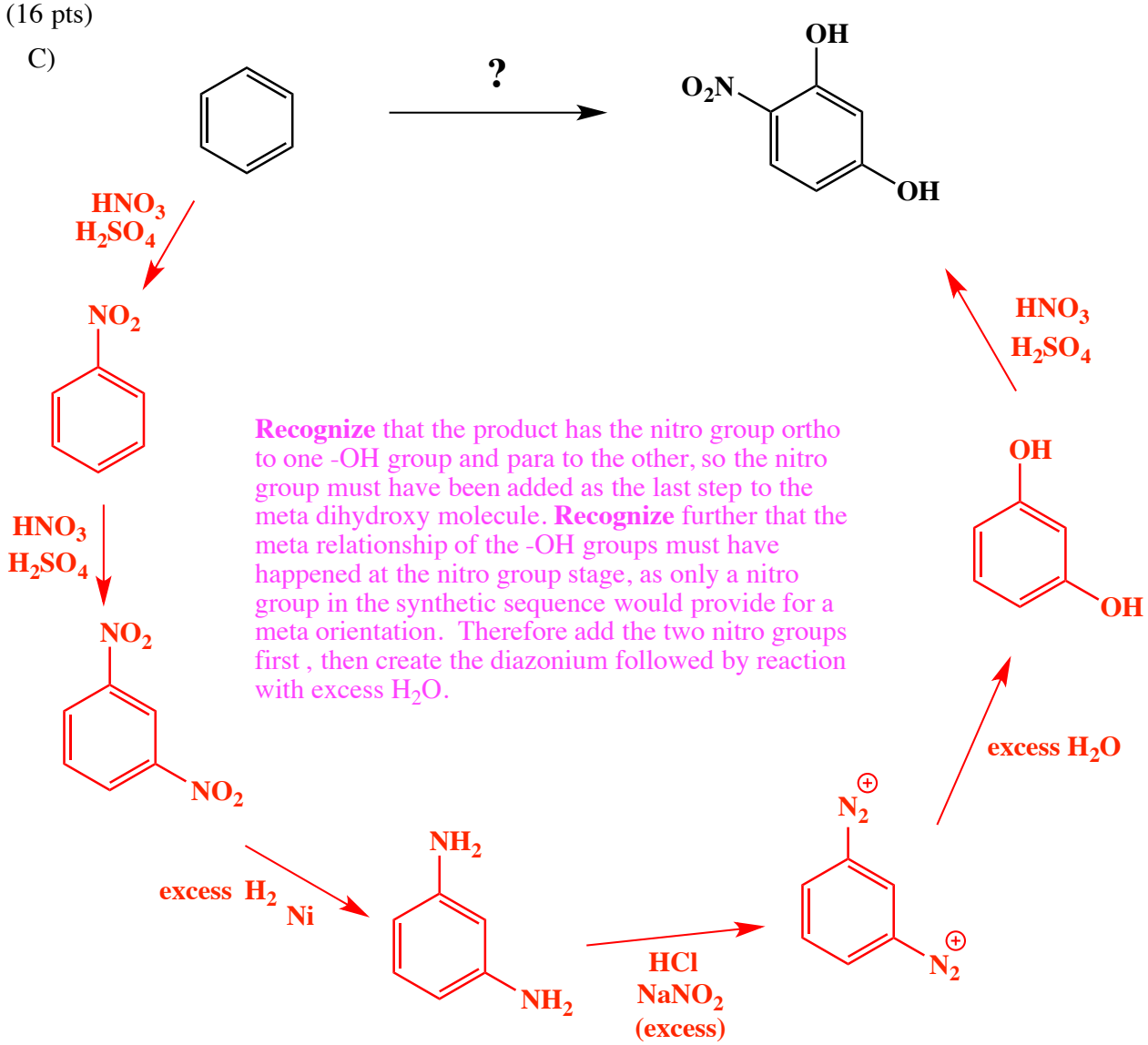
Recognize that because of the meta product, the nitro group must be added after the methyl group is oxidized, therby converting it from a "good" group, (methyl), to a "bad" group, (either a carboxylic acid or the ester). **Recognize** that once the carboxylic is made via oxidation of the benzylic methyl group, standard acid chloride formation then reaction with methanol gives the methyl ester. Note that you could skip the acid chloride step and carry out a Fischer esterification directly from the acid if you would like.

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)



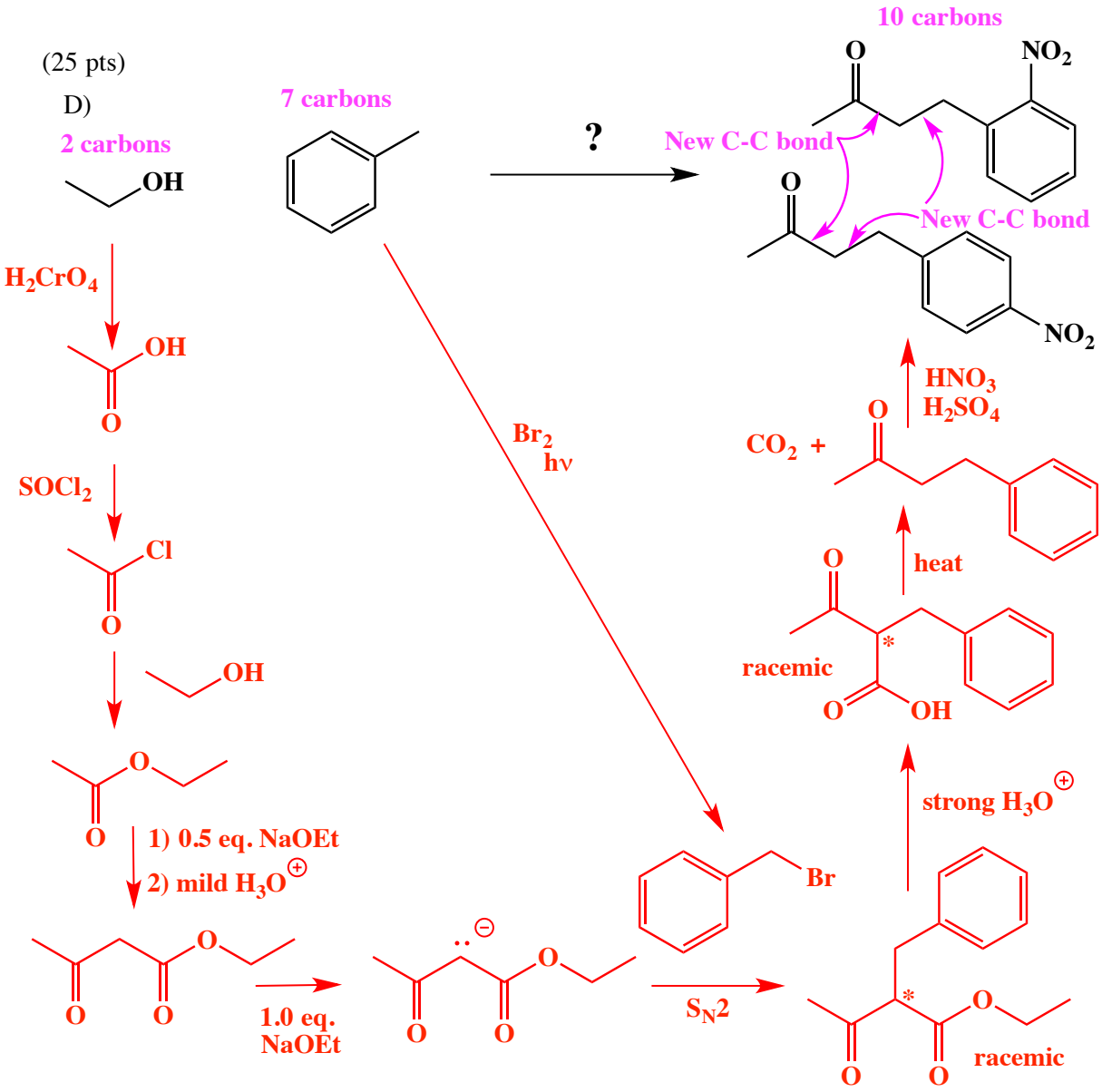
Recognize that the product has the nitro group ortho to one -OH group and para to the other, so the nitro group must have been added as the last step to the meta dihydroxy molecule. **Recognize** further that the meta relationship of the -OH groups must have happened at the nitro group stage, as only a nitro group in the synthetic sequence would provide for a meta orientation. Therefore add the two nitro groups first , then create the diazonium followed by reaction with excess H_2O.

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)



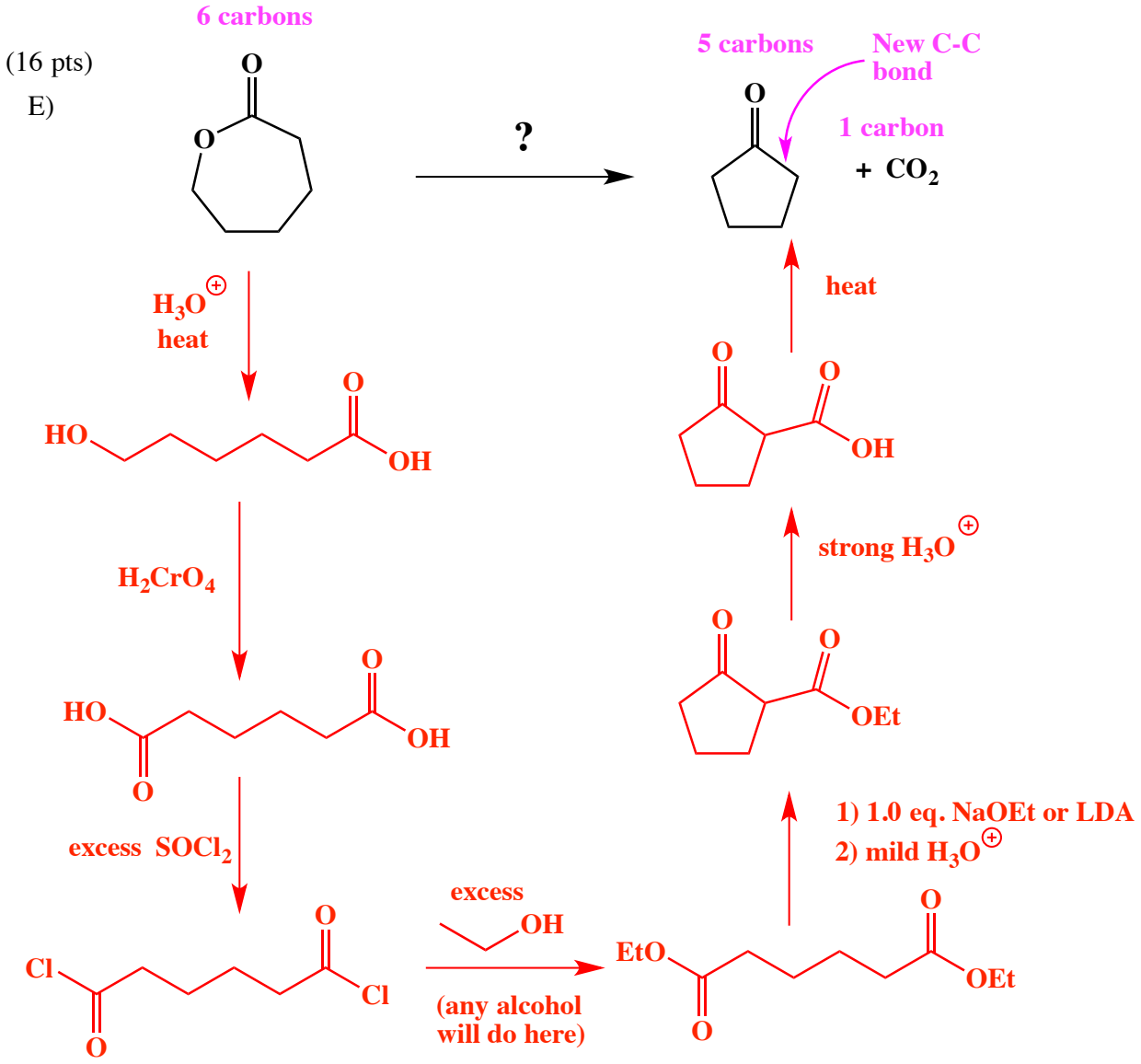
Recognize the nitro group is ortho and para to an alkyl group, meaning the nitro group was added last. **Recognize** the product as a methyl ketone, the KRE of an acetoester synthesis. Tracking the new C-C bond indicates that benzyl bromide is needed to alkylate the b-ketoester anion. **Recognize** that benzyl bromide can be made in one step from the starting aromatic molecule be reacting with Br_2 and hν. Finally, **recognize** that the acetoester can be made from a Claisen reaction of ethyl acetate, which comes from ethanol via oxidation to acetic acid followed by treatment with thionyl chloride and ethanol (as always, a Fischer esterification would be fine as well).

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)

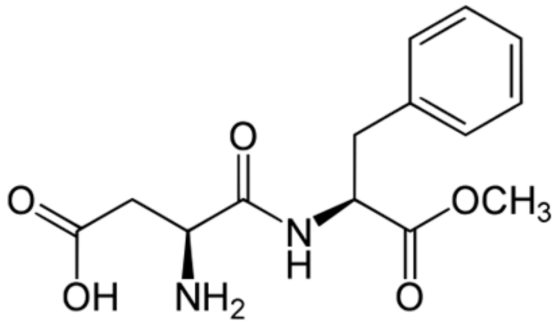


Recognize the product cyclic ketone as having one fewer carbons than the starting lactone combined with CO_2 as a product. Together, that suggests a decarboxylation, which implies a β-keto acid. A β-keto acid can be easily derived from a β-keto ester in a ring, the KRE of a Dieckmann condensation. **Recognize** that the required diester can be derived from opening up the starting lactone then oxidation to the diacid and the usual sequence of making an acid chloride followed by adding any alcohol. I used ethanol, but it does not matter which one you choose because it does not end up in the product. That is why you do not have to make the alcohol from the starting material by the way. Notice you could also have carried out a Fischer esterification to make the diester.

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 sweetner 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.

The low pH of diet coke combined with heating hydrolyzes the methyl ester (acid catalyzed ester hydrolysis) and the free carboxylic acid does not taste sweet.

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.

The protonation state drawn is not possible. The carboxylic acid cannot be protonated if the amine group is not protonated due to the respective pK_a's of these two groups (pK_a of a carboxylic acid is in the 3-5 range, and the pK_a of a ammonium group is in the 9-10 range).

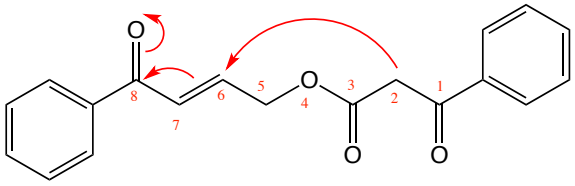
24.3 (2 pts) Aspartame is a chiral molecule, present as the single enantiomer shown. How many chiral centers are in aspartame?

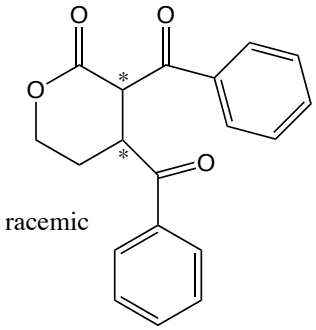
__2_____

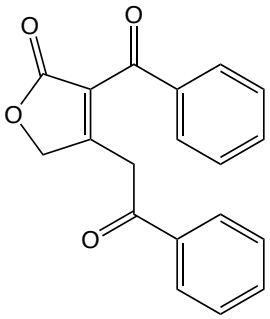
24.4 (2 pts) How many different stereoisomers are possible for aspartame?

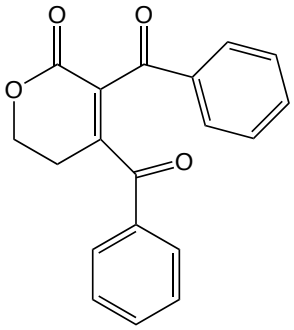
___4_____

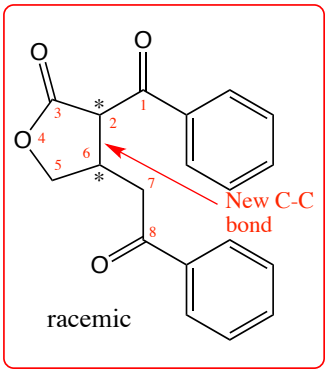
25 (8 pts) The following intramolecular Michael reaction is used to prepare important classes of molecules. From the following list, circle the product of the reaction shown:





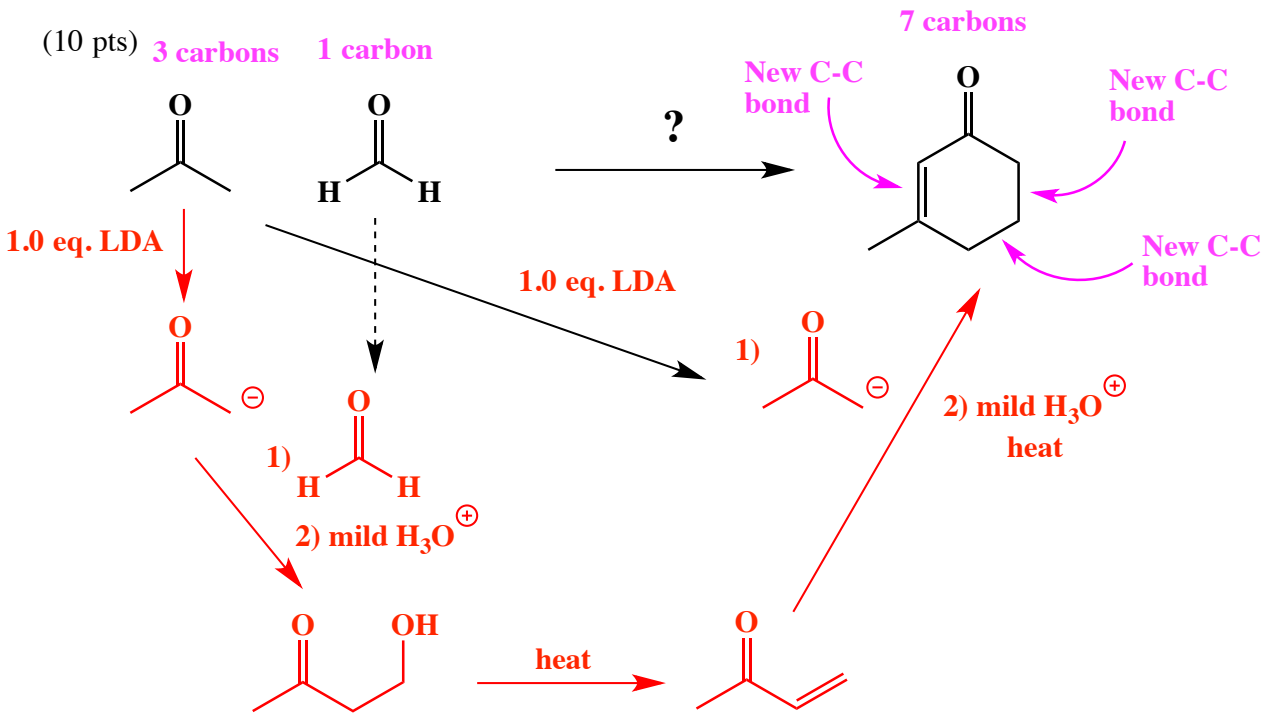






22. This one is extra credit. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and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

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



Recognize the product as the KRE of a Robinson between the α,β-unsaturated ketone shown and the enolate of the starting acetone. Recognize the required α,β–unsaturated ketone as being derived from an aldol between the acetone and formaldehyde starting materials followed by dehydration. Notice that I illustrated using LDA for the aldol, but a simple crossed aldol using catalytic NaOH would have worked just fine.