

X

NAME (Print): _____

Chemistry 320N
Dr. Brent Iverson
Final Exam
May 13, 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 cannot use a red, pink or orange 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		(82)
8		(24)
9		(36)
10		(23)
11		(30)
12		(17)
13		(19)
14		(21)
15		(37)
16		(11)
17		(16)
18		(13)
19		(22)
20		(9)
21		(6)
Total		(366)

Extra credit synthesis (pg 22)		(13)
Total		(366)

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

Use this page for scratch paper

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 six pages on this single sheet.

Question 1, page 2 (24 pts) True false questions.
As appropriate, circle True or False in each space corresponding to the statements on page 2.

- | | |
|-----------------------|------------------------|
| 1.1 <u>True</u> False | 1.7 <u>True</u> False |
| 1.2 True <u>False</u> | 1.8 <u>True</u> False |
| 1.3 <u>True</u> False | 1.9 True <u>False</u> |
| 1.4 True <u>False</u> | 1.10 <u>True</u> False |
| 1.5 <u>True</u> False | 1.11 <u>True</u> False |
| 1.6 True <u>False</u> | 1.12 <u>True</u> False |

Question 2, page 3 (8 pts) Write the word or symbol that best completes the sentences.

- 2.1 Anomeric
- 2.2 Axial
- 2.3 Glycosidic
- 2.4 Beta (β)

Question 3, page 3 (6 pts) Write the word or symbol that best completes the sentences.

- 3.1 Flat
- 3.2 2p
- 3.3 Pi

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

4 D

Question 5, page 4 (2 pts) Write the letter (A, B, C, or D) corresponding to the correct rank (most to least reactive with a wicked strong electrophile)

5 B

Question 6, page 4 (2 pts) Write the letter (A, B, C, or D) corresponding to the correct rank (most to least reactive with a nucleophile)

6 C

Question 7, page 5 (2 pts) Write the pH (2.0, 7.0, 9.0, 11.0) corresponding to the protonation state of the molecule

7 7.0

Question 8, page 5 (2 pts) Write the pH (2.0, 5.0, 9.0, 11.0) corresponding to the protonation state of the molecule

8 9.0

Question 9, page 6 (8 pts) State the type of orbital containing the lone pair of electrons indicated by the arrow.

9.1 sp² 9.2 2p 9.3 sp³ 9.4 2p

Question 10, page 6 (16 pts) Write the letter (A or B) corresponding to the MORE ACIDIC of the two molecules.

10.1 <u>B</u>	10.5 <u>A</u>
10.2 <u>B</u>	10.6 <u>B</u>
10.3 <u>A</u>	10.7 <u>B</u>
10.4 <u>A</u>	10.8 <u>A</u>

Question 11, page 7 (6 pts) Write the type of glycosidic bond indicated by the arrow. Answers might be α -1,4 or β -1,2, etc.

11.1 β -1,6 11.2 α -1,4 11.3 β -1,3

Question 12, page 7 (4 pts) Write the letter (A-D) that lists the carbohydrates indicated by the question.

12.1 B 12.2 D

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

1. (24 pts). **On page 1, circle True or False to indicate whether each of the following statements is true or false.**
- 1.1 The difference in energy between the $+1/2$ and $-1/2$ nuclear spin states is proportional to the strength of the magnetic field felt by the nucleus.
- 1.2 The difference in energy between the $+1/2$ and $-1/2$ nuclear spin states is inversely proportional to the strength of the magnetic field felt by the nucleus.
- 1.3 In NMR, energy of exactly the correct frequency (turns out to be radio frequency) can be absorbed by a nucleus resulting in excitation from the lower energy $+1/2$ spin state to the higher energy $-1/2$ spin state, a process referred to as resonance.
- 1.4 Protonation of a carbonyl oxygen atom in acid makes the carbonyl carbon atom much more nucleophilic (i.e. able to react with weaker electrophiles).
- 1.5 Protonation of a carbonyl oxygen atom in acid makes the carbonyl carbon atom much more electrophilic (i.e. able to react with weaker nucleophiles).
- 1.6 Alkyl Wittig reagents give predominantly "E" (trans) alkene products, while Wittig reagents with a carbonyl adjacent to the negative charge give predominantly "Z" (cis) products.
- 1.7 Alkyl Wittig reagents give predominantly "Z" (cis) alkene products, while Wittig reagents with a carbonyl adjacent to the negative charge give predominantly "E" (trans) products.
- 1.8 When reacting with acid chlorides and anhydrides, two equivalents of amine are required because the second equivalent is protonated and therefore not reactive. When reacting with esters, only one equivalent is required.
- 1.9 When reacting with esters, two equivalents of amine are required because the second equivalent is protonated and therefore not reactive. When reacting with acid chlorides and anhydrides, only one equivalent is required.
- 1.10 For electrophilic aromatic substitution, groups that are activating and ortho, para directing operate by stabilizing an adjacent positive charge through resonance (for groups with lone pairs on atoms attached to the ring) or hyperconjugation (for alkyl groups). These are sometimes called electron releasing groups.
- 1.11 For electrophilic aromatic substitution, halogens are deactivators due to inductive effects, but ortho, para directors due to pi donation, a resonance effect.
- 1.12 Staying physically fit for life is the most important element of being successful.

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

2. (8 pts). On page 1, fill in each blank with the word or symbol that best completes the following sentences.

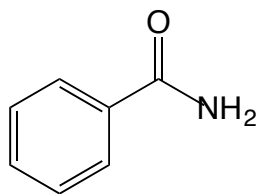
For a carbohydrate like glucose in **the cyclic hemiacetal form**, the carbon atom that was the carbonyl in the open chain form is called the _____ (2.1) carbon atom. For glucose, alpha is _____ (2.2), referring to the cyclic hemiacetal -OH group. The bond linking two monosaccharide units into a disaccharide is referred to as a(n) _____ (2.3) bond. In cellulose (wood), the linkage between glucose units is _____ (2.4), meaning that all the glucose linkages are equatorial leading to entirely flat chains that can pack together nicely to create a strong and rigid material.

3. (6 pts). On page 1, fill in each blank with the word (or symbol) that best completes the following sentences.

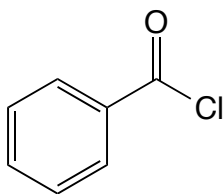
According to Hückel's rules, for a monocyclic molecule to be aromatic:

- 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.

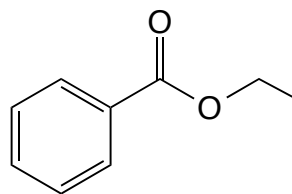
4. (2 pts). On page 1, write the letter (A, B, C, or D) corresponding to the order of reactivity of the following molecules reacting with a nucleophile such as water. Rank them starting with the most reactive (reacts the fastest) and ending with the least reactive (reacts the slowest).



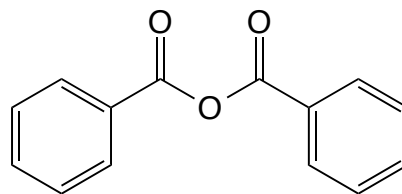
I



II



III



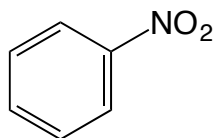
IV

Ranked in order of **most to least reactive with a nucleophile such as water:**

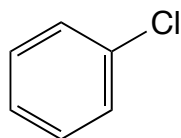
- A: I > II > III > IV
B: III > IV > II > I
C: III > II > IV > I
D: II > IV > III > I

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

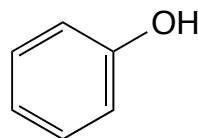
5. (2 pts). On page 1, write the letter (A, B, C, or D) corresponding to the order of reactivity of the following molecules reacting with a wicked strong electrophile. Rank them starting with the most reactive (reacts the fastest) and ending with the least reactive (reacts the slowest).



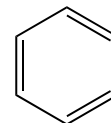
I



II



III



IV

Ranked in order of most to least reactive with a wicked strong electrophile:

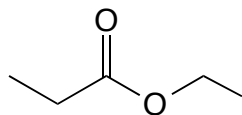
A: I > II > III > IV

B: III > IV > II > I

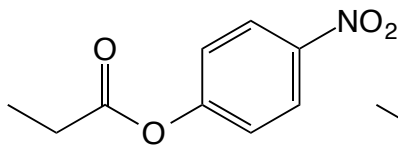
C: III > II > IV > I

D: II > IV > III > I

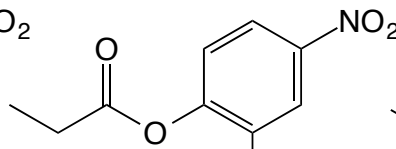
6. (2 pts). On page 1, write the letter (A, B, C, or D) corresponding to the order of reactivity of the following molecules reacting with a nucleophile such as water. Rank them starting with the most reactive (reacts the fastest) and ending with the least reactive (reacts the slowest).



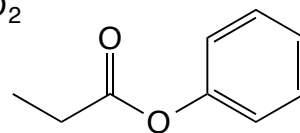
I



II



III



IV

Ranked in order of most to least reactive with a nucleophile such as water:

A: I > II > III > IV

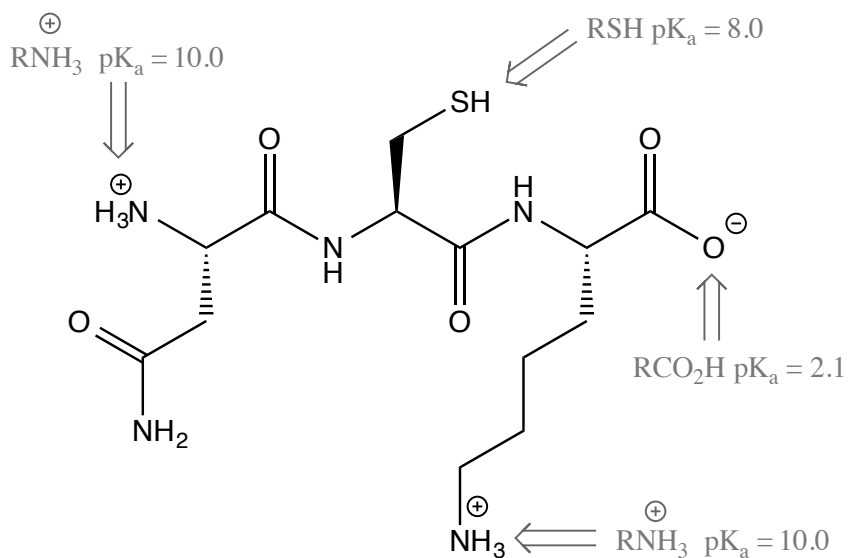
B: III > IV > II > I

C: III > II > IV > I

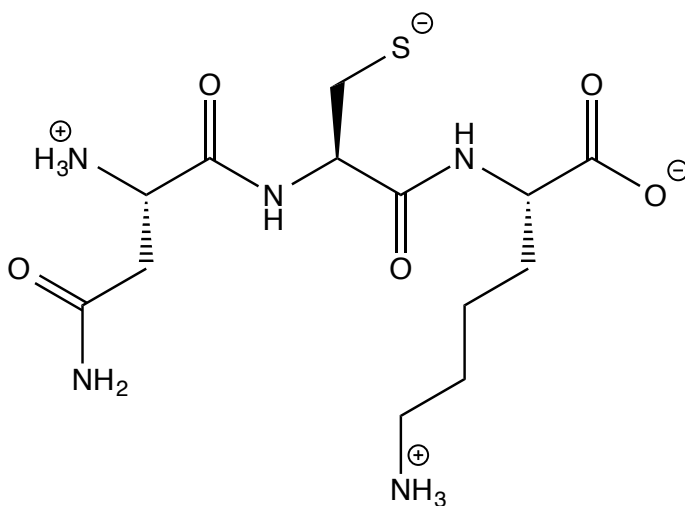
D: II > IV > III > I

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

7. (2 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, 7.0, 9.0 or 11.0?**

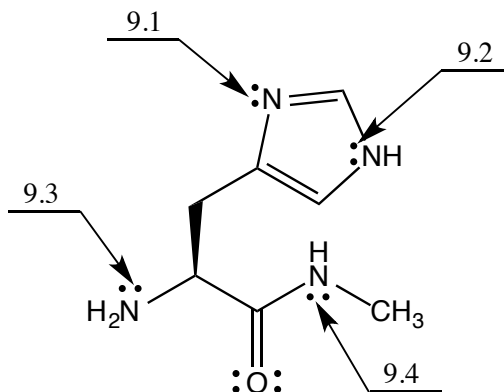


8. (2 pts). The same peptide is now drawn at a different pH. **Based on the protonation states of the different functional groups, is the pH of the new solution 2.0, 5.0, 9.0 or 11.0?**

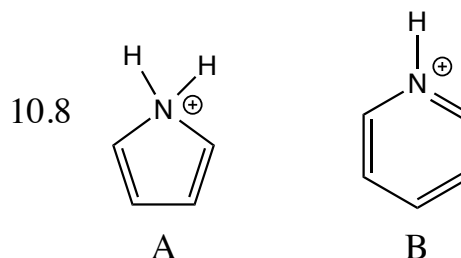
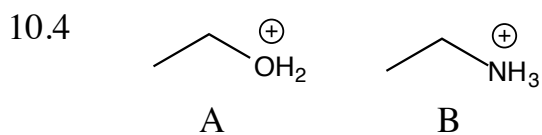
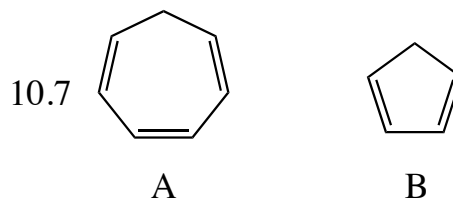
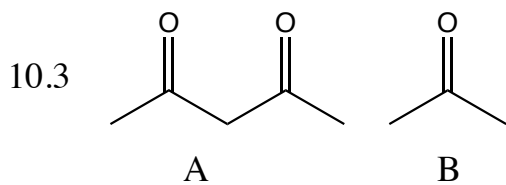
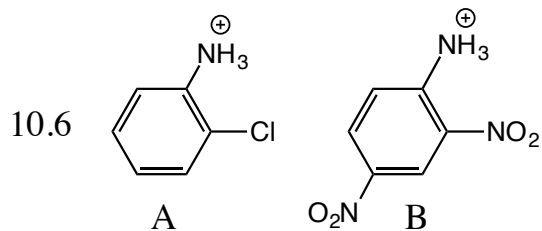
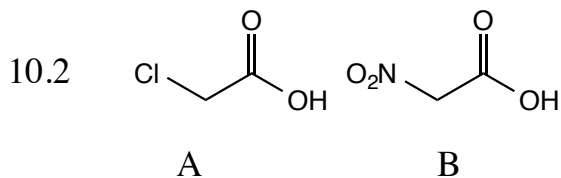
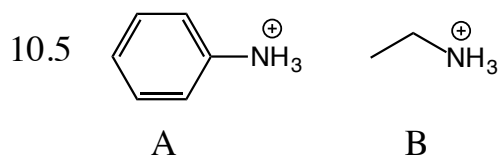
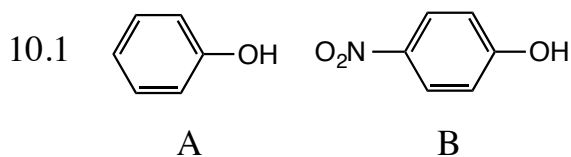


Write your answers to these questions on the answer sheet on page 1

9. (8 pts). On page 1, write the type of atomic orbital ($2p$, sp^3 , etc.) that contains the lone pair indicated by the arrows.

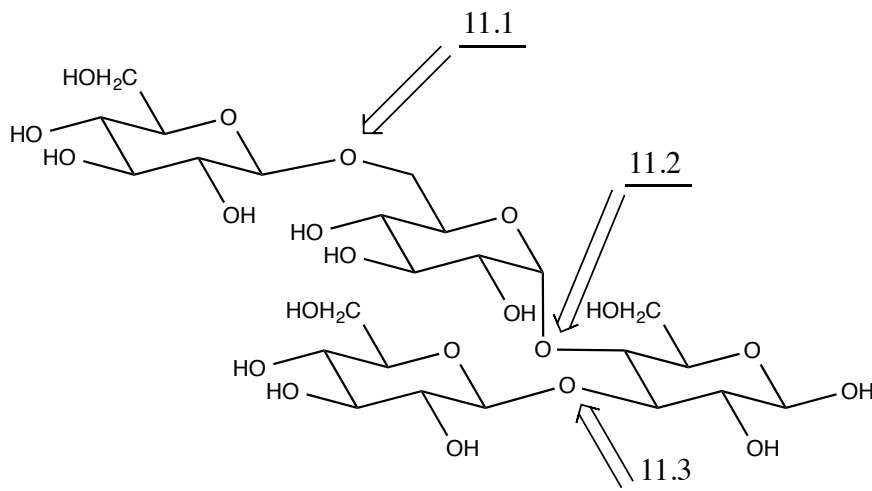


10. (16 pts). On page 1, for each pair of molecules, write the letter (A or B) corresponding to the MORE ACIDIC molecule.

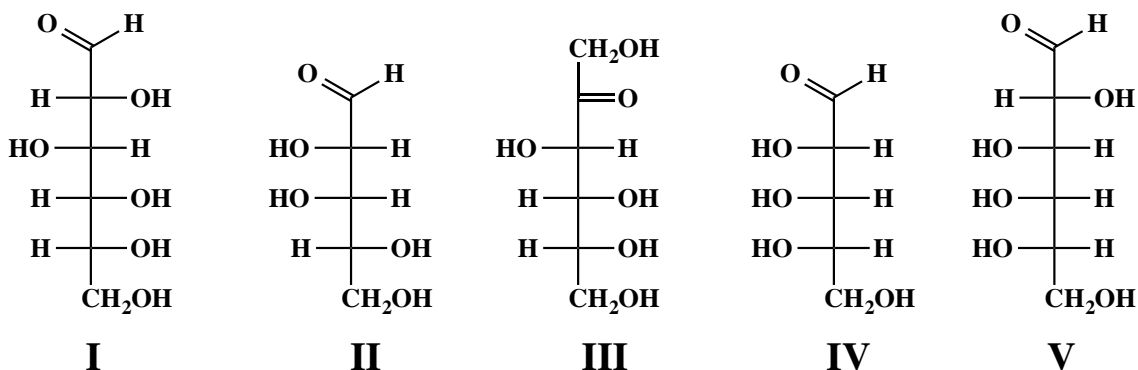


Write your answers to these questions on the answer sheet on page 1

11. (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.



12. (4 pts). Consider the following five carbohydrates a-e, drawn as Fischer projections.



- 12.1 On page 1, write the letter (A-D) corresponding to which of the five carbohydrates (I-V) are D-sugars?

A: I, II, III, IV, V
 B: I, II, III
 C: IV, V
 D: I, V

- 12.2 On page 1, write the letter (A-D) corresponding to which of the five carbohydrates (I-V) are aldohexoses?

A: I, II, III, IV, V
 B: I, II, III
 C: IV, V
 D: I, V

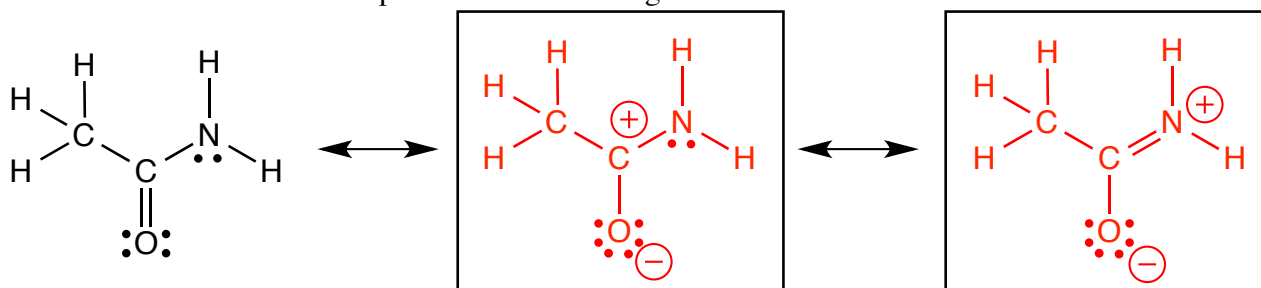
13. (2 pts) What is the most important question in chemistry?

Where are the electrons ?

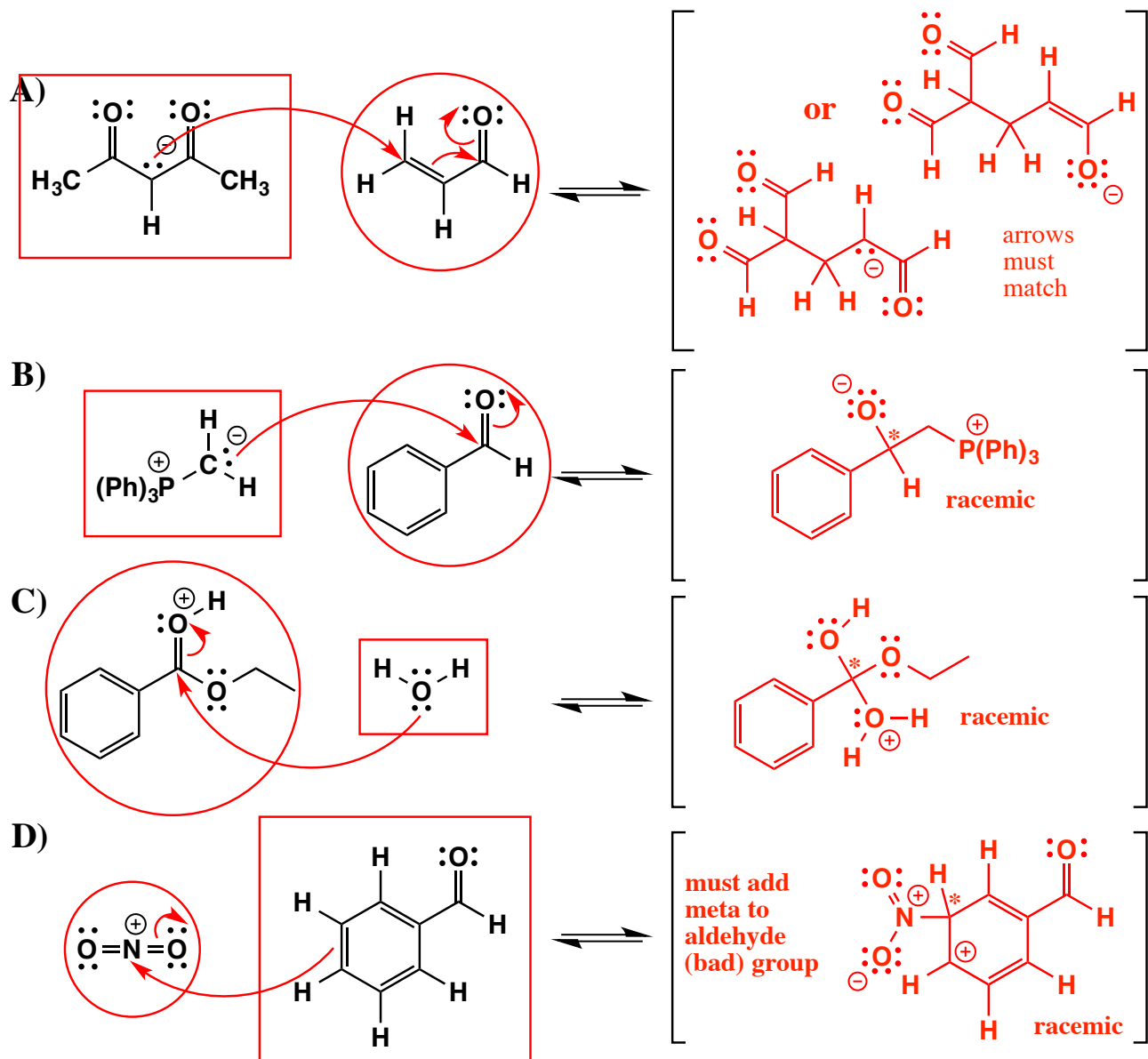
14. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here.

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.**

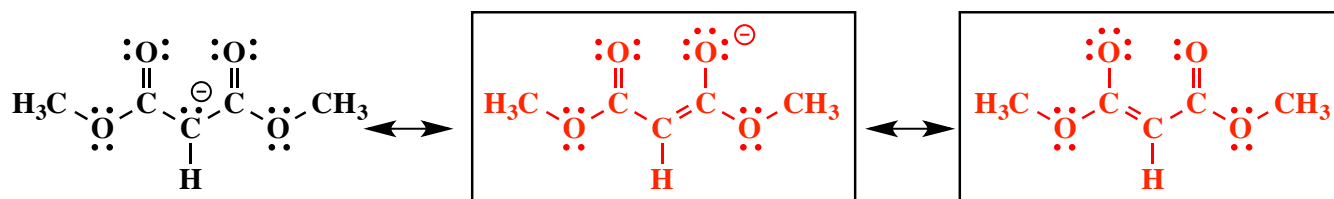
15. (8 points) Draw the two most important resonance contributing structures of the amide shown below. Be sure to show all lone pairs and formal charges. You do not have to draw arrows on this one.



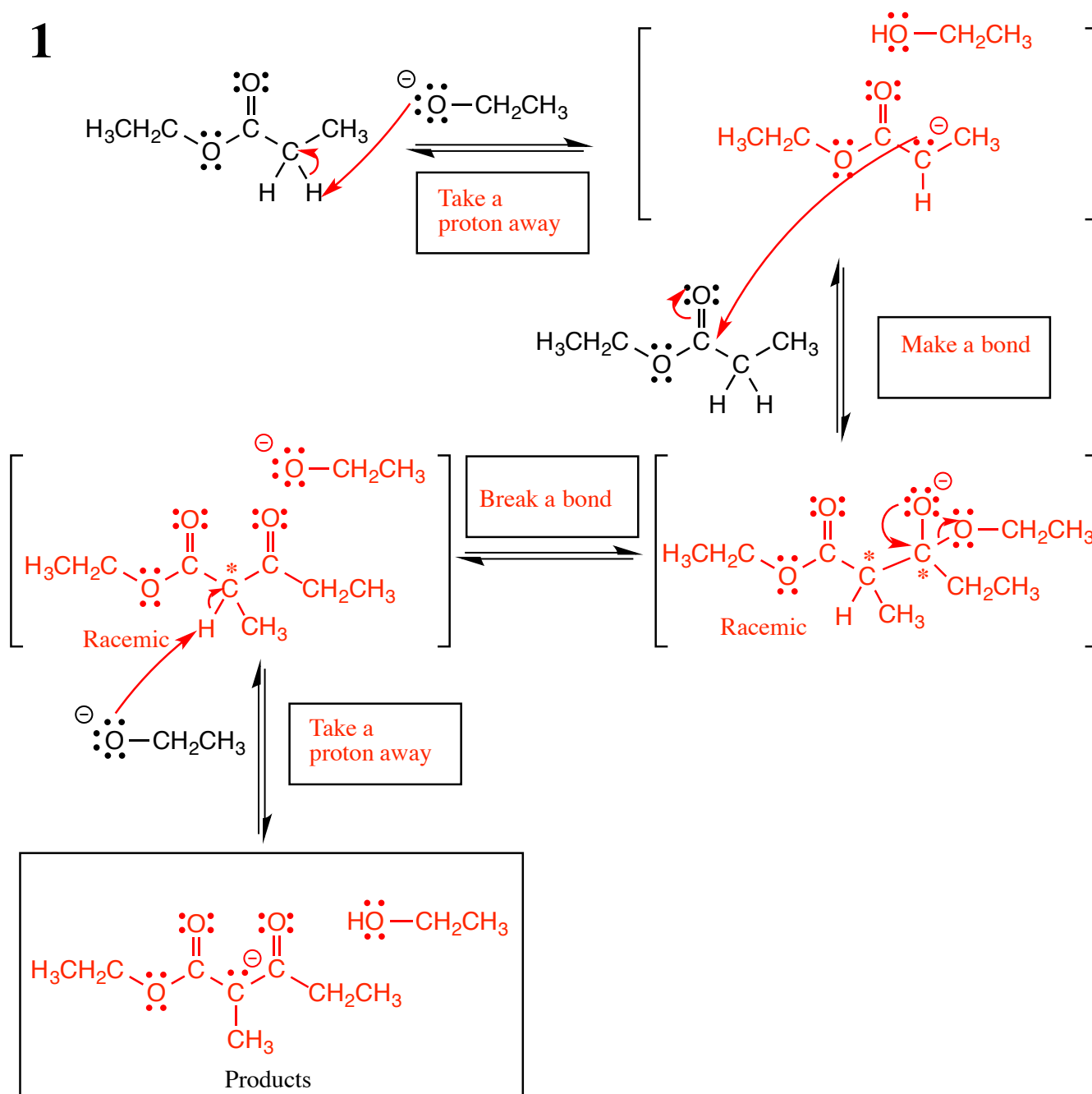
16. (28 pts) Each of the following is from a mechanism we covered in class over the semester. **Put arrows on the structures to show the flow of electrons then draw the structure of the intermediate formed.** We do not want you to finish the mechanisms, we are just covering one step from each one on this page. **Make sure to draw all lone pairs and formal charges. Put an asterisk next to any chiral centers you create and write racemic if appropriate. Finally, for each reaction step below, draw a BOX AROUND THE NUCLEOPHILE and CIRCLE THE ELECTROPHILE.**



17. (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.**

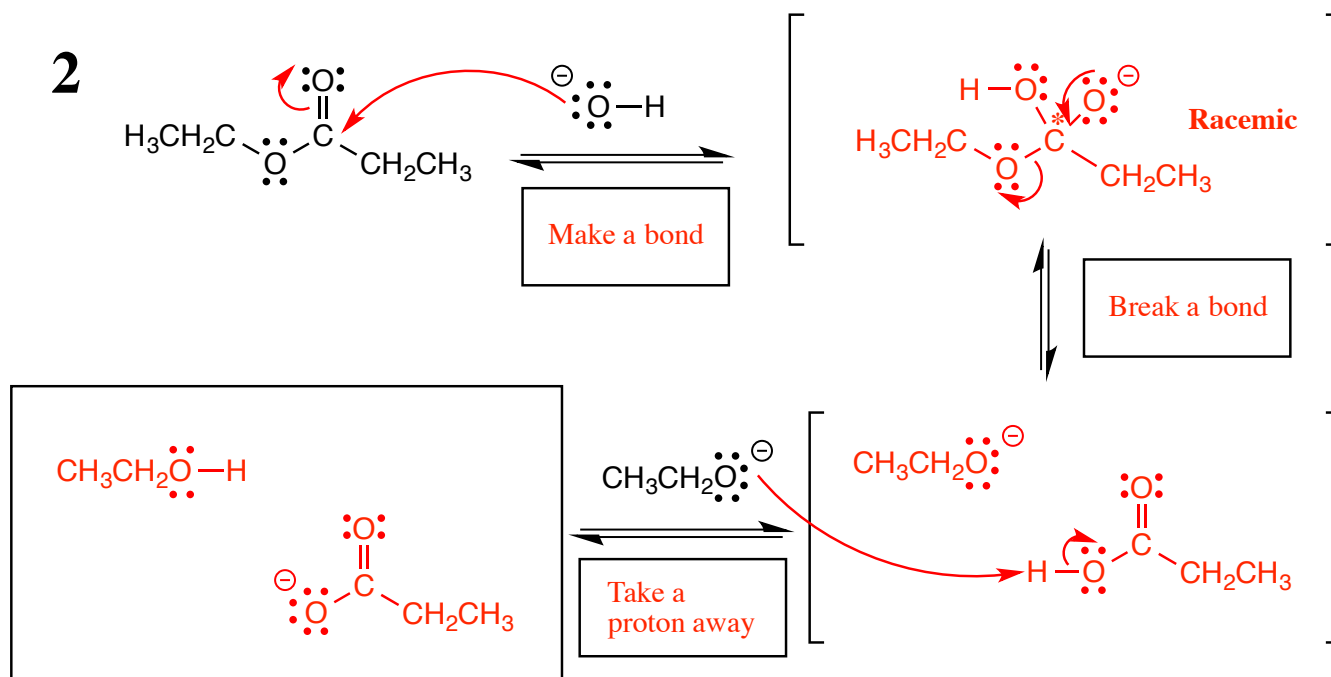


18. (23 pts) Complete the mechanism for the following Claisen reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN 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.).



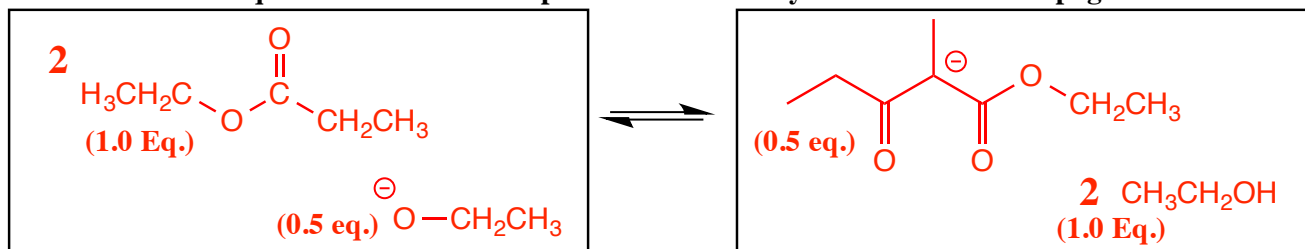
Note you will have to write a balanced equation for the above mechanism on PAGE 11

19. (18 pts) Complete the mechanism for the following base promoted hydrolysis 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.).

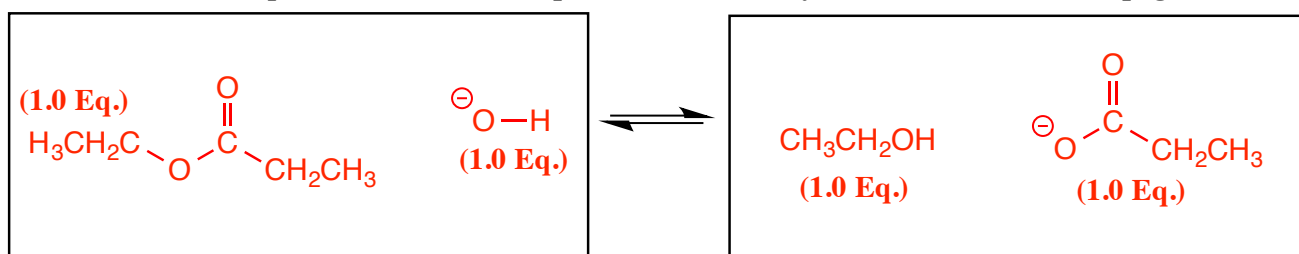


20. (12 pts) Write **BALANCED** equations for both mechanisms that you drew on the last two pages. Note that because we want balanced equations **you will need to specify the equivalents of each of the reagents you start with as well as the equivalents of each of the products made.**

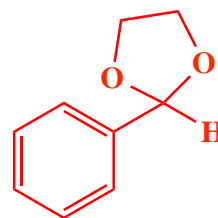
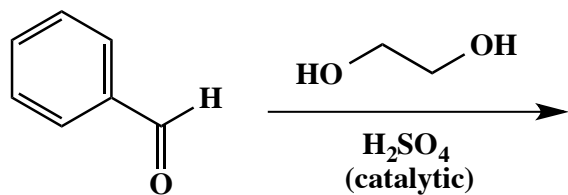
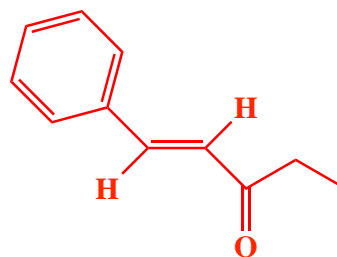
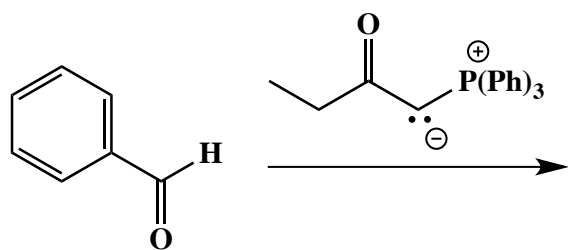
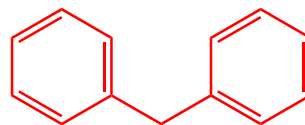
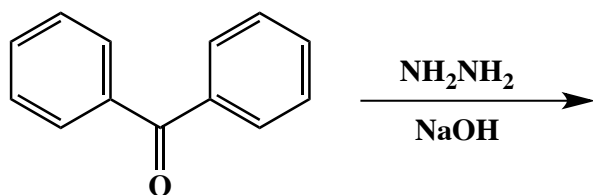
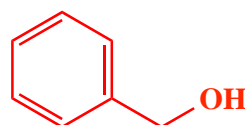
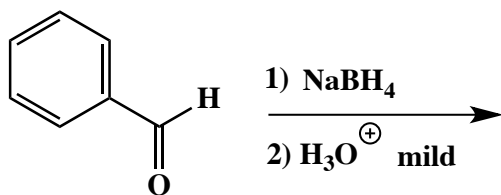
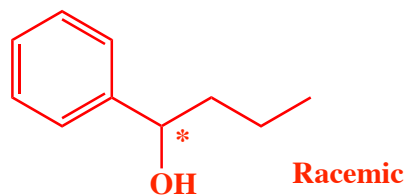
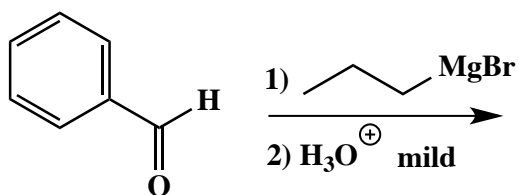
Write a balanced equation for the overall process described by mechanism 1 from page 10



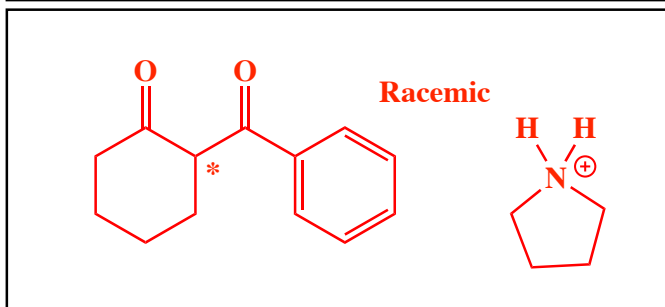
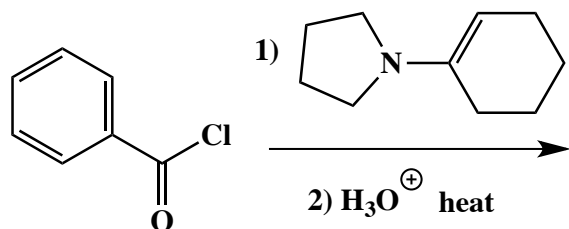
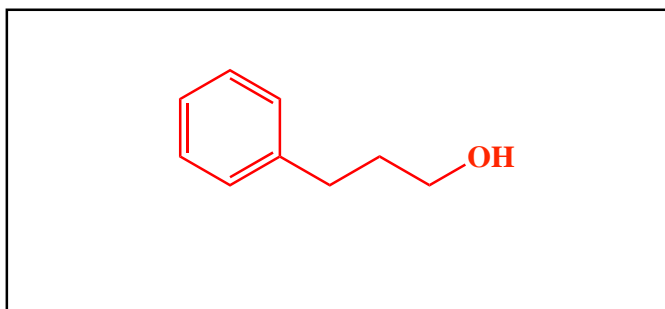
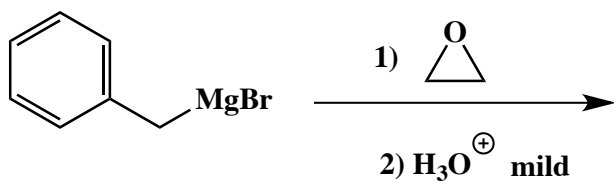
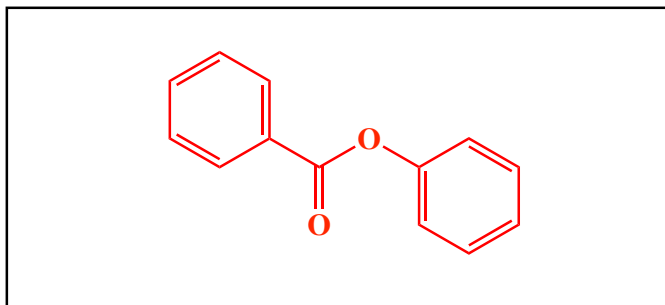
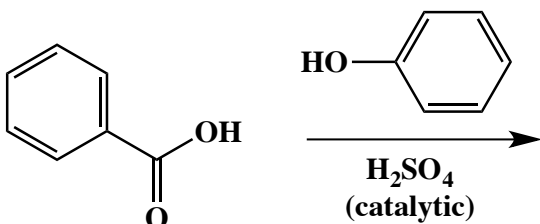
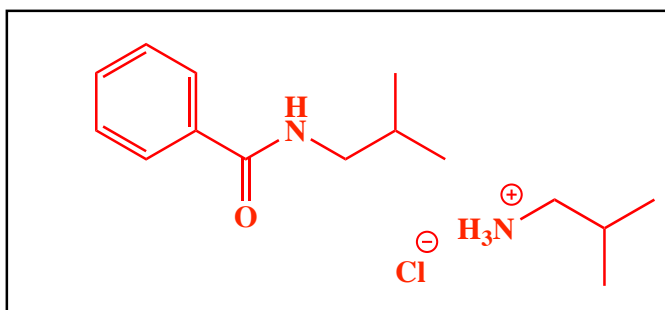
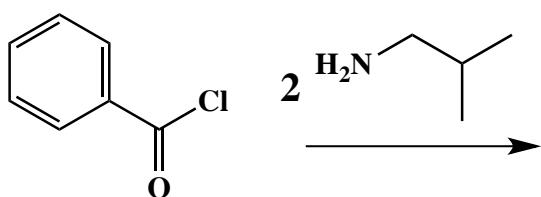
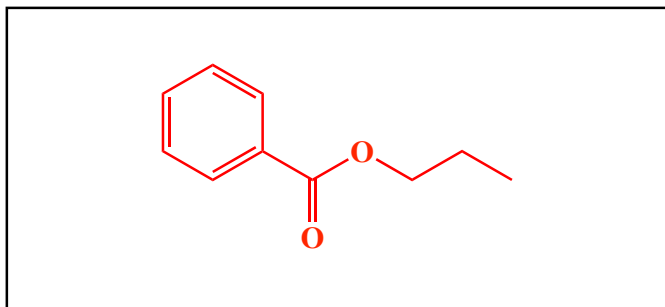
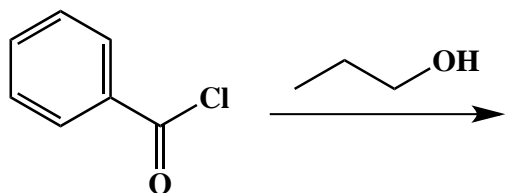
Write a balanced equation for the overall process described by mechanism 2 from this page



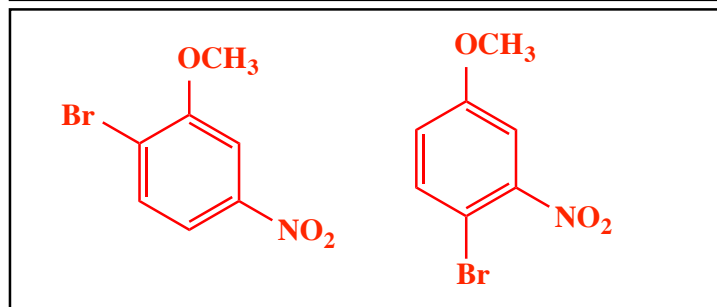
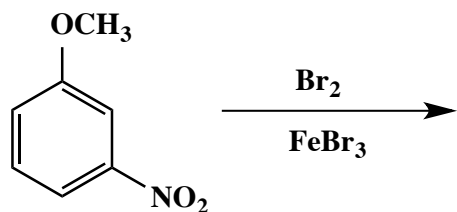
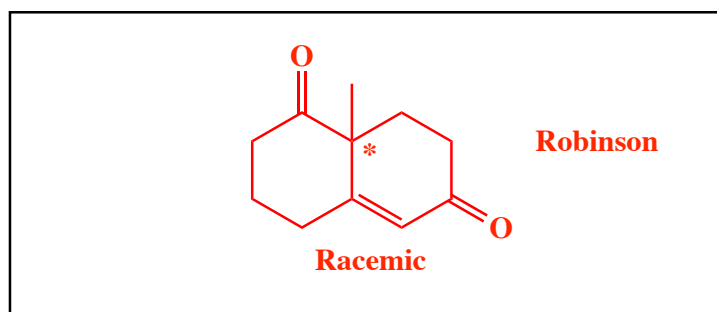
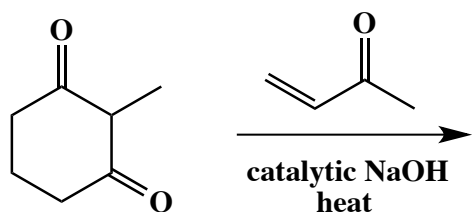
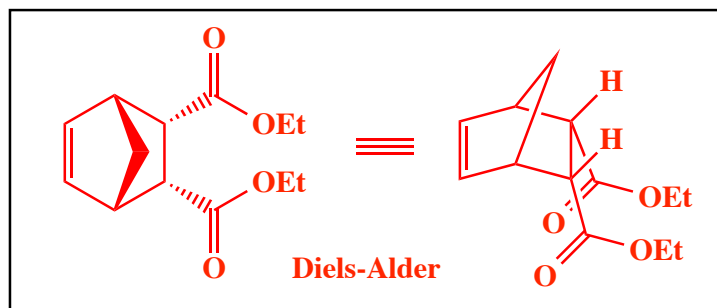
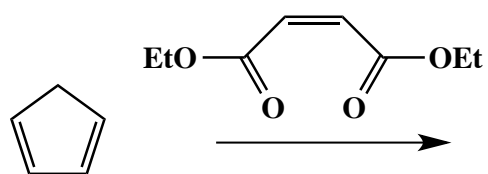
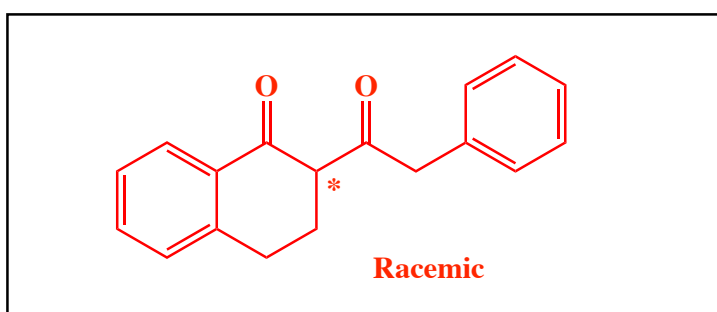
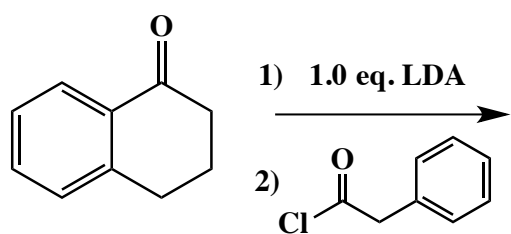
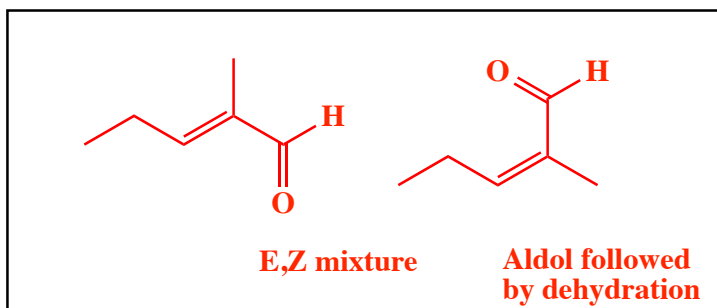
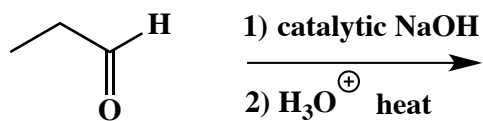
21. (3, 4, 5 or 6 pts.) Write the predominant carbon containing product or products that will occur for each transformation. If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and write racemic. No need for wedges and dashes. However, if an E,Z mixture is formed, you need to draw both!



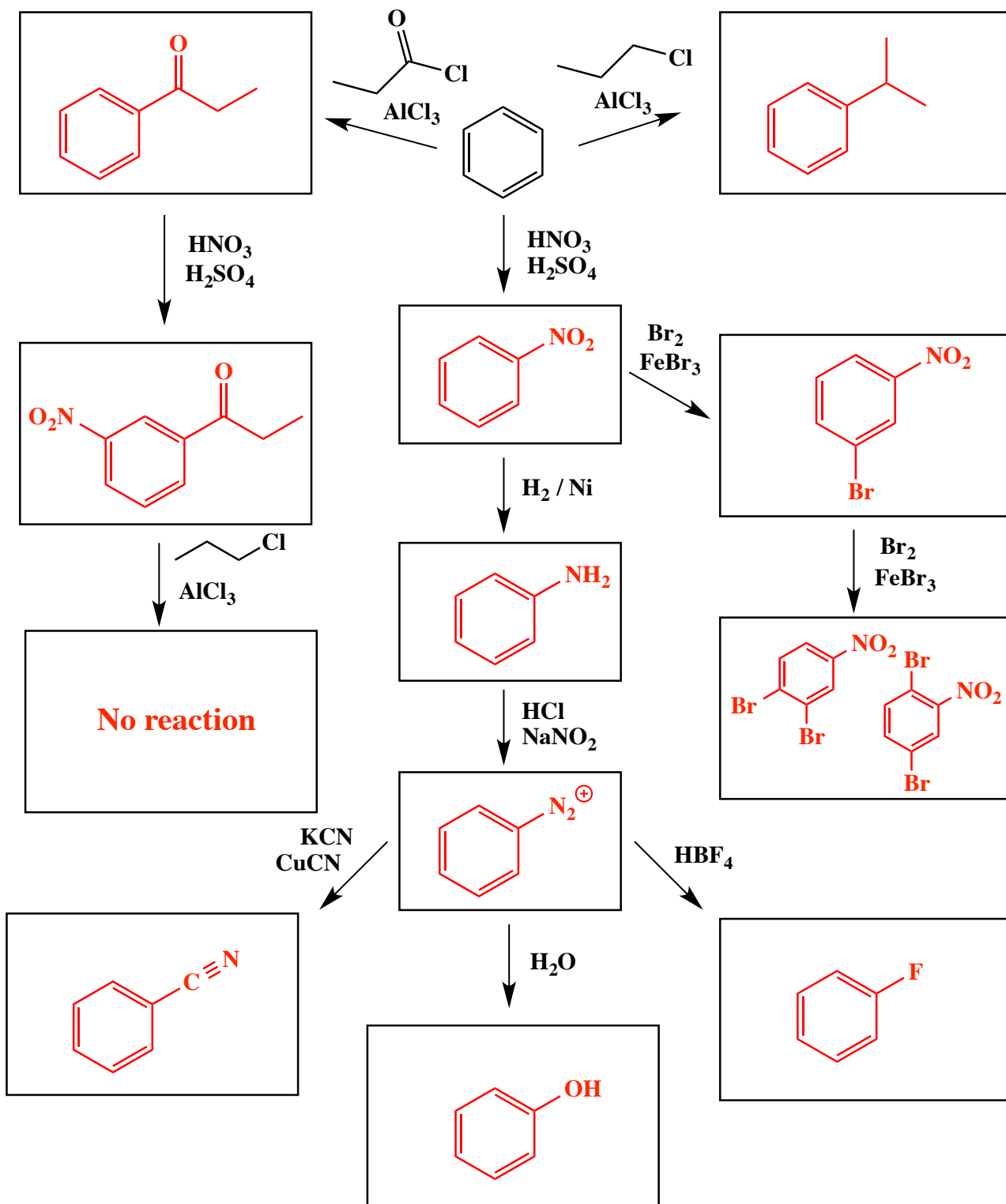
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21. (3, 4 or 5 pts.) Write the predominant carbon containing product or products that will occur for each transformation. If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, 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. Note that "no reaction" is an acceptable answer.

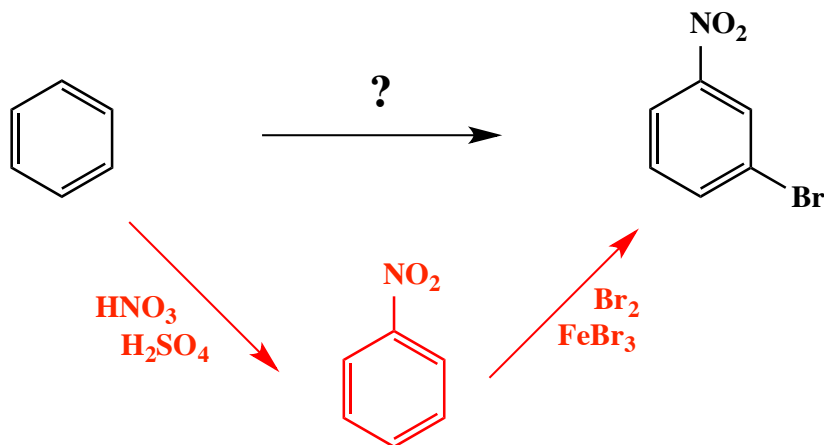


22. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic"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

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

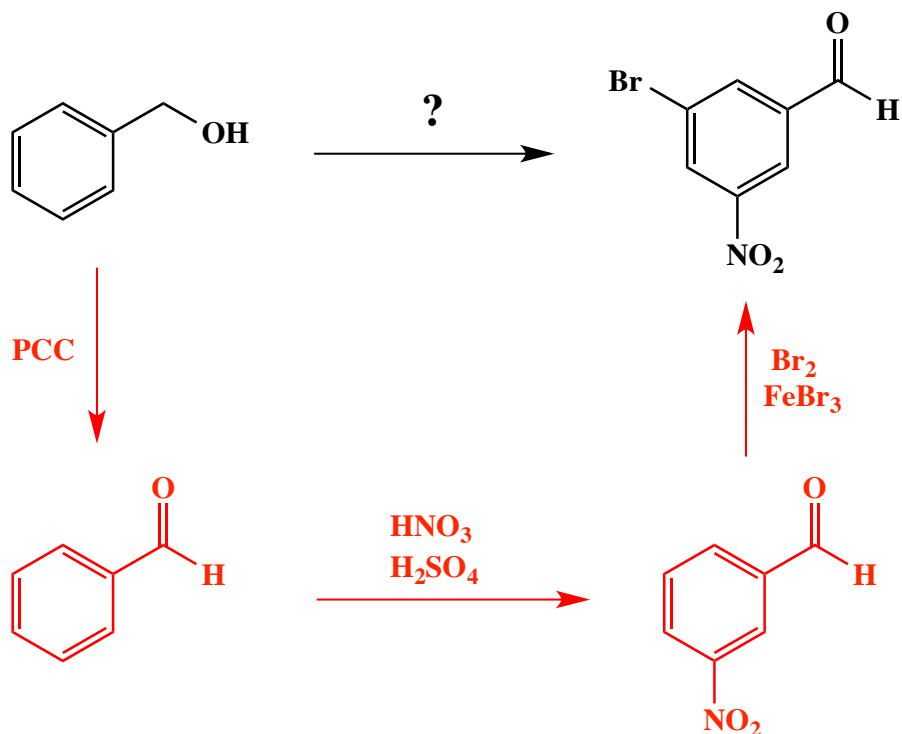
(4 pts)

A)



(7 pts)

B)

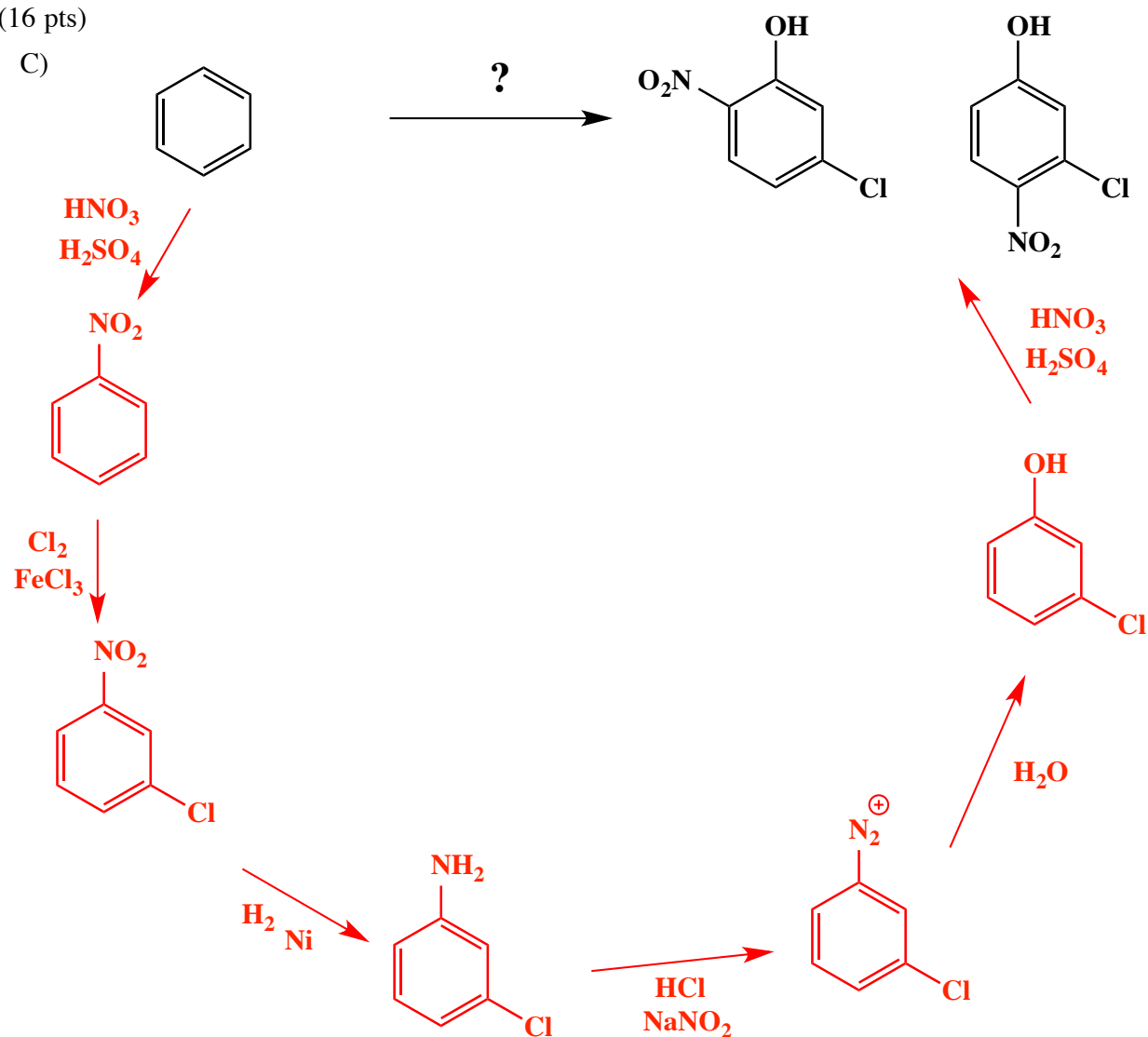


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Remember, all of the carbons of the product must come from the given starting material.

(16 pts)

C)

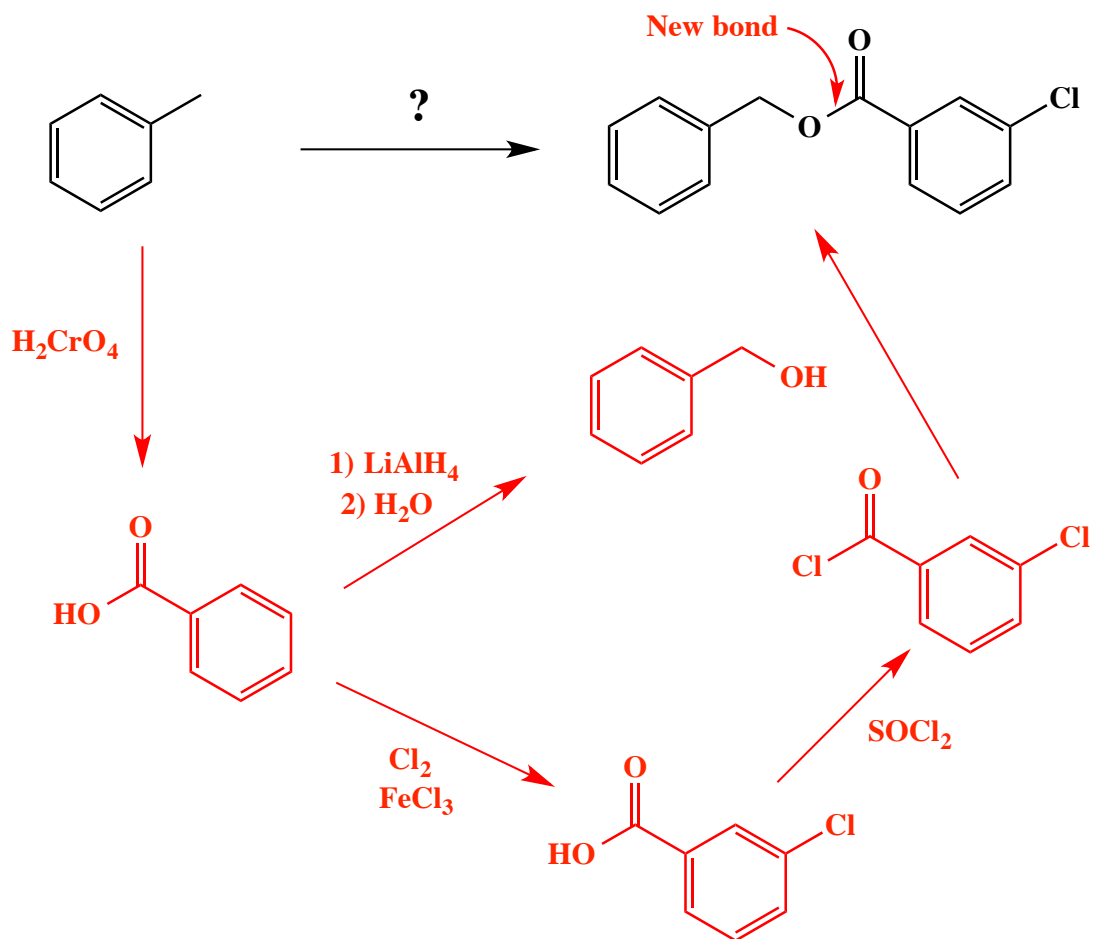


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Remember, all of the carbons of the product must come from the given starting material.

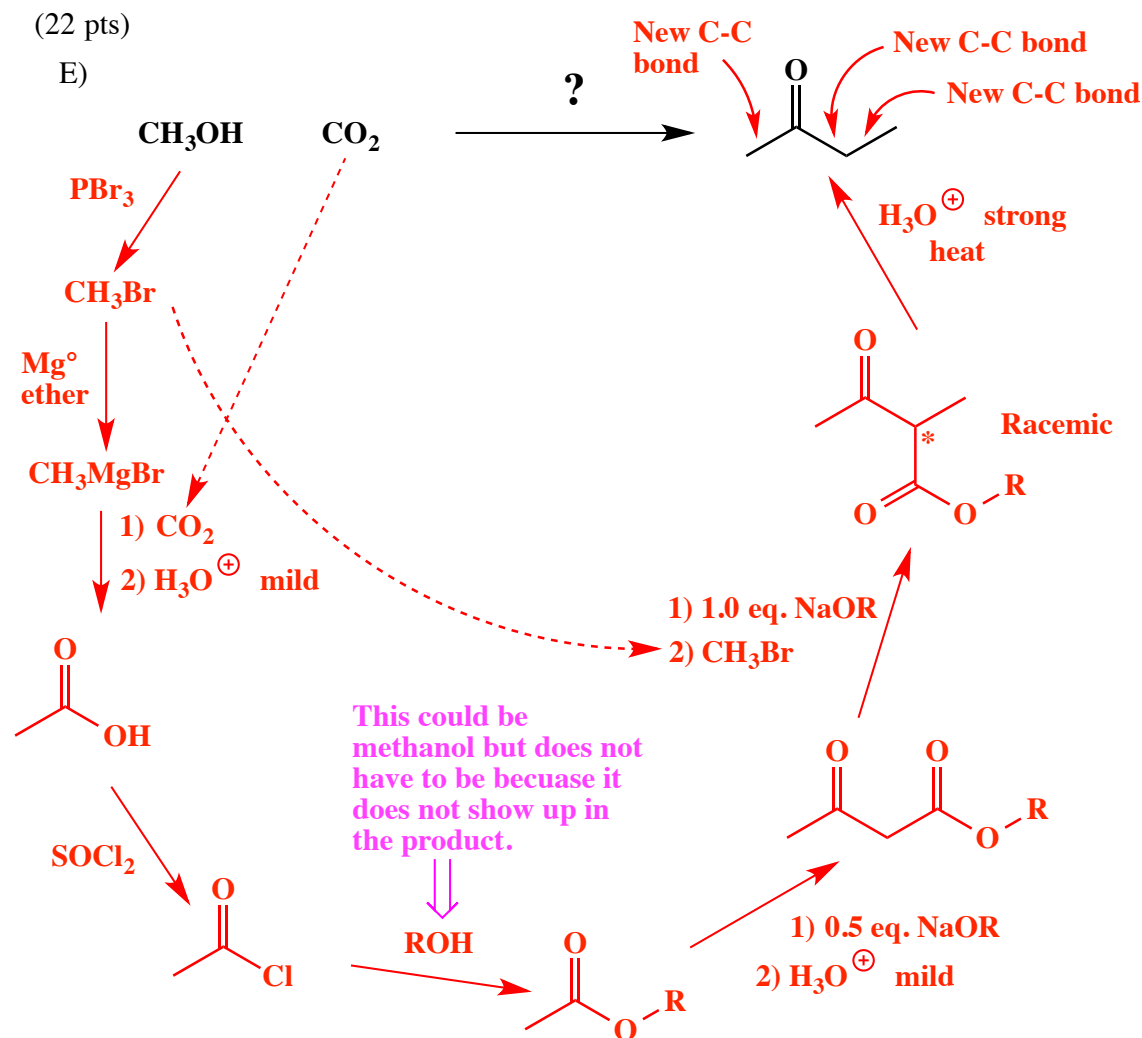
(13 pts)

D)

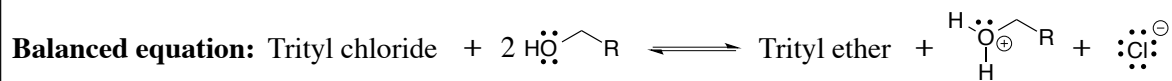
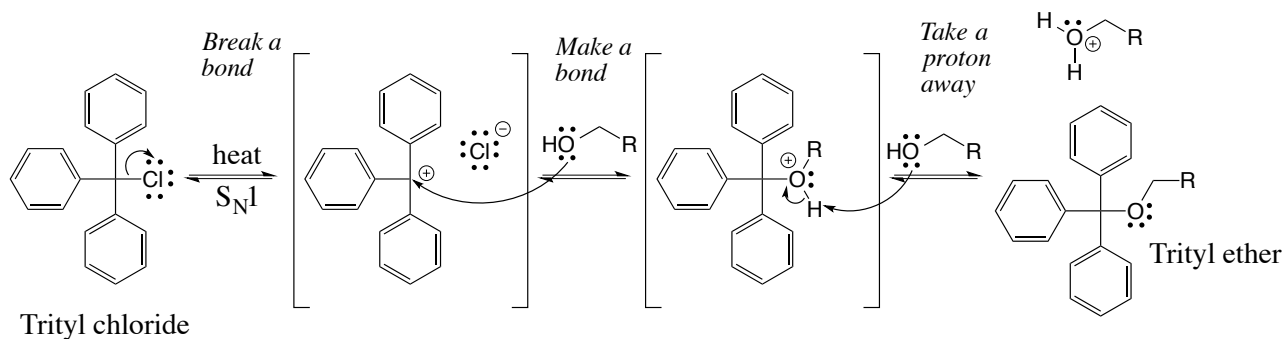


22. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to right "Racemic" where appropriate. Hint: This one is not as hard as you might think. TRUST YOUR KRE's!!

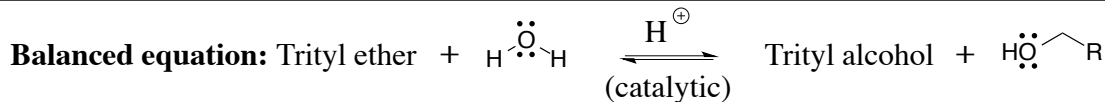
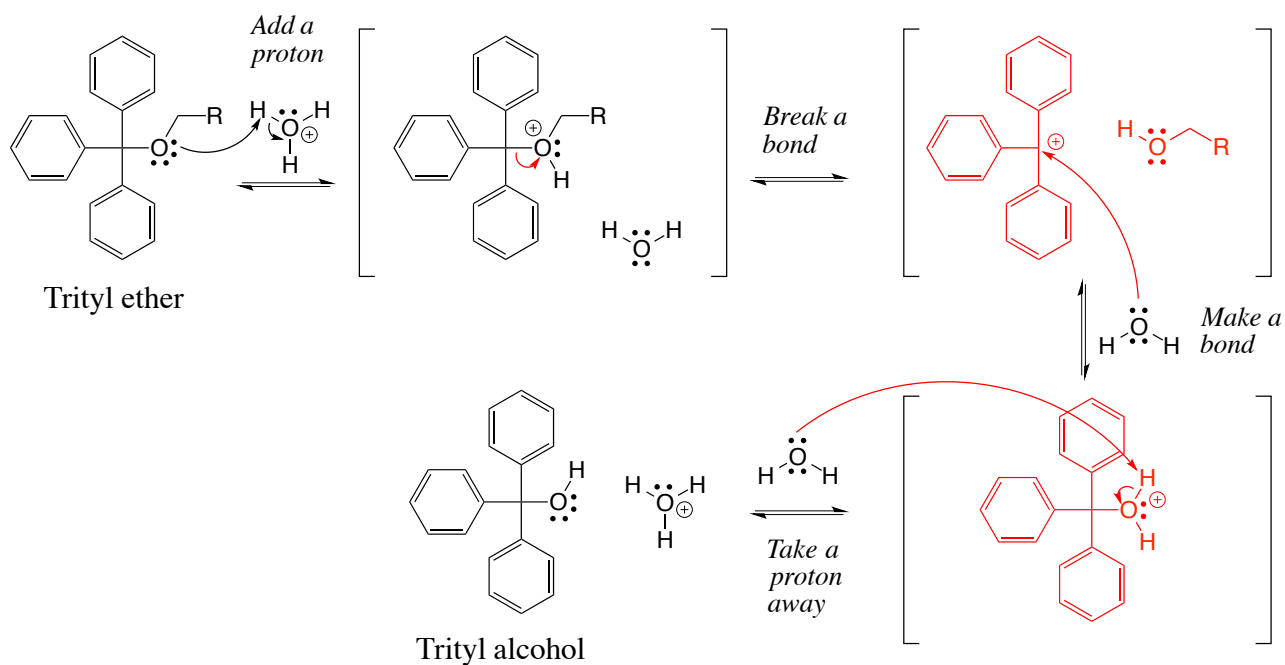
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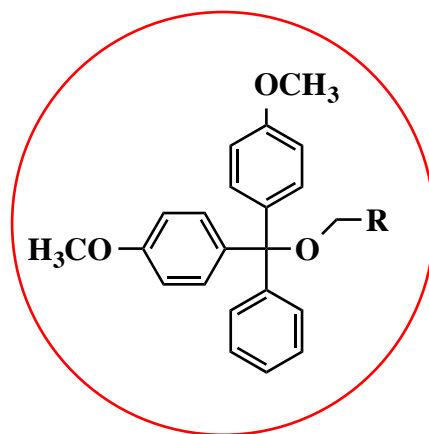
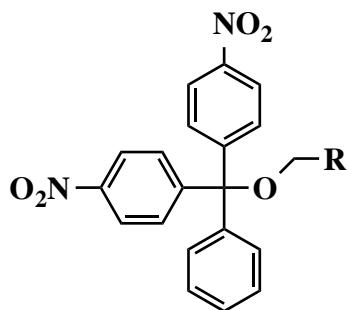
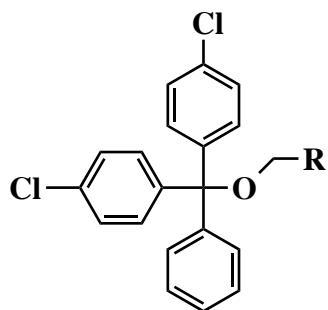
23. (16 pts total). Here is an “apply what you know” problem. Triphenylmethyl groups are used to protect alcohols and amines. The triphenylmethyl group is usually called “trityl” for short. The trityl group is added to an alcohol in an S_N1 process in which the alcohol, usually a primary alcohol, is heated with trityl chloride as shown to give the trityl ether.



(10 pts) Trityl ethers are stable to base and neutral conditions. They prevent alcohols from being deprotonated or acting as a nucleophile. Trityl ethers are removed in aqueous acid. **Fill in the structure of the missing key intermediates AND ALL MISSING ARROWS in the acid-catalyzed trityl ether hydrolysis reaction mechanism below. As always, show all lone pairs and formal charges.**



(6 pts) A trityl derivative is used to protect the primary alcohol function during the synthesis of oligonucleotides (DNA and RNA). As explained by the mechanism on the last page, the trityl group is removed in acid. It was determined that the trityl group was not quite reactive enough to come off under the mild acid conditions being used. As a result, a search was conducted for a trityl derivative that could be removed under milder acid conditions but is still stable enough to survive all the reaction conditions prior to its removal. The optimum trityl derivative has two of the three phenyl rings substituted. **Based on what you have learned since the last midterm and considering the mechanism you drew above, DRAW A CIRCLE AROUND the one derivative chosen because it comes off under milder acid conditions compared to unsubstituted trityl.**



This one is EXTRA CREDIT. It DOES NOT COUNT IN THE POINT TOTAL for the exam but it is a chance to add points to your score.

22. 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.

