NAME (Print): _____

SIGNATURE: _____

Chemistry 320N
Dr. Brent Iverson
Final Exam
May 10, 2017

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!!!

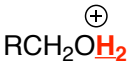
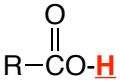
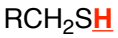
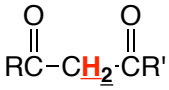
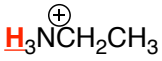
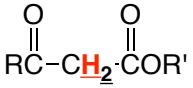
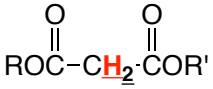
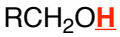
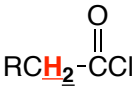
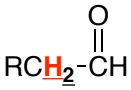
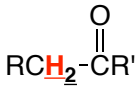
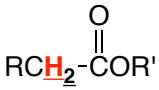
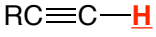
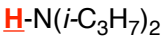
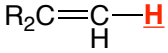
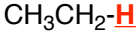
Page	Points	
1		(104)
7		(24)
8		(28)
9		(35)
10		(34)
11		(21)
12		(15)
13		(20)
14		(37)
15		(11)
16		(10)
17		(13)
18		(16)
19		(25)
20		(-)
21		(6)
Total		(399)

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
Thiols		8-9
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

This has been a difficult couple of weeks. Thank you for being an incredible class. The Longhorn family is strong. We proved that. We cannot change what happened, but we can each vow to be a little nicer to friends in need and a little more thoughtful around our families. The older I have become, the more I realize that helping other people, especially friends and family, is all that really matters.

In order to compensate for what we have been through combined with an early final timeslot, I wanted the format and even some questions to look very familiar to you. Best of luck.

Signature_____ Pg 1 _____(104)

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 (36 pts) Write the word or symbol that best completes the sentences.

1.1 aromatic
1.2 flat
1.3 2p
1.4 4n + 2
1.5 conjugation
1.6 smaller
1.7 longer
1.8 furanose
1.9 pyranose
1.10 hemiacetal
1.11 toward
1.12 away
1.13 alpha
1.14 beta
1.15 kinetic
1.16 reaction rate
1.17 thermodynamic
1.18 product stability

Question 2, 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)

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 acidic)

4 D

Question 5, page 4 (20 pts) Write the type of atomic orbital that contains the lone pair.

5.1 $2p$ 5.2 sp^2 5.3 $2p$ 5.4 sp^3

5.5 sp^3 5.6 $2p$ 5.7 $2p$ 5.8 sp^2

5.9 $2p$ 5.10 $2p$

Question 6, page 4 (2 pts) Write the pH (1.0, 5.0, 8.0, 11.0) corresponding to the protonation state of the molecule

6 1.0

Question 7, page 4 (2 pts) Total charge at pH 7.0

7 +1

Question 8, page 5 (4 pts) Write the type of glycosidic bond indicated by the arrow. Anwers might be α-1,4 or β-1,2, etc.

8.1 β-1,4 8.2 α-1,6

Question 9, page 5 (2 pts) Golden Rule 1 fill-in

9 valence

Question 10, page 5 (6 pts) Golden Rule 5-7 fill-in

10.1 Charges

10.2 Unpaired electrons

10.3 Pi electrons

Question 11, page 5 (4 pts) Golden Rule 8 fill-in

11.1 products

11.2 energy barrier

Question 12, page 5 (4 pts) Golden Rule 11 fill-in

12.1 nucleophiles

12.2 electrophiles

Question 13, page 5 (4 pts) Carbohydrate question

13.1 B 13.2 3

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

14.1 Nucleophile: B Electrophile A
14.2 Nucleophile: B Electrophile A
14.3 Nucleophile: A Electrophile B
14.4 Nucleophile: A Electrophile B
14.5 Nucleophile: A Electrophile B
14.6 Nucleophile: B Electrophile A
14.7 Nucleophile: B Electrophile A

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

1. (36 pts) **On page 1, fill in each blank with the word or words that best complete(s) the following sentences.**

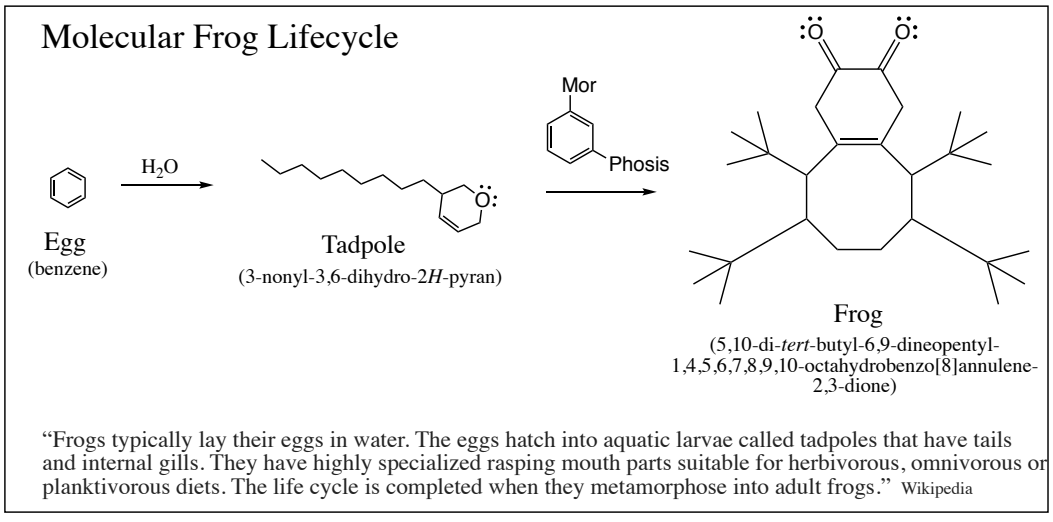
According to the Hückel definition, monocyclic molecules will be _____ (1.1) if they are
1) _____(1.2) ,
2) all the ring atoms have a _____ (1.3) orbital (the ring atoms are sp^2 hybridized or sp in rare cases)
3) there are _____ (1.4) pi electrons, where n = 0,1,2,3,4,5,6.....

For molecules with multiple double bonds, the greater the number of pi bonds in _____ (1.5) (we are looking for one key word) the _____ (1.6)(smaller/larger) the energy difference between filled and unfilled orbitals, so the _____ (1.7)(shorter/longer) the wavelength of light that is absorbed.

A five-membered ring formed by a carbohydrate is called a _____ (1.8) while a six-membered ring formed by a carbohydrate is called a _____ (1.9). In both cases, the ring is formed by an –OH group reacting with a carbonyl to give a cyclic _____ (1.10). When looking at a Fischer projection, groups that are horizontal are oriented (toward or away from) _____ (1.11) you, while groups that are vertical are oriented (toward or away from) _____ (1.12) you.

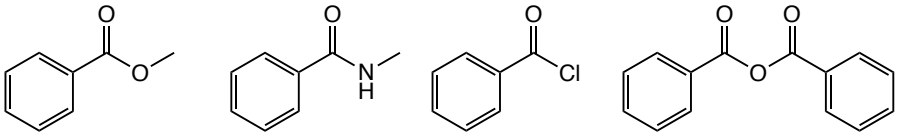
Both starch and cellulose are polymers of glucose, but starch has (alpha or beta) _____ (1.13) glycosidic bonds, so it is bent and therefore not rigid (potatoes). Cellulose has the glucose monomers linked via (alpha or beta) _____ (1.14) glycosidic bonds so it is flat and the chains can pack together nicely to create rigid cellulose (wood).

For the reaction of butadiene with HBr, the predominant product at low temperature is different from the predominant product at high temperature. At lower temperature, the reaction is said to be under _____ (1.15) control because all that matters is _____ (1.16) (reaction rate, or product stability). At higher temperature, the reaction is said to be under _____ (1.17) control because all that matters is _____ (1.18) (reaction rate, or product stability).



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

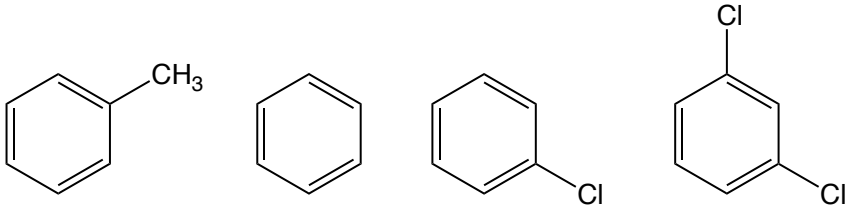
2. (2 pts) **On page 1, write the letter (A, B, C, or D) corresponding to the order of reactivity of the following molecules reacting with a nucleophile such as water. Rank them starting with the most reactive (reacts the fastest) and ending with the least reactive (reacts the slowest).**



I II III IV

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

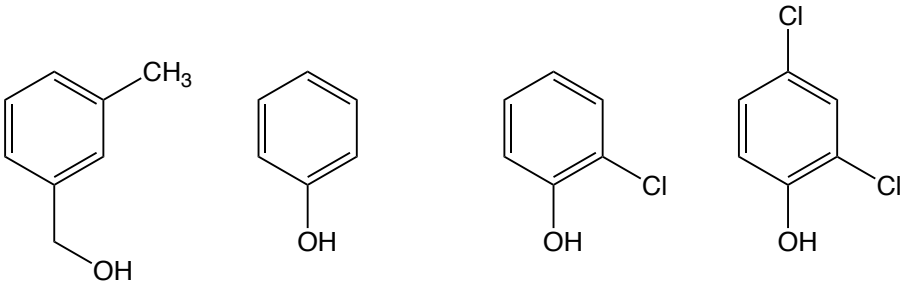
3. (2 pts) **On page 1, write the letter (A, B, C, or D) corresponding to the order of reactivity of the following molecules reacting with a wicked strong electrophile. Rank them starting with the most reactive (reacts the fastest) and ending with the least reactive (reacts the slowest).**



I II III IV

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

4. (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.**

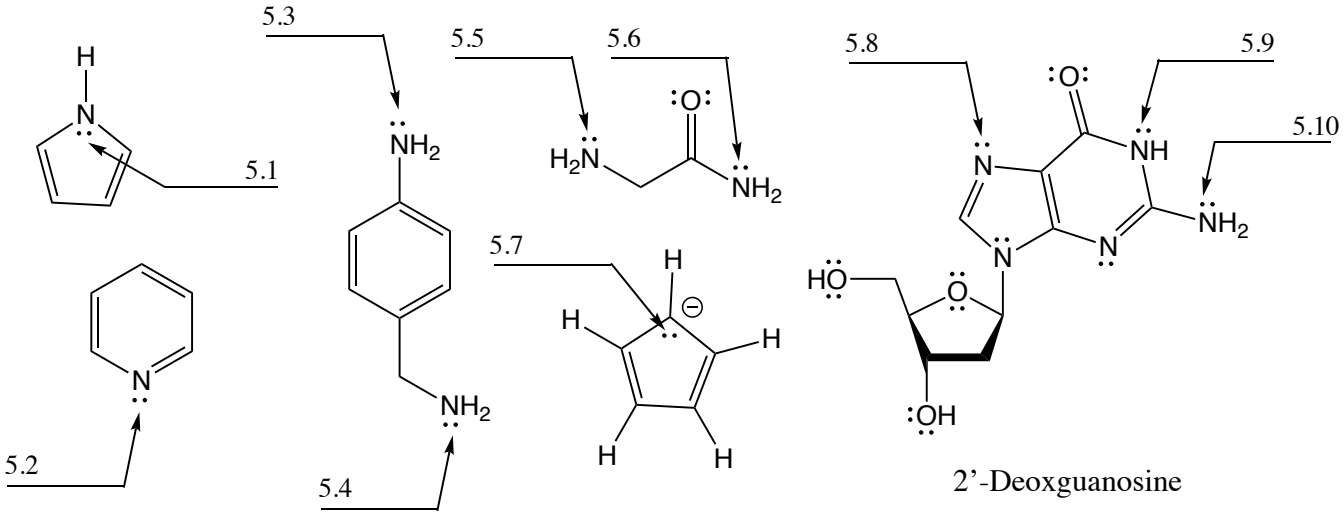


I II III IV

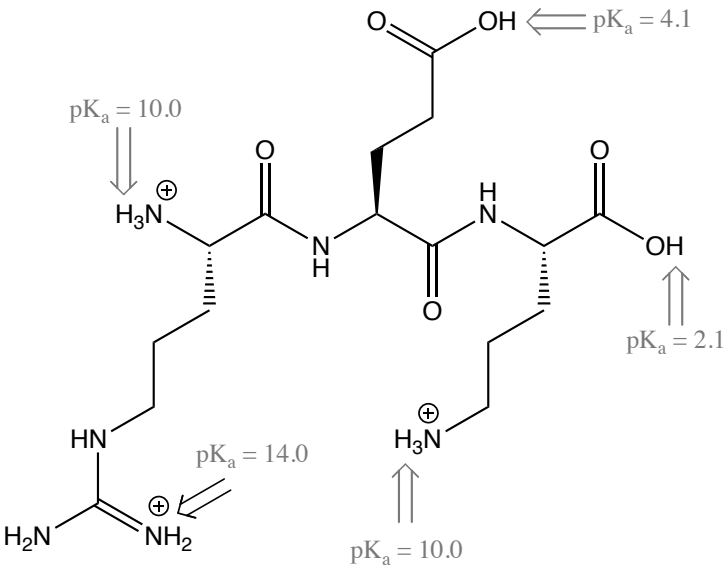
A: I > II > III > IV
B: IV > III > I > II
C: III > IV > I > II
D: IV > III > II > I

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

5. (20 pts) **Following are several molecules with atoms that have lone pairs. On page 1, write the type of atomic orbital (*sp*³, *2p*, etc.) that contains the lone pair indicated by the arrow.**



6. (2 pts) For the following peptide, the relevant pK_a values are provided. **Based on the protonation states of the different functional groups drawn below, is the pH of the solution 1.0, 5.0, 8.0 or 11.0?**



1.

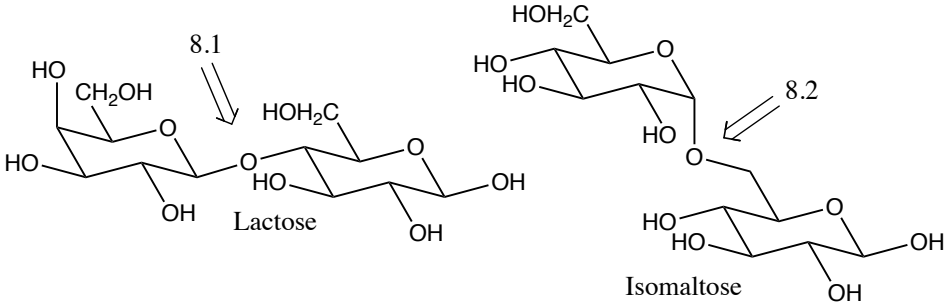
7. (2 pts) **What total charge would the above peptide have at pH 7.0?**

********** NOTICE THIS QUESTION**********

********** NOTICE THIS QUESTION**********

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

8. (2 pts). **On page 1, for the following disaccharide, write the type of glycosidic bond indicated by the arrow. The answer should be in the form α-1,4 or β-1,2, etc.**

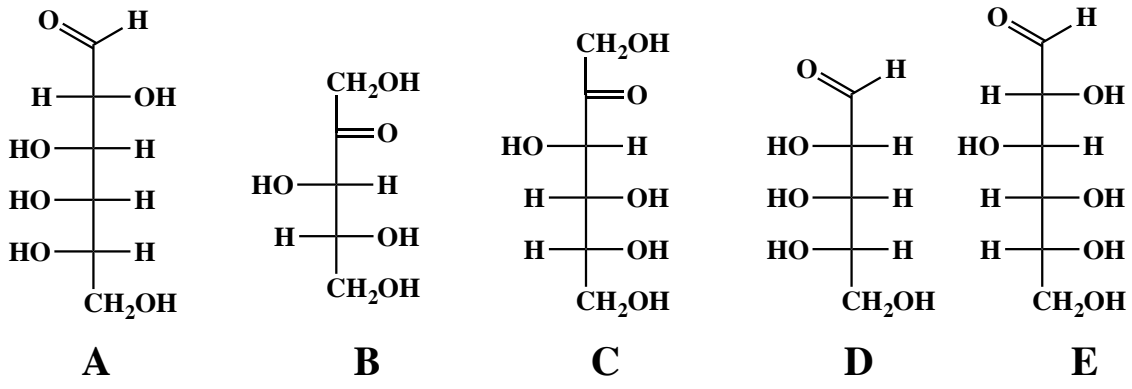


9. (2 pts) **According to the Golden Rule of Chemistry 1, "In most stable molecules all the atoms will have filled _____ shells".**

10. (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.**

11. (4 pts) **According to the Golden Rule of Chemistry number 8, "Reactions will occur if the _____**(11.1) **are more stable than the reactants and the _____** (11.2) **barrier is low enough." On page 1, fill in the two words that complete the Golden Rule of Chemistry number 8.**

12. (4 pts) **According to Golden Rule of Chemistry number 11, "Most bond making steps in reaction mechanisms involve _____** (12.1) **reacting with _____**(12.2)**."**

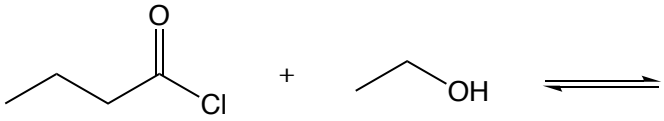


13.1 On page 1, write the letter (A-E) corresponding to which of the above five carbohydrates is a D-ketopentose

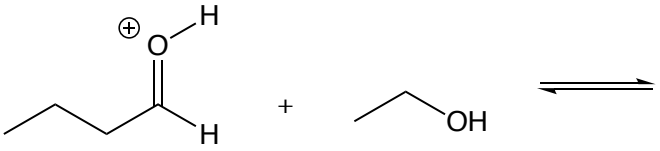
13.2 How many of the five carbohydrates above are of the D configuration?

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

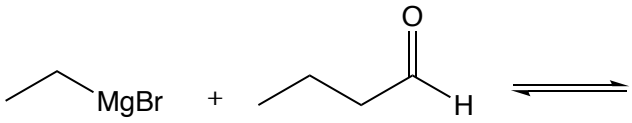
14. (2 pts each). On Page 1, for the following sets of reagents write the correct letter A or B to identify which is the nucleophile and which is the electrophile. You do not need to draw arrows or intermediates on this page.

14.1 

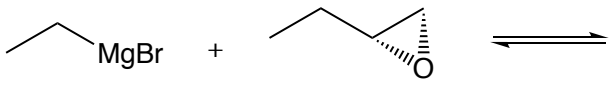
A **B**

14.2 

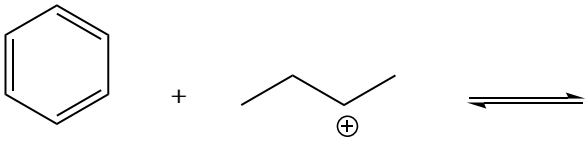
A **B**

14.3 

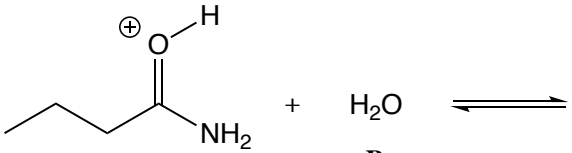
A **B**

14.4 

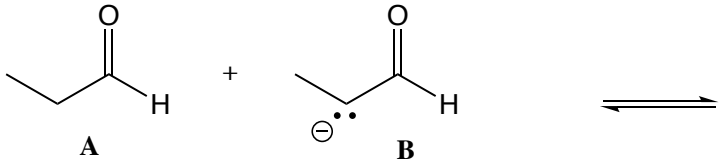
A **B**

14.5 

A **B**

14.6 

A **B**

14.7 

A **B**

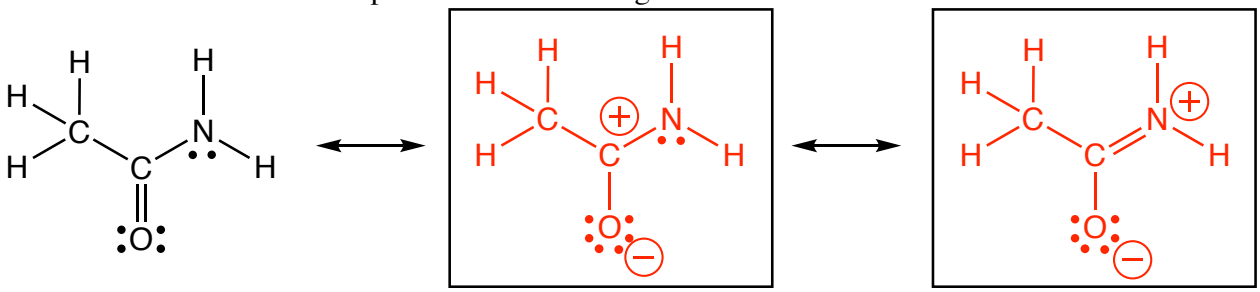
15. (2 pts) What is the most important question in chemistry?

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.

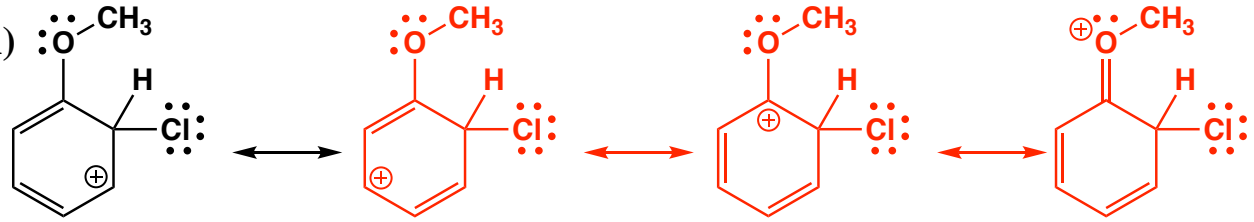
The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on the **same principles as NMR**, namely the **flipping (i.e. resonance) of nuclear spins of protons** by **radio frequency irradiation** when a patient is placed in a **strong magnetic field**. **Magnetic field 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.

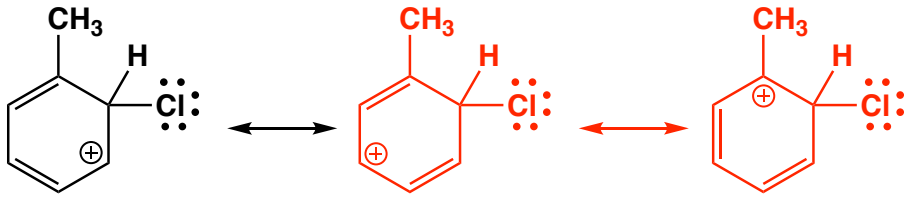


18. (16 pts) **Draw all of the <u>important</u> contributing structures for the following ions. You do NOT need to draw arrows for this one. Draw all bonds, charges and lone pairs that are missing from the following structures. Note: we provided template malecules for you to speed this up. Again, you need to draw all bonds, lone pairs and charges on the structures.**

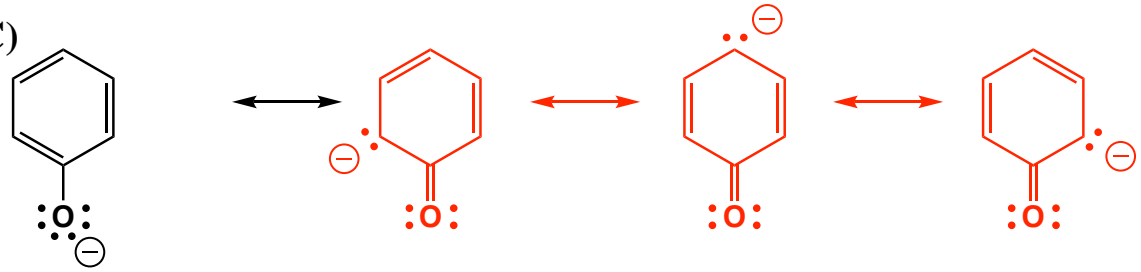
A)



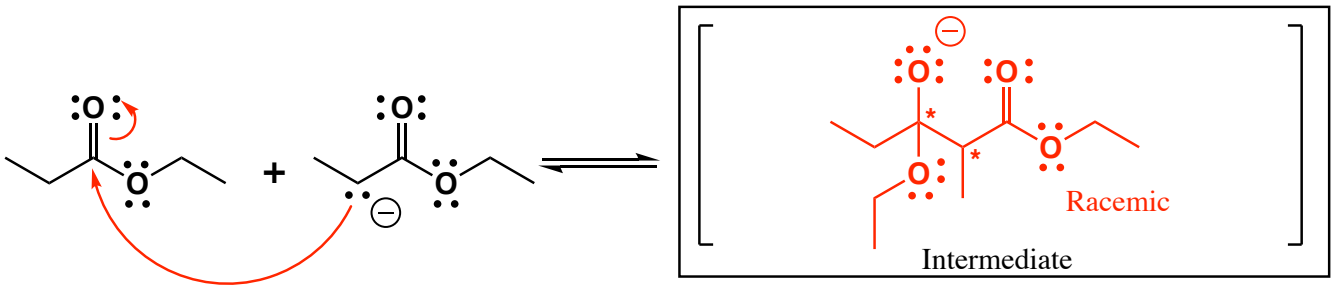
B)

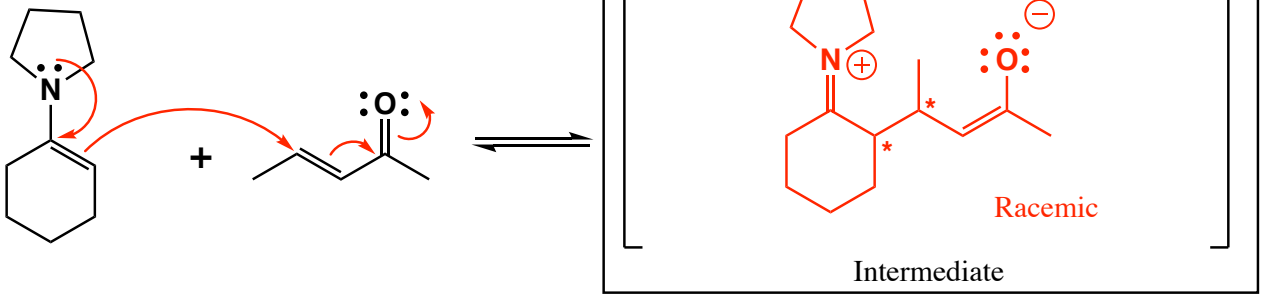


C)

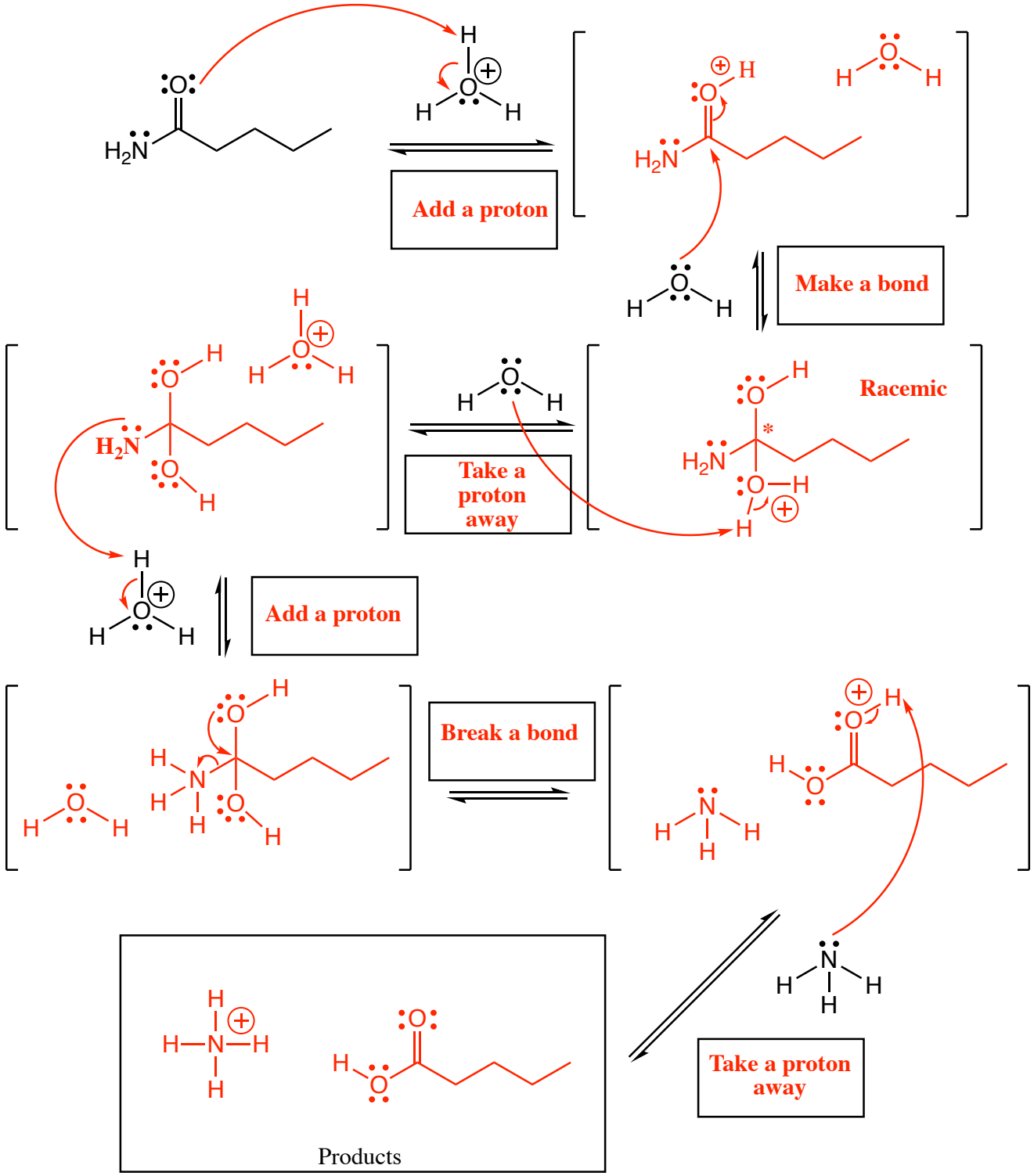


19. (12 pts) **Draw arrows on the following molecules and the structure(s) you expect to be formed in these reaction steps. Notice, in these reactions you will be drawing an intermediate, not a final product.**

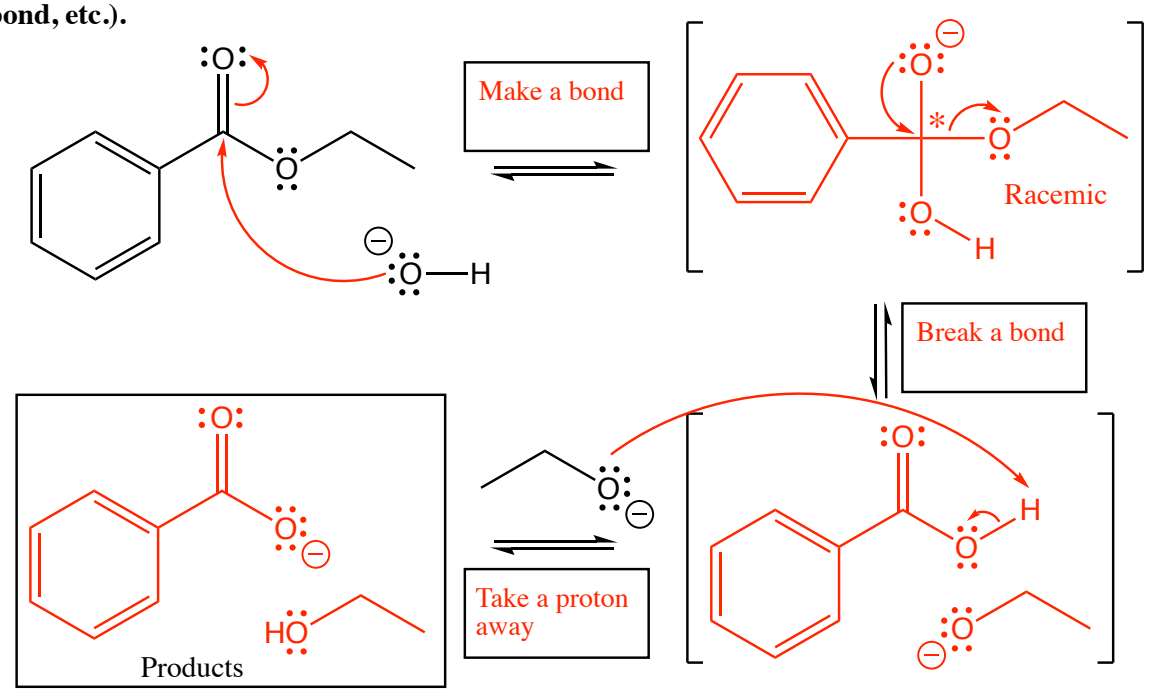


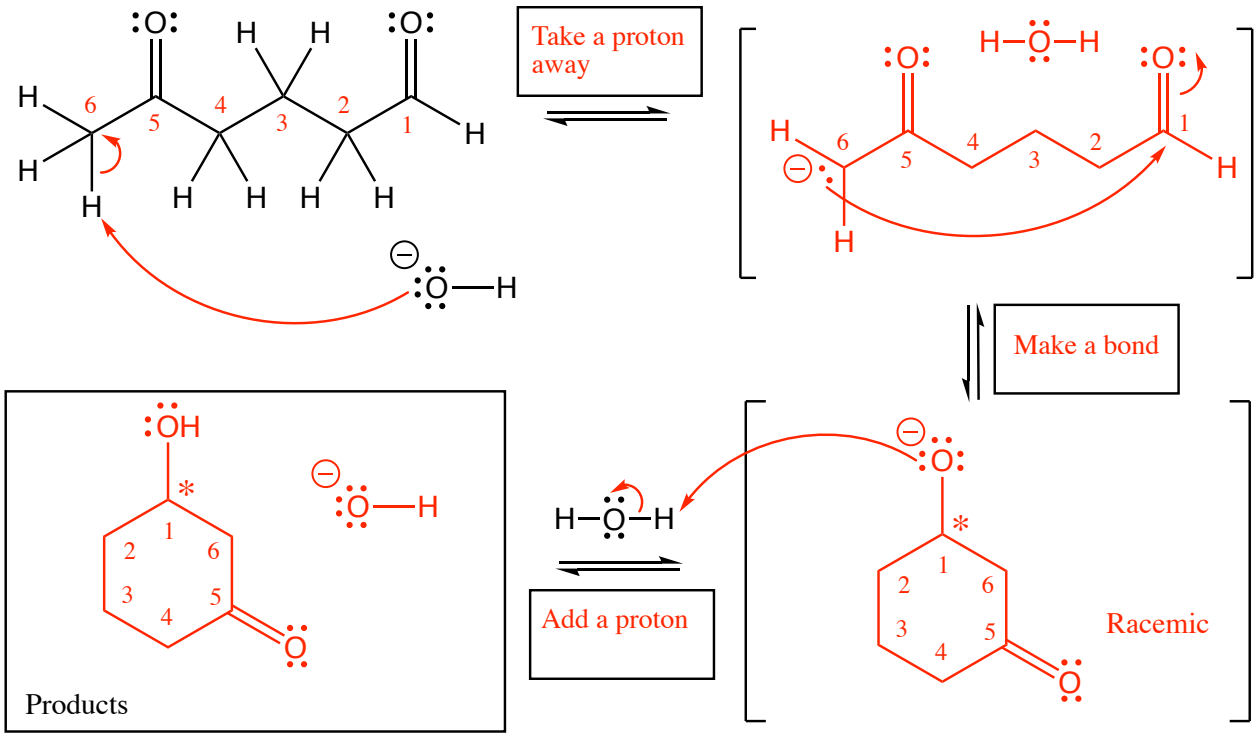


15. (35 pts) Complete the mechanism for the following amide hydrolysis reaction. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each 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.).**

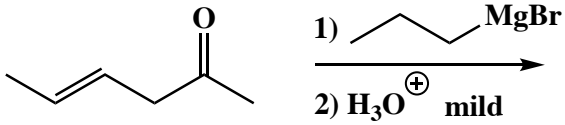


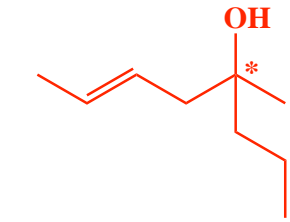
19. (34 pts) Complete the following ester hydrolysis (**2**) and aldol (**3**) reactions. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products 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.).**



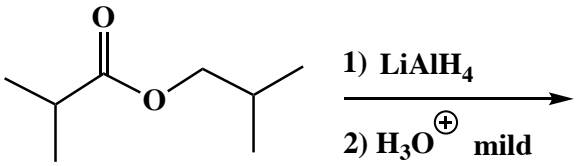


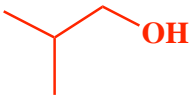
22. (3, 4, 5 or 6 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH.** If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk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

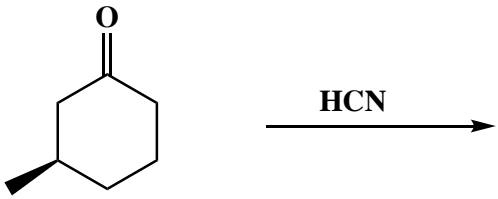


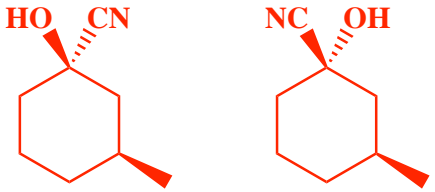


racemic

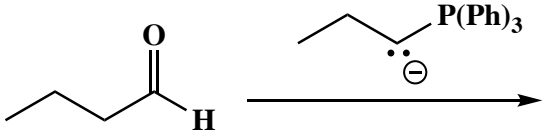


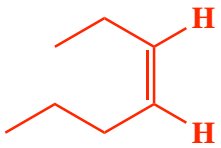
2 



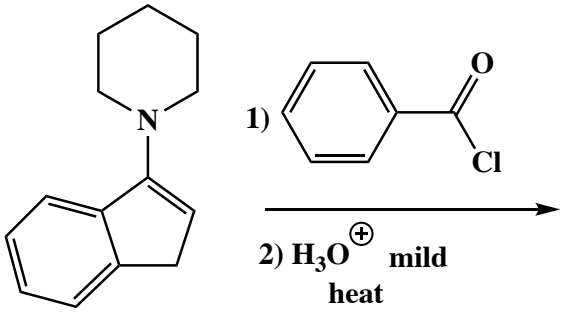


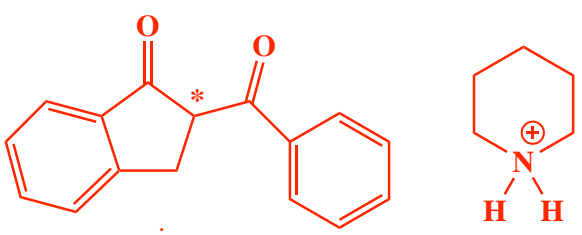
(not racemic)





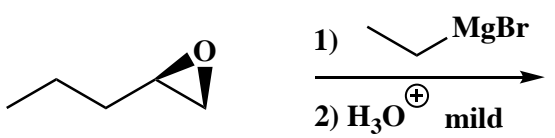
Z product

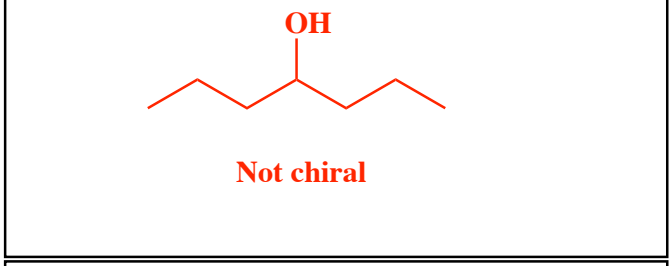


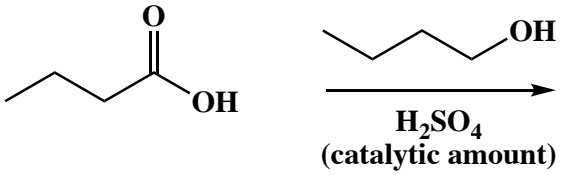


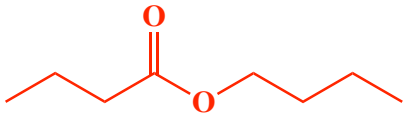
racemic

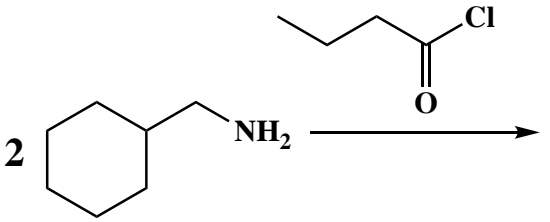
22. (3, 4, 5 or 6 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH.** If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk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

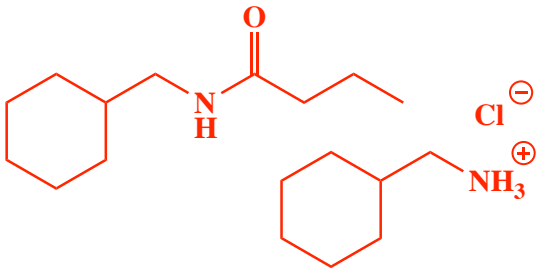


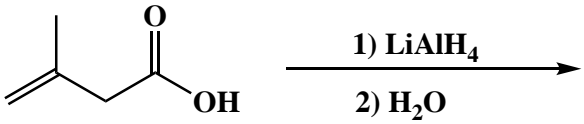


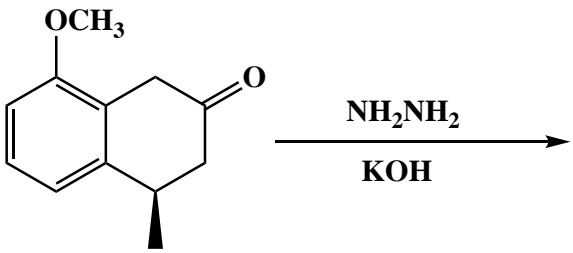


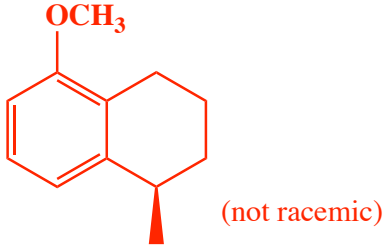




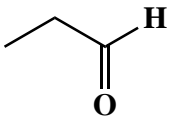






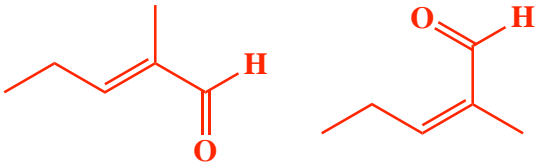


22. (3, 4, 5 or 6 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) and write racemic. No need for wedges and dashes. However, if an E,Z mixture is formed, you need to draw both!**

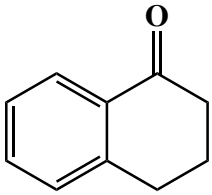


1) catalytic NaOH

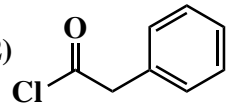
2) $H_3O^{\oplus}$ heat (dehydration)

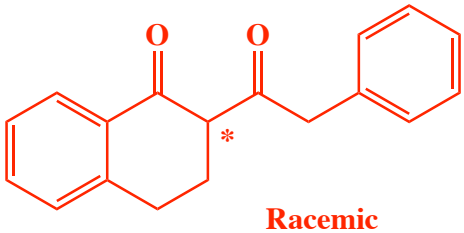


E,Z mixture

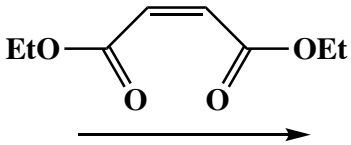


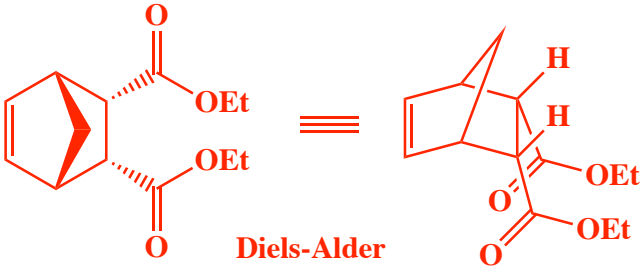
1) 1.0 eq. LDA

2) 

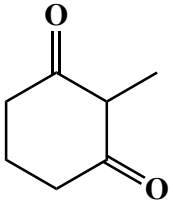


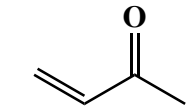
Racemic



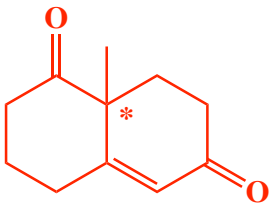


Diels-Alder



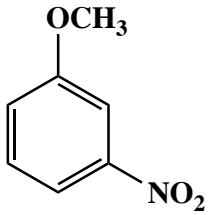


catalytic NaOH
heat



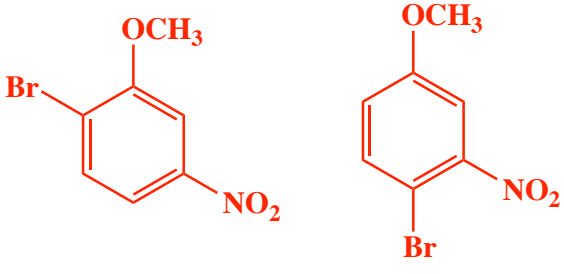
Robinson

Racemic

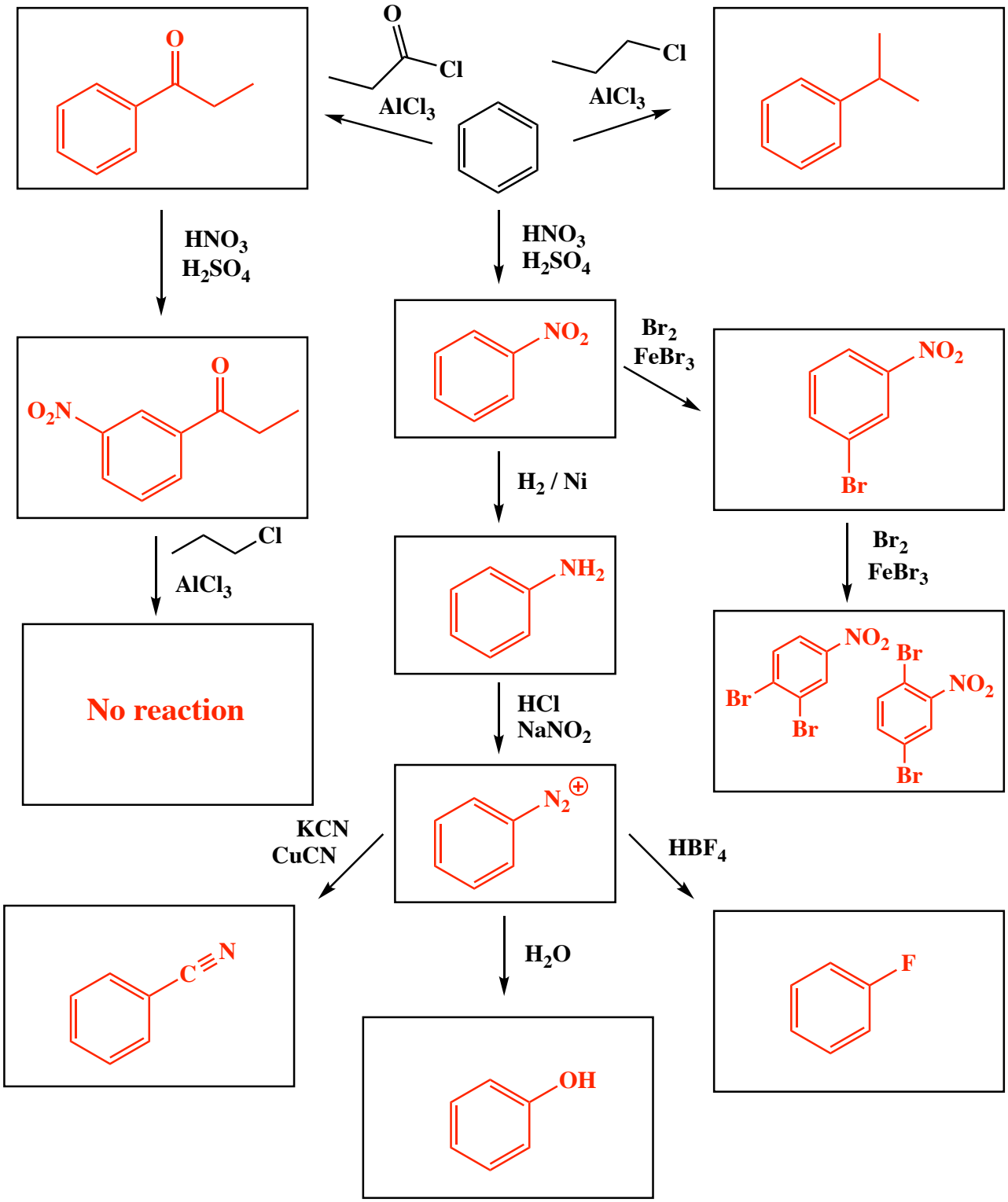


Br_2

$FeBr_3$



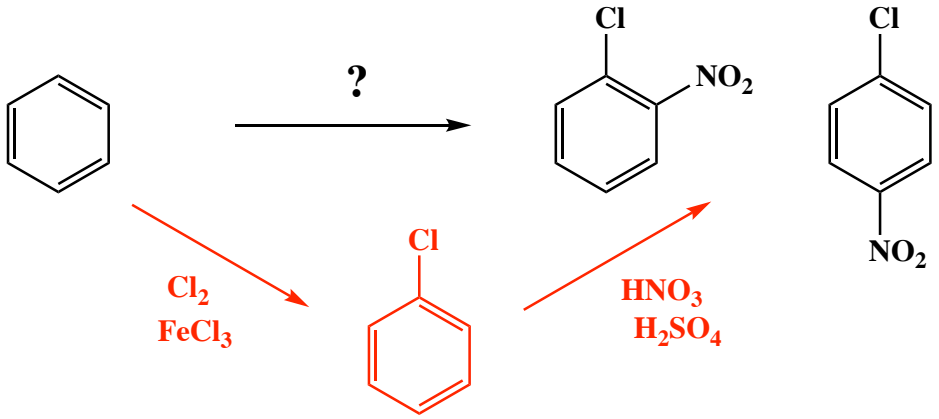
23. (3, 4 or 5 pts.) Write the predominant **carbon containing** product or products that will occur for each transformation. **If there are two carbon containing products, WRITE THEM BOTH. If a new chiral center is created and a racemic mixture is formed, label the chiral center with an asterisk (*) 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.**



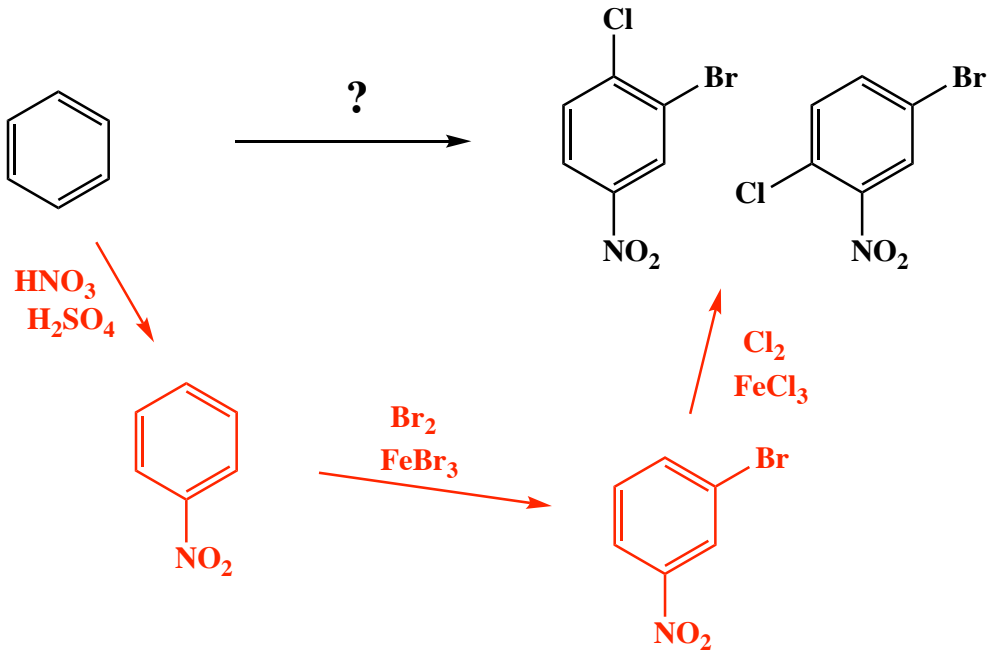
24. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to write "Racemic"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

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

A) (4 pts)



B) (7 pts)

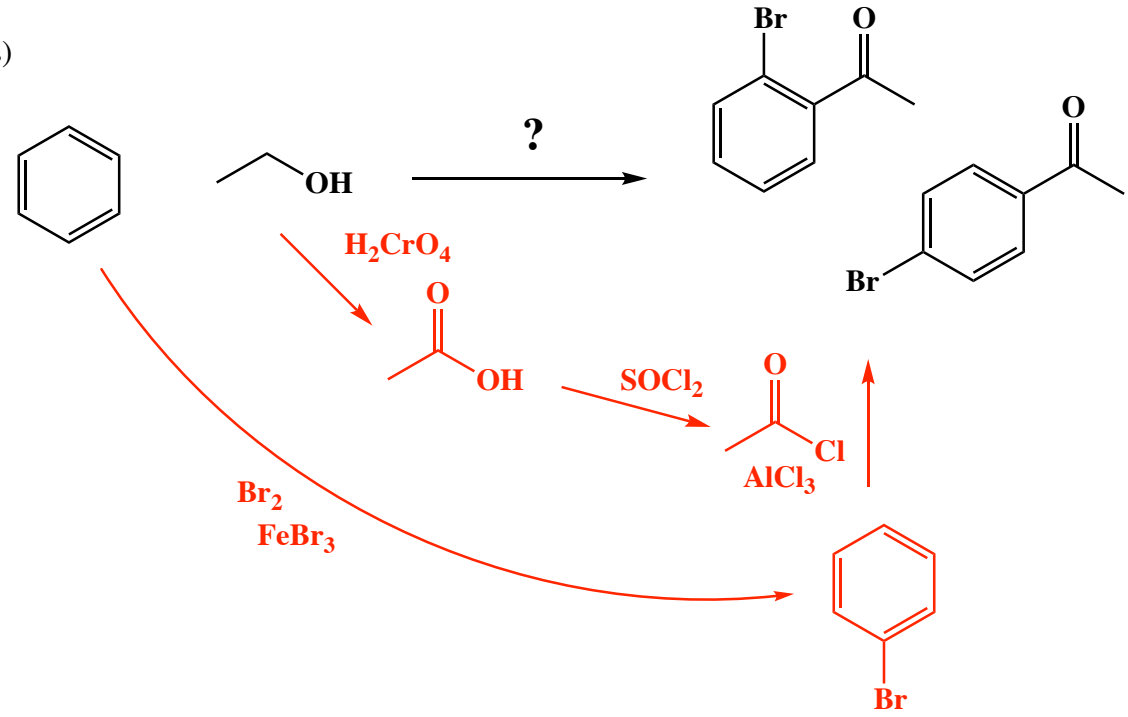


24. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to write "Racemic"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

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

(10 pts)

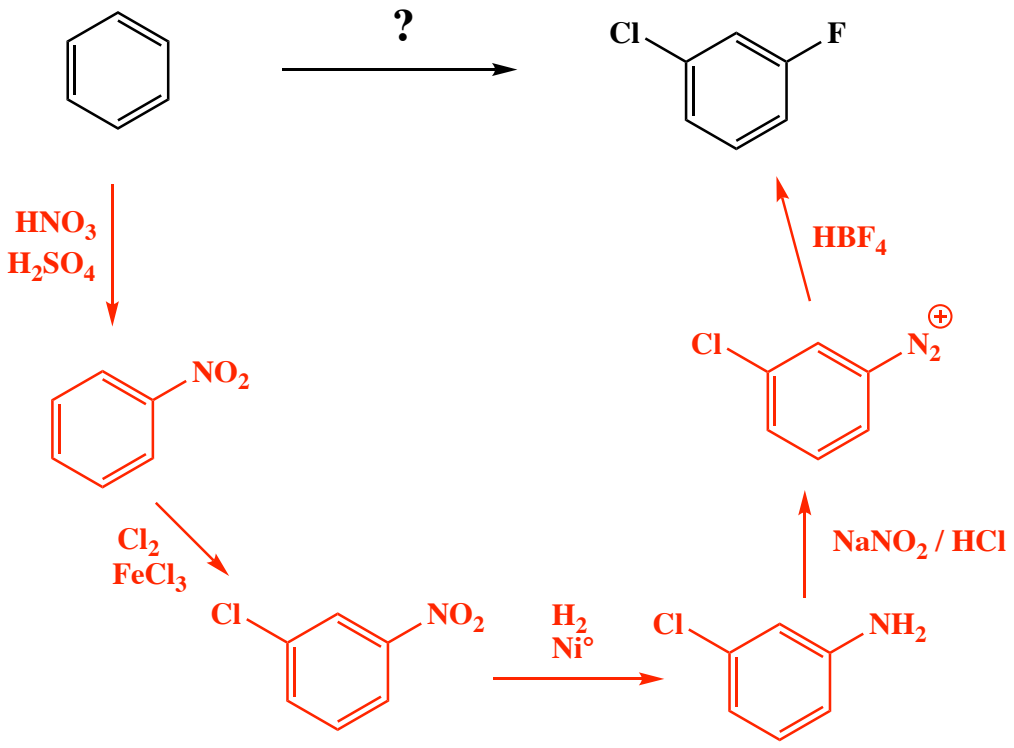
C)



24. 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 write "Racemic" where appropriate.

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

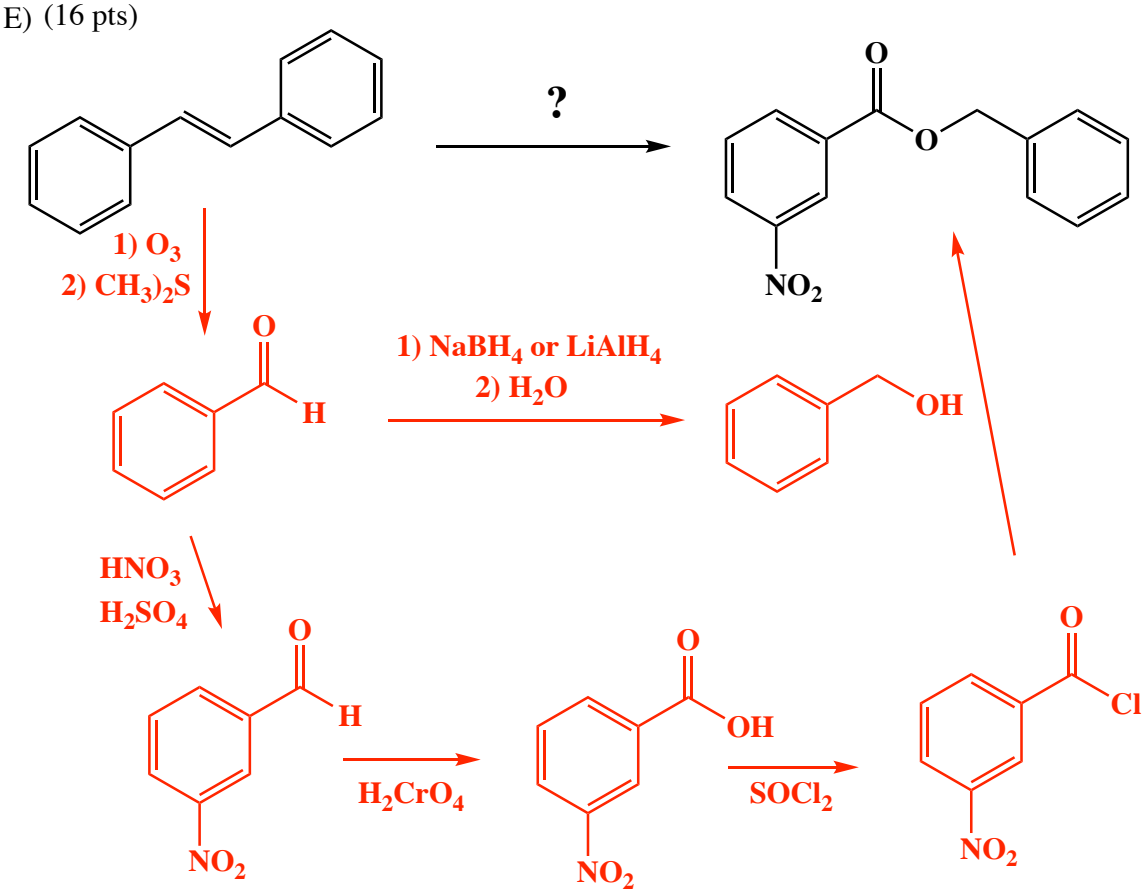
D) (13 pts)



24. 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 write "Racemic" where appropriate.

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

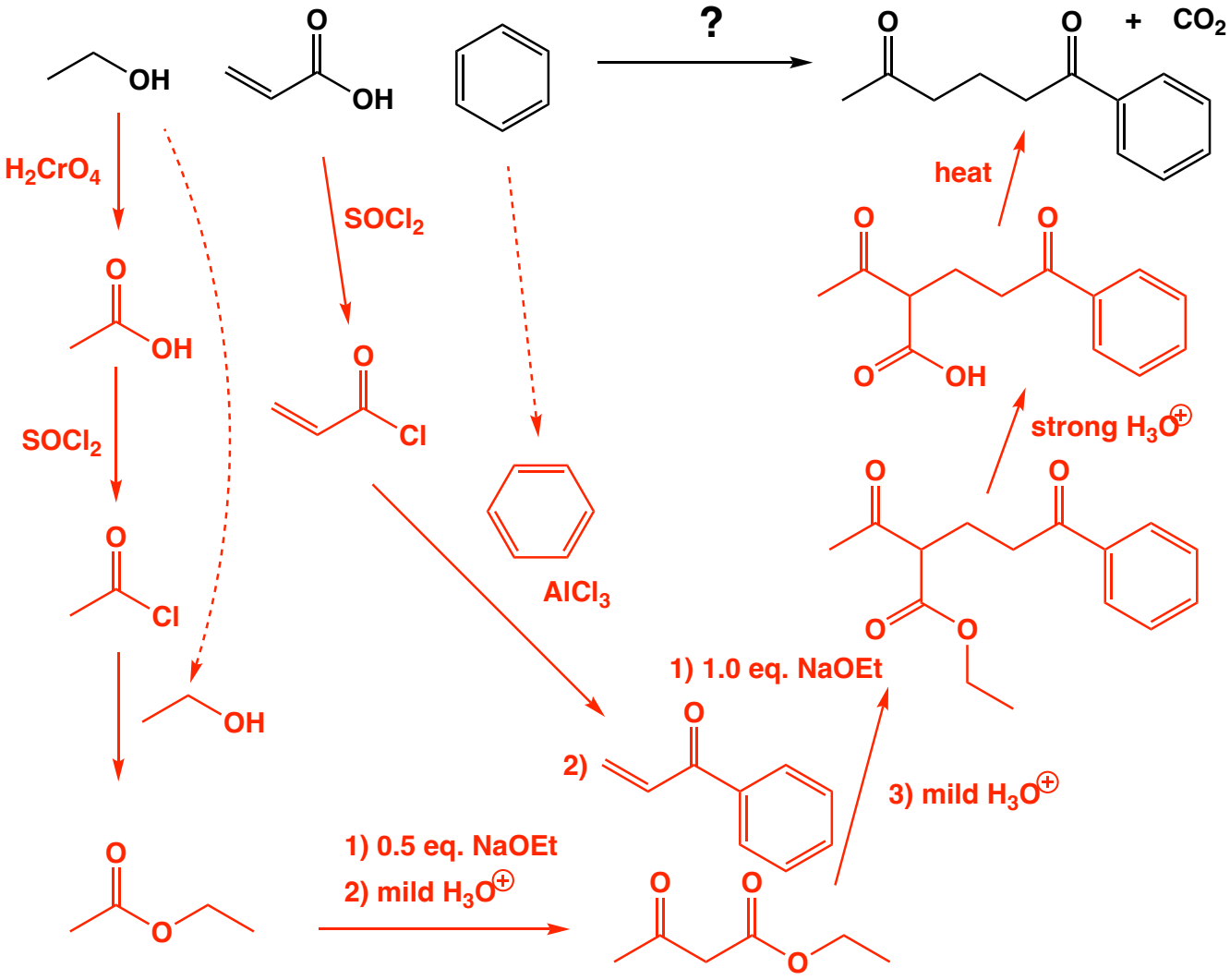
E) (16 pts)



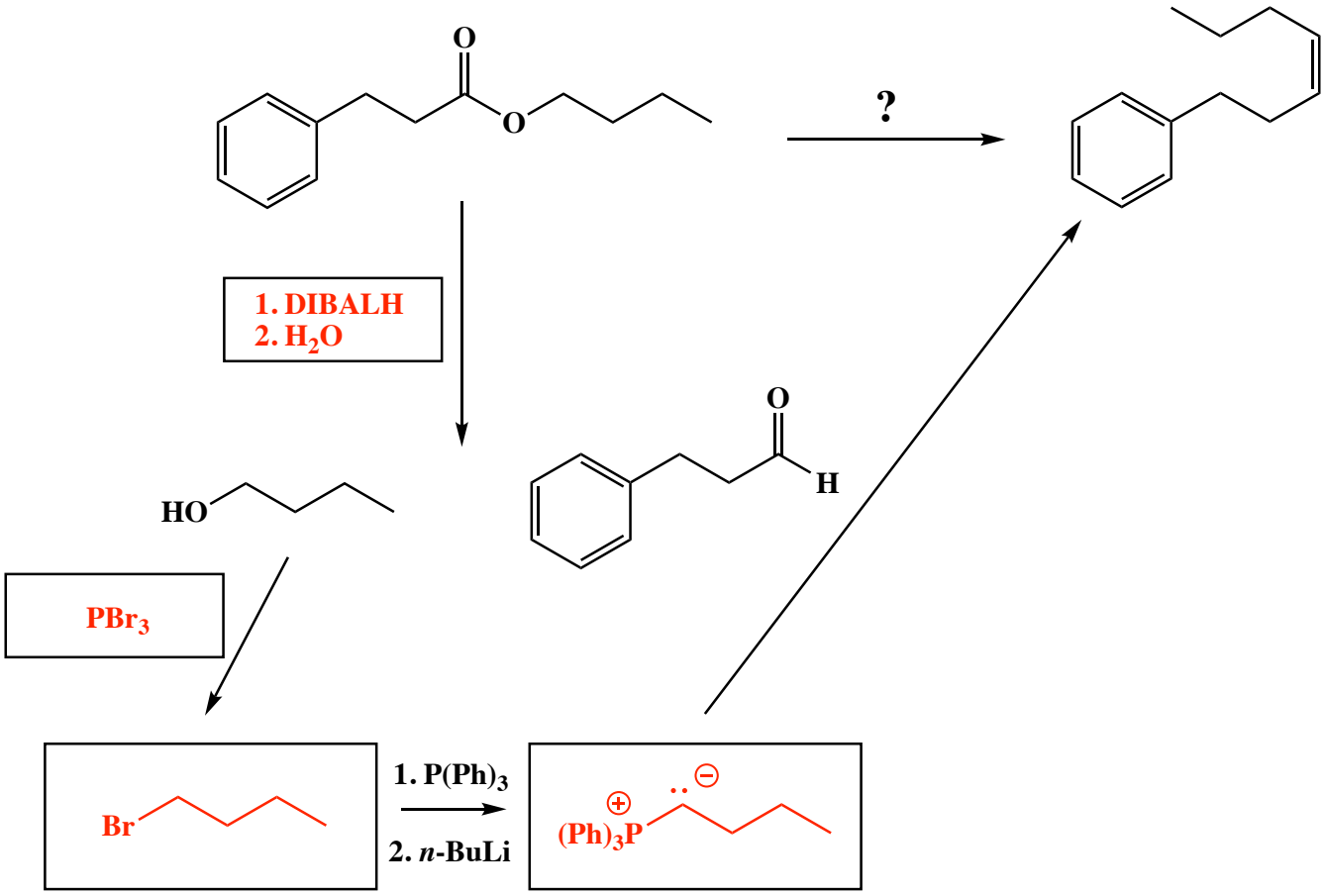
24. Using any reagents turn the starting material into the indicated product. All carbon atoms in the product must come from the starting material. Draw all molecules synthesized along the way. When in doubt, draw the molecule! Label all chiral centers with an asterisk (*) and make sure to write "Racemic"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

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

F) (25 pts)



25. (1 or 2 points) For this last one, fill in the boxes with the two reagents (the first one is "diabolical") and two structures needed to complete the synthesis.



This question is only worth 6 points, but it is intended to illustrate the power of the chemistry you have learned. In just four reactions you can convert an ester into an alkene! Note this is the exact reverse of what you were asked to do for the synthesis problem on page 18.

I have very much enjoyed getting to know all of you. As one of my favorite poets of the 20th century put it: “May your wishes all come true. May you build a ladder to the stars and climb on every rung. May you stay forever young. May your heart always be joyful and may your song always be sung. And may you stay forever young.” BD

Remember, run every chance you get. Being fit for your entire life is truly the best way to stay forever young.

Brent Iverson