NAME (Print): ______________________________

EID _______________

SIGNATURE: ______________________________

Chemistry 320N
1st Midterm Exam
February 15, 2024

Please print the first three letters of your last name in the three boxes

Please Note: Please take your time. You have three hours to take this exam. Please do not rush, we want you to show us everything you have learned this semester so far! Making careless mistakes is not good for anyone! If you find yourself getting anxious because of a problem, skip it and come back. Please do not second guess yourself! Keep track of the questions worth a lot of points. (This does not mean they are hard, it just means we think they cover important material.)

One last thing: I recommend you close your eyes for a moment, then take some nice deep breaths before you begin. YOU GOT THIS!

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!!!

Student Honor Code for the University of Texas at Austin

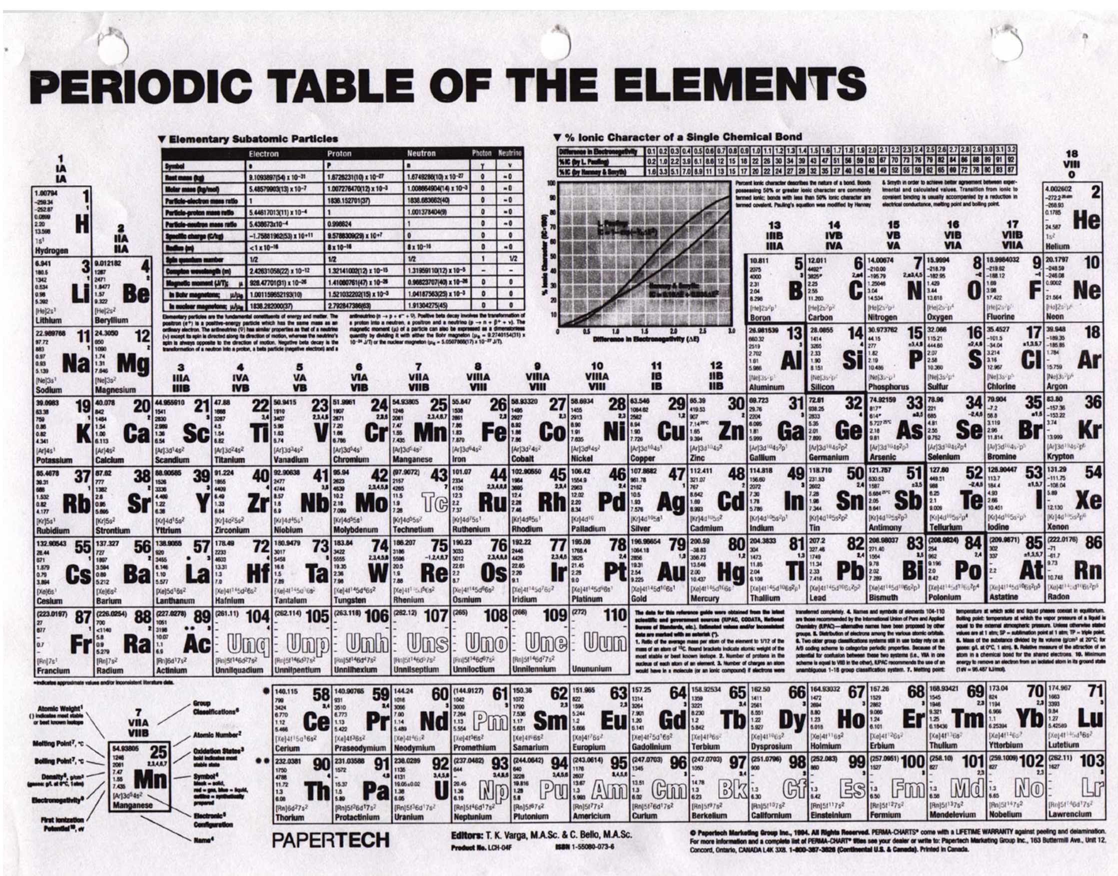
"I pledge, as a member of The University of Texas at Austin community, to do my work honestly, respectfully, and through the intentional pursuit of learning and scholarship."

Elaboration

1. I pledge to be honest about what I create and to acknowledge what I use that belongs to others.
2. I pledge to value the process of learning in addition to the outcome, while celebrating and learning from mistakes.
3. This code encompasses all of the academic and scholarly endeavors of the university community.

____

(Your signature)



Compound		pK_a
Hydrochloric acid	H-Cl	-7
Protonated alcohol	$RCH_2OH_2^{\oplus}$	-2
Hydronium ion	$H_3O^{\oplus}$	-1.7
Carboxylic acids	$R{-}C(=O)O{-}H$	3-5
Thiols	RCH_2SH	8-9
Ammonium ion	$H_4N^{\oplus}$	9.2
β-Dicarbonyls	$RC(=O){-}CH_2{-}C(=O)R'$	10
Primary ammonium	$H_3\overset{\oplus}{N}CH_2CH_3$	10.5
β-Ketoesters	$RC(=O){-}CH_2{-}C(=O)OR'$	11
β-Diesters	$ROC(=O){-}CH_2{-}C(=O)OR'$	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides	$RCH_2{-}C(=O)Cl$	16
Aldehydes	$RCH_2{-}C(=O)H$	18-20
Ketones	$RCH_2{-}C(=O)R'$	18-20
Esters	$RCH_2{-}C(=O)OR'$	23-25
Terminal alkynes	$RC{\equiv}C{-}H$	25
LDA	$H{-}N(i{-}C_3H_7)_2$	40
Terminal alkenes	$R_2C{=}CH{-}H$	44
Alkanes	$CH_3CH_2{-}H$	51

Signature______________________________ Pg 1 ______________(27)

1. (5 pts) What is the most important question in organic chemistry?

Where are the electrons?

2. (1 pt each) Fill in each blank with the word that best completes the sentences. Yep, this is the MRI paragraph!

The popular 1.____**medical**____ diagnostic technique of 2.____**magnetic**____

3.____**resonance**____ 4.____**imaging**____ (_5._**MRI**_) is based on the same

principles as NMR, namely the 6.____**flipping**____ (i.e. resonance) of

7.____**nuclear**____ spins of 8. __**H**__ atoms by radio 8.____**frequency**____

9.____**irradiation**____. 10. ____**Magnetic**____ 11.____**field**____

gradients are used to gain imaging information, and 12. ____**rotation**____ of the

13. ____**gradients**____ around the 14. ____**center**____ of the object gives imaging in

an entire plane (i.e. slice inside 15.____**patient**____). In an MRI image, you are looking at

individual 16.____**slices**____ that when 17.____**stacked**____ make up the three-

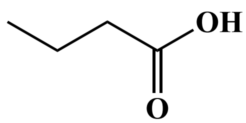
dimensional image of relative amounts of 18. ____**H**____ atoms,

especially the 19.____**H**____ atoms from 20.____**water**____ and

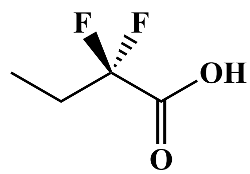
21.____**fat**____, in the different 22.____**tissues**____.

Signature________________________ Pg 2 ____________(18)

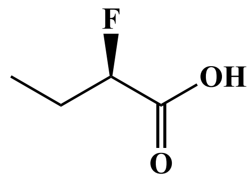
3. (1 pt each) Predict the relative acidities of the following molecules. Put the number 1 under the most acidic molecule, the number 4 under the least acidic molecule, and the numbers 2 and 3 under the other two stuctures as appropriate.



3



1



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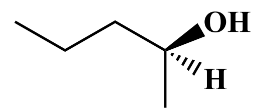
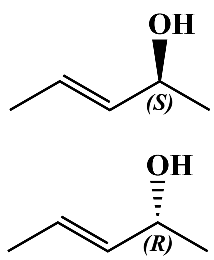
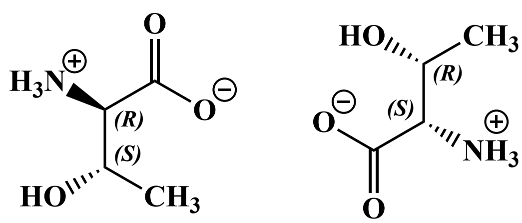


4

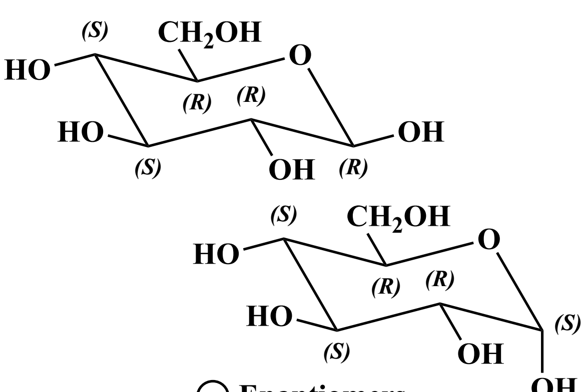
4. (3 pts each) Fill in the circle to identify the stereochemical relationship between each pair of molecules. Hint: You might want to determine *R* or *S* for each chiral center to help you answer the question.



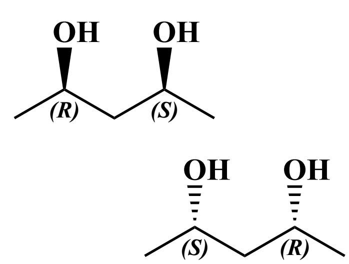
● **Enantiomers**
○ **Diastereomers**
○ **Same Molecule**



● **Enantiomers**
○ **Diastereomers**
○ **Same Molecule**



○ **Enantiomers**
● **Diastereomers**
○ **Same Molecule**

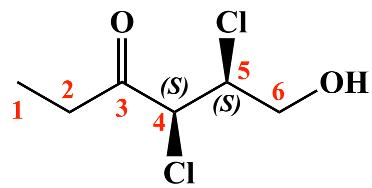


○ **Enantiomers**
○ **Diastereomers**
● **Same Molecule**

Signature_________________________ Pg 3____________(18)

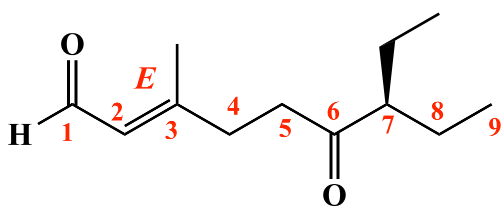
5. (6 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

A.



(4*S*,5*S*)-4,5-dichloro-6-hydroxyhexan-3-one
or (4*S*,5*S*)-4,5-dichloro-6-hydroxy-3-hexanone

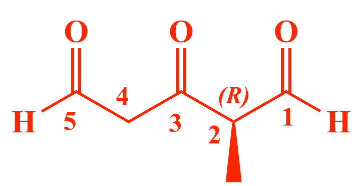
B.



(*E*)-7-ethyl-3-methyl-6-oxonon-2-enal
or (*E*)-7-ethyl-3-methyl-6-oxo-2-nonenal

C. In the box, draw the structure corresponding to the following IUPAC name.

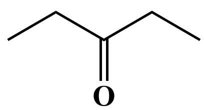
(*R*)-2-methyl-3-oxopentanedial



Signature______________________________

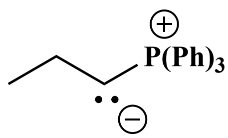
6. (13 pts) Being able to recognize the chemical personality of different species is one of the most important skills you can develop in Organic Chemistry. Fill in the appropriate circle to indicate whether each structure is a nucleophile or electrophile <u>in the mechanisms we have seen</u>. **Note that these species might be proton acids or bases in certain situations, but we will ignore that for this problem.**

6.1



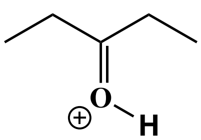
● **Electrophile**
○ **Nucleophile**

6.2



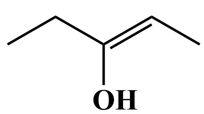
○ **Electrophile**
● **Nucleophile**

6.3



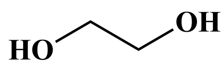
● **Electrophile**
○ **Nucleophile**

6.4



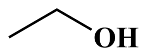
○ **Electrophile**
● **Nucleophile**

6.5



○ **Electrophile**
● **Nucleophile**

6.6



○ **Electrophile**
● **Nucleophile**

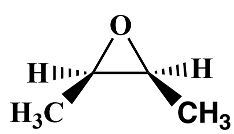
6.7 $NaBH_4$

○ **Electrophile**
● **Nucleophile**

6.8 Br_2

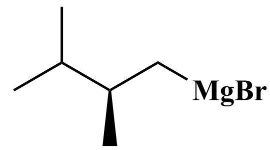
● **Electrophile**
○ **Nucleophile**

6.9



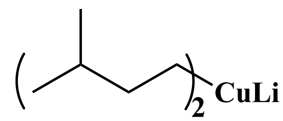
● **Electrophile**
○ **Nucleophile**

6.10



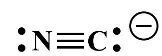
○ **Electrophile**
● **Nucleophile**

6.11



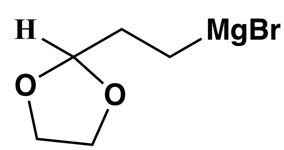
○ **Electrophile**
● **Nucleophile**

6.12



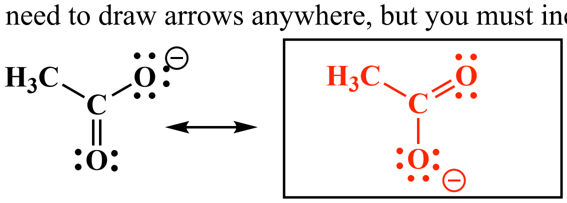
○ **Electrophile**
● **Nucleophile**

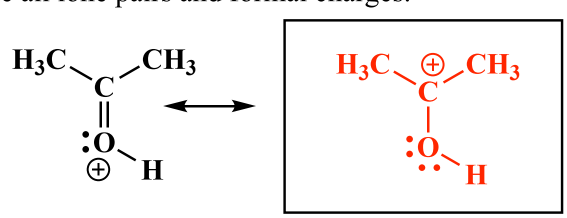
6.13

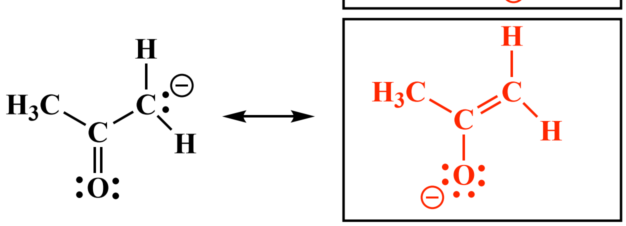


○ **Electrophile**
● **Nucleophile**

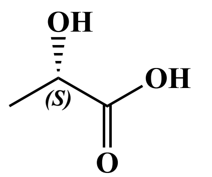
6 (cont.). (6 pts) For each structure below, draw the other importnat contributing structure. You do not need to draw arrows anywhere, but you must include all lone pairs and formal charges.







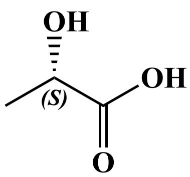
7. (4 pts each) (S)-Lactic acid is produced in our muscles during intense excercise when oxygen is scarce, such as **RUNNING 3.1 MILES or even farther**. The concentration of blood lactic acid is usually 1–2 mM at rest, but can rise to over 20 mM during intense exertion and as high as 25 mM afterward. Below are the two measured pKa values for (S)-lactic acid.



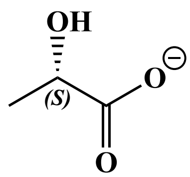
(*S*)-(+)-Lactic acid

pKa1 = 3.86 pKa2 = 15.1

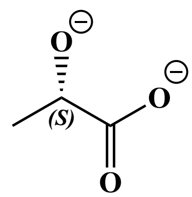
At neutral pH = 7.0, fill in the circle under the structure that is the predominant form of (*S*)-(+)-lactic acid.



Predominant form at pH = 7.0

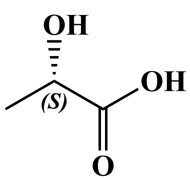


Predominant form at pH = 7.0

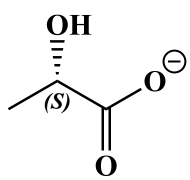


Predominant form at pH = 7.0

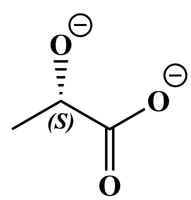
Lactic acid is commonly found is some foods such as sauerkraut and pickles. The pH of both of these foods can fall below 3. The low pH is important for keeping these foods from spoiling.



Predominant form at pH = 3.0

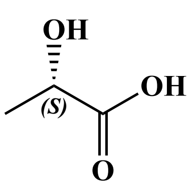


Predominant form at pH = 3.0

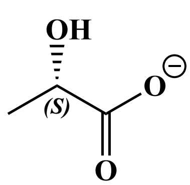


Predominant form at pH = 3.0

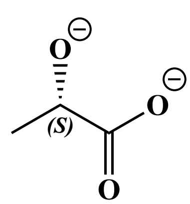
Lactic acid is soluble in alkaline solutions as well. What would be the predominant form of (*S*)-(+)-lactic acid in a solution of pH = 9.0



Predominant form at pH = 9.0



Predominant form at pH = 9.0

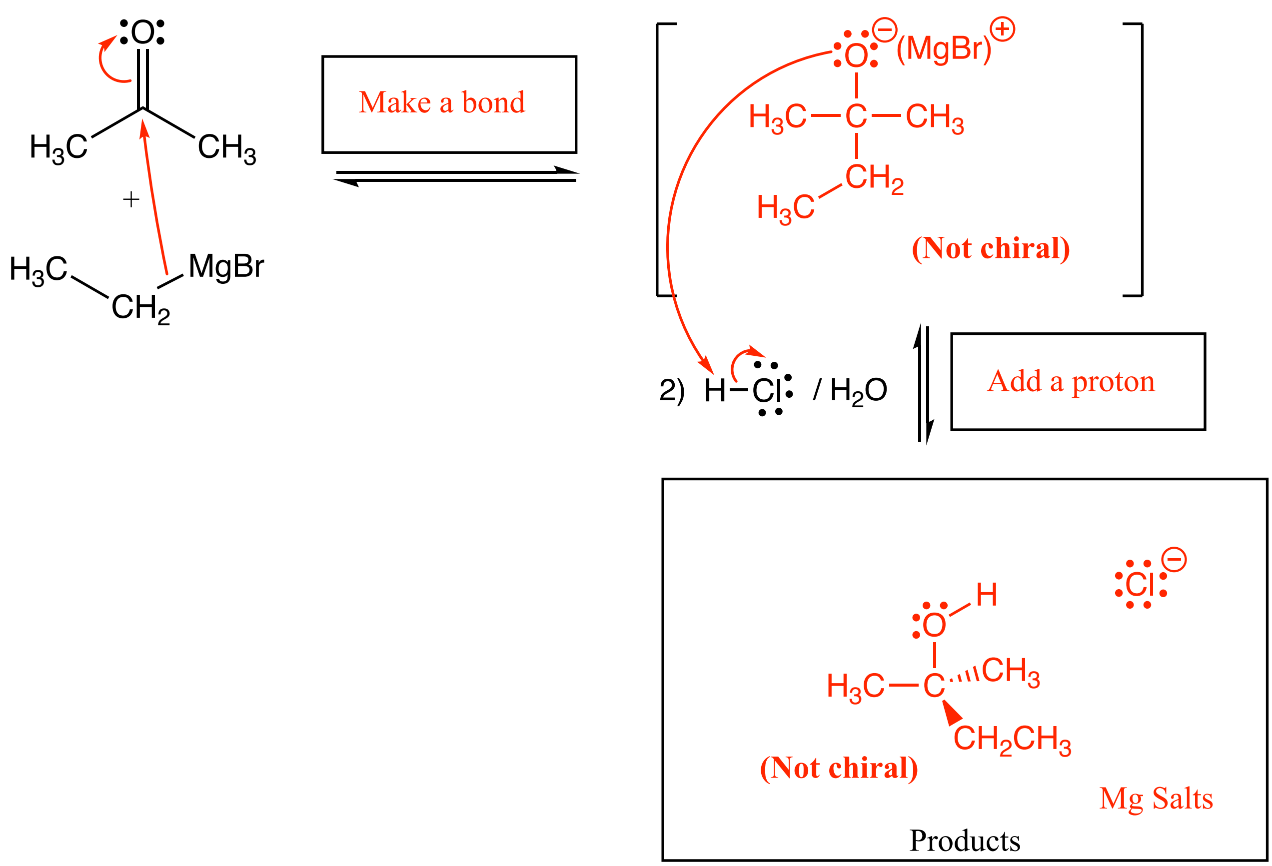


Predominant form at pH = 9.0

Signature____________________________ Pg 6 __________(15)

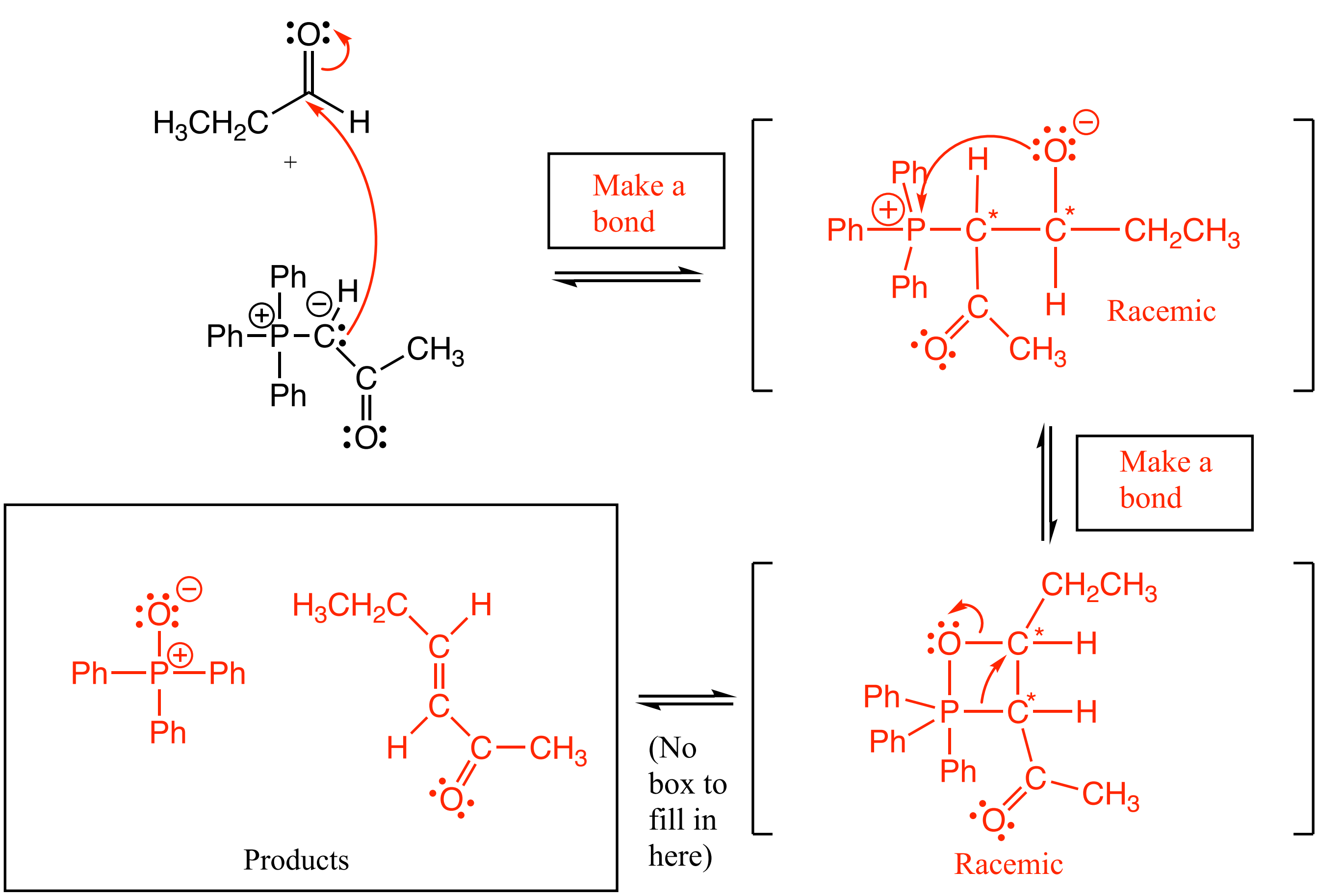
8. (15 pts) For these this reaction, use **arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. <u>FOR ALL CHIRAL PRODUCTS YOU MUST DRAW ALL ENANTIOMERS WITH WEDGES AND DASHES AND WRITE "RACEMIC' IF APPROPRIATE</u>. In the boxes provided by the arrows, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).**

Grignard Reaction with a Ketone

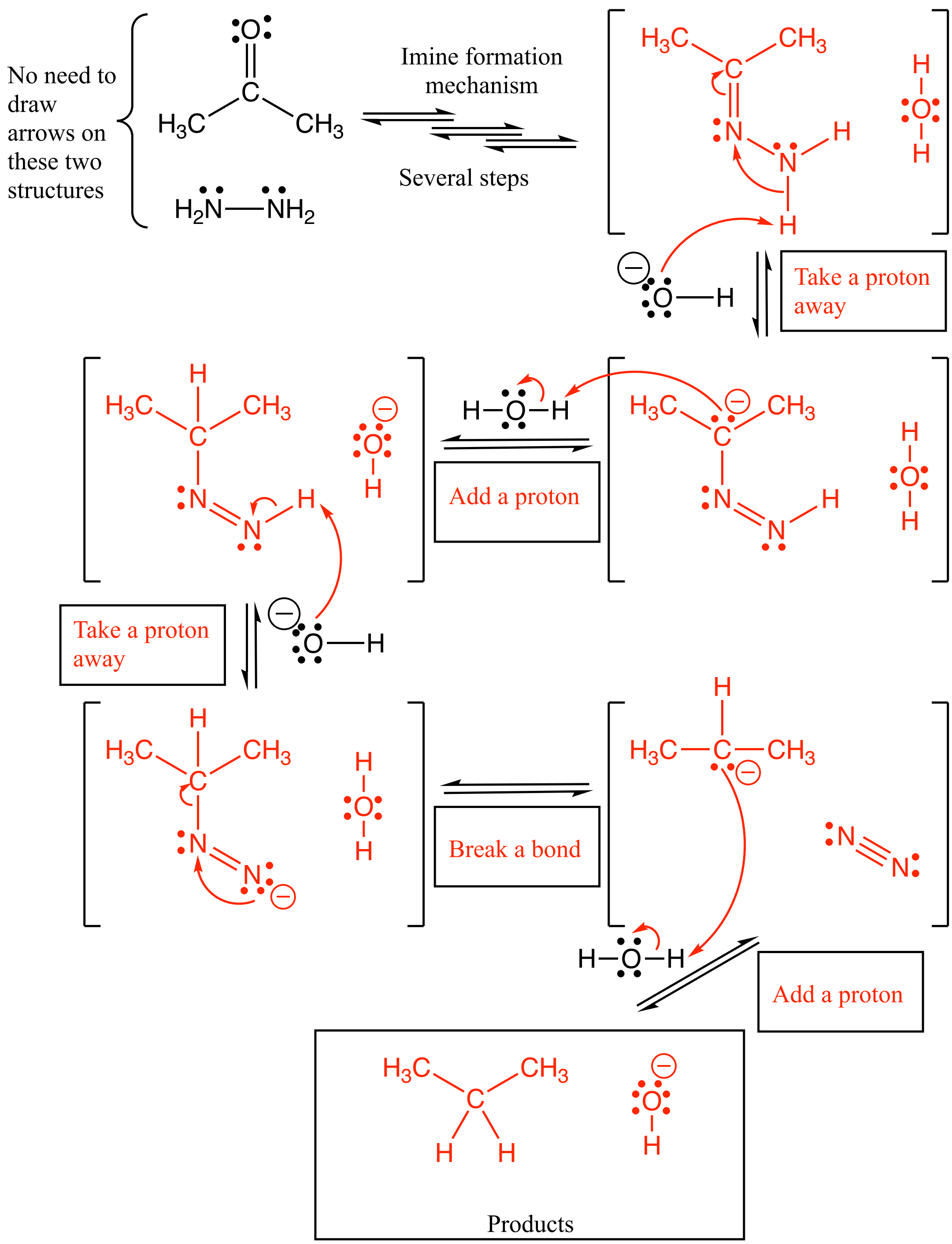


Signature_____________________________ Pg 7 __________(21)

9. (21 pts) For the following Wittig reaction, use **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, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. <u>FOR ALL CHIRAL PRODUCTS YOU MUST DRAW ALL ENANTIOMERS WITH WEDGES AND DASHES AND WRITE "RACEMIC' IF APPROPRIATE</u>. In the boxes provided by the arrows, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).**

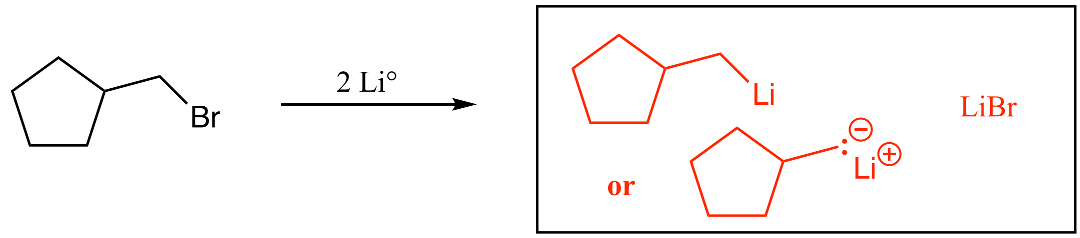


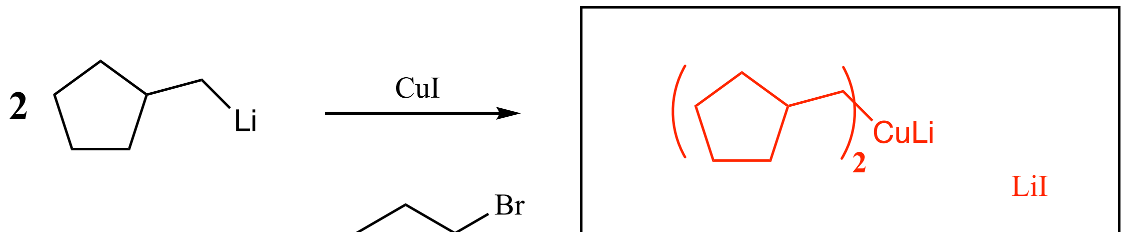
10. (34 pts) For this Wolff-Kishner reaction, use **arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. <u>FOR ALL CHIRAL PRODUCTS YOU MUST DRAW ALL ENANTIOMERS WITH WEDGES AND DASHES AND WRITE "RACEMIC' IF APPROPRIATE</u>. In the boxes provided by the arrows, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).**

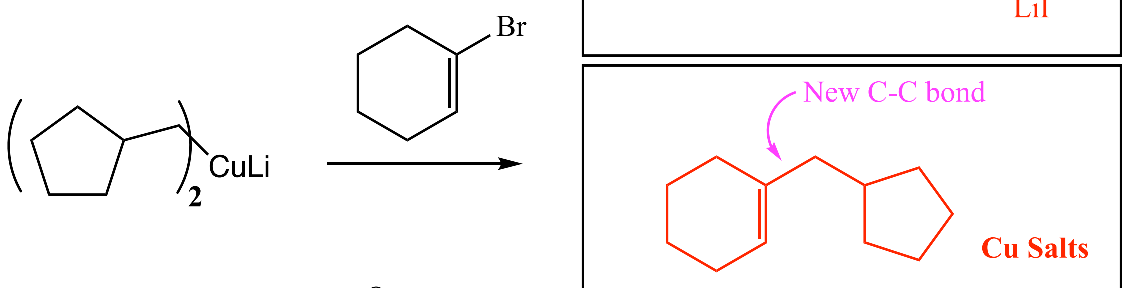


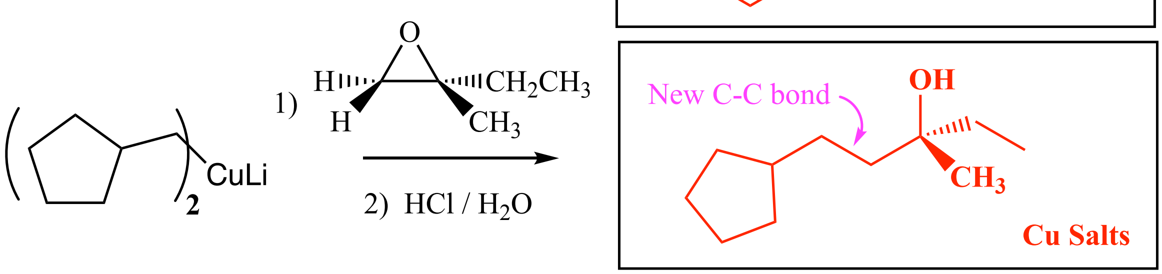
Signature___________________________ Pg 9 _____________(18)

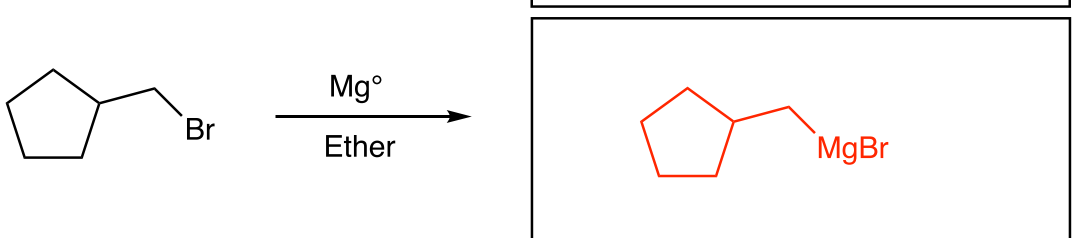
11. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges ( ) and dashes ( ) to indicate stereochemistry.
To get full credit, you only need to write the the major organic product for these.
You do not have to worry about the other products.

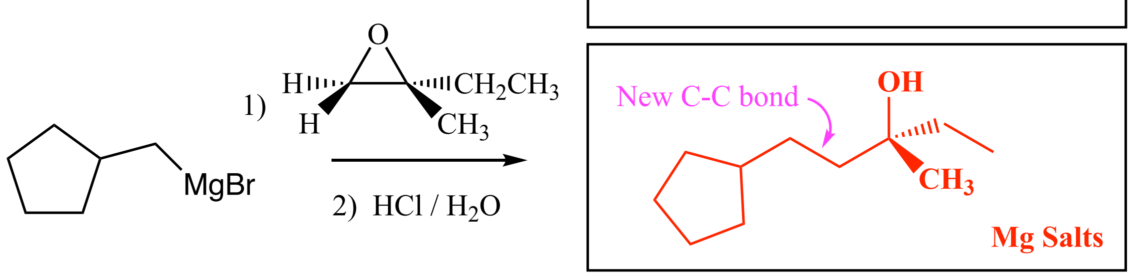




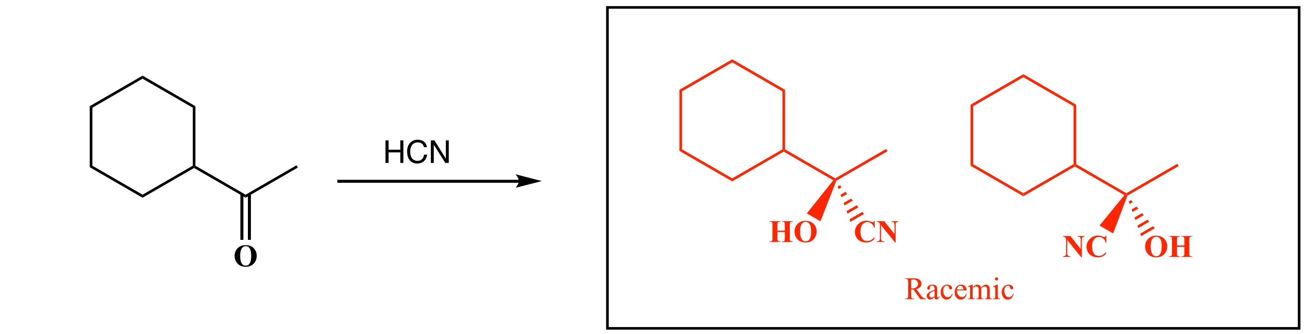


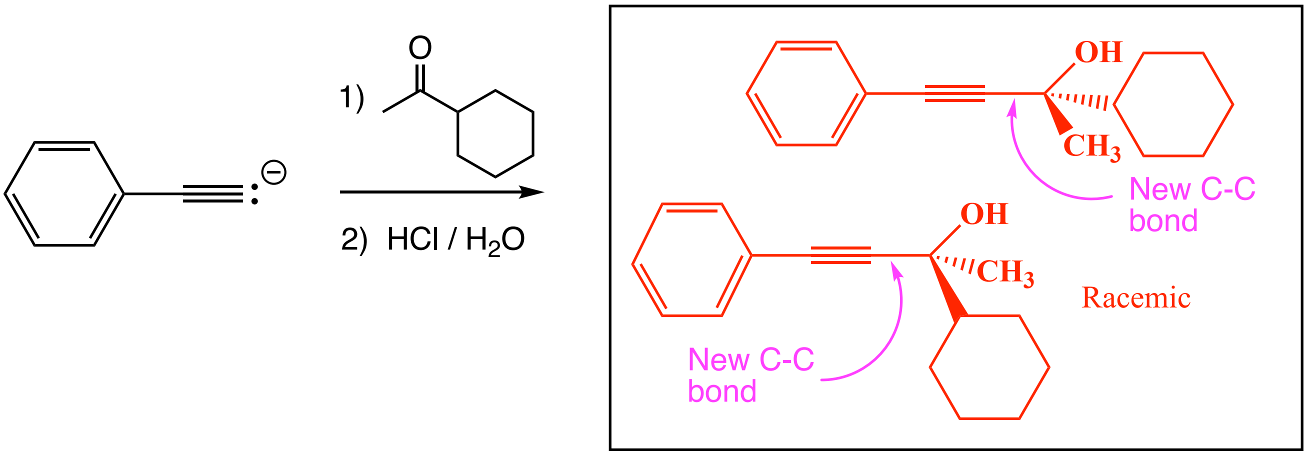


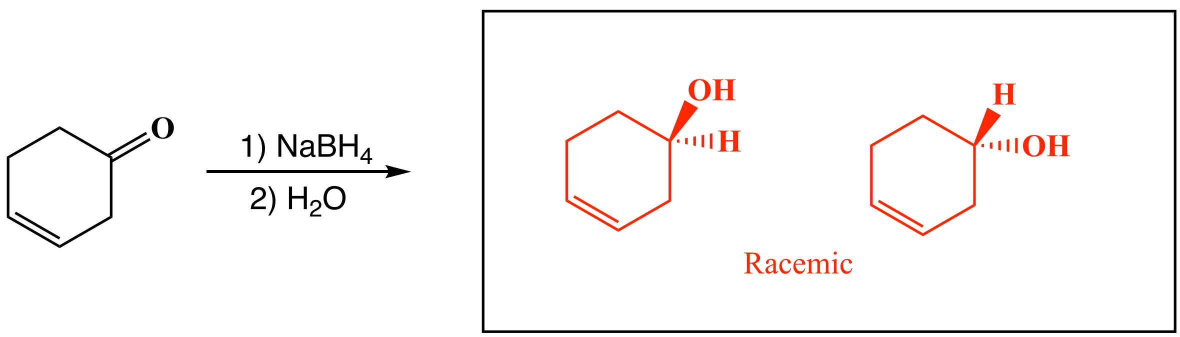


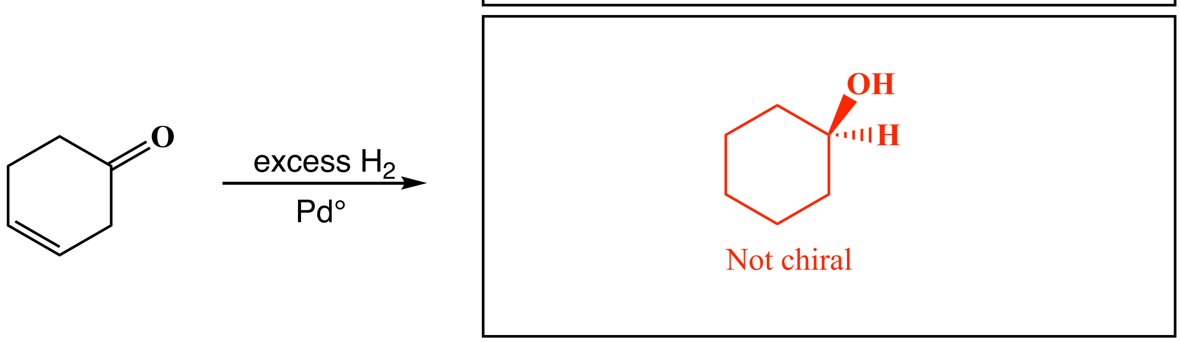


11. (cont.) (3, 4 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges ( ) and dashes ( ) to indicate stereochemistry. To get full credit, you only need to write the the major organic product for these. You do not have to worry about the other products.

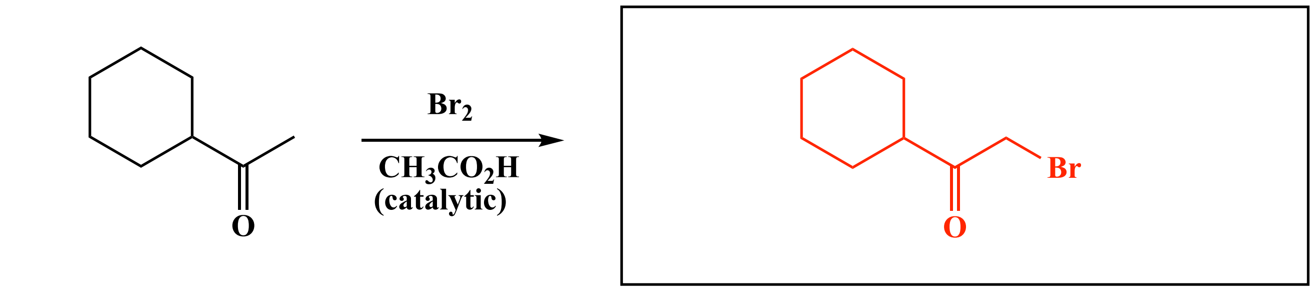


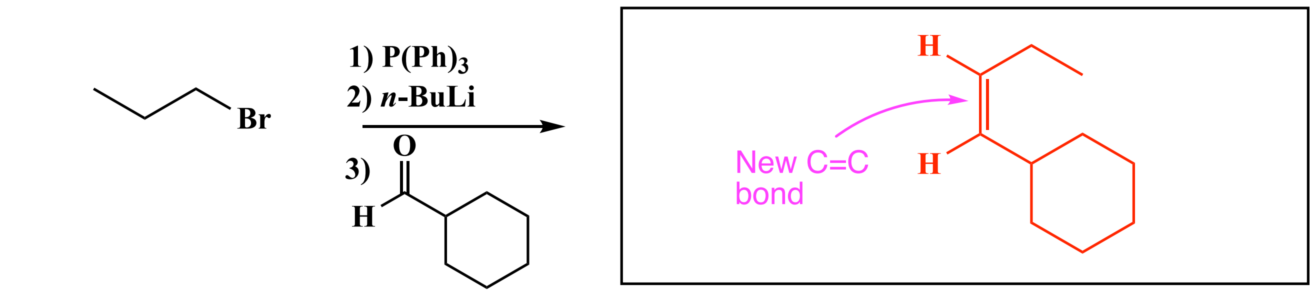


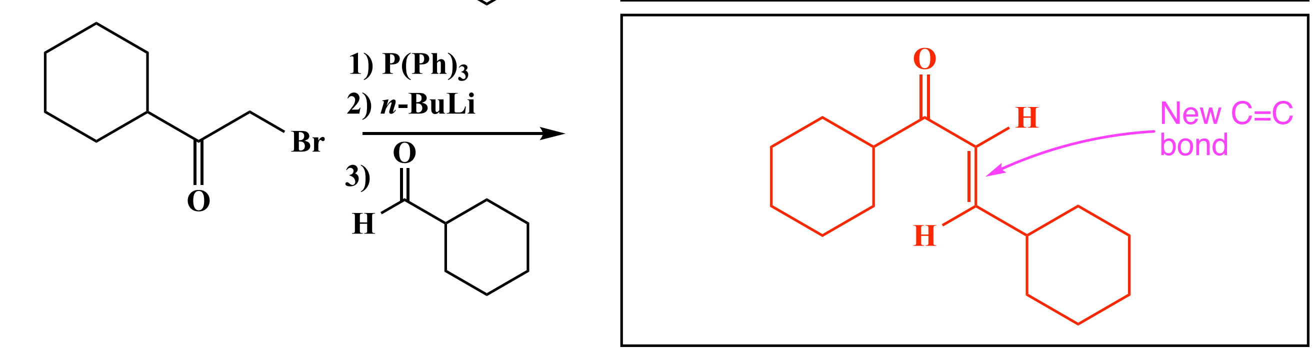


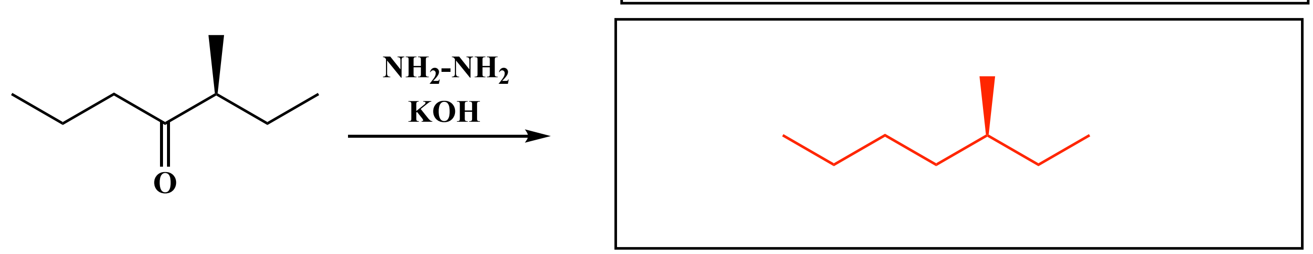


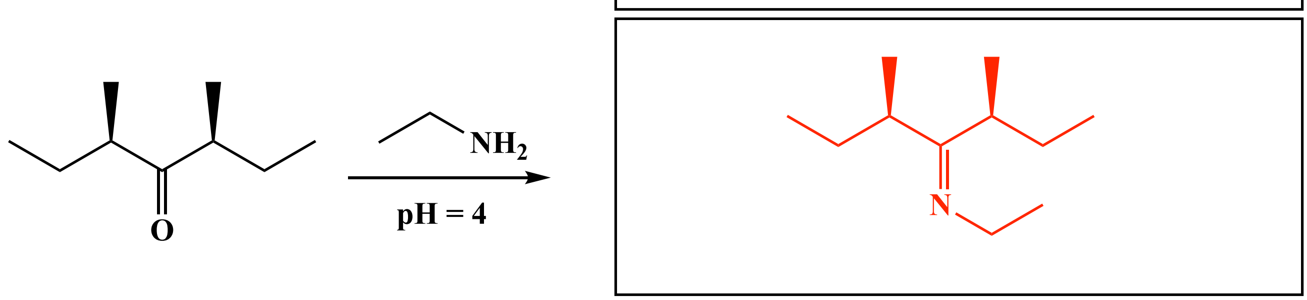
11. (cont.) (3, 4 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges ( ) and dashes ( ) to indicate stereochemistry. To get full credit, you only need to write the the major organic product for these. You do not have to worry about the other products.





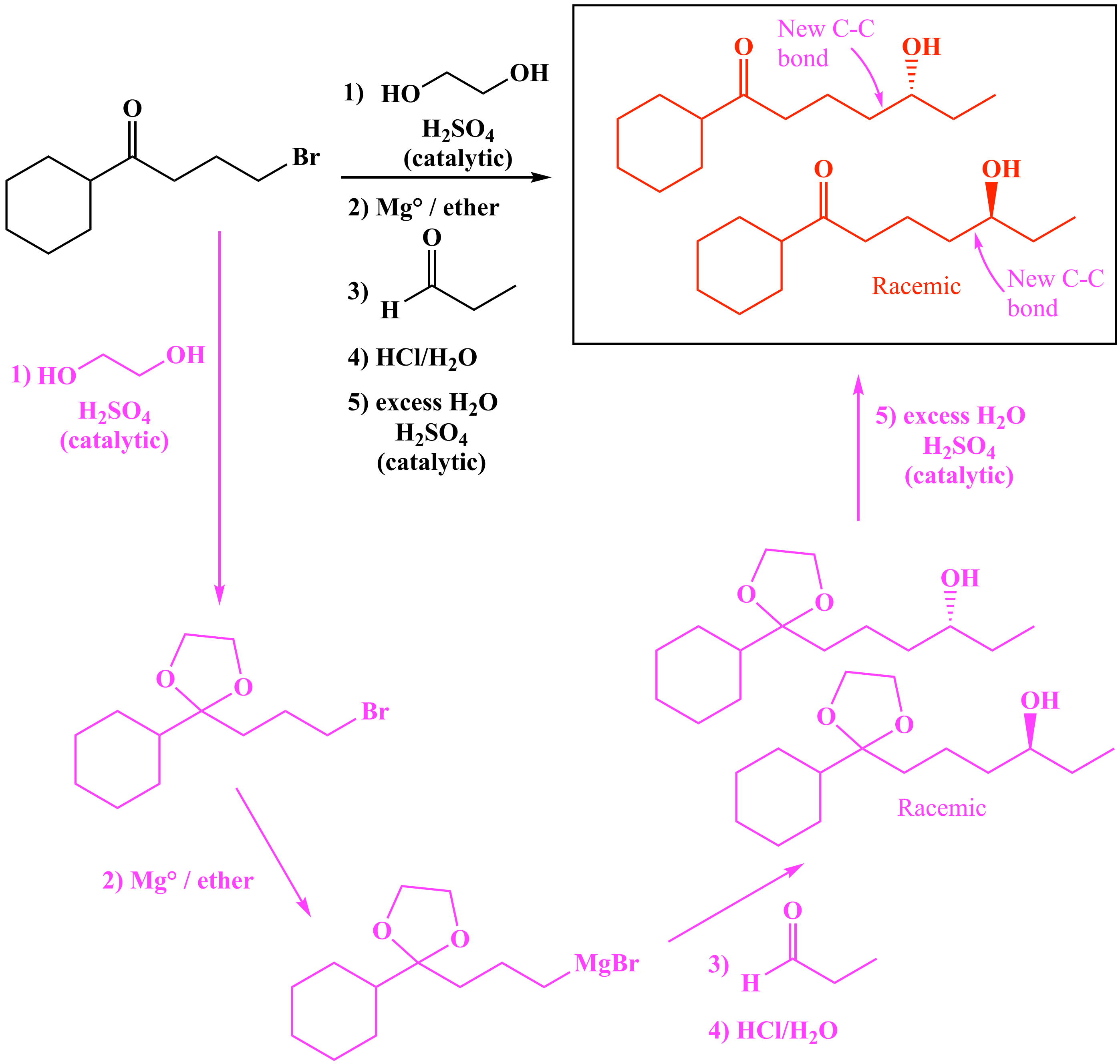




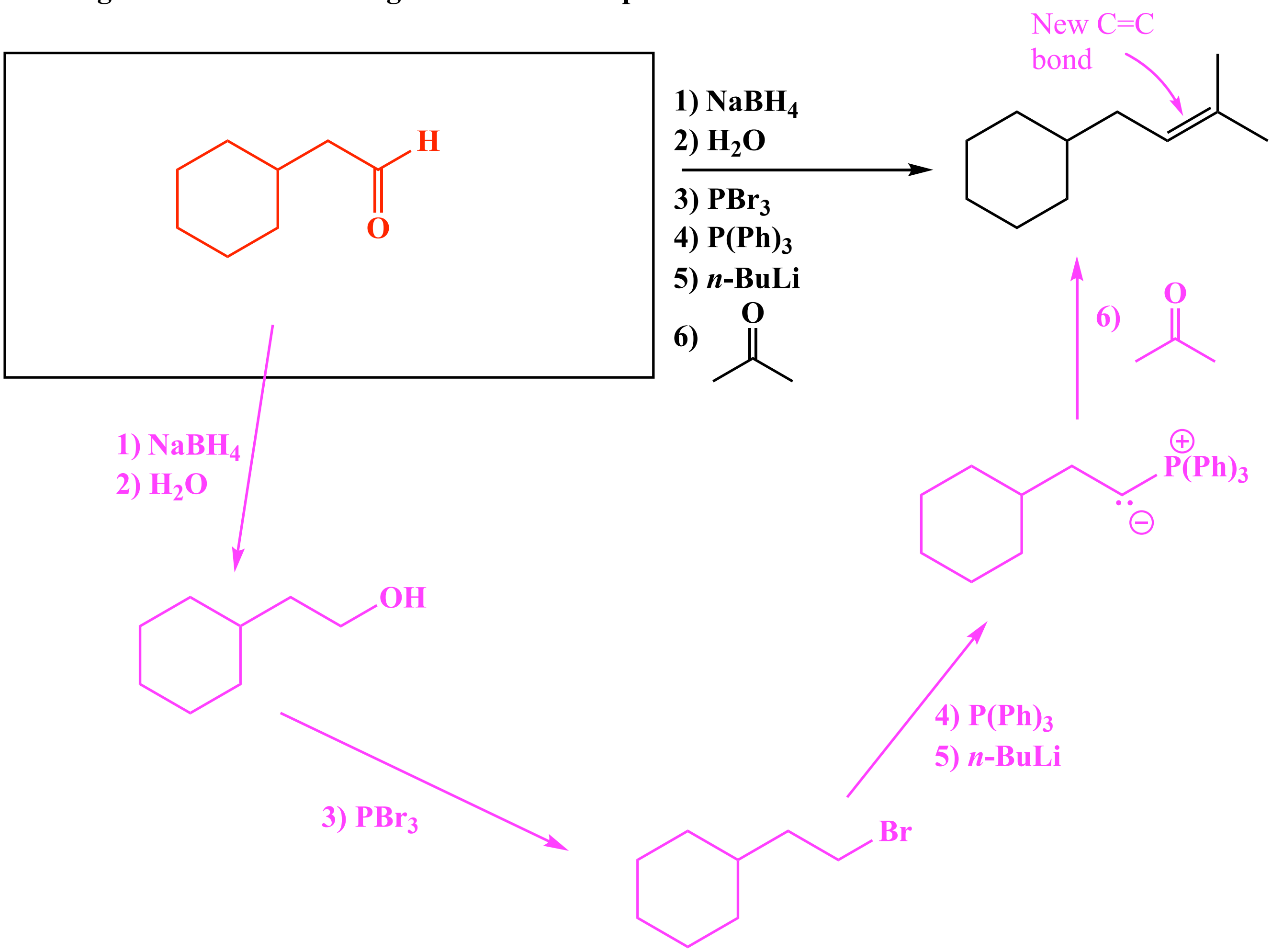


Signature___________________________ Pg 12 ____________(12)

12. (12 pts) Here is a warm-up for the synthesis problems. For the following series of reactions, write the **final** product(s) that you will see. Make sure draw all stereoisomers produced and to use wedges and dashes to indicate all stereochemistry, and you must write racemic if appropriate.

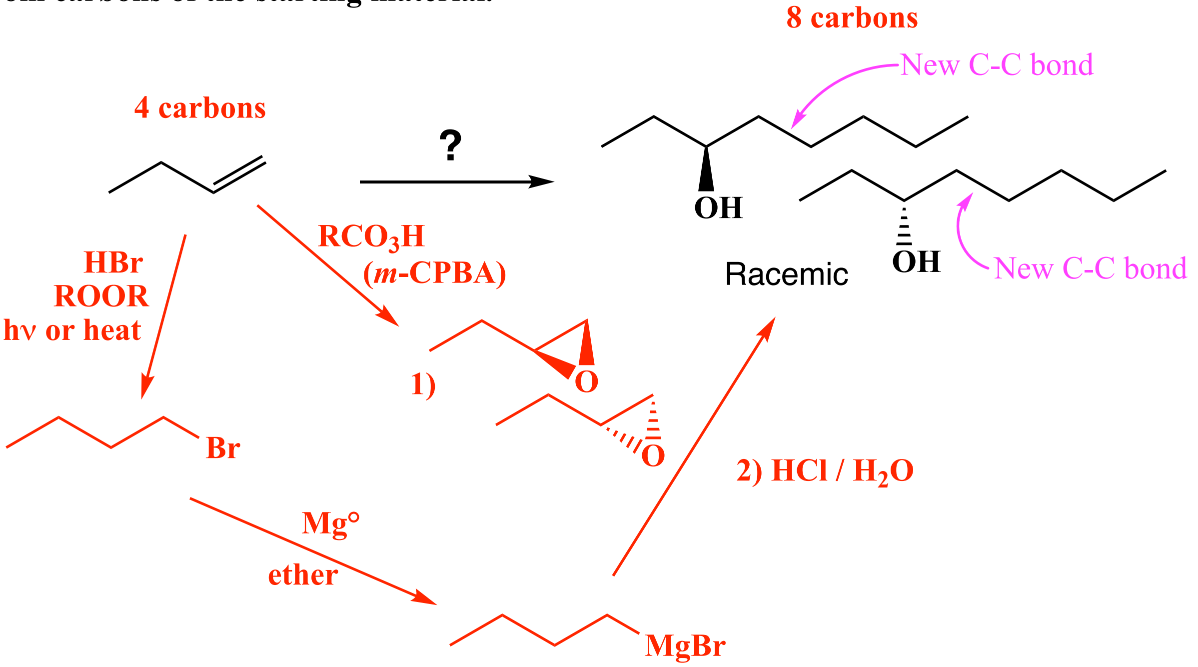


13. (12 pts) Here is a second warm-up for the synthesis problems. For the following series of reactions, we have given you the final product. Work backwards and **in the box provided write the structure of the starting material that would generate the final product shown.**



14. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

A) (10 pts)

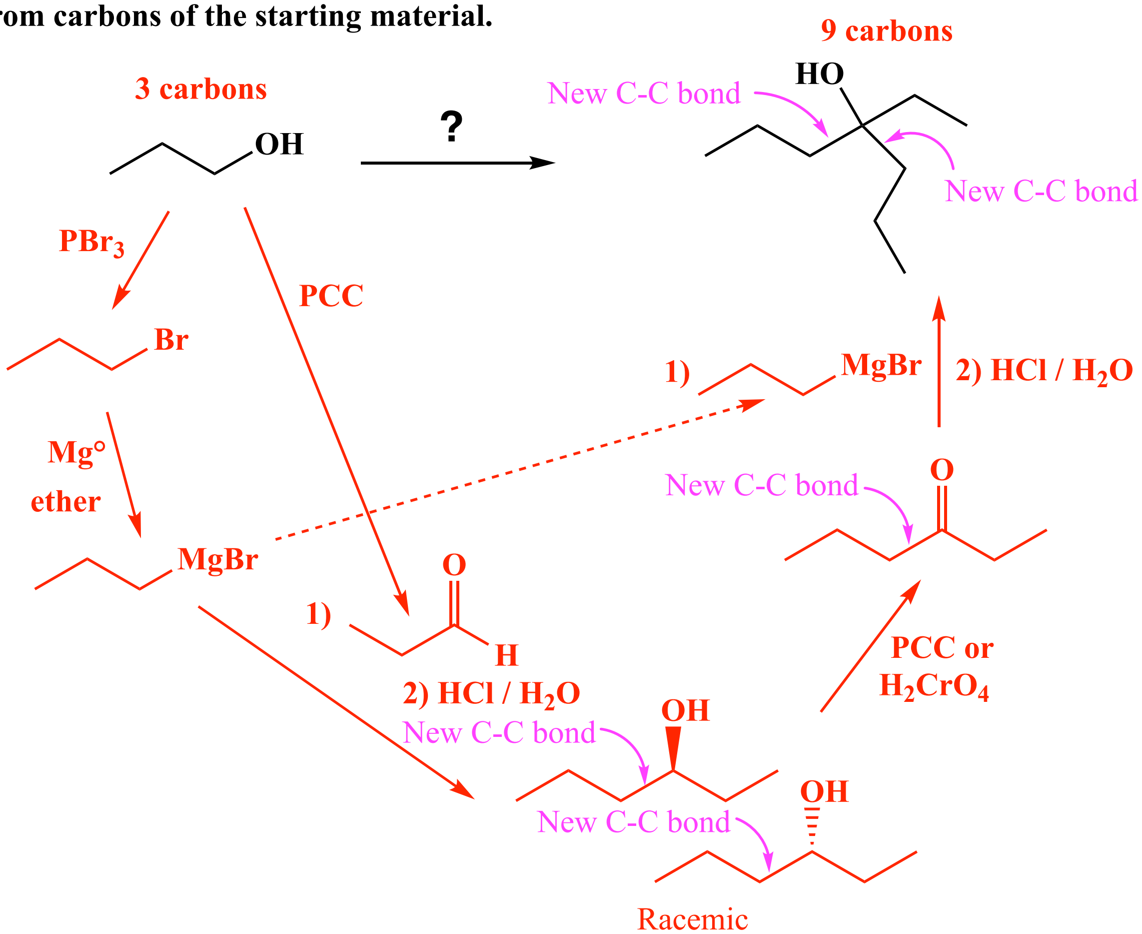


Recognize that the product has 8 carbons, while the starting material has four carbons. Therefore assume there is a new carbon-carbon bond between the 4th and 5th carbon atoms of the product as indicated. **Recognize** the KRE of an OH group two carbons from the new carbon-carbon bond, the product of a Grignard reagent reacting with an expoxide. **Recognize** the required epoxide can be made in one step from the starting alkene using RCO_3H. **Recognize** that the required Grignard reagent can be made in two steps from the starting alkene by first reacting with HBr in the presence of peroxides and light or heat to give the non-Markovnikov addition, followed by the usual Mg° and ether.

Signature_________________________ Pg 15 ___________(16)

14. (cont.). These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

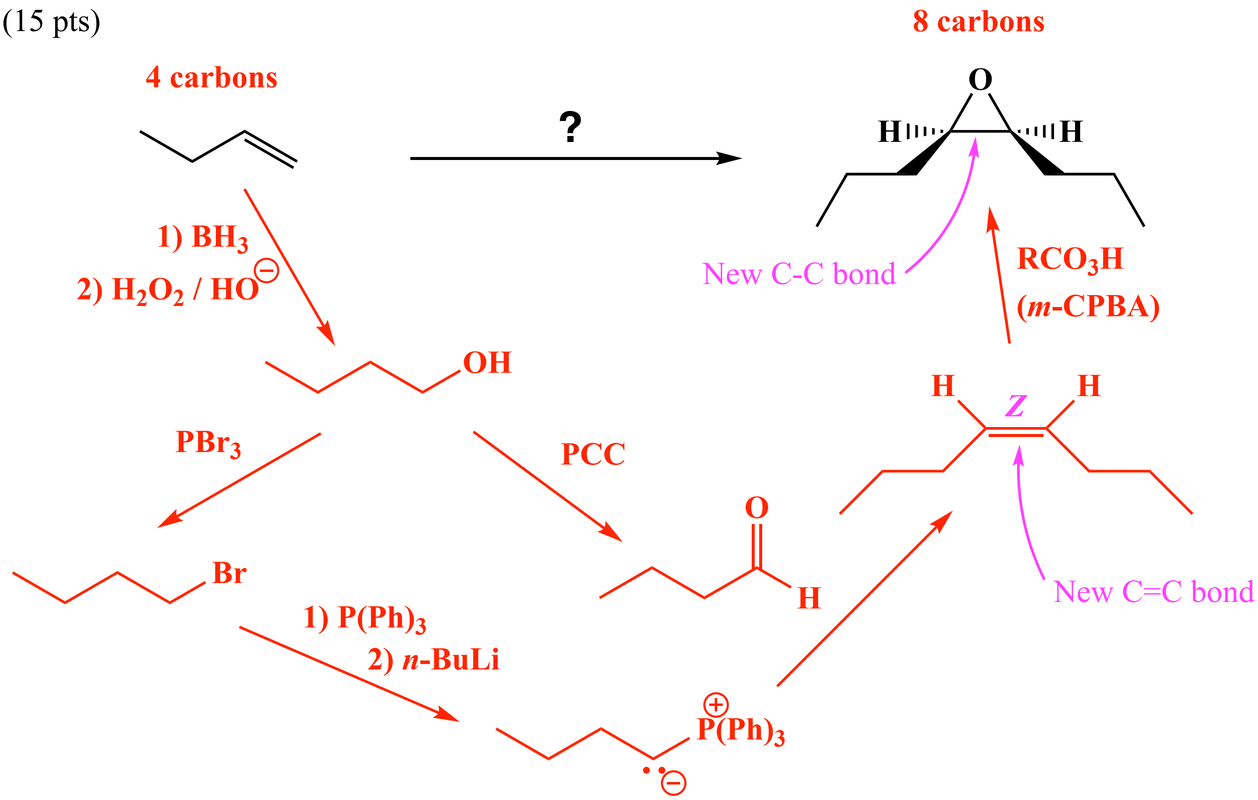
B) (16 pts)



Recognize that the starting material has 9 carbon atoms while the starting material has 3 carbon atoms. Therefore propose that two new carbon-carbon bonds are needed and they must be in the positions shown. **Recognize** the new carbon-carbon bonds are on the same carbon atom as the -OH group, the KRE of a six-carbon ketone reacting with a Grignard reagent as shown. **Recognize** that the required Grignard reagent can be made by first converting the starting alcohol to the bromoalkane using PBr3 then the usual Mg°/ether. **Recognize** that the required six-carbon ketone can be made from the oxidation of a six-carbon alcohol. This was the hardest thing to see in this problem. **Recognize** the six-carbon alcohol is the product of the same Grignard we already saw reacting with propanal, which in turn is made in one step from the starting alcohol using PCC.

14. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

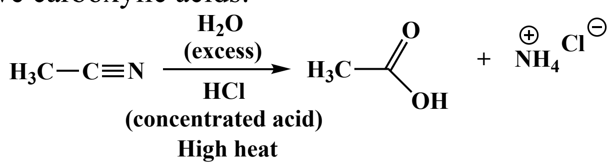
C) (15 pts)



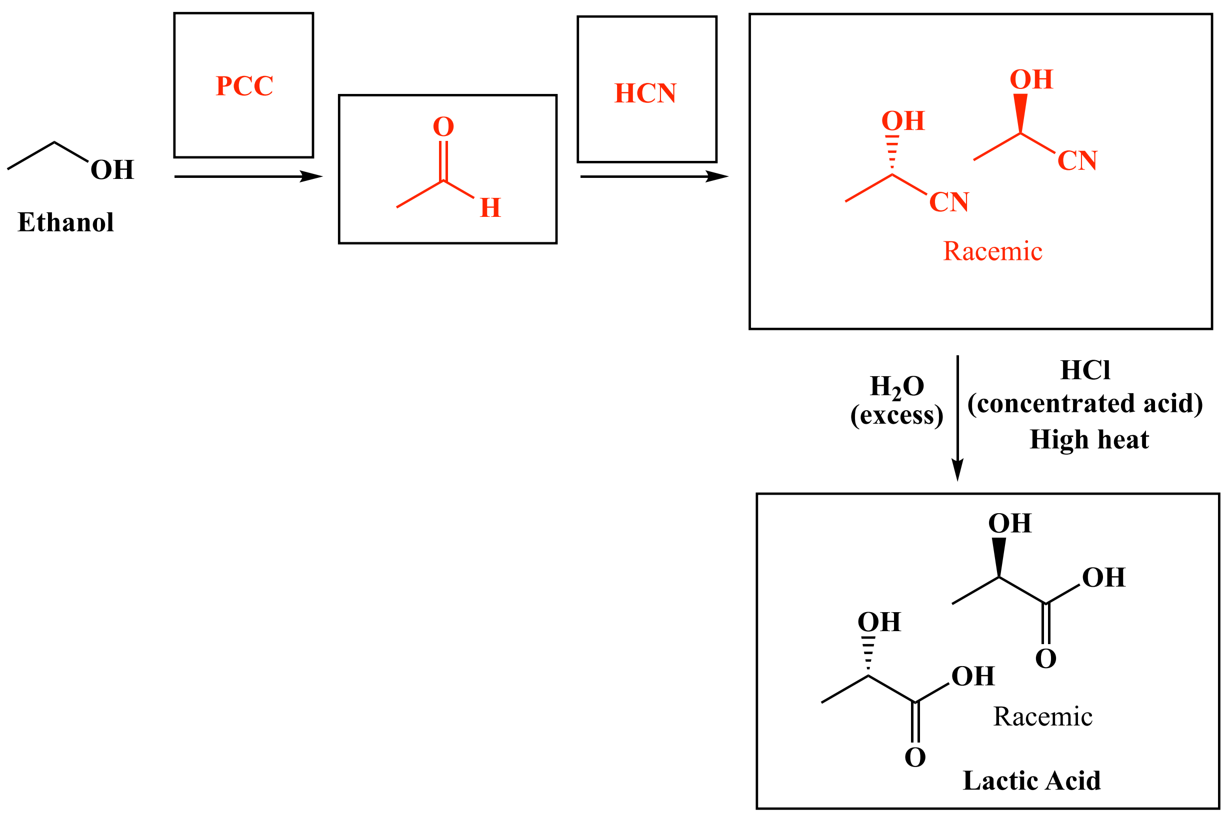
Recognize that the product has eight carbons and the starting material has 4 carbons, so a new carbon-carbon bond must be made between carbons 4 and 5 as shown. Recognize that the product epoxide is made from the *Z*-alkene as shown. **Recognize** the Z alkene with a new C=C bond between carbons 4 and 5 as being the product of a Wittig reaction between butanal and the four carbon Wittig reagent as shown. **Recognize** that butanal can be made from the staring alkene in two steps using hydroboration to give the non-Markovnikov alcohol followed by PCC. **Recognize** that the required Wittig reagent can be made from the same alcohol, followed by reaction with PBr_3 to give the bromoalkane, then 1) $P(Ph)_3$ and 2) *n*-BuLi.

15. (12 pts) Here is an "Apply What you Know" problem. You have not seen all of this directly, but based on what you know you CAN figure it out. **Polylactides**, more commonly known as polylactic acid (PLA), are a type of biodegradable plastic. PLA is part of the polyester family. PLA is known for its rigidity, glossiness, and clarity. It has good mechanical properties and is suitable for various processing techniques similar to conventional plastics. PLA is used for packaging materials (bottles, films, cups), biodegradable medical devices (sutures, pins, rods), 3D printing filaments, disposable tableware (plates, utensils) and agricultural products. One of the key benefits of PLA is its reduced environmental footprint during production because it is not derived from petroleum. Another key reason people are interested in PLA is that is biodegradable under industrial composting conditions. In other words, it can be broken down into water and carbon dioxide in only a few weeks. That contrasts with many common plastics that will remain in landfills for 400 to 1,000 years!

PLA is made entirely from lactic acid, which we saw on page 5 of this exam. One method of synthesizing lactic acid begins with ethanol. Here is what you have not learned yet: Nitrile groups react in water in the presence of concentrated HCl and heat to give carboxylic acids:

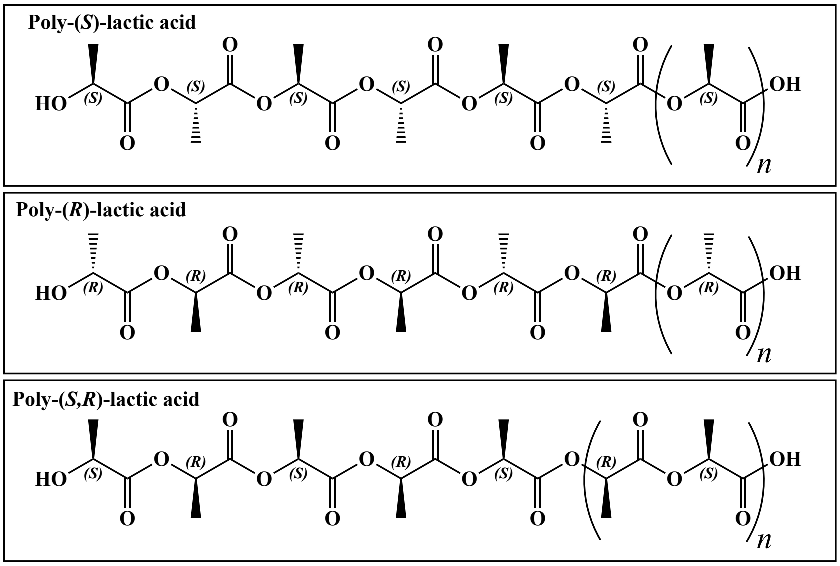


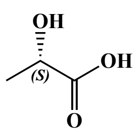
A) Lactic acid can be synthesized starting with ethanol, a renewable source of carbons atoms. Using chemistry you have learned, fill in the boxes with both the reagents and synthetic intermediates to complete the following synthesis of lactic acid:



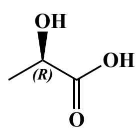
Signature____________________________ Pg 18 _____________(4)

B) Because lactic acid is chiral, polylactic acid comes in three forms. Below is the structure of the three polylactic acids. They are polymers in which the lactic acid units are bonded into a long chain through what are called ester bonds.





(*S*)-Lactic Acid



(*R*)-Lactic Acid

Note: The (*S*)-lactic acid is often called L-lactic Acid, and the (*R*)-lactic acid is often called D-lactic acid in accordance with an older method of naming stereoisomers in biochemistry. We are using the organic chemistry designations of (*S*) and (*R*) for this problem because you are more familiar with them.

As shown above, polylactic acid can be made from (S)-lactic acid, (R)-lactic acid or a racemic mixture of (S,R) lactic acid. Predict what will be true about the polylactic acids made from these three different starting materials and fill in the circle for the statement that is correct:

○ **All three materials will have identical properties (such as melting temperature, strength and brittleness).**

○ **The poly-(*S*)-lactic acid made from (*S*)-lactic acid and the poly-(*S,R*)-lactic acid made from (*S,R*)-lactic acid will have the same properties (such as melting temperature, strength and brittleness), the poly-(*R*)-lactic acid made from (*R*)-lactic acid will have different properties.**

○ **The poly-(*R*)-lactic acid made from (*R*)-lactic acid and the poly-(*S,R*)-lactic acid made from (*S,R*)-lactic acid will have the same properties (such as melting temperature, strength and brittlenesss), the poly-(*S*)-lactic acid made from (*S*)-lactic acid will have different properties.**

● **The poly-(*S*)-lactic acid made from (*S*)-lactic acid and the poly-(*R*)-lactic acid made from (*R*)-lactic acid will have the same properties (such as melting temperature, strength and brittleness), the poly-(*S,R*)-lactic acid made from (*S,R*)-lactic acid will have different properties.**

The poly-(*S*)-lactic acid and poly-(*R*)-lactic acid are essentially enantiomers (all the chiral centers are reversed) so they will have the same phyical properties. The poly-(*S,R*)-lactic acid is essentially a diasteromer of the other two, so it will have different properties.