NAME (Print): _____

EID _____

SIGNATURE: _____

Chemistry 320N
1st Midterm Exam
February 9, 2023

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!

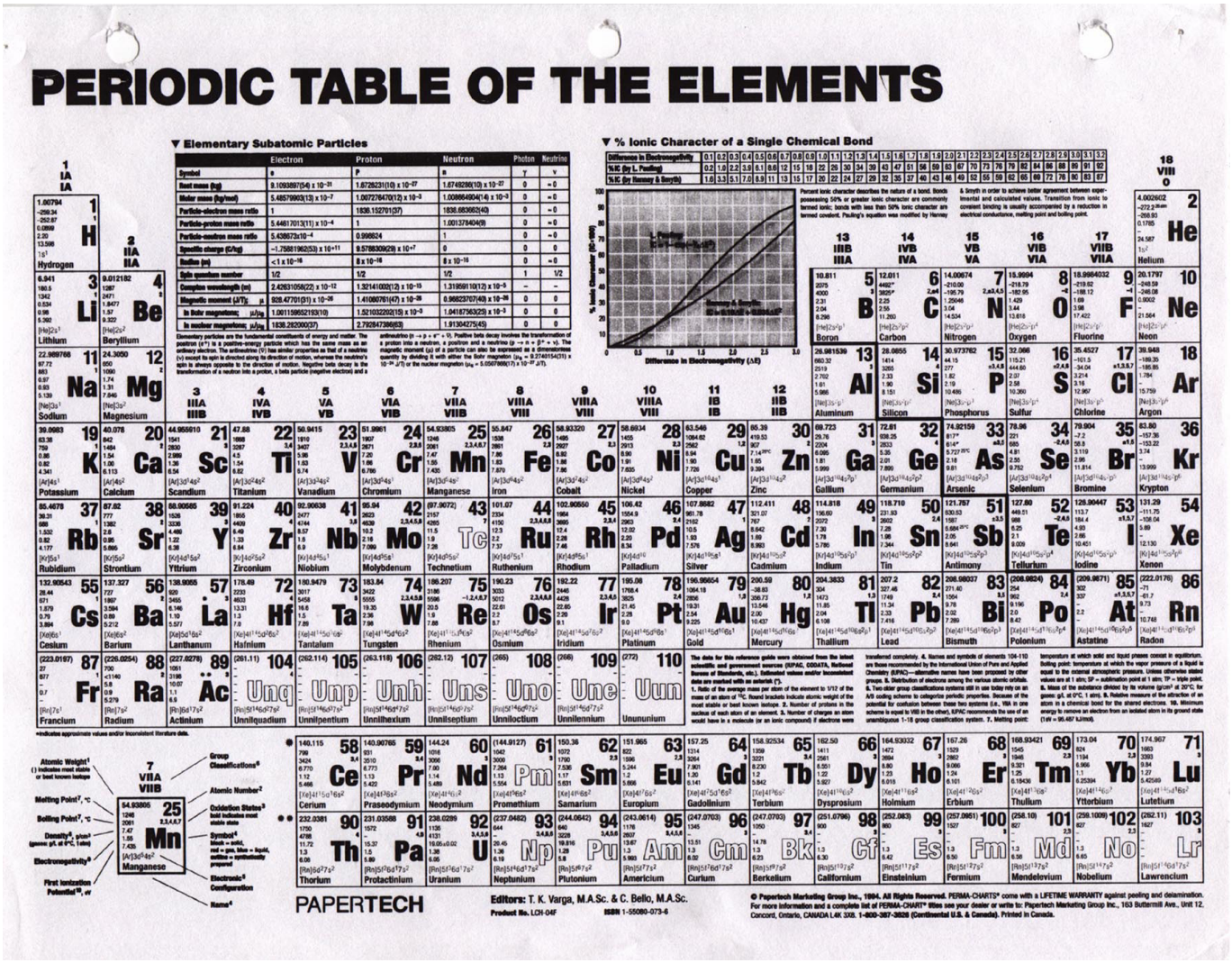
FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

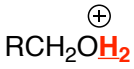
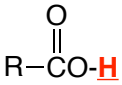
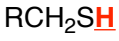
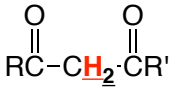
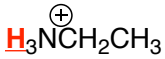
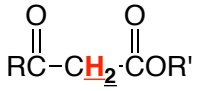
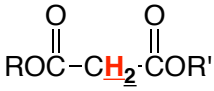
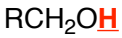
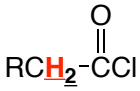
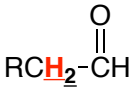
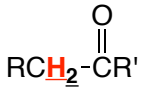
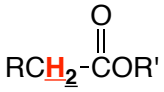
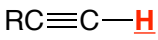
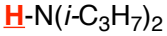
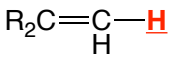
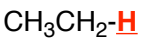
Student Honor Code

“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

Signature_____ Pg 1 _____(25)

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

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

The popular medical diagnostic technique of 1._____ 2._____

3._____ (_____) is based on the same principles as 4._____,

namely the flipping (i.e. 5._____) of nuclear spins of H atoms by

6._____ frequency irradiation when a patient is placed in a strong

7._____ 8._____. Magnetic field 9._____

are used to gain 10,_____ information, and rotation of the

11. _____ around the center of the object gives imaging in an entire plane (i.e.

12. _____ inside patient). In an MRI image, you are looking at individual

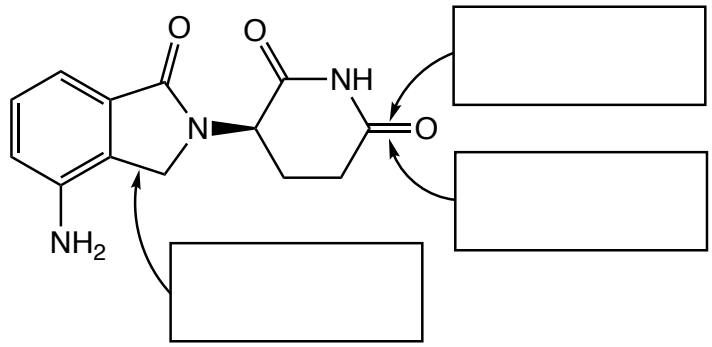
13._____ that when 14._____ make up the three-

dimensional image of 15._____ amounts of 16. _____ atoms,

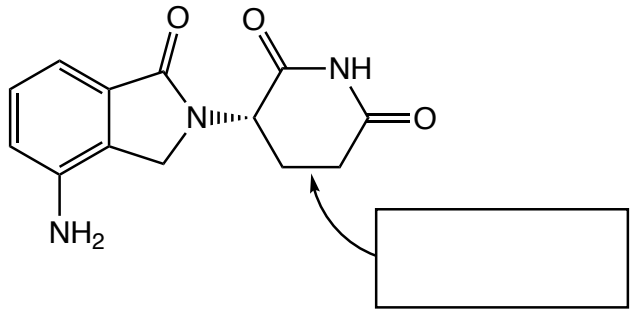
especially the 17._____ atoms from 18._____ and

19._____, in the different 20._____.

3. (2 pts each) In the spaces provided, indicate the type of bond, and the hybridized orbitals that overlap to form the bond. For example, one answer could be: **σCsp^3-H1s**

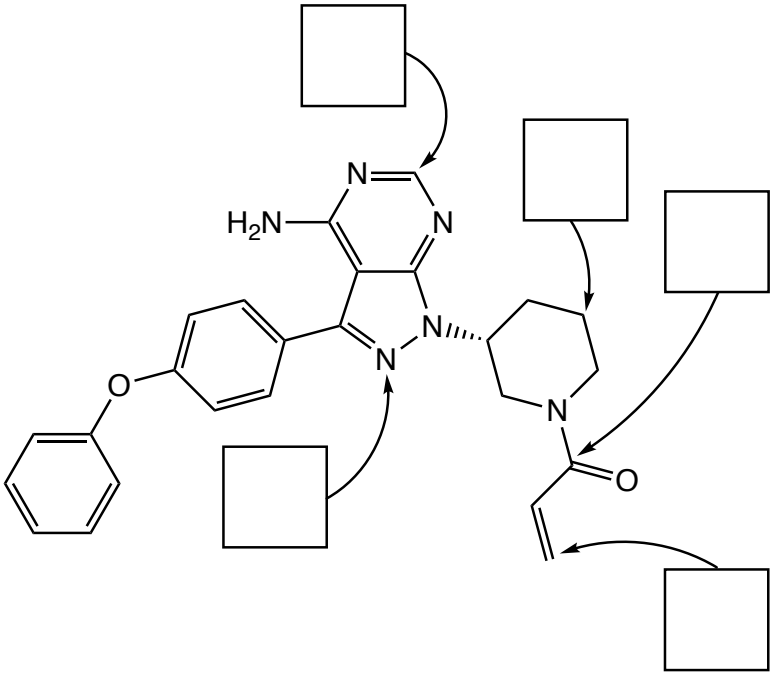


Note: for the multiple bonds, you can put the orbitals in any order, you just need to describe all the bonds.



Revlimid (sold as a reacemic mixture)
Company: Bristol Myers Squibb
2022 sales: $9.5 billion
Use: Treats cancers such as mulitple myeloma

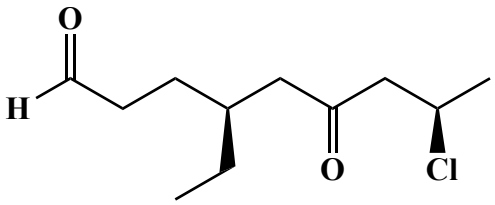
4 (1 pt each) In the spaces provided, write the hybridization state of the atoms indicated by the arrow.



Imbruvica
Comanies AbbVie, Johnson & Johnson
2021 sales: $9.8 billion
Use**:** Mantle cell lymphoma, chronic lymphocytic leukemia, Waldenstrom's macroglobulinemia, marginal zone lymphoma, chronic graft-versus-host disease
Diseases: Nonvalvular atrial fibrillation, deep vein thrombosis and pulmonary embolism

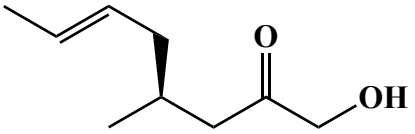
6. (6 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

A.



_____

B.



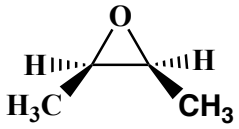
_____

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

(4*S*,5*S*,6*R*)-4,5,6-trimethyl-8-oxononanal

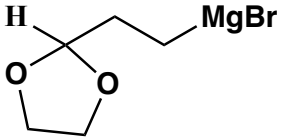
7. (17 pts) Being able to recognize the chemical personality of different species is one of the most important skills you can develop in Organic Chemistry. Fill in the appropriate circle to indicate whether each structure is a nucleophile or electrophile. Note that these species might be acids or bases in certain situations, but we will ignore that for this problem.

7.1



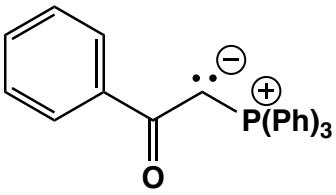
◯ Electrophile
◯ Nucleophile

7.2



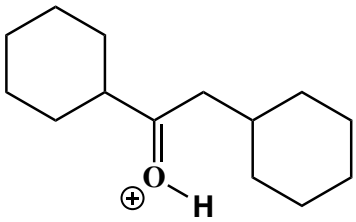
◯ Electrophile
◯ Nucleophile

7.3



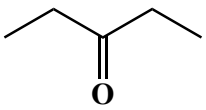
◯ Electrophile
◯ Nucleophile

7.4



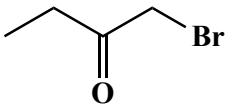
◯ Electrophile
◯ Nucleophile

7.5



◯ Electrophile
◯ Nucleophile

7.6

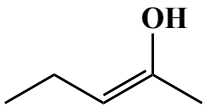


◯ Electrophile
◯ Nucleophile

7.7 $NaBH_4$

◯ Electrophile
◯ Nucleophile

7.8



◯ Electrophile
◯ Nucleophile

7.9 H_2O

◯ Electrophile
◯ Nucleophile

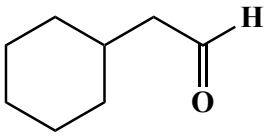
7.10 CH_3OH

◯ Electrophile
◯ Nucleophile

7.11 Br_2

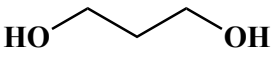
◯ Electrophile
◯ Nucleophile

7.12



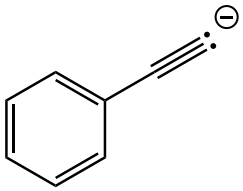
◯ Electrophile
◯ Nucleophile

7.13



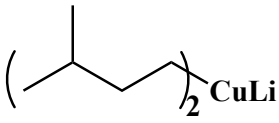
◯ Electrophile
◯ Nucleophile

7.14



◯ Electrophile
◯ Nucleophile

7.15

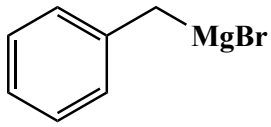


◯ Electrophile
◯ Nucleophile

7.16 $P(Ph)_3$

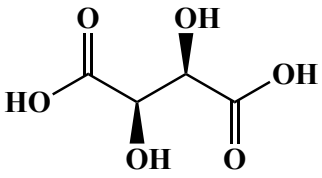
◯ Electrophile
◯ Nucleophile

7.17



◯ Electrophile
◯ Nucleophile

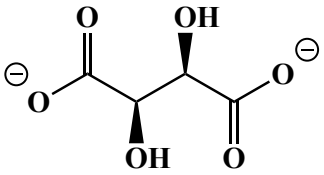
8. (4 pts each) (*2R,3R*)-(+)-Tartaric acid is found in wine. The two carboxylic acid groups have slightly different pKa values as listed below. The small difference makes sense because after the first carboxylic acid is deprotonated, that carboxlyate slightly raises the pKa of the second carboxylic acid in the molecule. Recall that an alcohol has a pKa value of around 16.



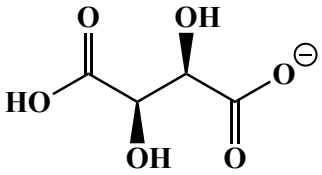
(*2R,3R*)-(+)-Tartaric acid

pKa1 = 2.98 and pKa2 = 4.4

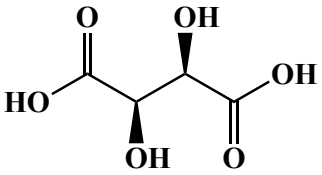
At neutral pH = 7.0, fill in the circle under the structure that is the predominant form of (*2R,3R*)-(+) Tartaric acid.



○ **Predominant form at pH = 7.0**

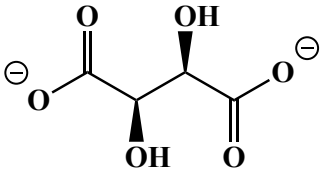


○ **Predominant form at pH = 7.0**

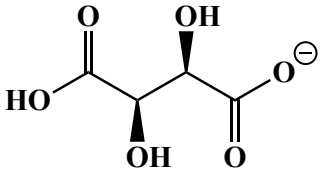


○ **Predominant form at pH = 7.0**

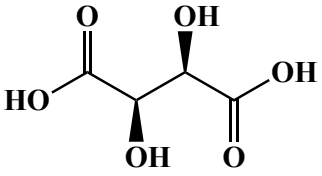
The pH of wine is below neutral and considrered acidic, usually in the pH = 3-4 range. Fill in the circle under the structure that is the predominant form of (*2R,3R*)-(+)-Tartaric acid if the pH of the wine is exactly pH = 3.5



○ **Predominant form at pH = 3.5**

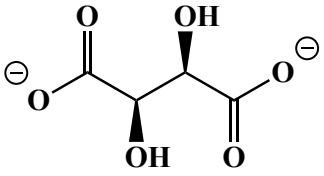


○ **Predominant form at pH = 3.5**

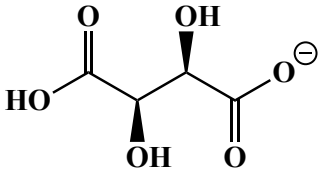


○ **Predominant form at pH = 3.5**

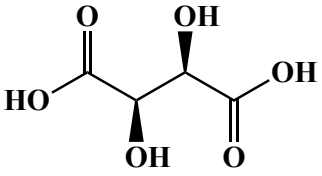
At a highly acidic pH = 2.0, fill in the circle under the structure that is the predominant form of (*2R,3R*)-(+)-Tartaric acid.



○ **Predominant form at pH = 2.0**



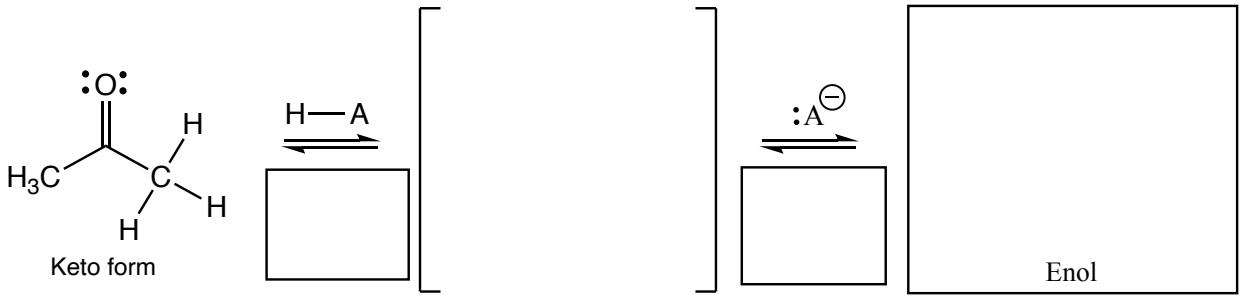
○ **Predominant form at pH = 2.0**



○ **Predominant form at pH = 2.0**

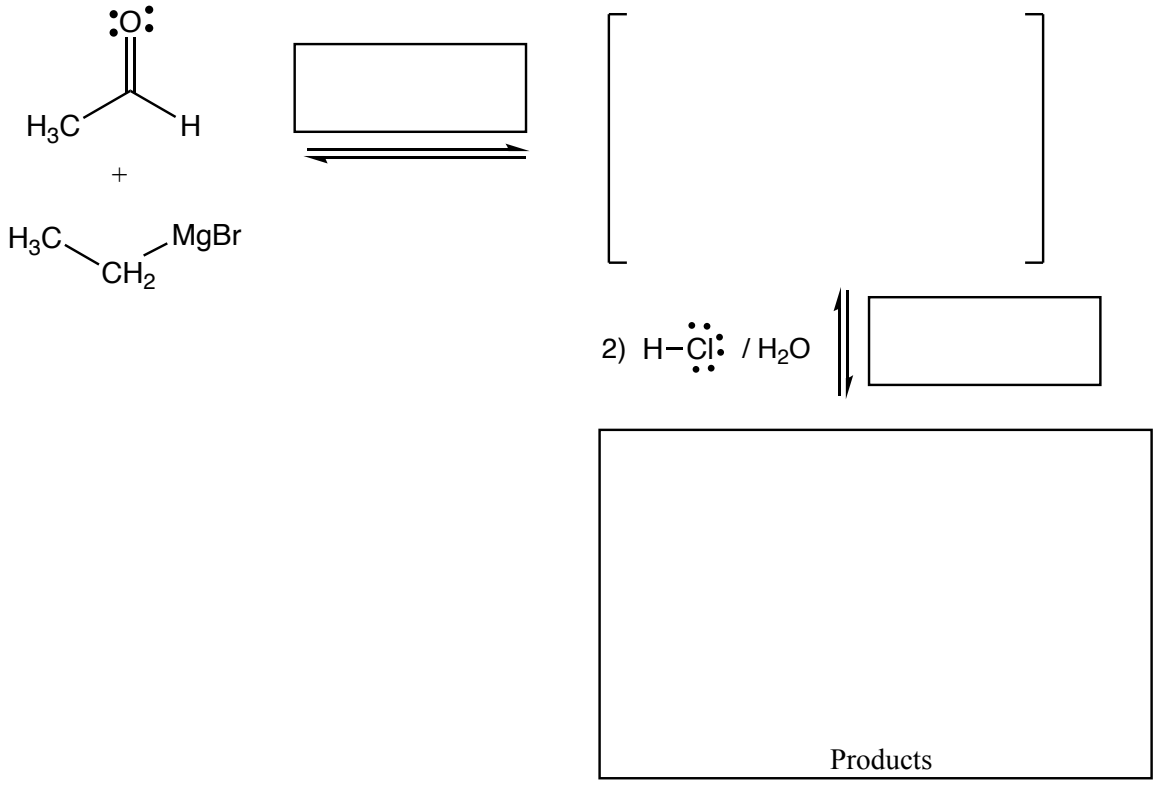
9. (32 pts) For these two reactions, use **arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, 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.).**

Acid-catalyzed Enol Formation

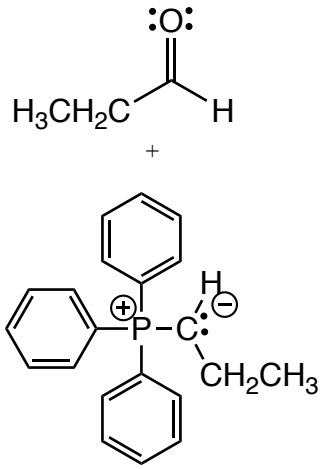


A = Any Neutral Acid

Grignard Reaction with a Ketone



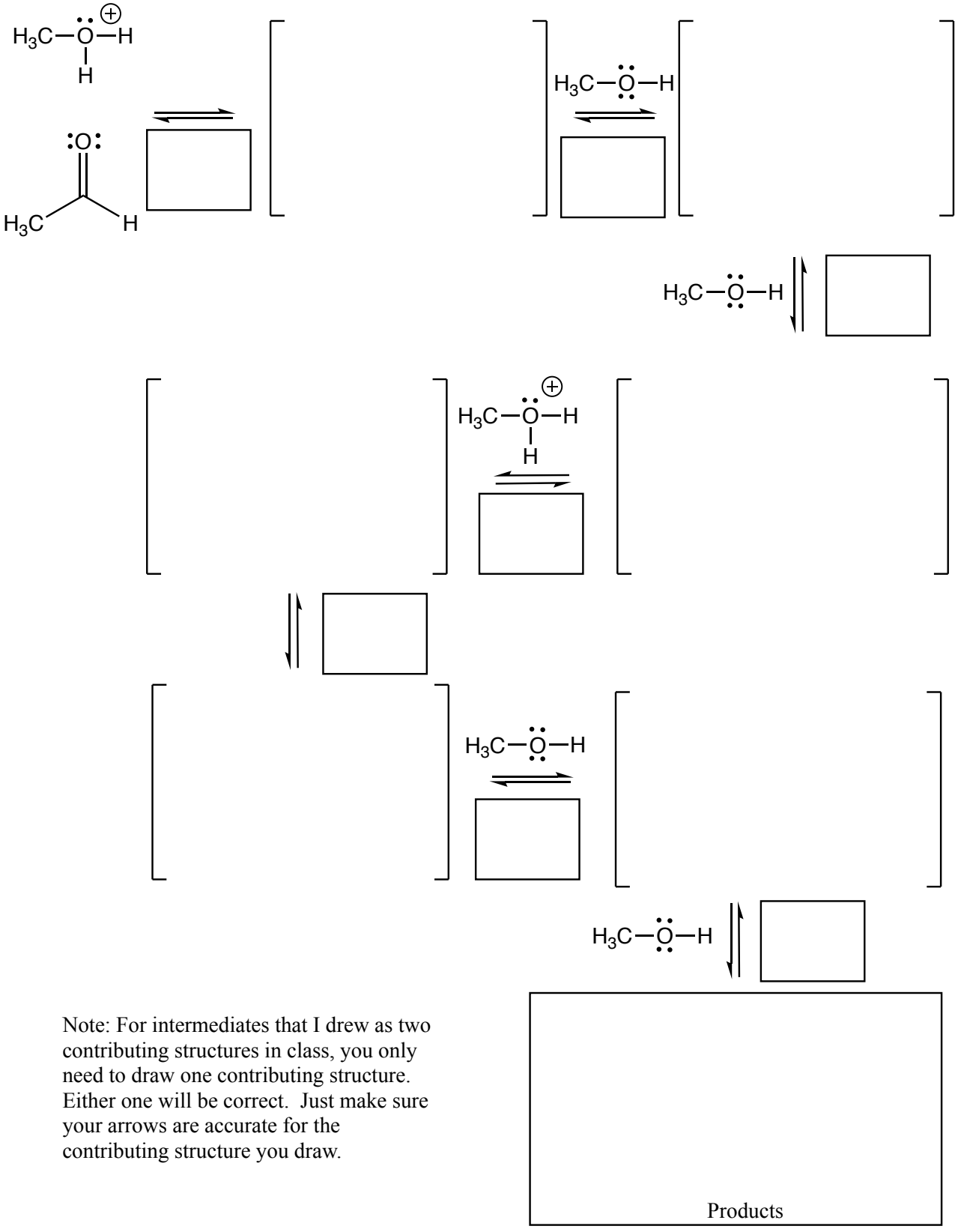
10. (21 pts) For the following Wittig reaction, use **arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN 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.).**



Products

(No box to fill in here)

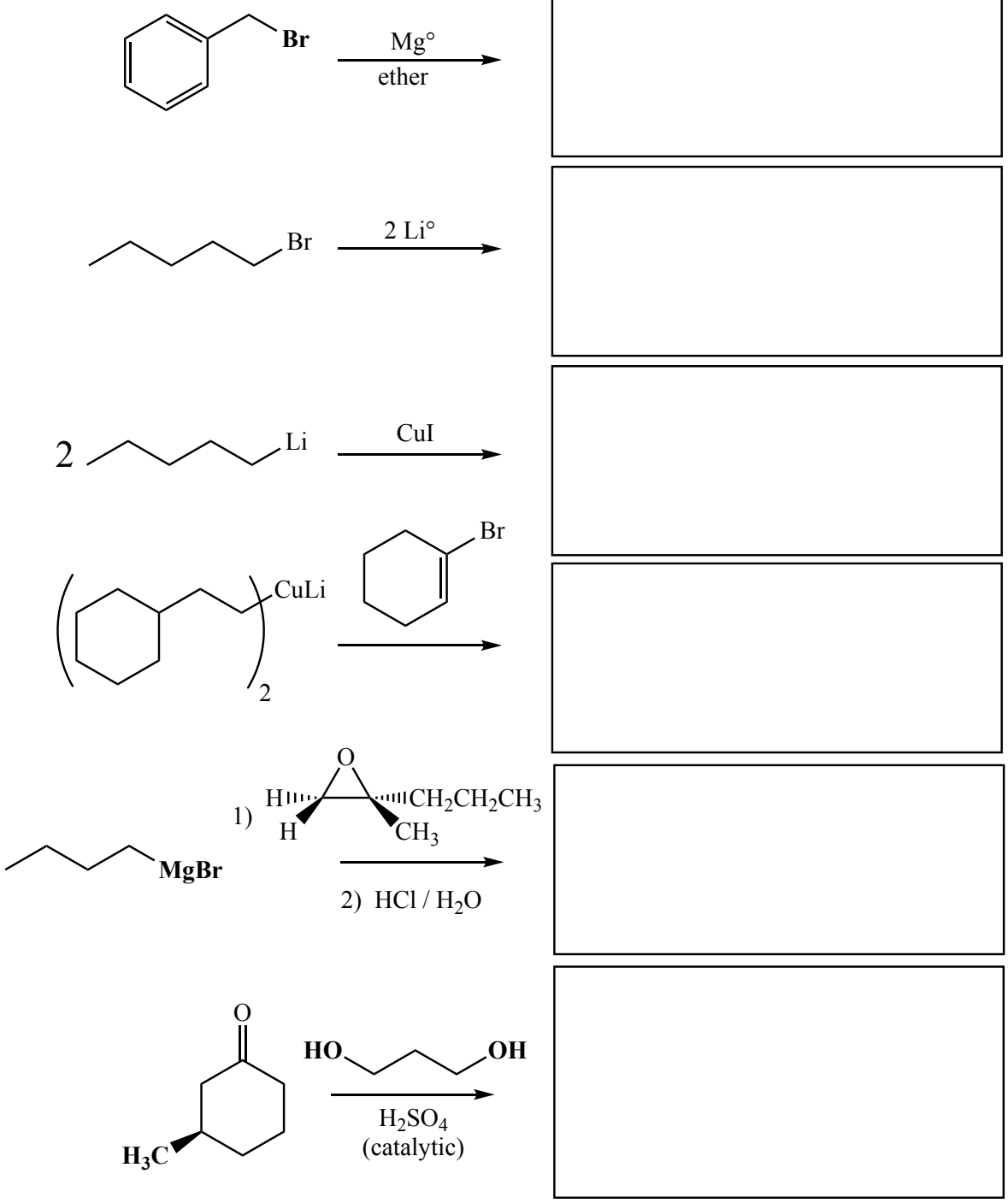
11. (54 pts) For the acetal formation mechanism on the following page, use **arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **IF A NEW CHIRAL 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.). I put this on its own page so you have more room to draw the stuctures.**



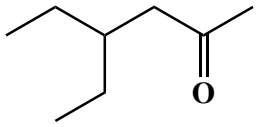
Note: For intermediates that I drew as two contributing structures in class, you only need to draw one contributing structure. Either one will be correct. Just make sure your arrows are accurate for the contributing structure you draw.

Products

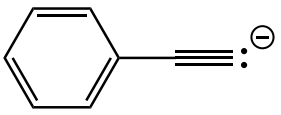
12. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. 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.

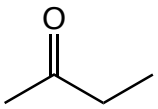


12. (cont.) (3, 4 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (····ıı) to indicate stereochemistry. 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.

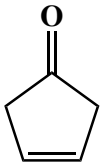


HCN →

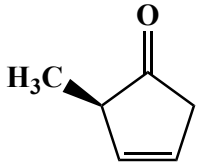


1) 

2) HCl / H_2O →

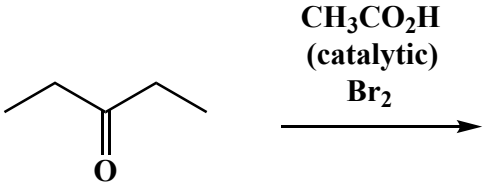


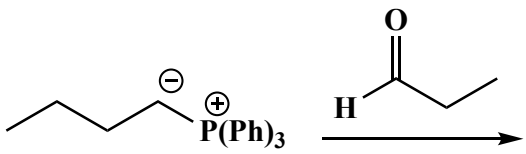
1) $NaBH_4$
2) H_2O →

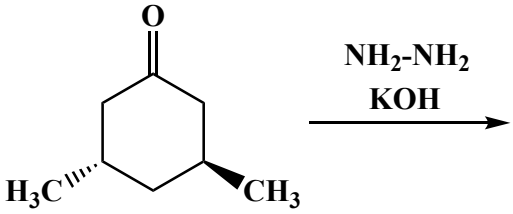


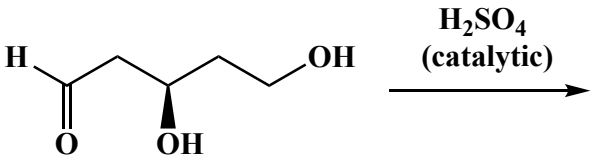
excess H_2
Pd° →

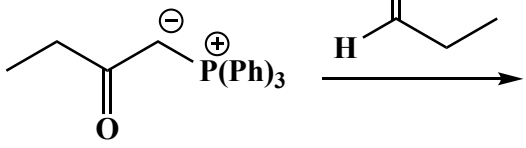
12. (cont.) (3, 4 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (····ıı) to indicate stereochemistry. 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.



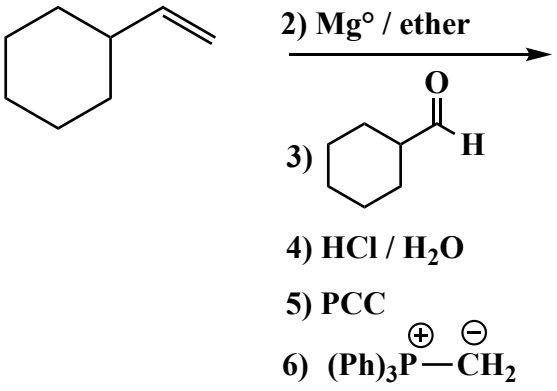




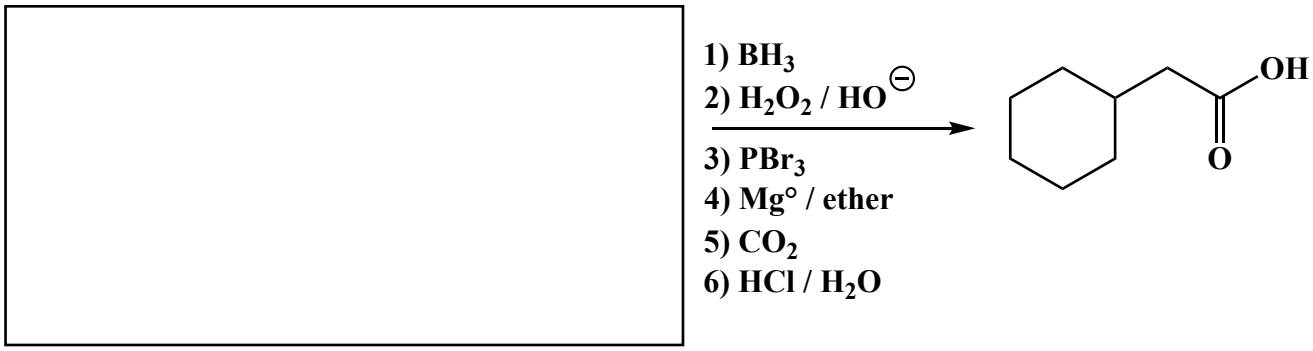




13. (12 pts) Here is a warm-up for the synthesis problems. For the following series of reactions, write the **final** product(s) that you will see. Make sure draw all stereoisomers produced and to use wedges and dashes to indicate all stereochemistry, and you must write racemic if appropriate.

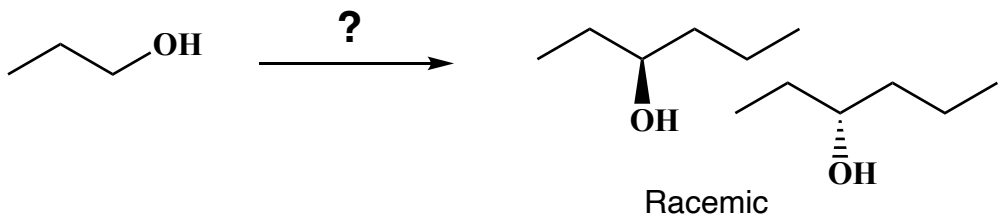


14. (12 pts) Here is a second warm-up for the synthesis problems. For the following series of reactions, we have given you the final product. Work backwards and **in the box provided write the structure of the starting material that would generate the final product shown.**



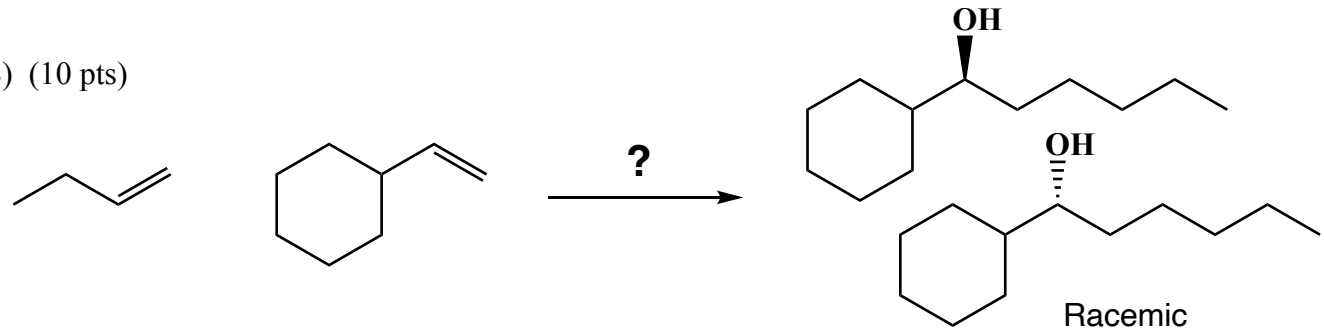
15. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized 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)



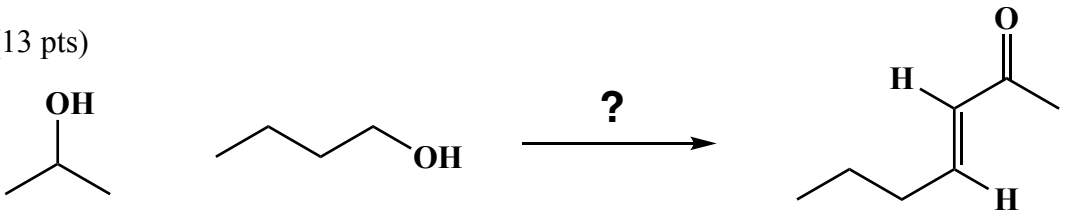
15. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule 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 materials.**

B) (10 pts)

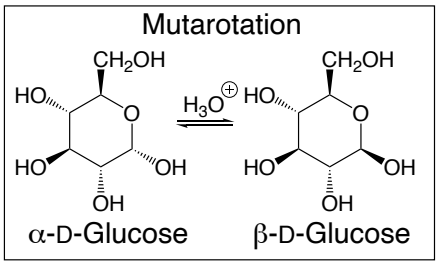


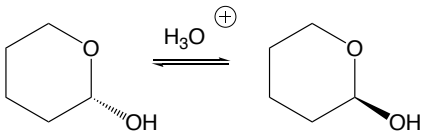
15. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized 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) (13 pts)



16. (24 pts) Here is an "Apply What you Know" Problem. You have not seen this directly, but based on what you know you CAN figure it out. We talked about the process called "mutarotation" in which alpha-D-glucose equilibrates with beta-D-glucose. The process emphasizes the reversible nature of cyclic hemiacetal formation. Shown below is mutarotation of D-Glucose as well as the analogous cyclic hemiacetal equilibration on the structurally most simple cyclic hemiacetal (shown on the right).





Recall that reversible reaction mechanisms involve the exact same intermediates in both directions, use what you know about hemiacetal formation to fill in the mechanism sheet below to complete the mechanism for how acid can catalyze the equilibration between cyclic hemiacetals.