NAME (Print): _____

EID _____

SIGNATURE: _____

Chemistry 320N
1st Midterm Exam
February 13, 2025

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!!!

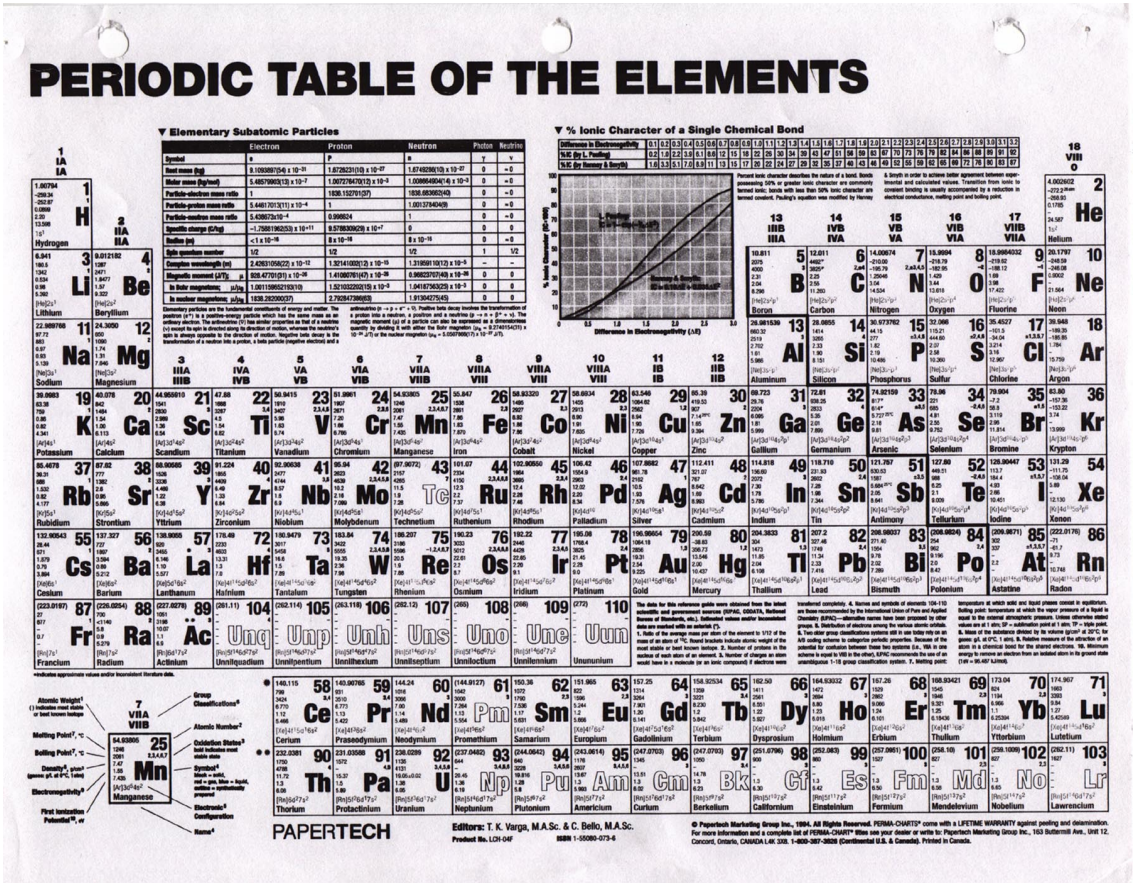
Student Honor Code for the University of Texas at Austin

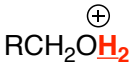
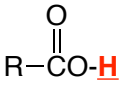
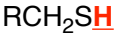
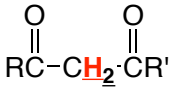
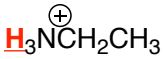
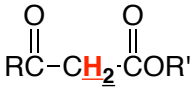
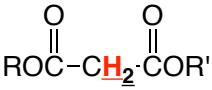
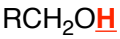
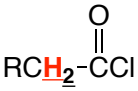
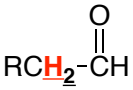
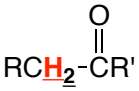
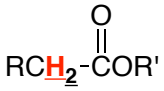
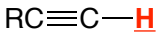
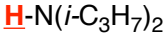
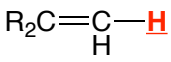
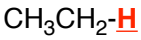
"I pledge, as a member of The University of Texas at Austin community, to do my work honestly, respectfully, and through the intentional pursuit of learning and scholarship."

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		-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 _____(29)

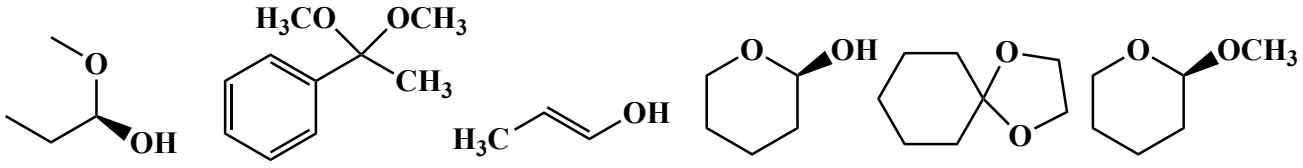
1. (5 pts) What is the most important question in organic chemistry?

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 medical diagnostic technique of 1.**magnetic** 2.**resonance** 3.**imaging** (**MRI**) is based on the same principles as 4.**NMR**, namely the flipping (i.e. 5.**resonance**) of nuclear spins of H atoms by 6.**radio** frequency irradiation when a patient is placed in a strong 7.**magnetic** 8.**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 9.**slices** that when 10.**stacked** make up the three-dimensional image of 11.**relative** amounts of H atoms, especially the H atoms from 12.**water** and 13.**fat**, in the different 14.**tissues**.

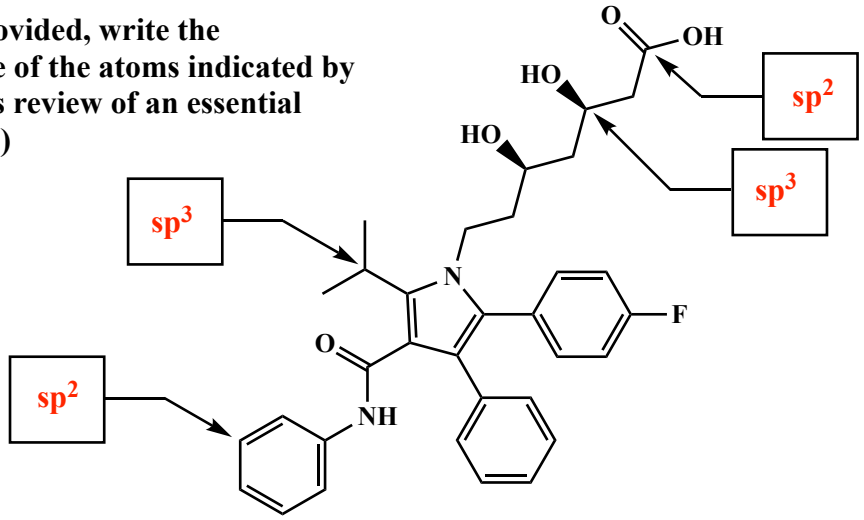
3. (2 pt each) Fill in each circle to indicate the appropriate name for the functional group in the following molecules and then indicate whether or not they are favored species at equilibrium.



○ Enol ● Hemiacetal ○ Acetal	○ Enol ○ Hemiacetal ● Acetal	● Enol ○ Hemiacetal ○ Acetal	○ Enol ● Hemiacetal ○ Acetal	○ Enol ○ Hemiacetal ● Acetal	○ Enol ○ Hemiacetal ● Acetal
○ Favored at equilibrium	● Favored at equilibrium	○ Favored at equilibrium	● Favored at equilibrium	● Favored at equilibrium	● Favored at equilibrium
● Not favored at equilibrium	○ Not favored at equilibrium	● Not favored at equilibrium	○ Not favored at equilibrium	○ Not favored at equilibrium	○ Not favored at equilibrium

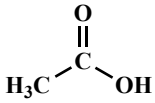
4. (8 pts) Lipitor (Atorvistatin) is a very important drug used to treat prevent atherosclerosis and heart disease. In 2023 it was 24th best selling drug, earning $2.2 billion in sales. Answer the following questions about lipitor.

A. In the boxes provided, write the hybridization state of the atoms indicated by the arrow. (This is review of an essential OChem 1 concept.)

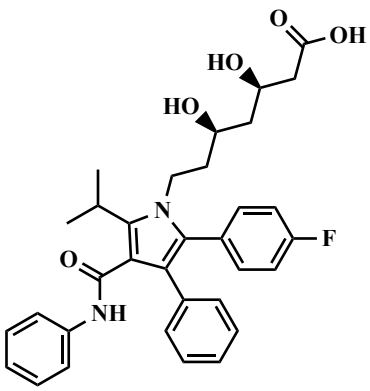


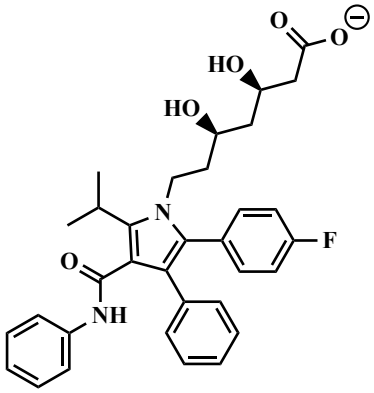
Lipitor (Atorvastatin)

B. (6 pts) Given that the pK_a value shown for acetic acid is typical for a carboxylic acid group, fill in the circle to indicate the pH at which the protonation state of lipitor shown above would be present. You might need to fill in more than one circle, as the given structure might be present at more than one of the pH values listed.



Acetic acid $pK_a = 4.76$

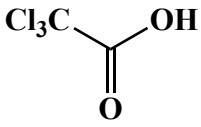




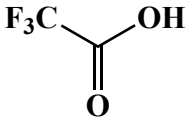
- ● The predominant form present at pH = 2
- ○ The predominant form present at pH = 7
- ○ The predominant form present at pH = 10

- ○ The predominant form present at pH = 2
- ● The predominant form present at pH = 7
- ● The predominant form present at pH = 10

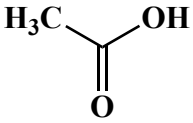
5. (4 pts) Predict the relative acidities of the following molecules. Put the number 1 under the most acidic molecule, the number 4 under the least acidic molecule, and the numbers 2 and 3 under the other two stuctures as appropriate.



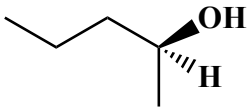
2



1

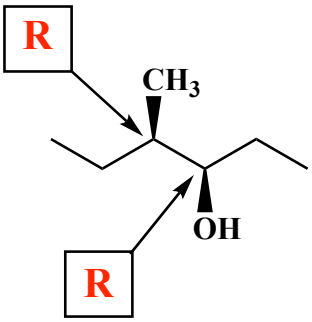


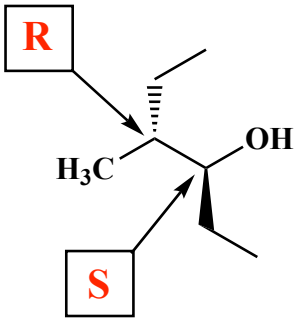
3



4

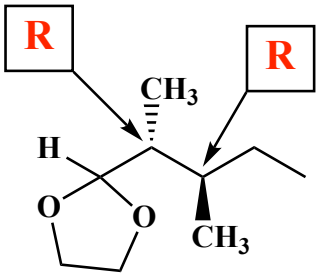
6. (12 pts) For each pair of molecules, fill in the boxes to label each chiral center as R or S then fill in the circle that indicates the appropriate relationship between the two molecules.

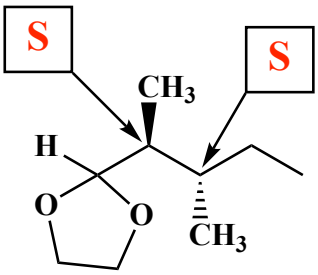




Relationship:

- ○ Enantiomers
- ● Diastereomers
- ○ Same molecule

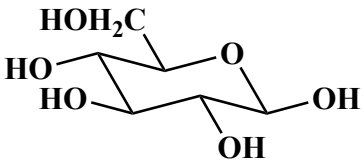




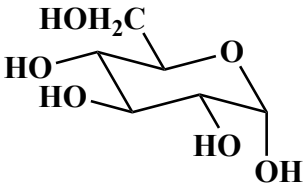
Relationship:

- ● Enantiomers
- ○ Diastereomers
- ○ Same molecule

7. (4 pts each) Fill in the circle to indicate the correct name for the glucose molecules shown.



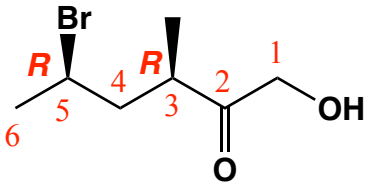
- ○ alpha(α) - D - Glucose
- ● beta(β) - D - Glucose



- ● alpha(α) - D - Glucose
- ○ beta(β) - D - Glucose

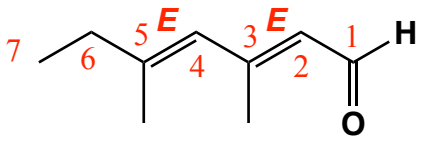
8. (4 pts each) Write an acceptable IUPAC name or draw a structural formula for the following molecules:

A.



(3*R*,5*R*)-5-bromo-1-hydroxy-3-methyl-2-hexanone
or
(3*R*,5*R*)-5-bromo-1-hydroxy-3-methylhexan-2-one

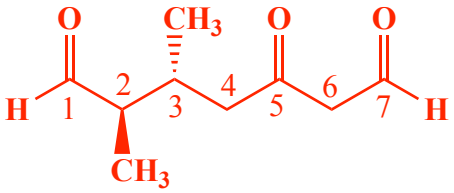
B.



(2*E*,4*E*)-3,5-dimethyl-2,4-heptadienal
or
(2*E*,4*E*)-3,5-dimethylhepta-2,4-dienal

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

(2*R*,3*R*)-2,3-dimethyl-5-oxoheptanedial

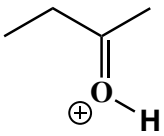


9. (11 pts) Being able to recognize the chemical personality of different species is one of the most important skills you can develop in Organic Chemistry. Fill in the appropriate circle to indicate whether each structure is a nucleophile or electrophile in the mechanisms we have seen. Note that these species might be acids or bases in certain situations, but we will ignore that for this problem.

9.1 $NaBH_4$

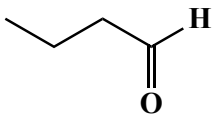
○ Electrophile
● Nucleophile

9.2



● Electrophile
○ Nucleophile

9.3

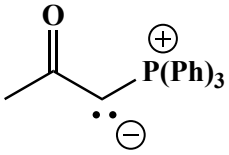


● Electrophile
○ Nucleophile

9.4 Br_2

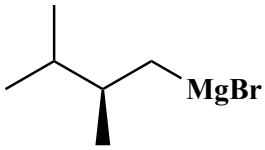
● Electrophile
○ Nucleophile

9.5



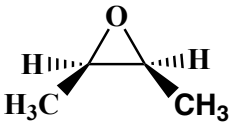
○ Electrophile
● Nucleophile

9.6



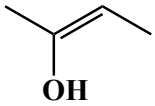
○ Electrophile
● Nucleophile

9.7



● Electrophile
○ Nucleophile

9.8

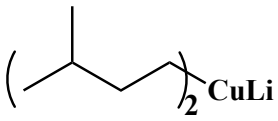


○ Electrophile
● Nucleophile

9.9 NH_2-NH_2

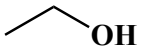
○ Electrophile
● Nucleophile

9.10



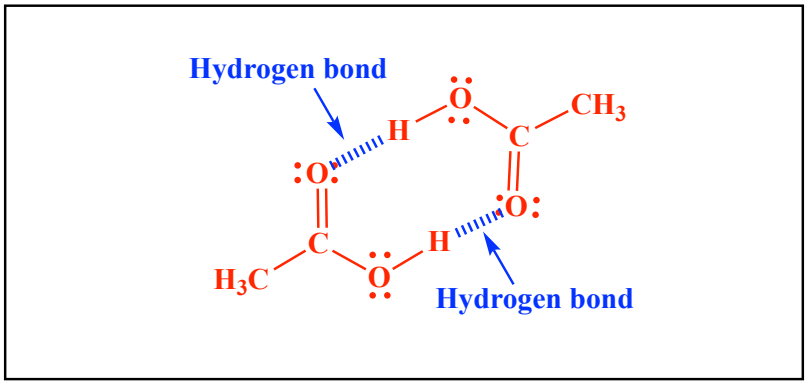
○ Electrophile
● Nucleophile

9.11



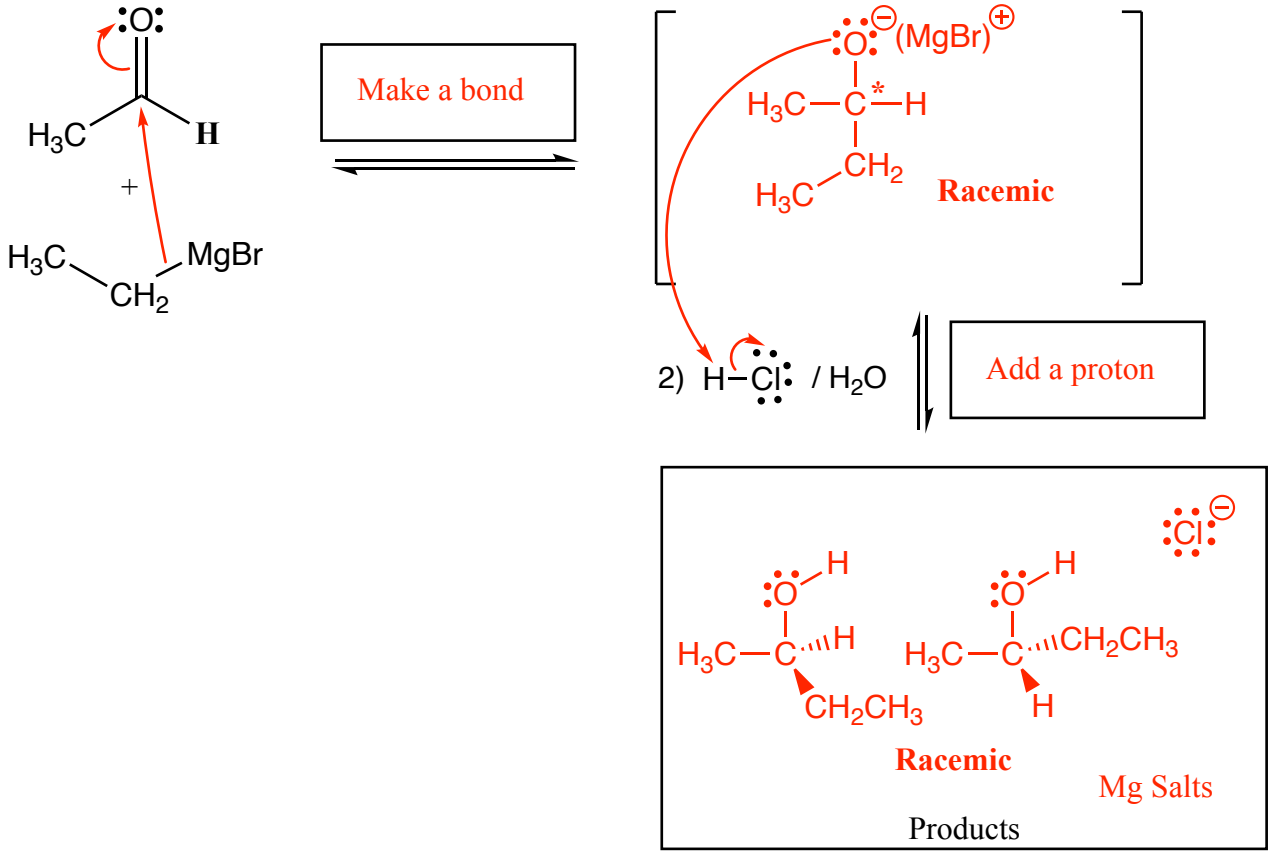
○ Electrophile
● Nucleophile

10. (6 pts) Carboxylic acids exist as a characteristic dimer in solution, held together with hydrogen bonds. In the box provided, draw the hydrogen bonded dimer of acetic acid. Indicate the hydrogen bonds as a dashed line, and draw all lone pairs on your stuctures. You saw this in lecture last Thursday.



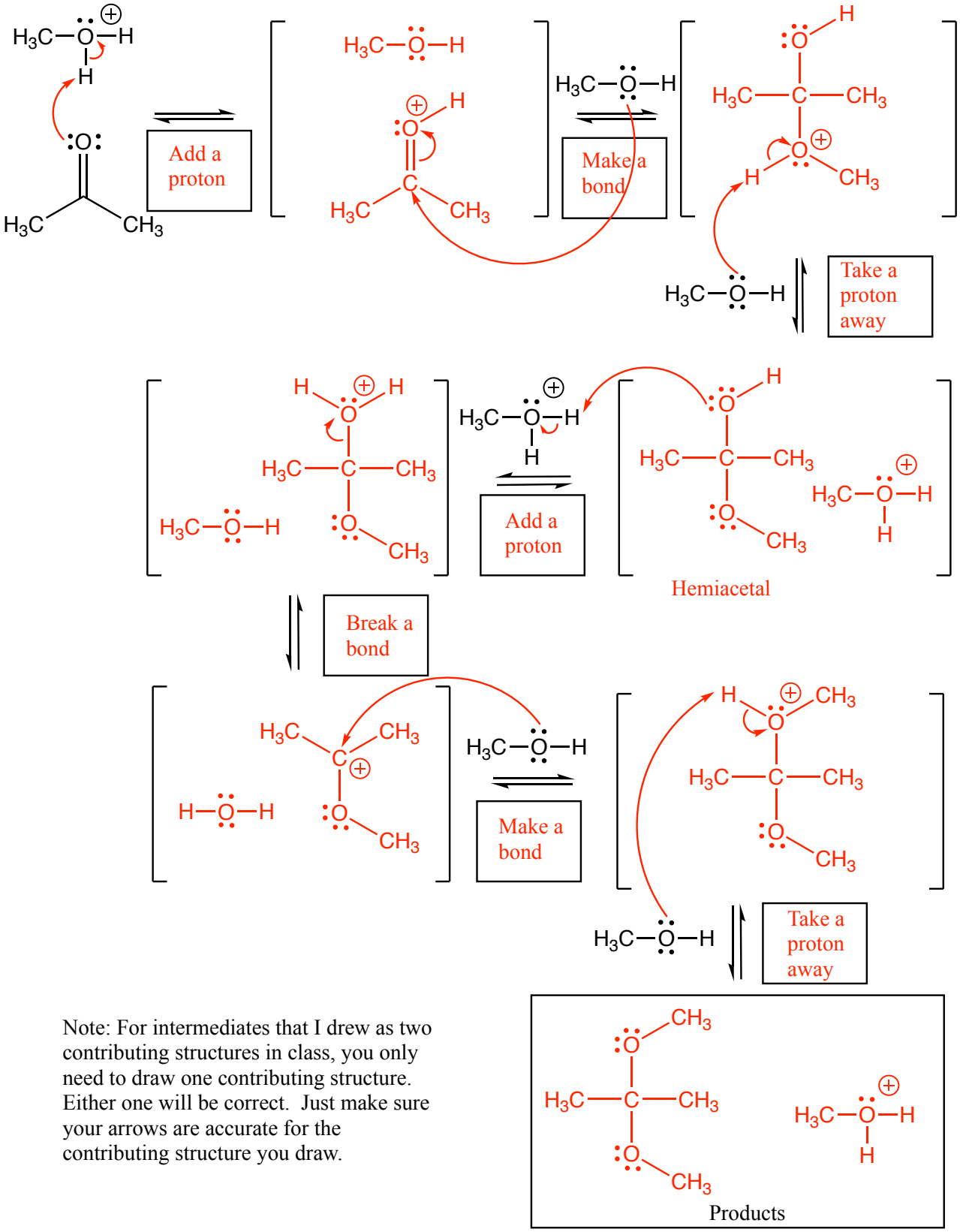
11. (12 pts) For this Grignard reaction, use **arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. <u>FOR ALL CHIRAL FINAL "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 an Aldehyde



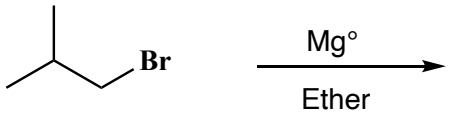
12. (45 pts) For the acetal reaction mechanism ON THE NEXT PAGE, use **arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **IF A NEW CHIRAL CENTER 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.).**

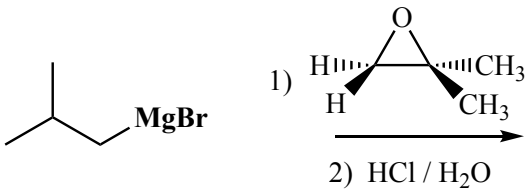
The mechanism did not fit on the same page as the directions, so use the directions on this page to fill in the mechanism on the next page!

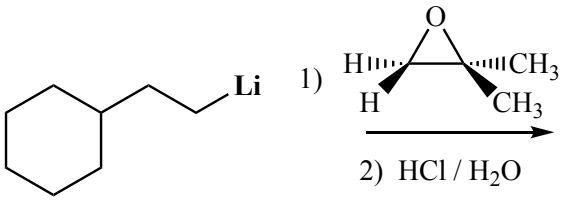


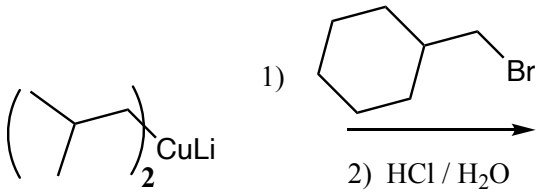
Note: For intermediates that I drew as two contributing structures in class, you only need to draw one contributing structure. Either one will be correct. Just make sure your arrows are accurate for the contributing structure you draw.

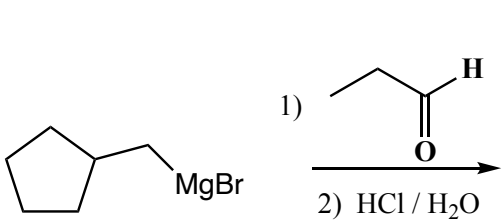
13. (3 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry. To get full credit, you only need to write the major organic product for these.
You do not have to worry about the other products.





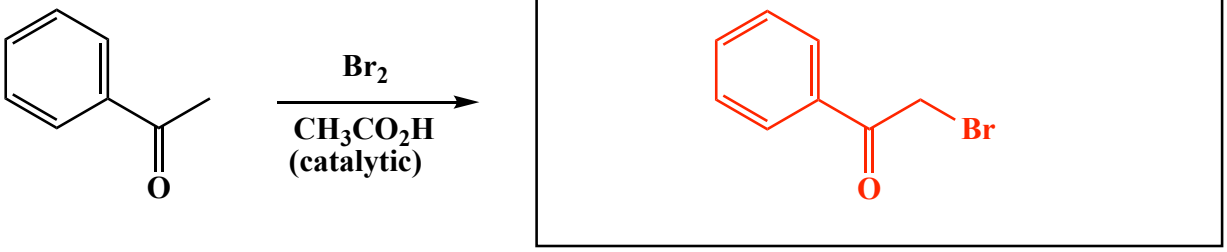


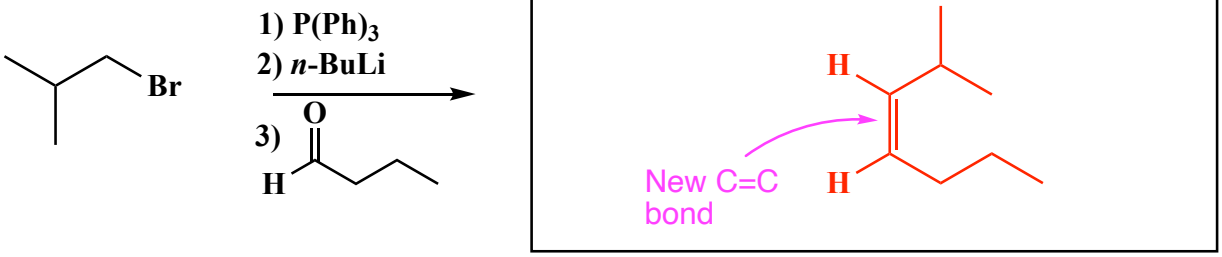


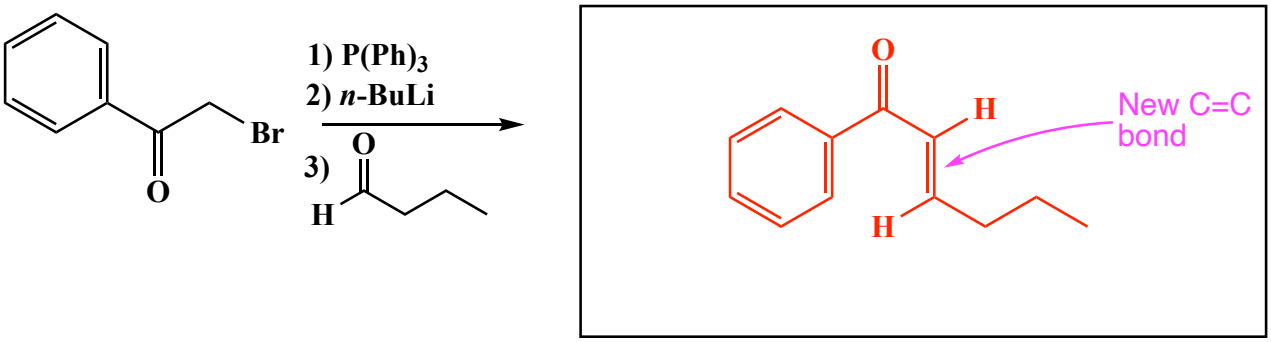


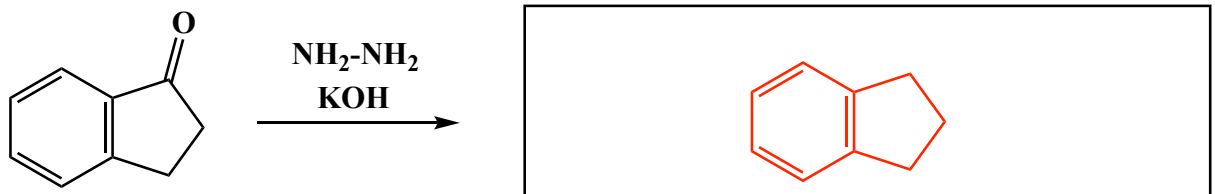
ugdxz

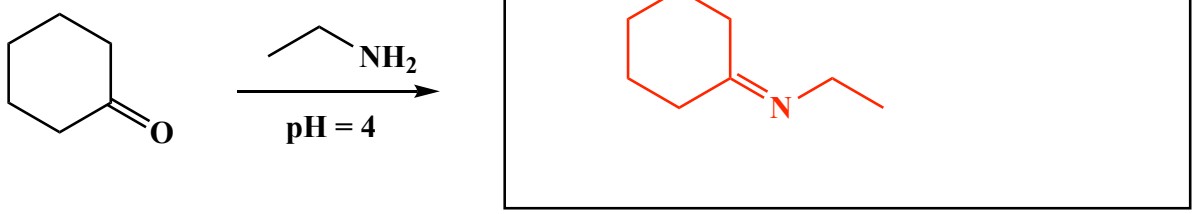
13. (cont.) (3, 4 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◄) and dashes (·····) to indicate stereochemistry.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



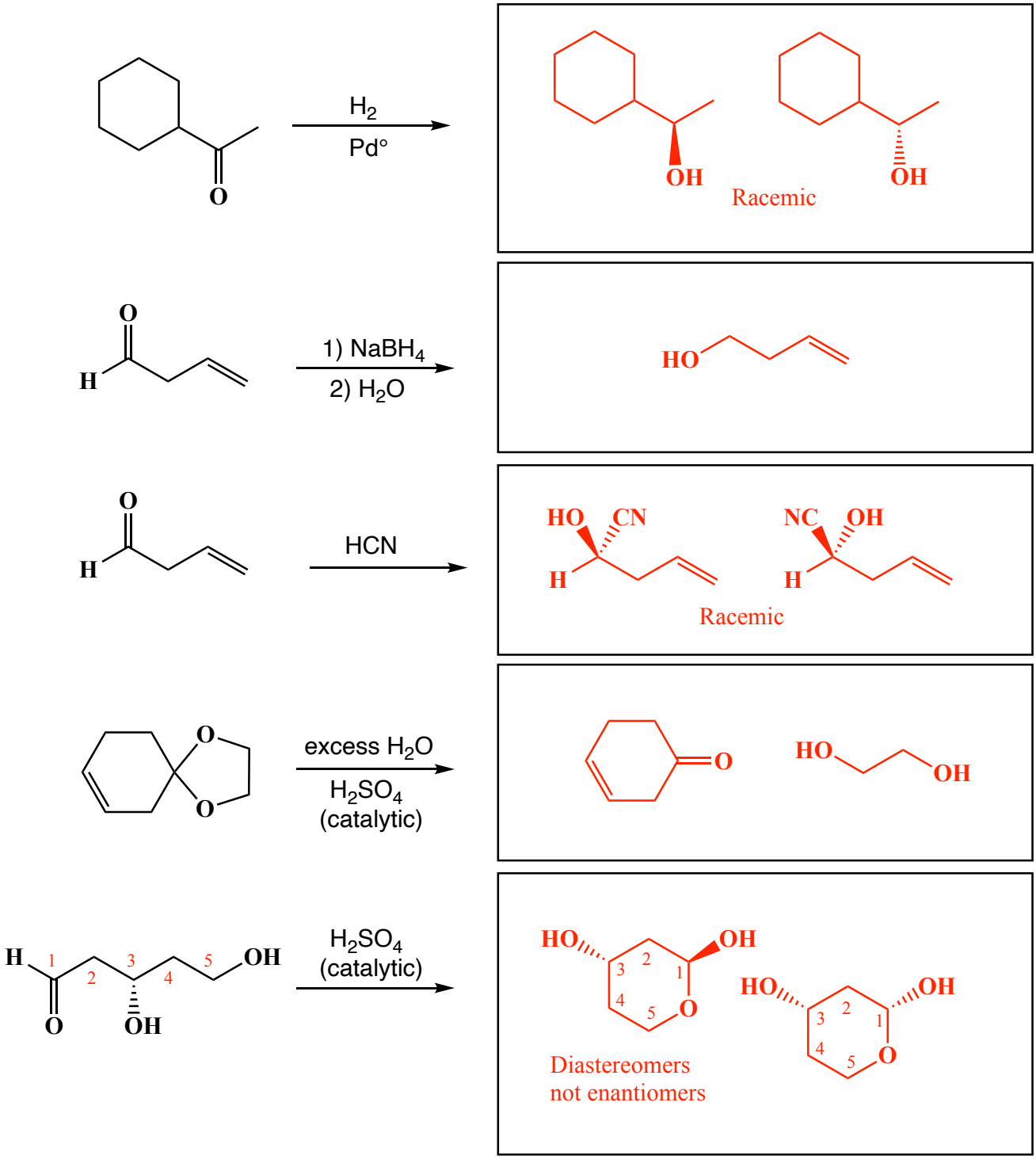




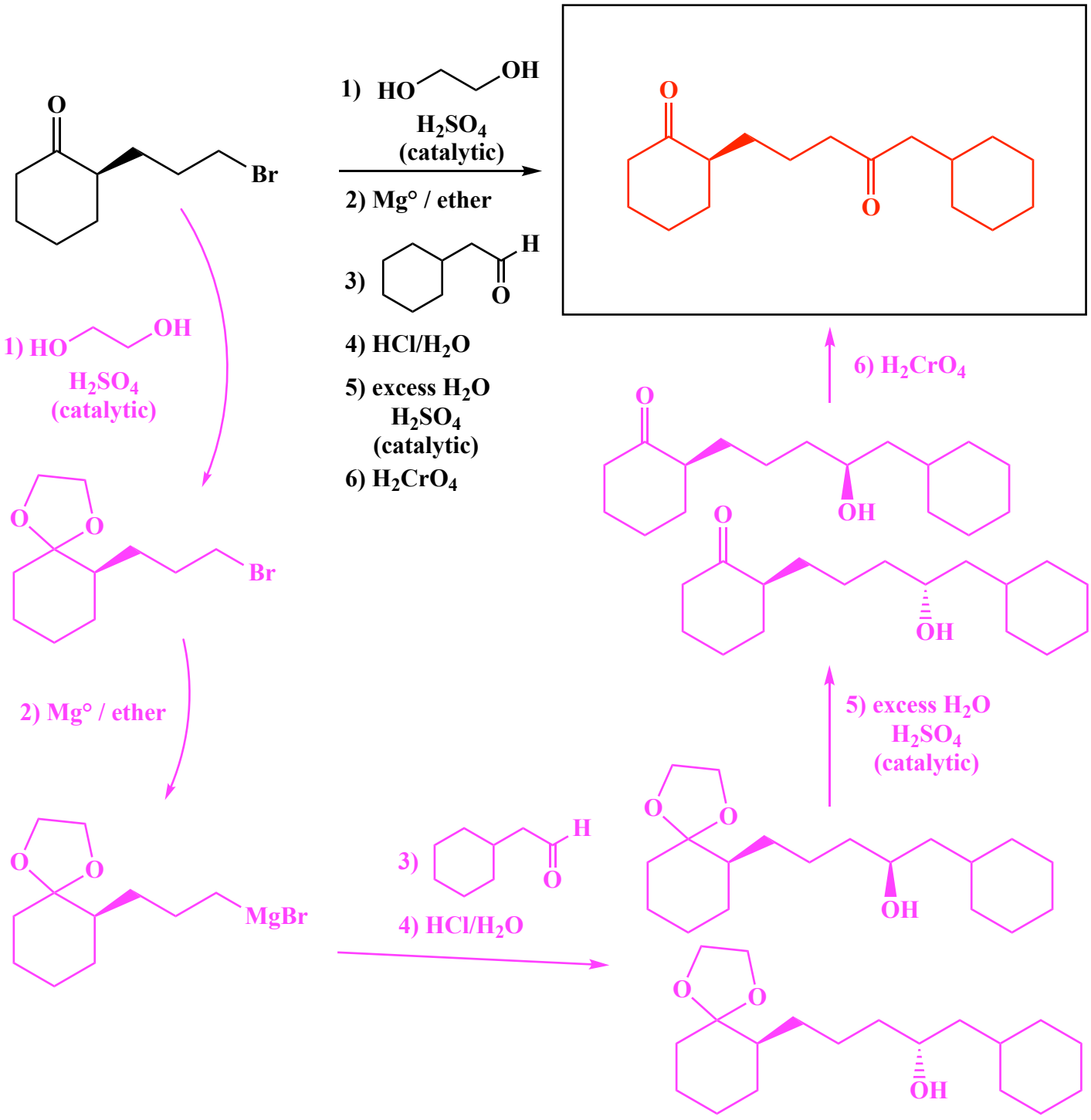




13. (cont.) (3, 4 or 5 pts.) Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (◀) and dashes (⋯) to indicate stereochemistry.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

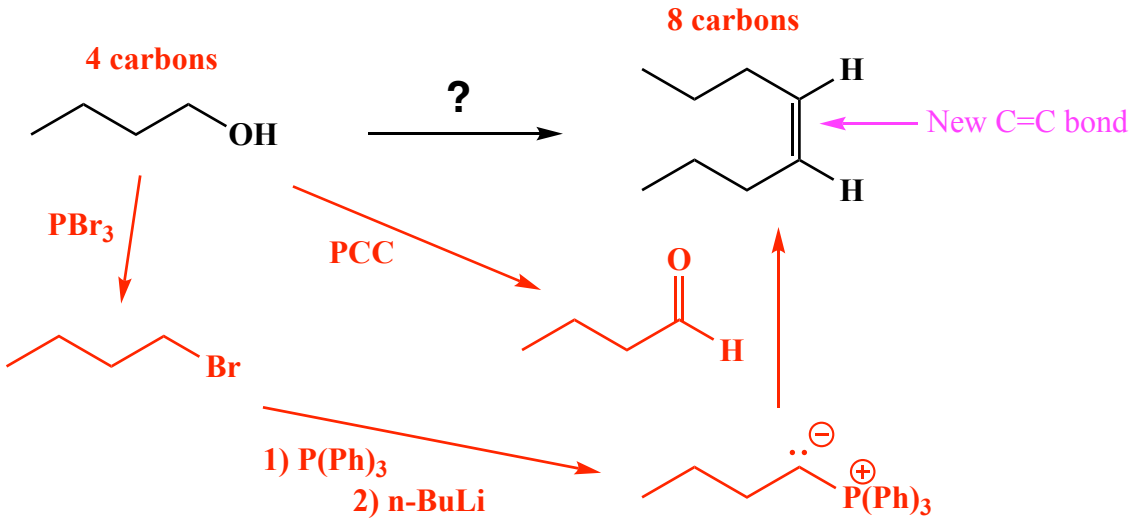


14. (10 pts) Here is a warm-up for the synthesis problems. For the following series of reactions, write the **final** product(s) that you will see. Make sure draw all stereoisomers produced and to use wedges and dashes to indicate all stereochemistry, and you must write racemic if appropriate.



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.**

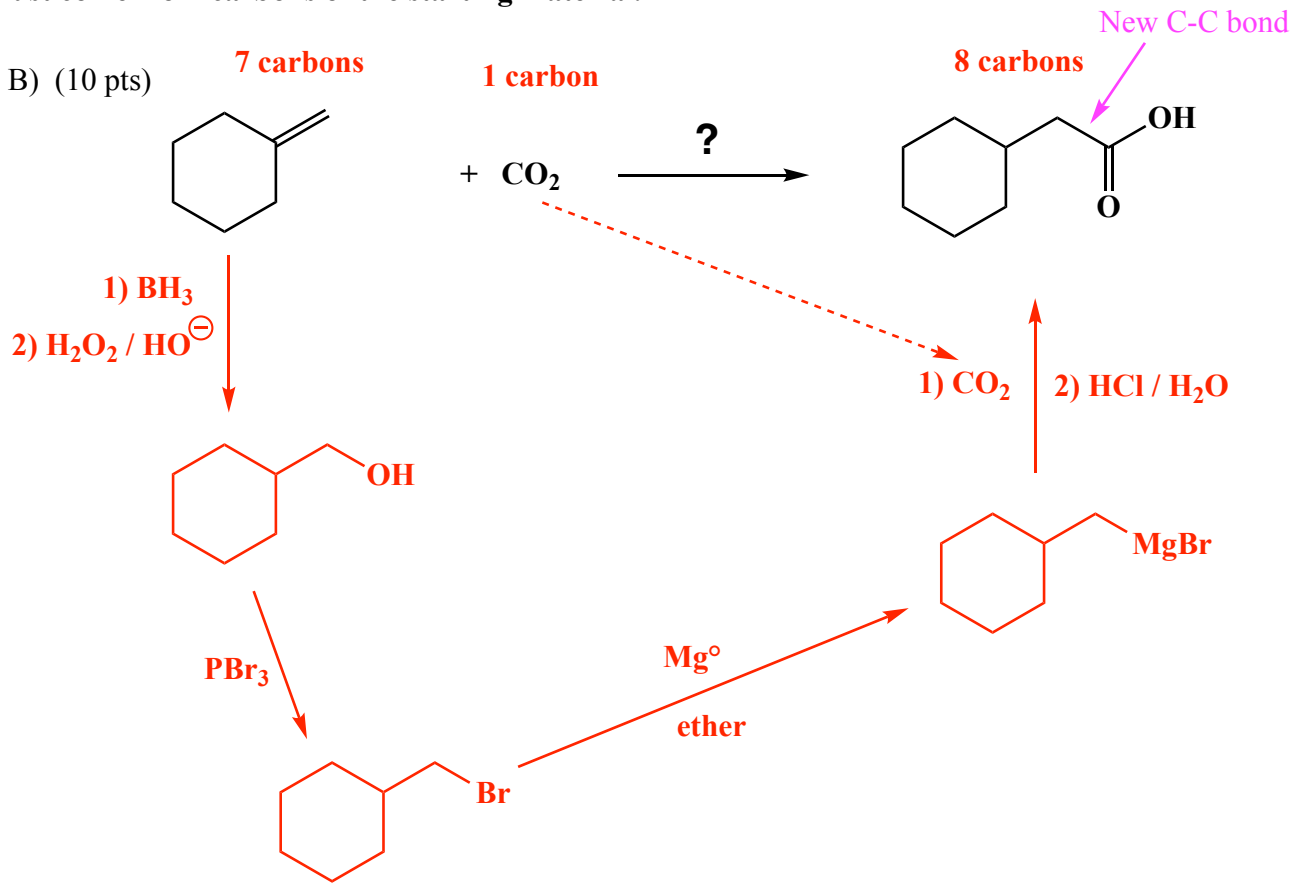
A) (10 pts)



Recognize the product is a Z alkene with 8 carbons. The starting material has 4 carbons, so predict the new C=C bond is the alkene. **Recognize** that the Z alkene with a new C=C is the KRE of a Wittig reaction with two four carbon pieces. You can make the required gour carbon aldehyde from the starting alchohol using PCC, and you can make the required four carbon Wittig reagent by converting the alcohol to the haloalkane using PBr_3, followed by the usual reaction with 1) $P(Ph)_3$ then 2) n-BuLi.

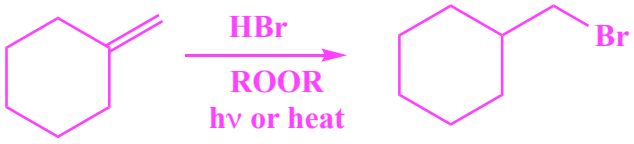
15. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized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

B) (10 pts)



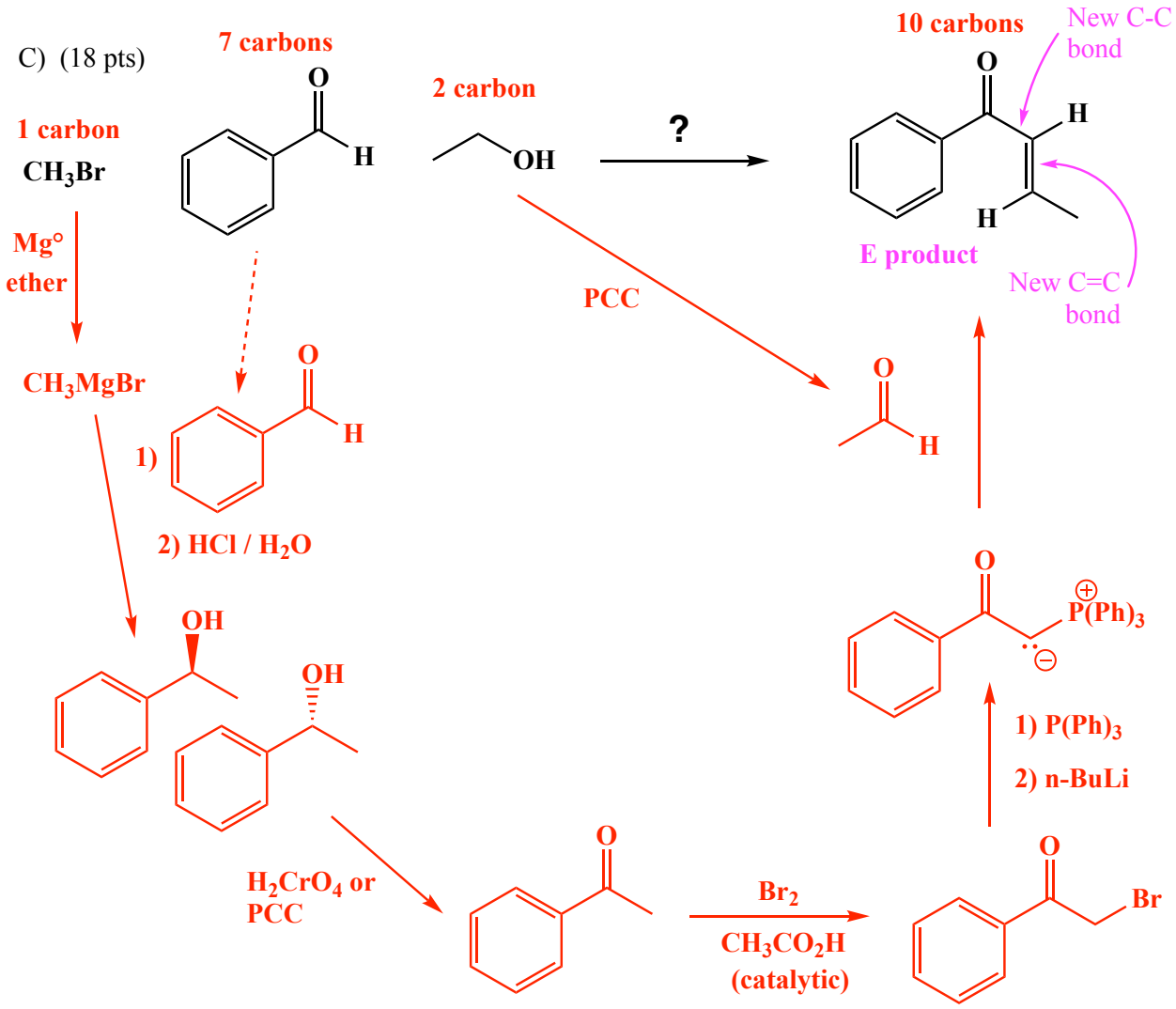
Recognize that the product has 8 carbons and the starting materials have 7 carbons and 1 carbons. Therefore the new carbon-carbon bond is between the last two carbons as shown. **Recognize** that a carboxylic acid with a new carbon-carbon bond to the carboxylic acid carbon is the KRE of a Grignard reagent reacting with CO_2, and of course, CO_2 is one of the starting materials. **Recognize** that the required 7-carbon Grignard reagent can be made from the starting 7 carbon alkene by first carrying out a non-Makovnikov addition of an OH group using 1) BH_3 followed by 2) H_2O_2 / $HO^{\ominus}$ to give the 7-carbon primary bromoalkane. Alternatively you could have created the 7-carbon primary bromoalkane directly from the starting alkene using HBr in the presence of peroxides (ROOR) with heat or light. Either way, treatment of the 7-carbon primary haloalkane with Mg° and ether gives the 7-carbon Grignard reagent.

Also a good answer:



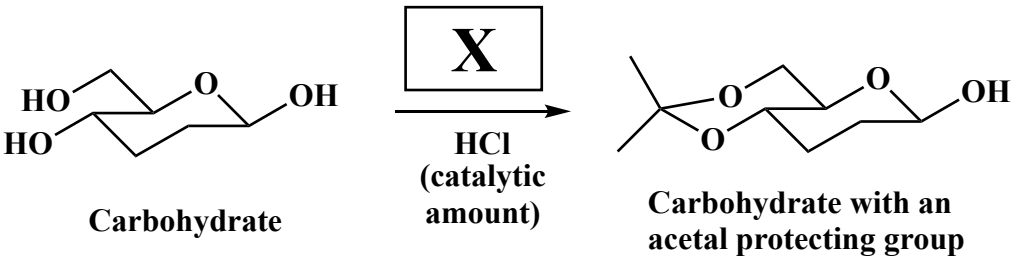
15 (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule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

C) (18 pts)



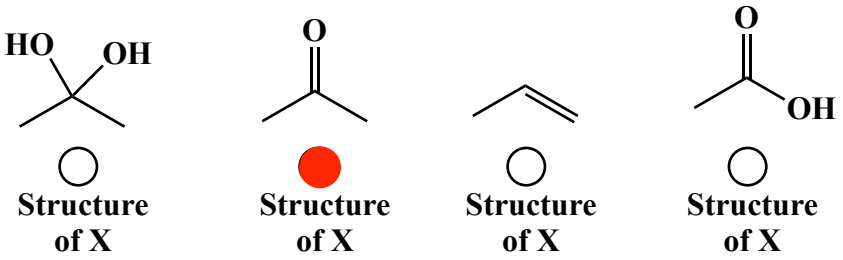
Recognize that the product has 10 carbons, and the starting materials have 1,2, and 7 carbons, so all three starting materials are used once. **Recognize** an E alkene in the product with an adjacent carbonyl group, the KRE of a Wittig reaction using an enolate Wittig reagent. Therefore, predict the C=C is one new bond and the other new C-C bond must therefore be between the carbonyl and the alkene. **Recognize** further that the aldehyde needed for the final Wittig is made from the ethanol starting material using PCC. **Recognize** that the haloketone needed to make the Wittig reagent can be made from the corresponding 8-carbon methyl ketone using the alphahalogenation reaction. The hard part of this synthesis is **recognizing** that the 8-carbon methyl ketone you need can be made from the starting aldehyde and methyl bromide by converting the latter into a Grignard reagent with Mg°/ether, carrying out the Grignard reaction then taking the resulting racemic secondary alcohol product to the 8-carbon methyl ketone using PCC or H_2CrO_4.

16. (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. A major effort in modern organic chemistry involves the synthesis of carbohydrates so that we can study their properties and biochemistry. It is common to use a protecting group to prevent -OH groups on carbohydrates from taking part in unwanted reactions. The following is a common strategy to protect nearby -OH groups on a carbohydrate using an acetal.



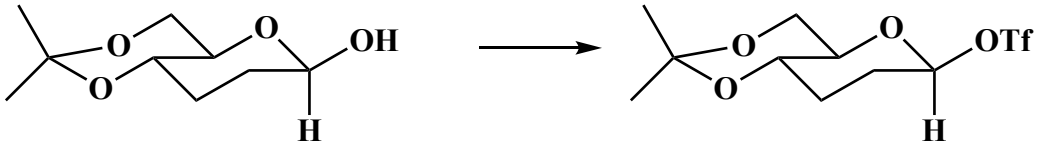
Carbohydrate **Carbohydrate with an acetal protecting group**

(4 pts) Look carefully at the carbohydrate with an acetal protecting group and fill in the circle beneath the molecule that corresponds to the appropriate structure "X".

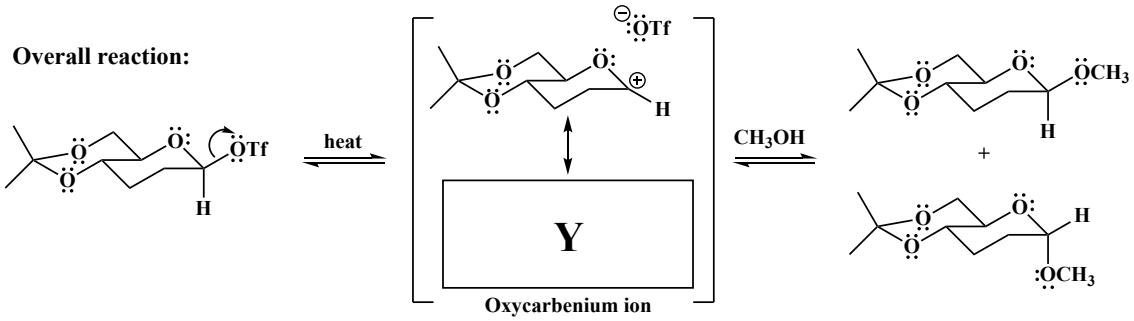


Structure of X **Structure of X** **Structure of X** **Structure of X**

Chemists use these protected carbohydrates to make new bonds at the anomeric carbon atom. They first turn the OH on the anomeric carbon into a great leaving group. Here -OTf corresponds to something called a triflate group, the structure of which is not important. All you need to know is that the -OTf group is a great leaving group.



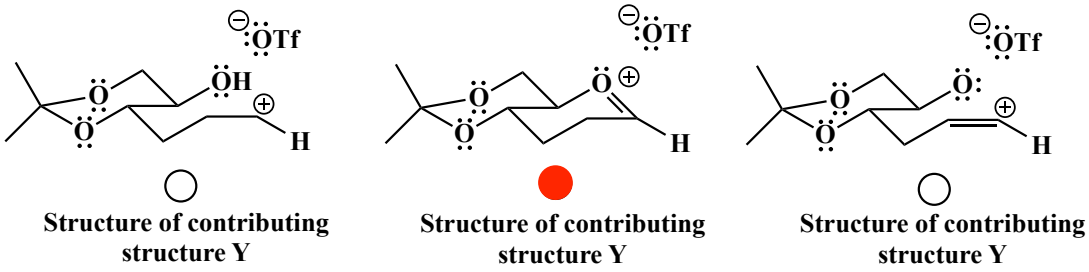
When these carbohydrates are heated, the leaving group departs to give a cation called an oxycarbenium ion intermediate that reacts with an alcohol such as methanol to make a new bond at the anomeric carbon as shown.



(4 pts) Fill in the appropriate circle. This overall reaction is best described as:

● **An S_N1 reaction** ○ **An S_N2 reaction** ○ **An E1 reaction** ○ **An E2 reaction**

(4 pts). Fill in the circle beneath the structure for Y that corresponds to the other important contributing structure of the oxycarbenium ion intermediate shown above.

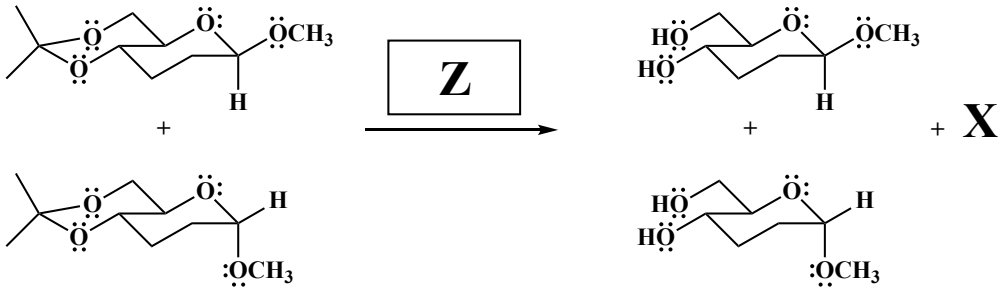


○ **Structure of contributing structure Y**

● **Structure of contributing structure Y**

○ **Structure of contributing structure Y**

To finish the reaction, the chemist must remove the acetal protecting group to regenerate the two -OH groups as well as give the reagent "X" from the first part of this problem.



(4 pts) Based on what you know about acetals, fill in the circle under the reagent(s) "Z" that a chemist should use to remove the acetal protecting group.

CH_3OH	NH_2-NH_2 $HO^{\ominus}$	1) $NaBH_4$ 2) H_2O	excess H_2O HCl or H_2SO_4 (catalytic amount)
○	○	○	●
Reagents that could be Z	**Reagents that could be Z**	**Reagents that could be Z**	**Reagents that could be Z**