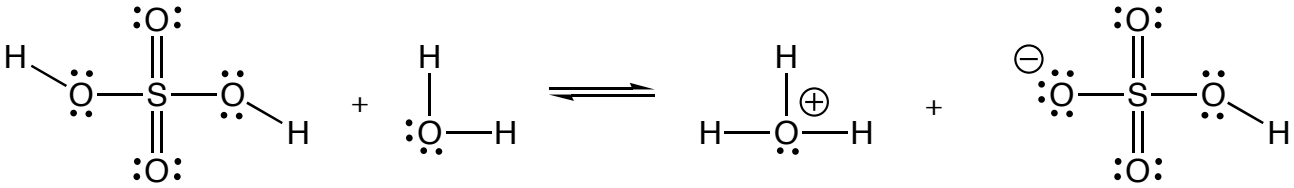
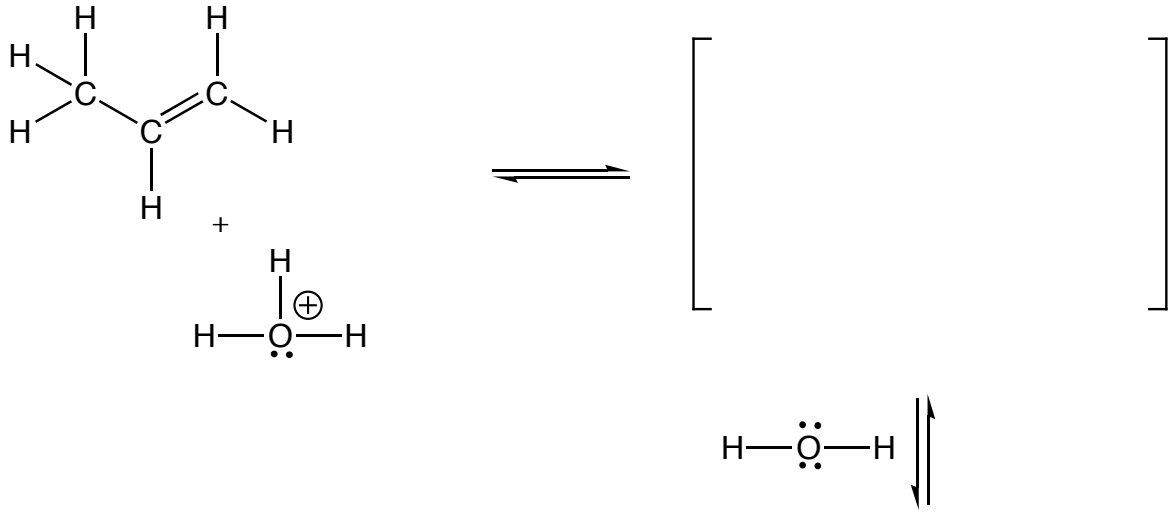
Acid-catalyzed Hydration of an Alkene





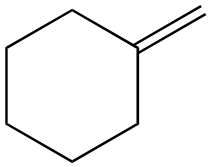
Products

Summary:

Regiochemistry:

Stereochemistry:

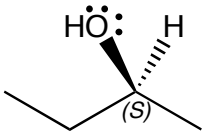
Example:



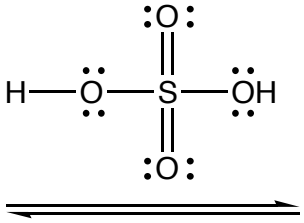
H_2O

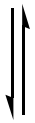
H_2SO_4 (catalytic amount)

2° or 3° Alcohol Dehydration

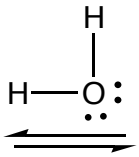


2° or 3° Alcohols





Products



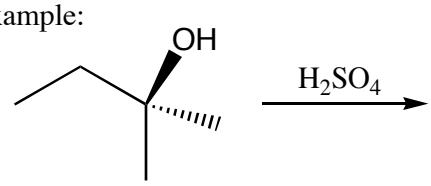
E1

Summary:

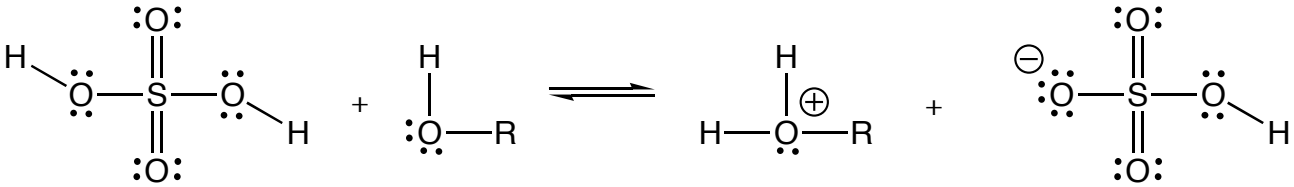
Regiochemistry:

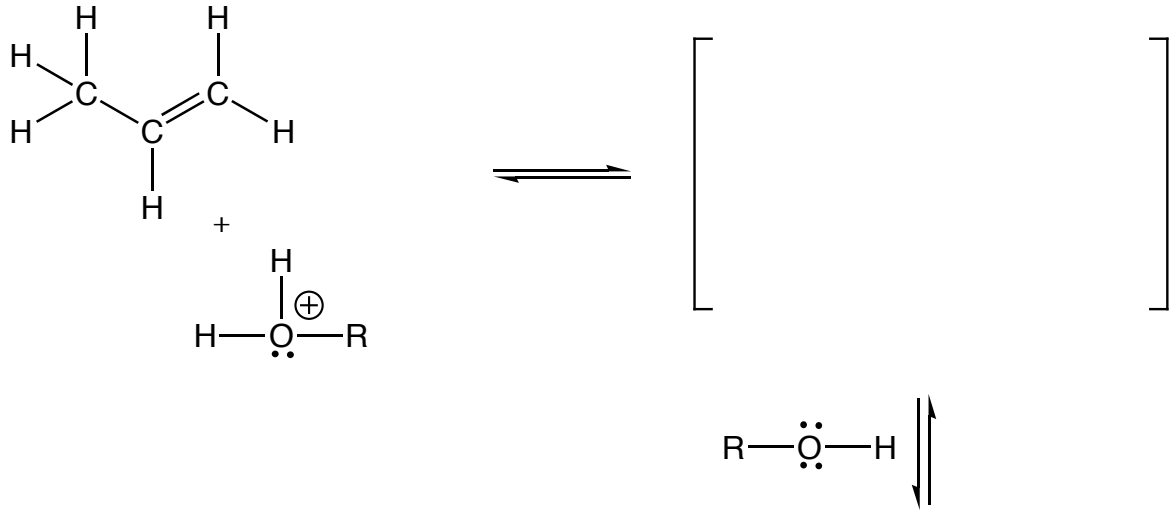
Stereochemistry:

Example:



Acid-catalyzed Reaction of an Alcohol with an Alkene





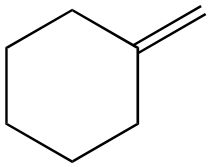
Products

Summary:

Regiochemistry:

Stereochemistry:

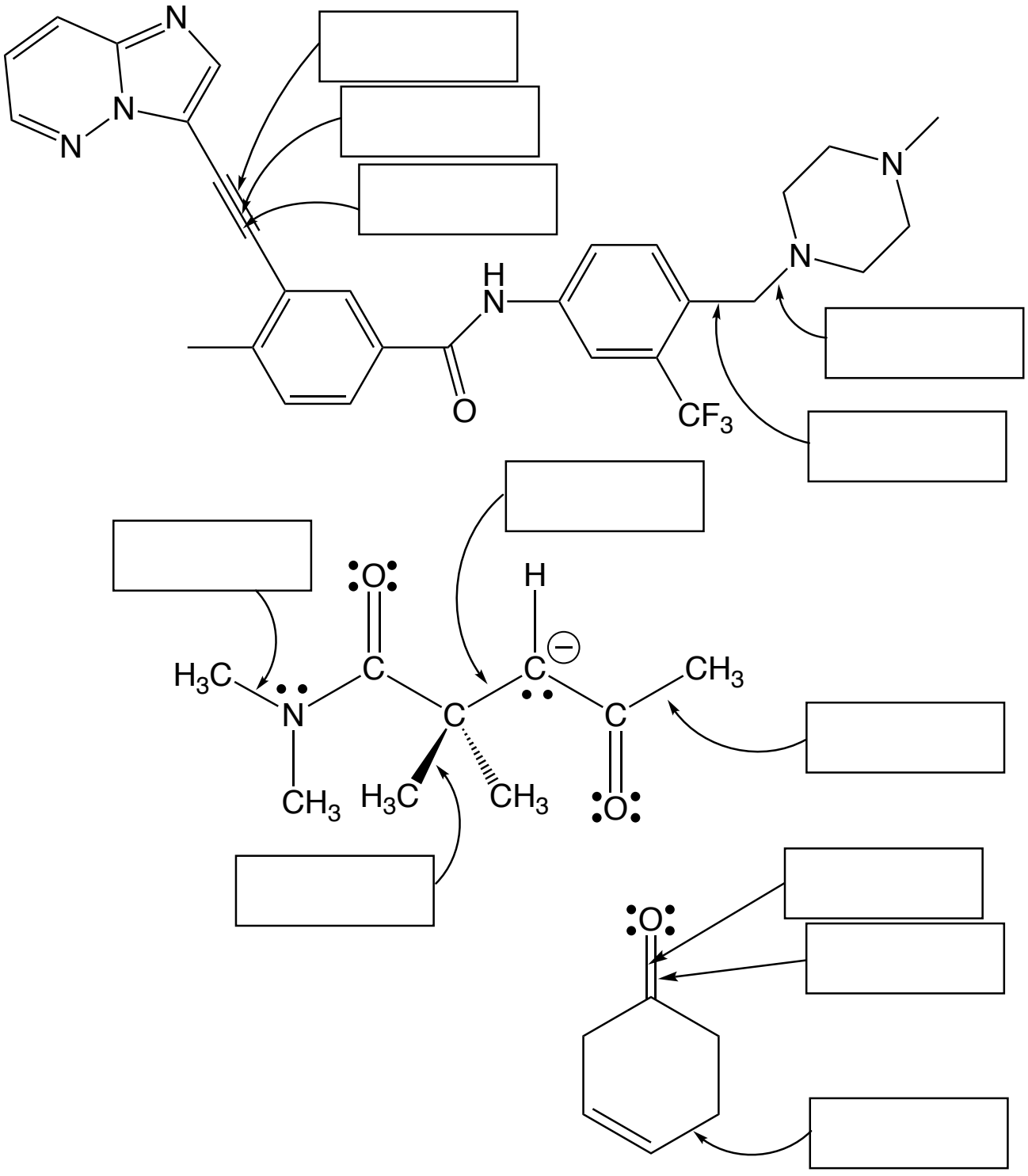
Example:



CH_3CH_2OH

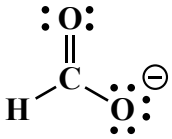
H_2SO_4 (catalytic amount)

17. (2 pts each) Describe each bond indicated with an arrow as the overlap of hybridized orbitals. For example, an answer might be $\sigma_{Csp^3\text{-}Csp^3}$

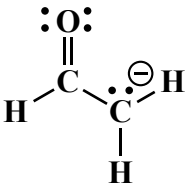


22. (22 points total). Here is an "apply what you know" problem in the form of an MCAT style passage.

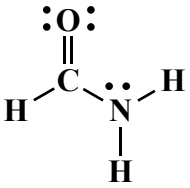
We have seen a number of molecules that contains a three-atom, delocalized pi bond (a "pi-way"). In partcular, we have seen a carboxylate ion, enolate ion, and of course, amides. Each of the three atoms donates a 2p orbital that overlap.



Carboxylate Ion

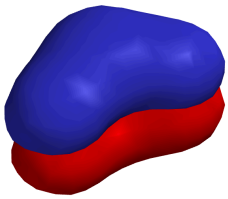


Enolate Ion

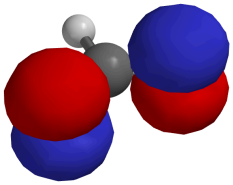


Amide

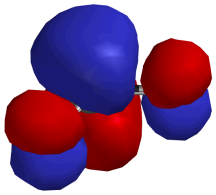
When the three 2p orbitals overlap, there are three pi molecular orbitals formed that extend over all three atoms. You have seen these before, and they are shown below:



Orbital A



Orbital B



Orbital C

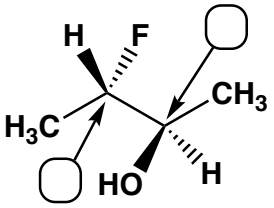
1. (4 pts) From the following choices, fill in the circle for the answer that accurately **lists the three molecular orbitals in order from lowest to highest energy**:

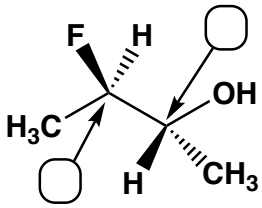
◯ Orbital A Orbital B Orbital C
◯ Orbital B Orbital C Orbital A
◯ Orbital A Orbital C Orbital B
◯ Orbital C Orbital B Orbital A

One of the more difficult parts of the analysis of delocalized pi bonding concerns how many electrons are involved in the pi molecular orbitals. Each of the ions shown above, the carboxylate ion, the enolate ion, and the amide, have the same number of pi electrons in the pi molecular orbitals.

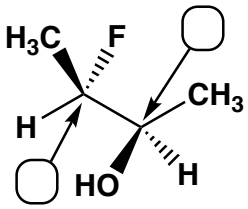
21. (38 pts) For each pair of molecules, on the line provided state the relationship between the two structures. Possible answers could be **enantiomers**, **diastereomers, consitutional isomers**, or **same molecule. Fill in the circle to indicate the correct relationship between the molecules shown. In the boxes provided next to each chiral center, write "R" or "S" to indicate the absolute stereochemistry present.**

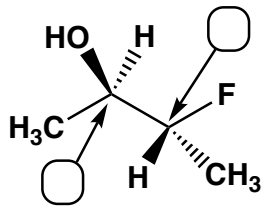
Relationship:



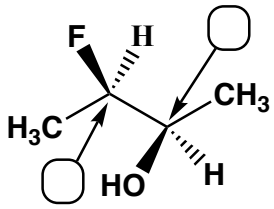


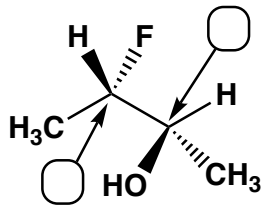
○ **enantiomers**
○ **diastereomers**
○ **constitutional isomers**
○ **same molecule**



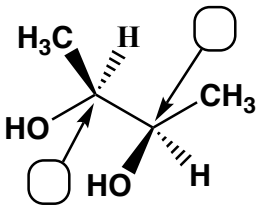


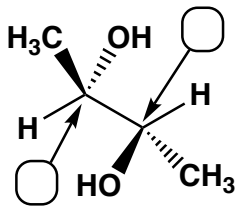
○ **enantiomers**
○ **diastereomers**
○ **constitutional isomers**
○ **same molecule**





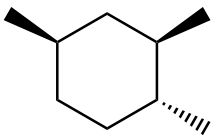
○ **enantiomers**
○ **diastereomers**
○ **constitutional isomers**
○ **same molecule**

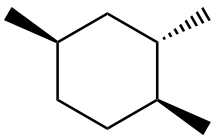




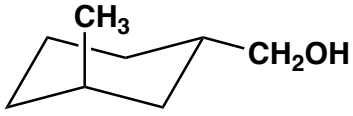
○ **enantiomers**
○ **diastereomers**
○ **constitutional isomers**
○ **same molecule**

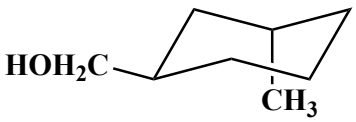
You do not need to label the chiral centers with "R" or "S" on these last two.





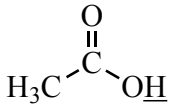
○ **enantiomers**
○ **diastereomers**
○ **constitutional isomers**
○ **same molecule**



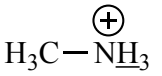


○ **enantiomers**
○ **diastereomers**
○ **constitutional isomers**
○ **same molecule**

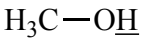
12. (15 pts) Complete the following four structures by adding appropriate numbers of lone pair electrons, H atoms, and formal charges to the atoms in the boxes. You must adjust your answers to indicate the predominant species at each indicated pH value. (You do not have to add anything such as H atoms to atoms not drawn in the boxes.) This problem is testing your understanding of the relationship of protonation state to pH to pKa values for certain functional groups we have discussed. Next, in the space provided, write the overall charge on each structure at the indicated pH. For your reference, here are the relevant pK_a values:



pK_a = 4.76

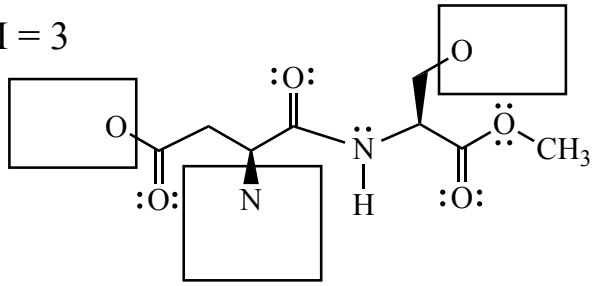


pK_a = 10.64



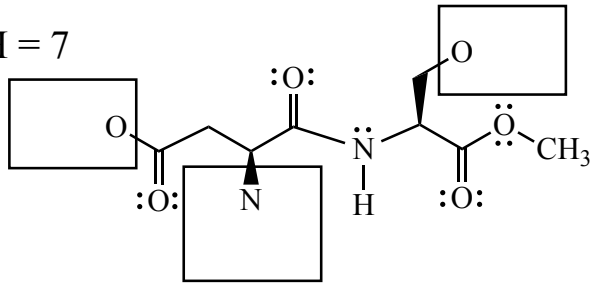
pK_a = 16

pH = 3



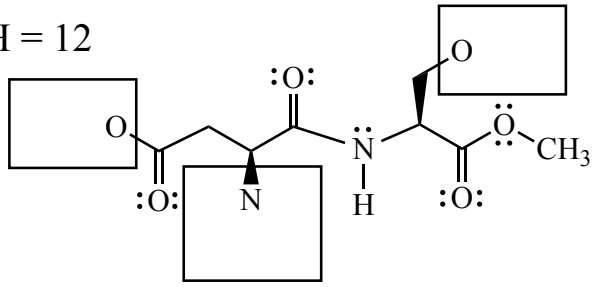
Total charge on molecule:_____

pH = 7



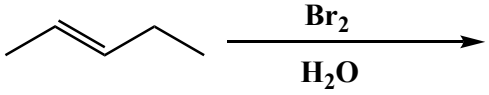
Total charge on molecule:_____

pH = 12

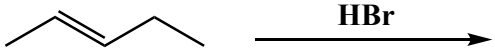


Total charge on molecule:_____

14. (9 or 11 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products if relevant and please remember that you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry as appropriate. When a racemic mixture is formed, you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES.

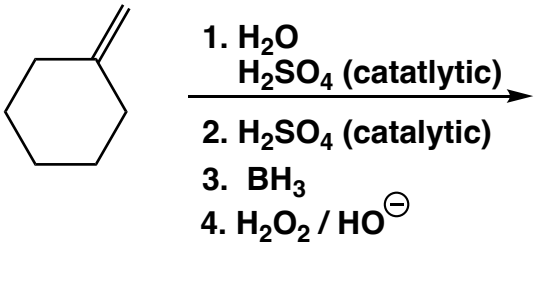
N. 

(2 pts) Will the product mixture you drew to the right rotate the plane of plane polarized light? _____

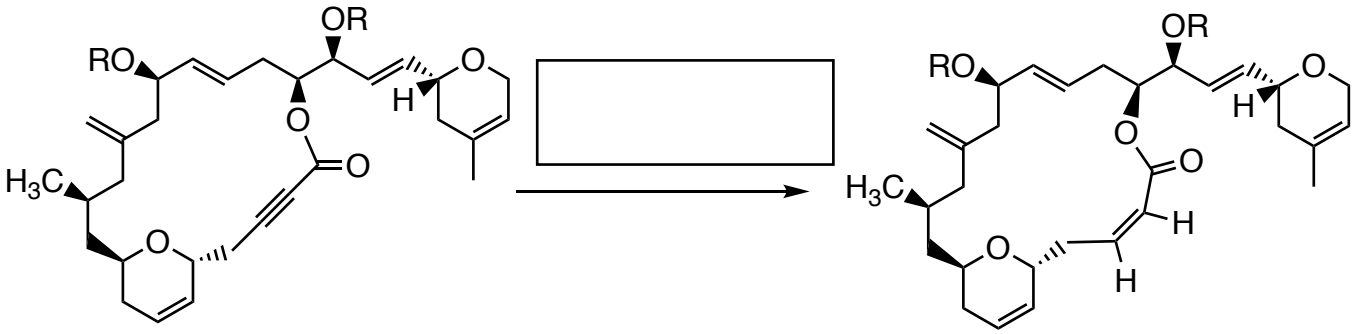
O. 

(2 pts) Will the product mixture you drew to the right rotate the plane of plane polarized light? _____

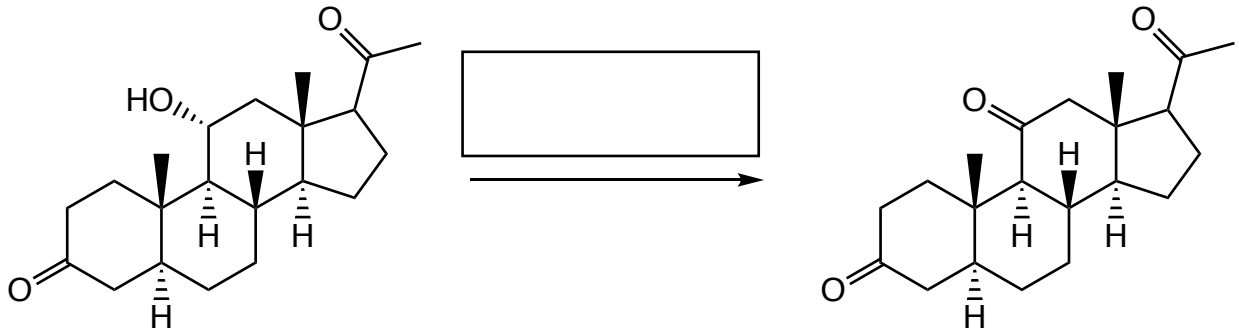
22. (8 pts) For the following sequence of reactions, **draw the final product(s)**. You only need to draw **the very last product(s) in the box provided**, although feel free to draw any other structures in the empty space provided. We will only grade the structure(s) in the box. As always, if a racemic mixture is created you need to draw both enantiomers using wedges and dashes and write "racemic".



19. (8 pts) The chemistry you have learned this semester is used in the synthesis of important pharmaceuticals. Here are two examples. Fill in the boxes with the reagent(s) required to carry out the transformation indicated.



Swamy, *et al.*, Tetrahedron Letters, 2018, 59, 419-429



Have a great holiday break!!

…And remember to run every chance you get!

18. 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.** OK, this is a long one. Work hard to Recognize that product and work backwards. You can do this!

E) (22 pts)