Circle one: I wish to have my exam put in the rack. I wish to pick up my exam.

Printed Name Answer Key .
(Please print clearly)

Signature _____.

CHEMISTRY 262

Exam IV
100 Points

April 24, 2013
6:30 – 8:30 PM

This exam has 7 problems on pages 2 through 8.

RULES

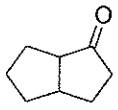
1. The use of a calculator and model kits are **not** permitted.
2. This exam is closed book and closed note. No aids other than writing implements are permitted.
3. Answer the questions in the spaces provided on this exam.
4. If you wish to ask a question about procedures or about a problem on the exam, raise your hand.

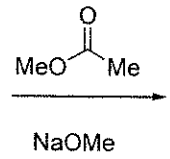
1. _____
2. _____
3. _____
4. _____
5. _____
6. _____
7. _____

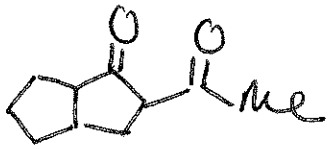
TOTAL: /100

1. Predict the major product or products that you would expect to be formed in **seven** of the following ten reactions (continued on the next page). If you feel that no reaction will occur, then answer no reaction. You may assume that each of the reactions is followed by a workup so that a neutral product is obtained. Be sure to answer **only** seven problems. If you answer more than seven, then *only your first seven will be graded.* (**21 points/ 3 pts. each**)

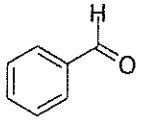
(a)

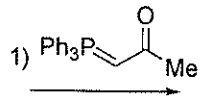


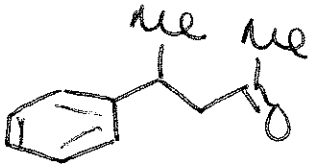




(b)







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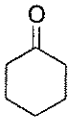

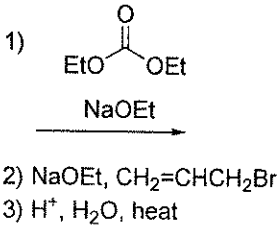

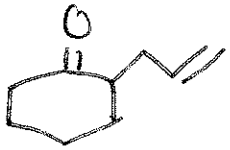

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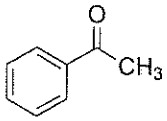

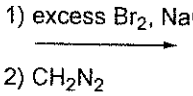

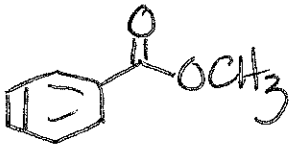

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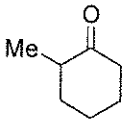

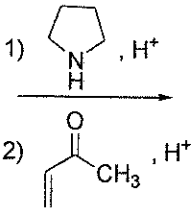

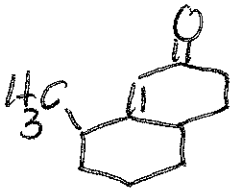

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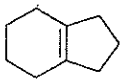

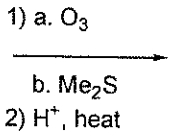

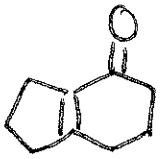

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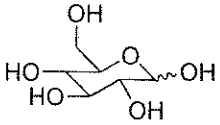

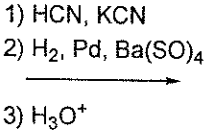

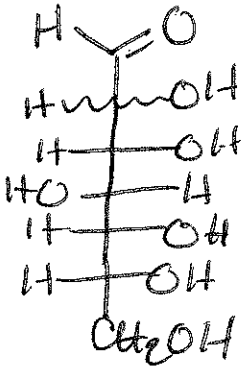

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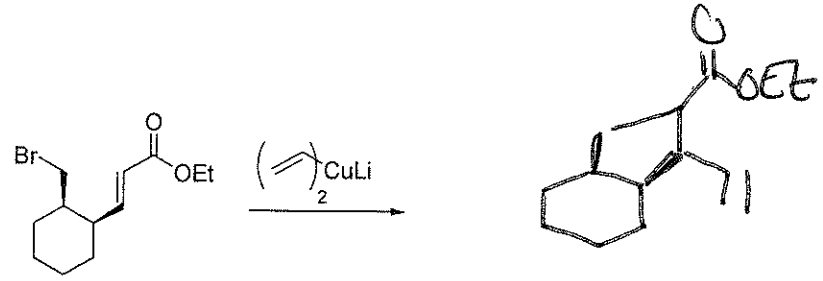
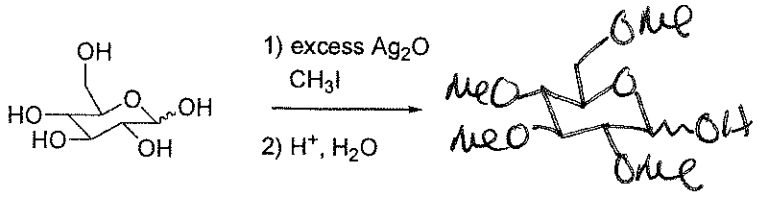


(i)



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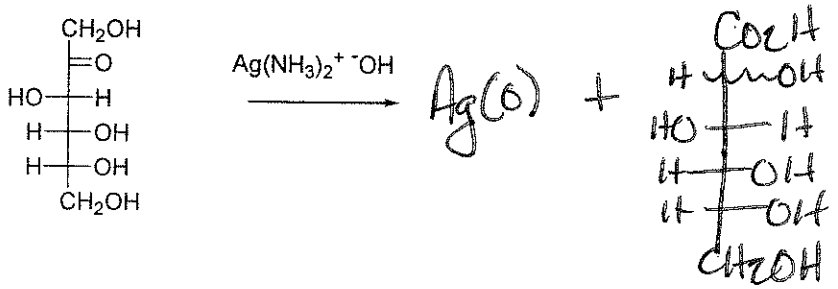
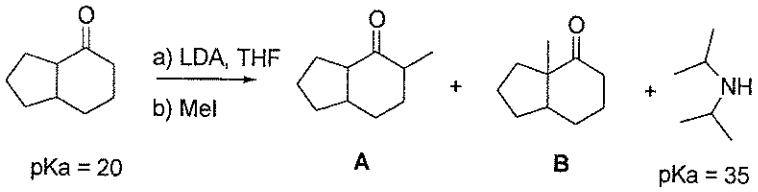
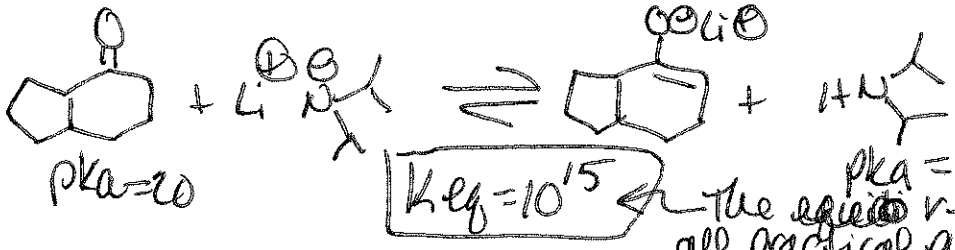


2. **a.** Use the starting material below to explain why lithium diisopropylamide (LDA) is a kinetic base. (**5 points**)





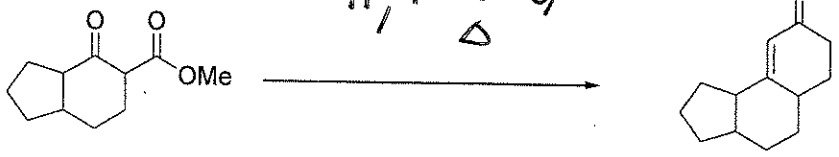
The equilibrium reaction is for all practical purposes not reversible

b. A student attempting to make product A with the reaction above instead obtained product B. When examining his experimental procedure, it was found that he made the intermediate enolate by adding the LDA base slowly to the starting ketone. What went wrong with his reaction? In other words, why did he get product B? (**5 points**)

The slow addition of base to the ketone leads to a small amount of enolate and a lot of remaining starting material. The starting material is a proton source that equilibrates the enolate.

3. Fill in the reagents needed for accomplishing **three** of the five following transformations. More than one step may be required. Be sure to answer **only** three problems (**9 points/ 3 pts. each**)

a)



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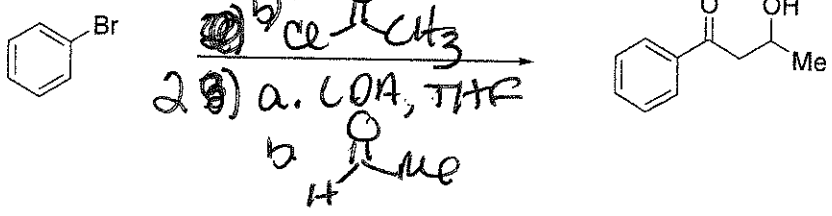

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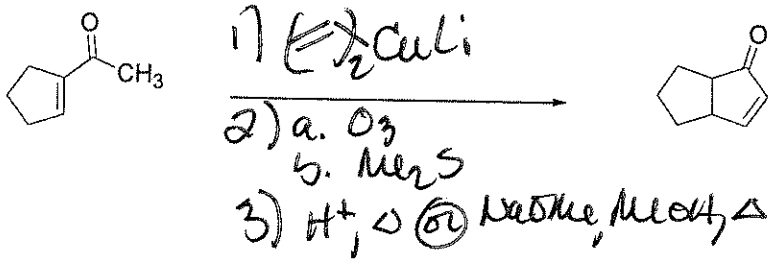
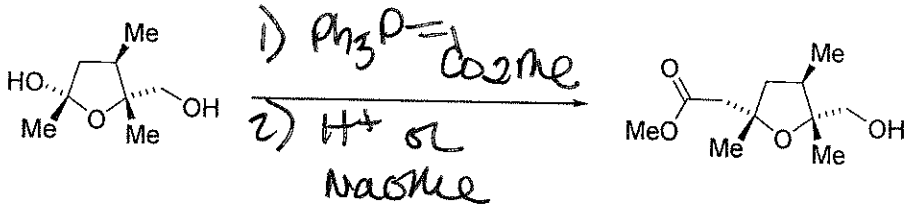
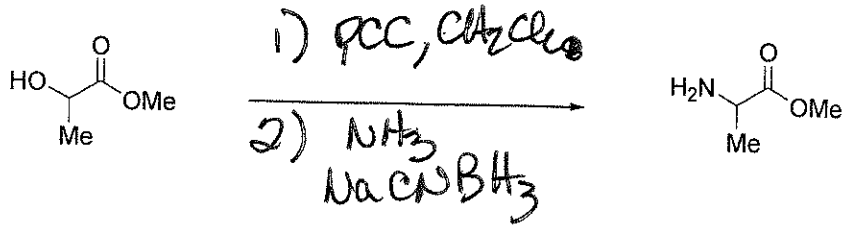


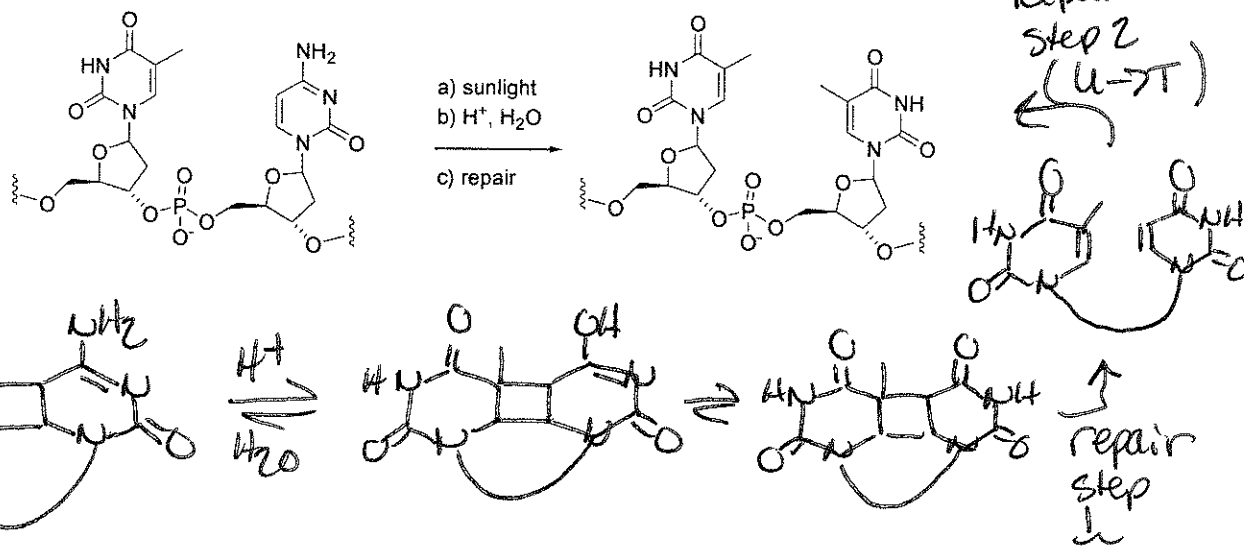
d)



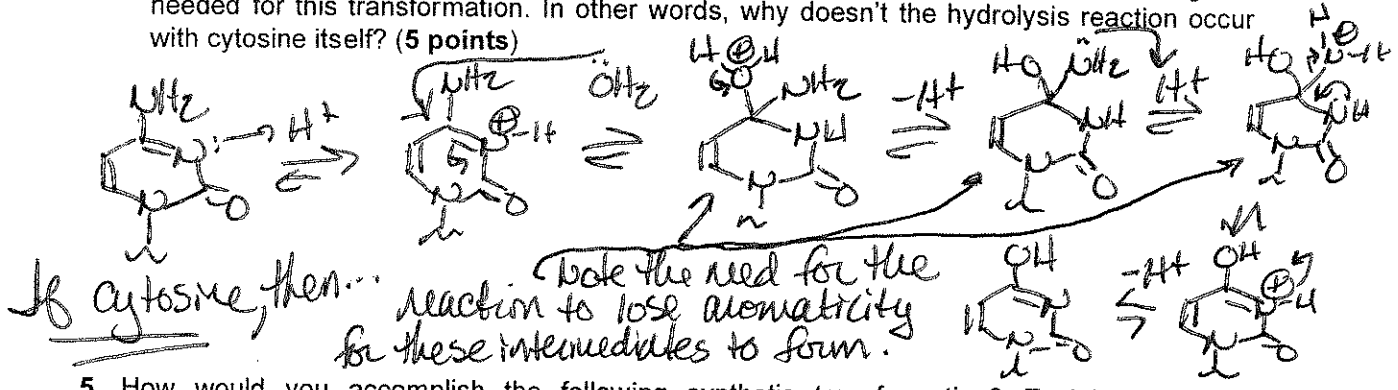
e)



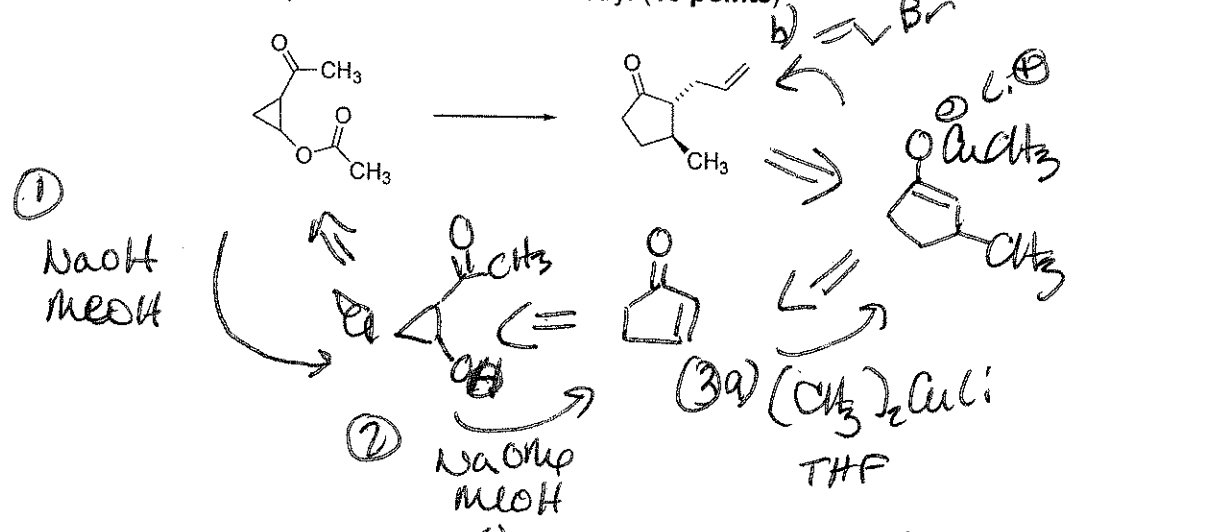
4. **a.** Show the key intermediates (you can leave the sugars and phosphodiester bond out of your drawings) involved in the following transformation. (**5 points**)



b. Use a "curved-arrow" mechanism for the hydrolysis reaction to explain why sunlight is needed for this transformation. In other words, why doesn't the hydrolysis reaction occur with cytosine itself? (**5 points**)

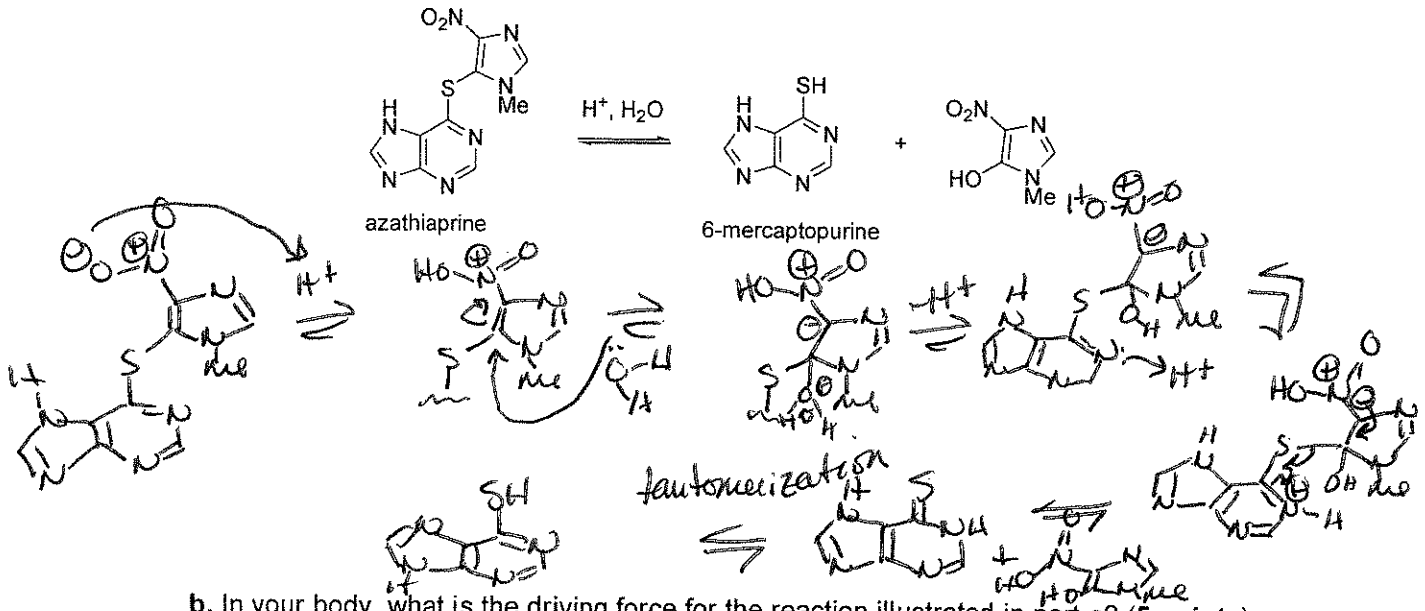


5. How would you accomplish the following synthetic transformation? Explain why your synthesis would lead to the required trans stereochemistry. (**10 points**)



6. Mechanisms:

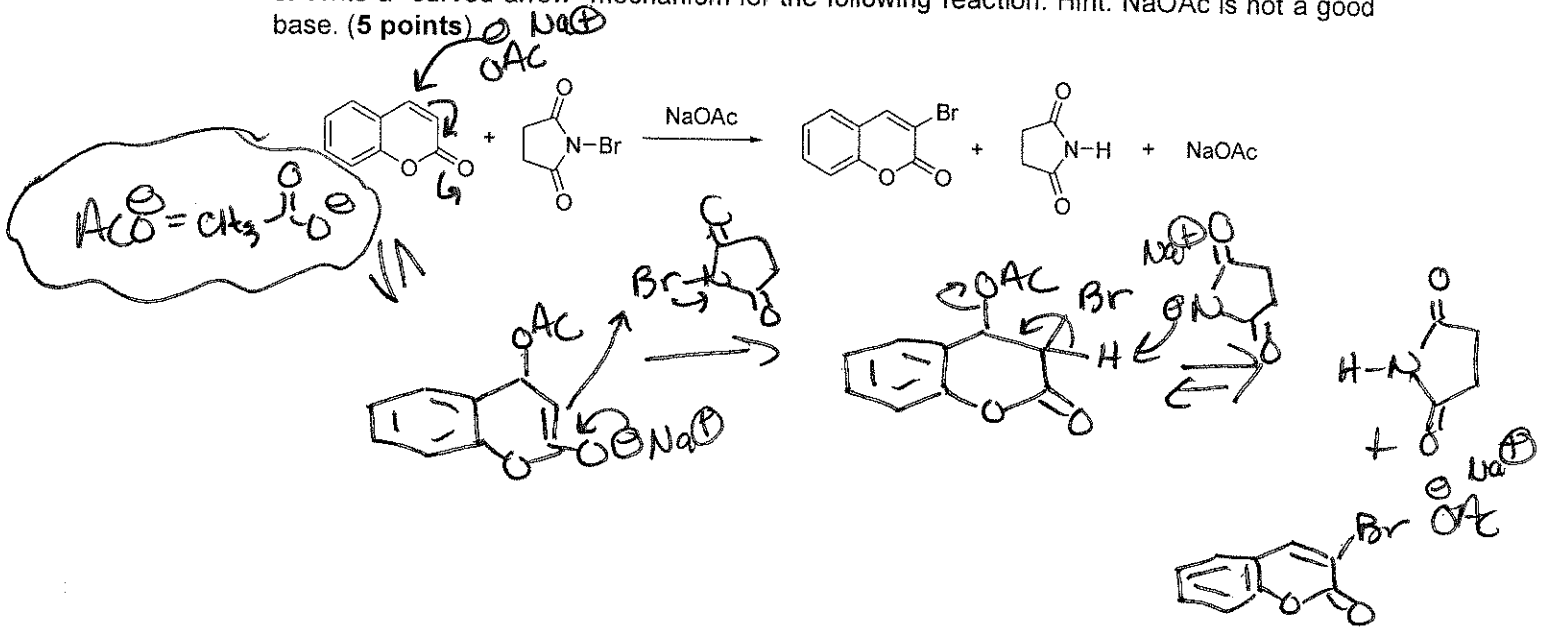
a. Write a "curved-arrow" mechanism for the following transformation. (**5 points**)



b. In your body, what is the driving force for the reaction illustrated in part a? (**5 points**)

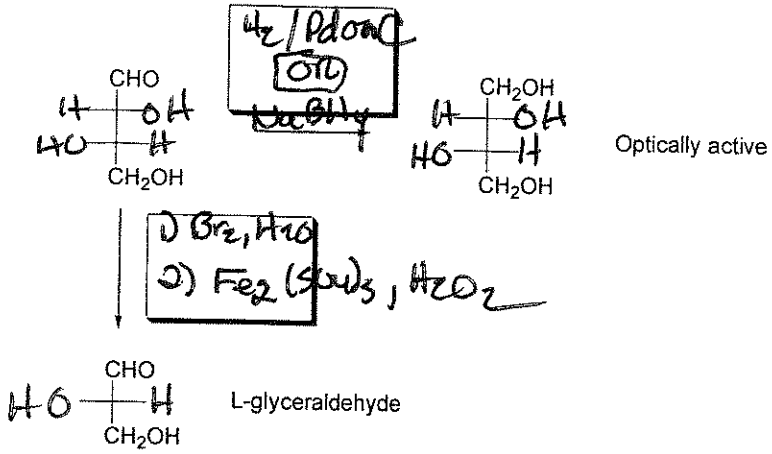
The solvent is water. The high concentration of water pushes the equilibrium to the product

c. Write a "curved-arrow" mechanism for the following reaction. Hint: NaOAc is not a good base. (**5 points**)

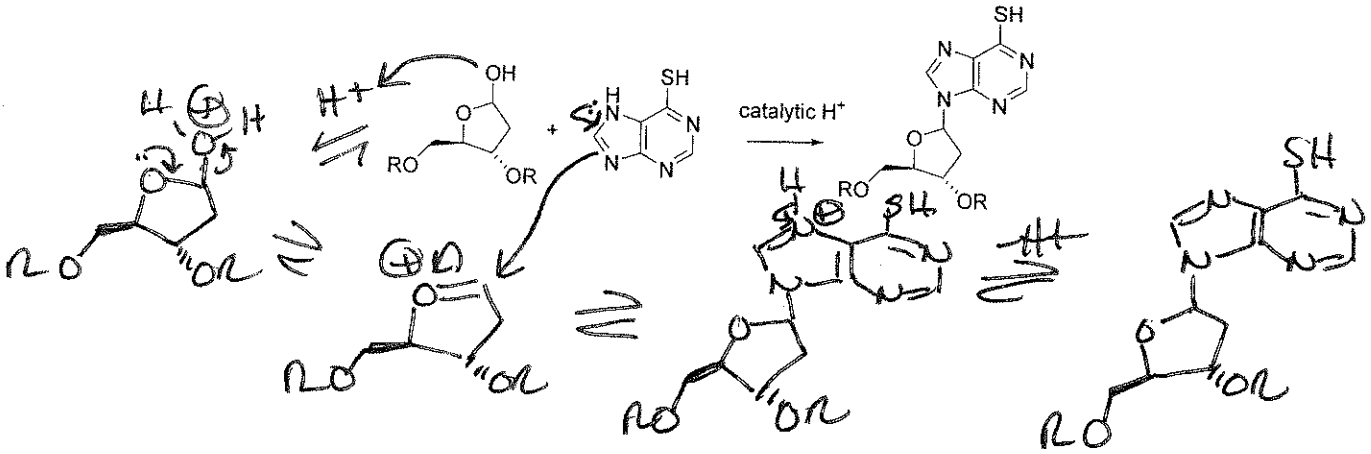


7. "Fun" with sugars:

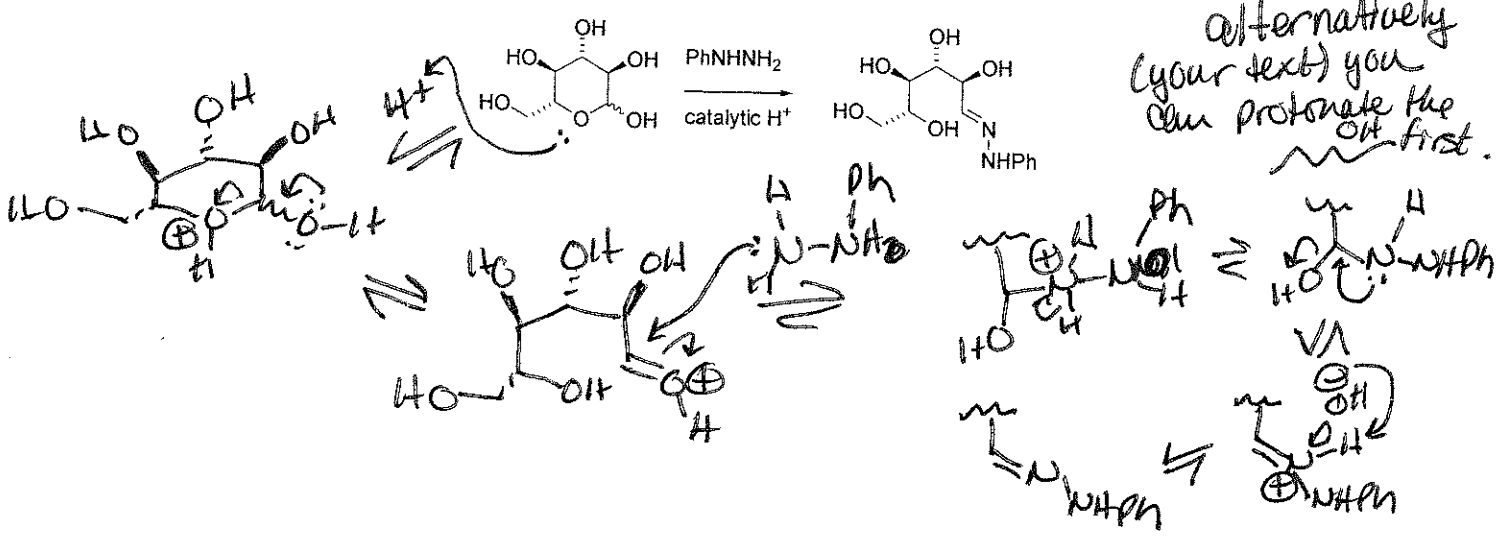
a. For the scheme below, fill in the missing "OH's" and reagents. (**5 points**)



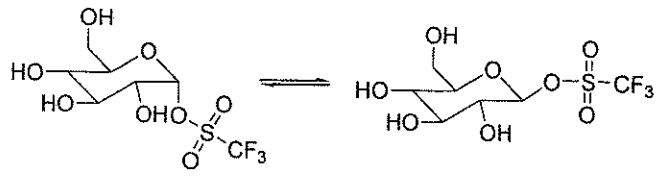
b. In your body, 6-mercaptopurine is incorporated into a nucleoside which then interferes with DNA synthesis. Write a "curved-arrow" mechanism for formation of the nucleoside. (**5 points**)

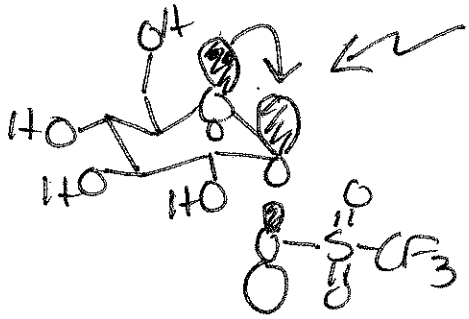


c. Sugars can be precipitated nicely as hydrazone derivatives. Write a "curved-arrow" mechanism that illustrates how this happens? (**5 points**)



d. In the following sugar derivative, the trifluorosulfonate group prefers to be in the axial position because of the "anomeric effect". Draw a molecular orbital picture that illustrates the anomeric effect. (**5 points**)





Donation of the lone-pair electrons to the σ^*-orbital of the axial C-O bond. This cannot happen with the equatorial C-O bond.

e. The trifluorosulfonate group is a strong electron-withdrawing group. Does this favor or disfavor the axial stereochemistry at the anomeric carbon? Why? (**5 points**)

It favors the axial C-O bond. The stronger the electron-withdrawing group, the more the σ^*-orbital can accept e⁻-density. The presence of the electron-withdrawing group lowers the energy of σ^* making it better able to overlap with the non-bonding lone pair electrons.