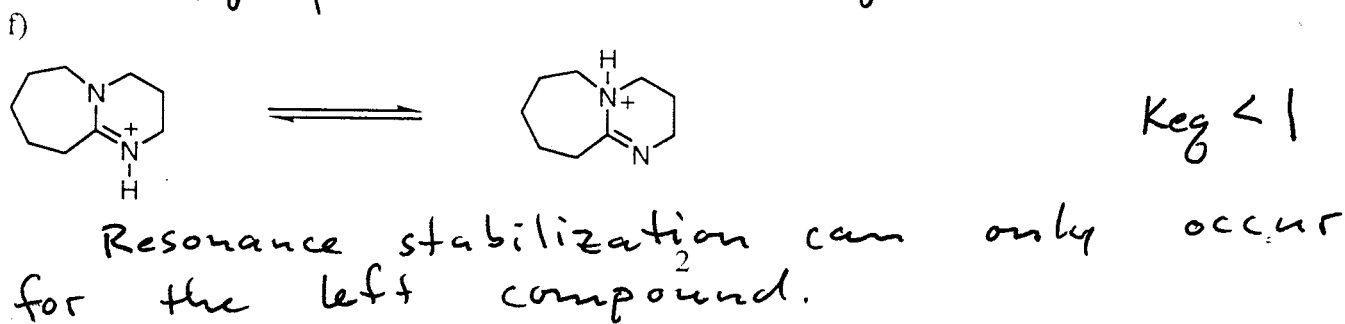
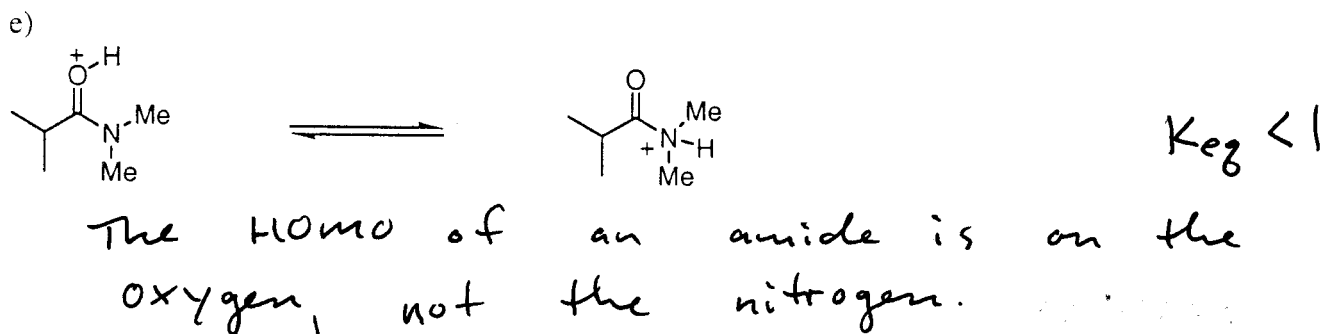
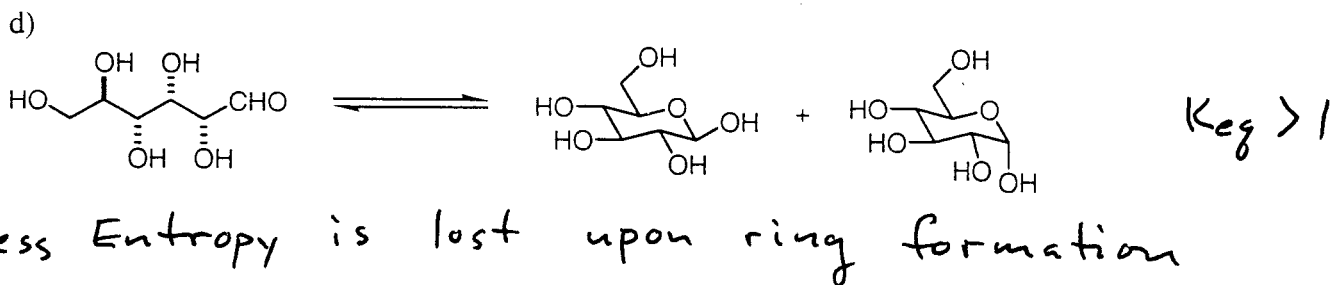
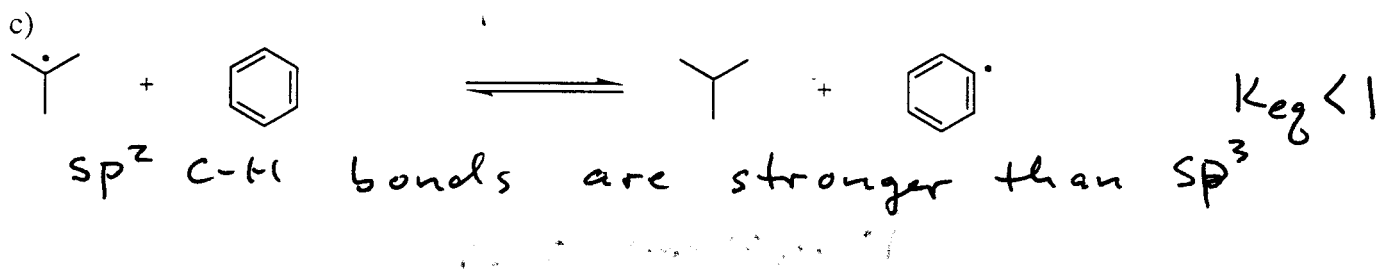
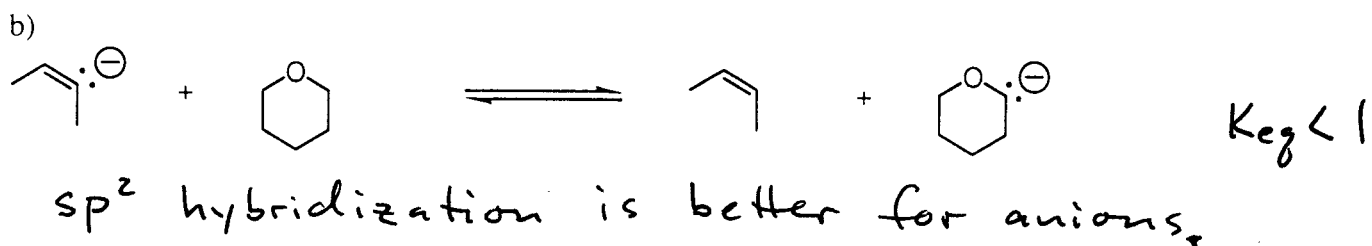
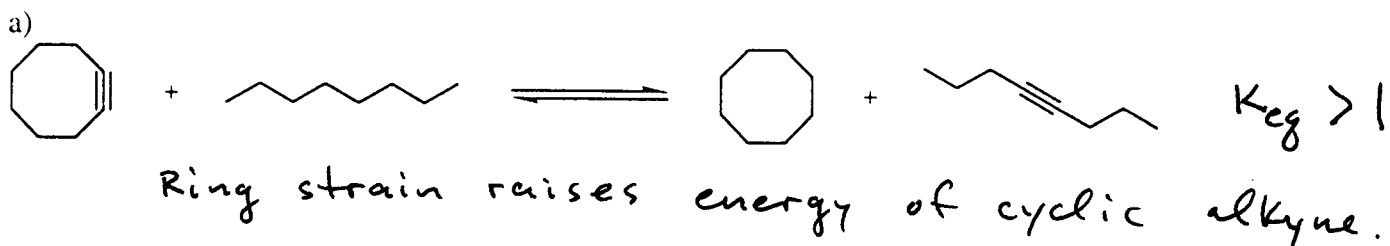
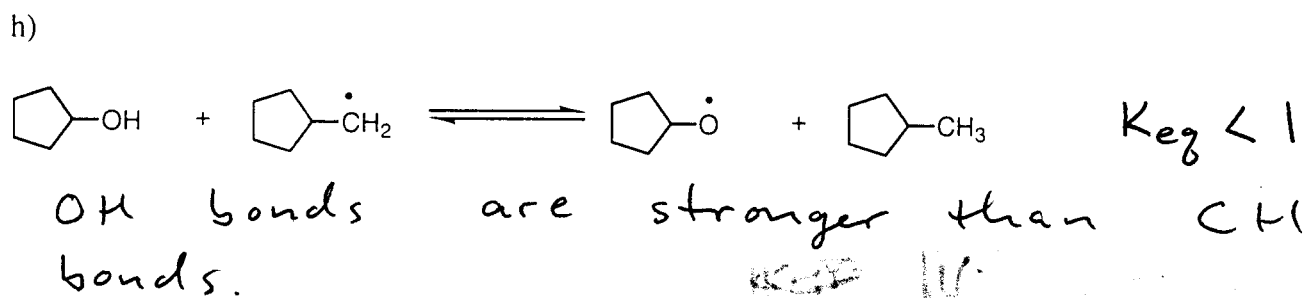
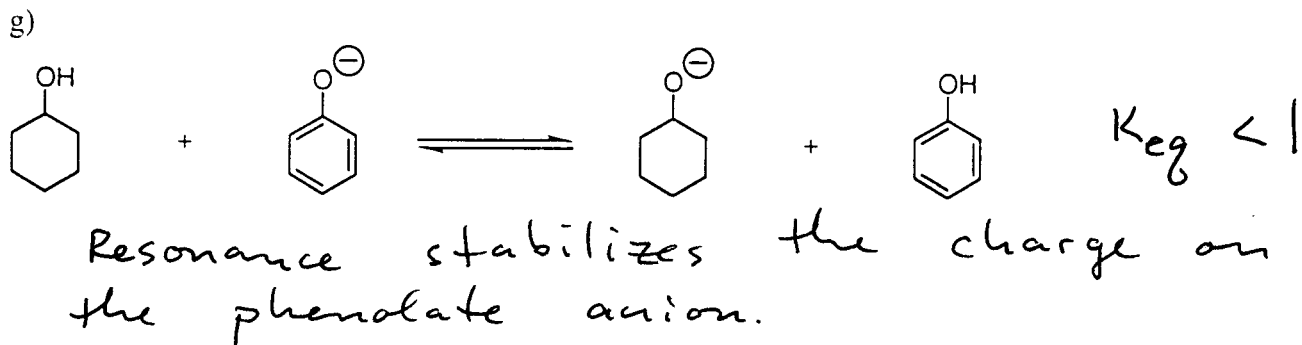
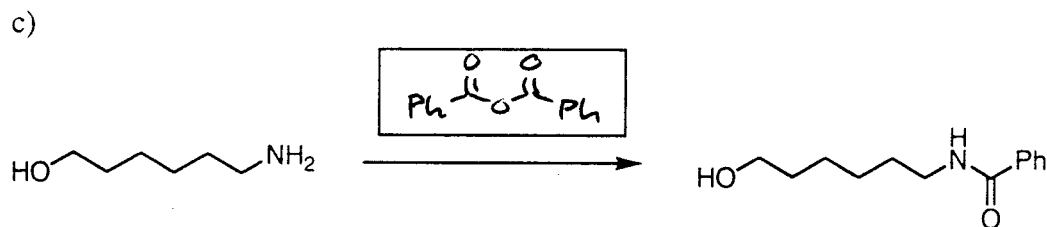
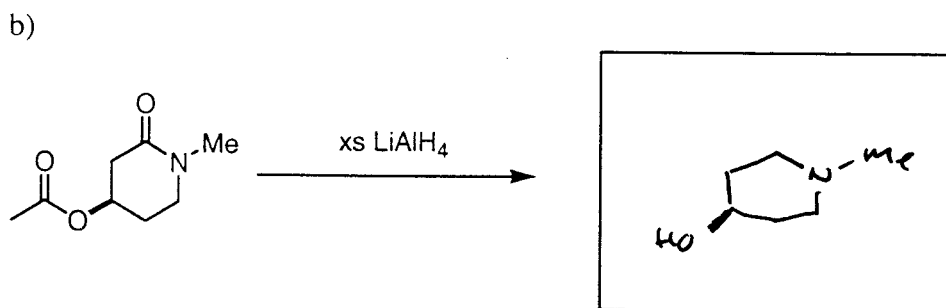
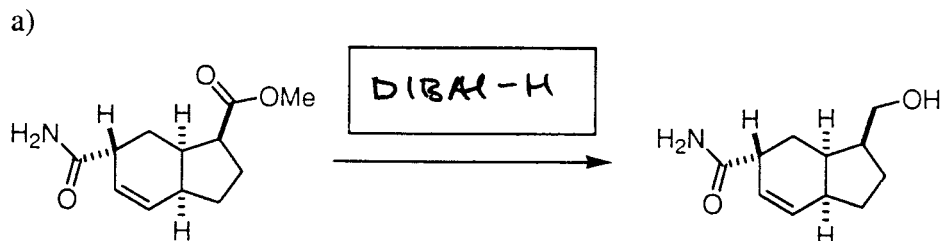


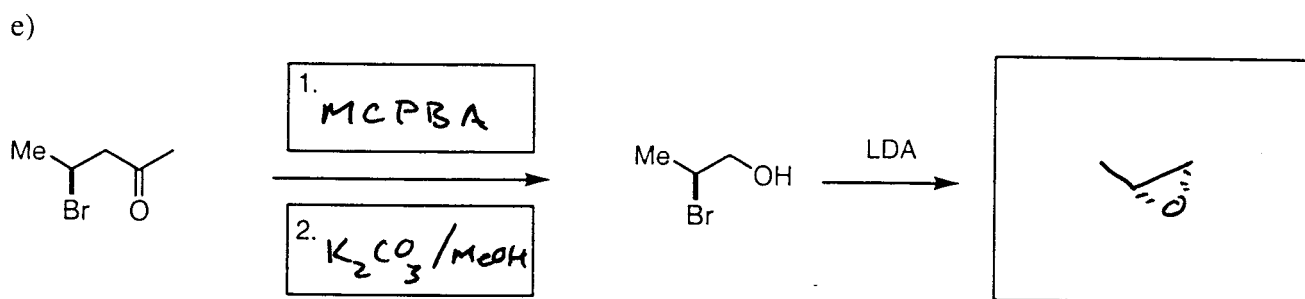
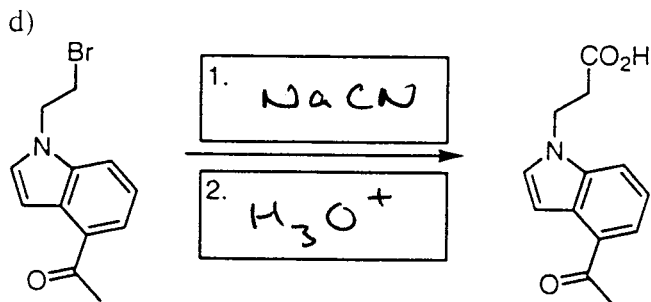
1. For each of the following hypothetical equilibria, predict whether the value of K_{eq} is > 1 , $= 1$, or < 1 . Provide an explanation for your answer in 10 words or less (16 points).



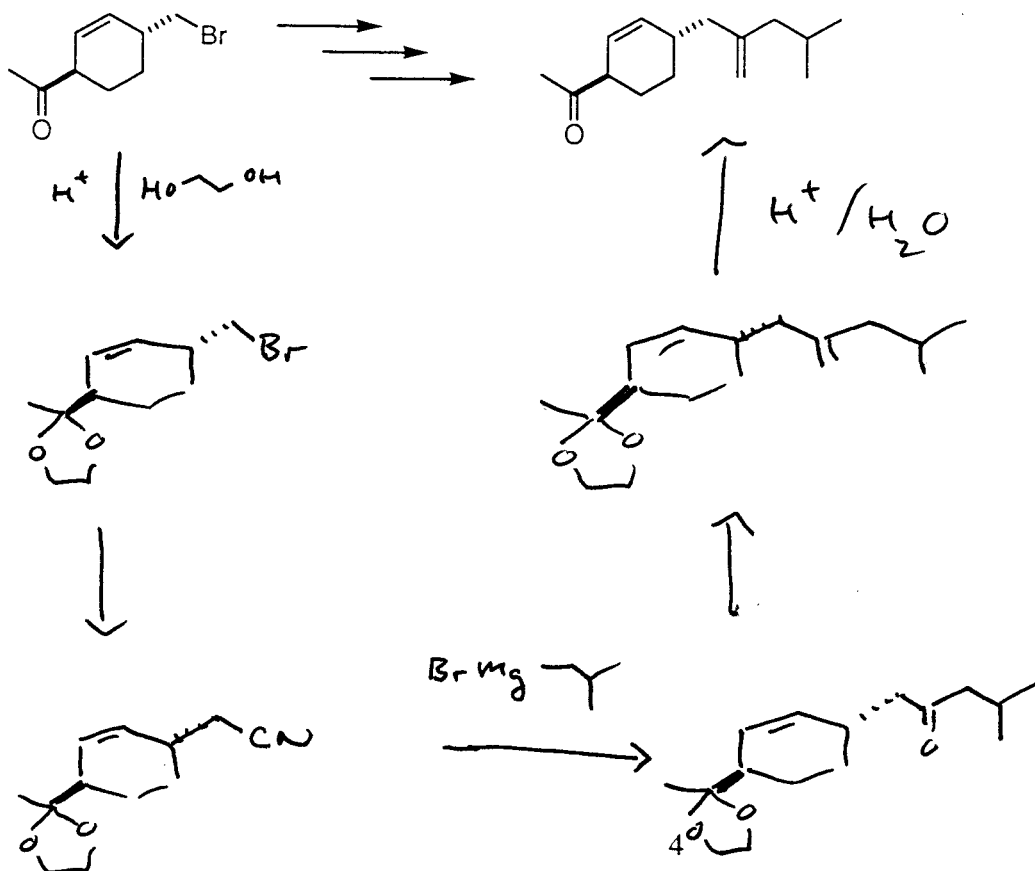


2. A major focus of this course is the ability to perform selective transformations on complex substrates. Provide reagents or products as indicated for the following transformations. Remember: separate boxes are not provided for workup steps (12 points).

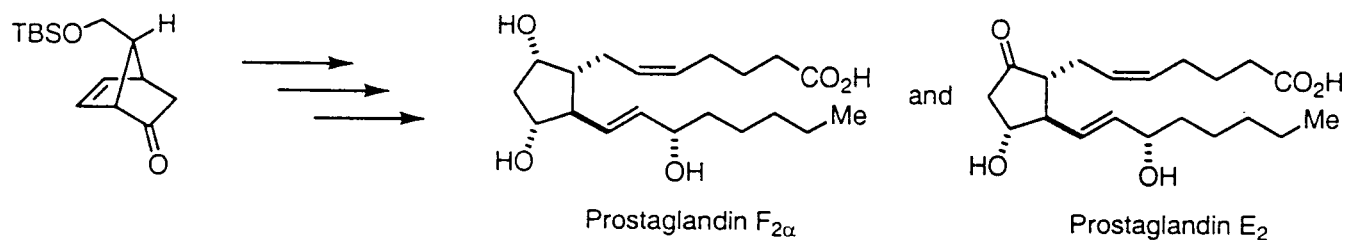




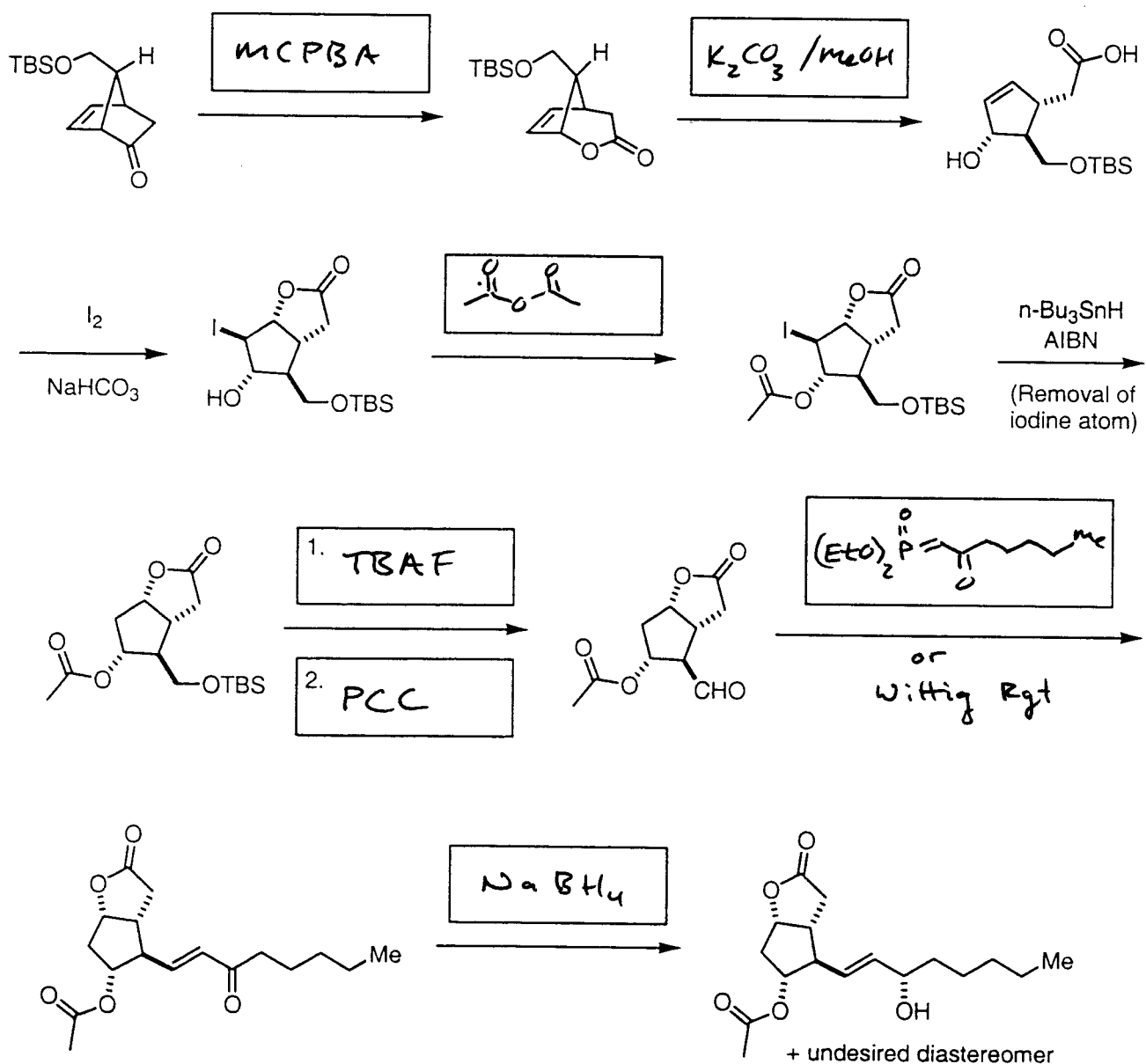
3. Provide a sequence of synthetic steps for the following transformation. You may use any reagents that you wish, but the building blocks that are incorporated into the structure must be made up of 4 carbons or less (10 points).



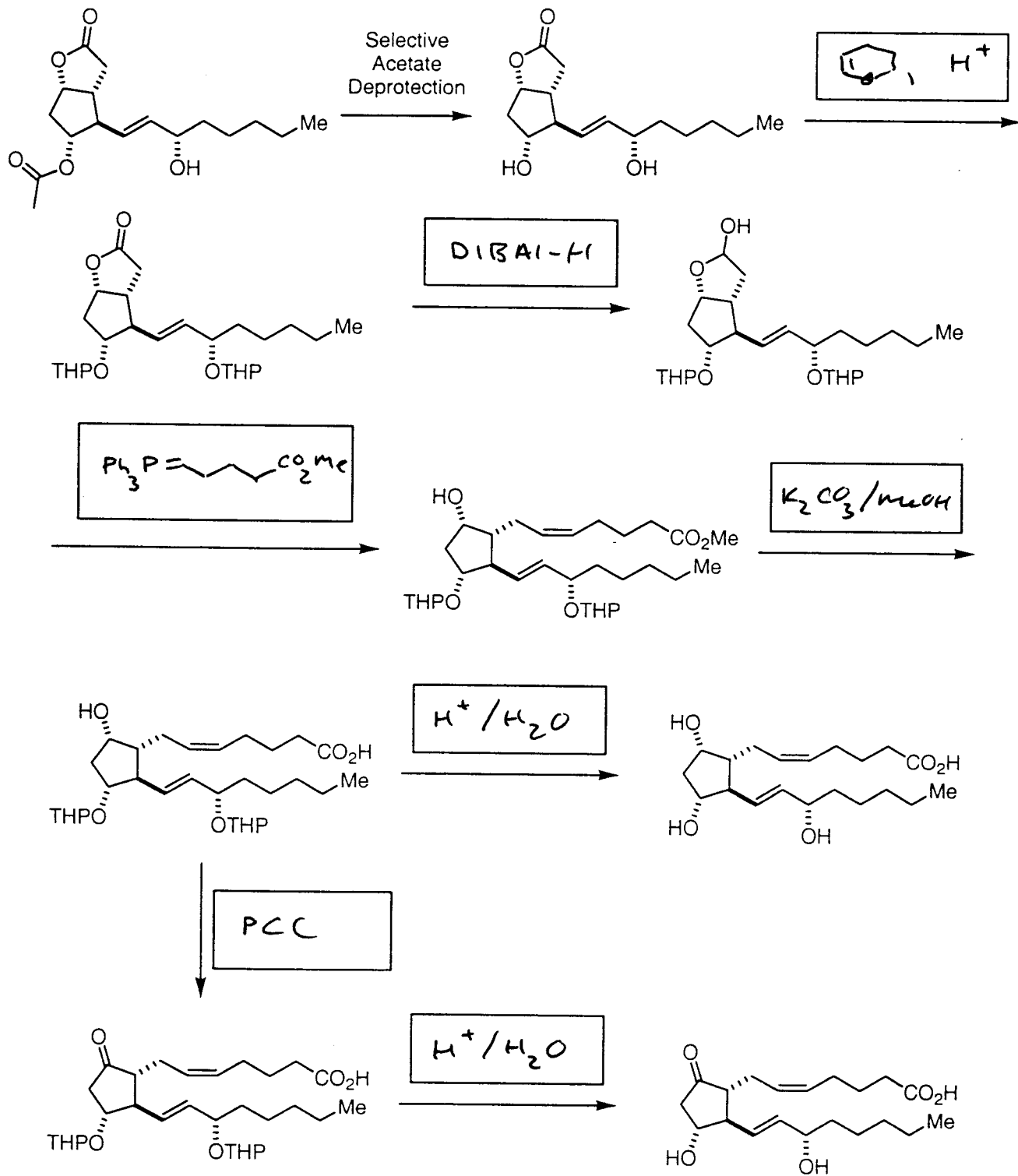
4. Prostaglandins are a class of highly active biomolecules, and thus are of potential interest as drug candidates. In 1969, Prof. E. J. Corey published a general strategy for the preparation of several of these compounds. This route has been adapted by several pharmaceutical companies, and has been carried out on multi-kilogram scale:



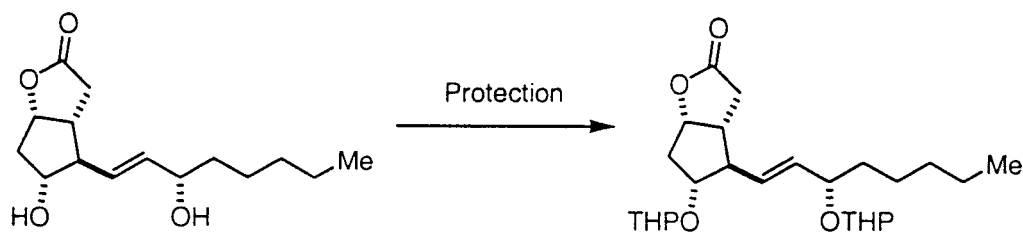
Surprisingly, nearly all of the reactions he used in the synthesis are in the Chem 112B synthetic toolkit. In the boxes provided, fill in the reagents that you would recommend for each of the following transformations (28 points):



4. (Continued)

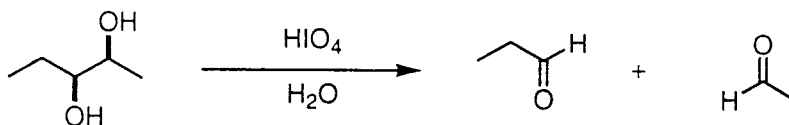


5. Assuming enantiomerically pure starting material, what is the maximum number of product spots that you might expect to see by TLC for the following protection reaction? Justify your answer IN 15 WORDS OR LESS (4 points).

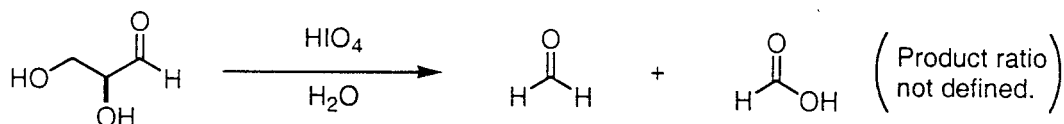


4. Each THP group adds a chiral center.
 $2^2 = 4$ diastereomers.

6. As discussed in class, 1,2-diols can be cleaved to afford two new carbonyl compounds using either HIO_4 or NaIO_4 in aqueous solution:

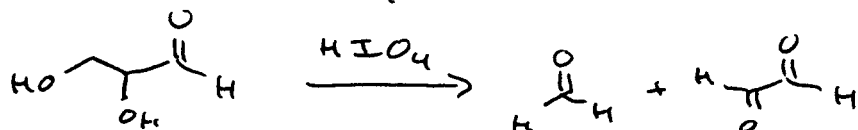


However, when glyceraldehyde is subjected to the same reaction conditions, a mixture of formaldehyde and formic acid is obtained:

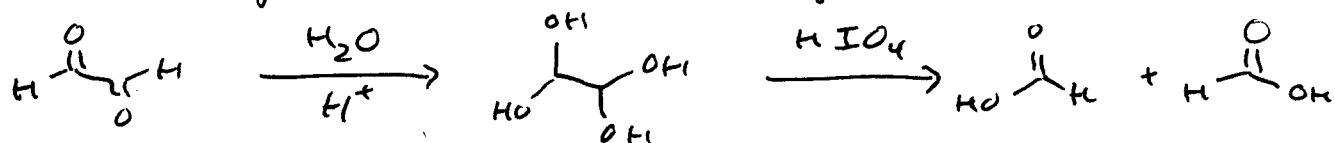


Provide a clear explanation for the formation of these two products and indicate the ratio in which you would expect to obtain them. Note: you do not need to supply a full mechanism--only the specific steps of it that are needed to justify your answer (8 points).

The first step cleaves the diol:

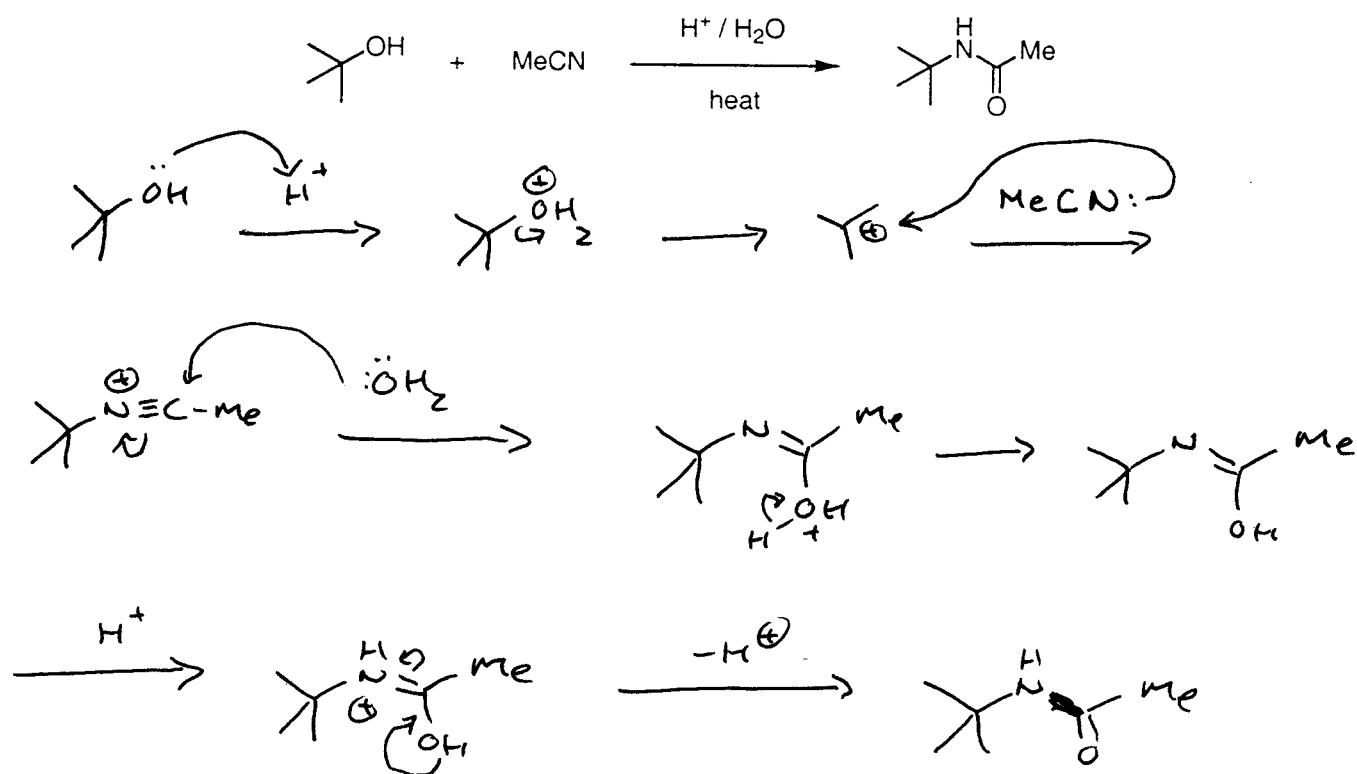


The dialdehyde then forms a hydrate, which undergoes diol cleavage:



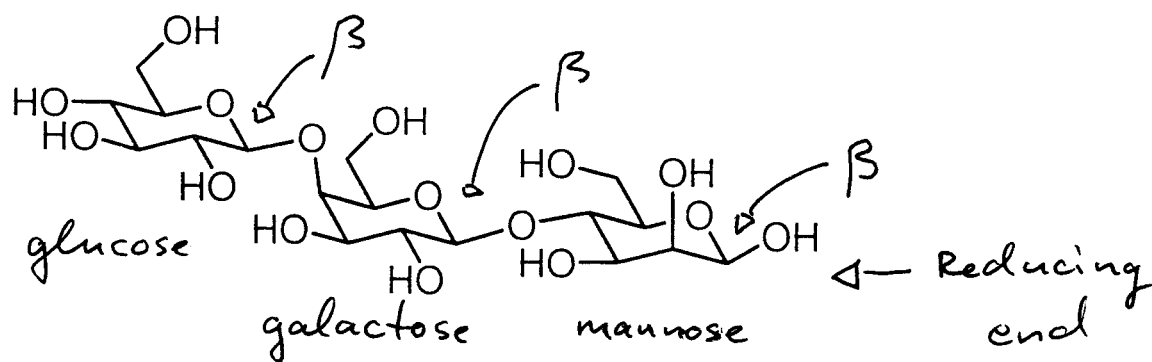
Thus, 1 eqv of CH_2O and 2 eqv of HCO_2H are formed.

7. Provide a mechanism for the following transformation (8 points):



8. A new carbohydrate, ahamindrose, has recently been isolated from a marine organism:

ahamindrose:

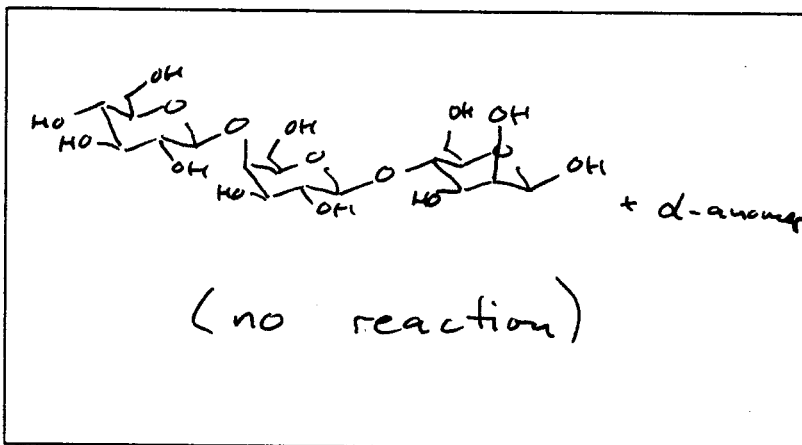
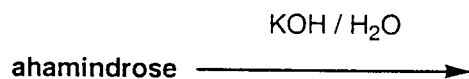


a) On the molecule above, circle and identify the basic building blocks. Also identify each linkage as α or β , and indicate the reducing end (5 points).

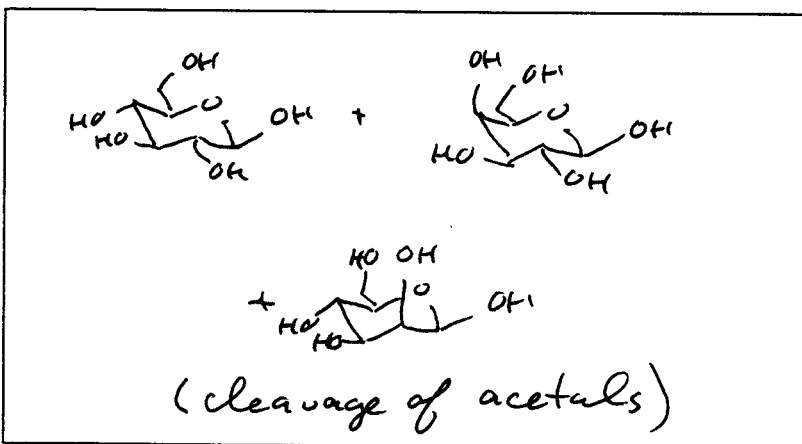
8. (Continued)

Predict the reaction products when ahamindrose is exposed to the following conditions (9 points):

b)



c)



d)

