Final Examination for **Chem 313**

7:00 p.m. December 10, 2015; **Time: 2.5 hours**

This examination consists of **11** pages, including this cover page and three pages of scrap paper. It is out of 100 points. You may remove the pages of scrap paper.

Last Name Answer Key First Name _____

Signature _____ Student Number _____

Student Conduct during Examinations

Each examination candidate must be prepared to produce, upon the request of the invigilator or examiner, his or her UBCcard for identification.

Examination candidates are not permitted to ask questions of the examiners or invigilators, except in cases of supposed errors or ambiguities in examination questions, illegible or missing material, or the like.

No examination candidate shall be permitted to enter the examination room after the expiration of one-half hour from the scheduled starting time, or to leave during the first half hour of the examination. Should the examination run forty-five (45) minutes or less, no examination candidate shall be permitted to enter the examination room once the examination has begun.

Examination candidates must conduct themselves honestly and in accordance with established rules for a given examination, which will be articulated by the examiner or invigilator prior to the examination commencing. Should dishonest behaviour be observed by the examiner(s) or invigilator(s), pleas of accident or forgetfulness shall not be received.

Examination candidates suspected of any of the following, or any other similar practices, may be immediately dismissed from the examination by the examiner/invigilator, and may be subject to disciplinary action: i. speaking or communicating with other examination candidates, unless otherwise authorized; ii.purposely exposing written papers to the view of other examination candidates or imaging devices; iii. purposely viewing the written papers of other examination candidates; iv. using or having visible at the place of writing any books, papers or other memory aid devices other than those authorized by the examiner(s); and, v. using or operating electronic devices including but not limited to telephones, calculators, computers, or similar devices other than those authorized by the examiner(s)—(electronic devices other than those authorized by the examiner(s) must be completely powered down if present at the place of writing). Examination candidates must not destroy or damage any examination material, must hand in all examination papers, and must not take any examination material from the examination room without permission of the examiner or invigilator.

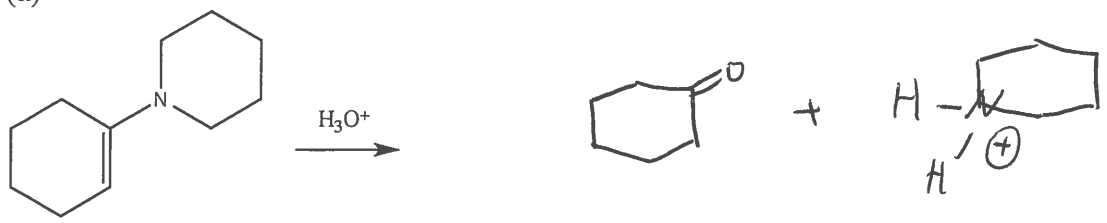
Notwithstanding the above, for any mode of examination that does not fall into the traditional, paper-based method, examination candidates shall adhere to any special rules for conduct as established and articulated by the examiner.

Examination candidates must follow any additional examination rules or directions communicated by the examiner(s) or invigilator(s).

1. [34]	_____
2. [5]	_____
3. [5]	_____
4. [8]	_____
5. [6]	_____
6. [8]	_____
7. [7]	_____
8. [6]	_____
9. [8]	_____
10. [7]	_____
11. [6]	_____
Total [100]	_____

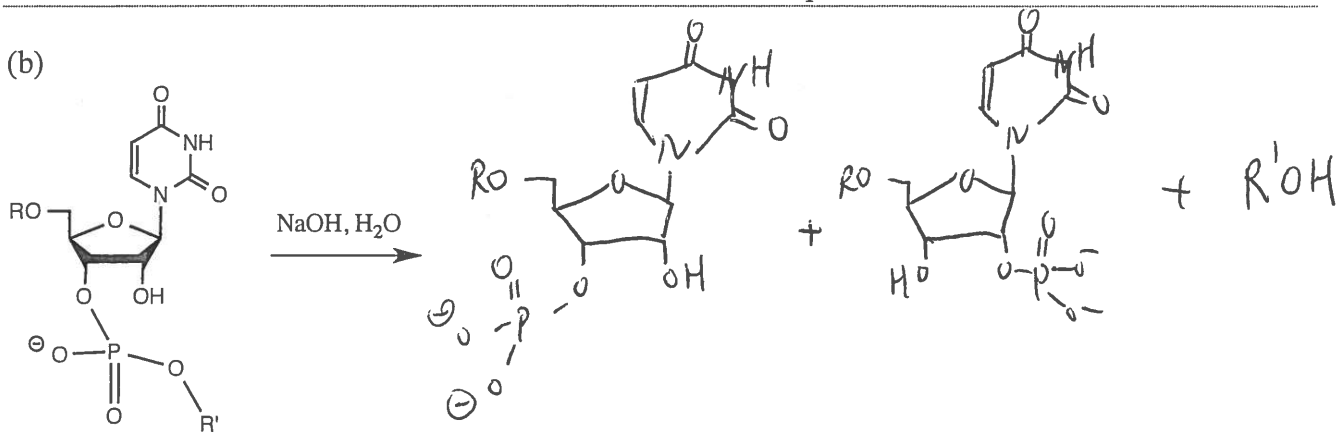
1. [34 points] Predict the major products of the reactions below. Show stereochemistry where appropriate. Equations might not be balanced.

(a)



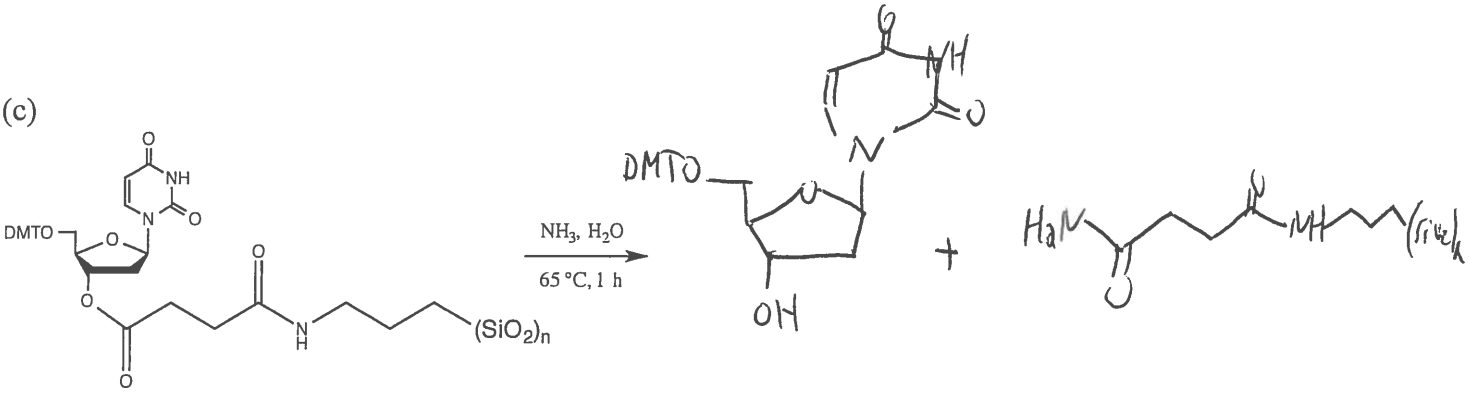
Draw two products

(b)



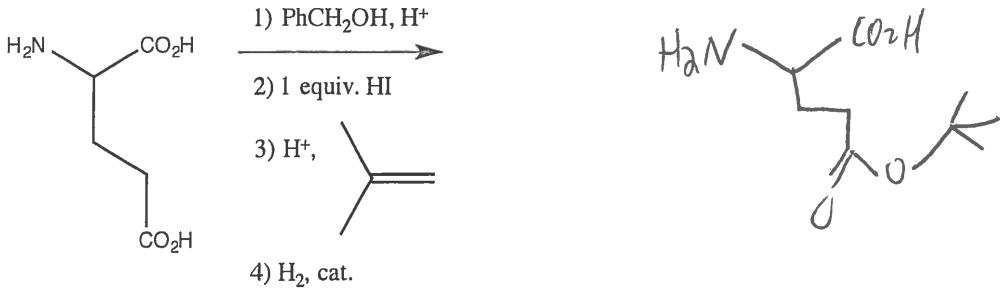
Draw two isomeric products plus an additional by-product;

(c)



Draw two products

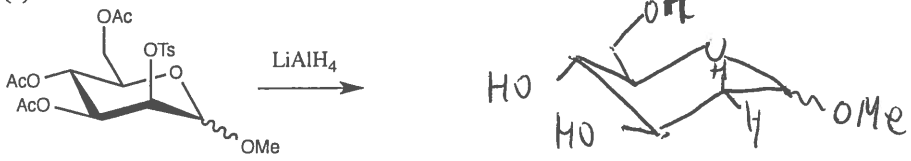
(d)



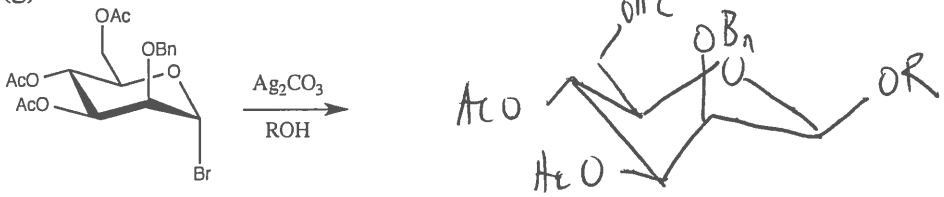
1. (continued)

(e)

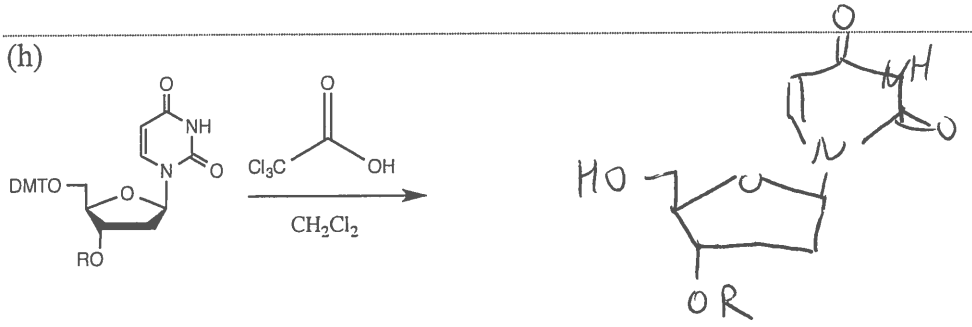
(f)



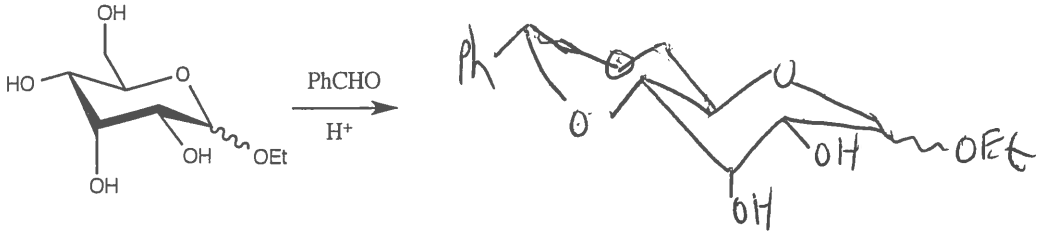
(g)



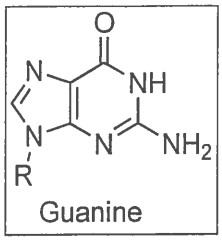
(h)

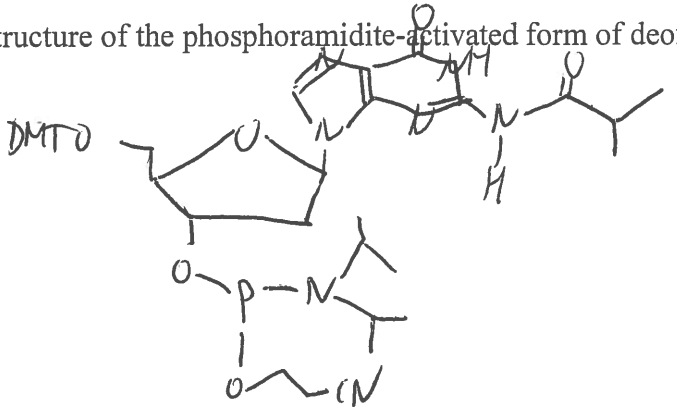


(j)

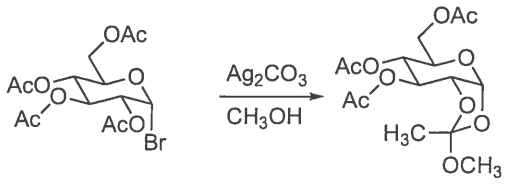


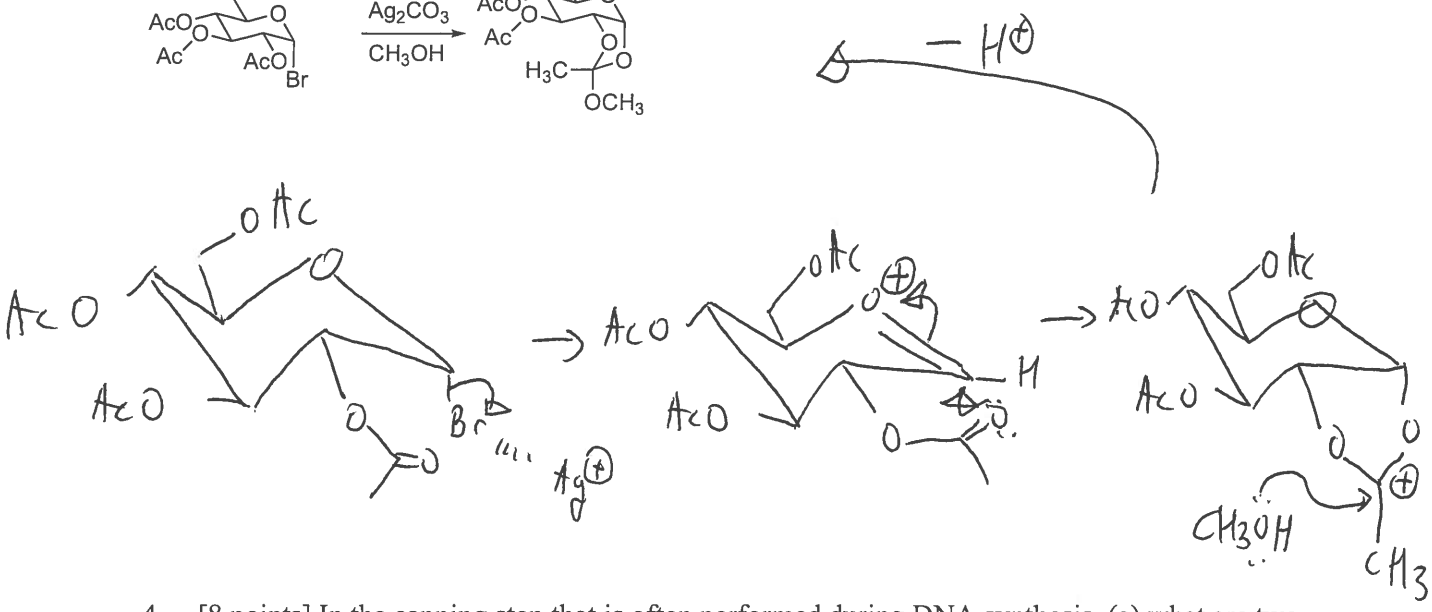
2. [5 points] Draw the structure of the phosphoramidite-activated form of deoxyguanosine used in DNA synthesis.





3. [5 points] Under Koenigs-Knorr conditions, an orthoester (shown below, right) often forms. Propose a mechanism for this transformation. (Org. Bioorg. Chem. **2010** 497)





4. [8 points] In the capping step that is often performed during DNA synthesis, (a) what are two potential functions of the reagent *N*-methylimidazole? (See part (b) for hints.)

(a) Base

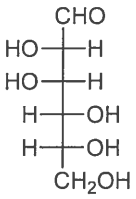
(b) nucleophilic catalyst

(b) For each function above, explain what the consequence might be if *N*-methylimidazole is not present during the capping process. Hint: one consequence is small; the other is large.

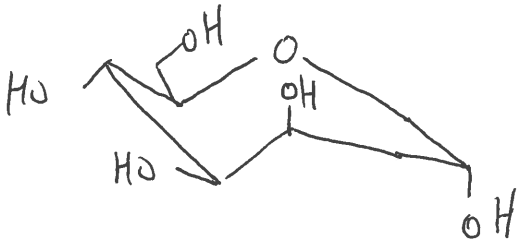
(a) If no base is present, CH_3CO_2H builds up. This acid is strong enough to deprotect DMT's, which would lead to unwanted capping of 5'OH's.

(b) The rxn would be slower.

5. [6 points] (a) Draw the structure of α-D-mannopyranose in its most stable conformation.

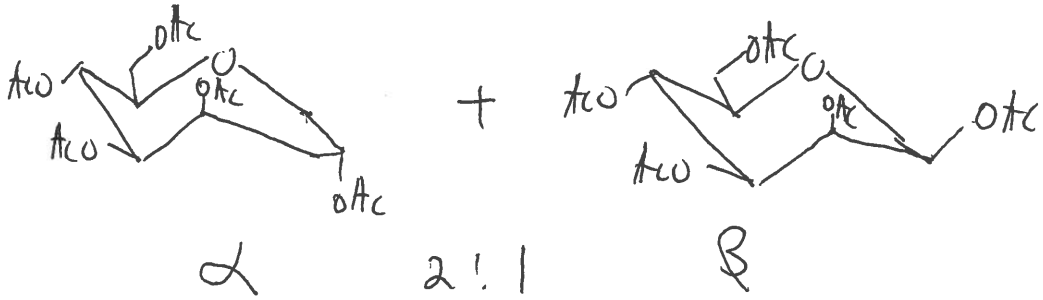


D-mannose

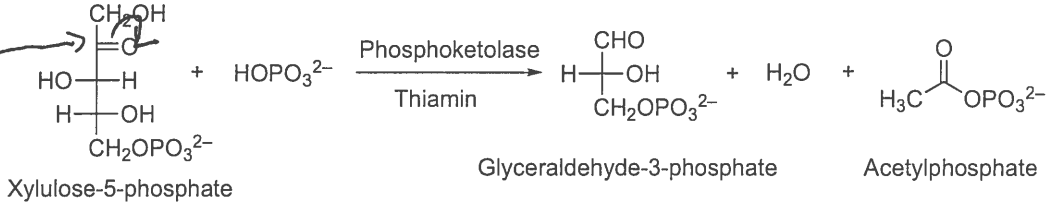


(b) Draw the structures of the products of the reaction below. Indicate which is α, and which is β. Estimate the ratio of α:β.

D-mannose $\xrightarrow[\text{pyr}]{Ac_2O}$ (α:β = 2:1, 0 °C)



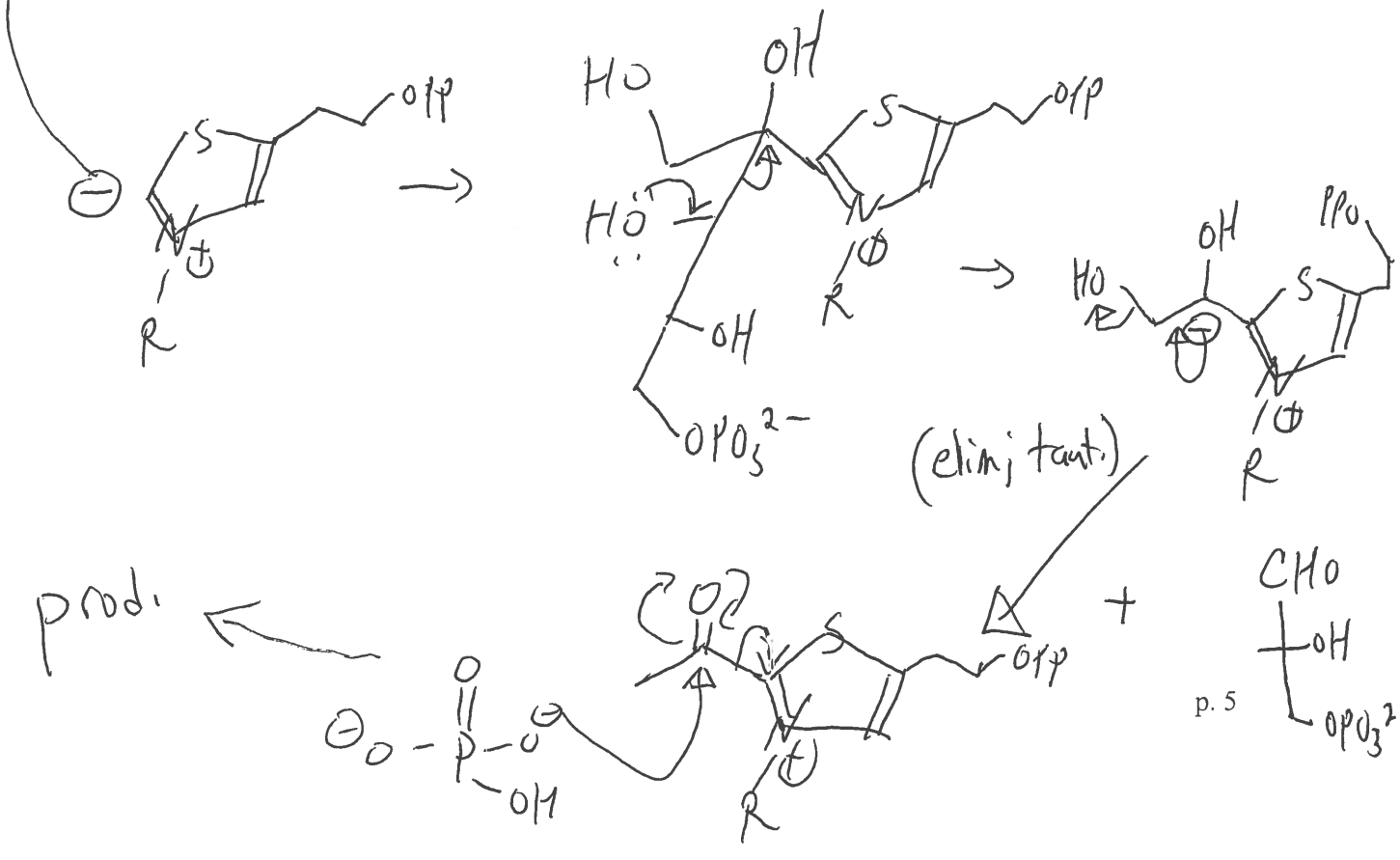
6. [8 points] Propose a mechanism for the thiamin catalyzed reaction below.



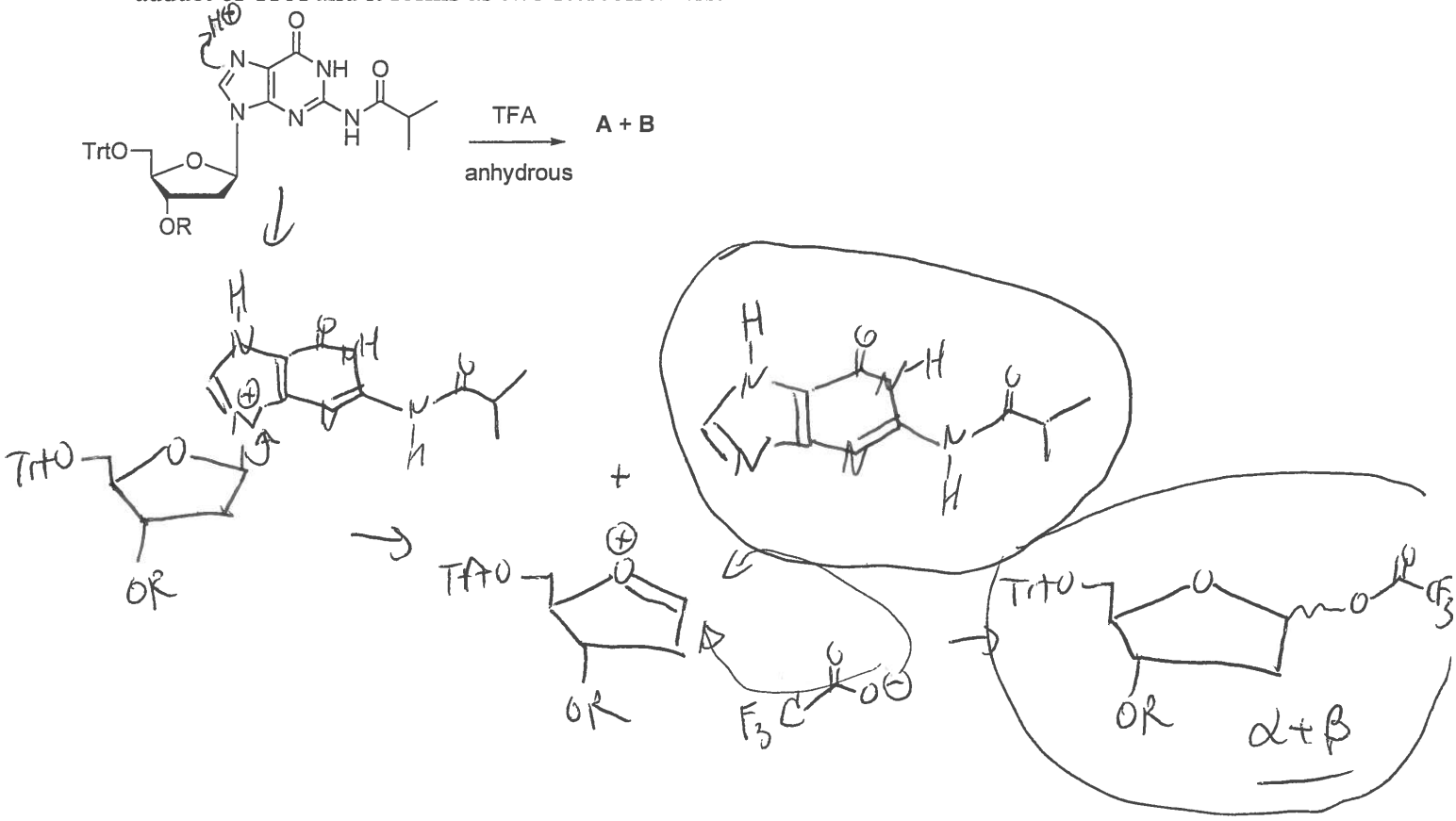
Xylulose-5-phosphate

Glyceraldehyde-3-phosphate

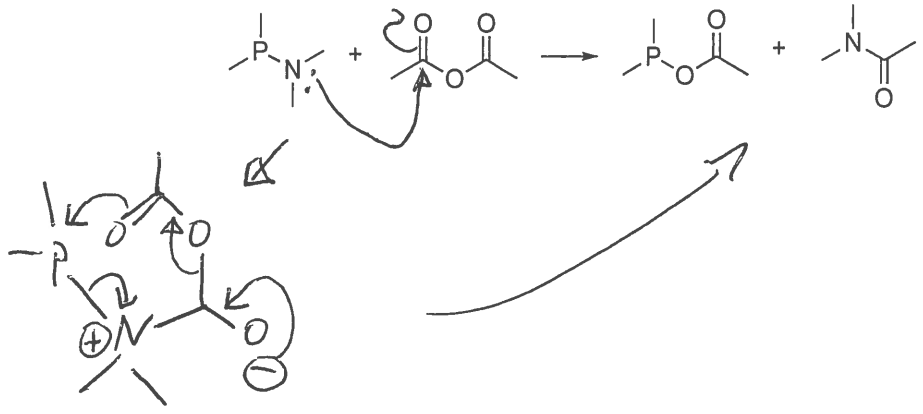
Acetylphosphate



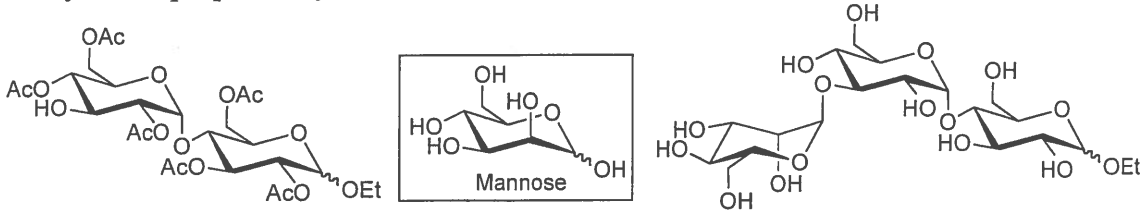
7. [7 points] DMT is 100 times "more acid labile to acid-promoted cleavage than the parent trityl group, and its removal leads to much less unwanted cleavage of the glycosidic linkages, especially of purine 2'-deoxyribonucleosides." (Org. Biomol. Chem. **2005** 3851) Starting from 5'-trityl protected guanosine (below), propose a mechanism for the unwanted cleavage reaction that occurs under more acidic (e.g., TFA) conditions. Choose neutral species for **A** and **B**. Leave OR and OTrt intact (to save time). Regarding protonation sites, several are acceptable. Hint: one product is an adduct of TFA and it forms as two stereoisomers.



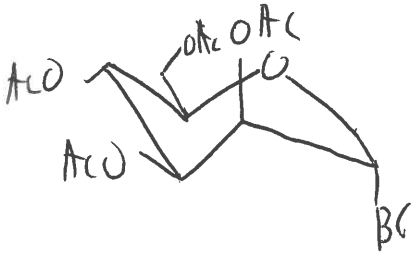
8. [6 points] It has been suggested that the transformation below may involve a 6-membered transition state (J. Phys. Org. Chem. **2004** p. 1). Propose a mechanism.



9. [8 points] Using mannose and the disaccharide shown on the left as your only starting carbohydrates, propose a synthesis for the trisaccharide shown on the right.



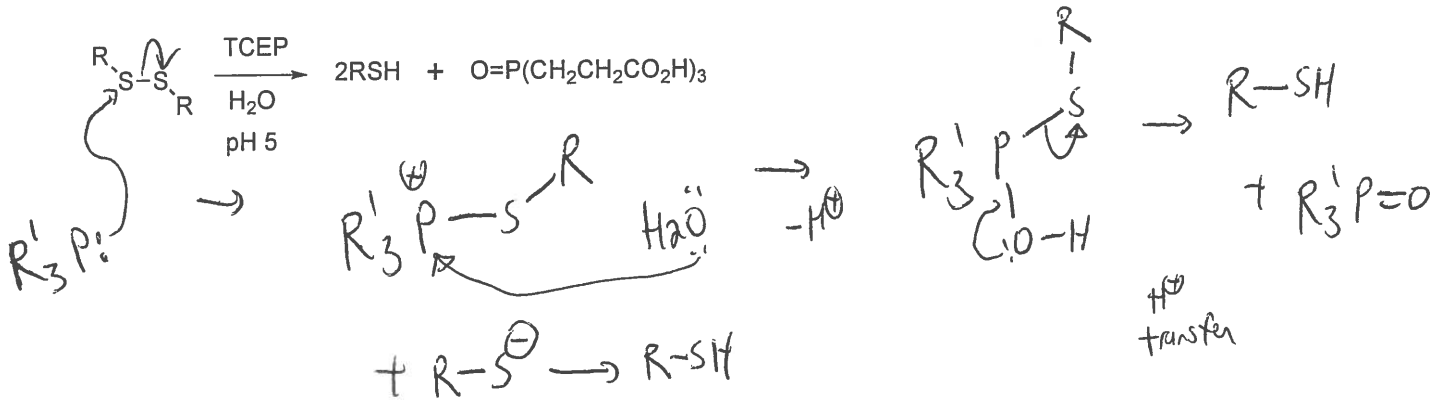
1) Ac_2O, pyr
2) HBr



1) Disacch., Ag_2CO_3
2) $MeO^{\ominus}$, MeOH

product

10. [7 points] TCEP, tris(2-carboxyethyl)phosphine, $P(CH_2CH_2CO_2H)_3$, is often used instead of DTT as it is more stable in air, it does the same job even more irreversibly, and it works well at pH 5. Propose a mechanism for the transformation below. (J. Org. Chem. **1991**, *56*, 2548; **2007**, *72*, 8298)



11. [6 points] Propose a mechanism for the reaction below which is catalyzed by the enzyme serinehydroxymethyltransferase: