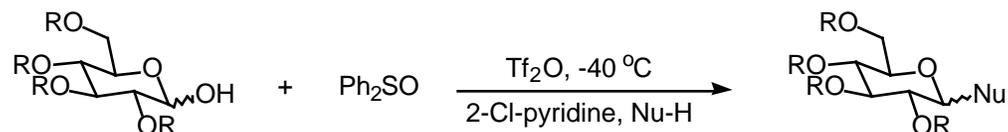
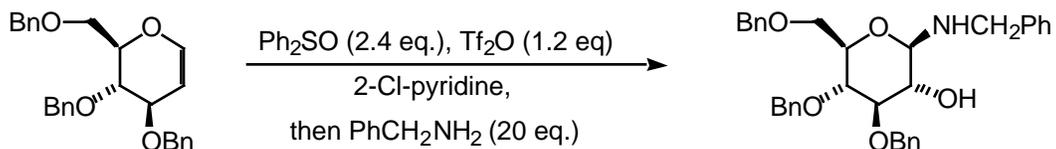


Organic Cume October 1999

- (20 pts) Describe, via equations, three methods for forming a glycosidic linkage. Do not include the methodology discussed by Professor David Gin.
- Professor David Gin proposed a direct dehydrative glycosylation procedure based on the use of diphenyl sulfoxide and triflic anhydride:

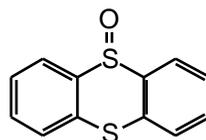
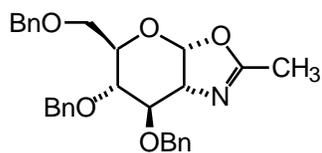


- (20 pts) Give two possible mechanisms for the reaction with particular emphasis on two possible ways in which the hemiacetal might be activated.
 - (10 pts) When the OH was labelled with oxygen-18, the diphenylsulfoxide obtained after the reaction contained a significant amount of the label. Which of your two mechanisms fits that piece of information?
- (10 pts) What is the potential problem in using DMSO instead of diphenyl sulfoxide in a reaction like this?
 - (10 pts) Perbenzylated glucose glycal can react with dioxirane and the resulting product treated with a mild Lewis acid and alcohol to give a glycoside. Write an equation for the first reaction.
 - (20 pts) Professor Gin applied his methodology to glucals. An example is shown below:



Give two possible mechanisms for this reaction given that when ^{18}O labelled diphenyl sulfoxide is used in the reaction, there is essentially complete transfer of the label to the hydroxy group in the product.

6. (10 pts) When the glucal used in the last question is treated with thianthrene-S-oxide, triflic anhydride and N-TMS acetamide, the oxazoline shown below is produced in 70% yield. Give a mechanism for the formation of this compound.



thianthrene-S-oxide