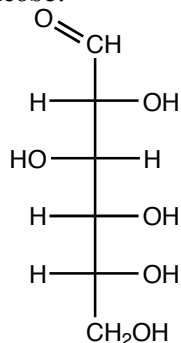
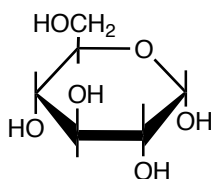


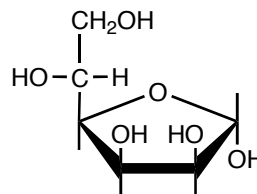
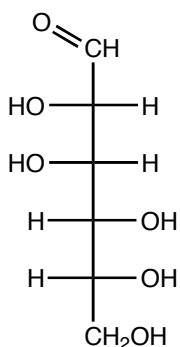
1. a. (6 pts.) Draw the linear form of glucose.



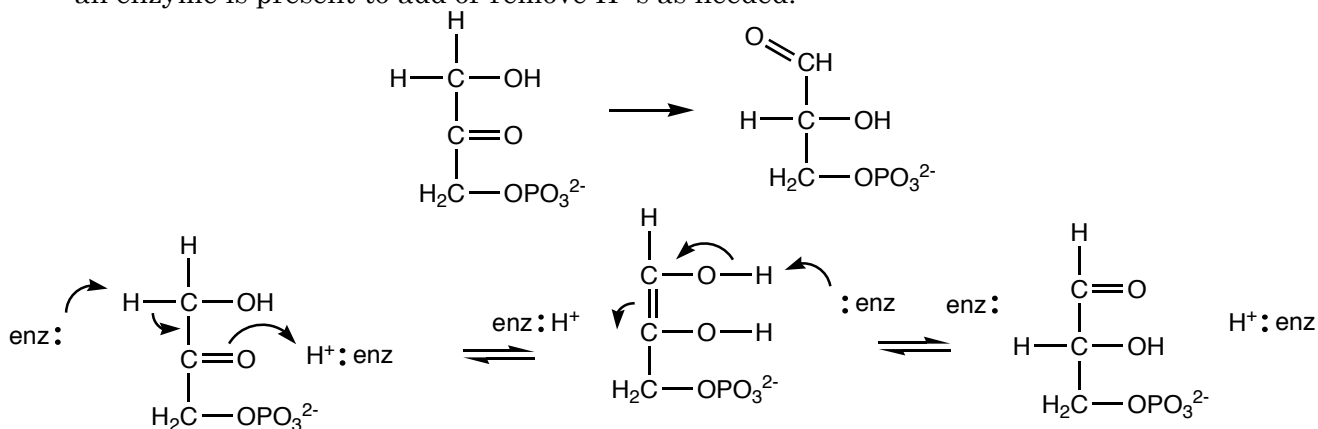
- b. (6 pts.) D-glucose typically exists in its pyranose form. Draw α -D-glucofuranose.



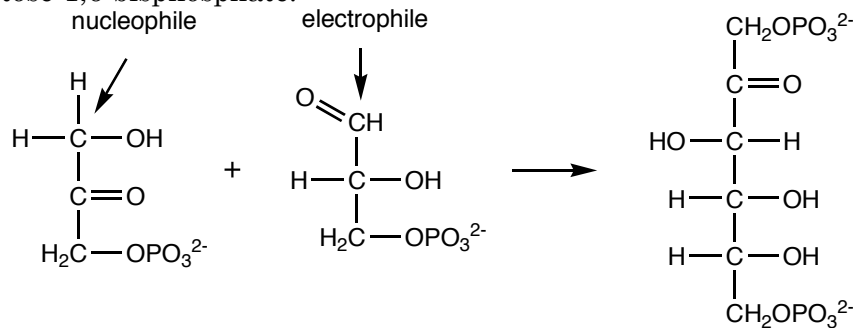
2. (6 pts.) The linear form of D-mannose is drawn below. D-mannose can exist as a furanose. Draw α -D-mannofuranose.



3. (8 pts.) The isomerization of dihydroxyacetonephosphate to glyceraldehyde-3-phosphate occurs through an enediol intermediate. Draw the mechanism of the reaction. Assume that an enzyme is present to add or remove H^+ 's as needed.



4. In gluconeogenesis, dihydroxyacetonephosphate combines with glyceraldehyde-3-phosphate to form fructose-1,6-bisphosphate.



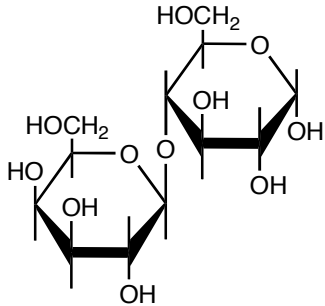
(2 pts.) Is C-3 on fructose from the dihydroxyacetonephosphate or the glyceraldehyde-3-phosphate? **dihydroxyacetonephosphate**

(2 pts.) Is C-4 on fructose from the dihydroxyacetonephosphate or the glyceraldehyde-3-phosphate? **glyceraldehyde-3-phosphate**

(2 pts.) Which carbon atom acts as the nucleophile for the reaction?

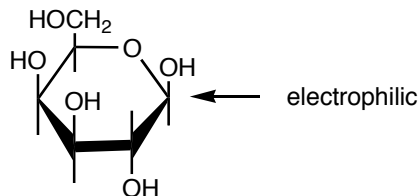
(2 pts.) Which carbon atom acts as the electrophile for the reaction?

5. (8 pts.) Can α -lactose, drawn below, be converted to β -lactose via mutarotation, explain?



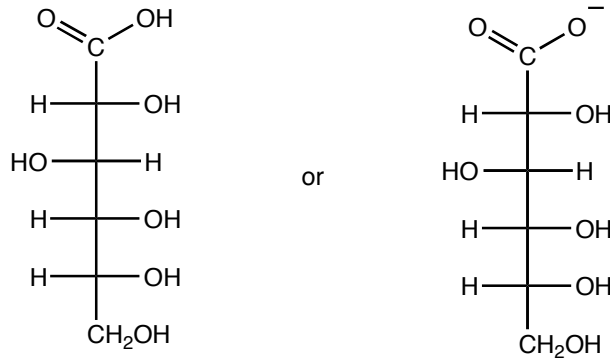
Yes, the hemiacetal on the glucose ring can be opened. Thus, the hemiacetal can convert from its α form to its β form.

6. a. (4 pts.) Label the nucleophilic sites on the sugar drawn below.
 b. (4 pts.) Label the most electrophilic carbon on the sugar drawn below.

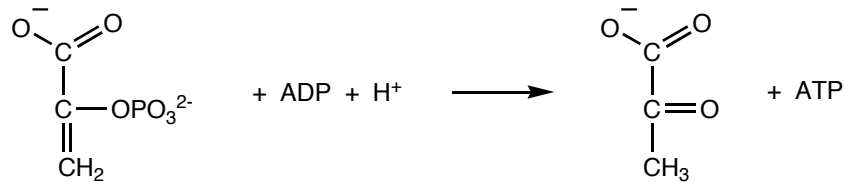


All of the alcoholic oxygen atoms are nucleophilic. The anomeric carbon is the most electrophilic site.

7. (6 pts.) C-1 of glucose can be oxidized to form glucoaldonic acid. Draw glucoaldonic acid (the linear form, not the lactone form).

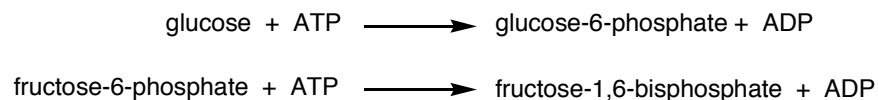


8. (8 pts.) The ΔG for the conversion of phosphoenolpyruvate and ADP to pyruvate and ATP is very favorable. What is it that makes this reaction favorable (the reaction is drawn below).



The conversion of the unstable enol to the more stable ketone drives this reaction to completion.

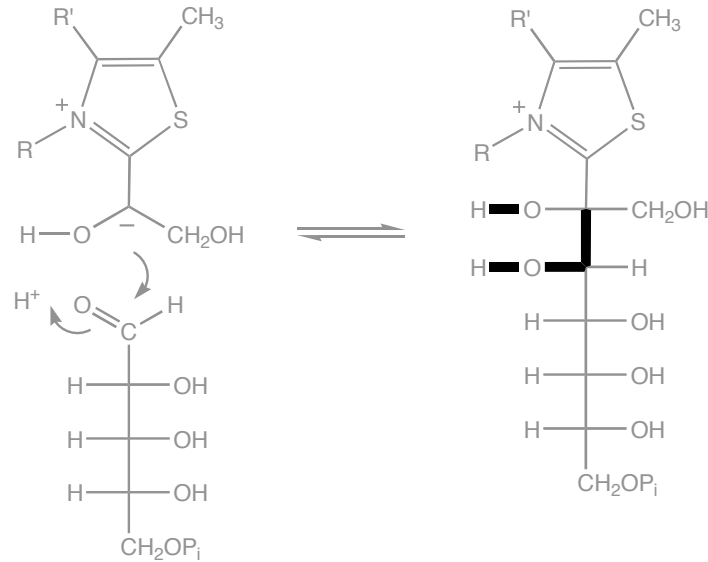
9. Many of the reactions in gluconeogenesis are the reverse of the reactions in glycolysis. However, there are three irreversible steps in glycolysis. Two of the three reactions are drawn below.



(8 pts.) If the reactions drawn above are irreversible, then how are the conversions from glucose-6-phosphate to glucose and fructose-1,6-bisphosphate to fructose-6-phosphate accomplished in gluconeogenesis.

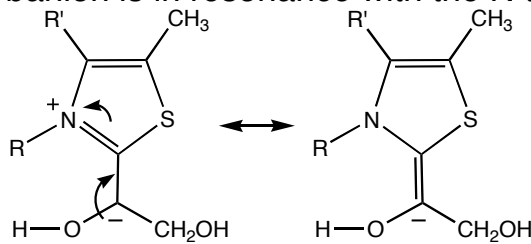
Instead of trying to form ATP from ADP, in gluconeogenesis, the phosphoesters are simply hydrolyzed to produce the sugars and a phosphate group. Since ATP is not formed, and the hydrolysis of a phosphoester linkage is favorable, the phosphorylated sugars are easily converted to their unphosphorylated forms.

10. In the pentose-phosphate pathway, transketolase transfers a ketone from D-xylulose to D-ribose. A step in the mechanism is drawn below.



- a. (6 pts.) Draw the correct bonds in the product.
- b. (4 pts.) Carbanions are normally quite unstable, but the carbanion on the upper left exists long enough for one molecule to move out of the active site and another to move into the active site. What is it that makes this carbanion unusually stable?

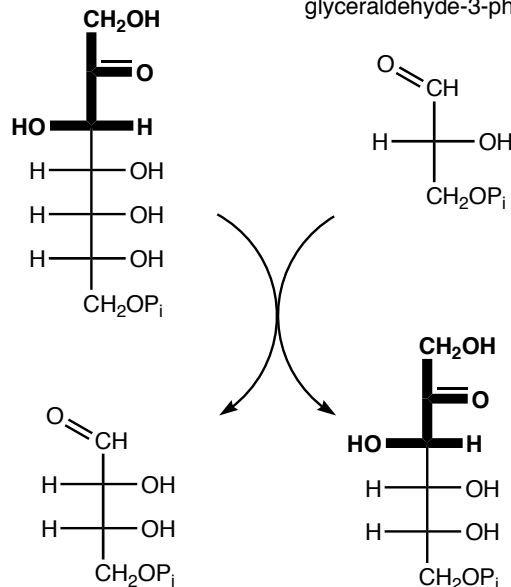
Resonance. The carbanion is in resonance with the N to C double bond.



11. In the reaction drawn to the right, carbon atoms are transferred from sedoheptulose to glyceraldehyde-3-phosphate to form fructose-6-phosphate and erythrose-4-phosphate.

sedoheptulose-7-phosphate

glyceraldehyde-3-phosphate



- a. (5 pts.) Indicate which atoms are transferred from sedoheptulose to glyceraldehyde-3-phosphate.
- b. (5 pts.) Indicate which atoms in the fructose-6-phosphate came from the sedoheptulose.