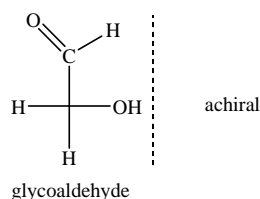


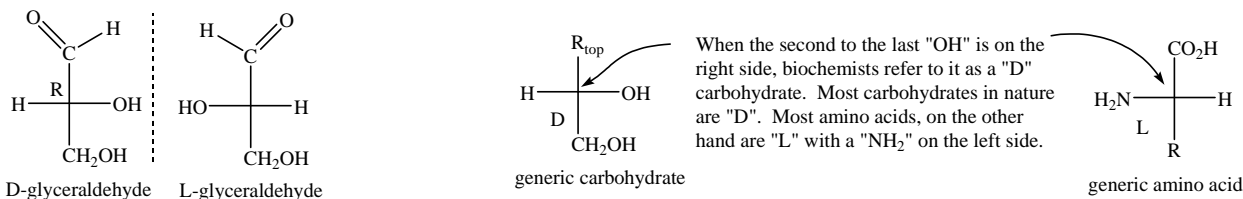
## Carbohydrates

The following carbohydrates show a small sampling of Nature's choices for energy use, structural support and also serve as recognition targets in cells. Nature almost exclusively picks one enantiomer of a pair, though apparently some bacteria can make both enantiomers. When drawn as a Fischer projection the common stereoisomer has the second to the last OH on the right side. In Biochemistry, this is referred to as the "D" isomer. If the second to last OH were on the left side in a Fischer projection it would be referred to as the "L" isomer. There is no logical reason for these designations. They must be memorized, as do the positions of all of the other "OH" groups up the chain. "Reducing carbohydrates" have an aldehyde carbon at C1 and can be 2Cs, 3Cs, 4Cs, 5Cs, 6Cs or more in length. Glucose is probably the most famous of the carbohydrates. Some of these are shown below. How many chiral centers does each example have? Through tautomeric changes an aldehyde carbohydrate (glucose) can be converted into a keto carbohydrate (fructose). How many stereoisomers are possible for each length of carbon? What are the absolute configurations of any chiral centers? What stereochemical relationship does the first stereoisomer as A (then B, C, etc.) have to the others? Are there any meso structures. (See problem below.)

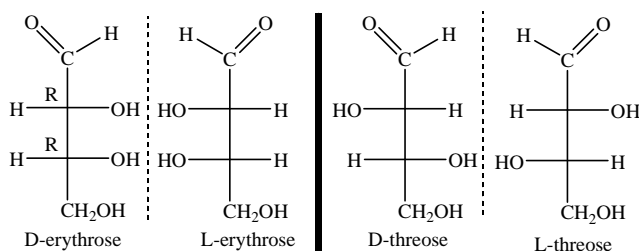
A unique two carbon aldose carbohydrate is possible, but not technically considered a carbohydrate, 2-hydroxyethanal



Three carbon aldose carbohydrates – two possible (enantiomers), both are 2,3-dihydroxypropanal



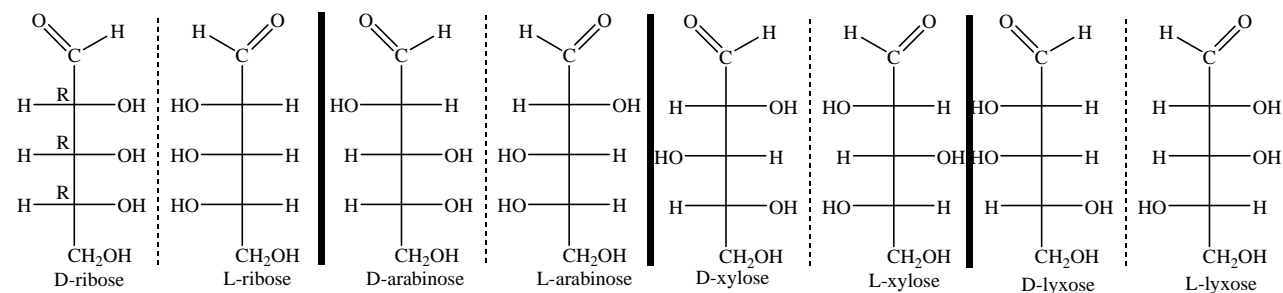
Four carbon aldose carbohydrates – four possible, all are 2,3,4-trihydroxybutanal (enantiomers and diastereomers)



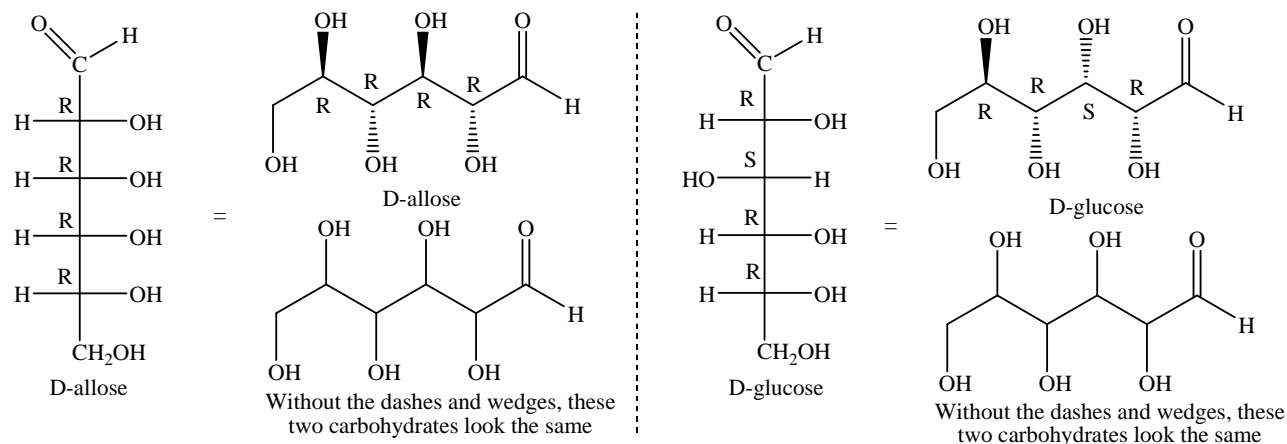
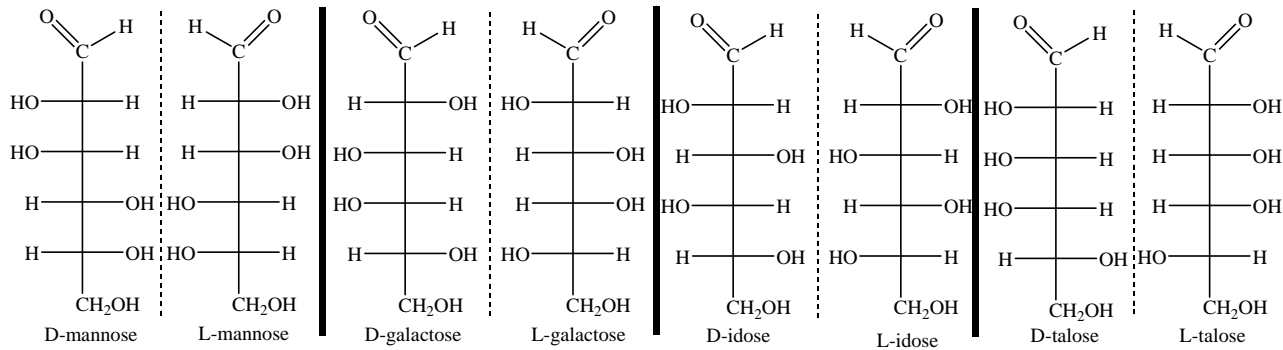
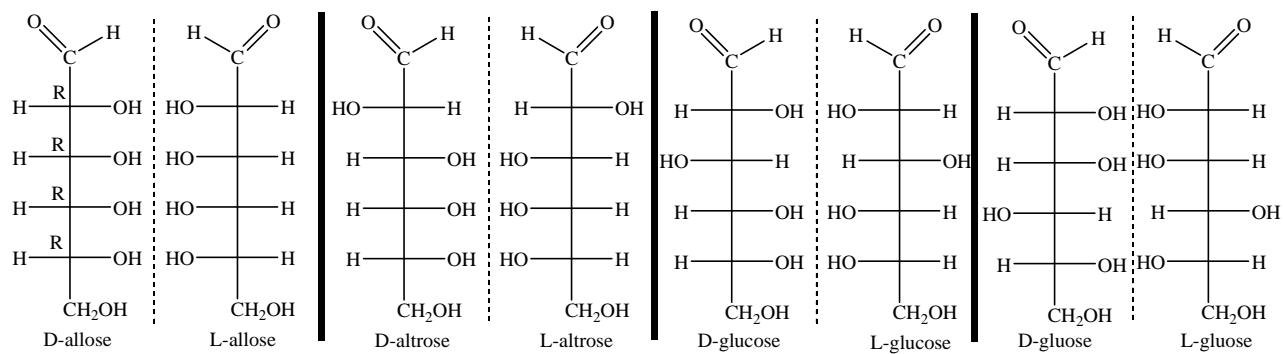
Biochem names are all different. Organic names are easier. All of these are 2,3,4-trihydroxybutanal.

- 1 = (2R,3R)-2,3,4-trihydroxybutanal
- 2 = (2S,3S)-2,3,4-trihydroxybutanal
- 3 = (2S,3R)-2,3,4-trihydroxybutanal
- 4 = (2R,3S)-2,3,4-trihydroxybutanal

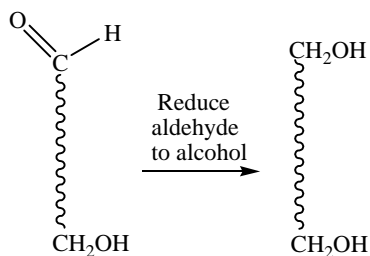
Five carbon aldose carbohydrates – eight possible, all are 2,3,4,5-tetrahydroxypentanal (enantiomers and diastereomers)



Six carbon aldose carbohydrates – 16 possible, all are 2,3,4,5,6-pentahydroxyhexanal (enantiomers and diastereomers)



Problem – What would happen to the number of stereoisomers in each case above if the top aldehyde functionality were reduced to an alcohol functionality (a whole other set of carbohydrates!)? A generic structure is provided below to show the transformation. Nature makes some of these too. How many chiral centers does each example have? How many stereoisomers are possible for each length of carbon? What are the absolute configurations of any chiral centers? Specify the first stereoisomer as A (then B, C, etc.) and state what each relationship is to the others. Are there any meso structures.



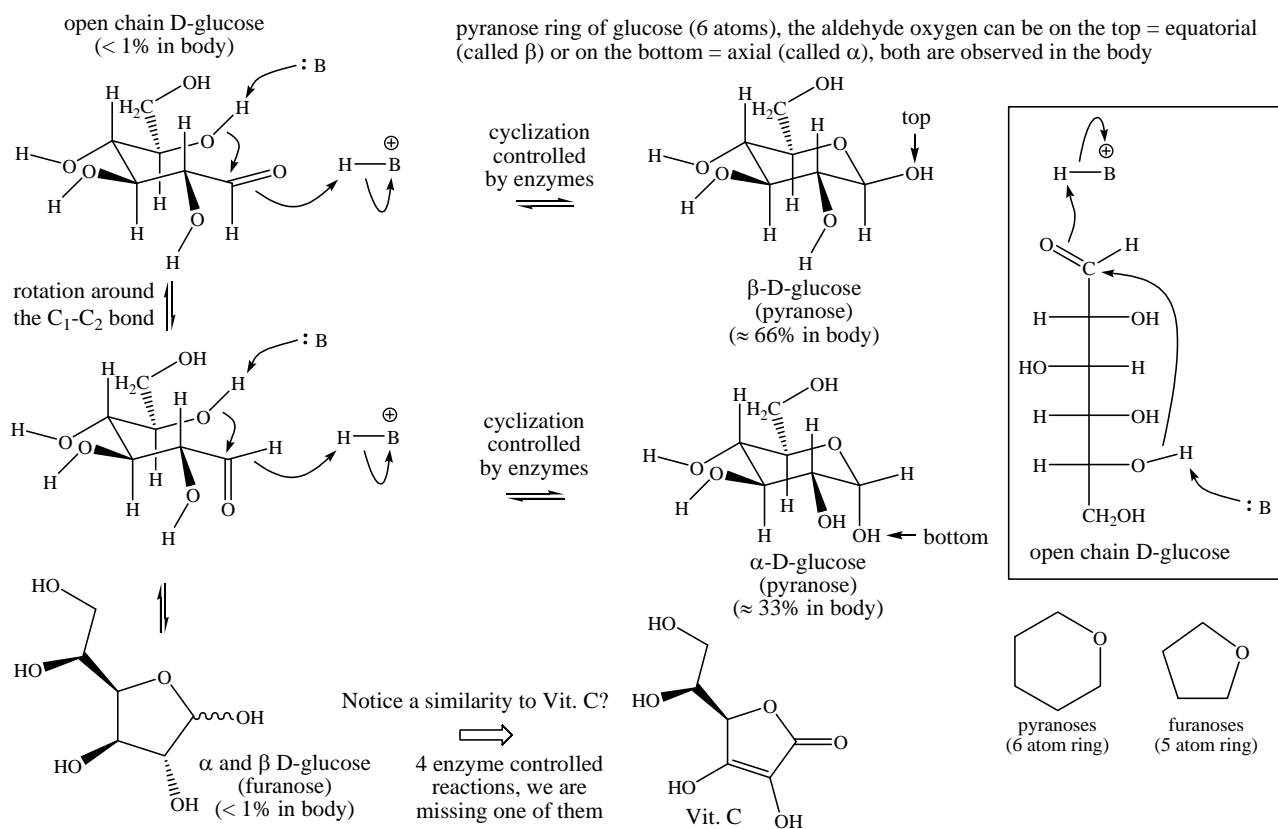
Three carbon tri-ol carbohydrate = becomes only one structure (glycerol), which is achiral

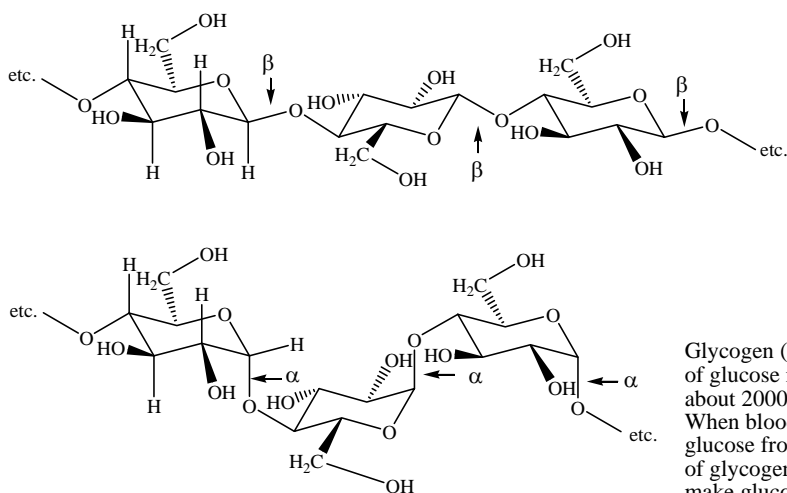
Four carbon tetra-ol carbohydrates = becomes three stereoisomers (one meso pattern)

Five carbon penta-ol carbohydrates = becomes four stereoisomers (two meso patterns, one duplication)

Six carbon hexa-ol carbohydrates = becomes ten stereoisomers (two meso patterns, two duplications)

D-glucose is the most common choice of the 6 carbon examples above (can you think of a possible reason?). Even though it is a single sugar, Nature can arrange glucose in many possible ways. Only a few are shown below.

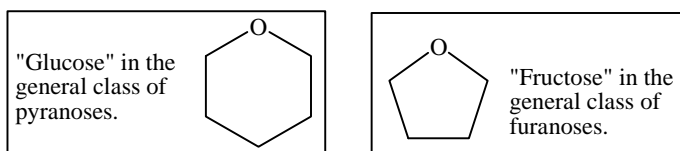




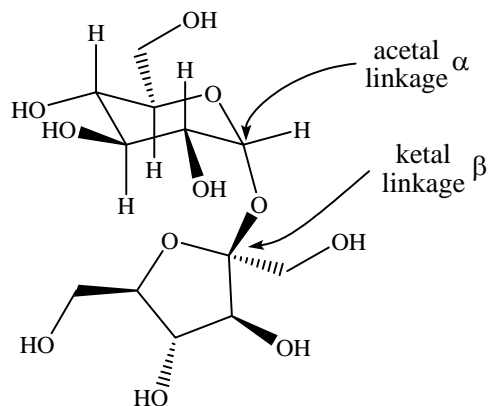
Cellulose consists of long flat chains of glucose molecules (about 15,000) connected with the  $\beta$  linkage, about 40 chains per fiber. It is said that cellulose accounts for about 1/2 of all the carbon in the biosphere and about  $10^{15}$  kg of cellulose are synthesized and degraded every year. About 90% of cotton is cellulose. In our plant food it is referred to as dietary fiber or roughage. Ruminants and termites can break down cellulose with the help of microorganisms.

Glycogen (our glucose storage system) consists of helices of glucose molecules connected with the  $\alpha$  linkage. We have about 2000 Kcals of energy stored in this way in our liver. When blood levels of glucose get low, our liver starts to release glucose from our glycogen stores. When you start to run out of glycogen your body switches over to fat metabolism to make glucose (gluconeogenesis).  $\alpha(1,4)$  linkages are shown but there are also some  $\alpha(1,6)$  linkages in glycogen.

Disaccharides are two sugars linked together ( $\alpha$  or  $\beta$ ). Common carbohydrate possibilities have 3C, 4C, 5C and 6C structures and the carbonyl group can be an aldehyde or a ketone. As mentioned above, the 6C sugars can be six atom heterocycles (pyranoses such as glucose) or five atom heterocycles (furanoses such as fructose). Sucrose and lactose are two of the more famous disaccharides.

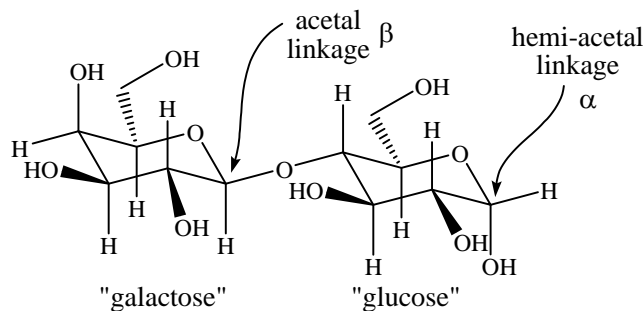


sucrose - found in beets and sugar cane



$\alpha$ -D-glucopyranosyl-(1 $\rightarrow$ 2)- $\beta$ -D-fructofuranoside

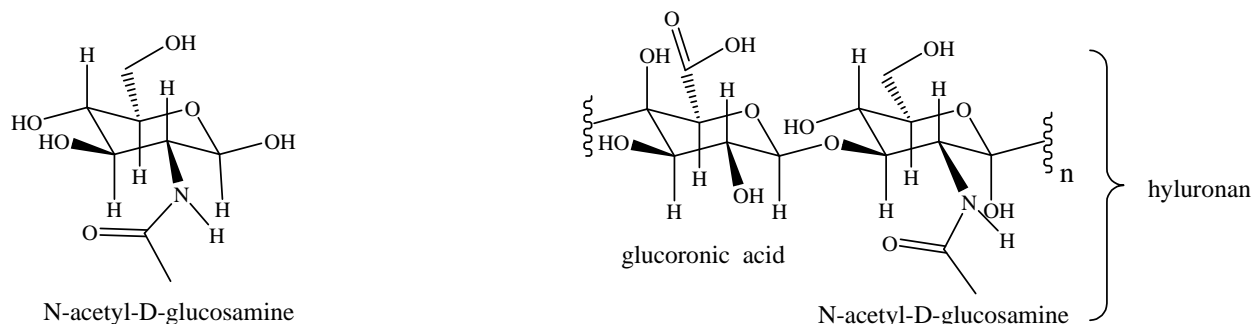
lactose - found in mother's milk



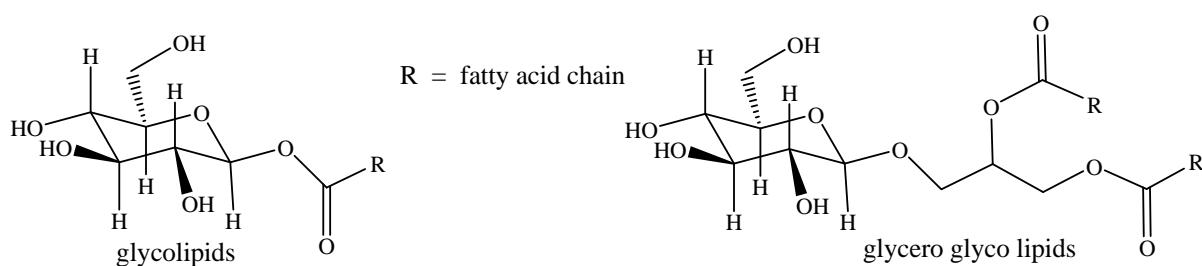
$\beta$ -D-galactopyranosyl-(1 $\rightarrow$ 4)- $\alpha$ -D-glucopyranose

The nomenclature of biochemistry often appears more complicated than the nomenclature of organic chemistry.

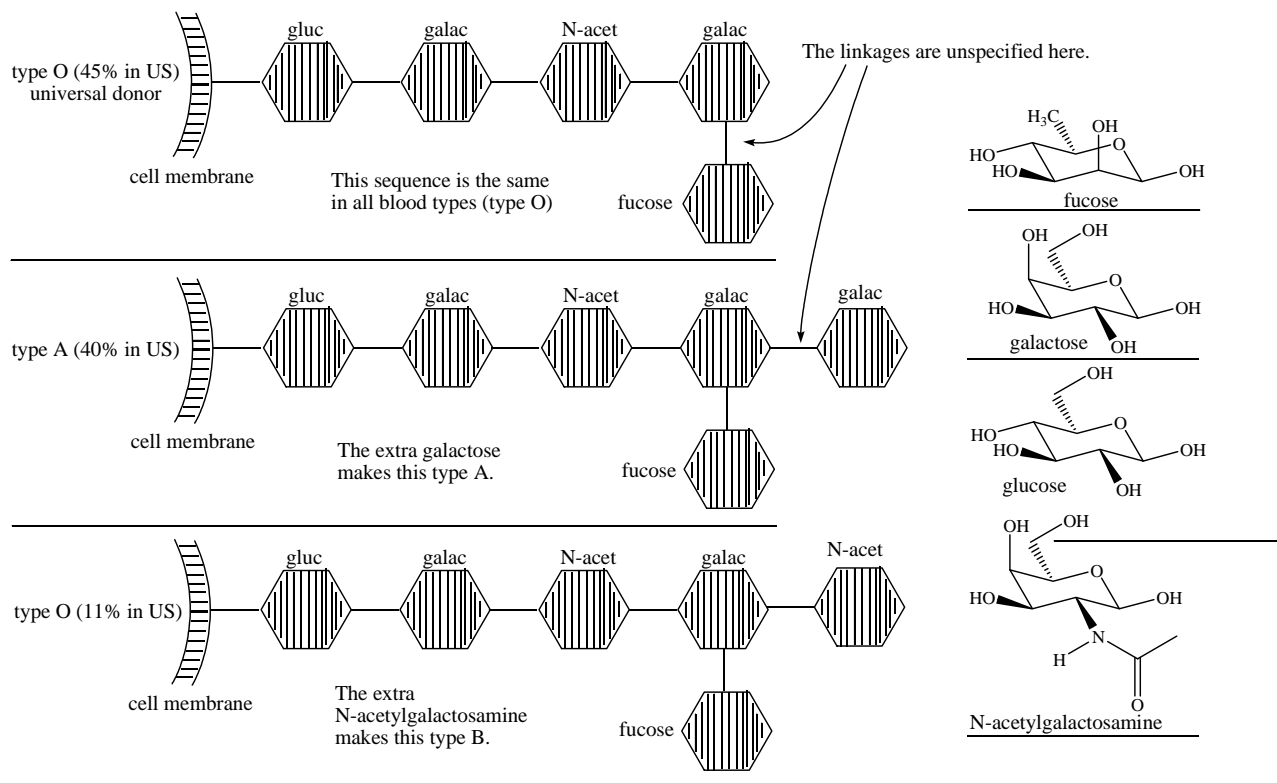
There are approximately 60 amino sugars known, having many important functions. N-acetylglucosamine is part of a biopolymer in bacterial cell walls and a major component of the cell walls of most fungi. It is also the monomeric unit of the polymer chitin, which forms the outer coverings of insects and crustaceans. When polymerized with glucuronic acid, it forms hyaluronic acid, which is a polymer with a molecular weight in the millions. A 150 pound body has about 15 grams of hyaluronic acid in it.



Glycolipids can serve as markers for cellular recognition and are found on the outer surface of all eukaryotic cell membranes. They extend from the phospholipid bilayer into the aqueous environment outside the cell where it acts as a recognition site for specific chemicals as well as helping to maintain the stability of the membrane and attaching cells to one another to form tissues.

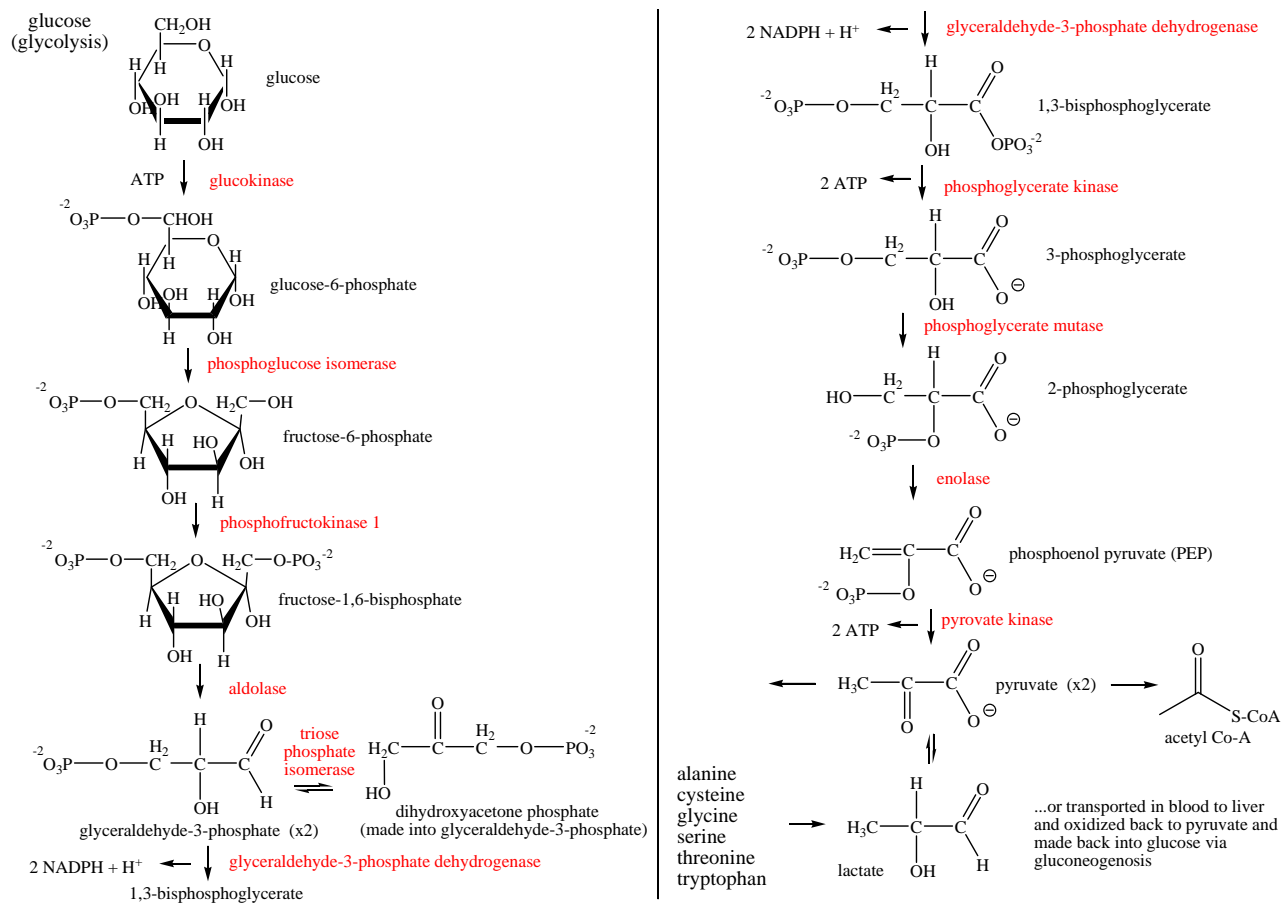


Blood types are based, in part, on carbohydrate coatings linked to lipid molecules on the outer cell membranes. There is also a soluble form linked to proteins in the blood. About 75% of type A individuals have a repeat of the 3 terminal sugars. Type AB (4% in the US) have both A and B patterns on their cell surfaces and are universal acceptors. There is some variation in the position number of the connections and the  $\alpha/\beta$  linkage is not indicated. Science News (vol 151, p 24, 1-11-97) discusses enzymes from chicken livers (type A) and coffee beans (type B) that can cleave the single sugar at the end of the cell coatings. This would convert type A and type B to type O, which would allow for universal donation. The article discusses the possible commercial production for blood donations. There are over 7,000,000,000 (billion) people on the earth. Every one of us has a unique biochemical profile that is uniquely recognized by our immune system. The blood types give you a hint at how this is possible.

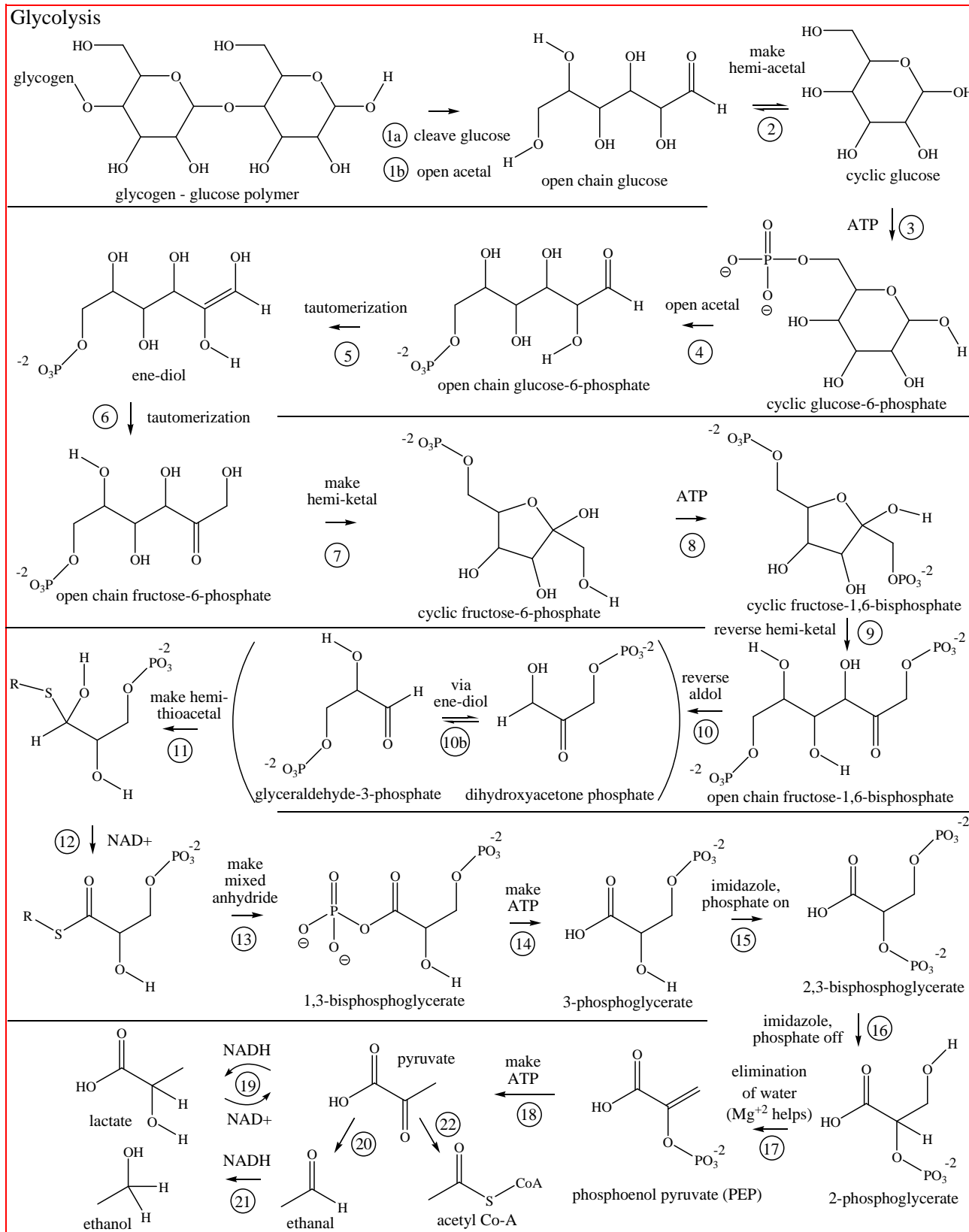


Cycles

1. Glycolysis – simple version (not all steps are shown in the usual cycle)



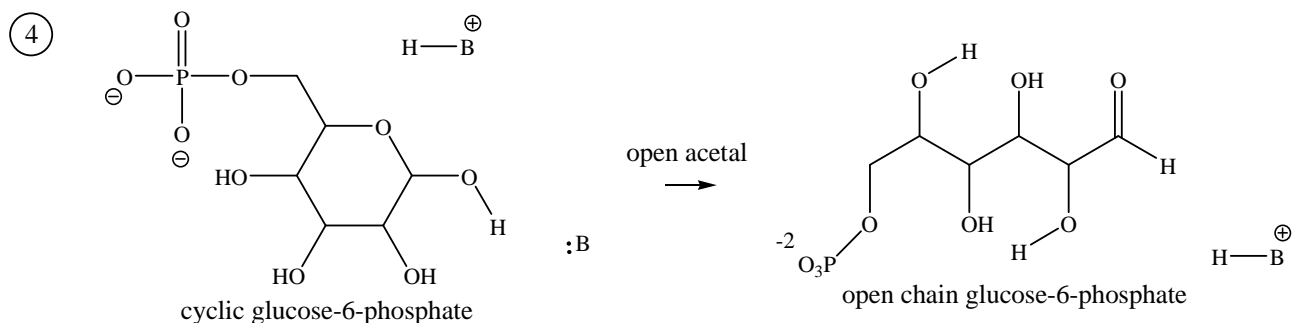
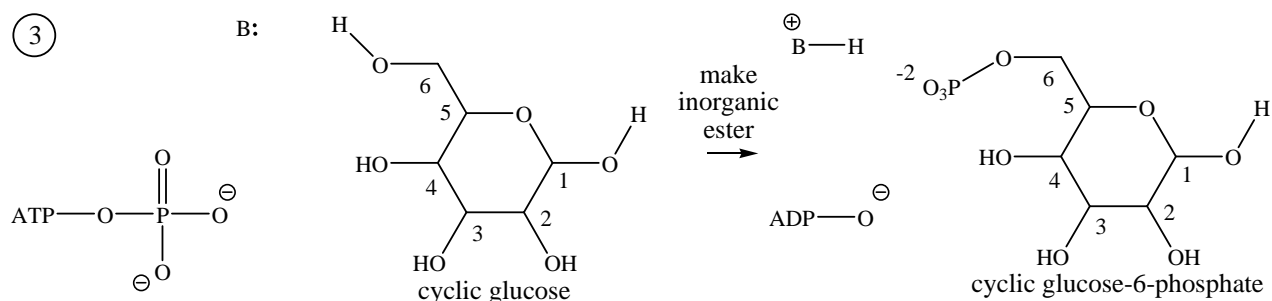
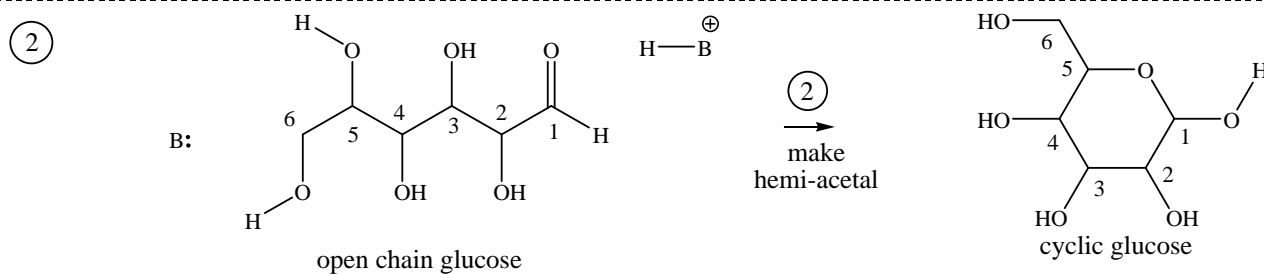
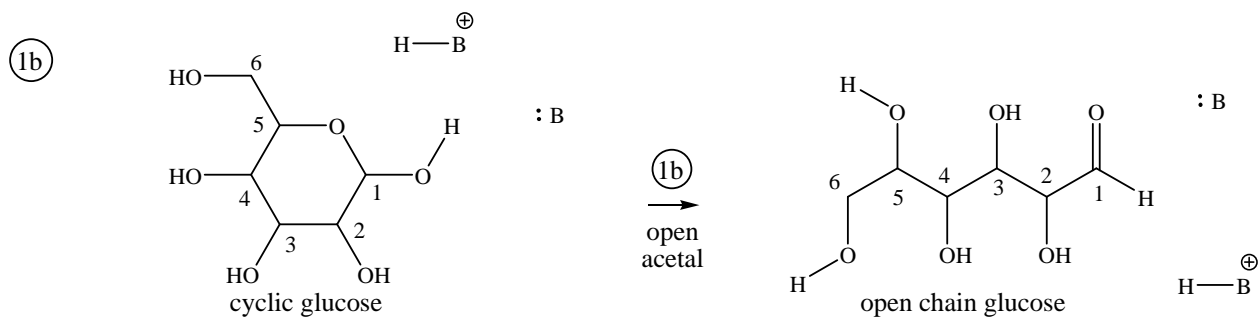
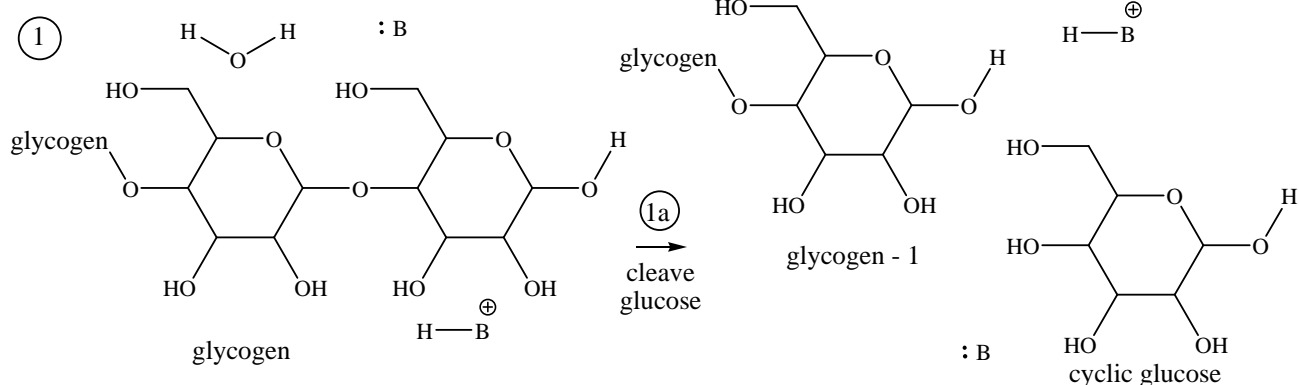
Glycolysis – long version

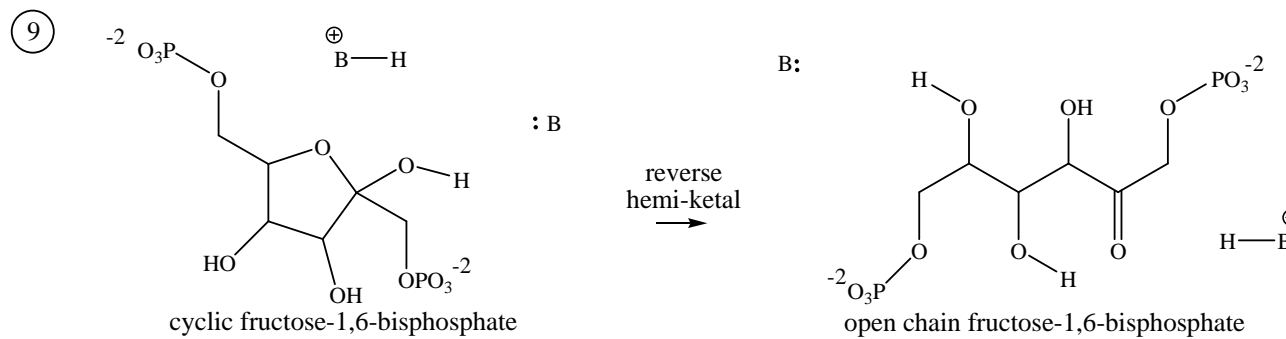
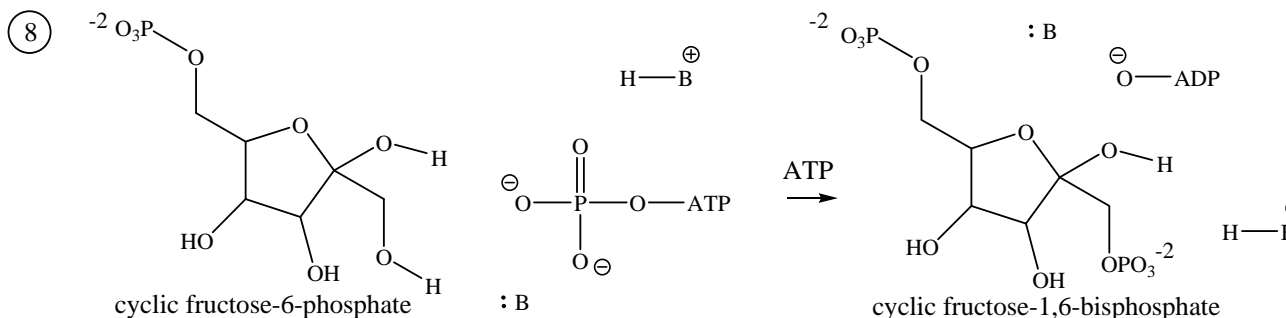
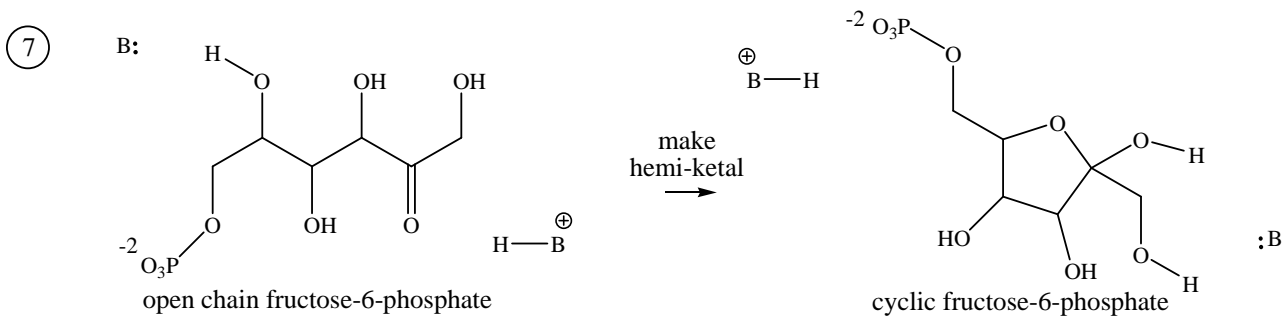
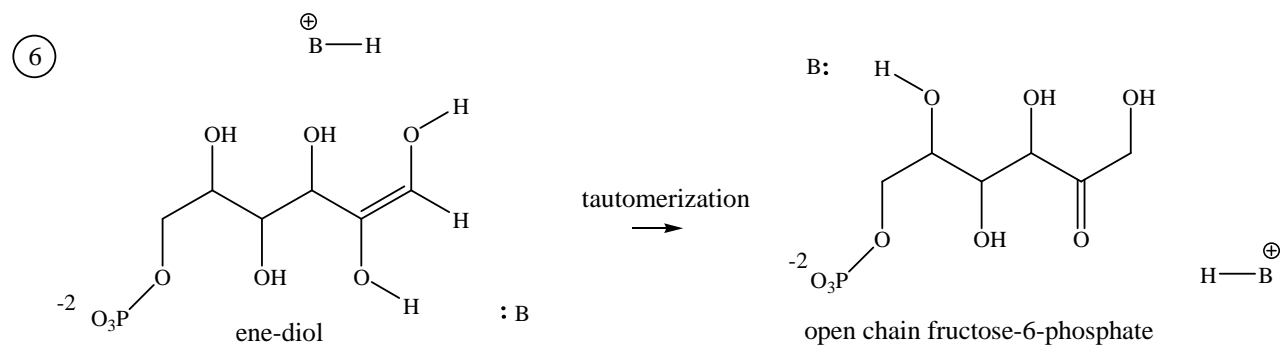
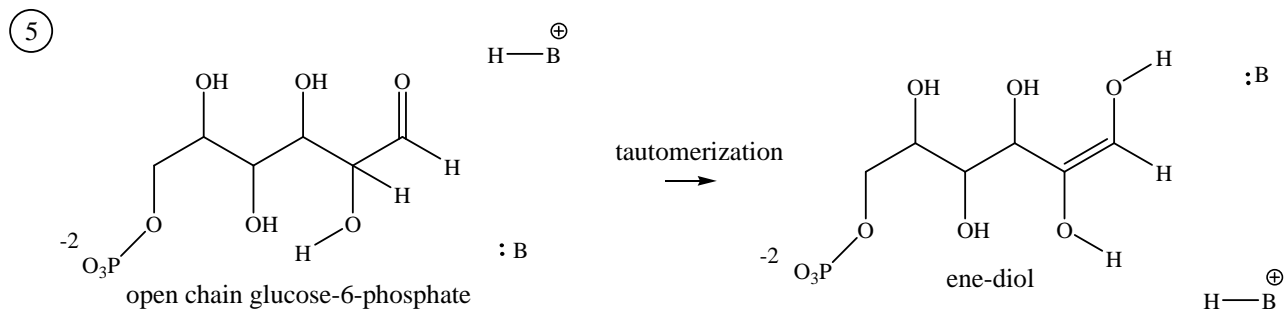




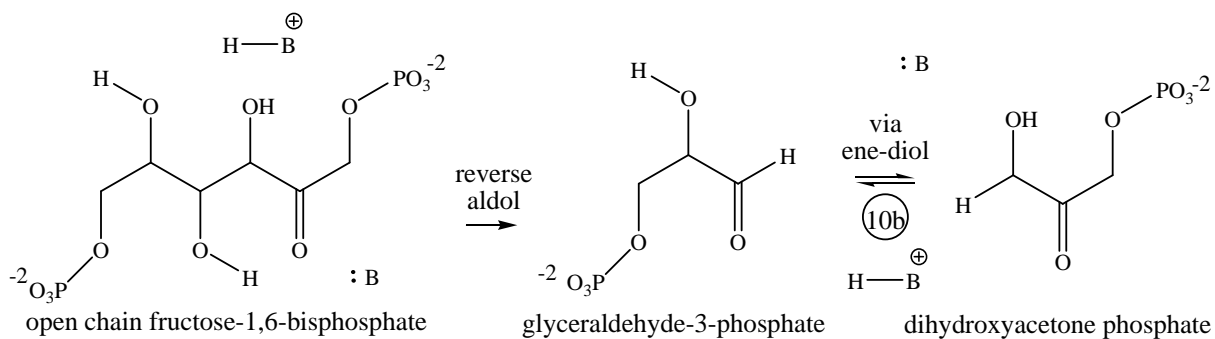
## Glycolysis step by step

Mechanism steps without arrows. B: = base and B+-H = acid. Add in necessary arrows to show electron movement. Stereochemistry is omitted. Each step is under enzyme control. Possible answers are shown below.

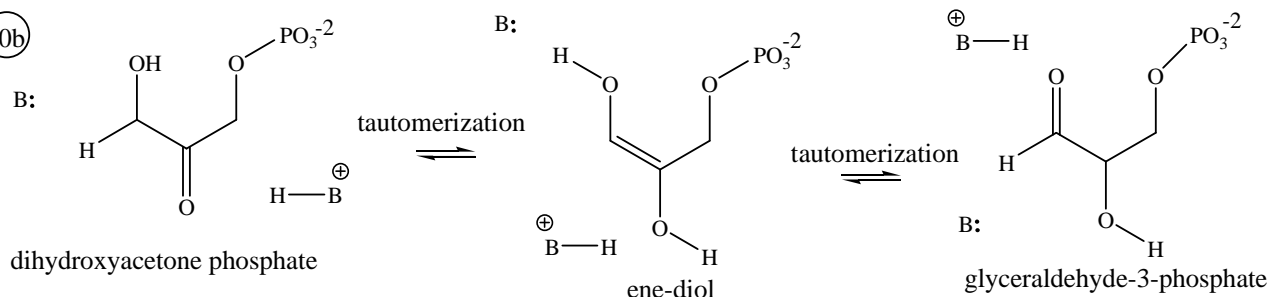




(10)



(10b)



(10)

imine alternative to keto retroaldol (actually protonated iminium ion)

