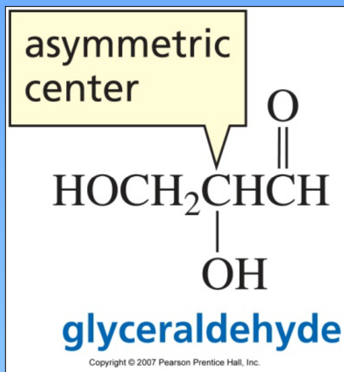
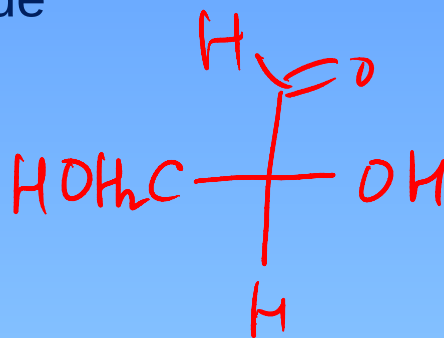
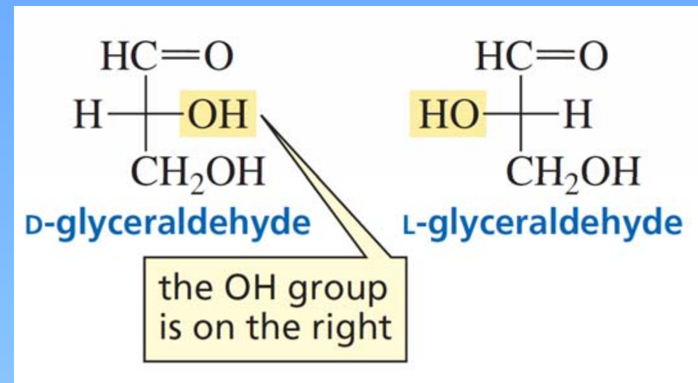
Stereochemistry: D and L Notation

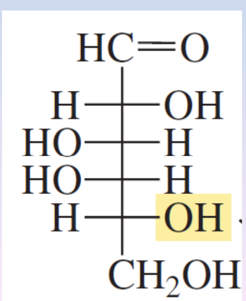
- Glyceraldehyde

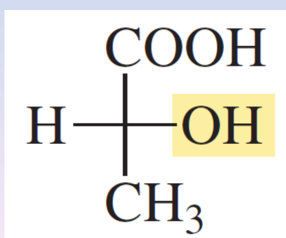


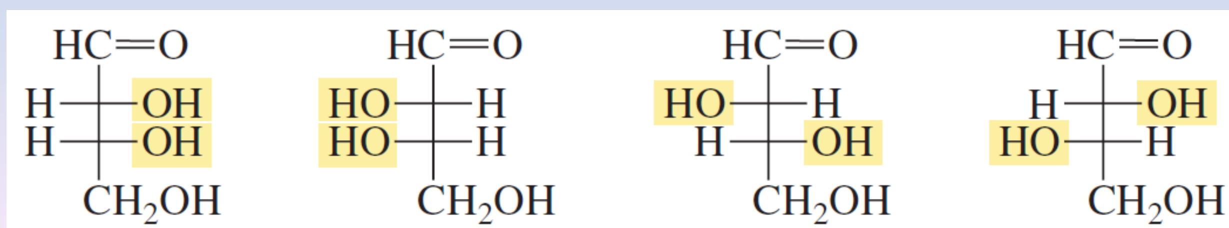




- D and L Notation: used to describe the configurations of carbohydrates and amino acids. Rules:
  - In a Fischer projection, the carbonyl group is always placed on/close to the top
  - If the OH attached to the bottom-most asymmetric center is on the right, then a D-sugar; If on the left, a L-sugar
  - All the natural sugars are D-sugars



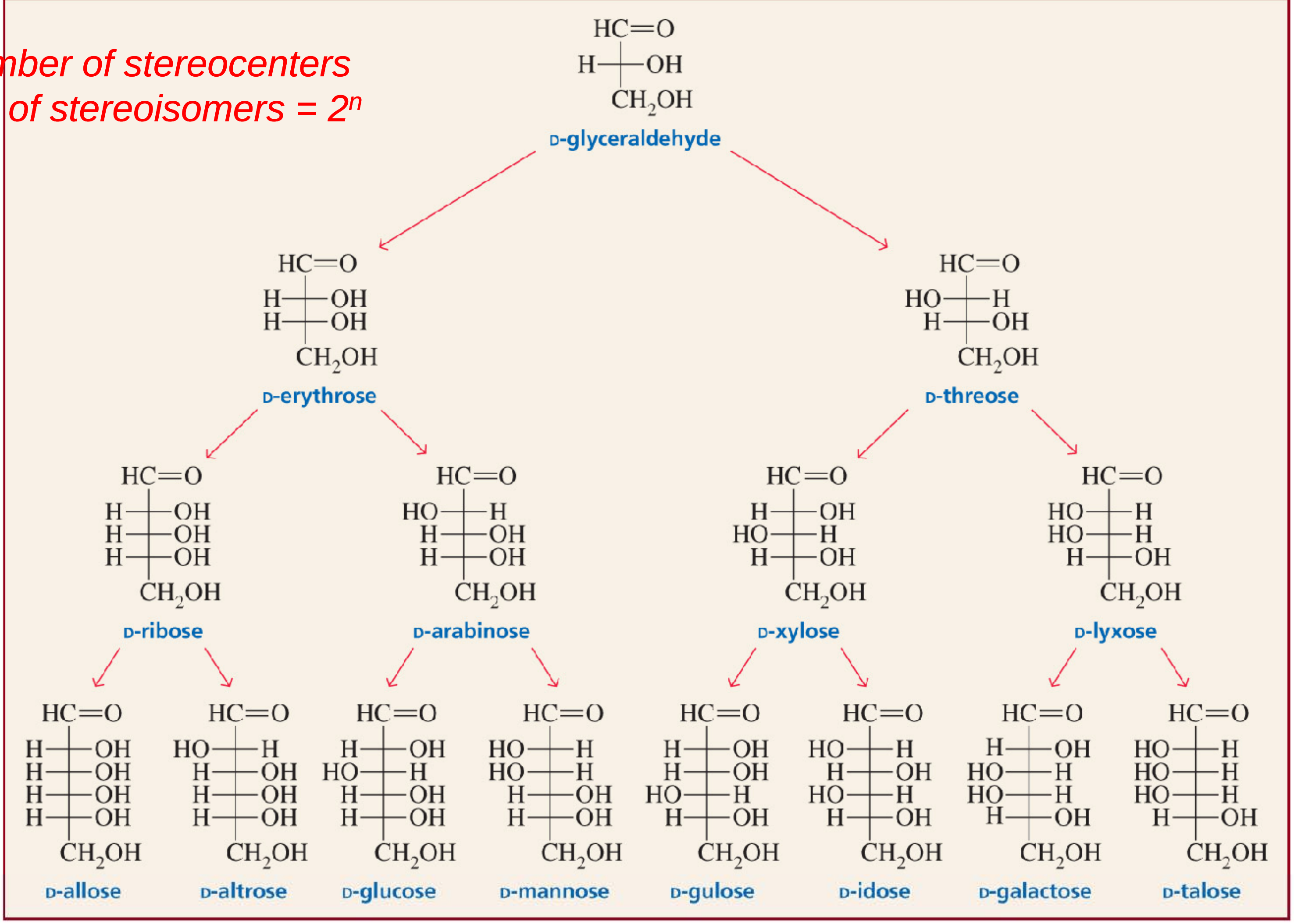




Configurations of D-Aldose

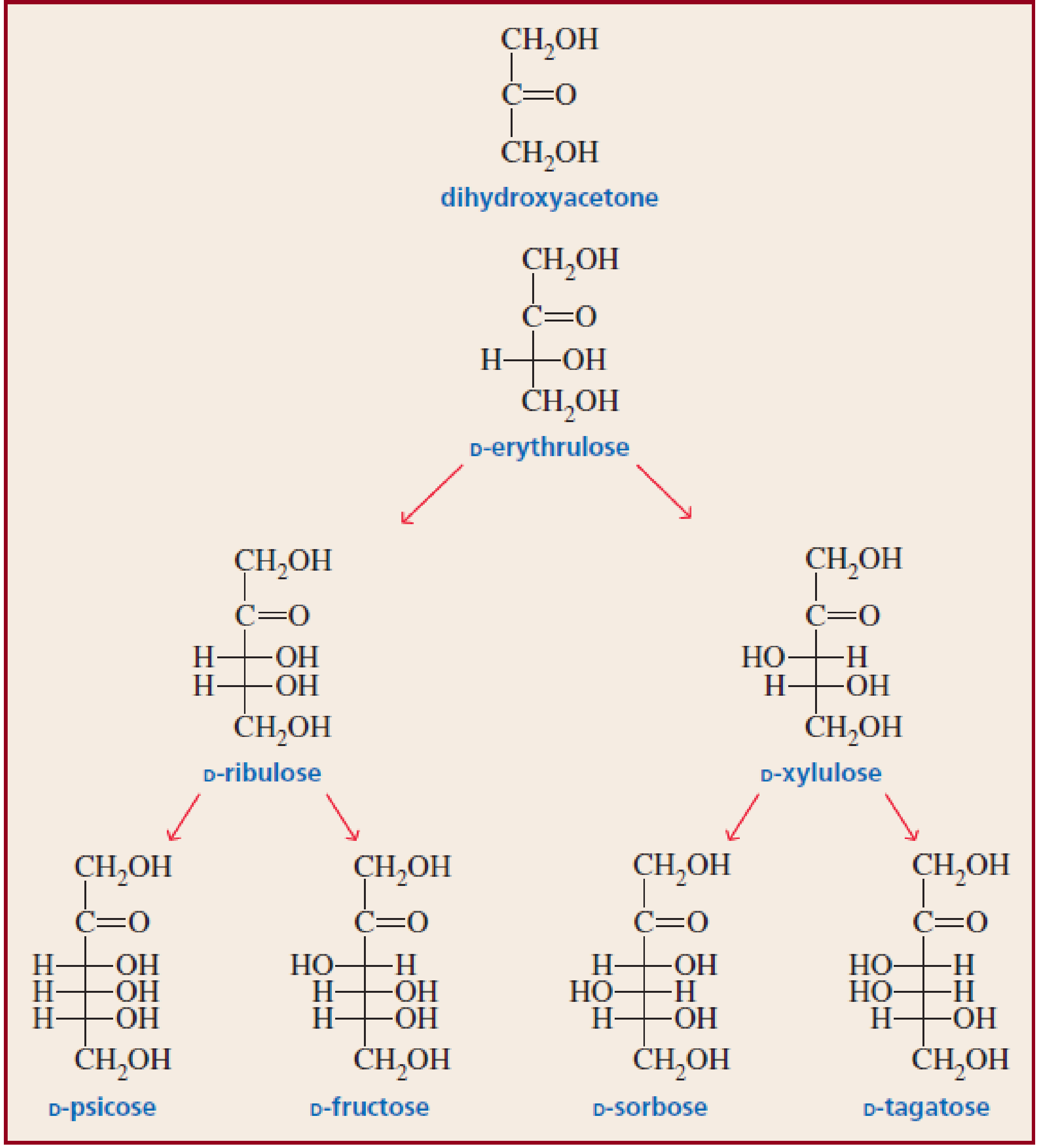
n is number of stereocenters
Number of stereoisomers = 2^n

Table 21.1 Configurations of the D-Aldoses



Configurations of Ketose

Table 21.2 Configurations of the D-Ketoses



- Comparing to aldoses, ketoses have one less chiral carbon center
- For example:
  - Aldohexoses such as glucose have 4 chiral centers, so 2^4 diastereoisomers
  - Ketohexoses such as fructose have only 3 chiral centers, so 2^3 diastereoisomers.

Practice Problem

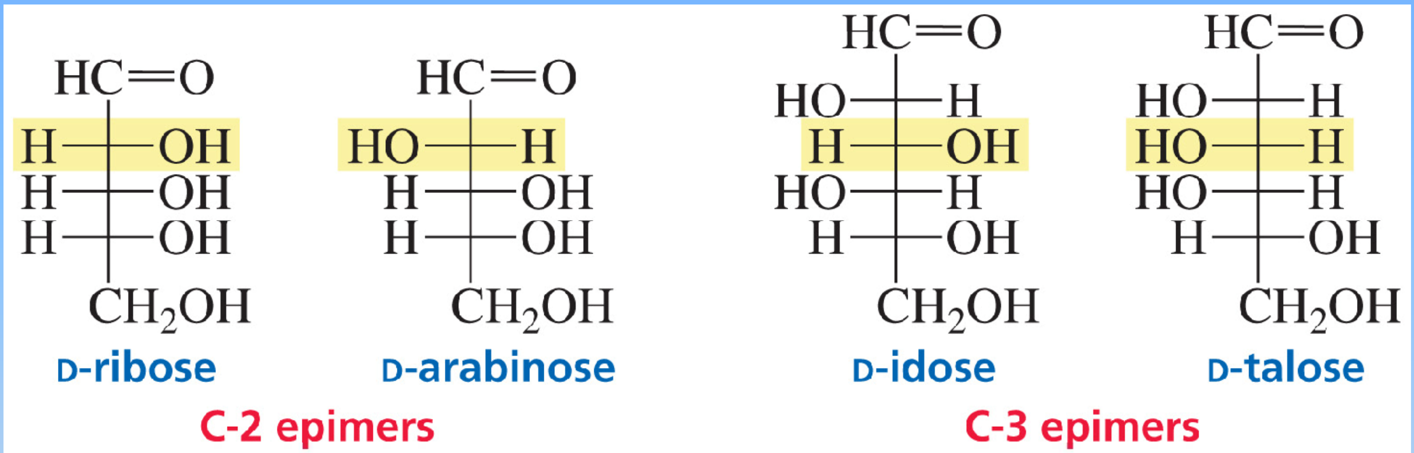
How many stereoisomers are possible for

a. 2-ketoheptose

b. an aldoheptose

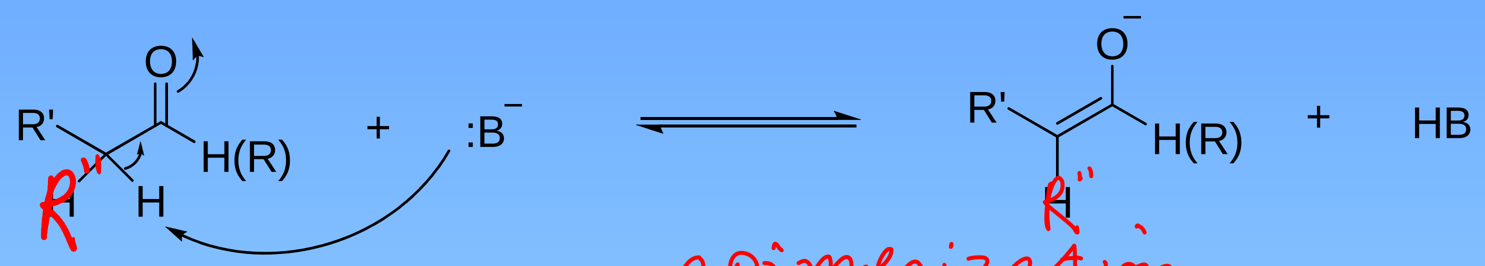
Stereochemistry: Epimers

- Epimers: diastereomers that differ in configuration at only one asymmetric center

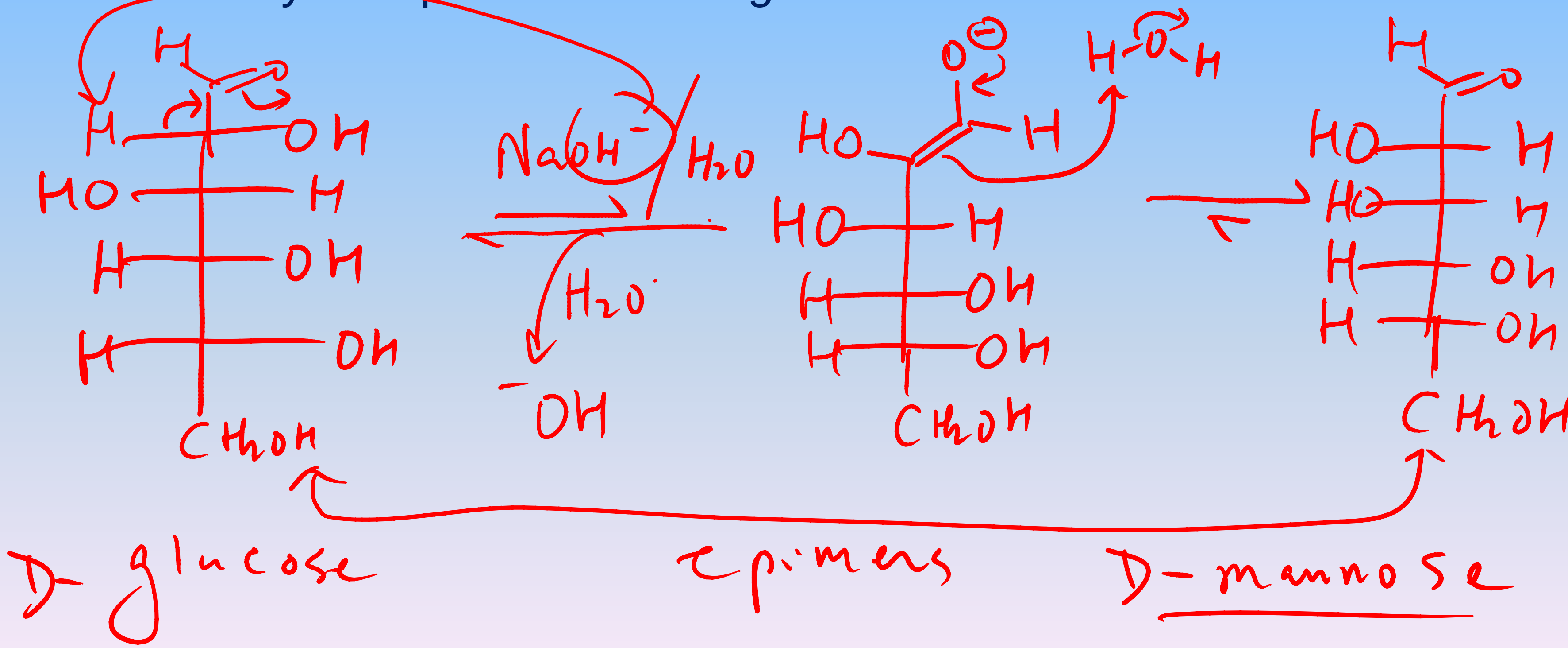


Reactions of Monosaccharides: Basic Conditions

- Typical reactivities of aldehydes/ketones under basic conditions

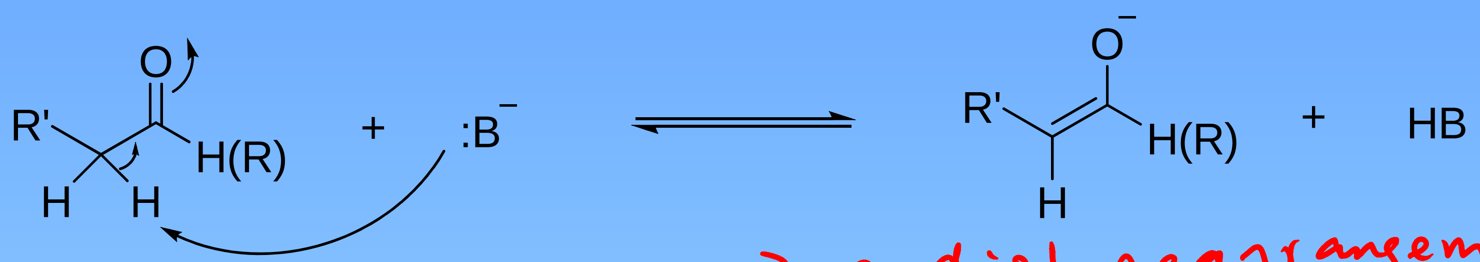


- base-catalyzed epimerization: *D-glucose and D-mannose*



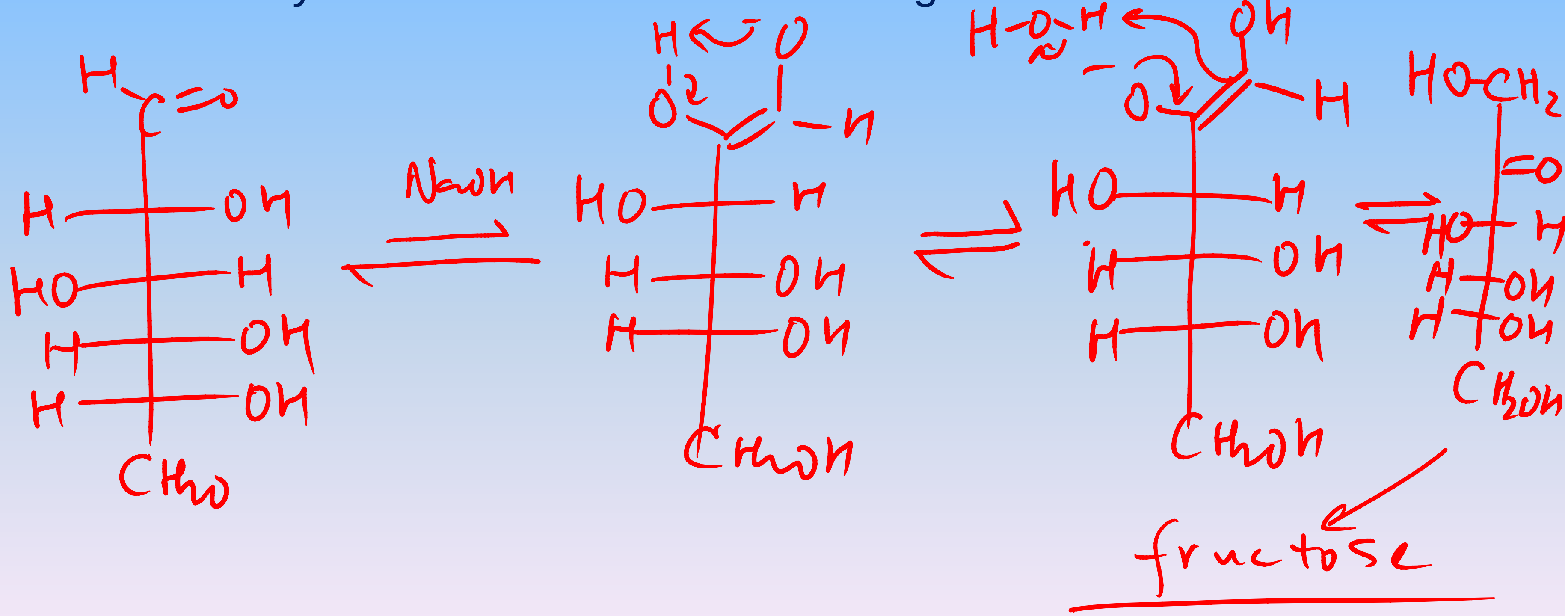
Reactions of Monosaccharides: Basic Conditions

- Typical reactivities of aldehydes/ketones under basic conditions



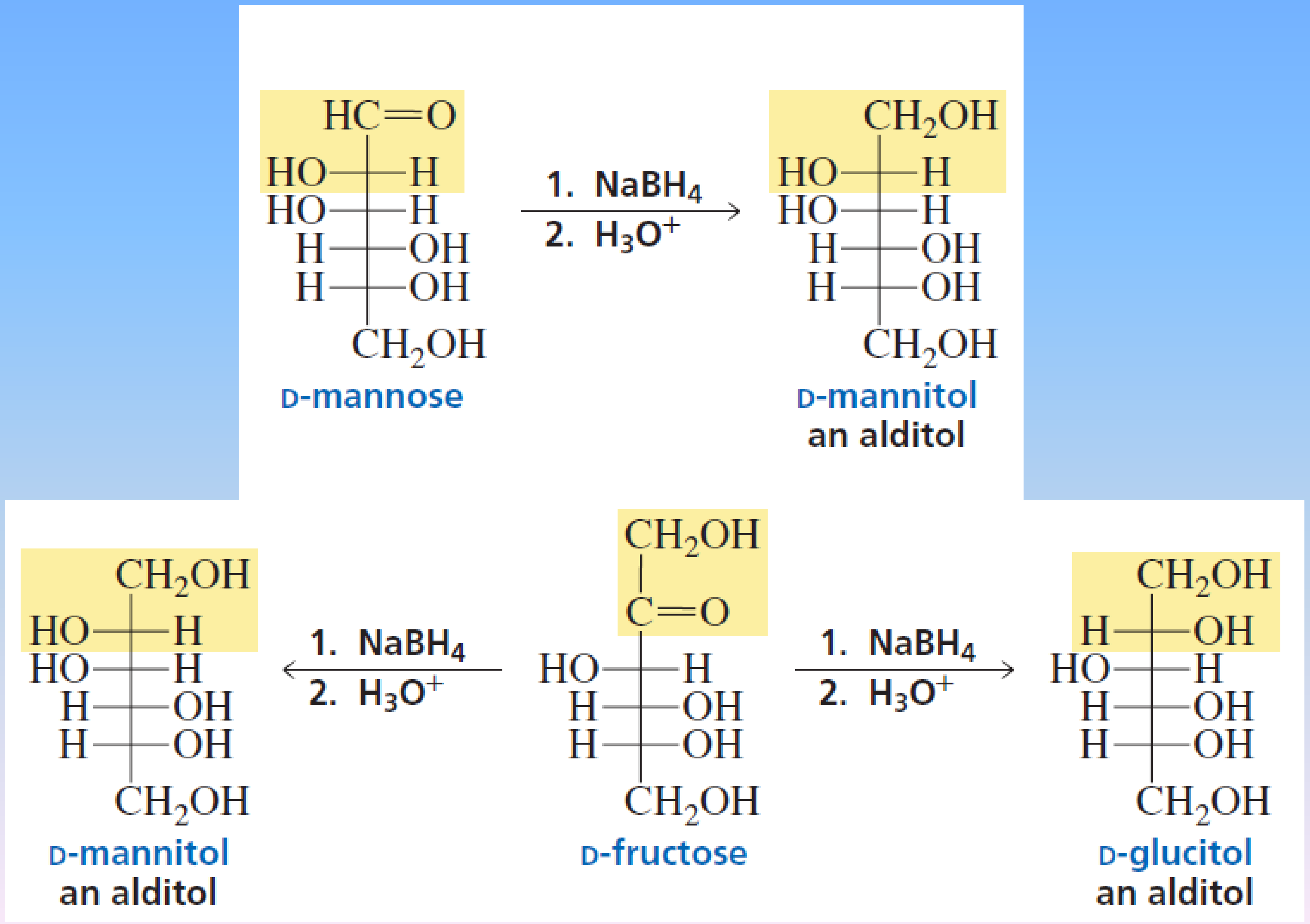
endiol rearrangement

- base-catalyzed isomerization between D-glucose and D-fructose



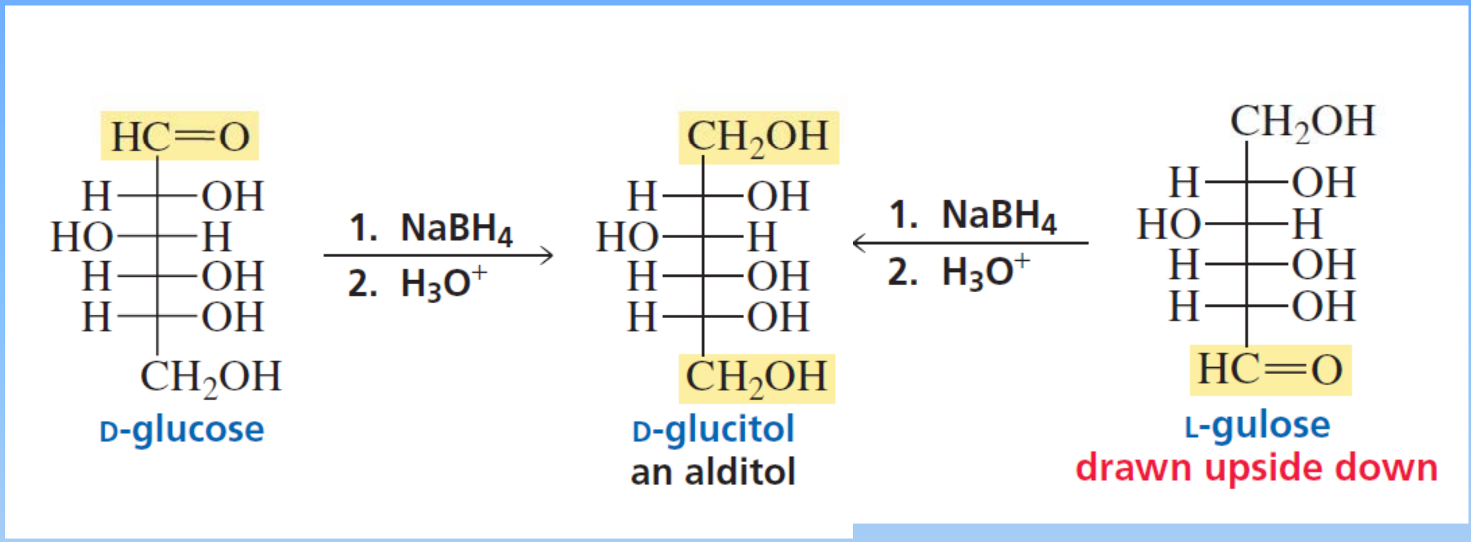
Reactions of Monosaccharides: Reduction

- Reduction of an aldose forms an alditol
- Reduction of a ketose, however, form two alditols.



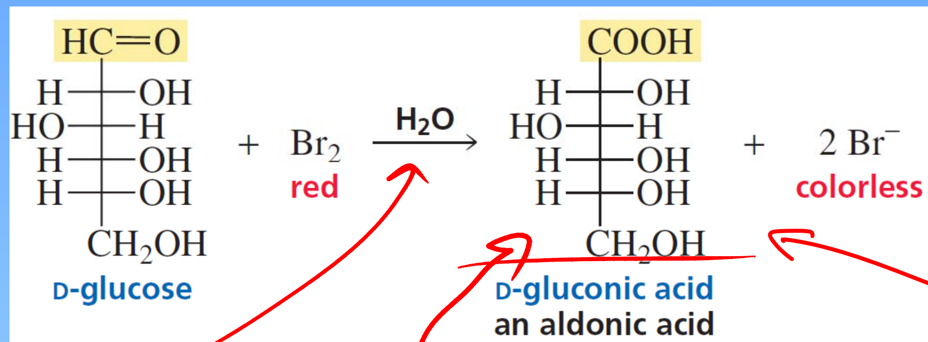
Reactions of Monosaccharides: Reduction

- One alditol can be formed via reduction of two different aldose



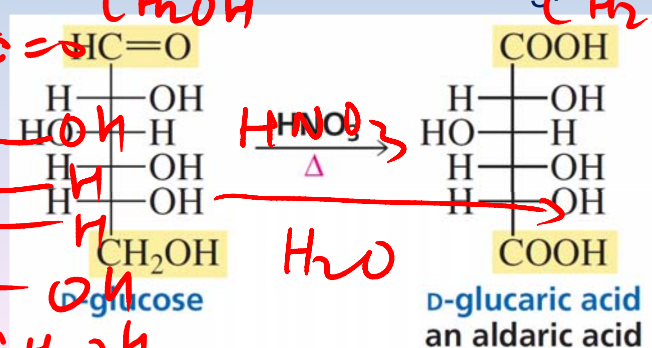
Reactions of Monosaccharides: Oxidation

- Br_2 in H_2O: only oxidize aldoses into aldonic acids (not oxidizing ketose)



- Ag^+, NH_3, OH^- (tollens' reagent– named after Bernhard Tollens)
  - Both ketoses and aldose are oxidized.

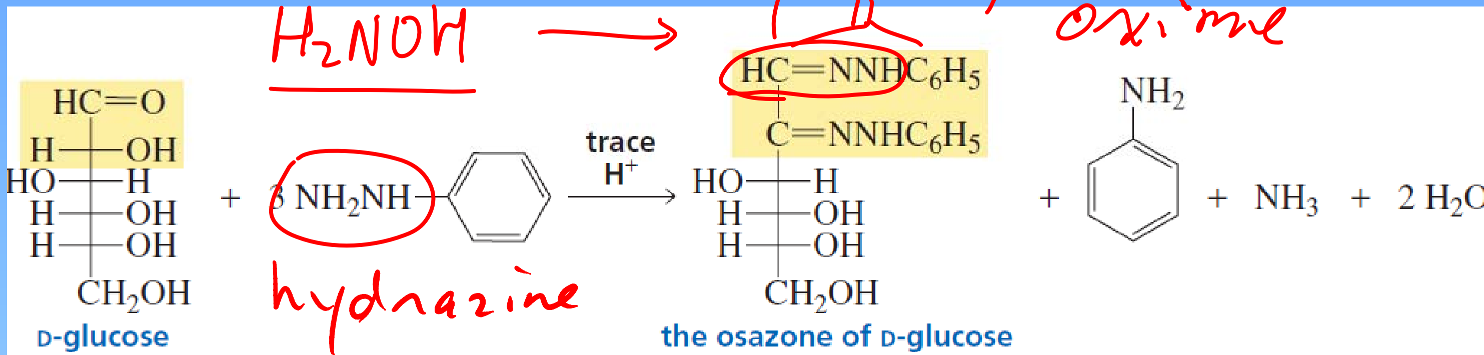
- Stronger oxidants such as HNO_3, 1° OH group could be oxidized.



Aldonic acid
Aldaric acid

Reactions of Monosaccharides: Osazones

- Reaction of aldose/ketose with hydrazine to form crystalline osazone



- Which monosaccharides can form the following osazone?