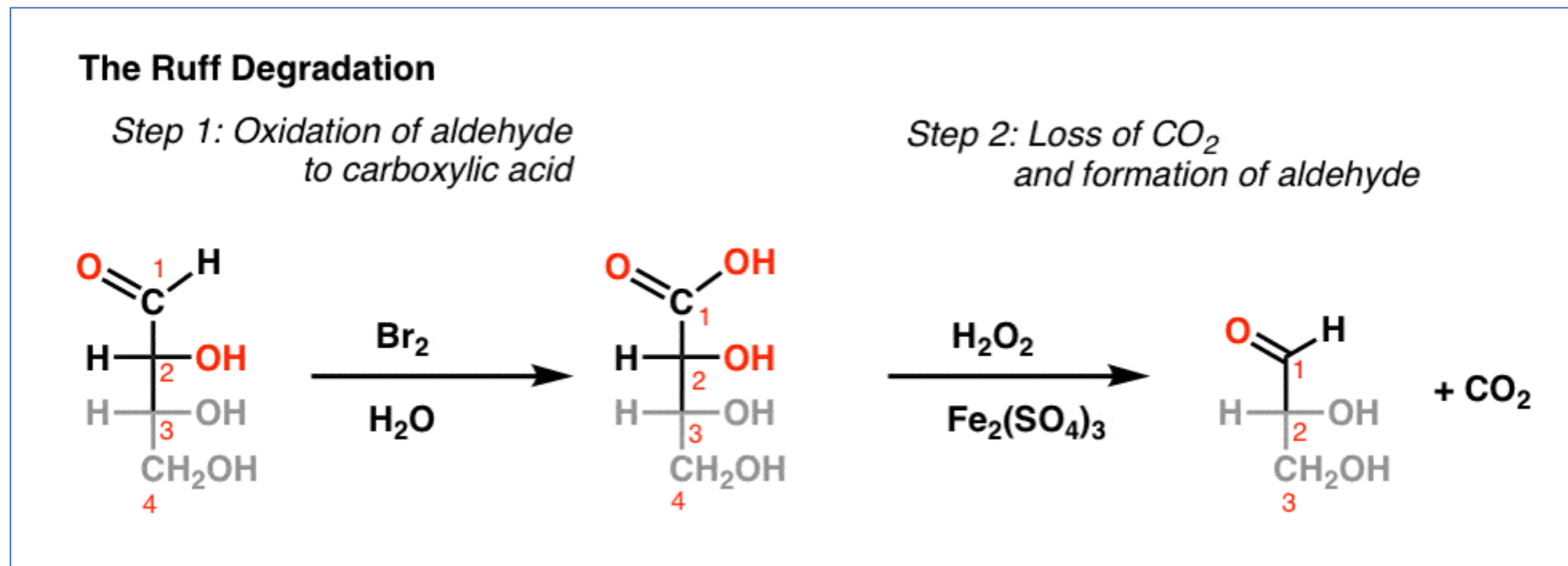


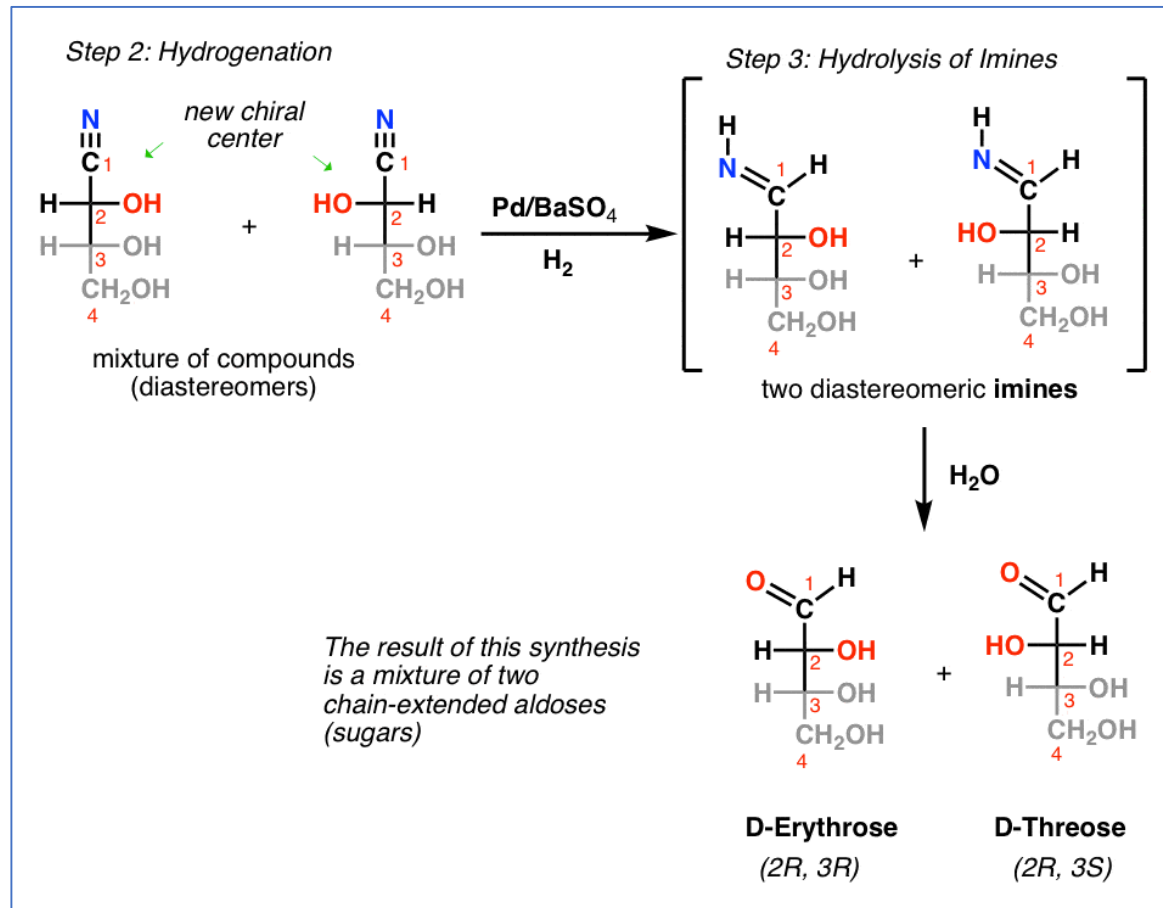
## The Ruff Degradation

- Aldose chain is shortened by oxidizing the aldehyde to  $-\text{COOH}$ , then decarboxylation. In the Ruff degradation, the calcium salt of an aldonic acid is oxidized with hydrogen peroxide.
- Ferric ion catalyzes the oxidation reaction, which cleaves the bond between C-1 and C-2, forming an aldehyde.
- The calcium salt of the aldonic acid prepared from oxidation of an aldose with an aqueous solution of bromine and then adding calcium hydroxide to the reaction mixture.



## The Kiliani–Fischer Synthesis

- ❖ The Kiliani-Fischer Synthesis is a method for extending a carbohydrate chain by a single carbon.
- ❖ The Kiliani-Fischer Synthesis involves addition of cyanide ion to an open-chain aldehyde (in the case of aldoses) which is then partially reduced and then hydrolyzed to give a new aldehyde.
- ❖ In the absence of chiral reagents, a mixture of diastereomers will be produced.



## Disaccharides

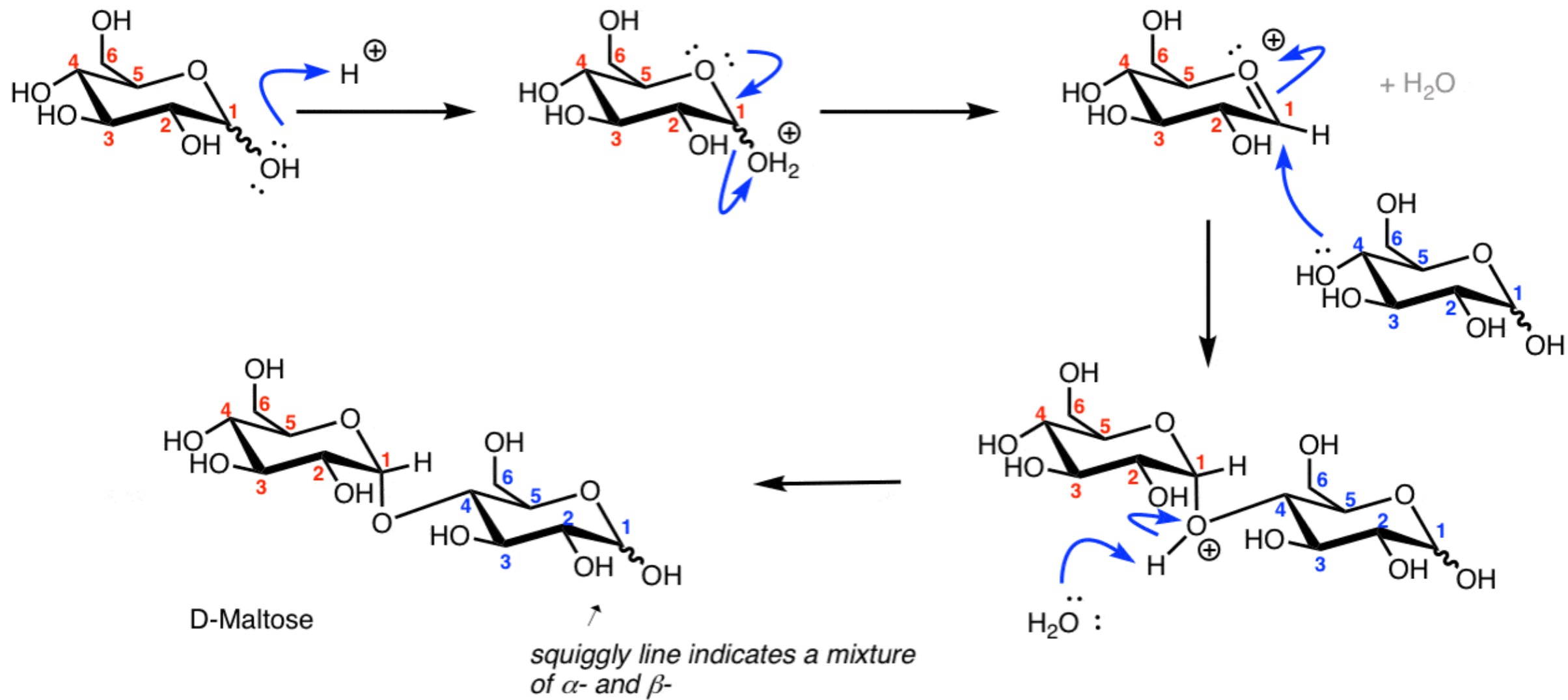
- ❖ If the glycoside or acetol is formed by reaction of the anomeric carbon of a monosaccharide with OH group of another monosaccharide molecule, then the glycoside product is a disaccharide
- ❖ The anomeric carbon can react with any of the hydroxyl groups of another monosaccharide unit to form a disaccharide.
- ❖ Disaccharides can be categorized by the position of the hydroxyl group of another monosaccharide making up the glycoside.

Disaccharides have *three* naturally occurring glycosidic linkages

- ❖ 1-4' link: The anomeric carbon is bonded to oxygen on C-4 of second monosaccharide.
- ❖ 1-6' link: The anomeric carbon is bonded to oxygen on C-6 of second monosaccharide.
- ❖ 1-2' link: The anomeric carbons of the two monosaccharide unit are bonded through an oxygen.

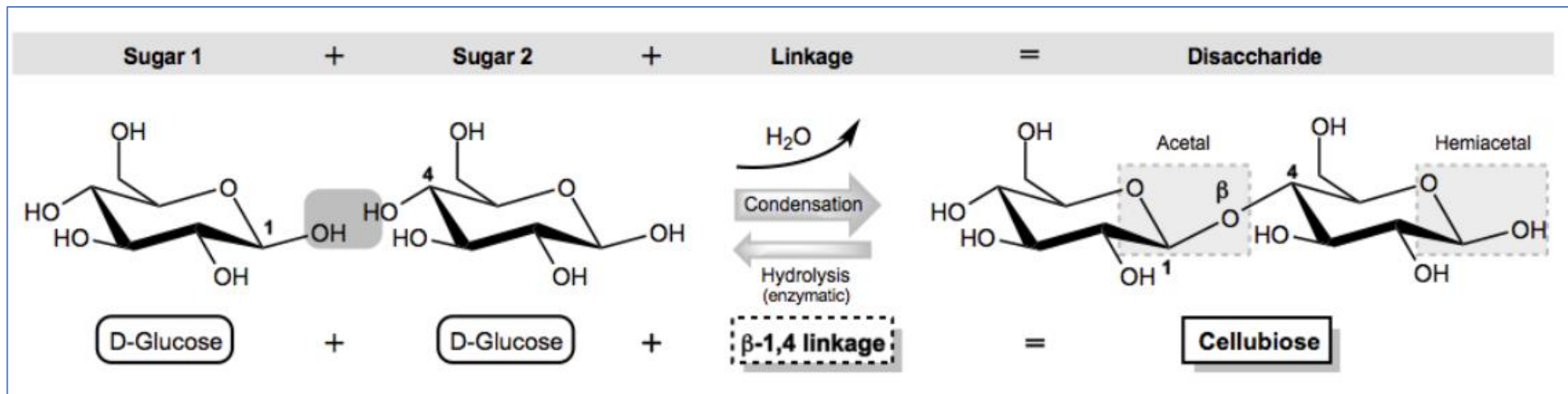
The “prime” superscript indicates that –OH group bonded carbon position of the second monosaccharide unit,  $\alpha$ - and  $\beta$ -configuration given by based on the configuration at the anomeric carbon of the first monosaccharide unit.

## Maltose formation from two equivalents of glucose - mechanism

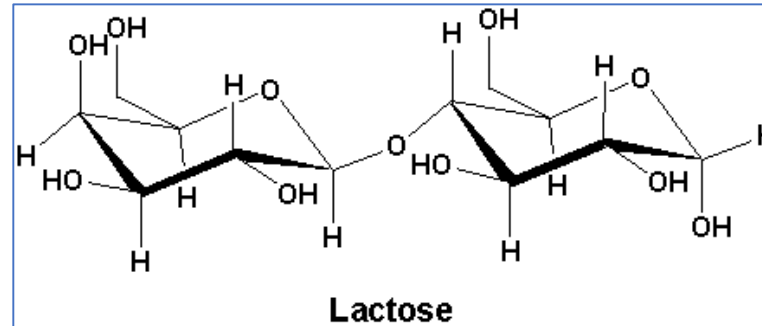


**1-4' Glycosides:** These represent the most common naturally occurring disaccharides. The linkage is between C-1 of one sugar subunit and C-4 of the other. For example, *maltose* is a disaccharide with two D-glucose units bearing 1,4'-glycosidic linkage. The stereochemistry of this linkage is  $\alpha$ . So, the glycosidic linkage is called  $\alpha$ -1,4'-glycosidic linkage.

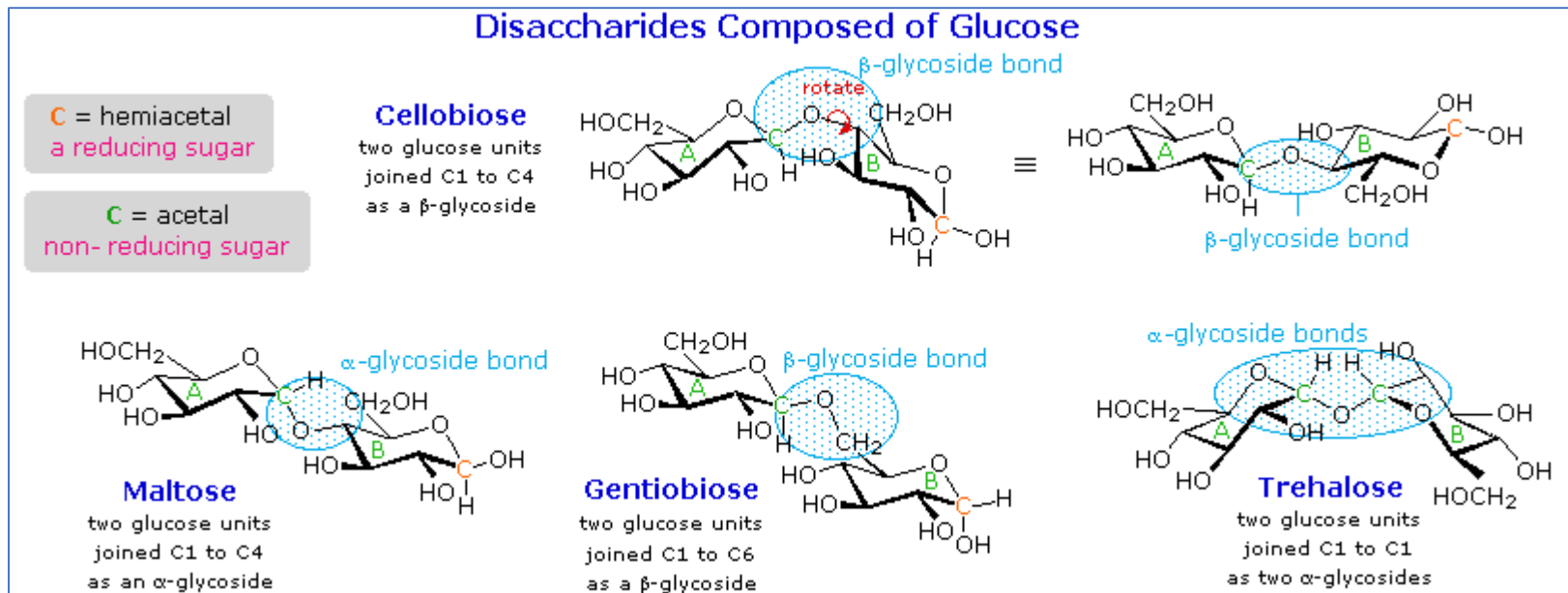
*Cellobiose* also contains two D-glucose subunits. The only difference from maltose is that the two glucose subunits are joined through a  $\beta$ -1,4'-glycosidic linkage.



*Lactose*, a disaccharide present in milk, contains D-galactose (non-reducing) and D- glucose (reducing) monosaccharide units. These units are hooked together by a  $\beta$ -1,4'- glycosidic linkage.



**1-6' Glycosides:** The anomeric carbon of one unit hooked by the oxygen of the terminal carbon (C-6) of another monosaccharide unit. Example, *gentiobiose* is a sugar with two glucose units joined by a  $\beta$ -1,6'-glucosidic linkage.



**1-2' Glycosides:** The glycosidic bond is hooked between the two anomeric carbon of the monosaccharide units. For example, *sucrose* contains a D-glucose subunit and a D-fructose subunit, which have been joined by a glycosidic bond between C-1 of glucose (in the  $\alpha$ -position) and C-2 of fructose (in the  $\beta$ -position).

