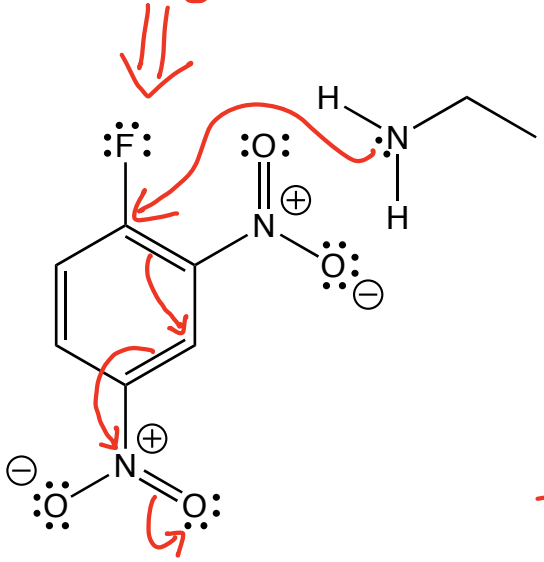
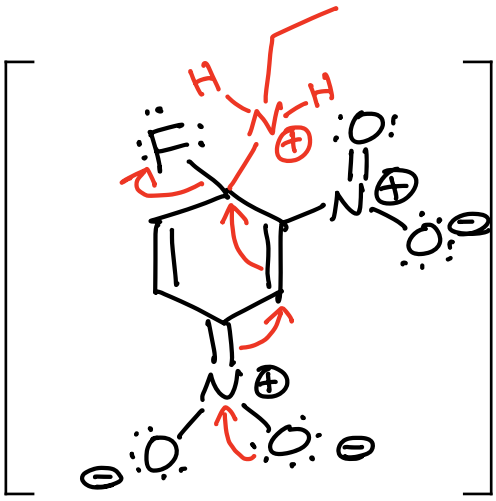
Nucleophilic Aromatic Substitution Module

VERY electron deficient aromatic ring because of all the electron withdrawing groups

Nucleophilic Aromatic Substitution



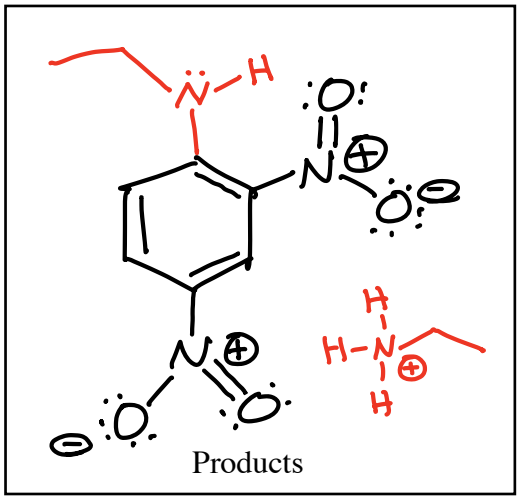
Make a bond



Meisenheimer complex

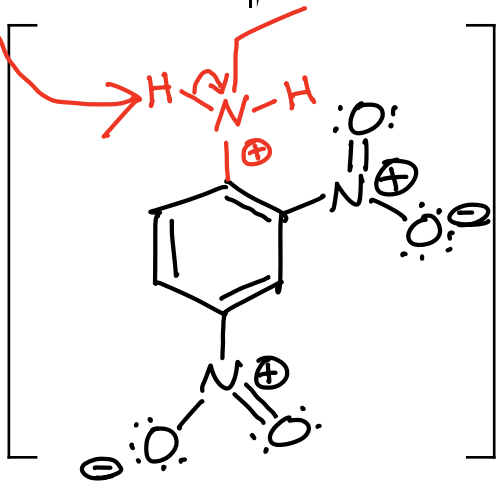
The timing of this last deprotonation step is uncertain

Break a bond



Products

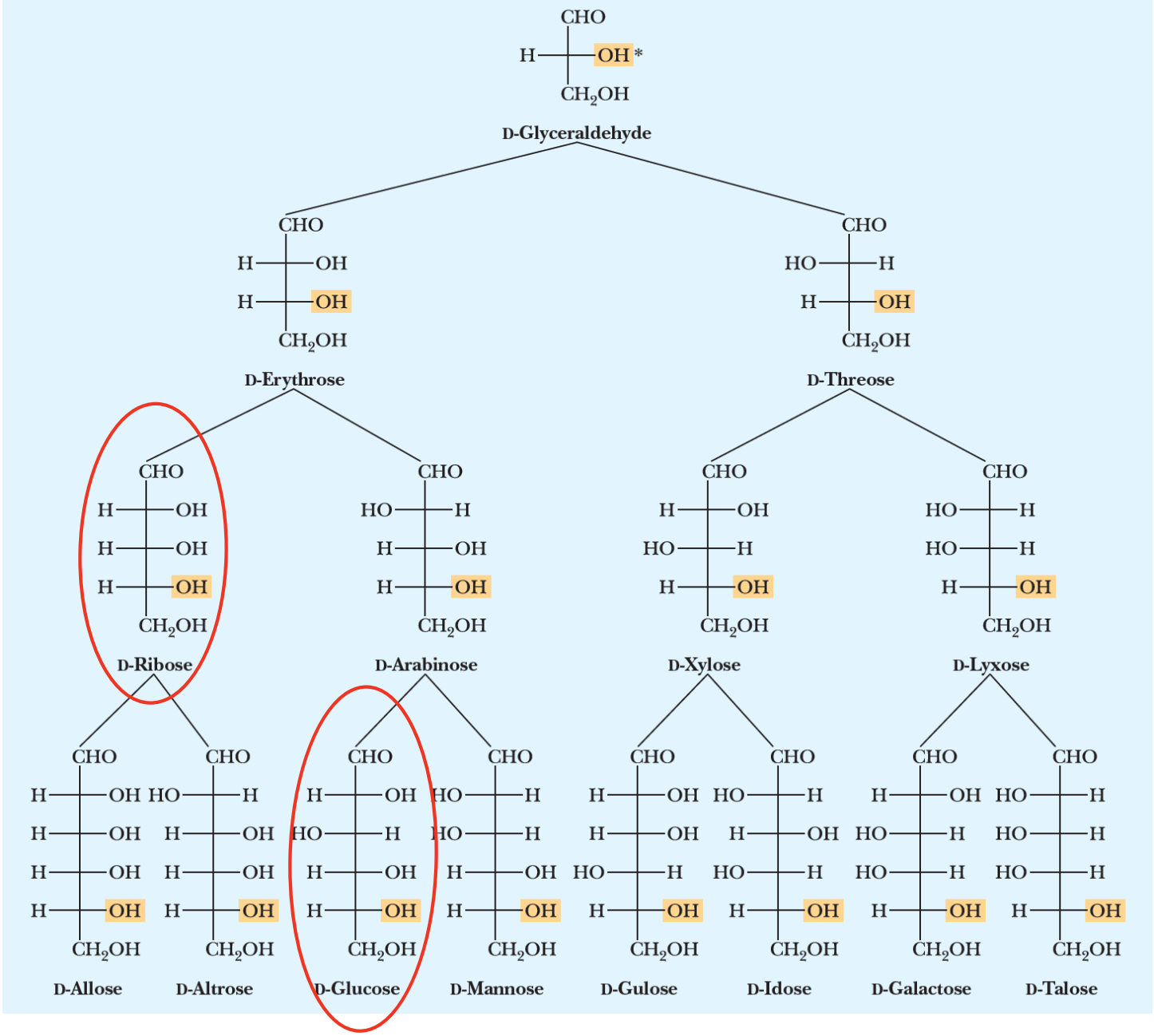
Take a Proton Away



This reaction is relatively rare, and this is the only example you will see in this class

Carbohydrate Chemistry Module 1

Table 25.1 Configurational Relationships Among the Isometric D-Aldotetroses, D-Aldopentoses, and D-Aldohexoses



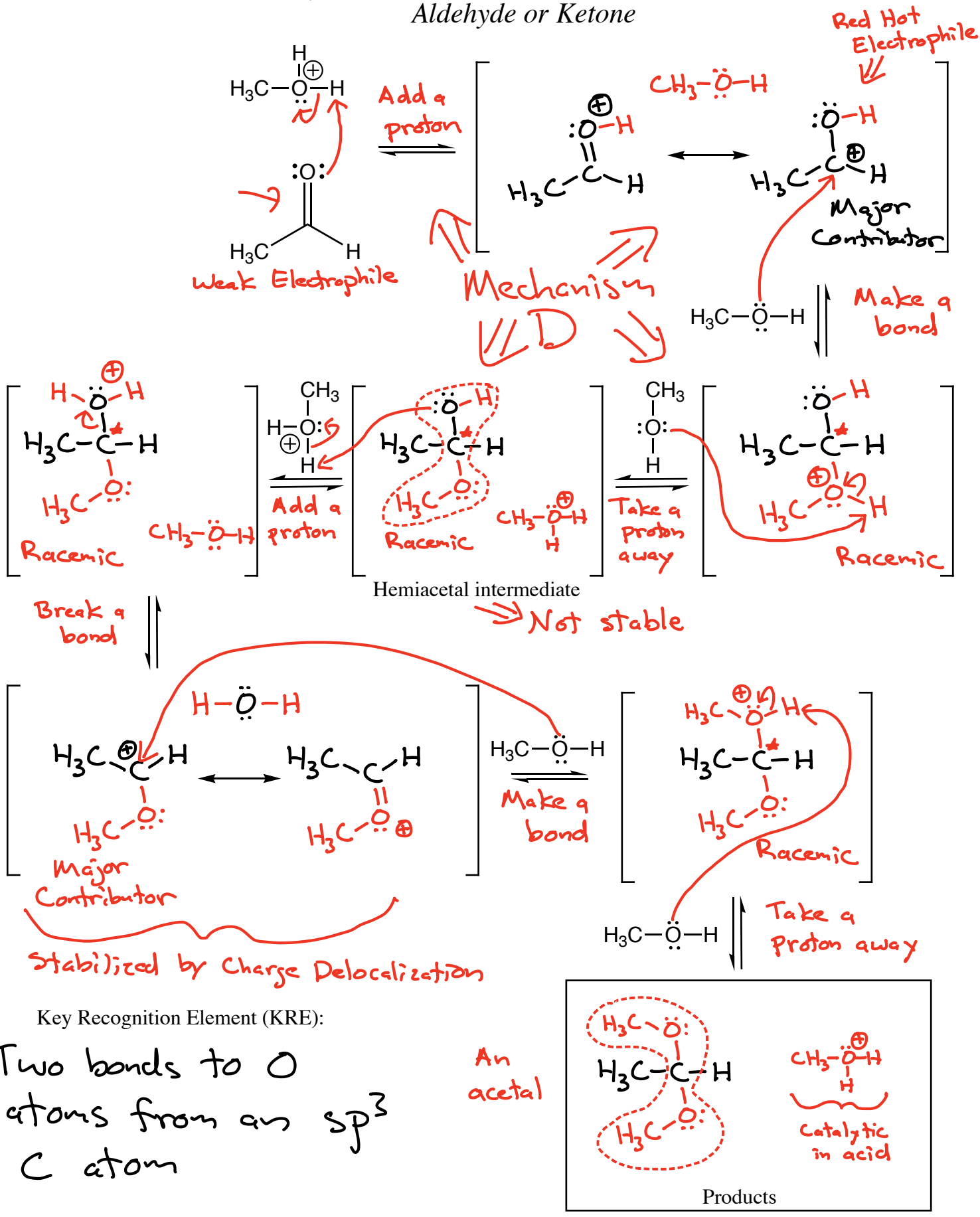
Alpha Is Axial

(Beta is equatorial)

H_2SO_4

"Hey, does that thing have a hemi in it?" "SWEET!" !

Acid Catalyzed Hemiacetal and Acetal Formation From an Aldehyde or Ketone

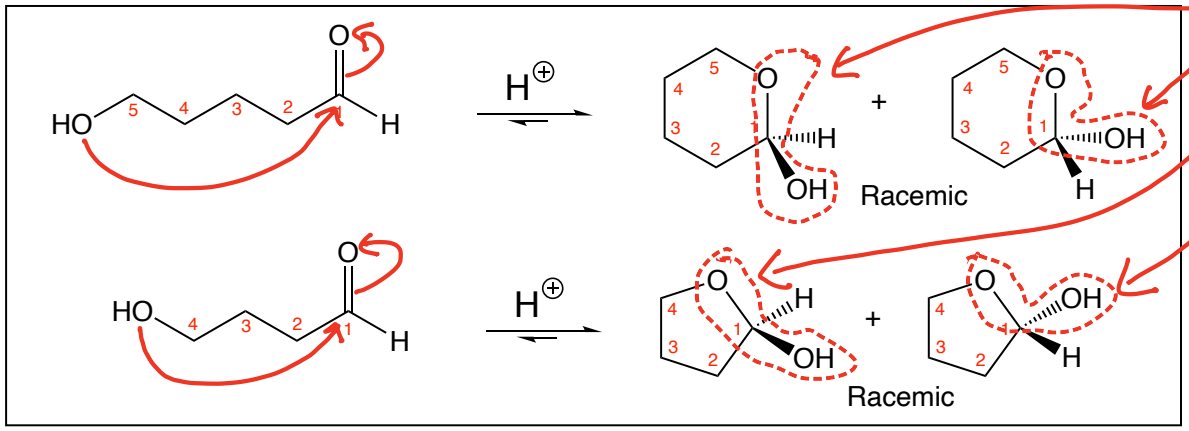


Key Recognition Element (KRE):

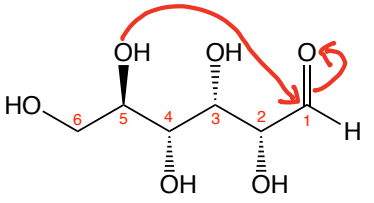
Two bonds to O atoms from an sp^3 C atom

Cyclic Hemiacetals and Carbohydrates

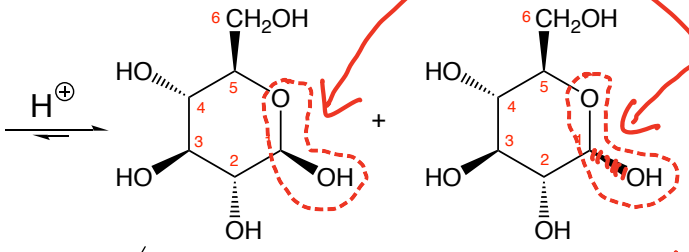
Cyclic hemiacetals



The cyclic form of hemiacetals are stable-"SWEET!"
→ The chelate effect



D-**Glucose**
(open chain form)

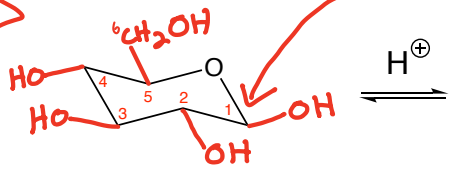


Cyclic Hemiacetals

"SWEET!"

Anomeric Carbon

This interconversion is called "mutarotation"

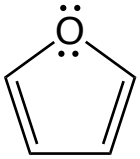


β-D-**Glucose** α-D-**Glucose**

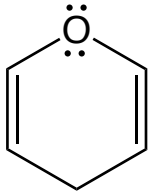
Biochemists call these two forms "anomers"

More stable → every group is equatorial!

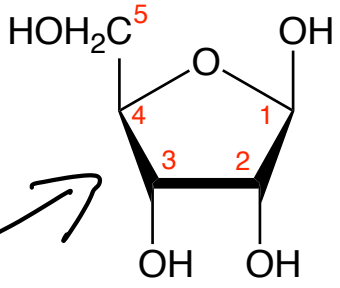
Less stable → one -OH is axial



Furan



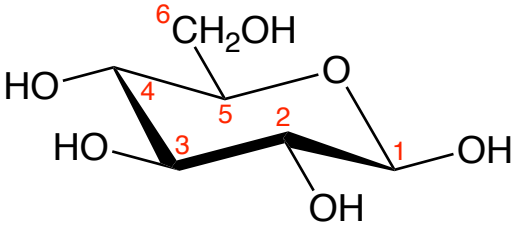
Pyran



A furanose

β-D-Ribose

or β-D-Ribofuranose

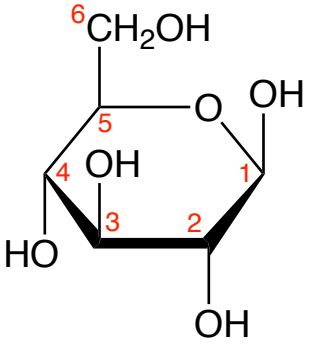


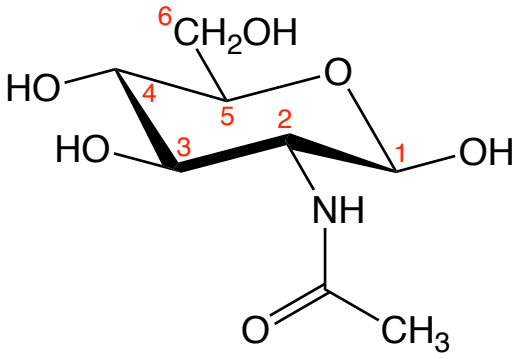
A pyranose

β-D-Glucose

or β-D-Glucopyranose

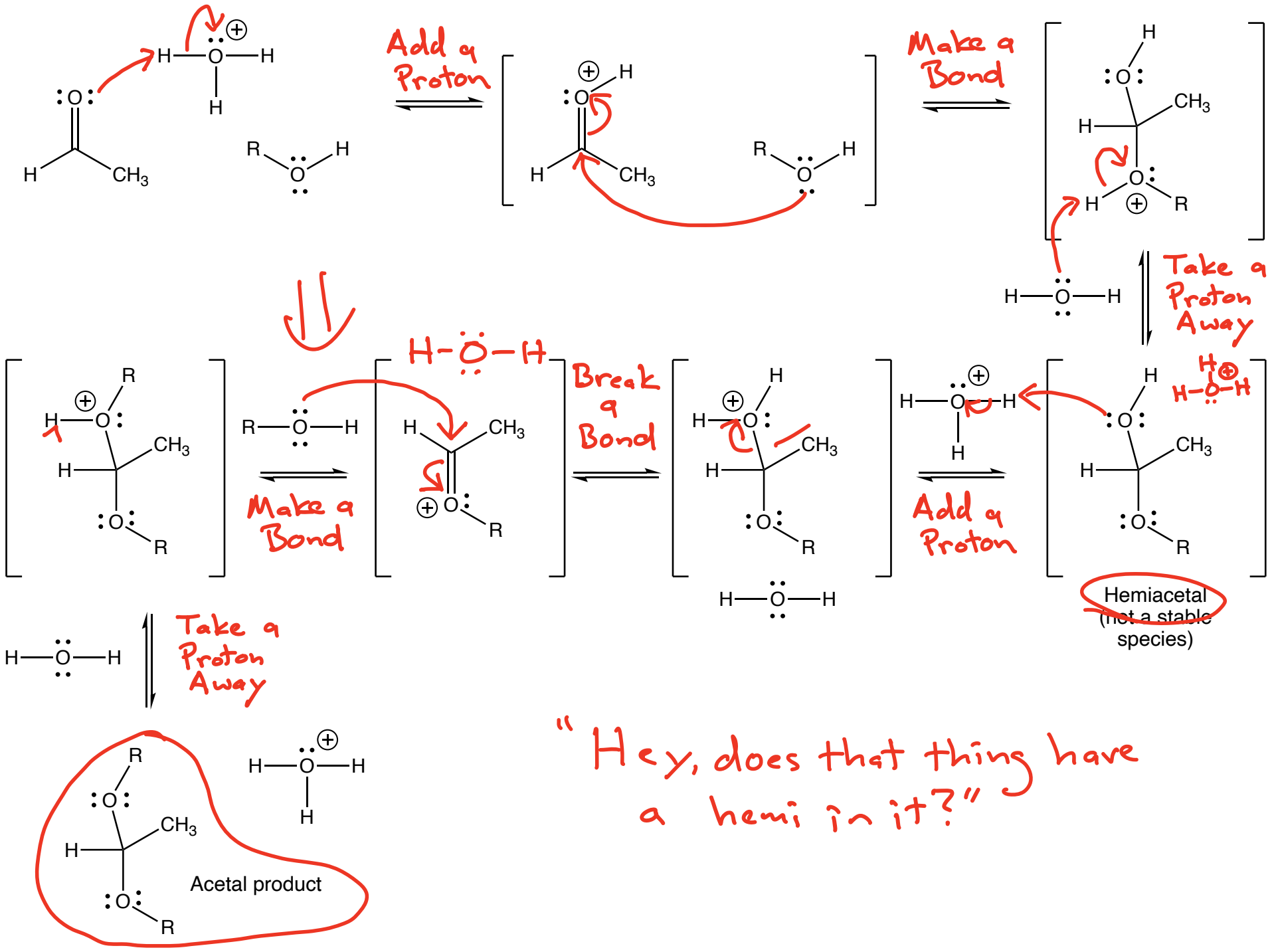
This is called a Haworth projection

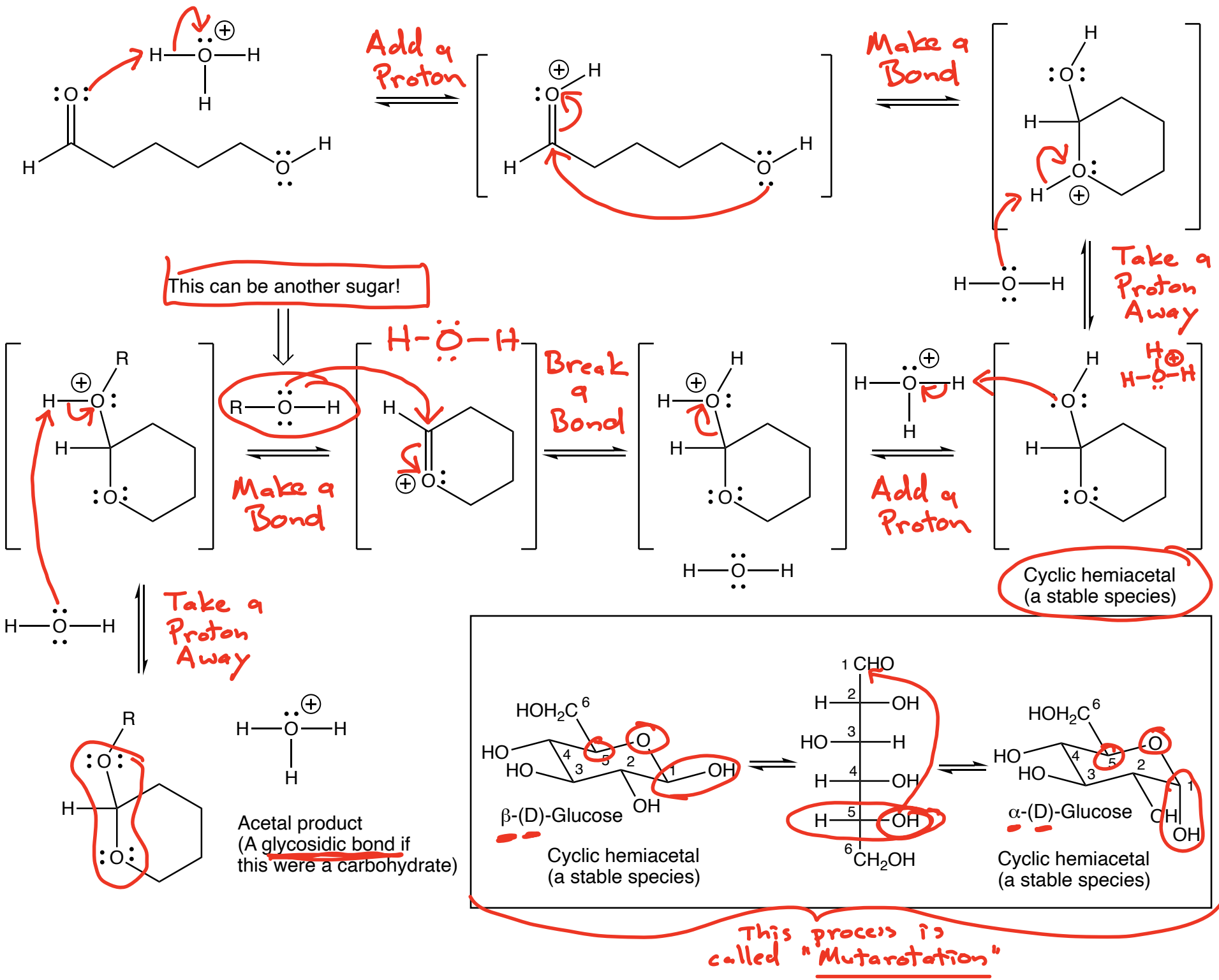


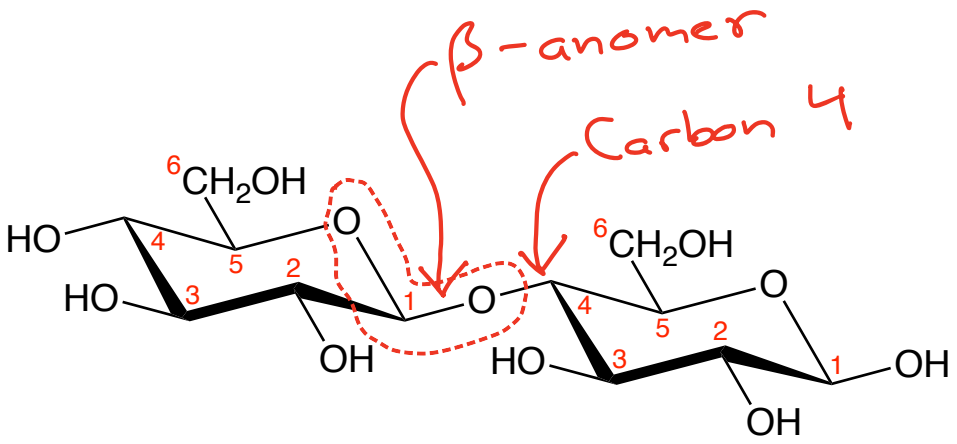


N-Acetyl-D-Glucosamine
(GlcNAC)

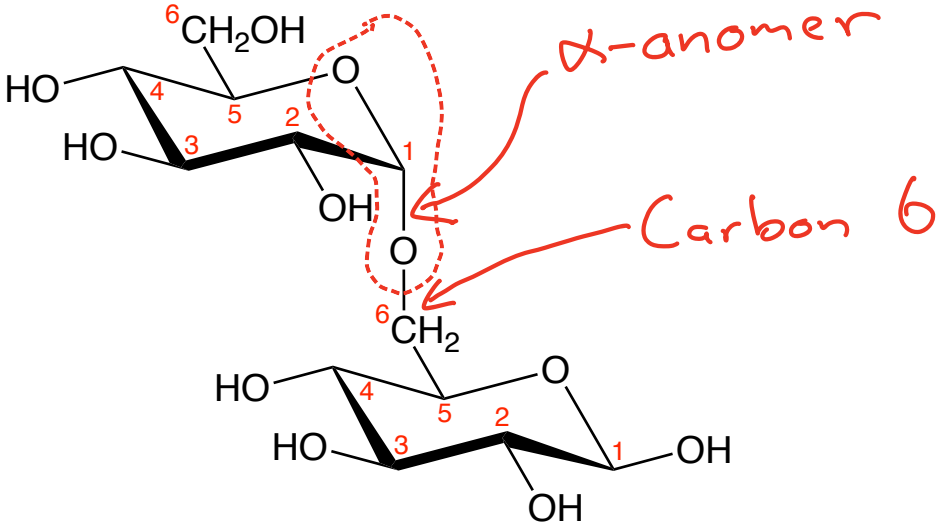
Carbohydrate Chemistry Module 2


Add a Proton
Make a Bond
Take a Proton Away
Break a Bond
Make a Bond
Add a Proton
Take a Proton Away
Hemiacetal (not a stable species)
Acetal product
"Hey, does that thing have a hemi in it?"


Add a Proton
Make a Bond
Take a Proton Away
This can be another sugar!
Make a Bond
Break a Bond
Add a Proton
Take a Proton Away
Cyclic hemiacetal (a stable species)
Acetal product (A glycosidic bond if this were a carbohydrate)
β-(D)-Glucose
Cyclic hemiacetal (a stable species)
α-(D)-Glucose
Cyclic hemiacetal (a stable species)
This process is called "Mutarotation"

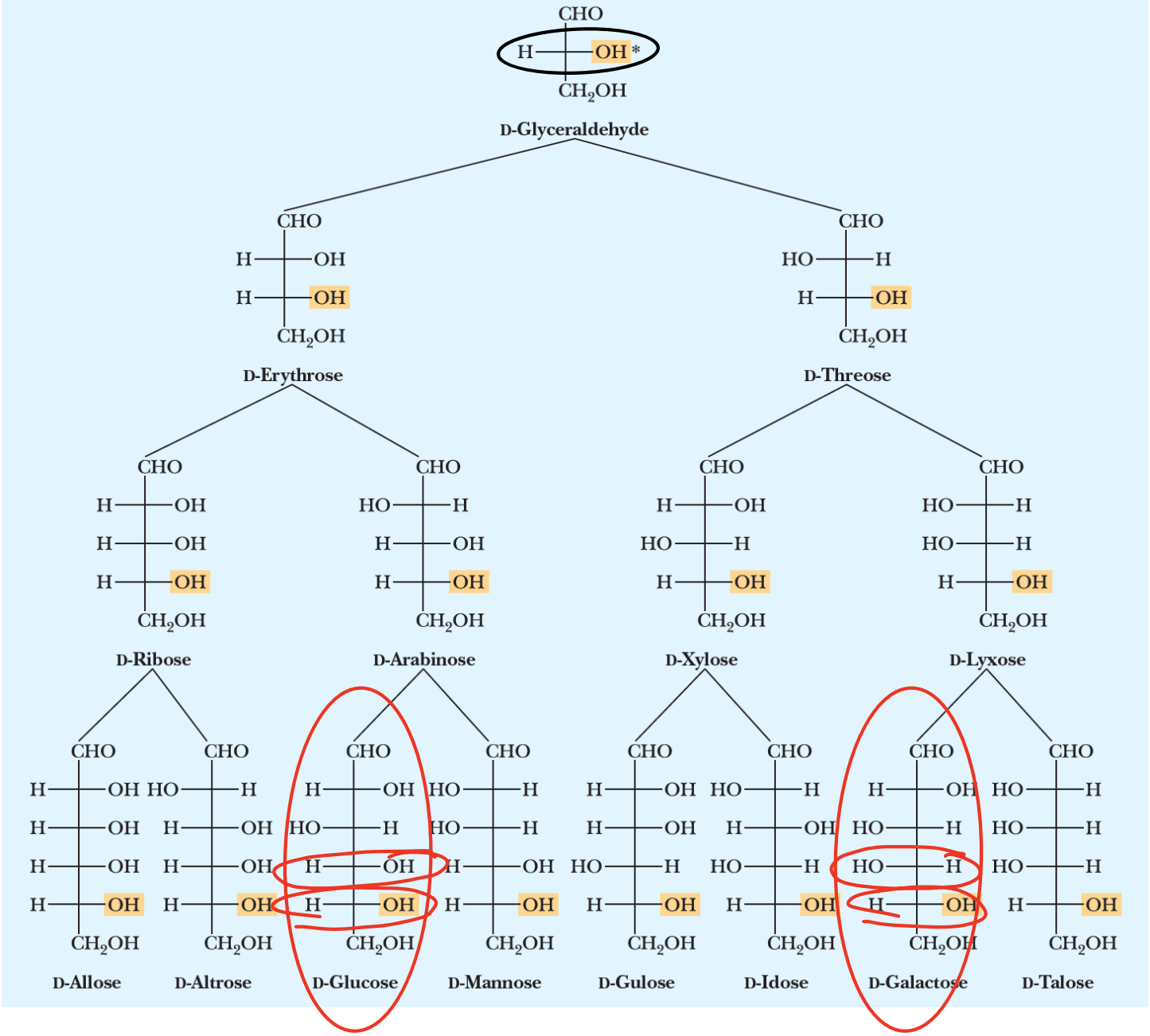


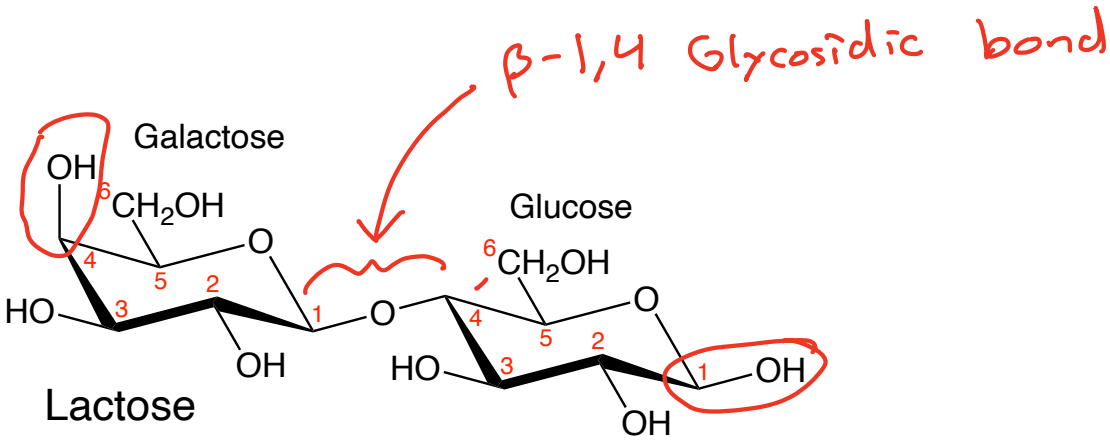
This is a β-1,4-Glycosidic Bond

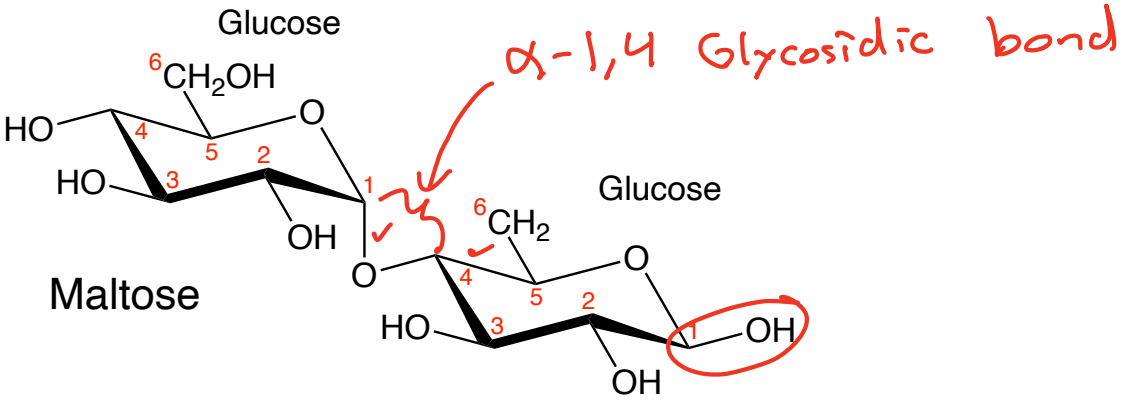


This is an α-1,6-Glycosidic Bond

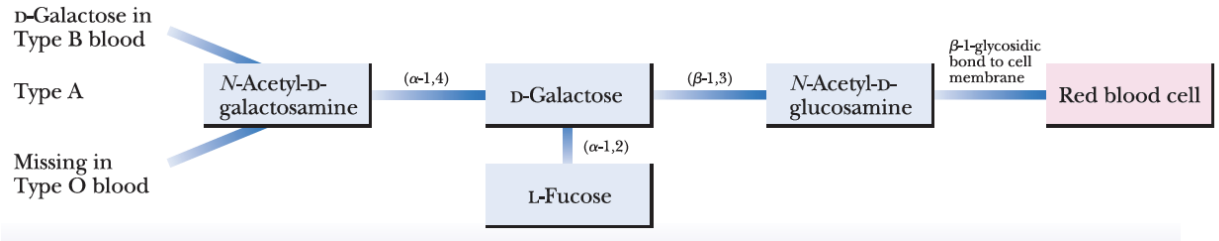
Table 25.1 Configurational Relationships Among the Isometric D-Aldotetroses, D-Aldopentoses, and D-Aldohexoses





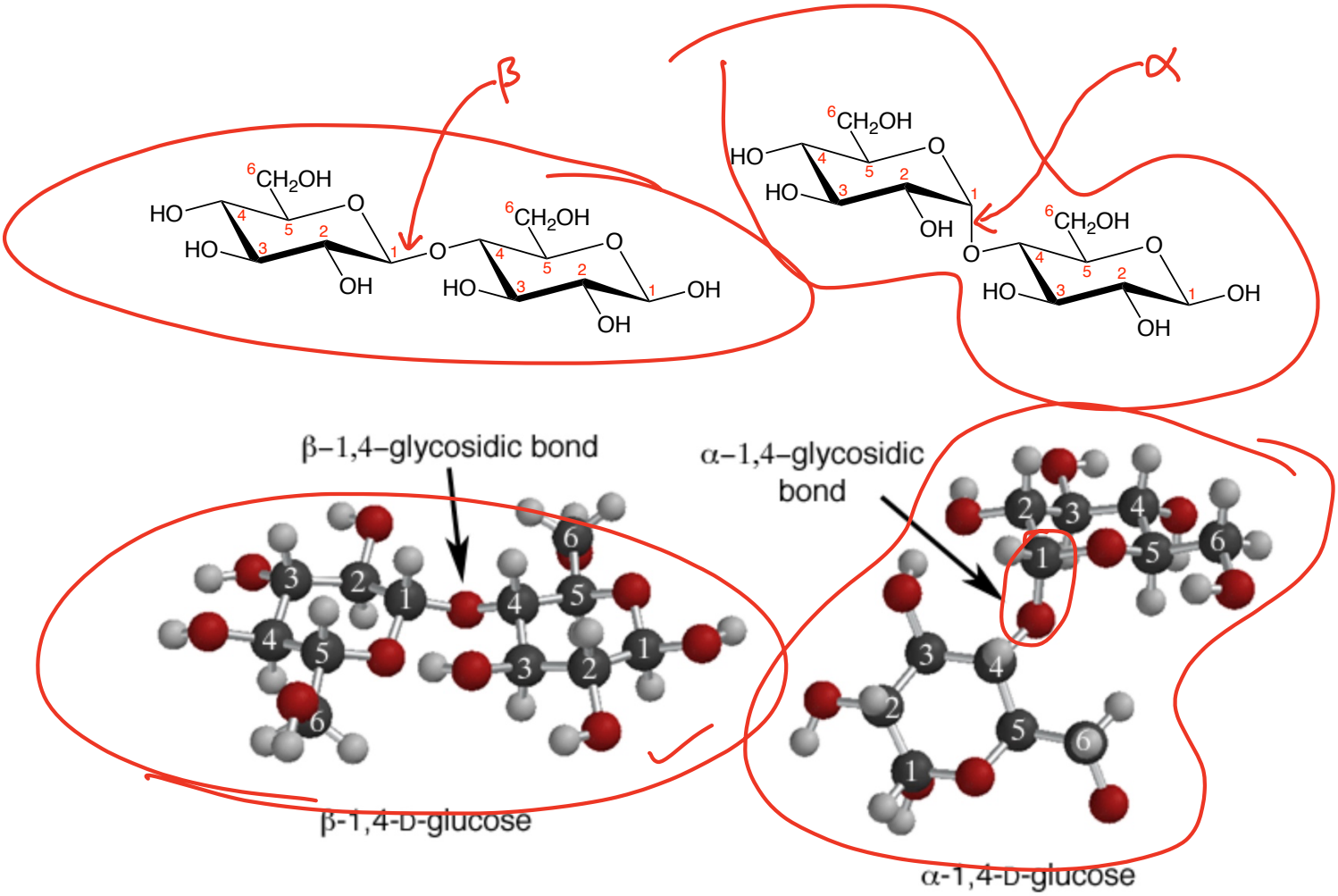


We can link more carbohydrates together, always at Carbon 1, with α or β linkages at carbons 2, 3, 4 or 6

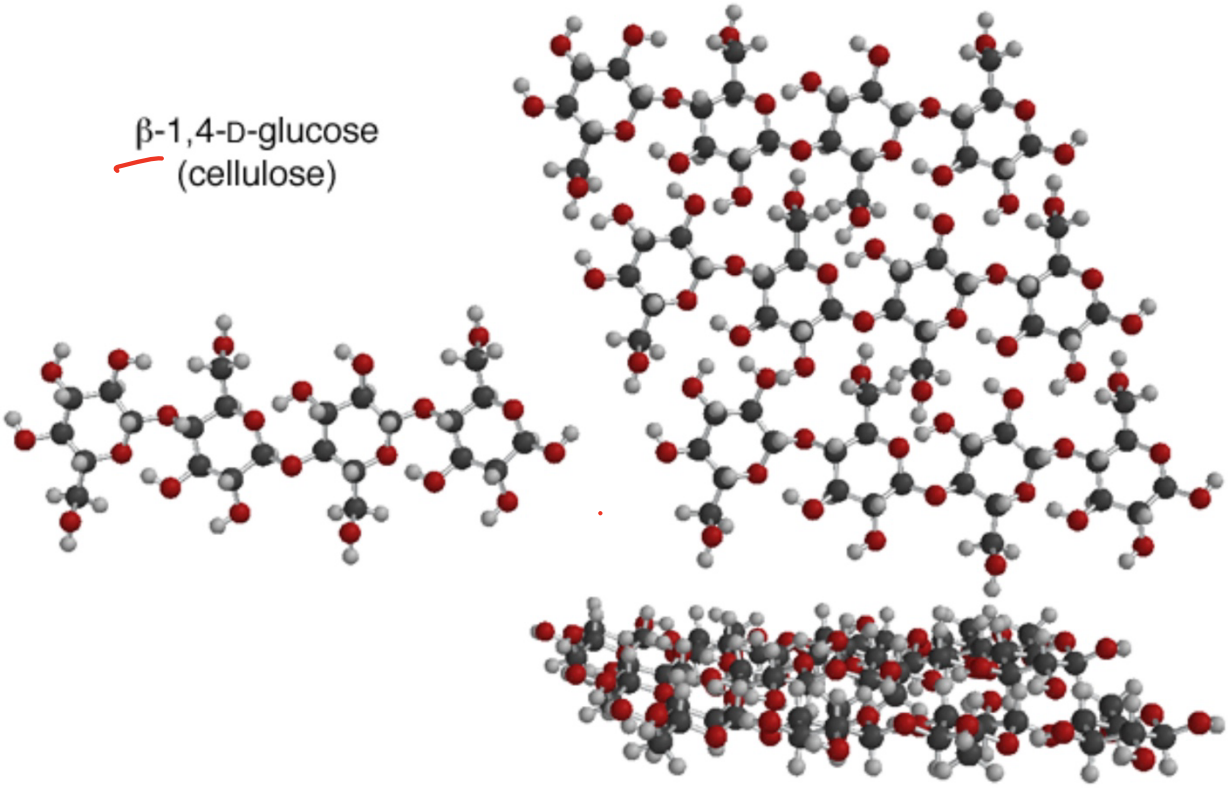


VS.

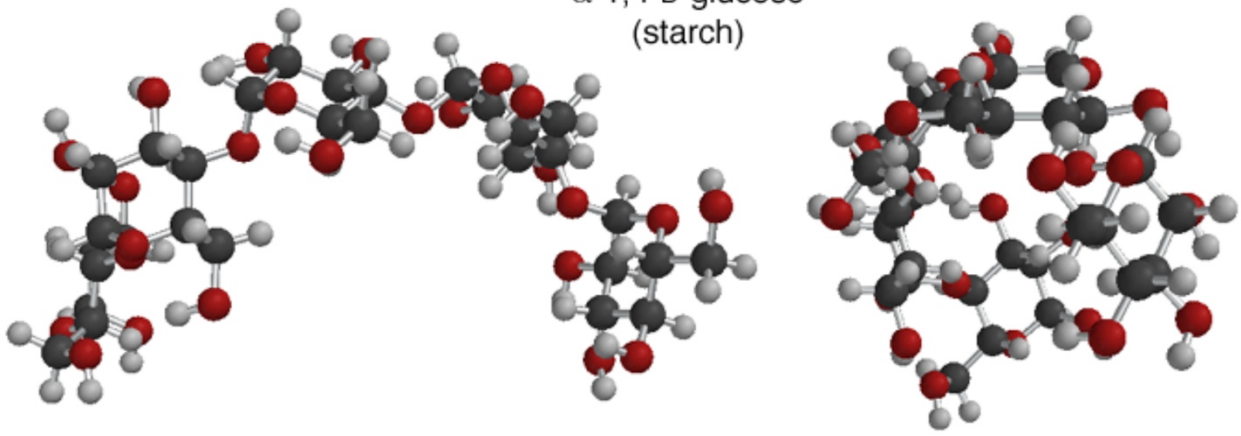
What is the difference —
They are both polymers
of D-Glucose


β
α
β–1,4–glycosidic bond
α–1,4–glycosidic bond
β-1,4-D-glucose
α-1,4-D-glucose

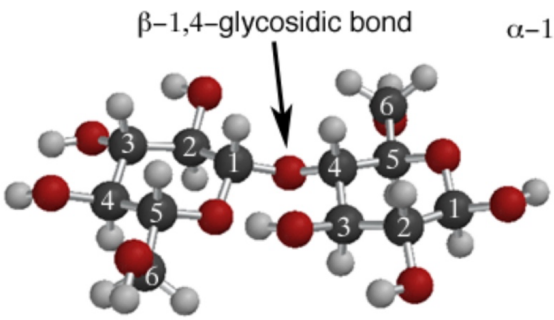
β-1,4-D-glucose
(cellulose)



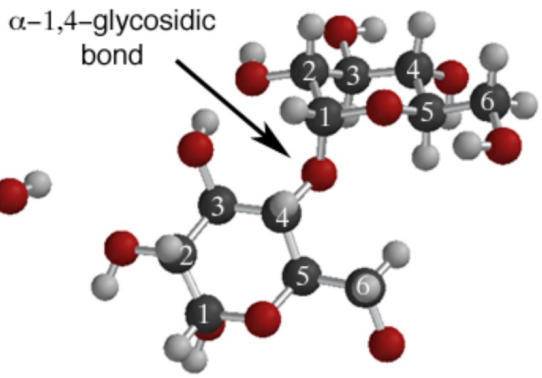
α-1,4-D-glucose
(starch)



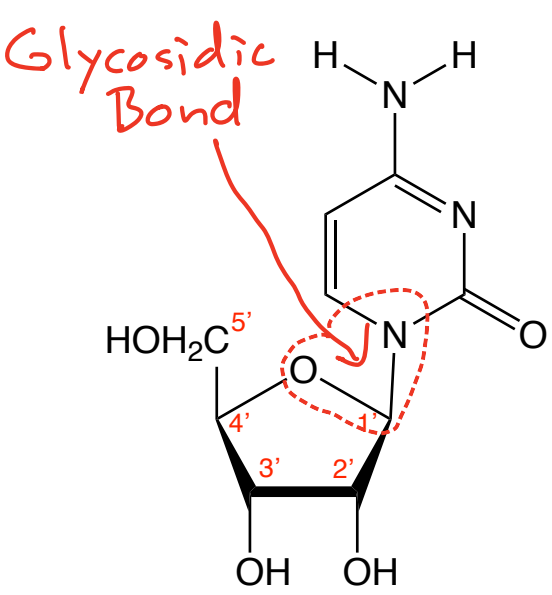
Vs.



β-1,4-D-glucose



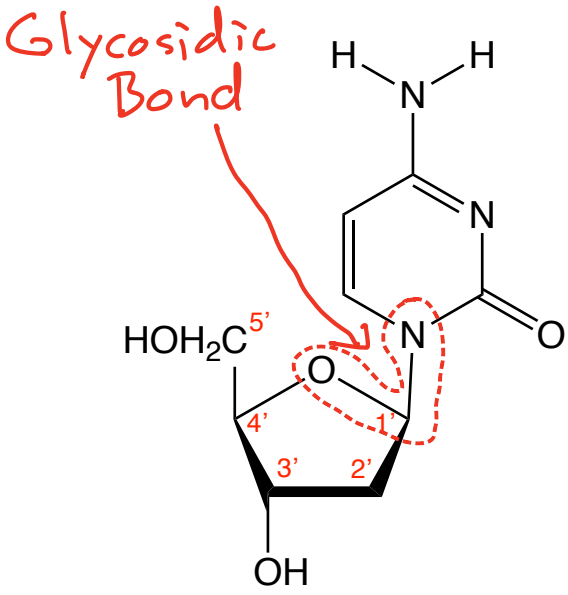
α-1,4-D-glucose



D-Ribose

⇓

RNA



D-2'-Deoxyribose

⇓

DNA