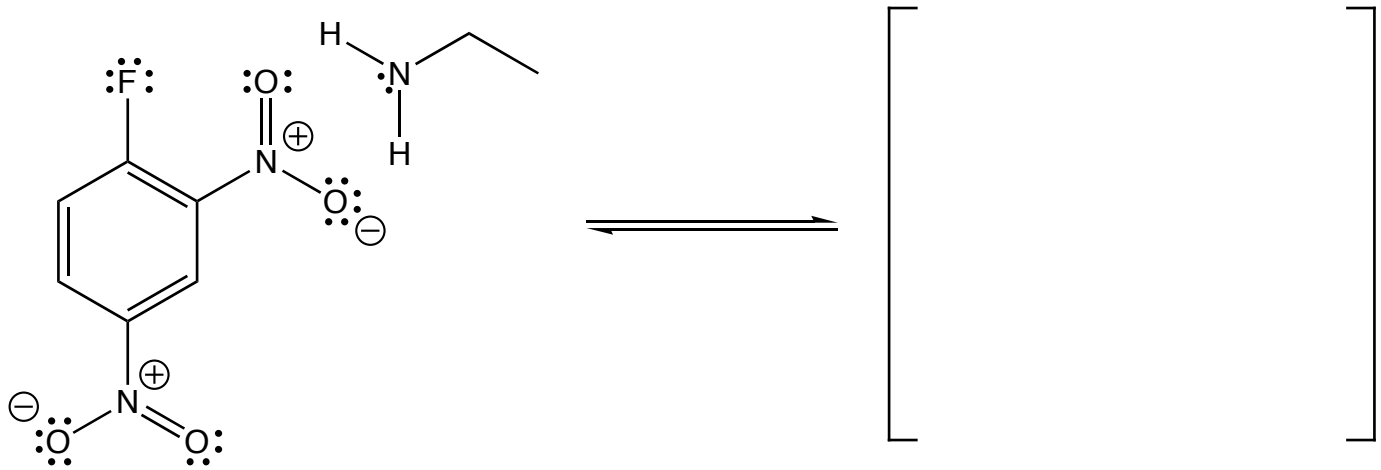
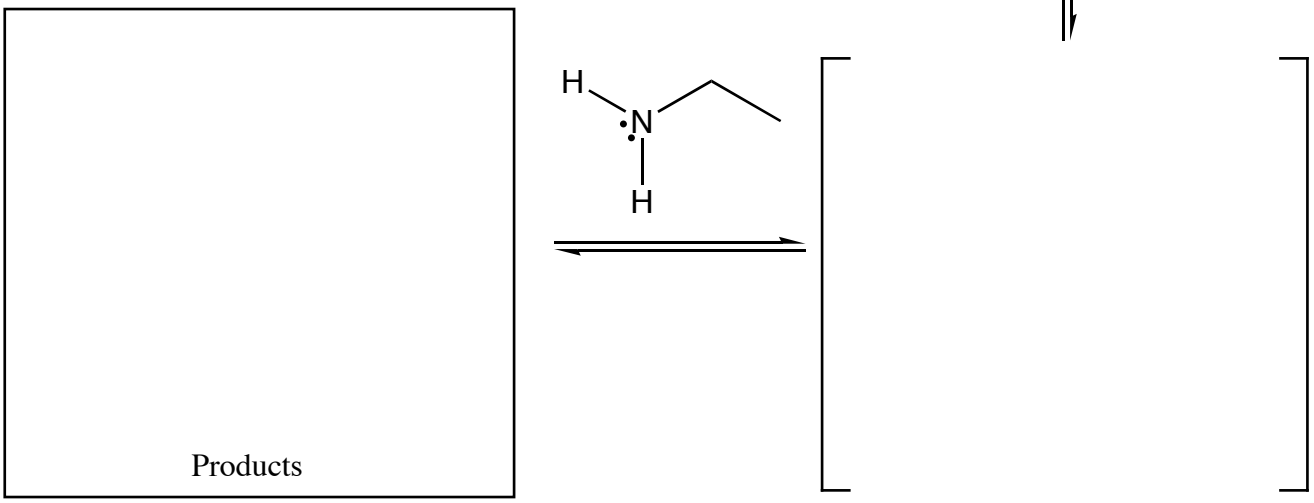
Nucleophilic Aromatic Substitution Module

Nucleophilic Aromatic Substitution



Meisenheimer complex



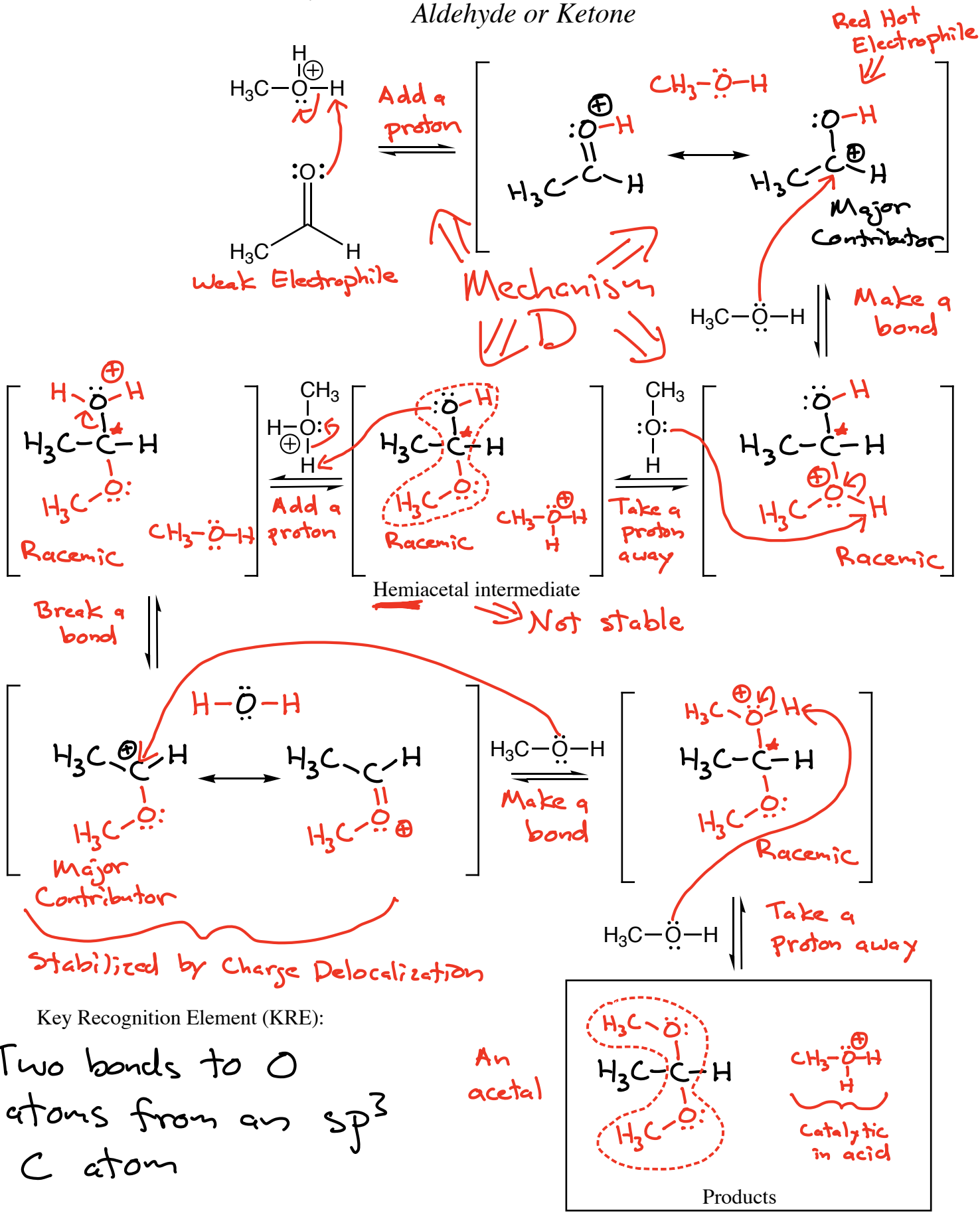
Products

Carbohydrate Chemistry Module 1

H_2SO_4

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

Acid Catalyzed Hemiacetal and Acetal Formation From an Aldehyde or Ketone

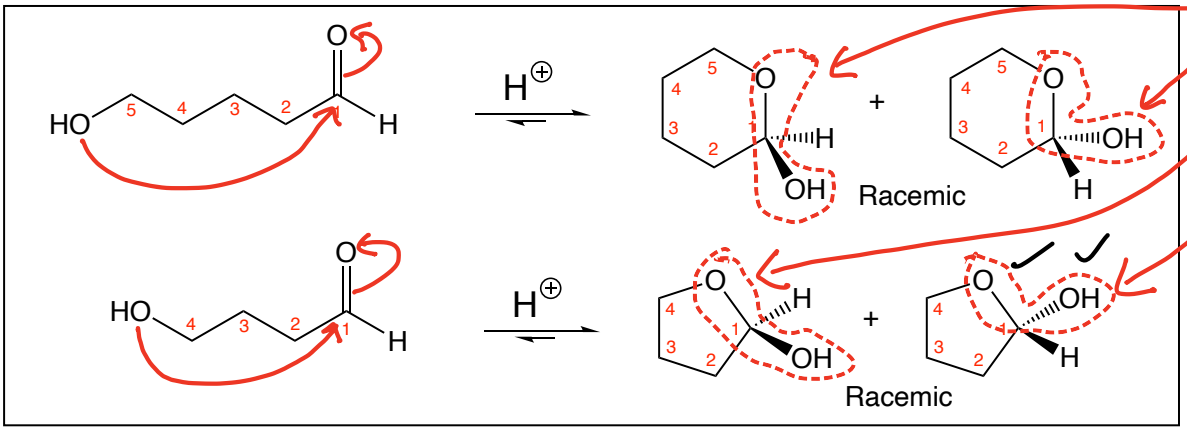


Key Recognition Element (KRE):

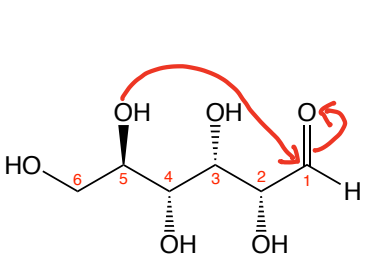
Two bonds to O atoms from an sp^3 C atom

Cyclic Hemiacetals and Carbohydrates

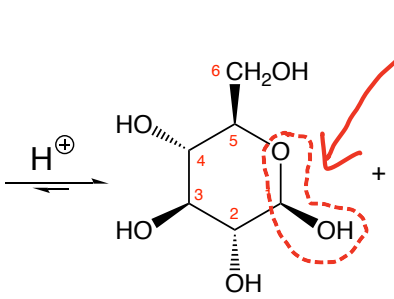
Cyclic hemiacetals



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



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

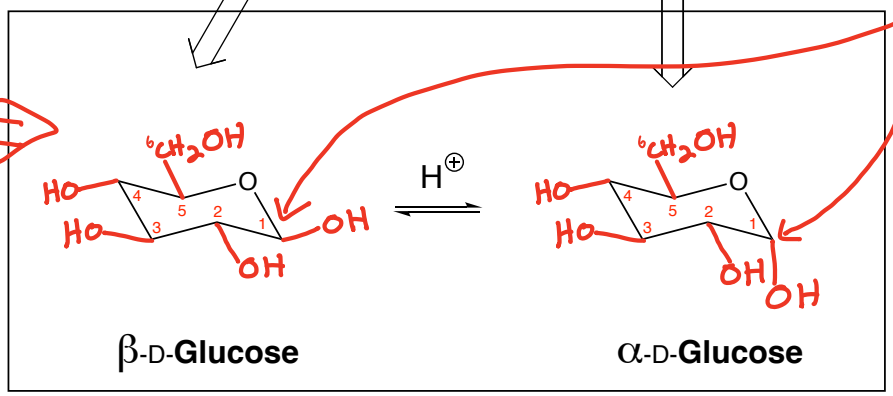


Cyclic Hemiacetals

"SWEET!"

Anomeric Carbon

This interconversion is called "mutarotation"



Biochemists call these two forms "anomers"

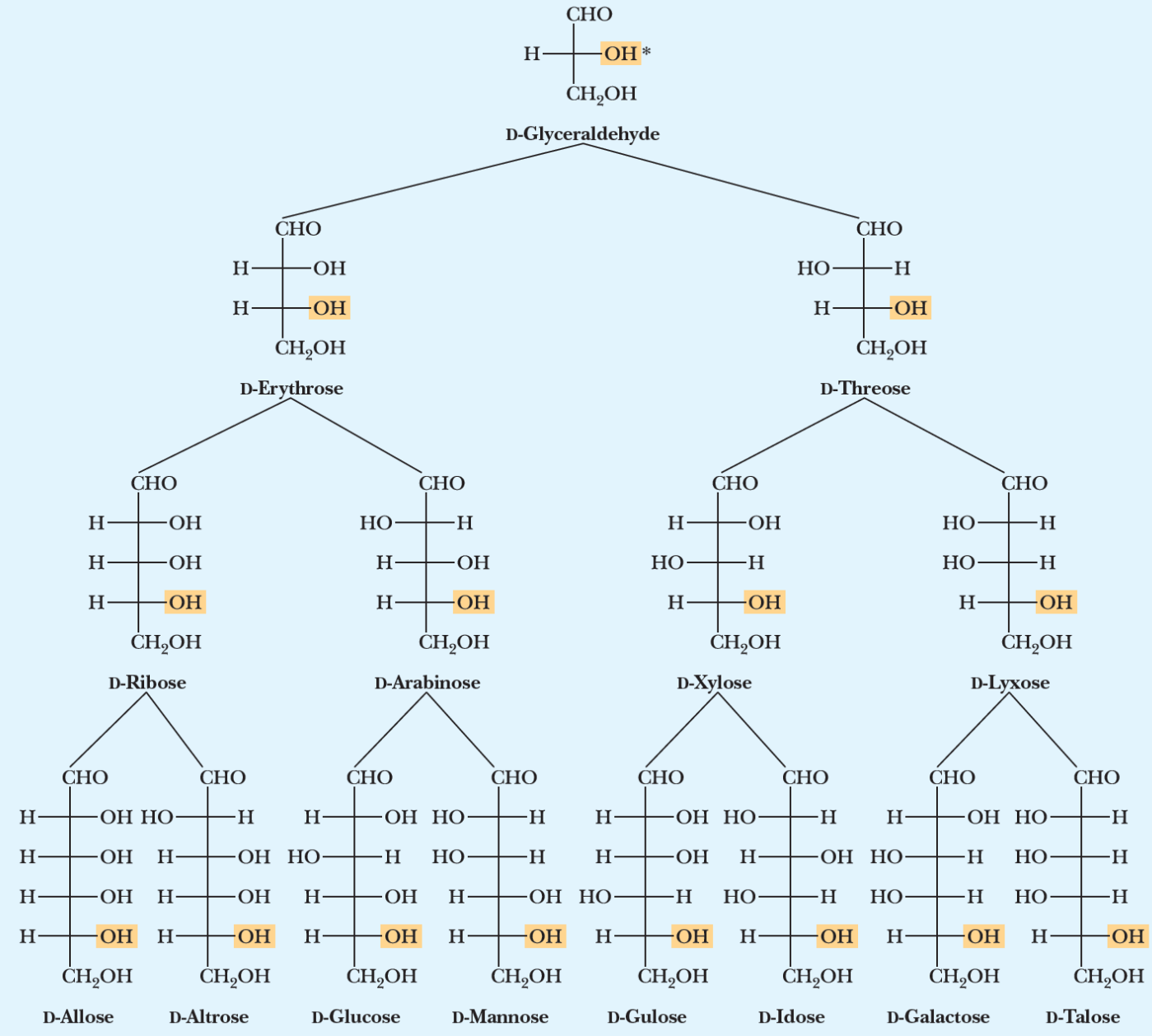
β-D-Glucopyranose
means "6-mebered ring"

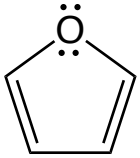
More stable → every group is equatorial!

α-D-Glucopyranose

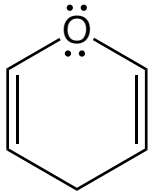
Less stable → one -OH is axial

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

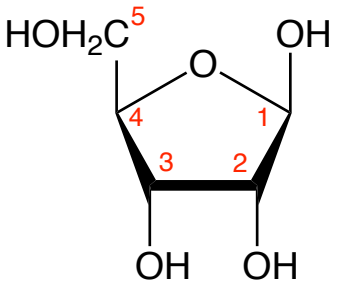


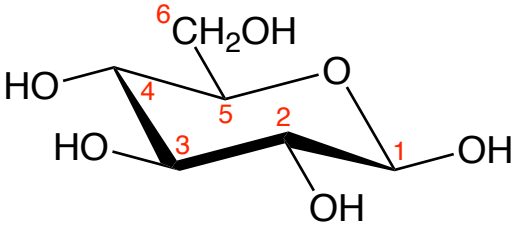

O

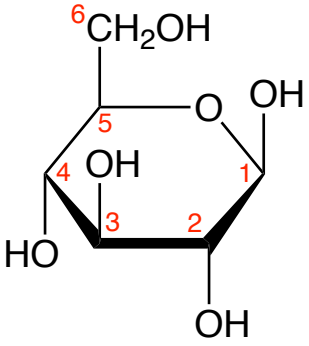
Furan

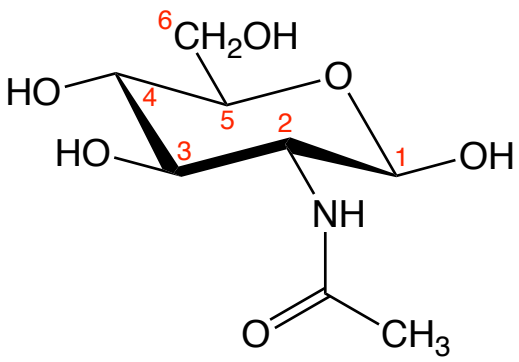

O

Pyran


HOH2C
5
OH
O
4
1
3
2
OH
OH

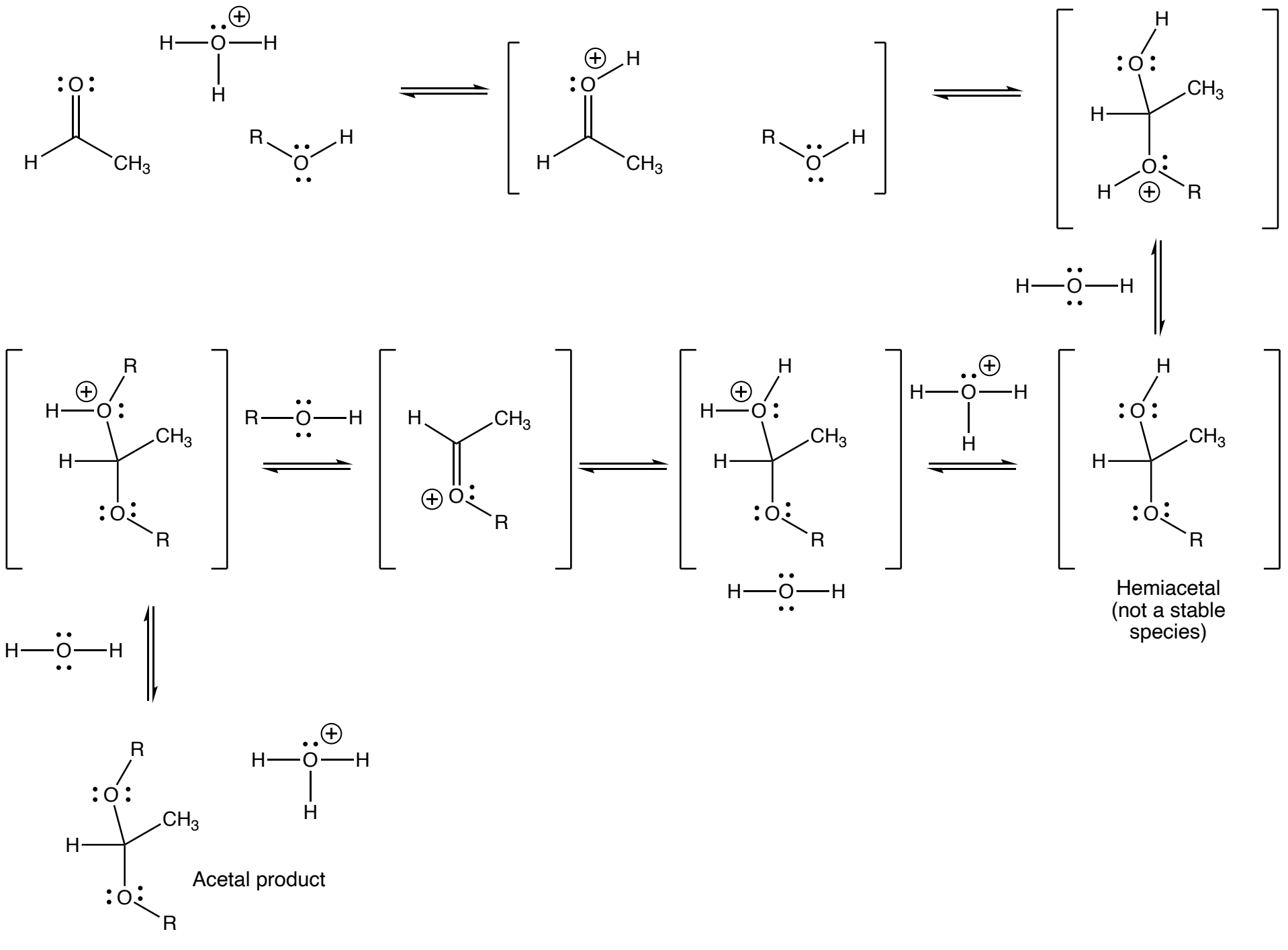

6
CH2OH
HO
4
O
5
2
HO
3
1
OH
OH

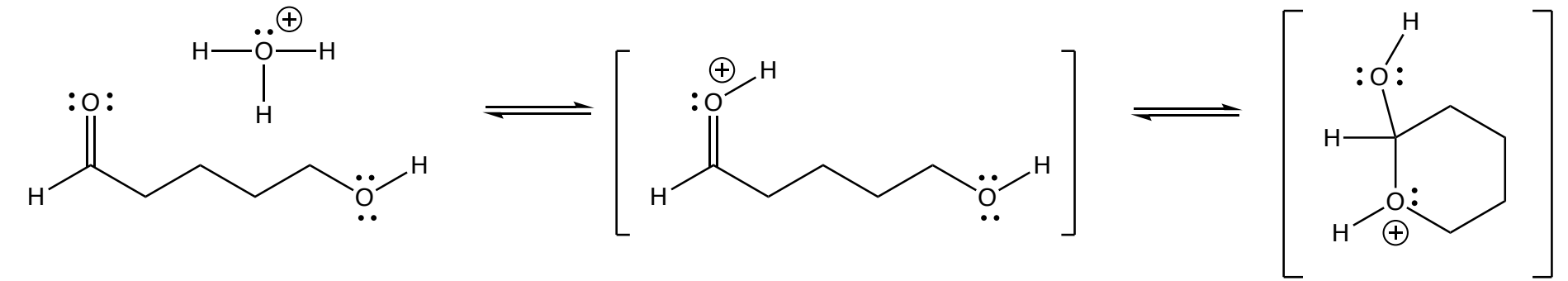

6
CH2OH
O
OH
5
4
OH
1
3
2
HO
OH



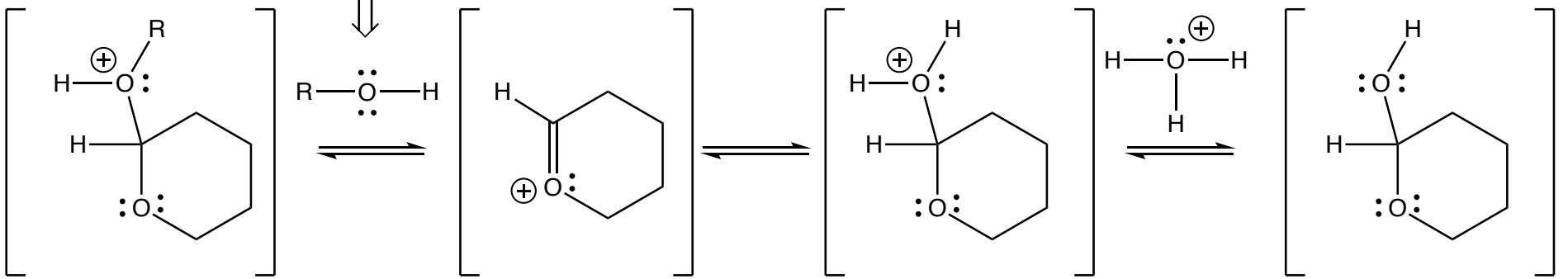
N-Acetyl-D-Glucosamine
(GlcNAC)

Carbohydrate Chemistry Module 2

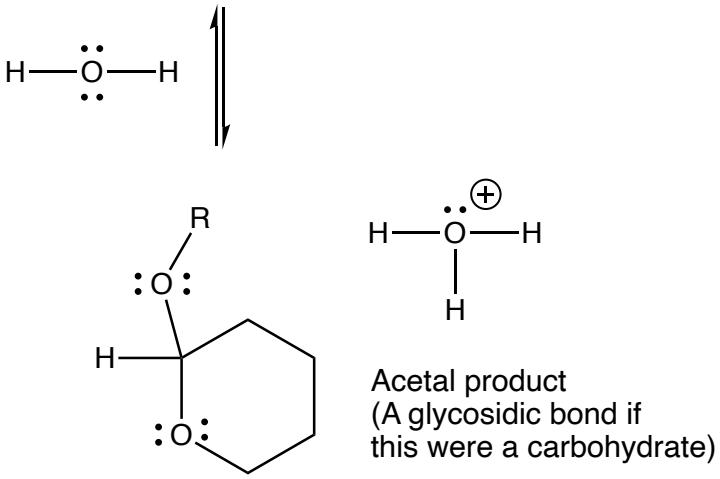

Hemiacetal
(not a stable
species)
Acetal product



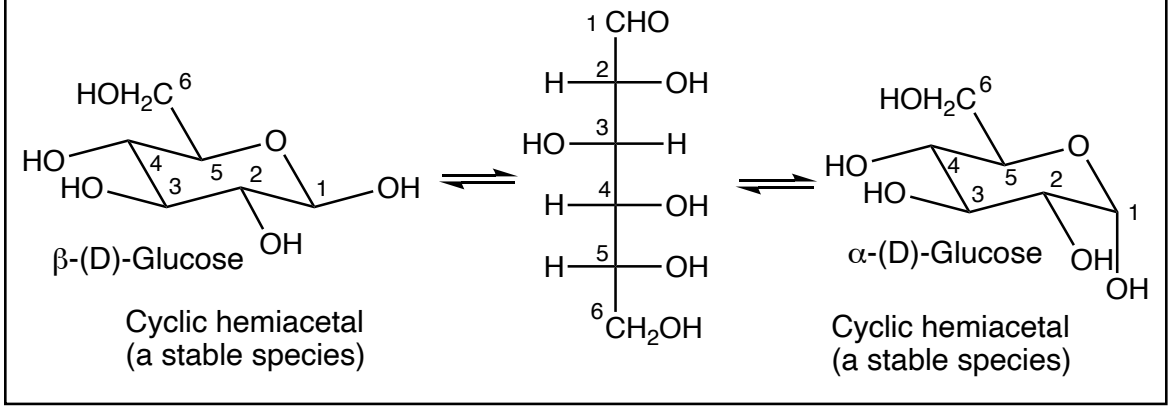
This can be another sugar!

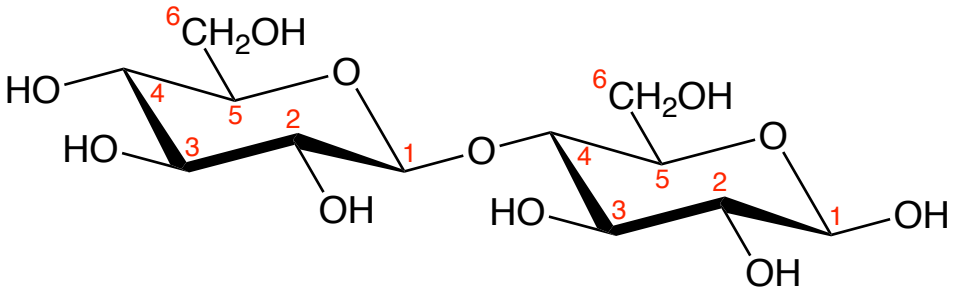


Cyclic hemiacetal
(a stable species)



Acetal product
(A glycosidic bond if
this were a carbohydrate)




6CH2OH
HO
O
4
5
2
HO
3
1
O
OH
6CH2OH
O
4
5
2
HO
3
1
OH
OH

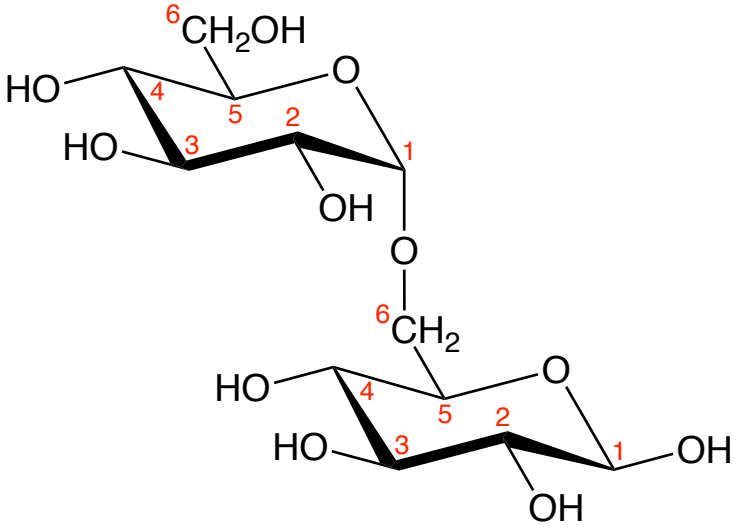
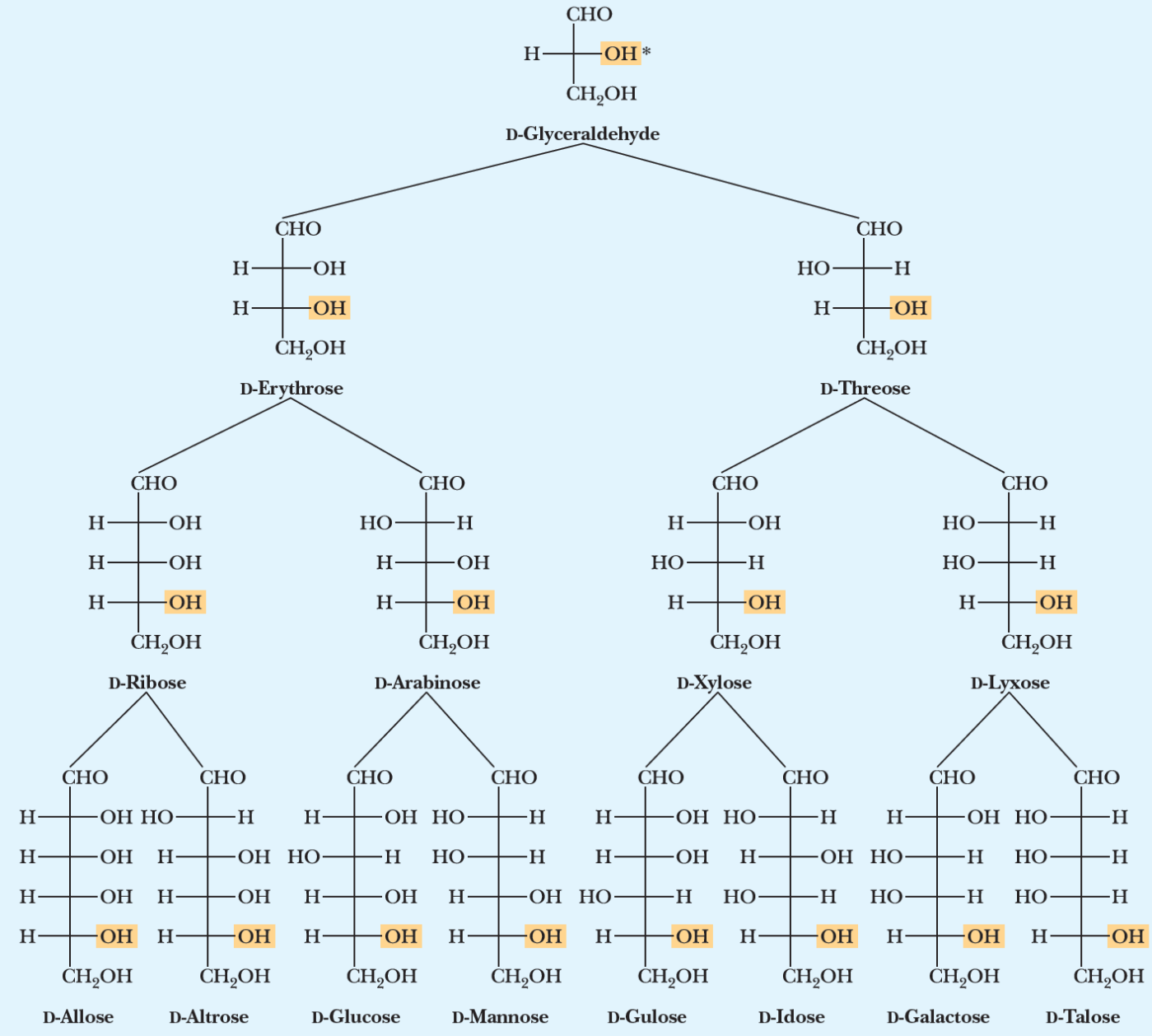
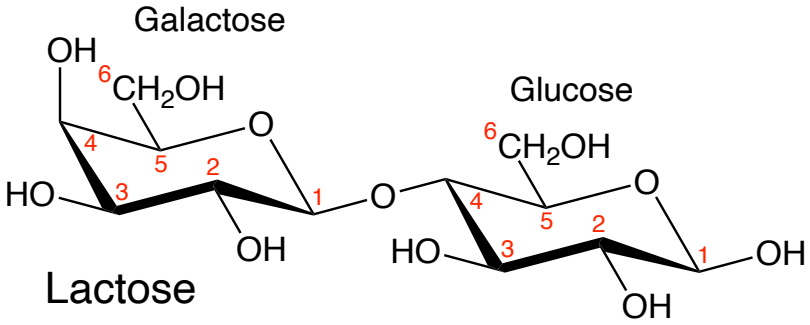
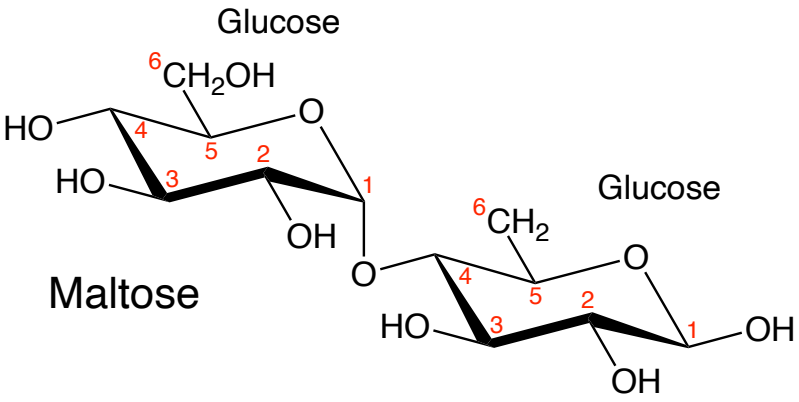
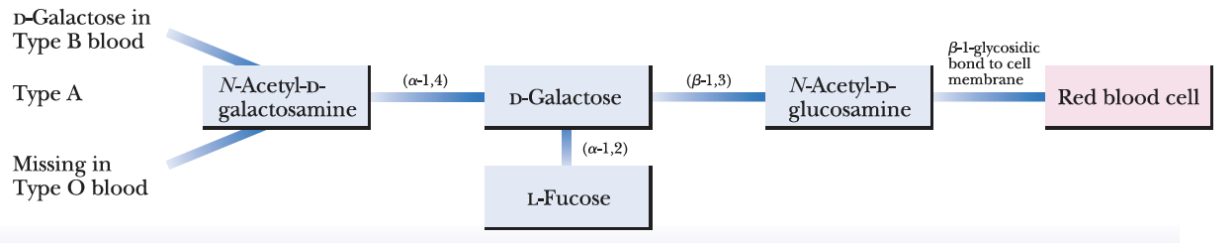

6CH2OH
HO
O
4
5
2
HO
3
1
OH
O
6CH2
HO
O
4
5
2
HO
3
1
OH
OH

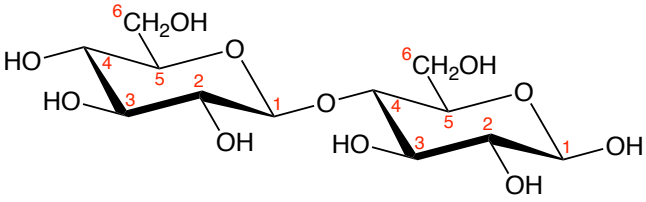
Table 25.1 Configurational Relationships Among the Isomeric D-Aldotetroses, D-Aldopentoses, and D-Aldohexoses

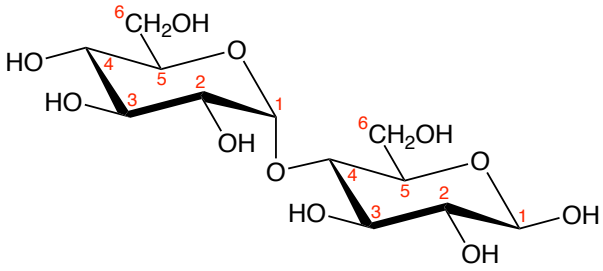


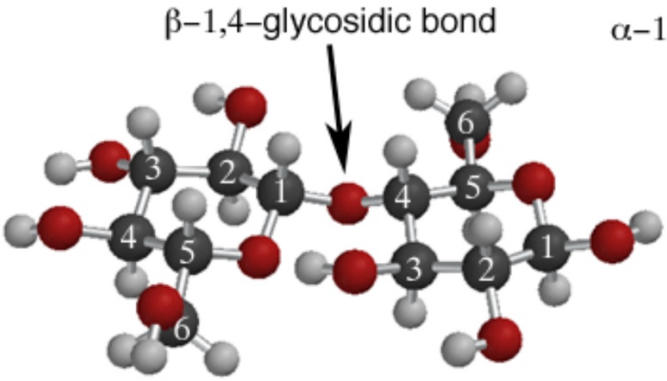

Galactose
OH
6CH2OH
O
4
5
2
HO
3
1
O
OH
Glucose
6CH2OH
O
4
5
2
HO
3
1
OH
OH
Lactose


Glucose
6CH2OH
O
HO
4
5
2
HO
3
1
OH
Glucose
6CH2
O
4
5
2
O
HO
3
1
OH
OH
Maltose

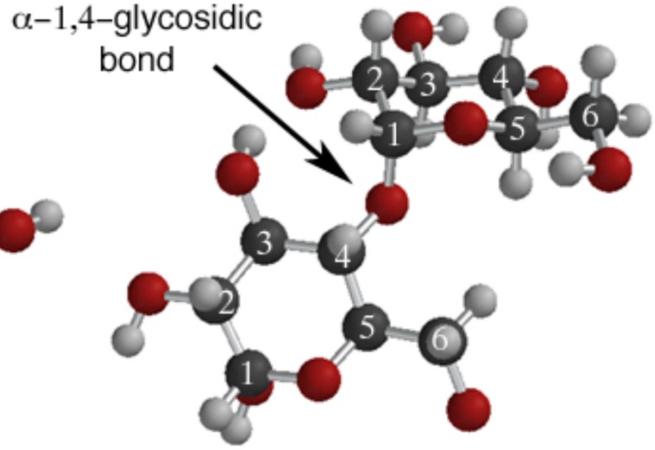

D-Galactose in Type B blood
Type A
Missing in Type O blood
N-Acetyl-D-galactosamine
(α-1,4)
D-Galactose
(β-1,3)
N-Acetyl-D-glucosamine
β-1-glycosidic bond to cell membrane
Red blood cell
(α-1,2)
L-Fucose





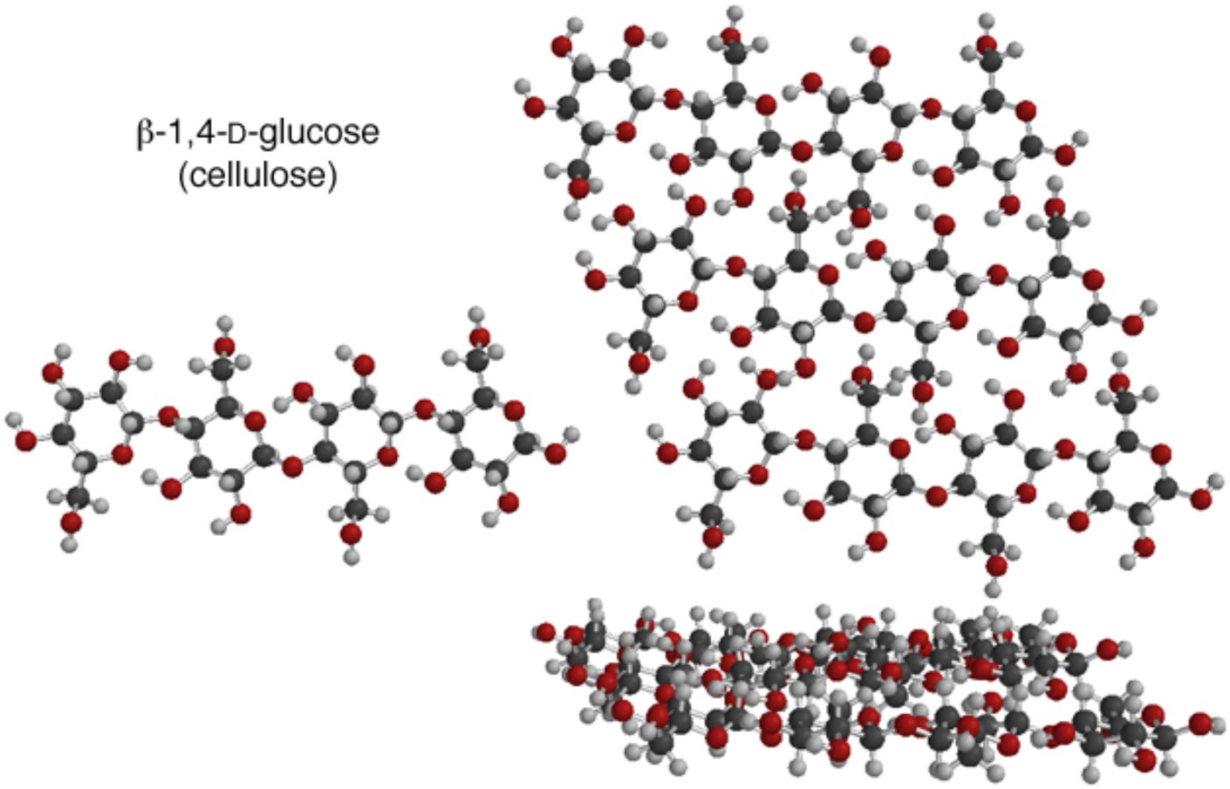


β-1,4-D-glucose

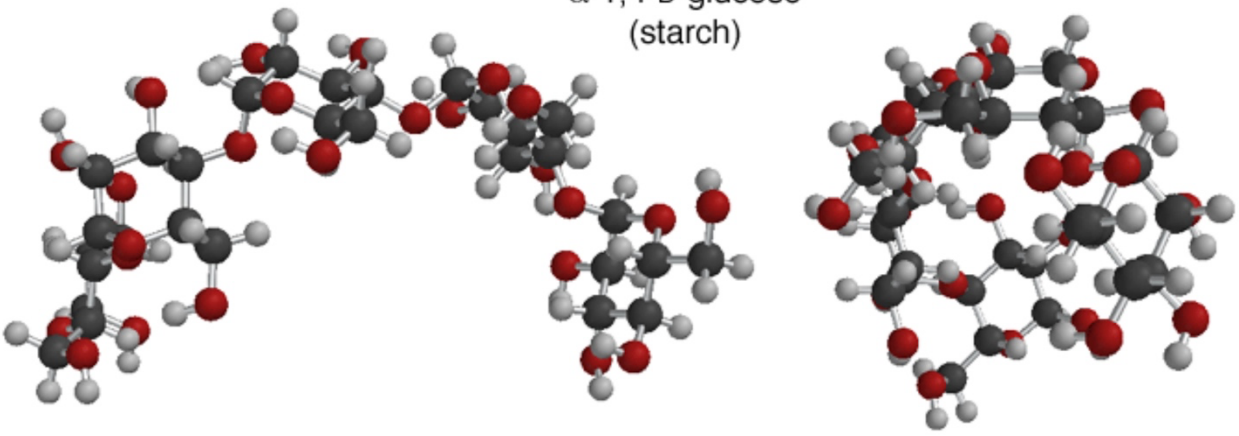


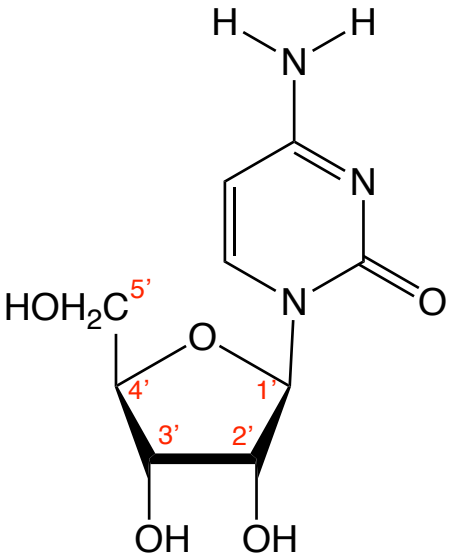
α-1,4-D-glucose

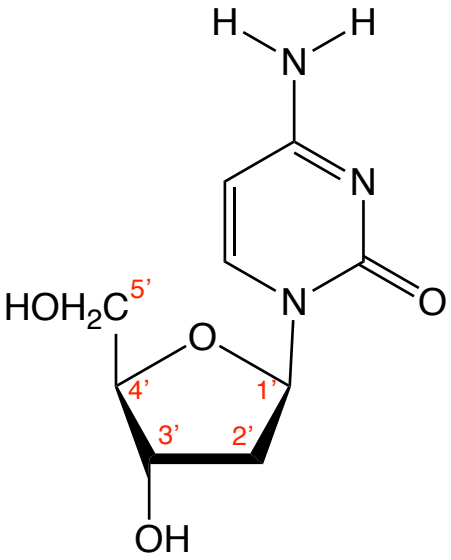
β-1,4-D-glucose
(cellulose)



α-1,4-D-glucose
(starch)




H
H
N
N
N
O
HOH2C
5'
O
4'
1'
3'
2'
OH
OH


H
H
N
N
N
O
HOH2C
5'
O
4'
1'
3'
2'
OH