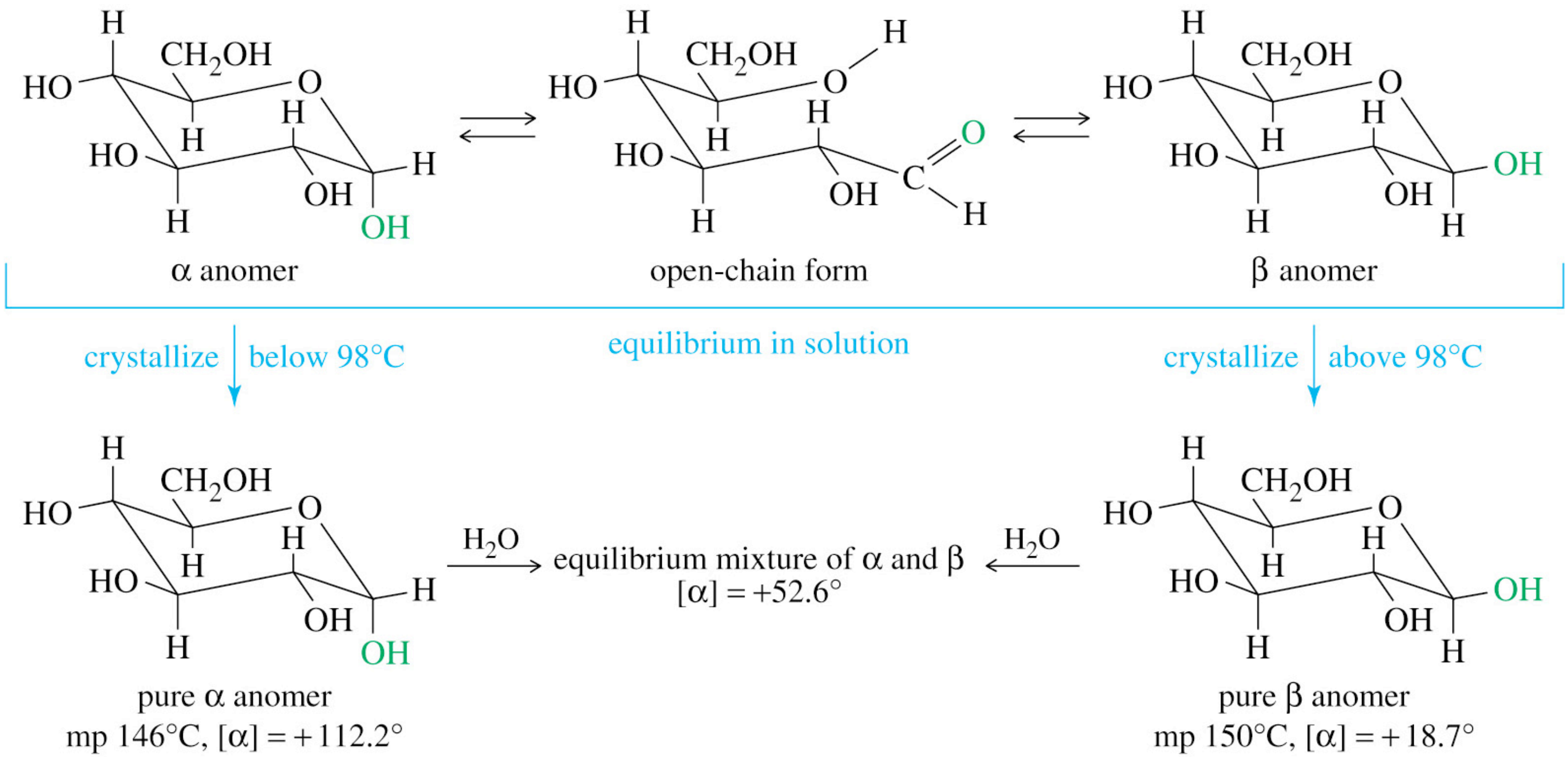
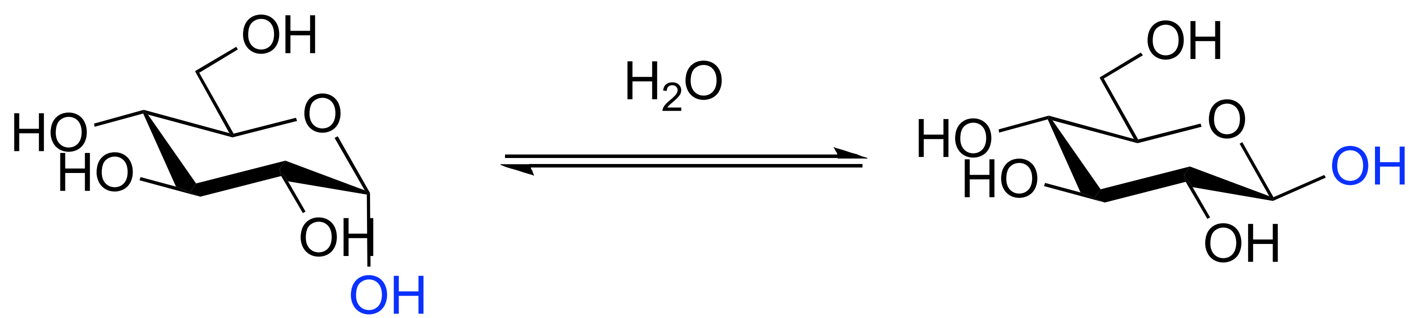
Reactions of the anomeric center-I


α anomer
open-chain form
β anomer
equilibrium in solution
crystallize below 98°C
crystallize above 98°C
H2O
equilibrium mixture of α and β
[α] = +52.6°
pure α anomer
mp 146°C, [α] = +112.2°
pure β anomer
mp 150°C, [α] = +18.7°

The anomeric centre



α-glucopyranose

38%

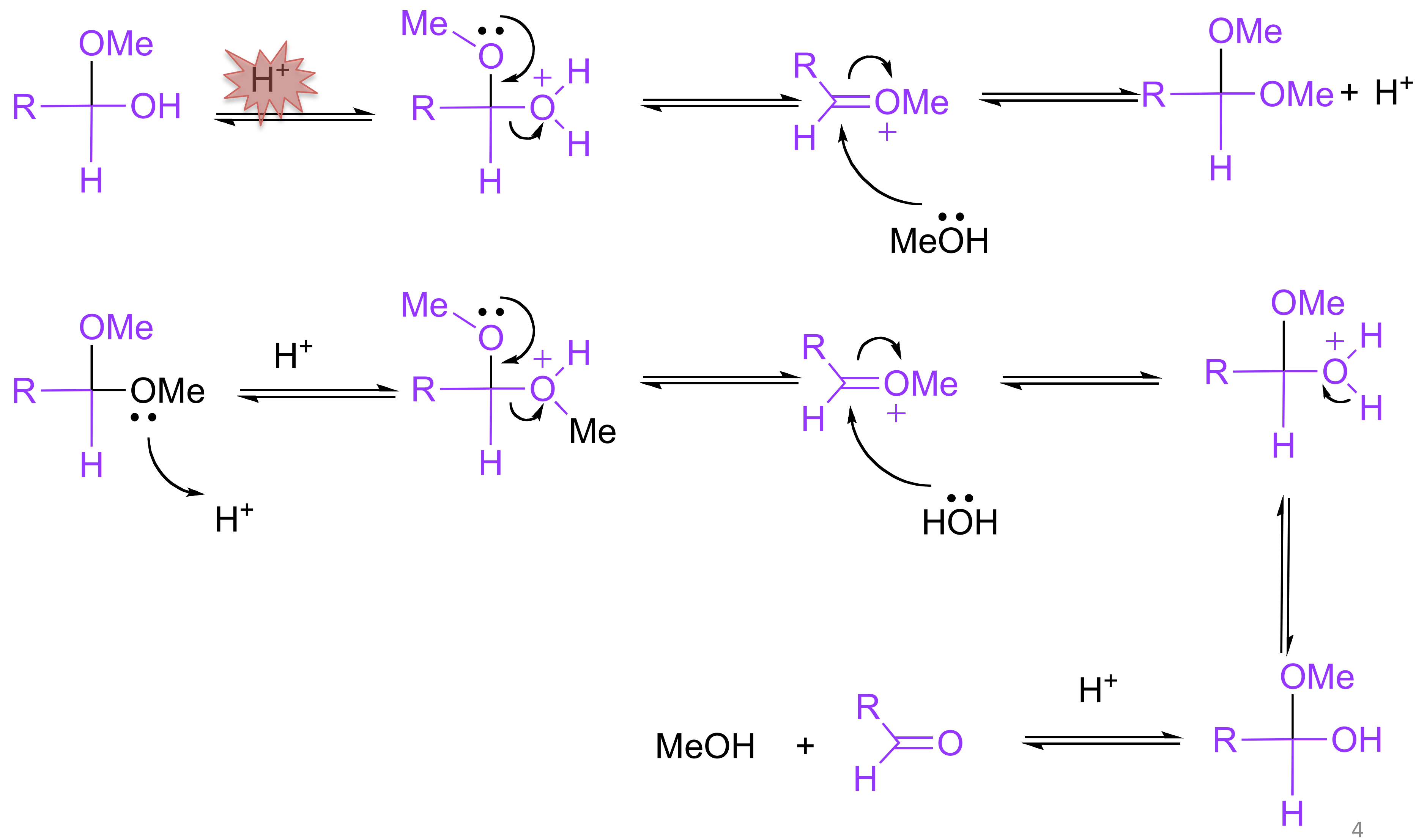
β-glucopyranose

62%

Axial

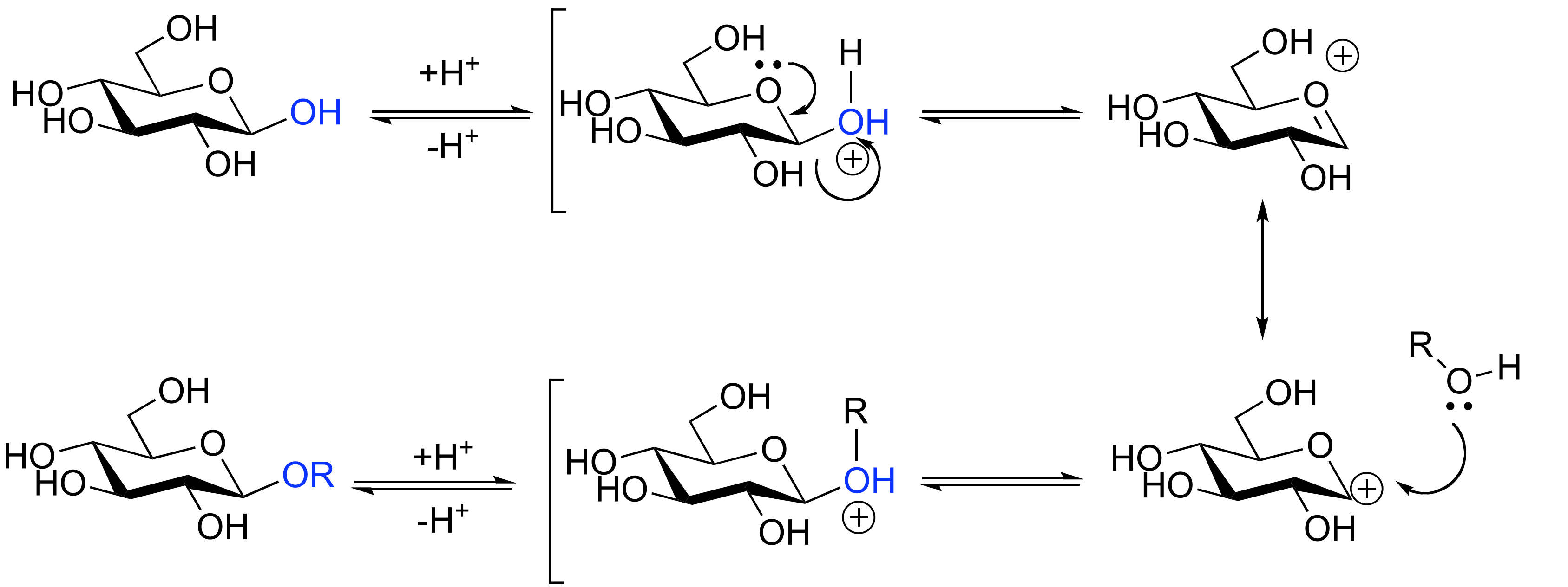
Equatorial

Acetal formation and hydrolysis



Acetals and hemiacetals are in the same oxidation state as carbonyls and it is therefore not surprising that they are readily interconverted and you should think of the process of aldehyde-to-hemiacetal-to-acetal as one reversible rxn.

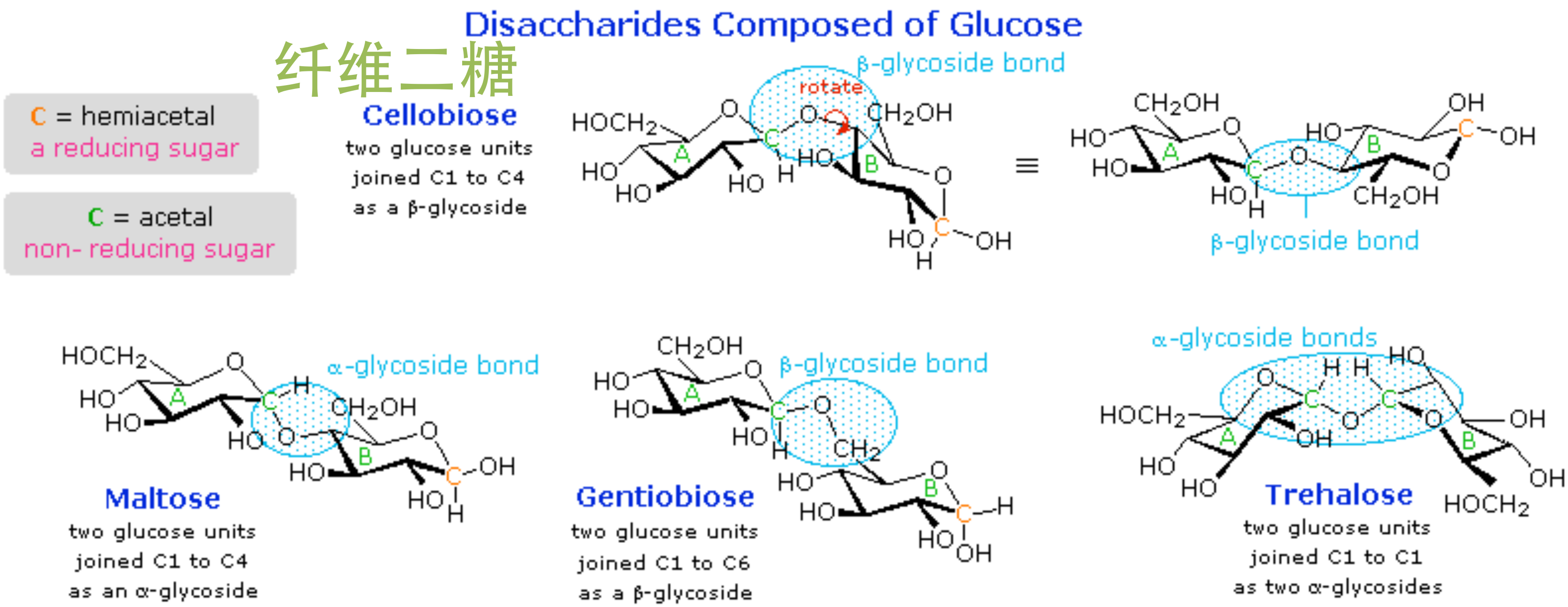
Fischer glycosylation



Glycosyl cation

Presence of an oxygen substituent α to the anomeric carbon, makes any carbocation formed there more stable

纤维二糖



麦芽糖

龙胆二糖

海藻糖

Maltose, Malt sugar

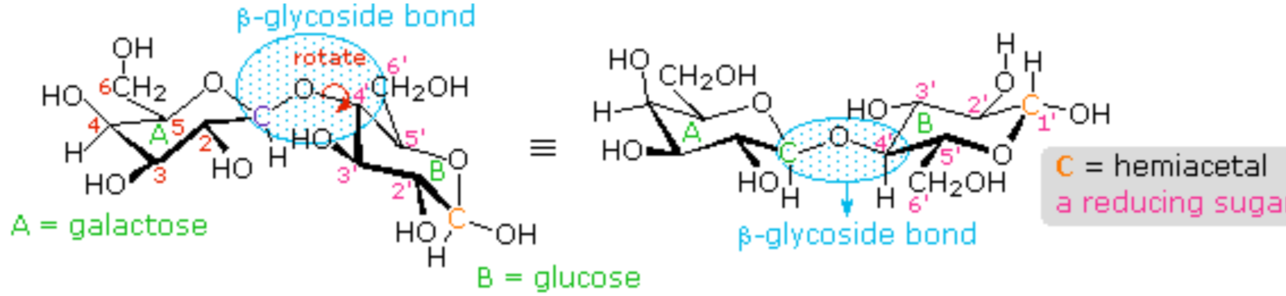
beautybodyandskin.com

buyfoodsale.com

Lactose

4-O-β-D-Galactopyranosyl-D-glucose

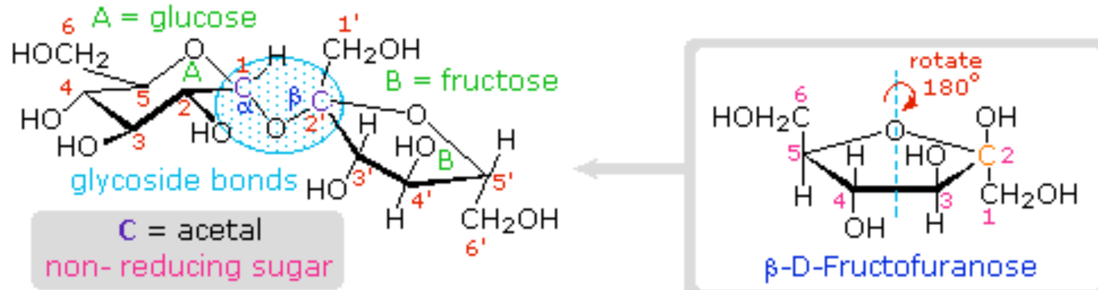
[β-anomer is drawn]

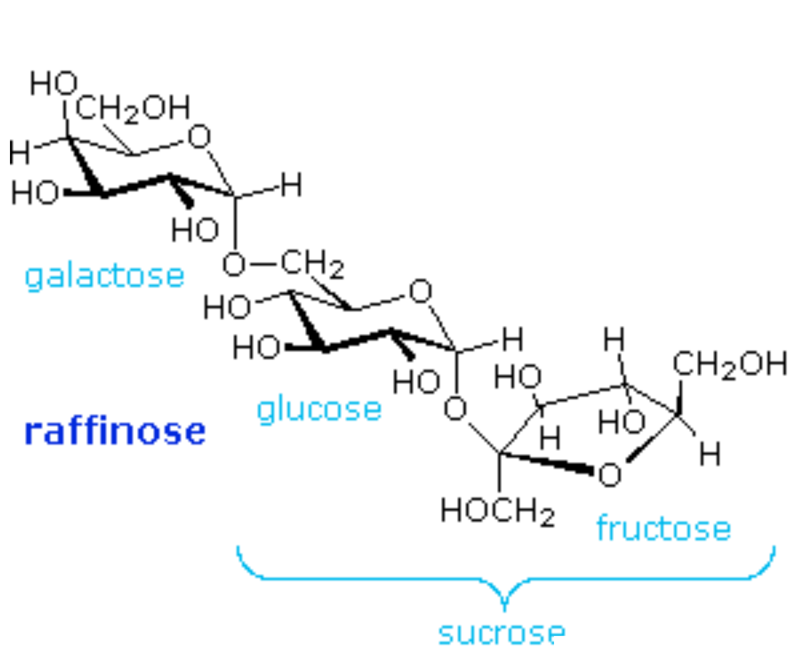


Sucrose

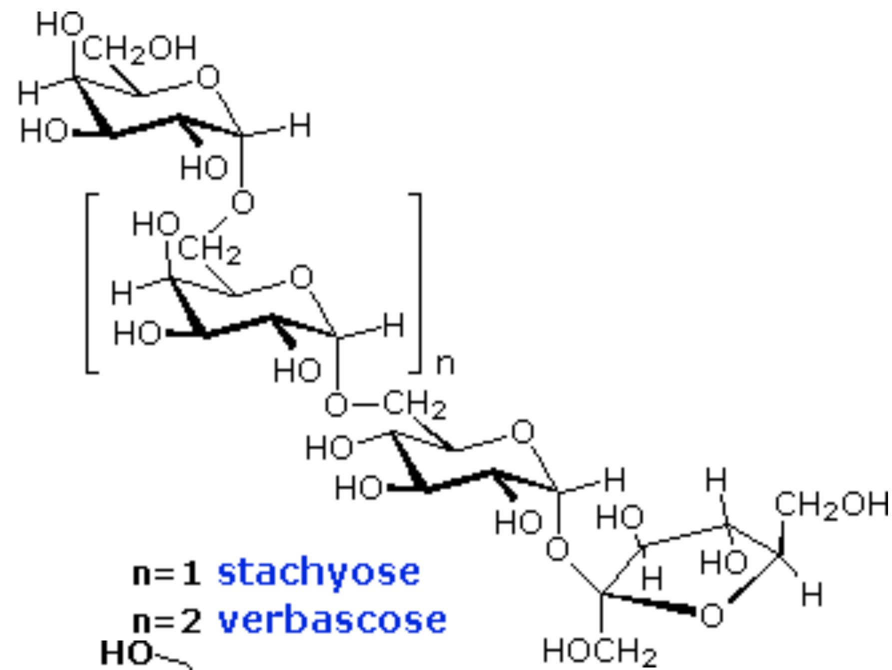
α-D-Glucopyranosyl-β-D-fructofuranoside

β-D-Fructofuranosyl-α-D-glucopyranoside



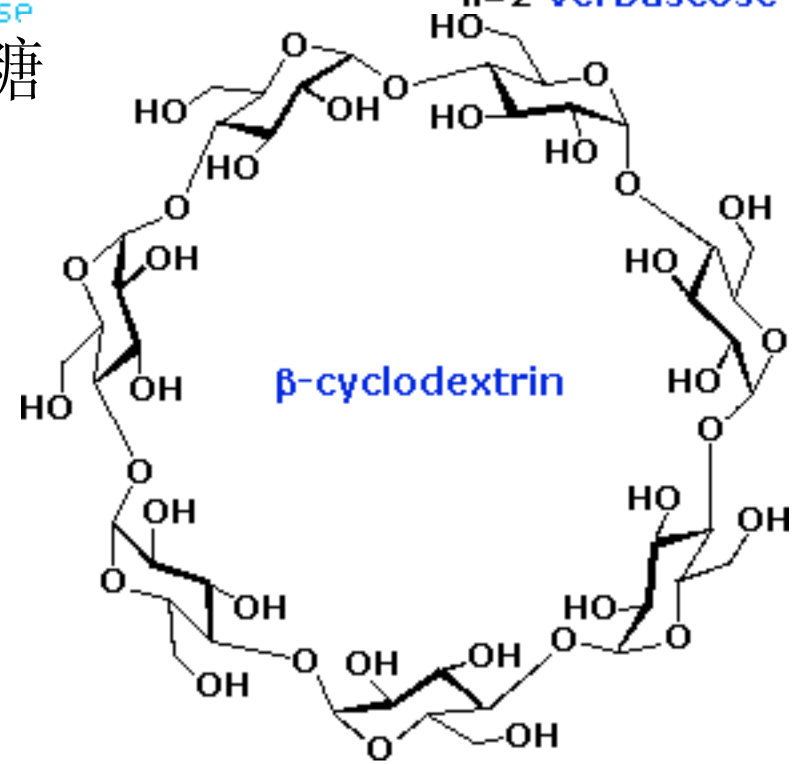


棉子糖，蜜三糖



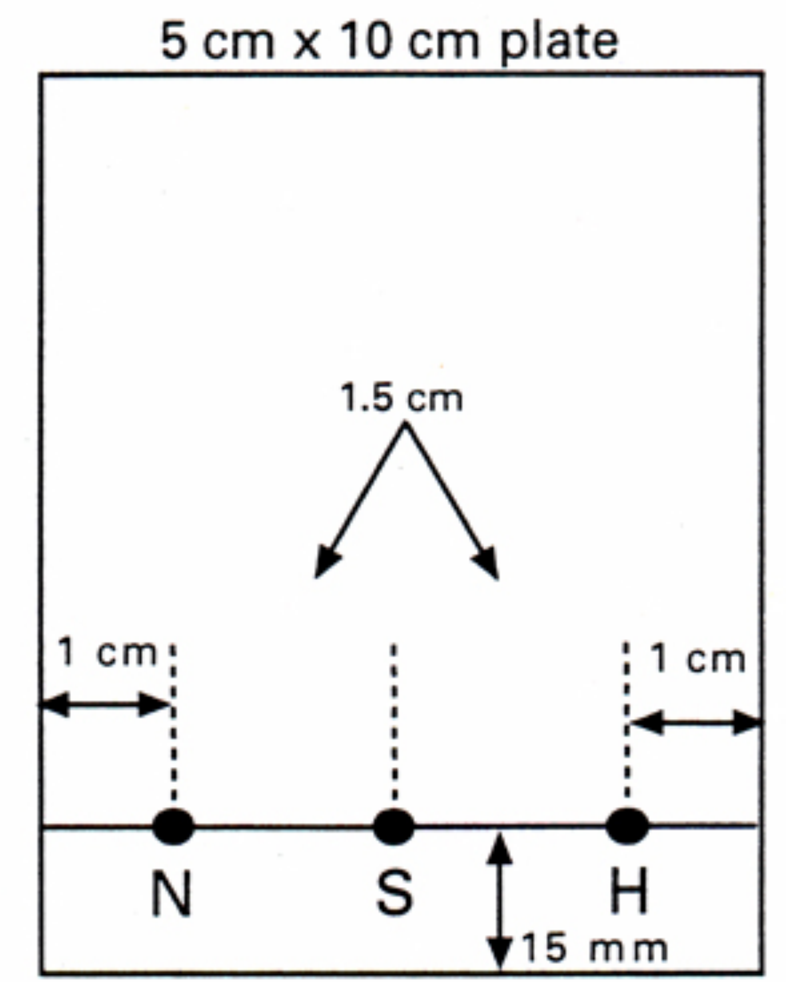
水苏糖

毛蕊花糖

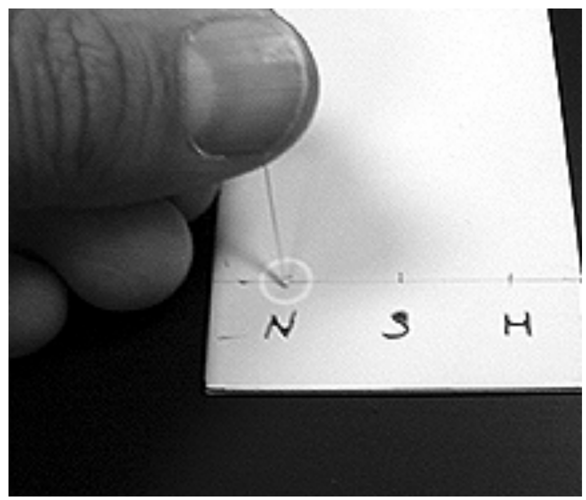


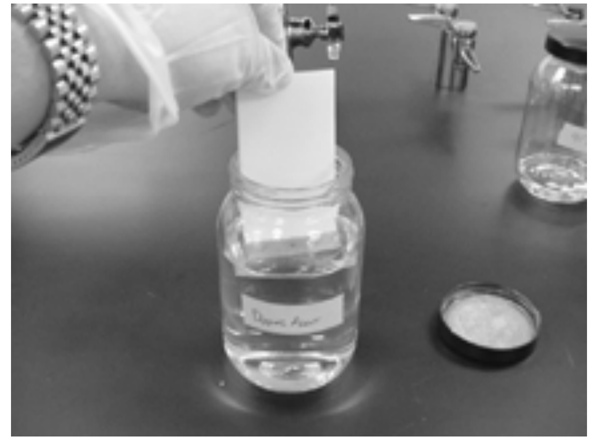
环糊精

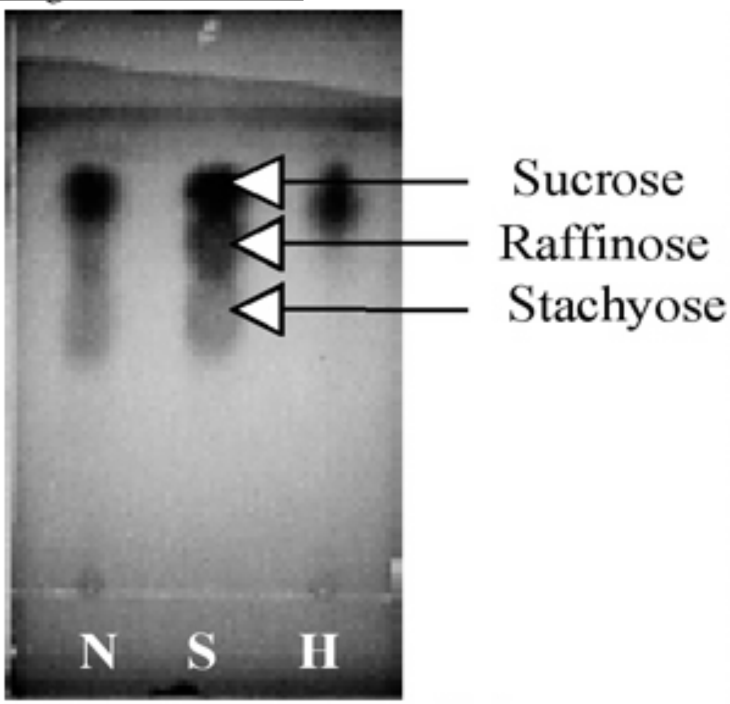
thin-layer chromatography (TLC)



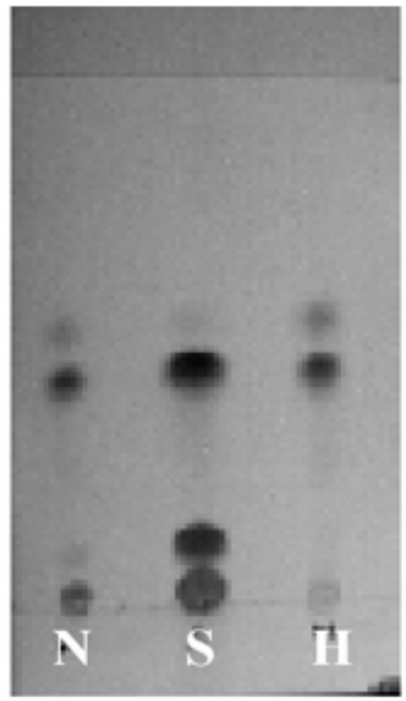
"N" for normal soybean
"S" for sugar standards
"H" for high sucrose soybean





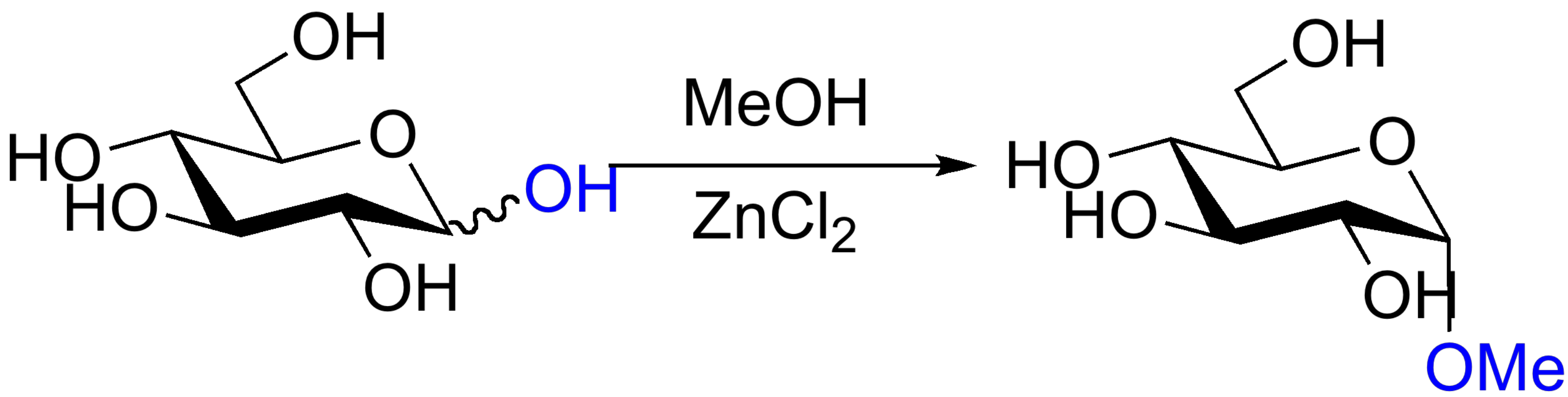


70% isopropyl alcohol



91% isopropyl alcohol

http://www.biotech.iastate.edu/lab_protocols/HSSB-TLC_Student.html



Fischer glycosidation/glycosylation

Equilibrium reaction

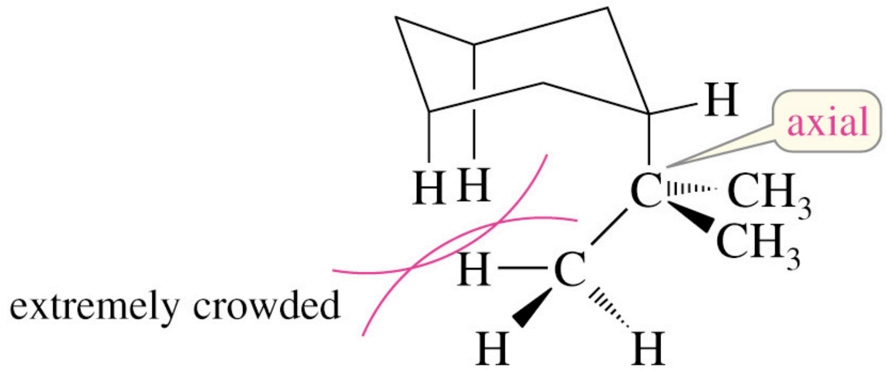
Treated with aqueous acid can reverse the reaction

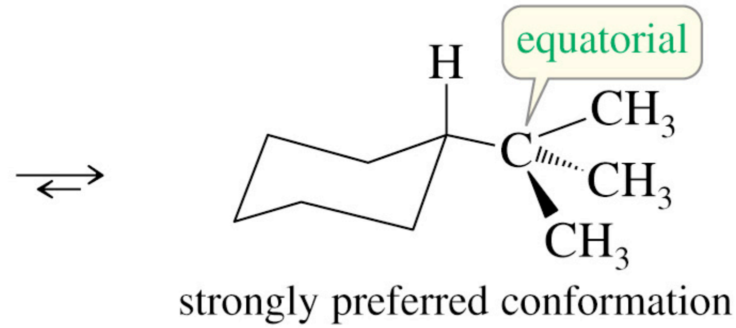
Source of anhydrous acid: Bronsted acid/Lewis acid

Under thermodynamic control

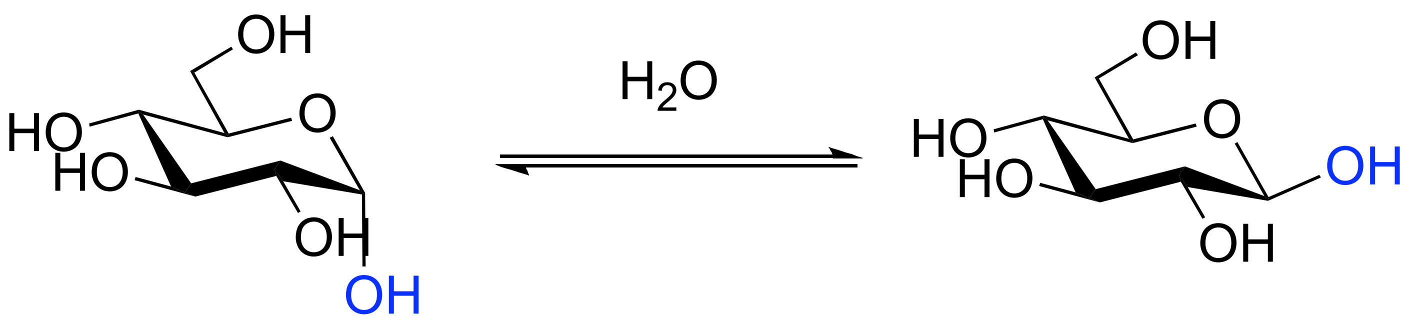
Stable under almost all other conditions except aqueous acid

PROTECTION OF ANOMERIC CENTER





Steric effect

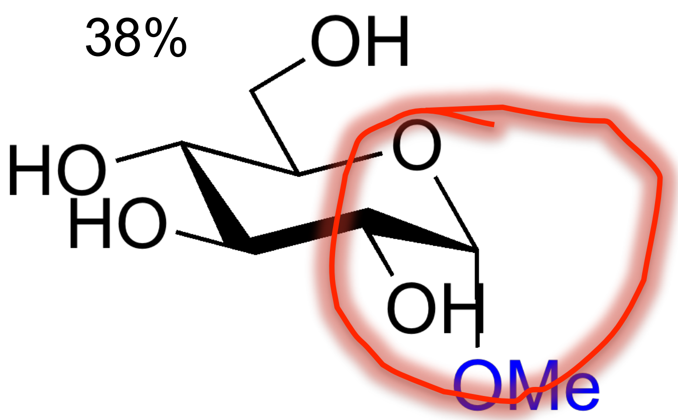


α-glucopyranose

38%

β-glucopyranose

62%

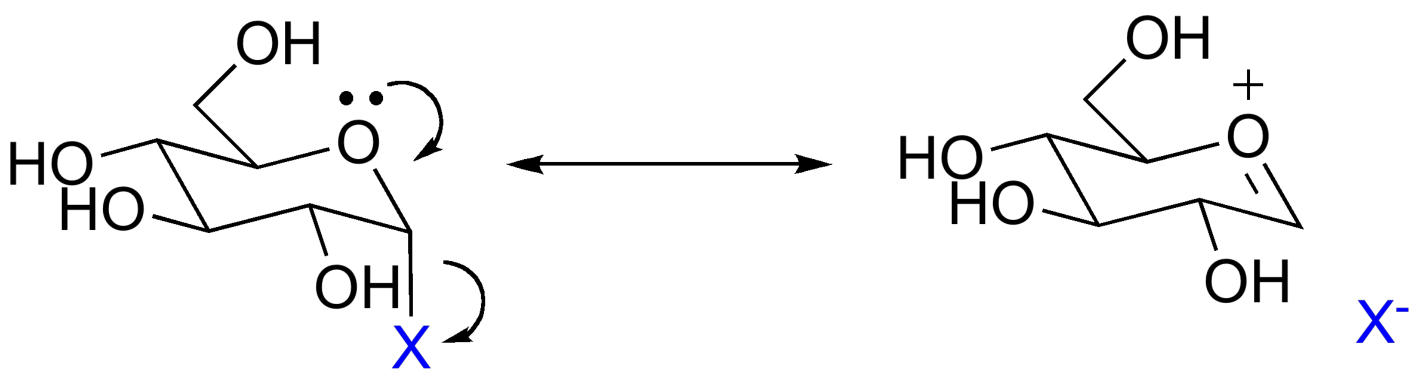


Thermodynamic stable pdt

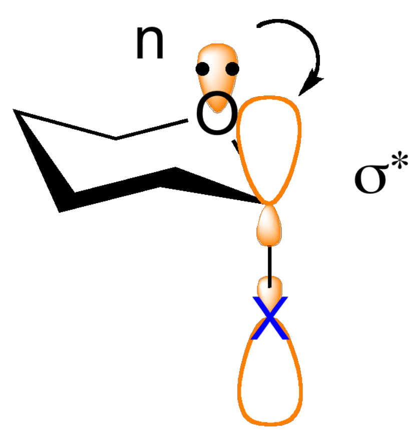
Anomeric effect

Electronegative substituents on a pyranose ring prefer to occupy an axial rather than an equatorial orientation

(A)



(B)



Effective only:

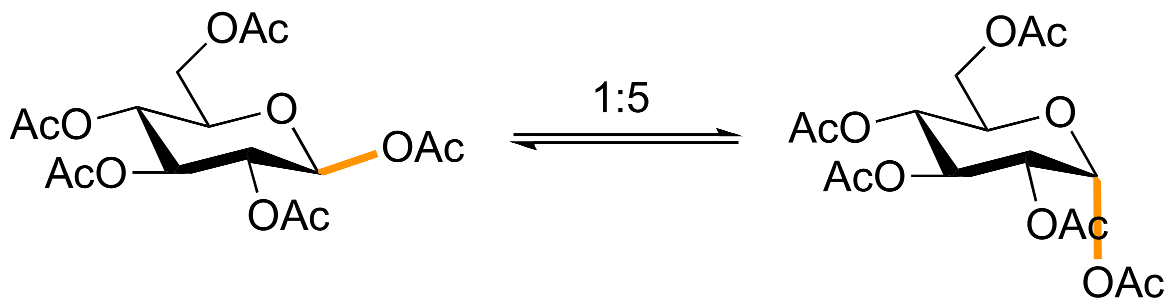
X = electronegative atom, O, F, Cl, Br……

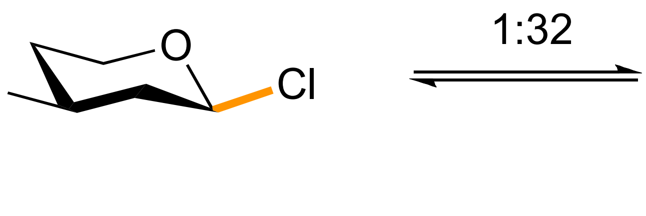
No stabilising electronic interaction
at equatorial position

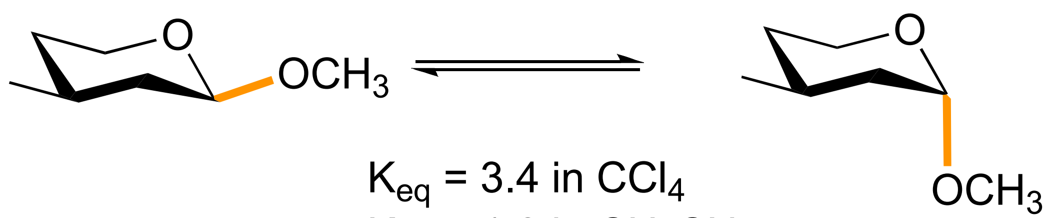
Several consequences:

Shortening of O-C ring bond length

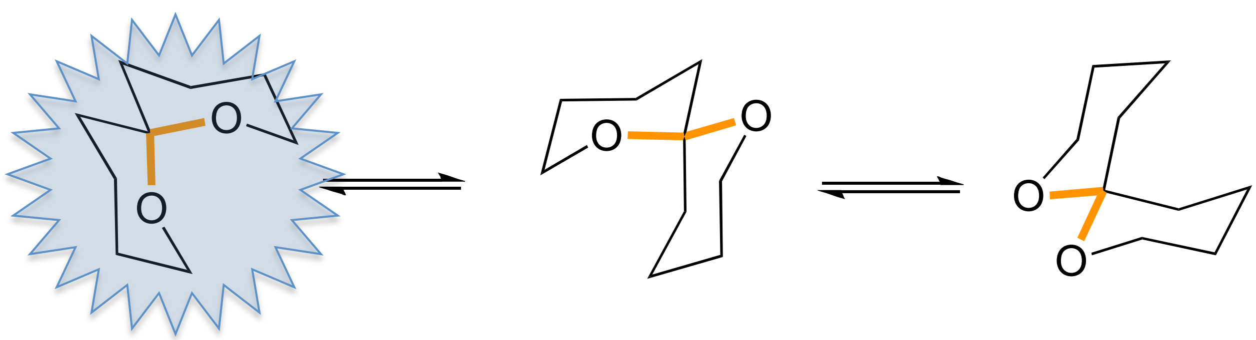
Lengthening of C-X bond



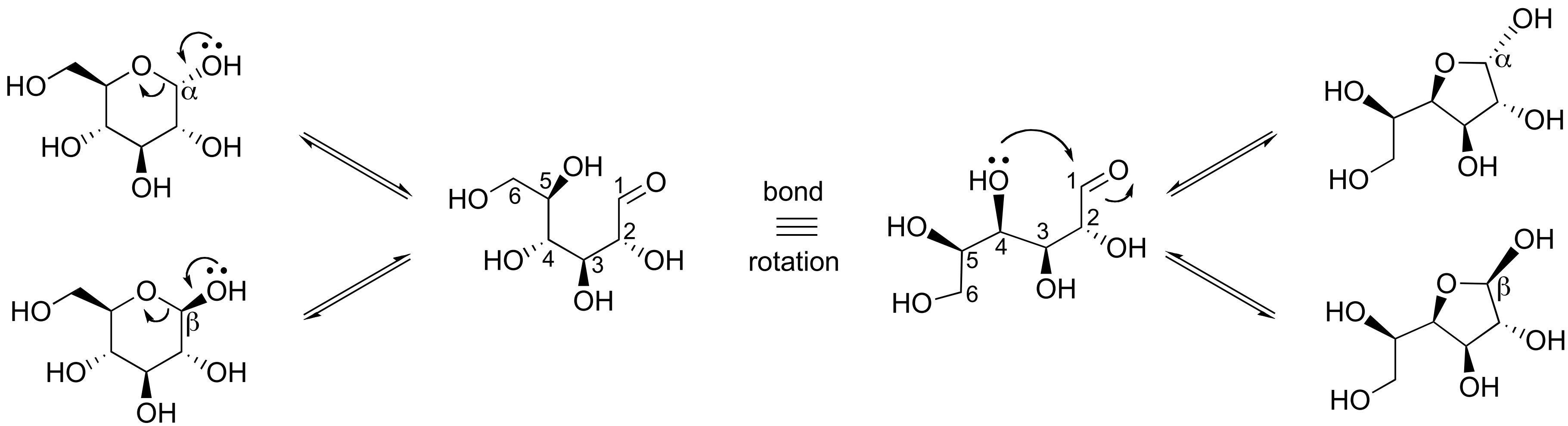


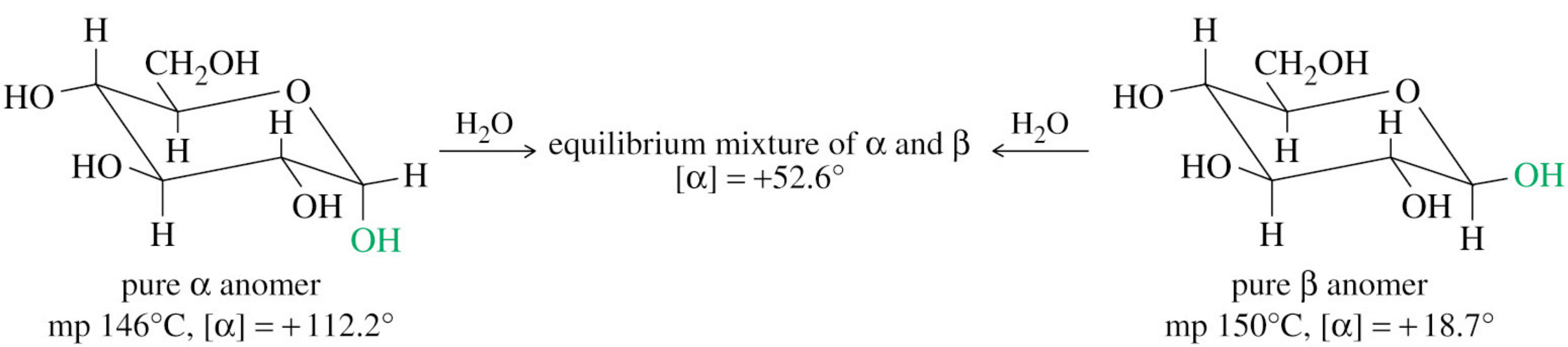


K_{eq} = 3.4 in CCl_4
K_{eq} = 1.8 in CH_3CN



Mutarotation （变旋现象）





Position of the equilibrium

Glucose: thermodynamic stability of pyranose ring

In this case, all substituents can adopt equatorial positions

Other sugars may have larger amounts of the furanose form at equilibrium

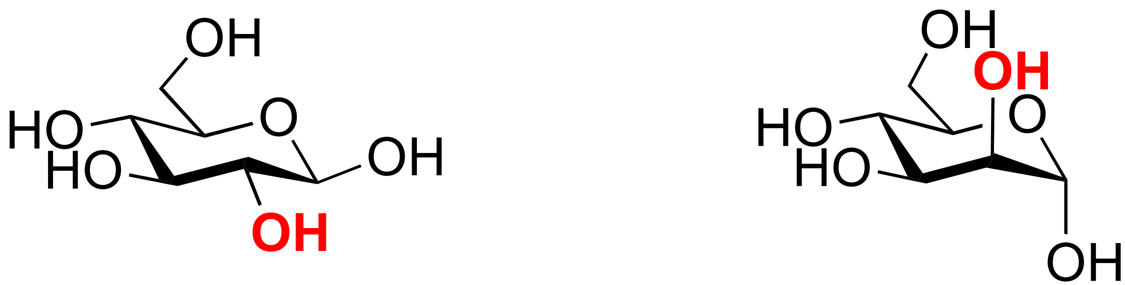
Relative amounts of α and β pyranose pdt

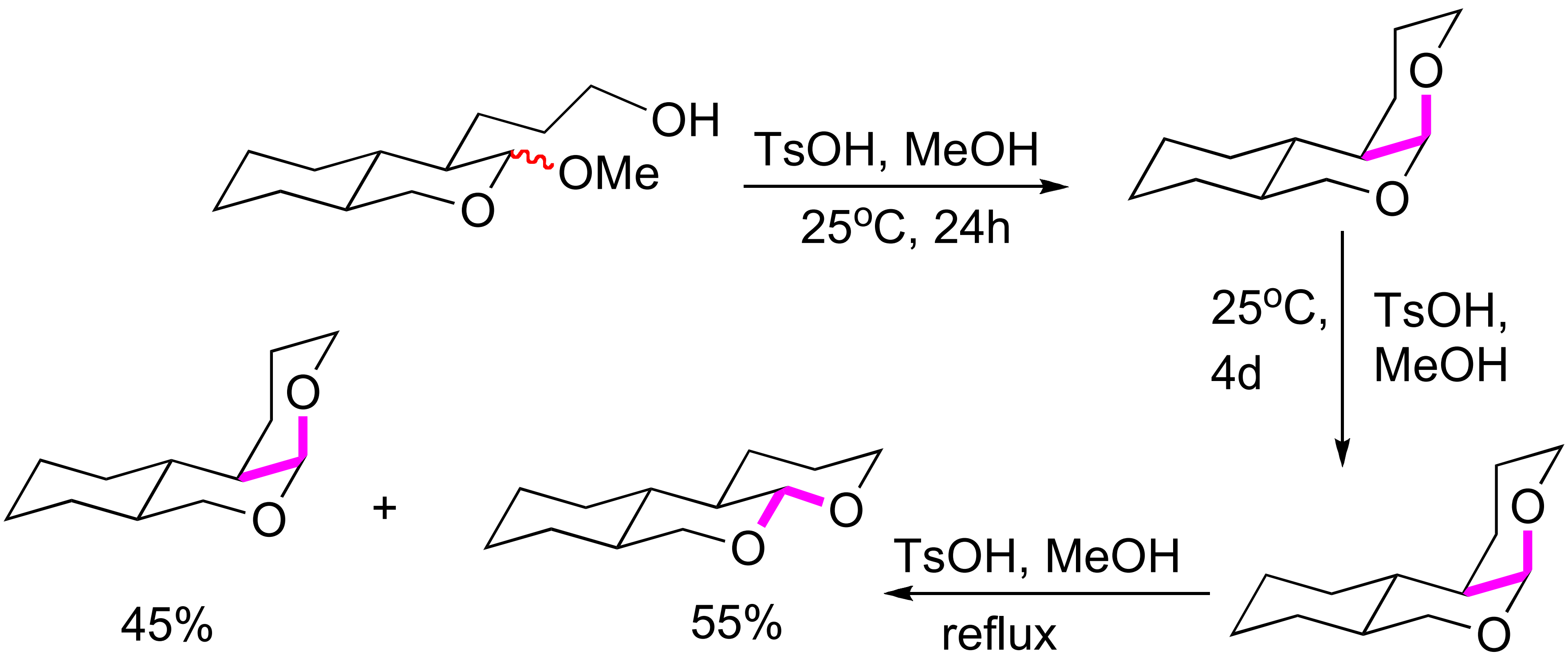
Anomeric effect of α form

Steric effects favor equatorial substituents

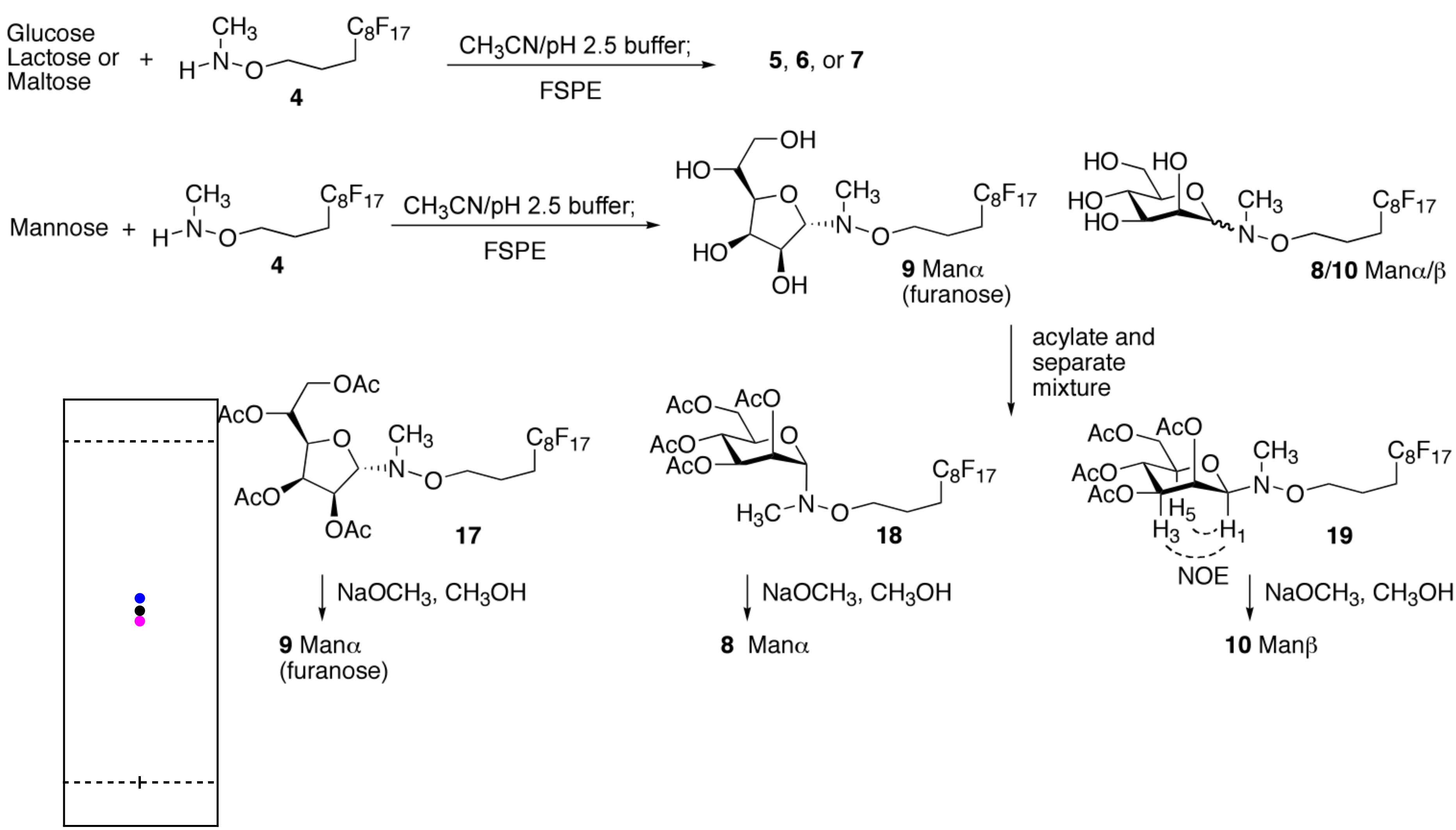
Steric effect may, at least in part, counteract the anomeric effect

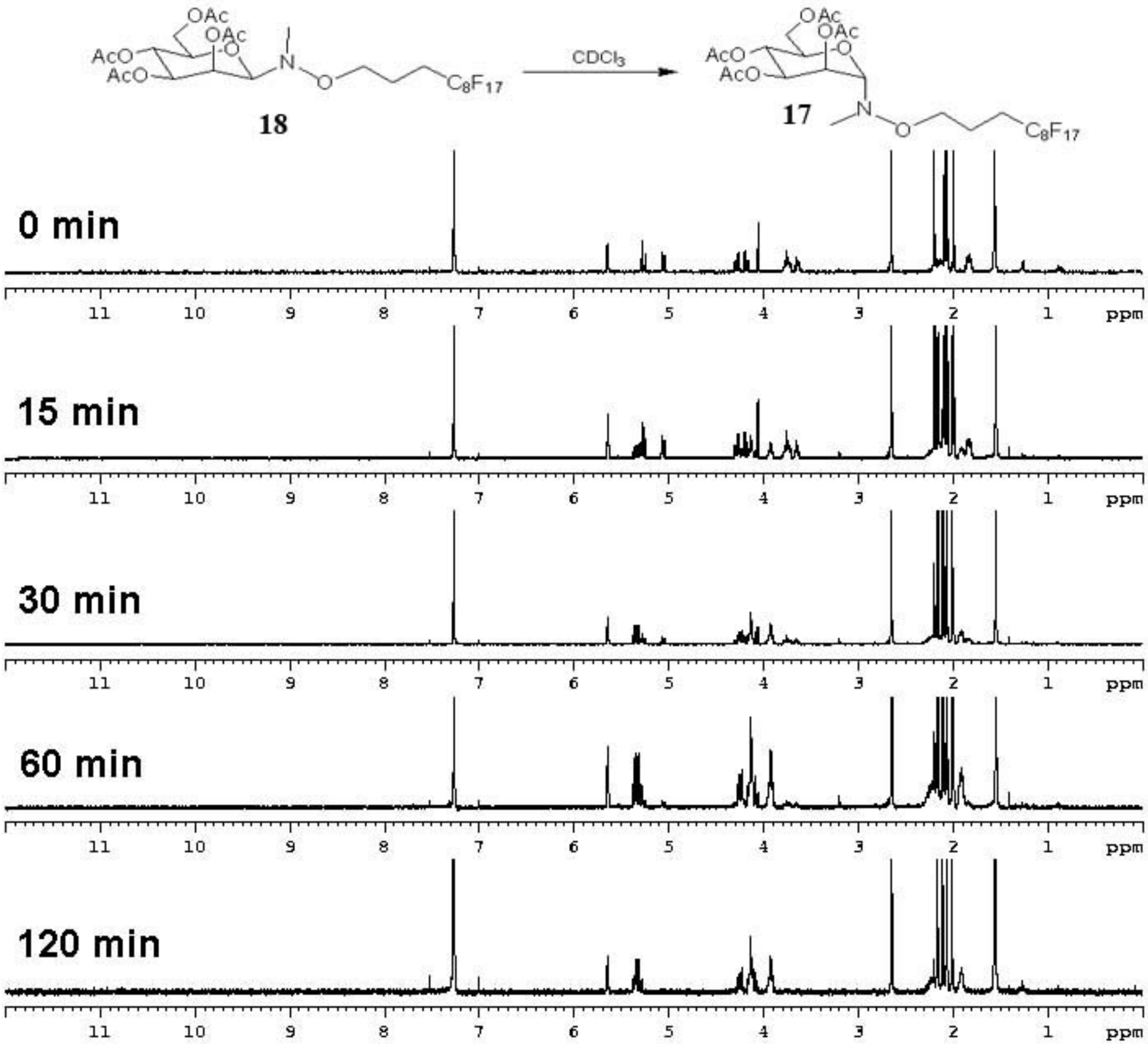
Competition between electronic effects (favor α anomer) and steric effects (favor α anomer)


OH
HO
HO
OH
OH
OH
OH
HO
HO
O
OH
O


OH
OMe
O
TsOH, MeOH
25oC, 24h
O
O
25oC,
4d
TsOH,
MeOH
O
O
TsOH, MeOH
reflux
O
O
+
O
O
45%
55%

My experience





AcO
AcO
OAc
OAc
O
N
O
C8F17
18
CDCl3
17
0 min
15 min
30 min
60 min
120 min
11 10 9 8 7 6 5 4 3 2 1 ppm

Summary

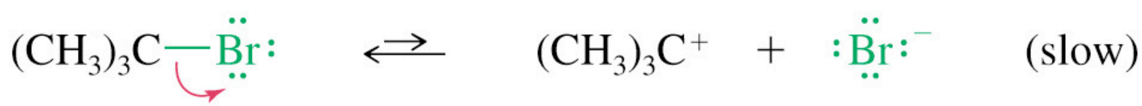
To understand the underlying reasons for the anomeric effect and to be aware of some of the other consequences

To understand and describe the process of mutarotation

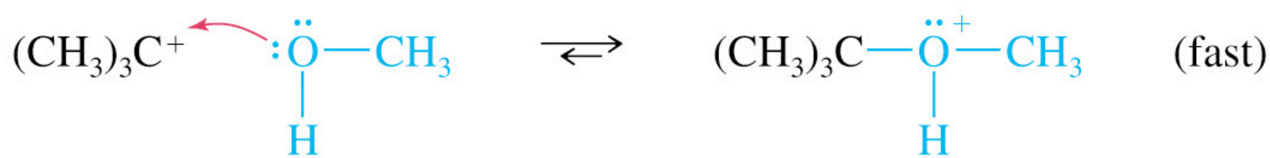
To be able to ratinalise the relative proportions of α/β and furanose/pyranose forms present at equilibrium for glucose

SN1

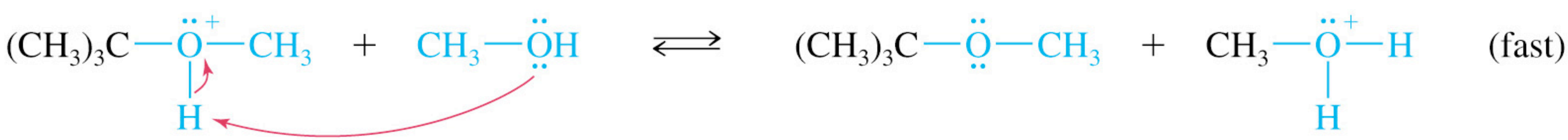
Step 1: Formation of carbocation (rate limiting)

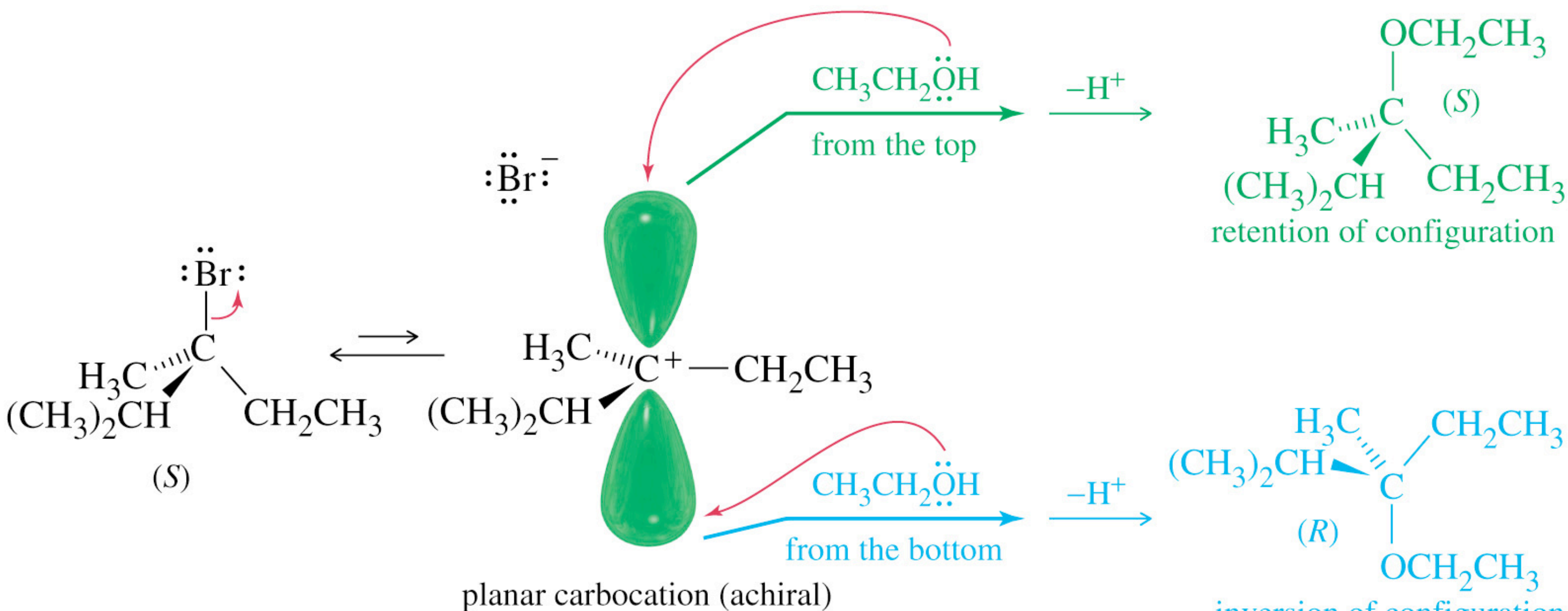


Step 2: Nucleophilic attack on the carbocation

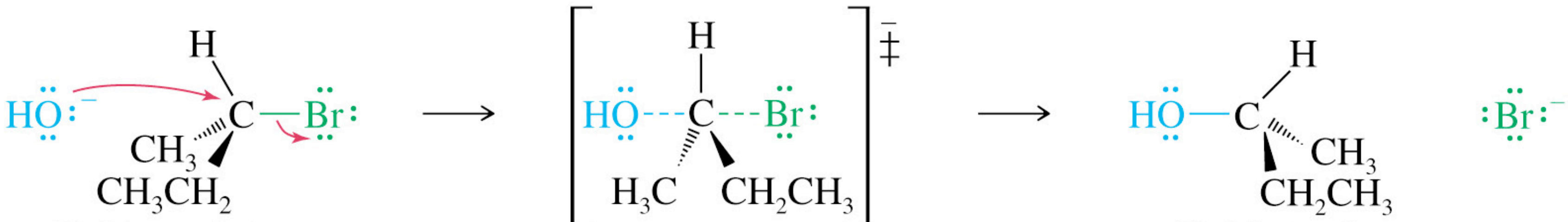


Final Step: Loss of proton to solvent

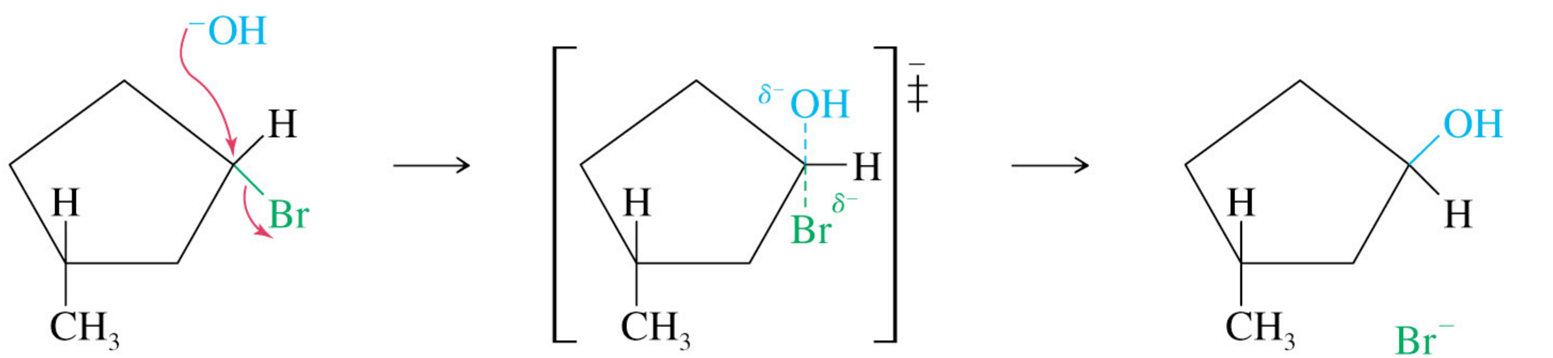



:Br:
(S)
:Br:⁻
planar carbocation (achiral)
CH3CH2ÖH
from the top
−H⁺
(S)
retention of configuration
CH3CH2ÖH
from the bottom
−H⁺
(R)
inversion of configuration

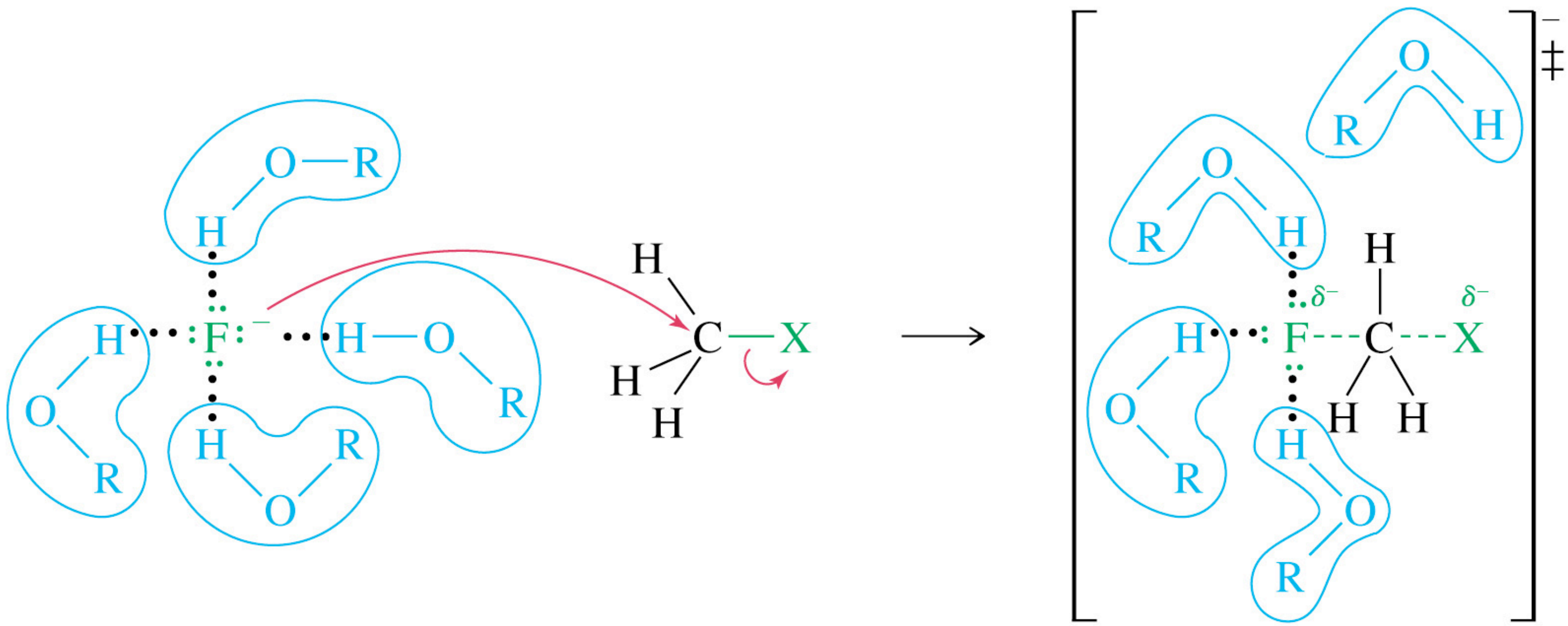
Inversion of configuration in the S_N2 reaction



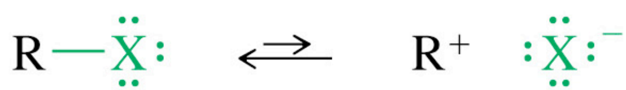
(*S*)-2-bromobutane (*R*)-2-butanol



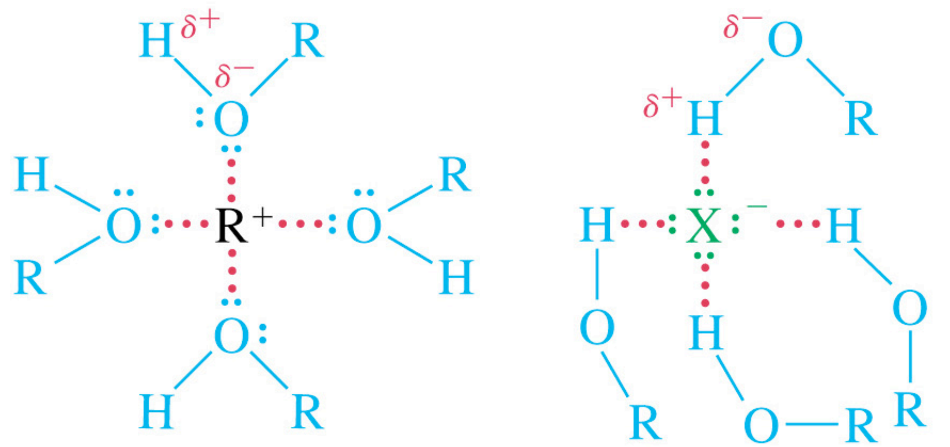
cis-1-bromo-3-methylcyclopentane transition state *trans*-3-methylcyclopentanol



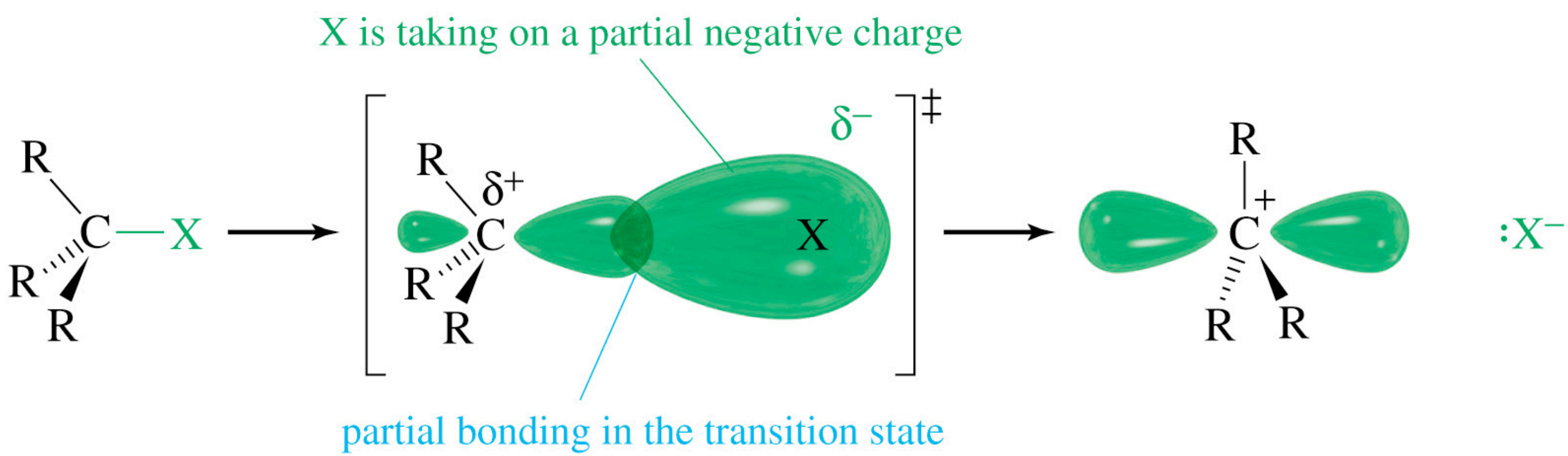
solvent partially stripped
off in the transition state



ionization



solvated ions


X is taking on a partial negative charge
R
C
X
R
R
R
δ+
C
R
R
δ−
X
‡
R
+
C
R
R
:X−
partial bonding in the transition state

SWEETING AGENTS

one of five types of taste sensed by humans.

Sweetness, saltiness, sourness, bitterness and savouriness.

Sucrose is the standard sweetener used in cuisine.

A less expensive alternative known as high fructose corn syrup (HFCS)

developed in the late 1950's

widely used in baked goods and beverages

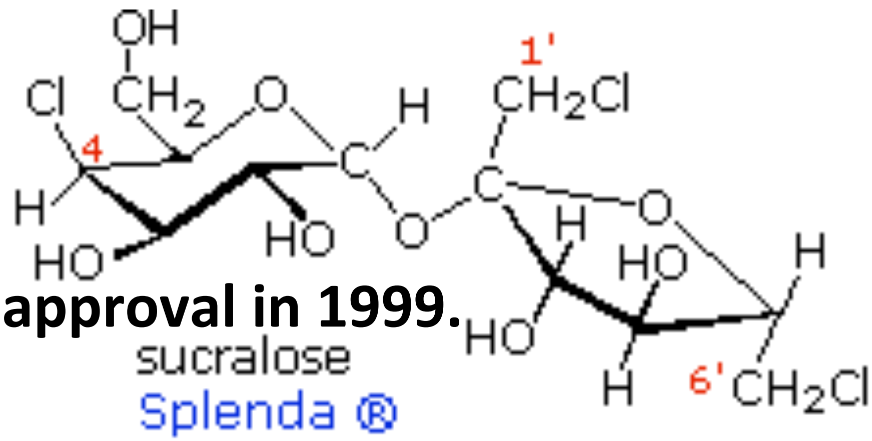
HFCS is made from corn syrup by enzymatic conversion of glucose to fructose.

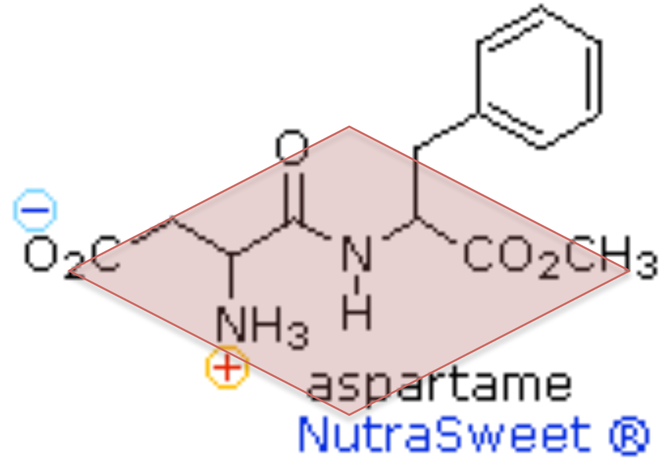
Fructose is 2.3 times as sweet as glucose and 75% sweeter than sucrose, then HFCS provides a practical substitute for sucrose in a variety of applications, and is available in compositions ranging from 45 to 90% fructose.

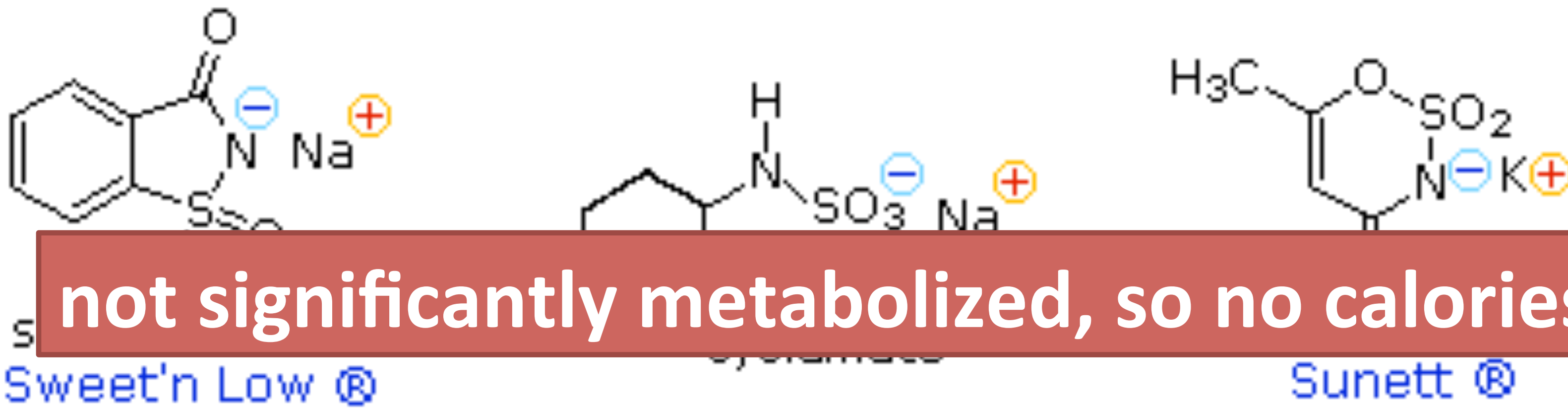
Since the specific rotation of these sugar solutions changes from +66.5º for pure sucrose to -22.0º for the hydrolysis mixture (fructose is strongly levorotatory), the resulting glucose fructose mixture is called **invert sugar**.

invertase

FDA approval in 1999.



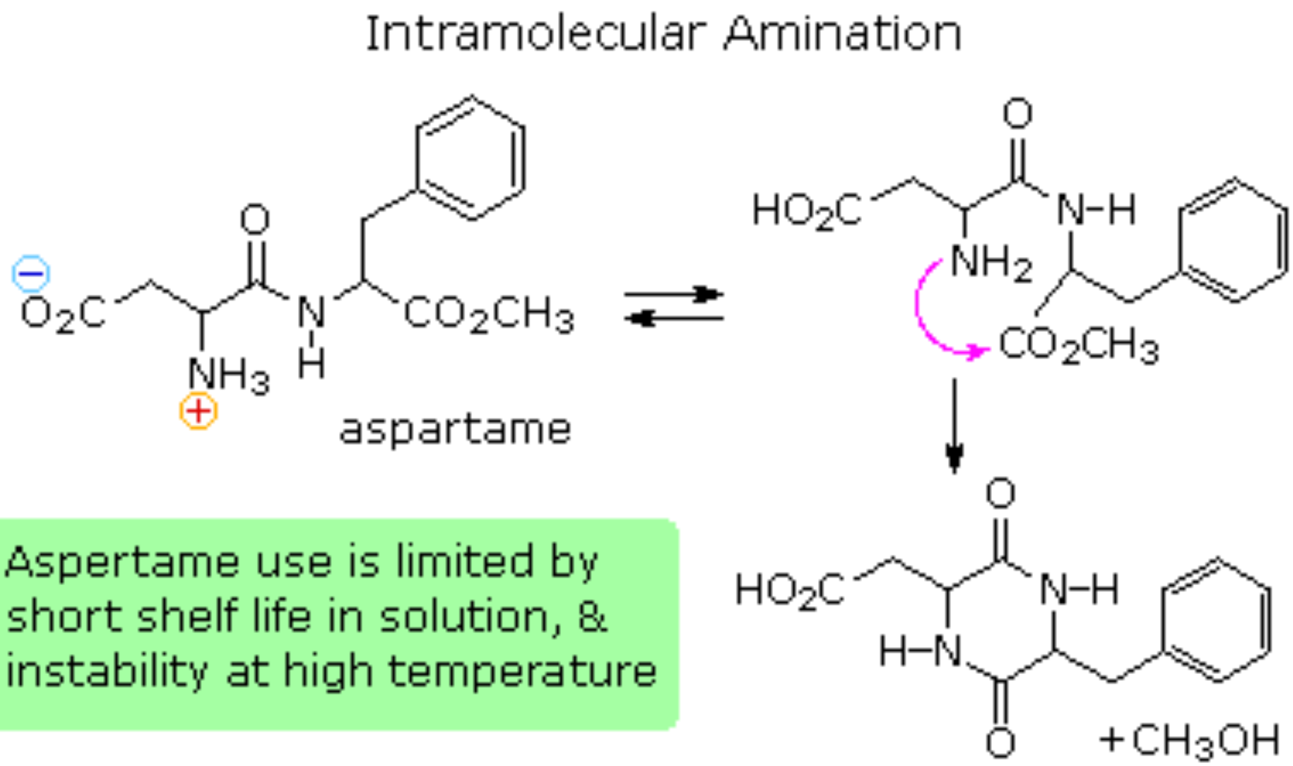




not significantly metabolized, so no calories

in 1879
at Johns Hopkins University

Compound	sucralose	saccharin	acesulfame-K	aspartame	cyclamate	fructose	sucrose	glucose	maltose	lactose
Sweetness	600	300	200	180	30	1.7	1.0	0.7	0.3	0.15



Aspertame use is limited by short shelf life in solution, & instability at high temperature

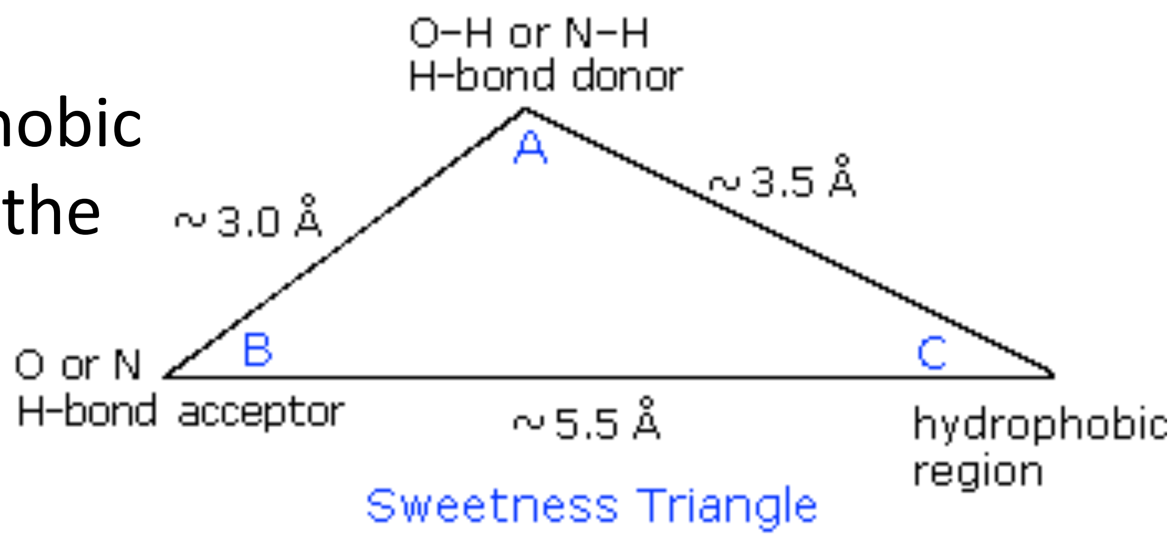
Sweet triangle

For sweetness to be perceived, molecules of a substance must activate receptor sites in taste bud proteins on the tongue.

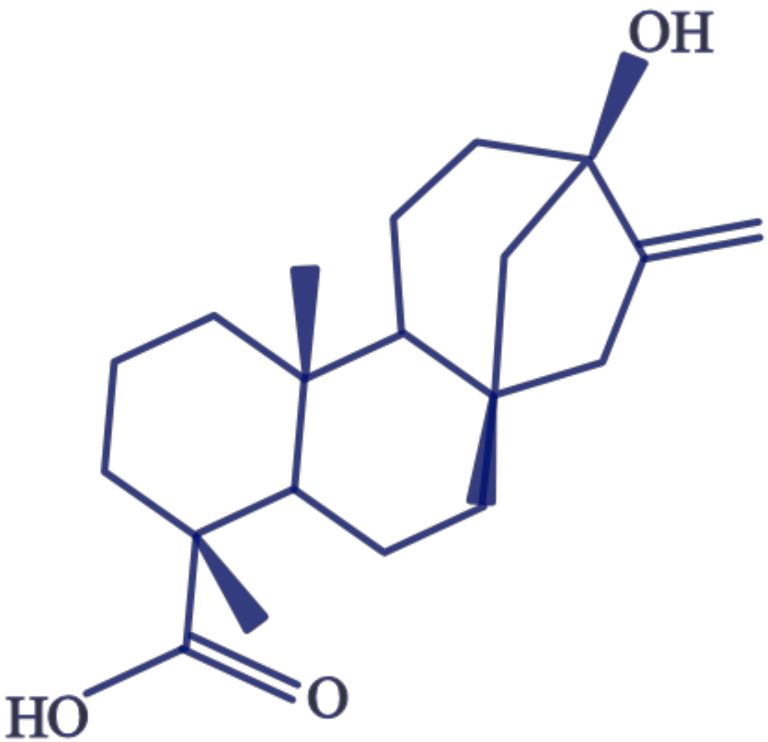
The A(H) and B regions encompass functions of higher electronegativity,

the distance between A and B (2.4 A - 4.0 A)

C, represents a hydrophobic and lipophilic region of the molecule

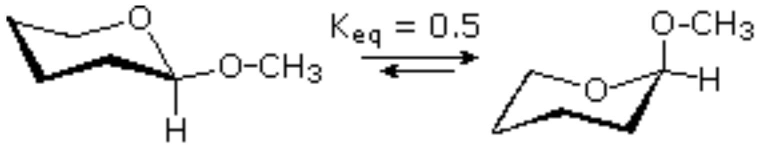


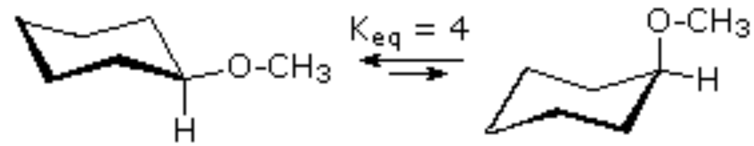
甜菊醇

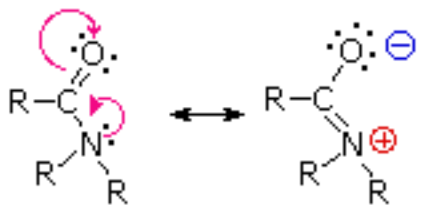


Stevia rebaudiana Bertoni

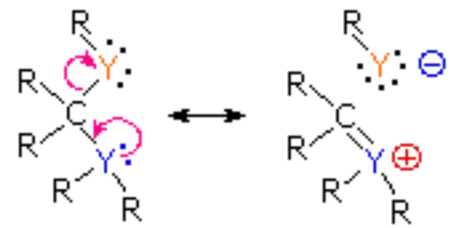
Steviol



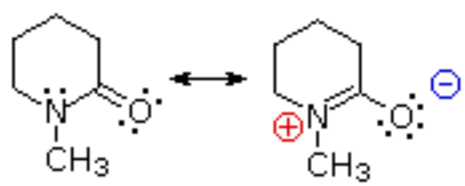




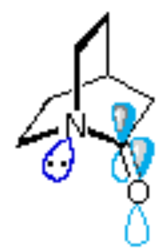
n-π resonance in amides



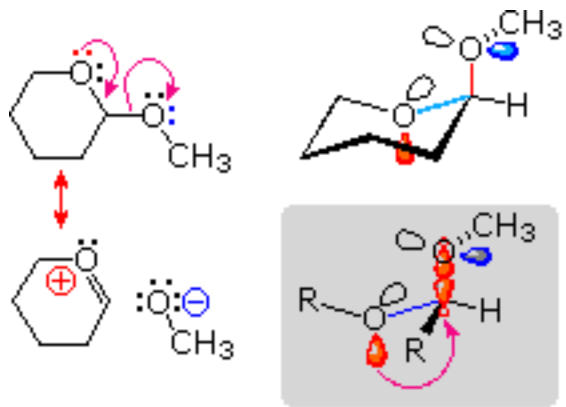
n-σ resonance (Y = N, O, Cl ---)



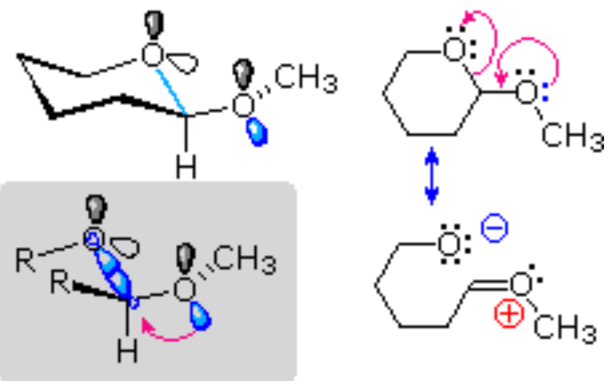
pK_a = 0.5
C=O 1658 cm^{-1}



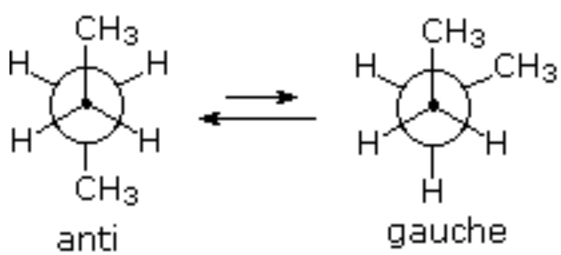
pK_a = 5.3
C=O 1760 cm^{-1}



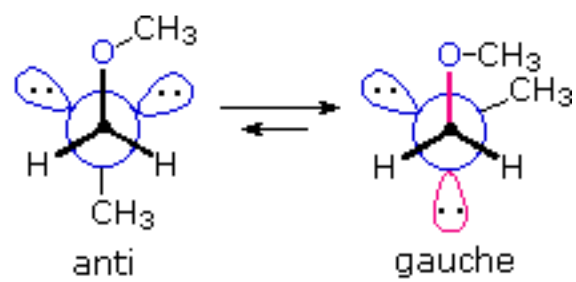
anomeric stabilization type 1



anomeric stabilization type 2



Butane



Dimethoxymethane