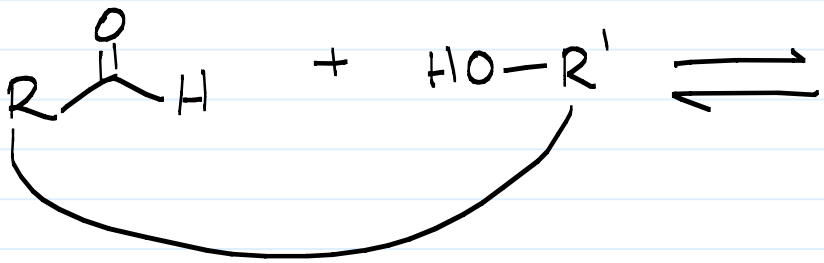
Sugars

Note Title 5/8/2014

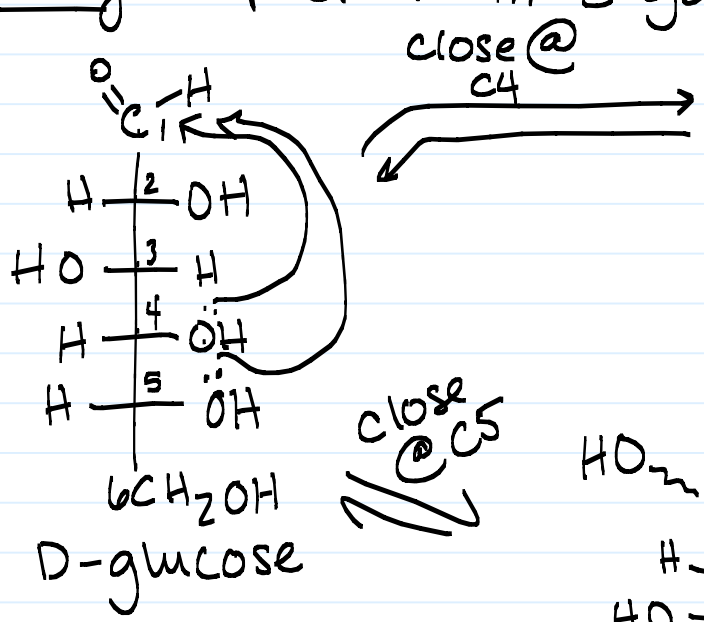
Recall:

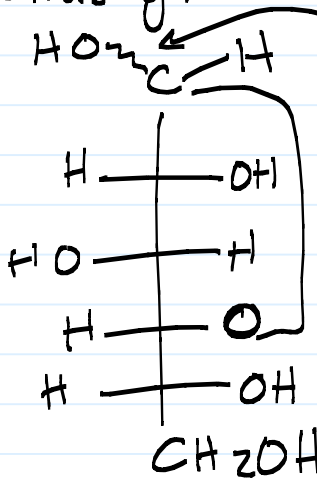


hemiacetal

→ favored if 5- or 6-membered ring can form.

Really important in sugar chemistry!

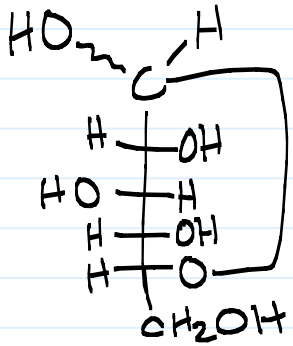




squiggle to indicate both configurations exist

5-membered ring = "furanose"

furan

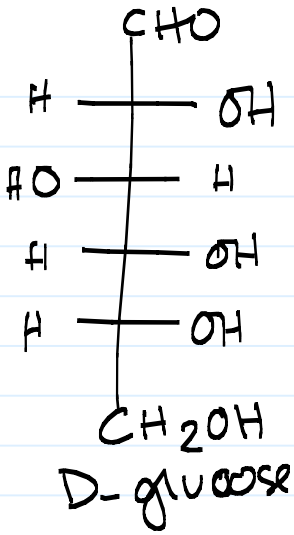


6-membered ring = "pyranose"

pyran

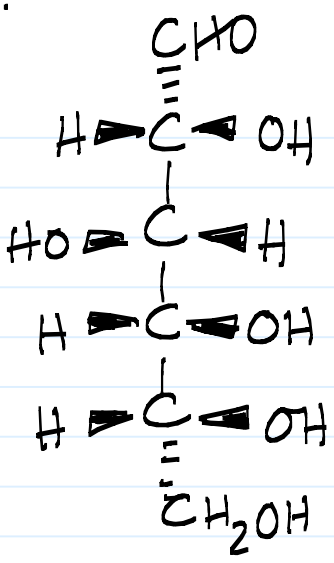
For glucose
Open < 0.05%
pyranose > 99.95%

Haworth form:

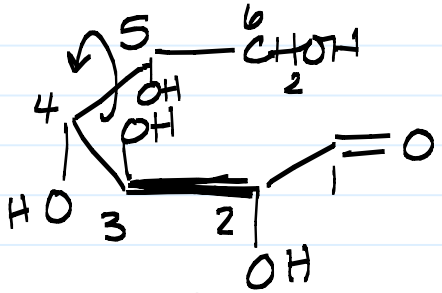


D-glucose

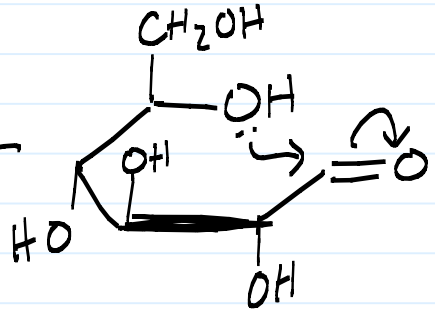
=

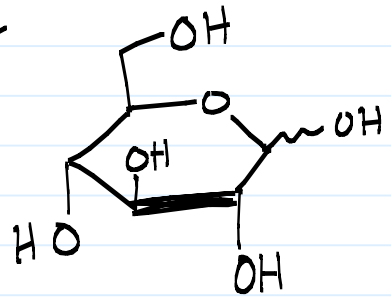


rotate + wrap around an imaginary cylinder



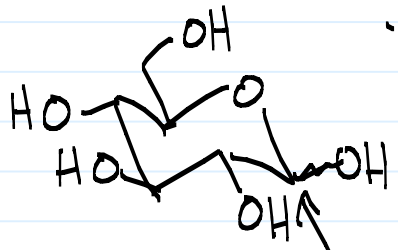
Rotate around C4-C5

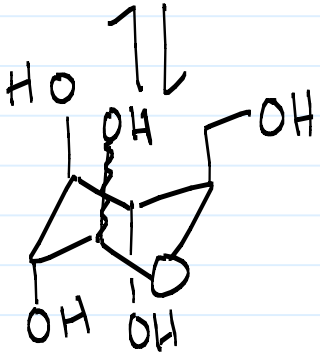




Haworth form

"relax" to chair



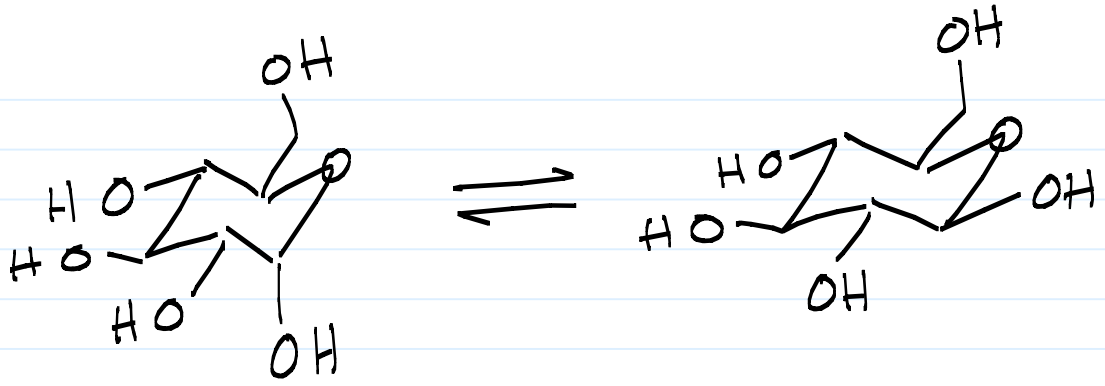


anomeric carbon.

Both configurations exist (squiggle)

For glucose:

pyranose



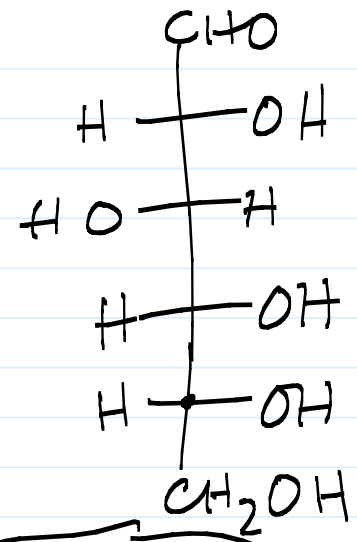
α-glucose ⇌ β-glucose

α-pyranose : β-pyranose : α-furanose : β-furanose

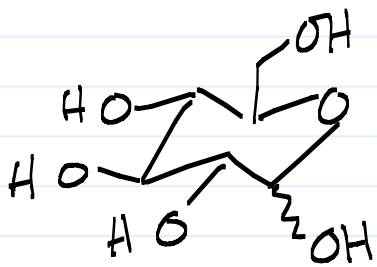
36 : 64 : <1 : <1

* Easiest to do with model kit!

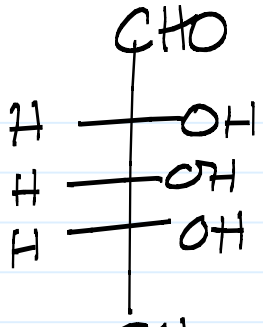
Sugars you should know by name:

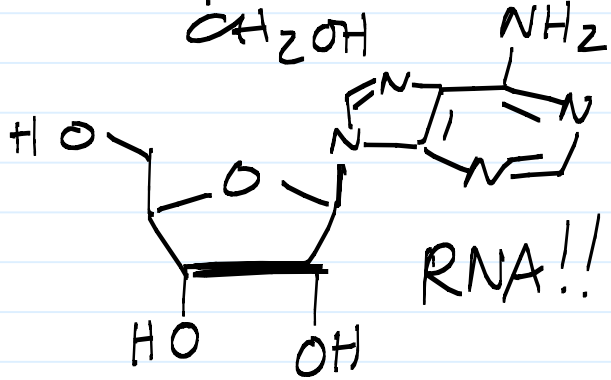


glucose



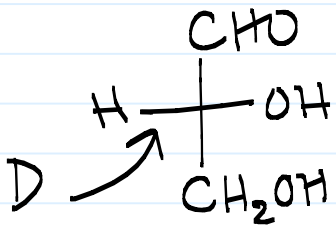
Ribose





RNA!!

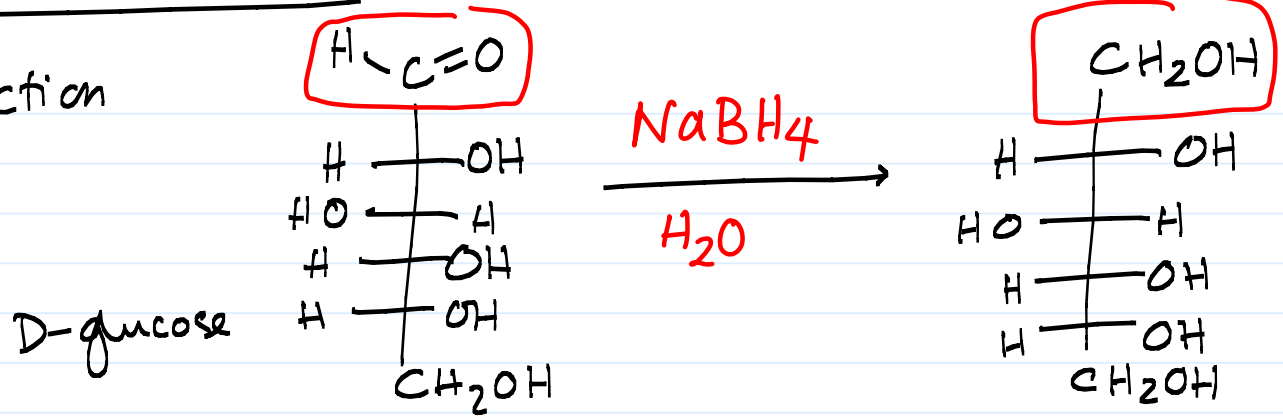
D vs. L glyceraldehyde



Dihydroxyacetone

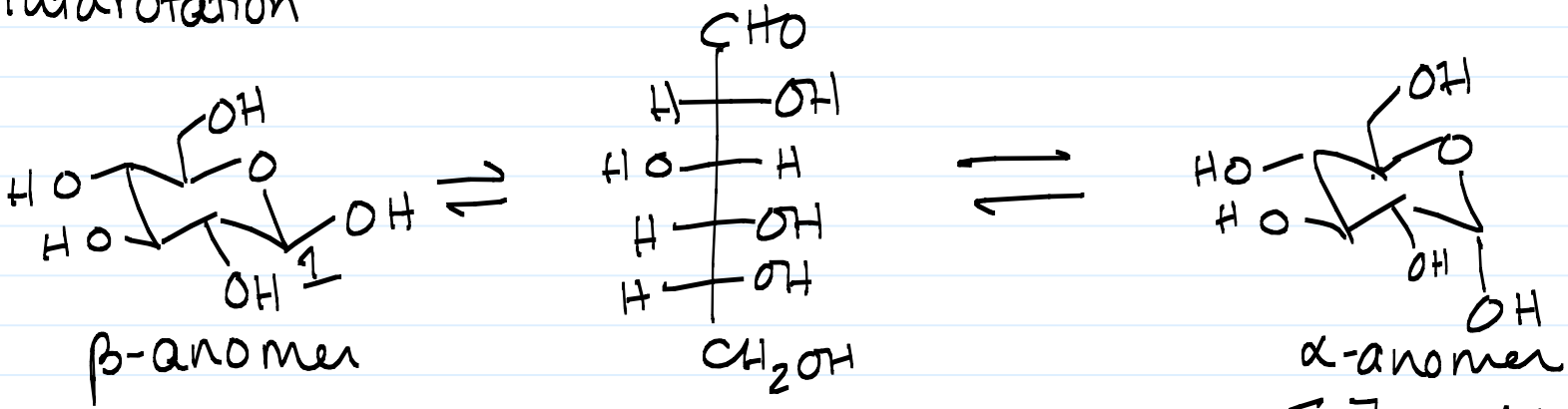
Rxns of Sugars

- Reduction



Note: $NaBH_4$ can reduce any aldehyde (more mild than $LiAlH_4$). Doesn't touch esters, carboxylic acids, etc.

- Mutarotation



β-anomer

Pure: $[\alpha] = +18.7°$

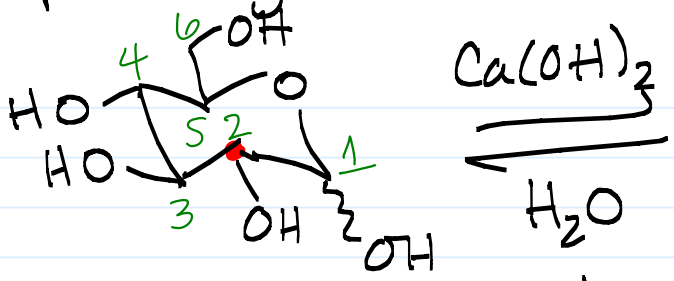
α-anomer

$[\alpha] = +112°$

Aqueous Solution: $[\alpha] = +52.7°$

Practice: Draw mech!!

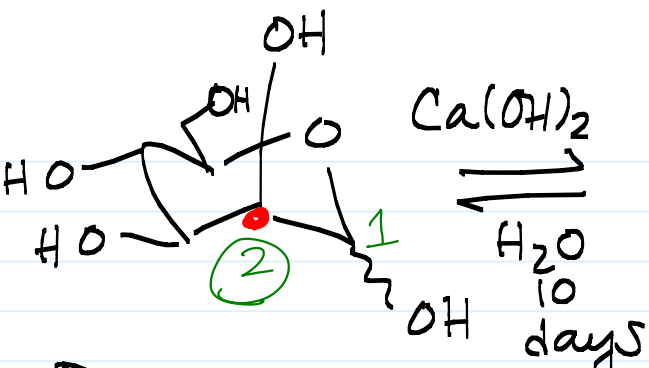
- Epimerization in Base



$Ca(OH)_2$ ⇌ H_2O, 10 days

D-glucopyranose

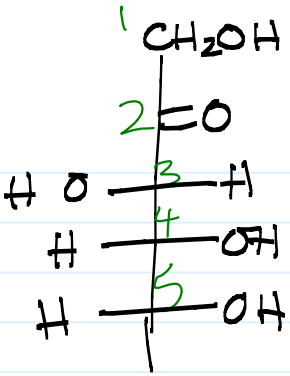
63.4%



$Ca(OH)_2$ ⇌ H_2O, 10 days

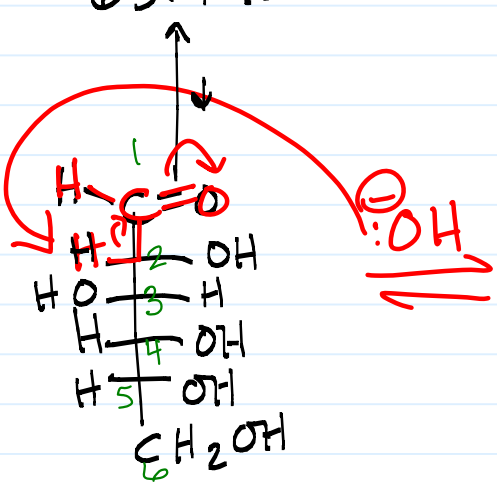
D-mannopyranose

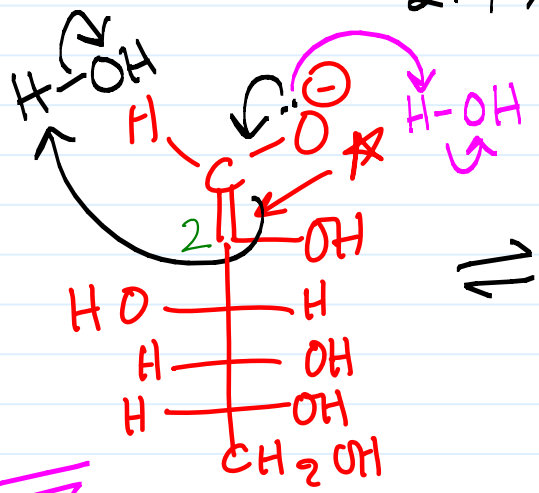
2.4%

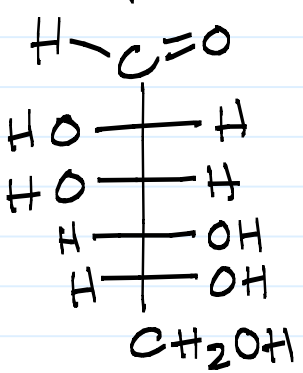


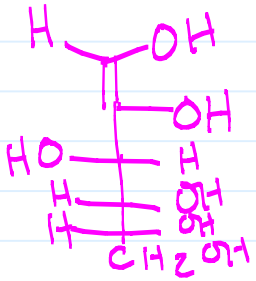
D-fructose

30.9%

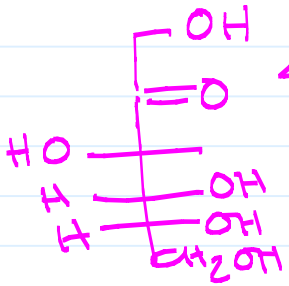








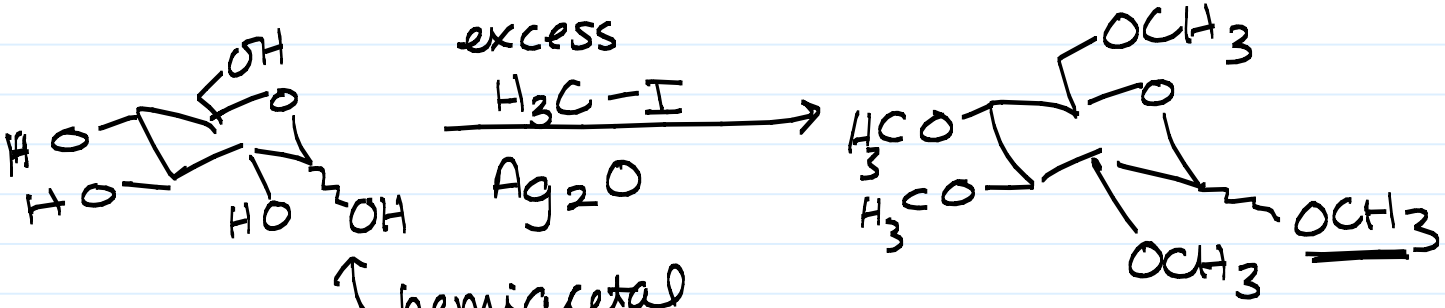
tautomerize



fructose

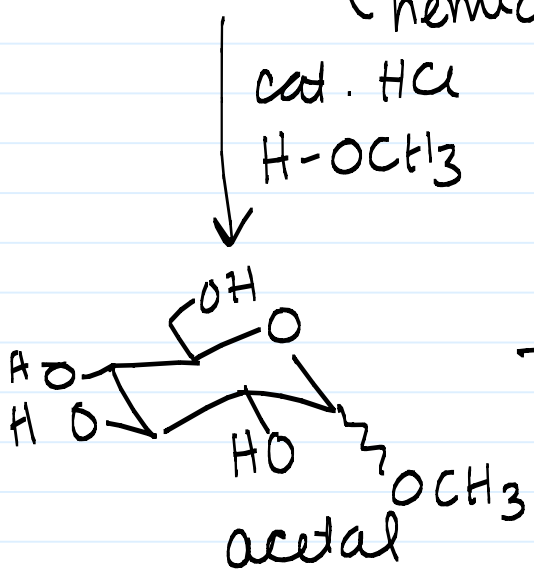
- Ether Form'n

Recall: $R-OH \longrightarrow R-O-R'$

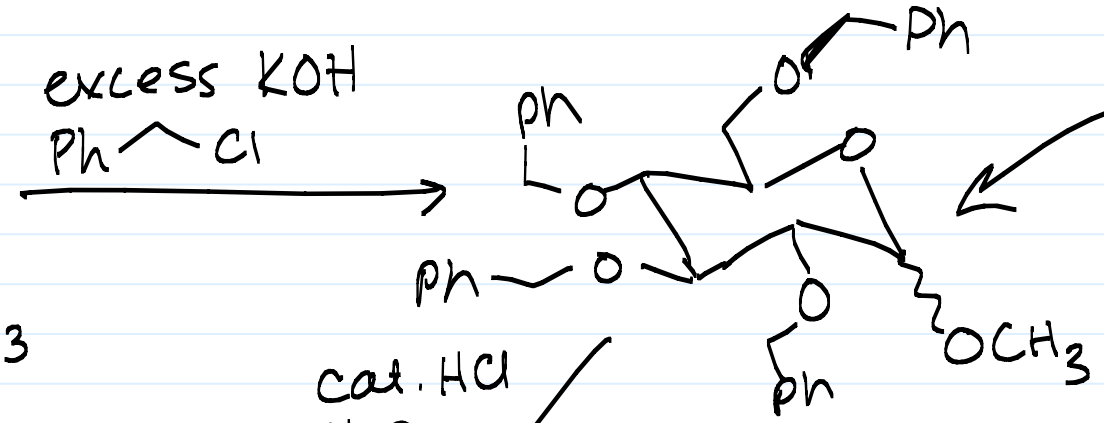


↑ hemiacetal

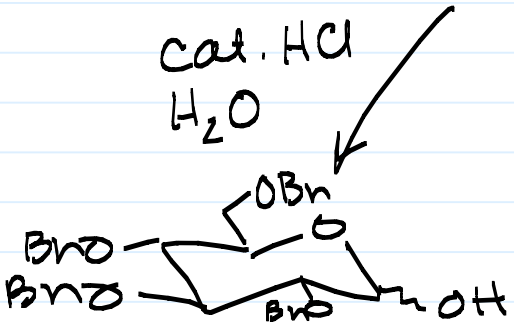
PRACTICE: Draw mech's!!



acetal



Acetal stable under basic conditions.



Bn = CH_2Ph

- Ester Formation