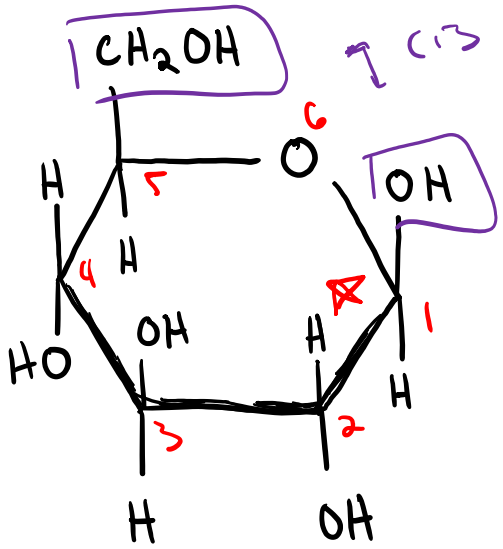
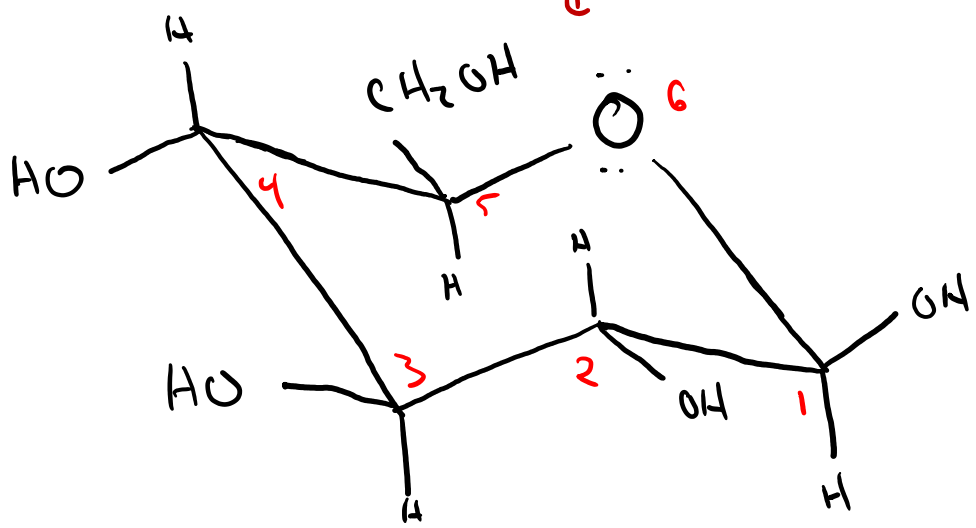
Reactions of Carbohydrates

4/17/2023

Chair Structures of Pyranoses



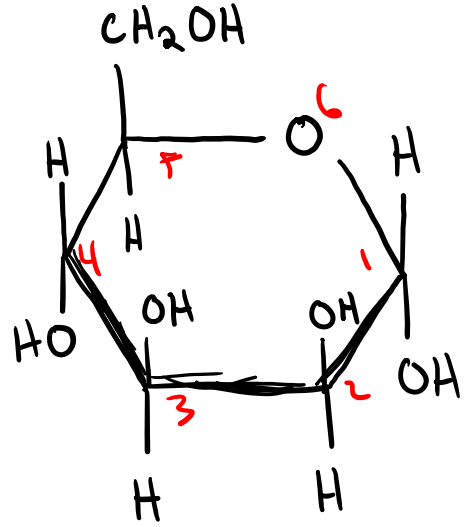
right rear corner

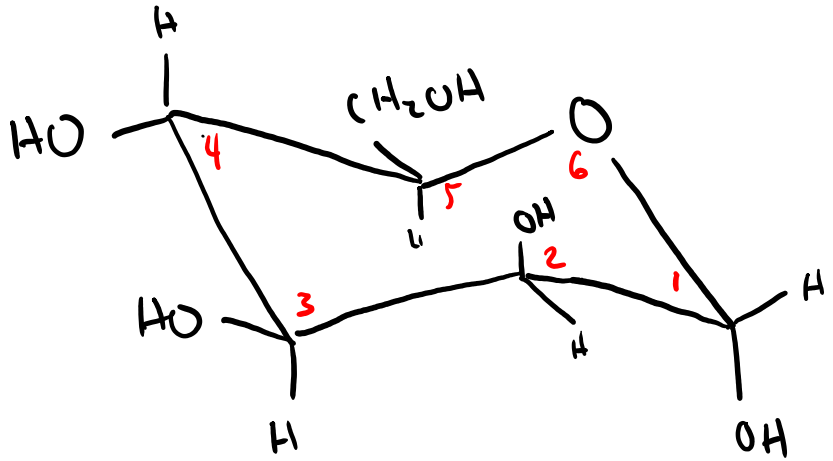


β - D - Glucopyranose

all OH & CH_2OH are equatorial!

very stable (most common sugar)





α - D - Mannopyranose

Practice:

draw

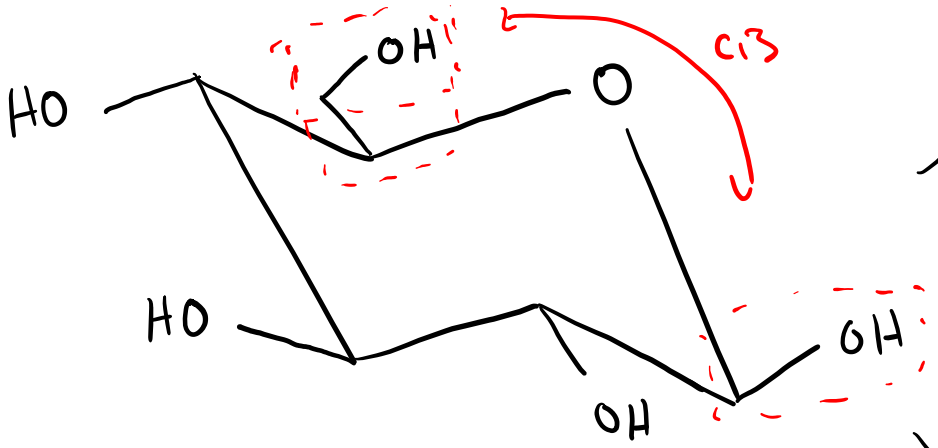
β - L mannopyranose

Reactions of Carbohydrates

(24.6)

Alcohols as nucleophiles (not new to us!)

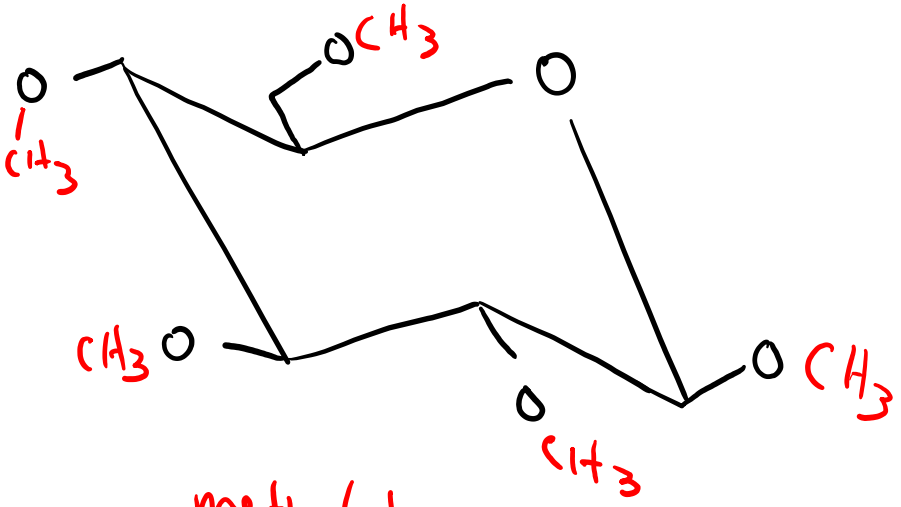
β - D-glucose



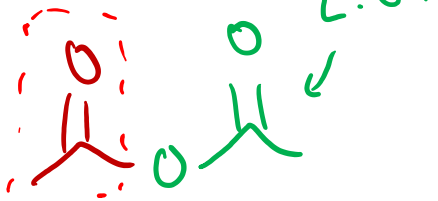
CH_3-I

excess

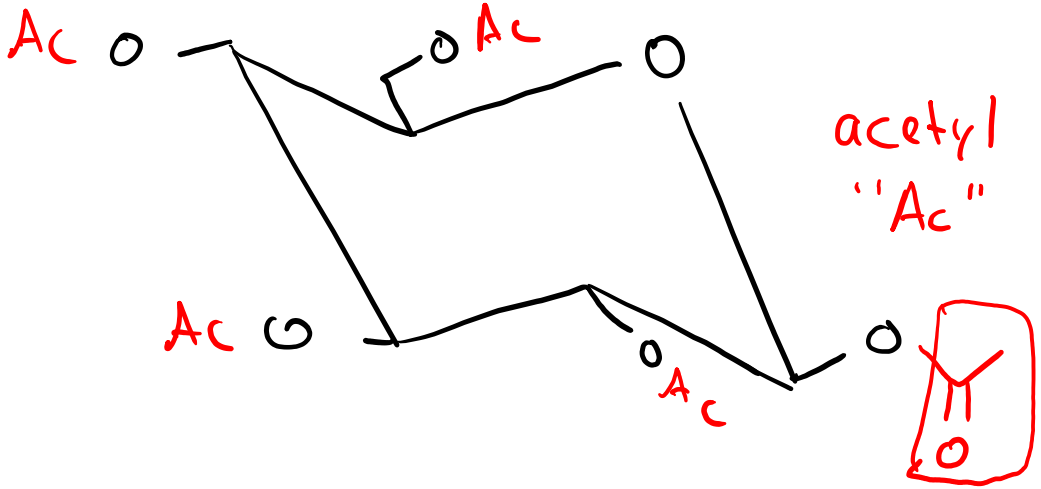
excess pyridine



methylation of glucose



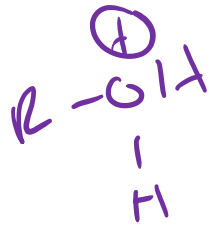
excess pyridine



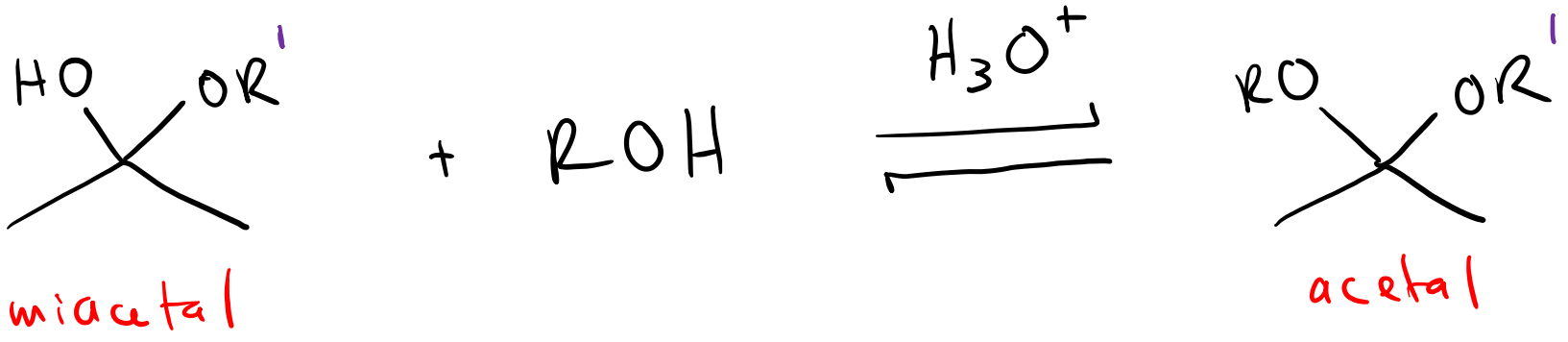
acetyl "Ac"

R-OH

$(CH_3)_3C-I$



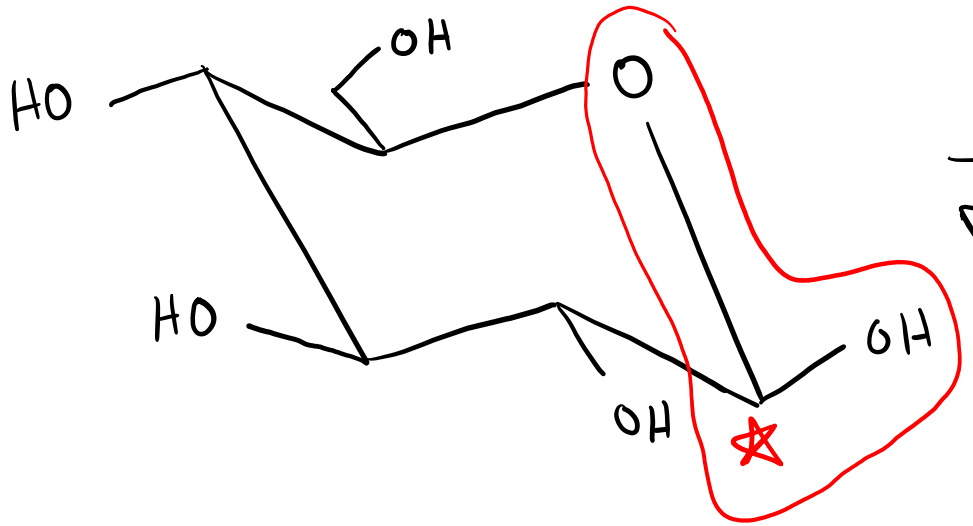
Glycoside Formation (hemiacetal → acetal)



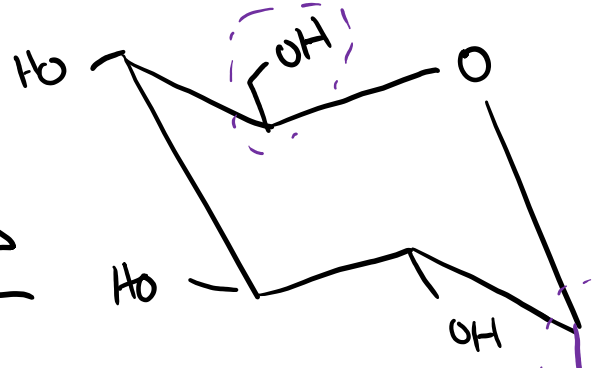
hemiacetal

acetal

☆ only the anomeric -OH changes ☆



HCl



trans

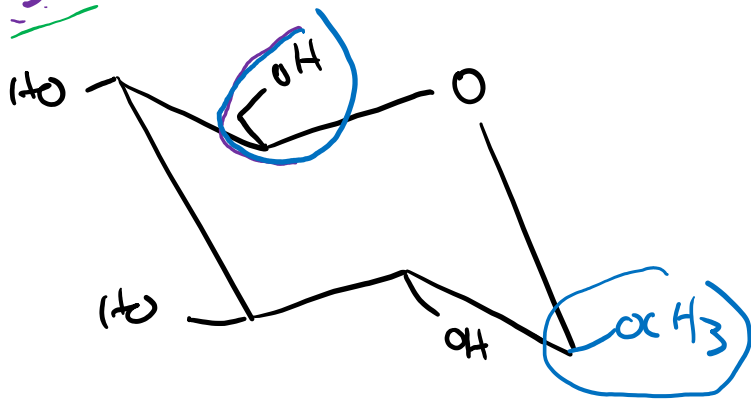
α-

~33%

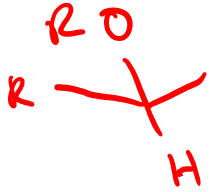
+

~66%

β-

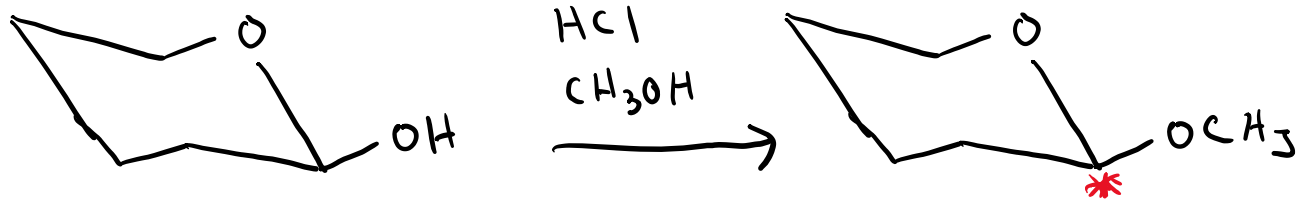


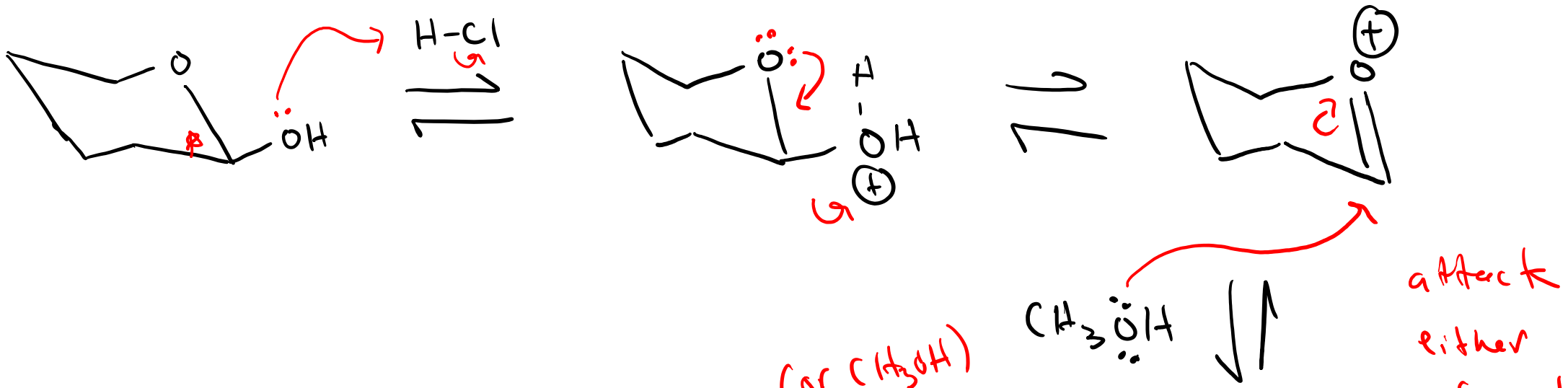
+ CH_3OH

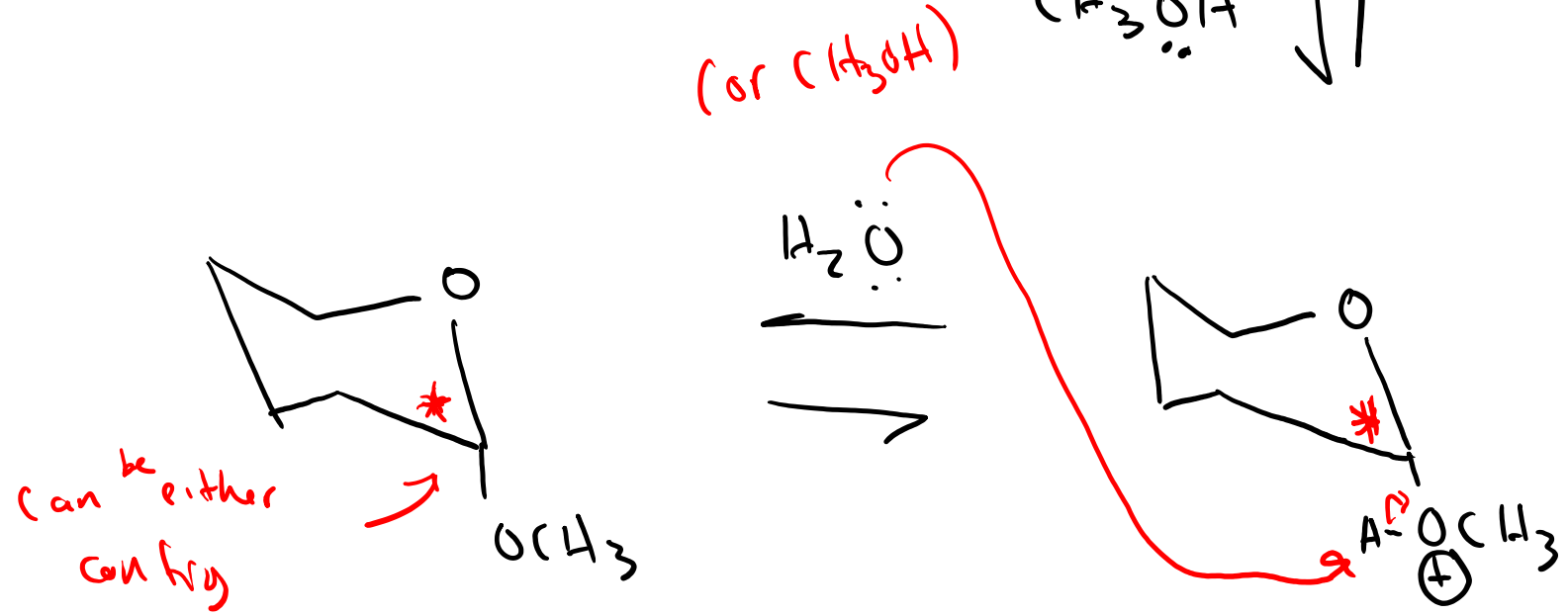


↳ hemiacetal

Glycoside Formation: Mechanism

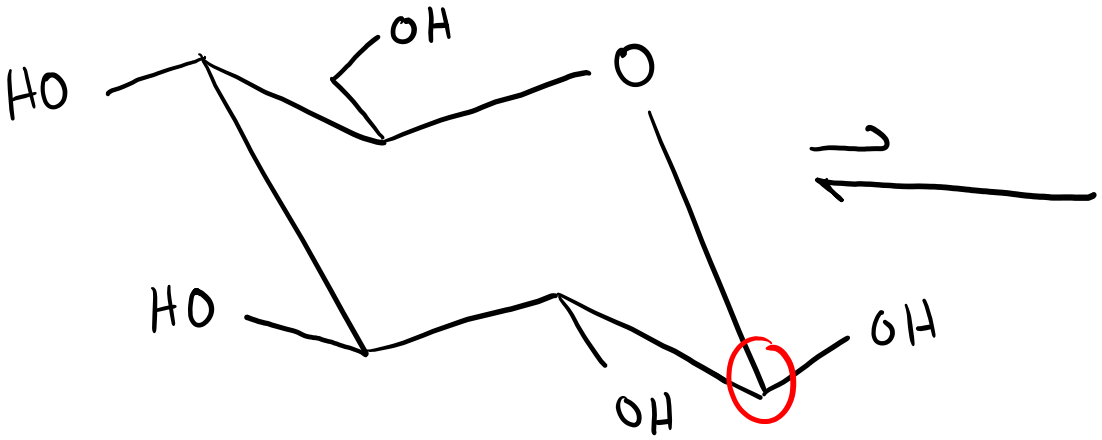


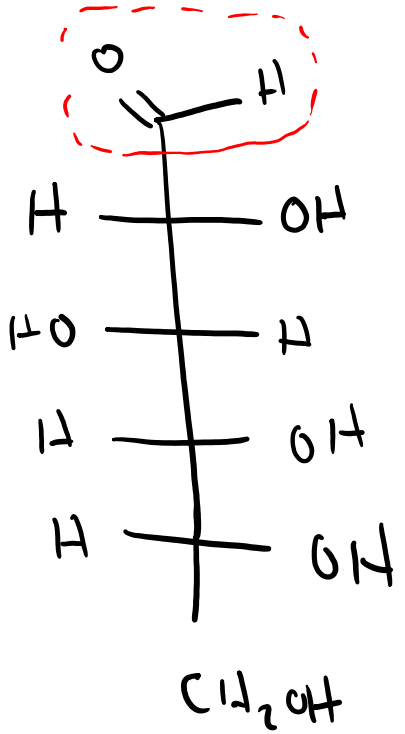




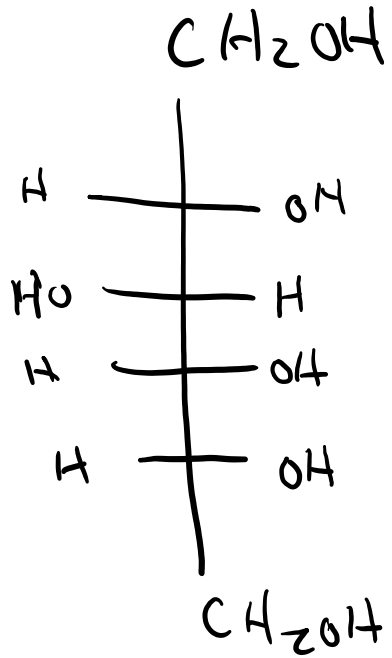
Reduction of Carbohydrates

Hydride transfer!





1) $NaBH_4$
2) H_3O^+



no C=O

to reduce

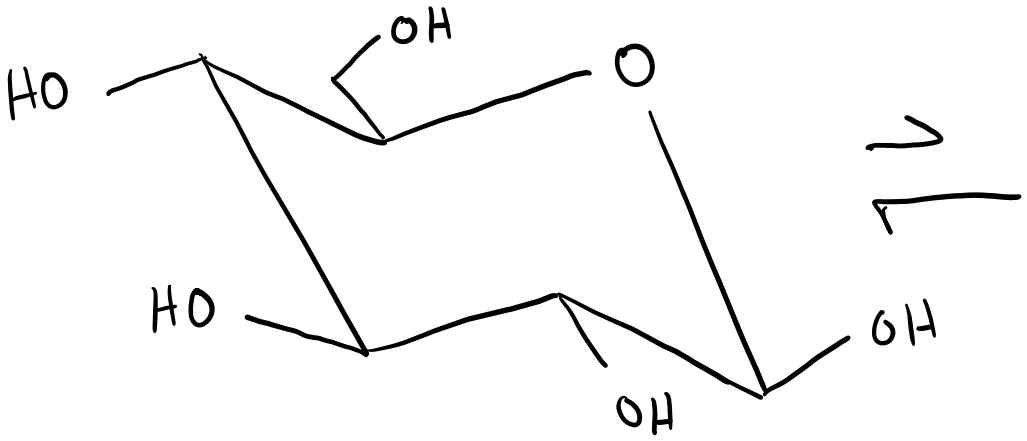
99% ring

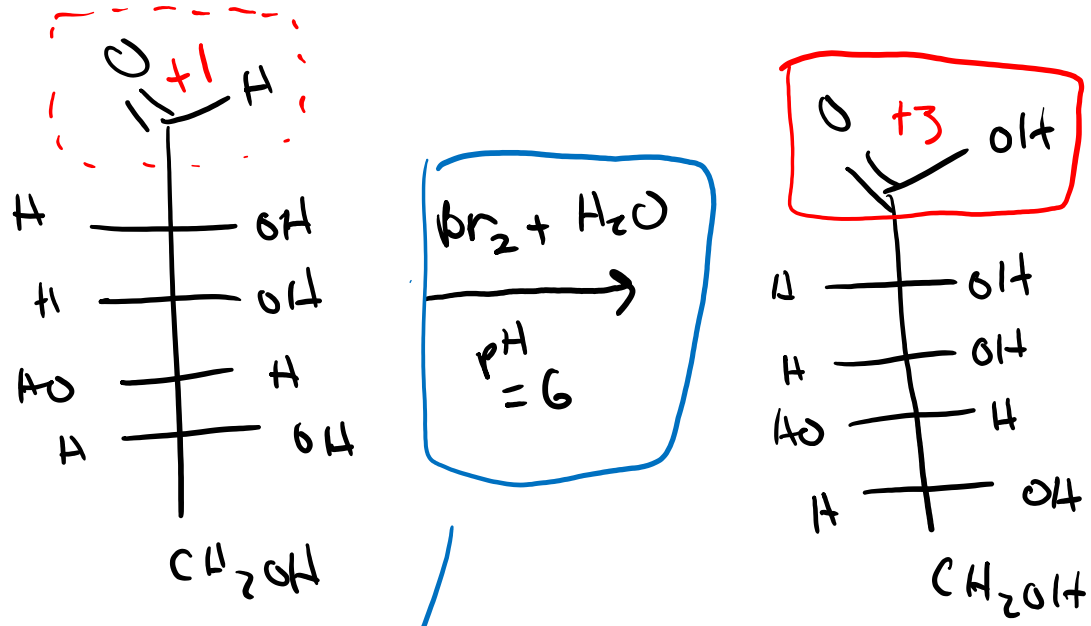
~1% chain

@ equilibrium

Le Chatelier's principle!

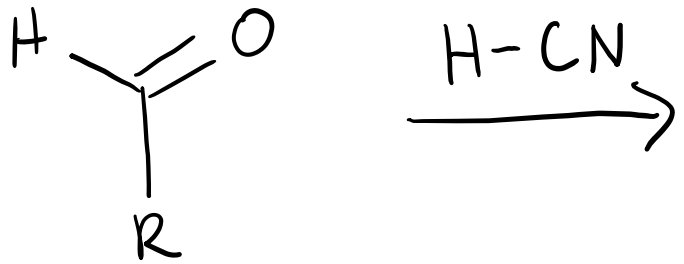
Oxidation of Carbohydrates





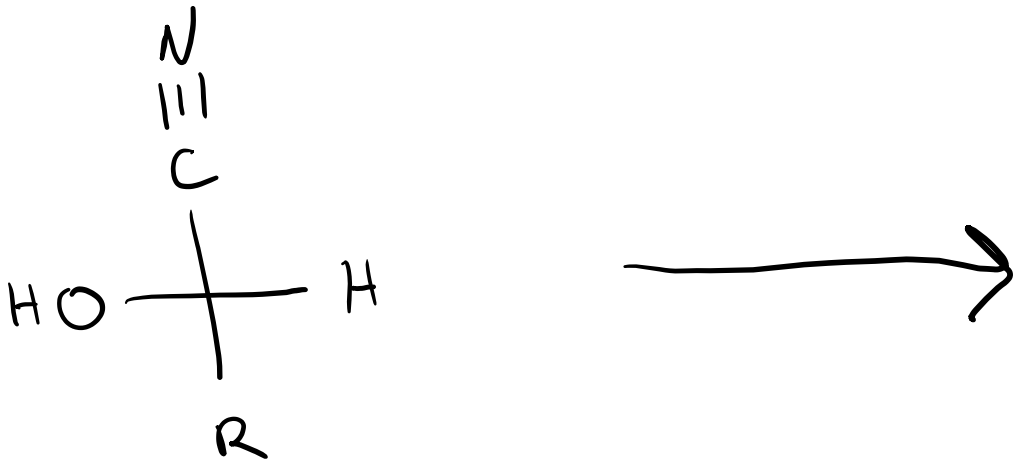
- weak ox. agent
- Selective for aldehyde over alcohol

Chain Lengthening: Kiliani-Fischer Synthesis

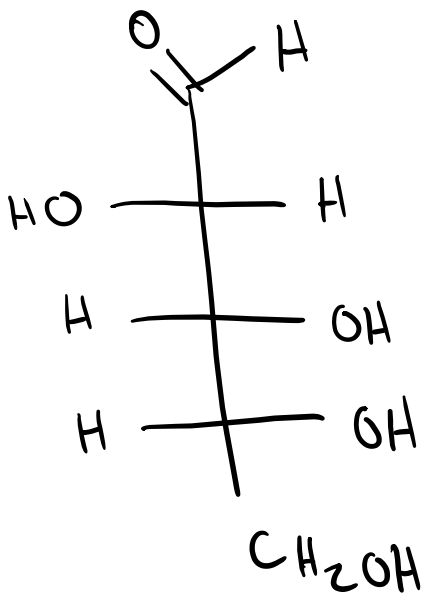


Mechanism:

Chain Lengthening: Kiliani-Fischer Synthesis



Chain Lengthening: Kiliani-Fischer Synthesis



D- Arabinose

1) HCN

2) H_2 +

Pd / $BaSO_4$

H_2O