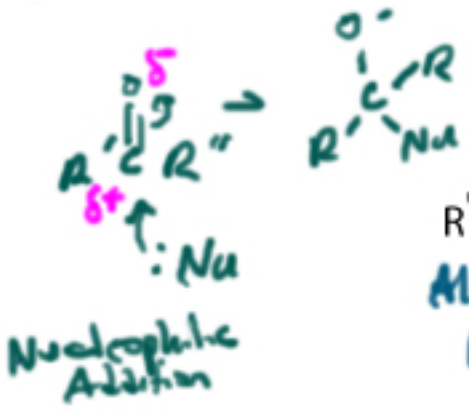
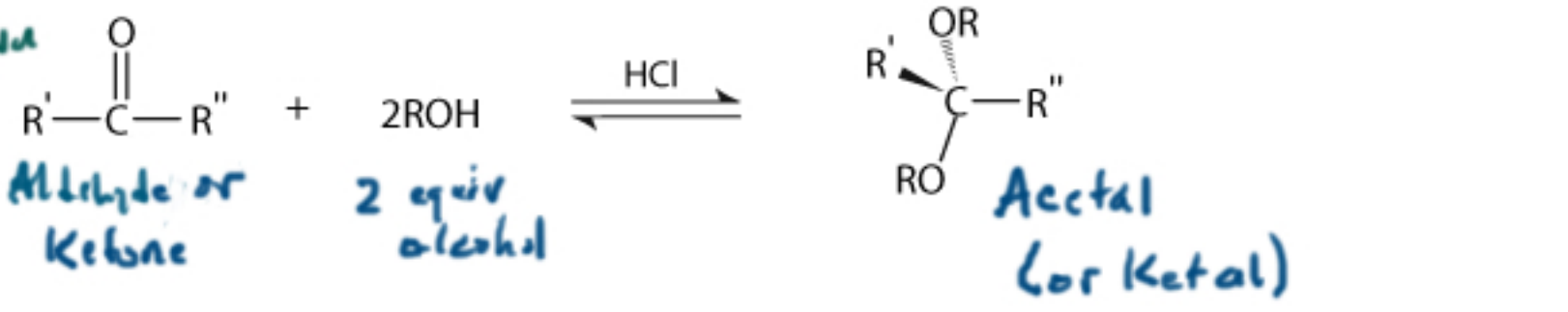
Module 6

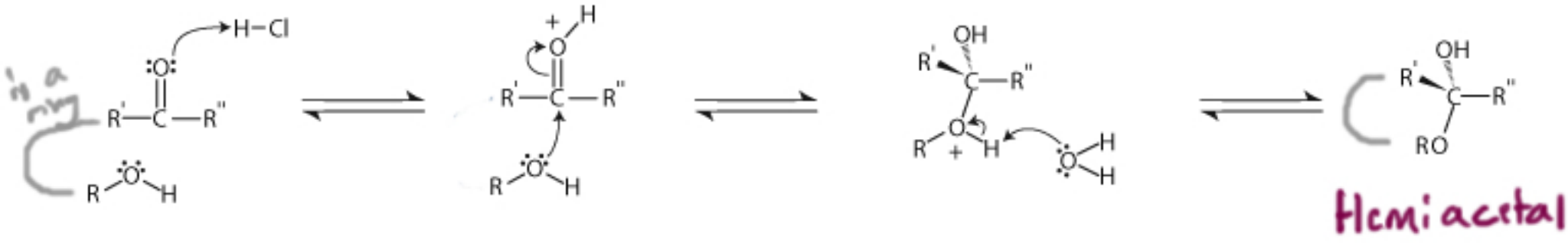
Reactions of Aldehydes and Ketones

Session Slides with Notes

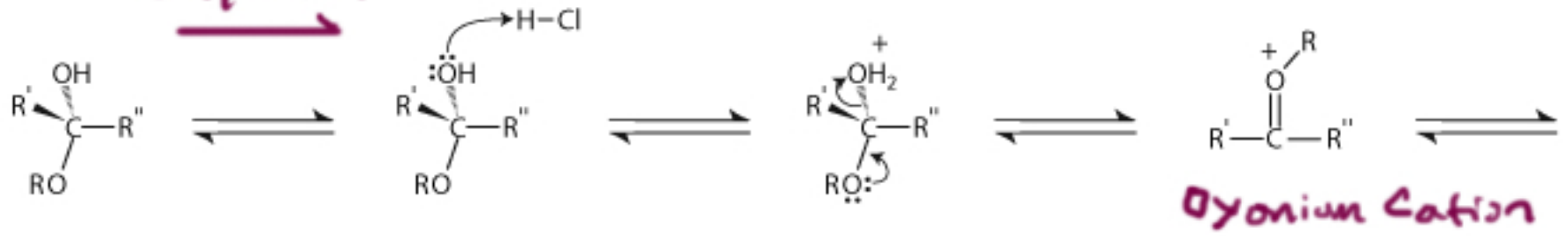
Acetal Formation

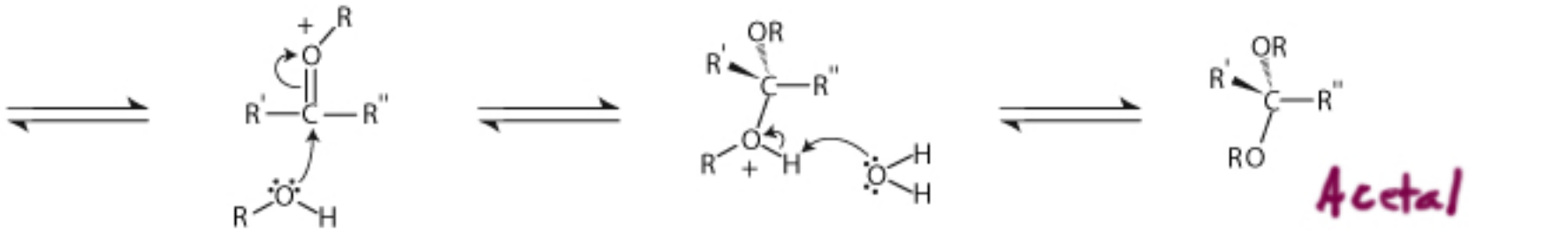






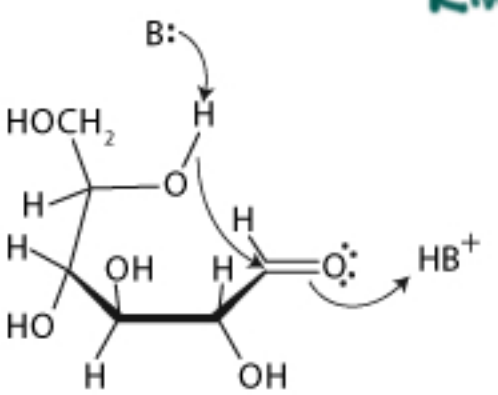
Dehydration →

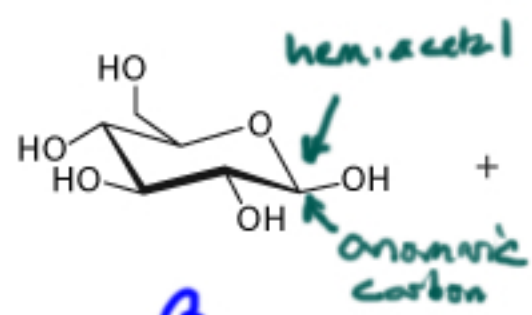




Benchtop - used to protect carbonyl groups

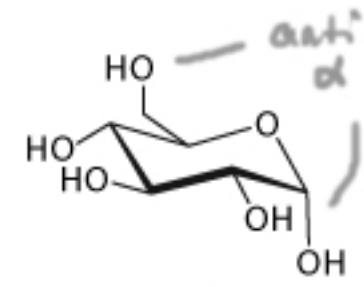
Ring Formation in Glucose (Hemiacetal Formation)





β

≈ 65%

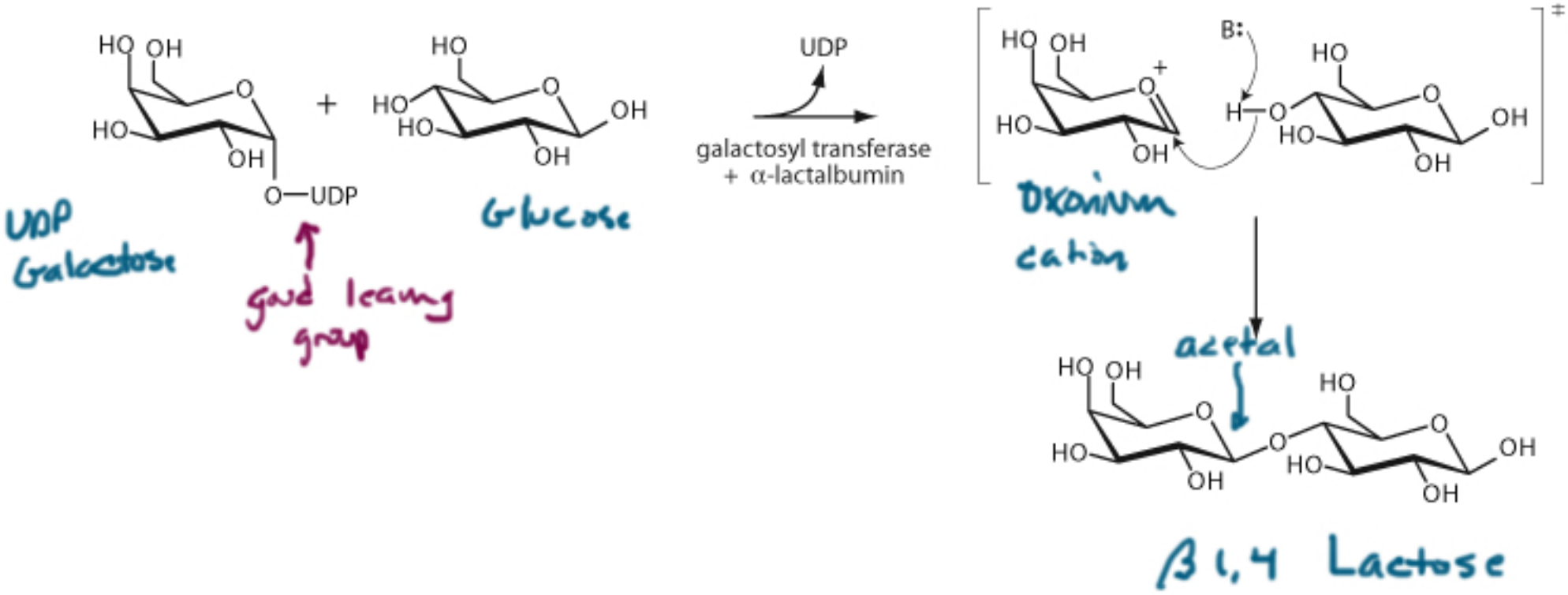


α

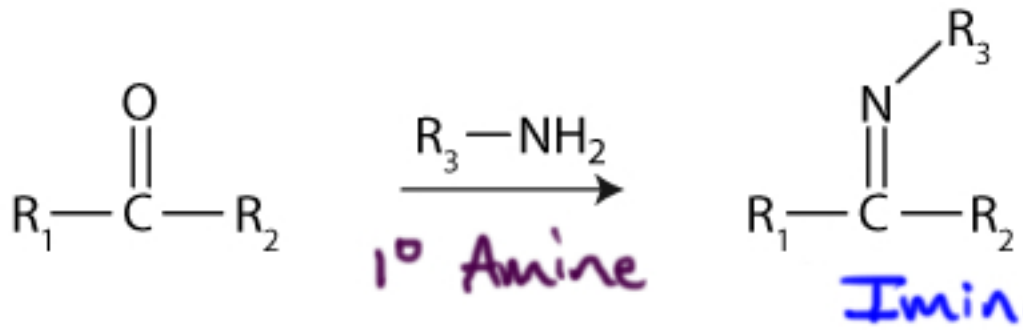
≈ 33%

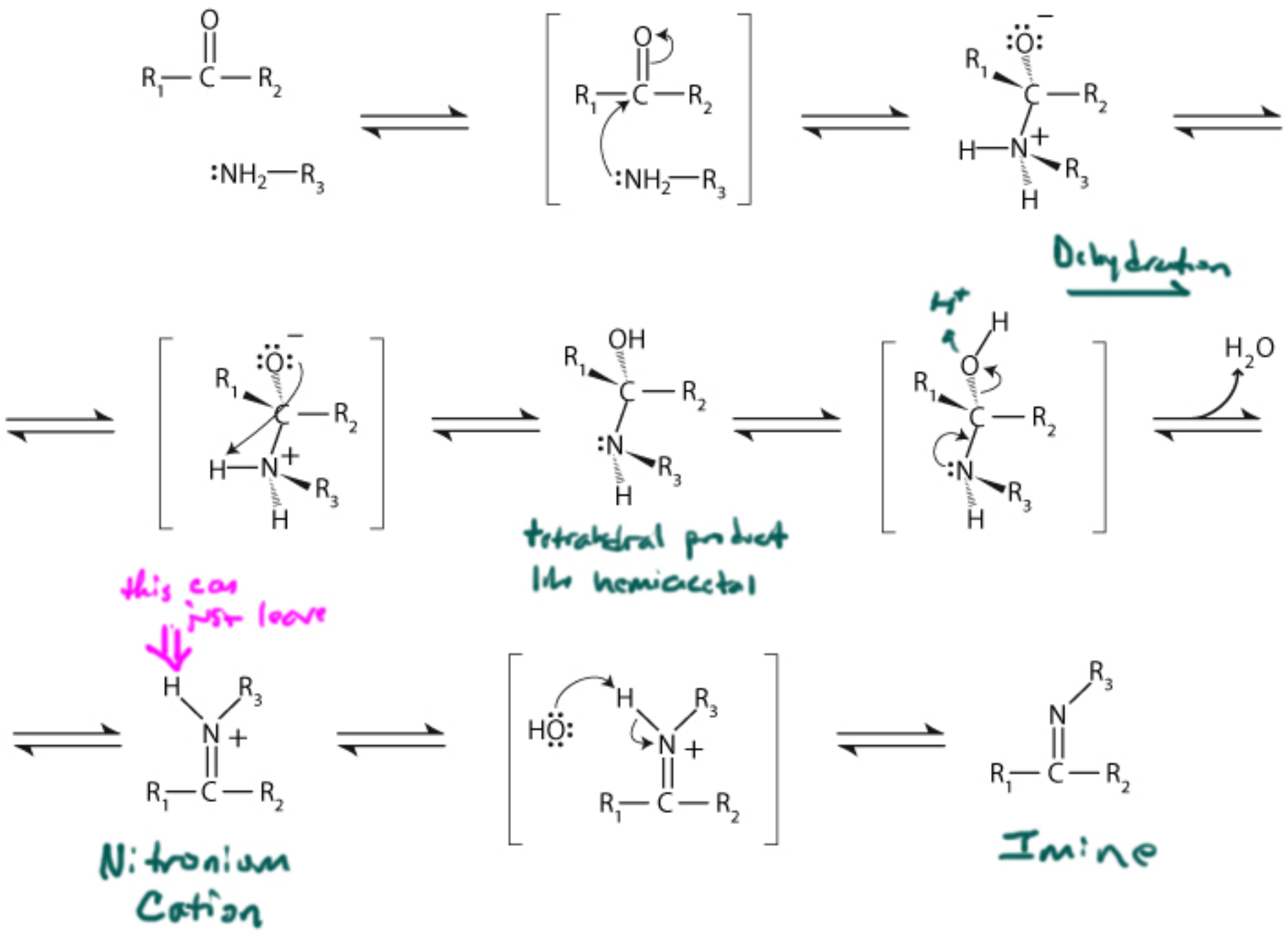
2 anomers of D-glucopyranose

Forming a Glycosidic Bond (bit step 2 of acetal formation)

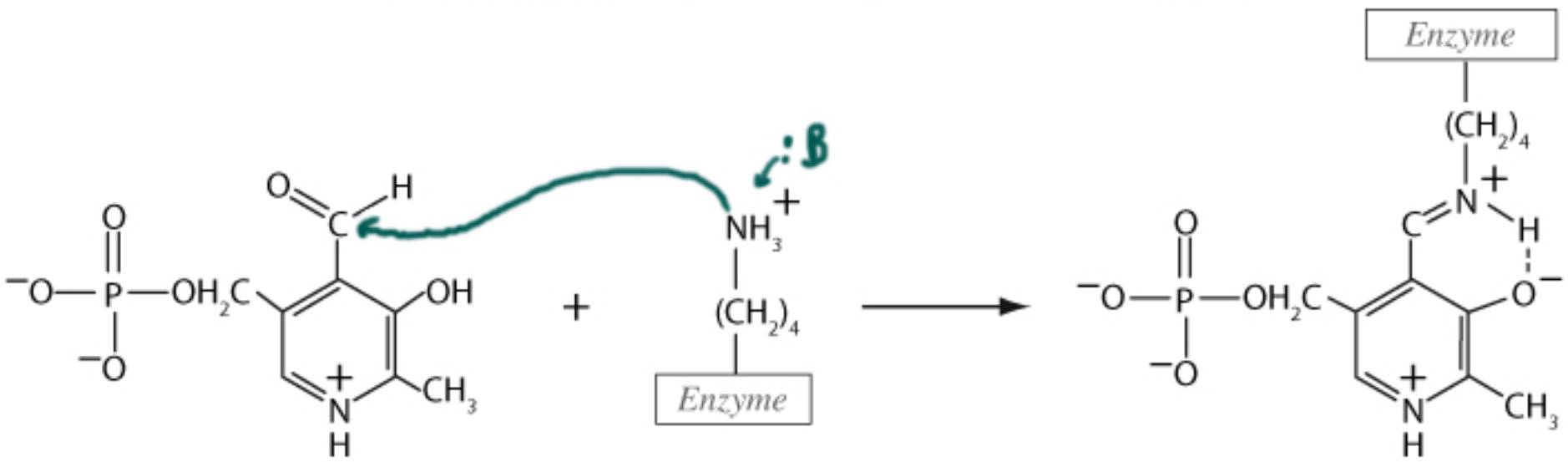


Imine Formation



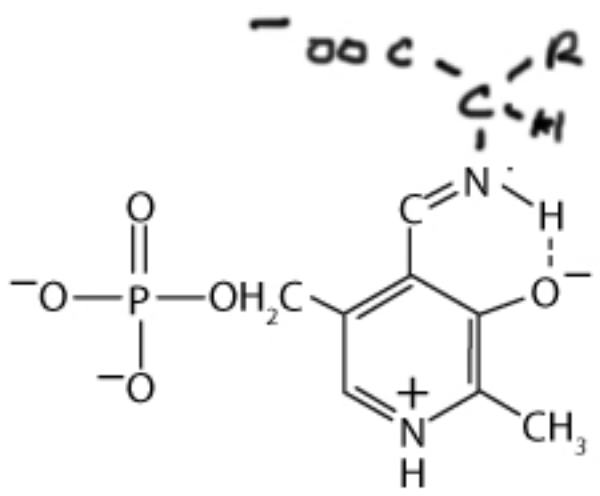


Formation of Enzyme PLP Schiff Base



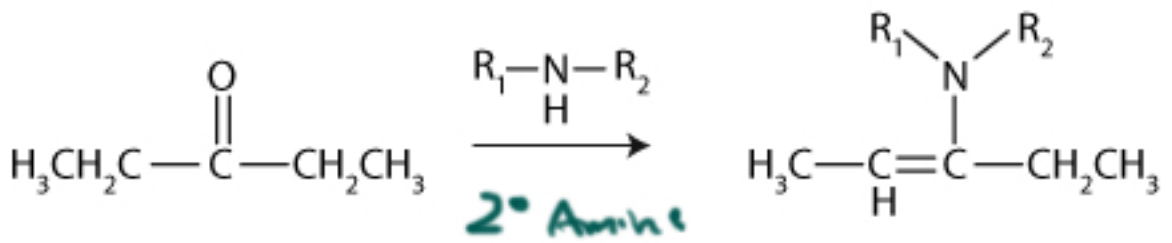
PLP

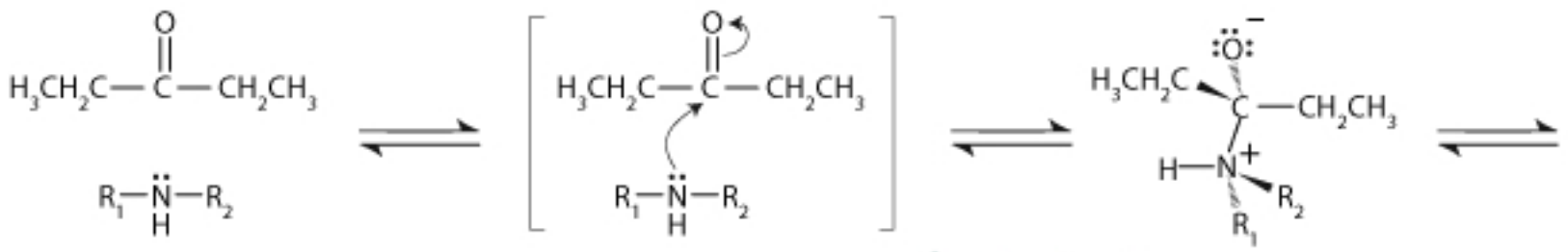
"the amino acid cofactor"

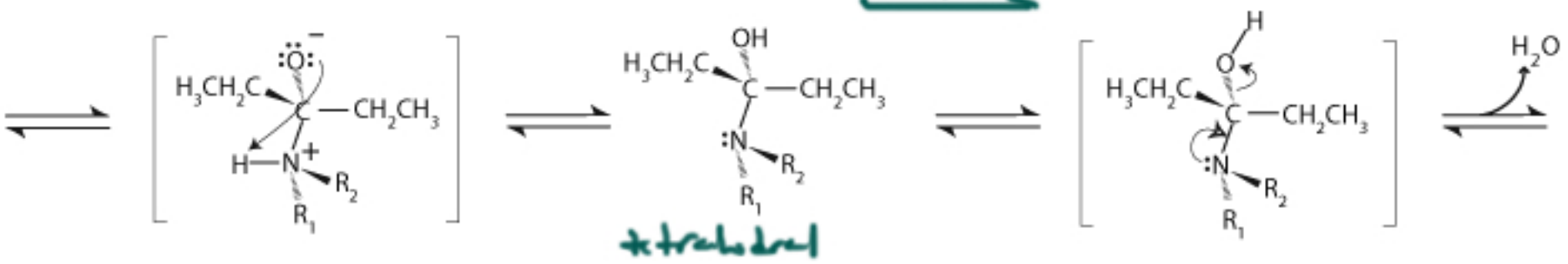


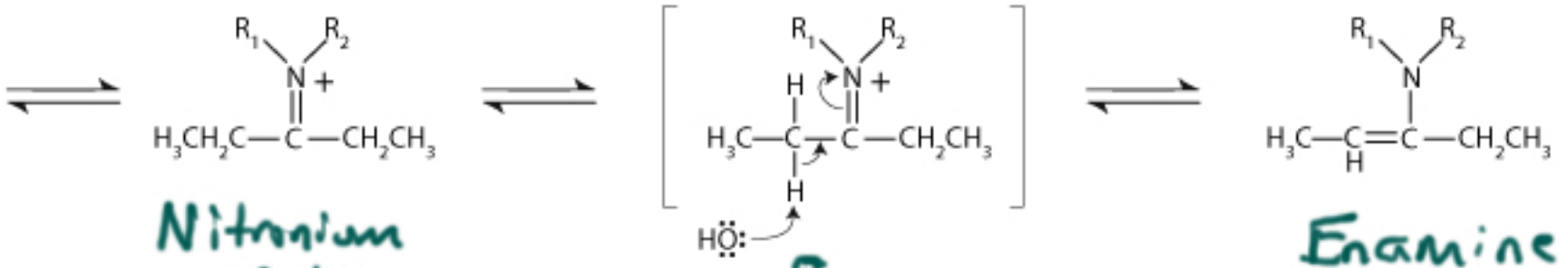
amino acid PLP Schiff base

Enamine Formation



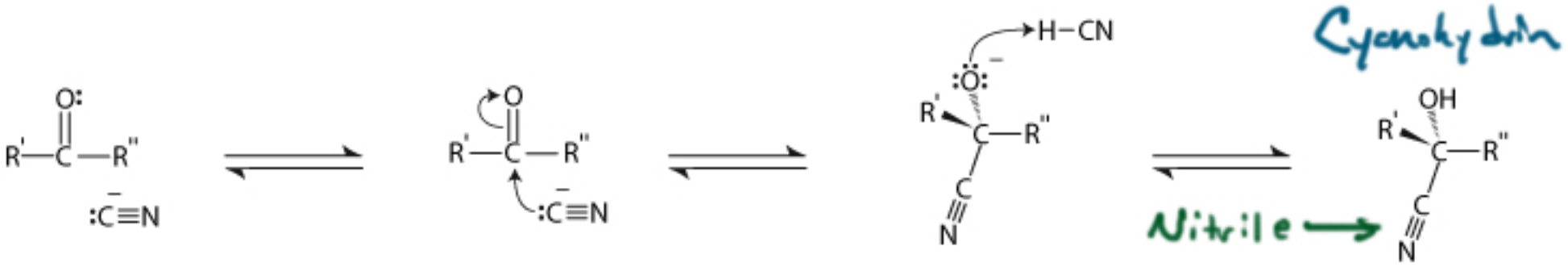






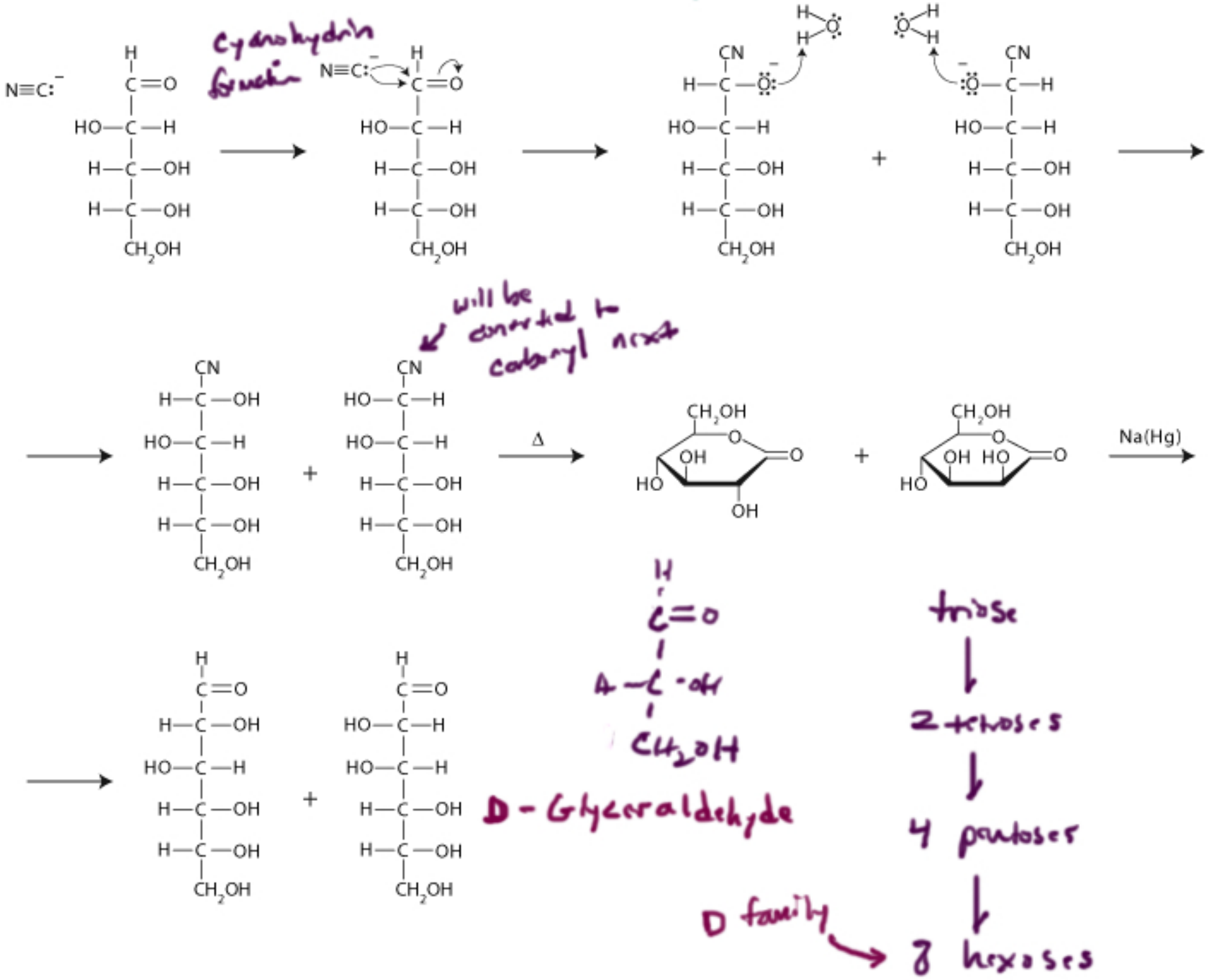
Transfer of an α hydrogen

Cyanohydrin Formation



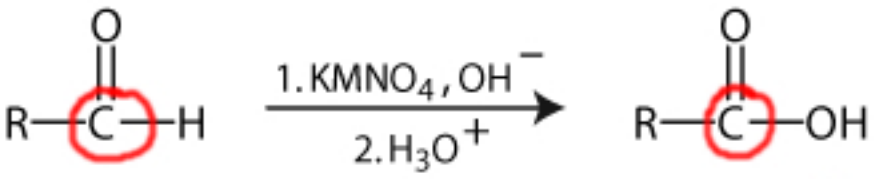
Hydrolysis of Nitrile | $2 H_2O$ (or OH^-)

Kiliani Fischer Synthesis



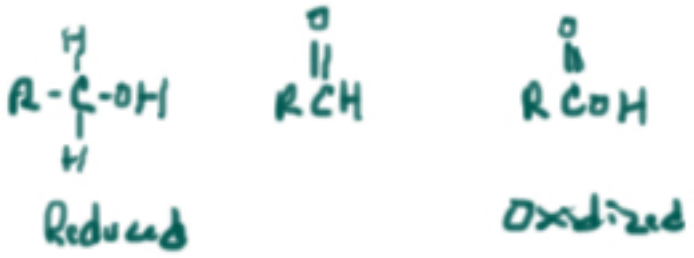
Steps of the Kiliani-Fischer synthesis of D-glucose and its C-2 epimer, D-mannose, from D-arabinose

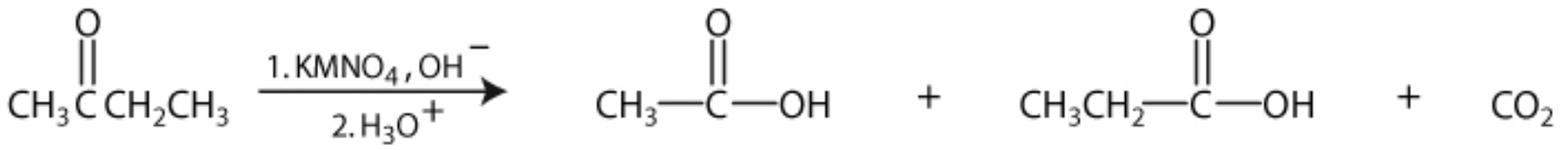
Oxidation of Aldehydes and Ketones



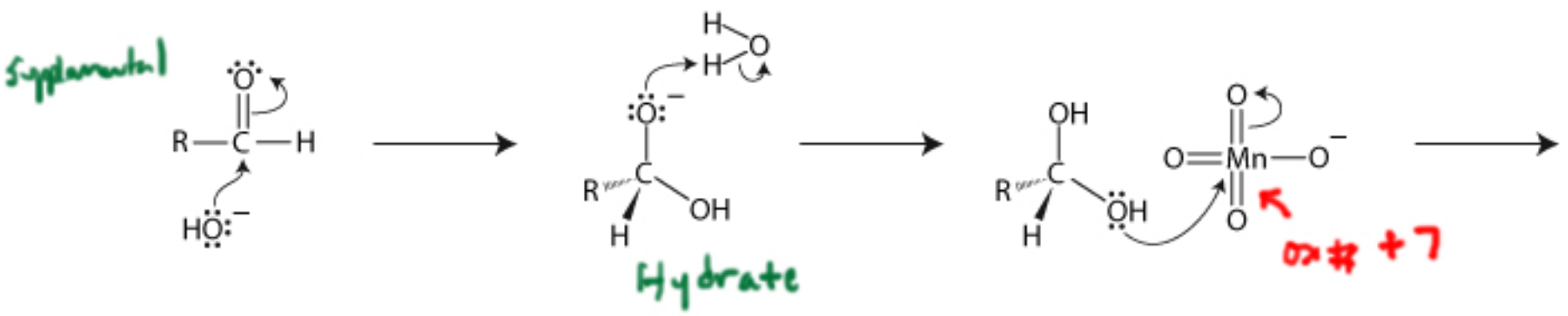
ox # +1

ox # +3

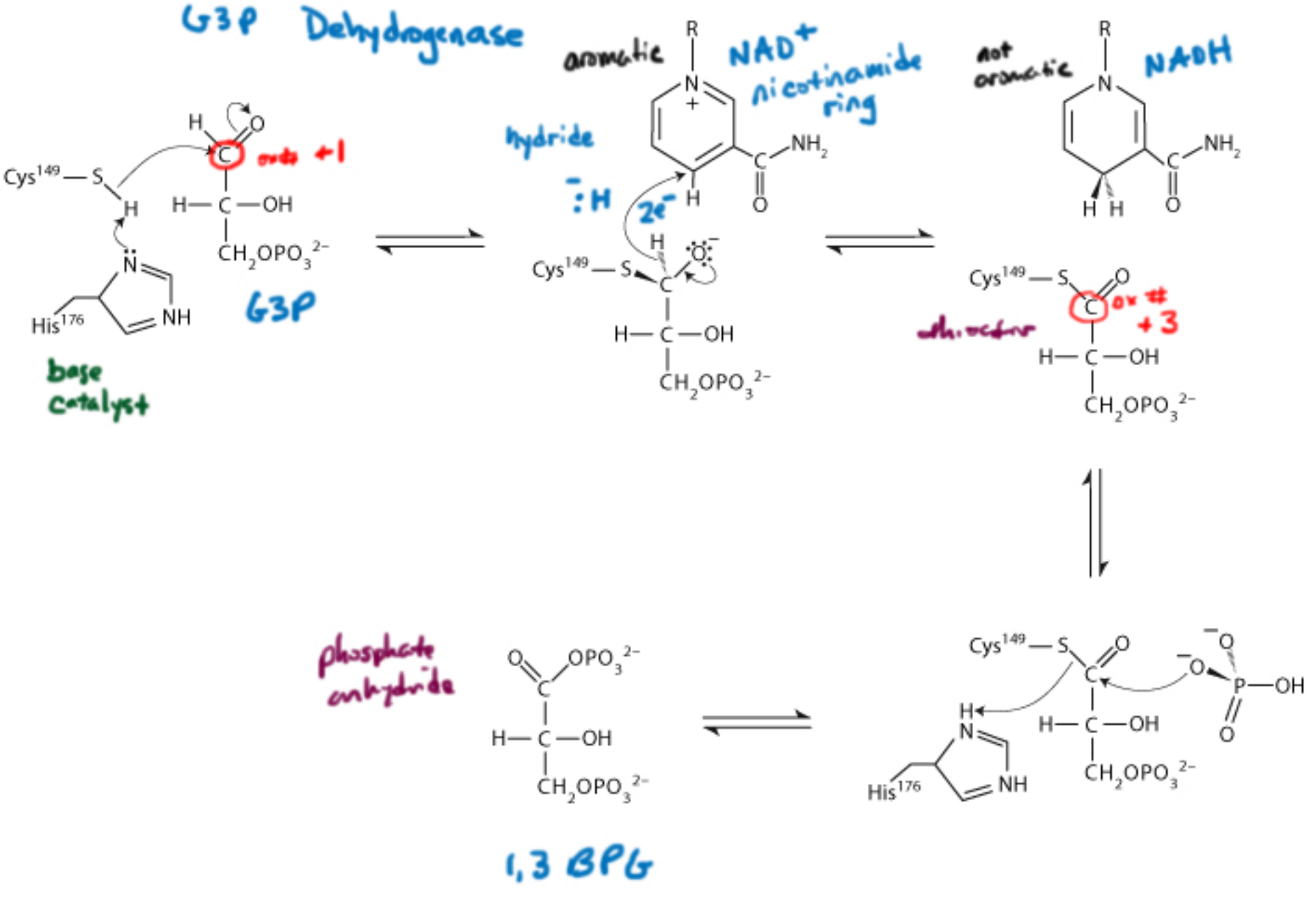




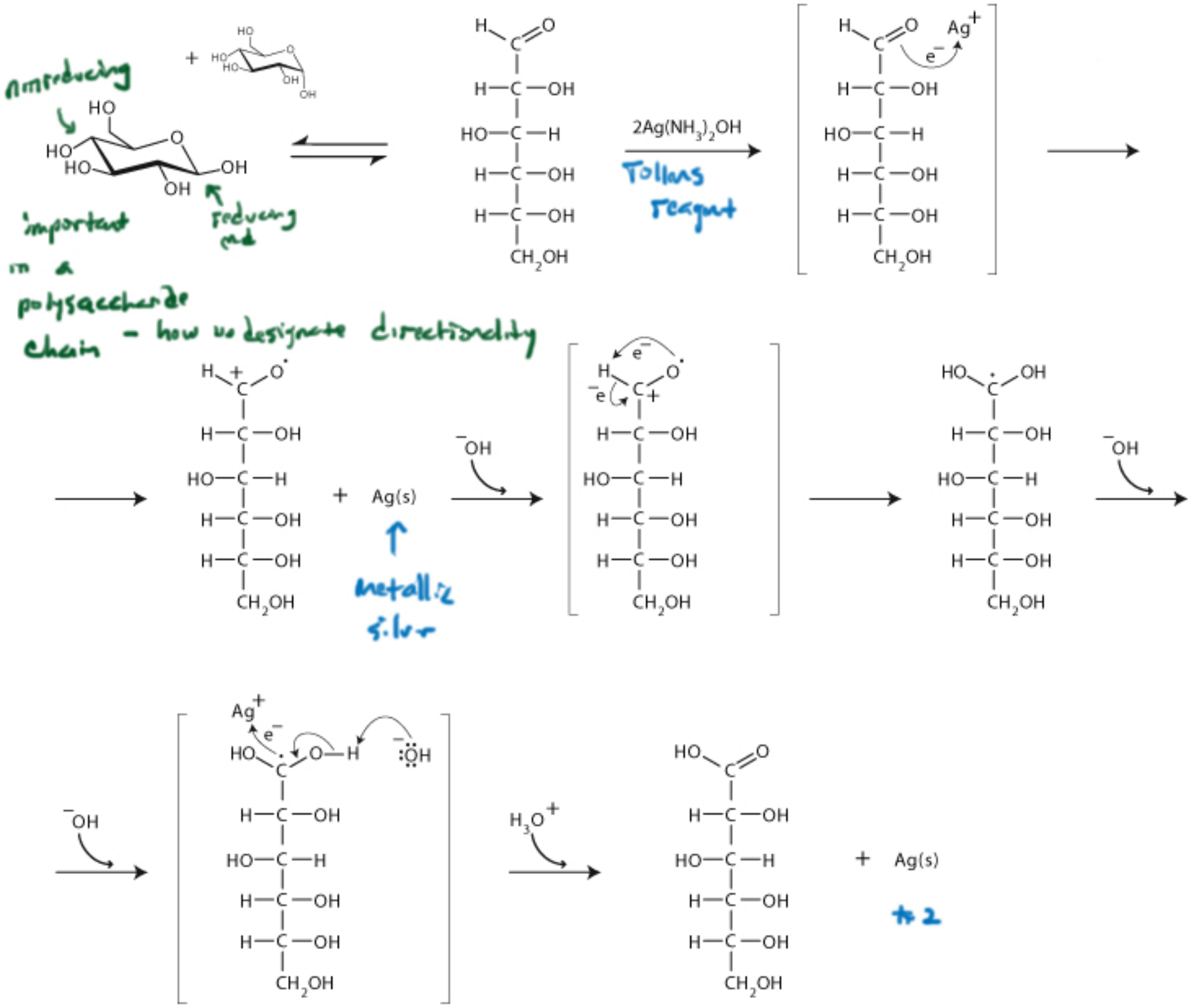
symmetrical



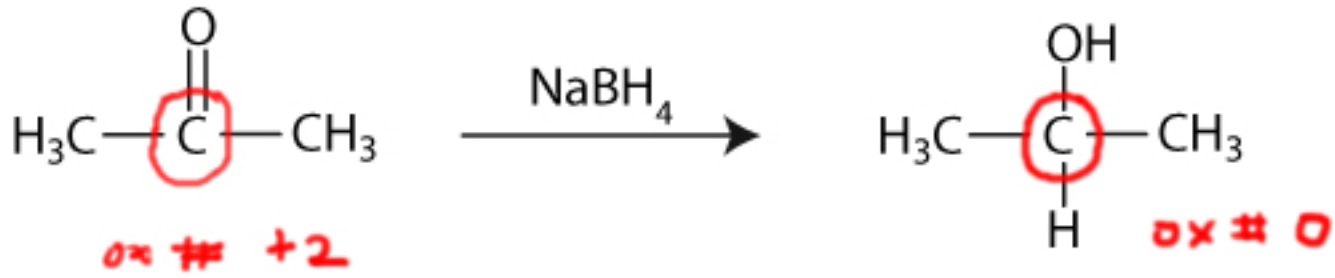
G3P Dehydrogenase

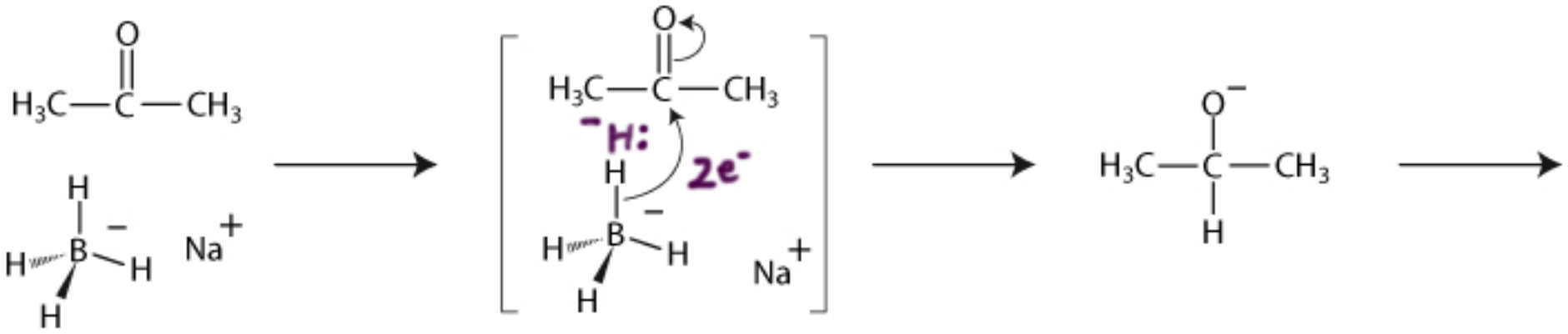


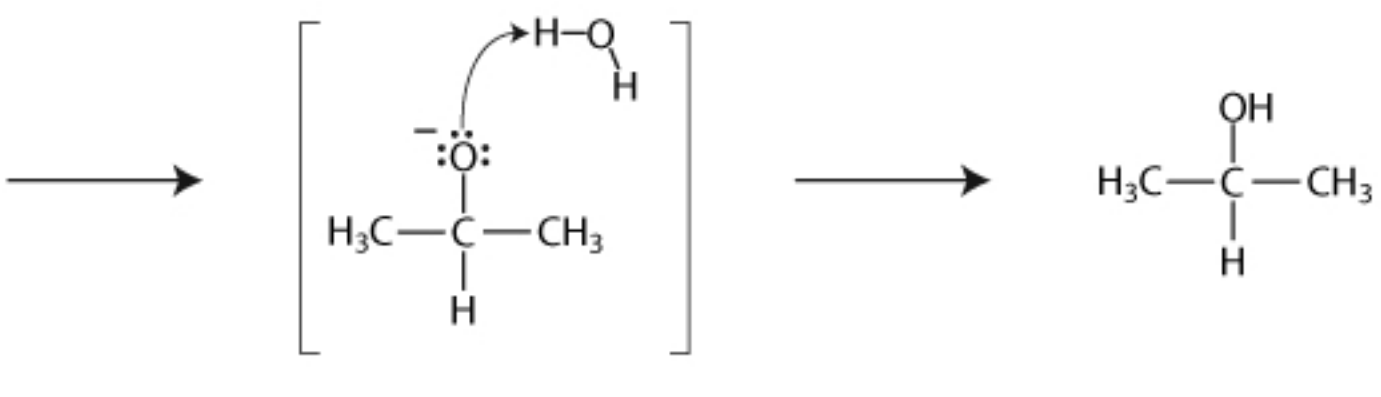
Tollens Test for reducing sugars



Reduction of Aldehydes and Ketones

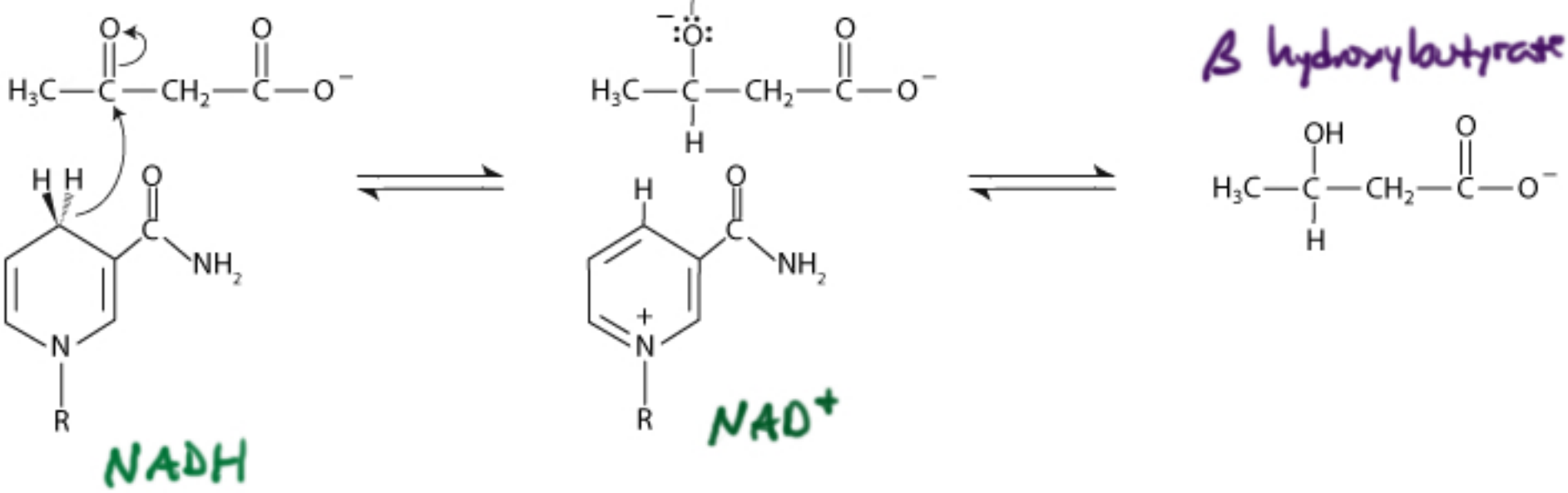






β Hydroxybutyrate Dehydrogenase

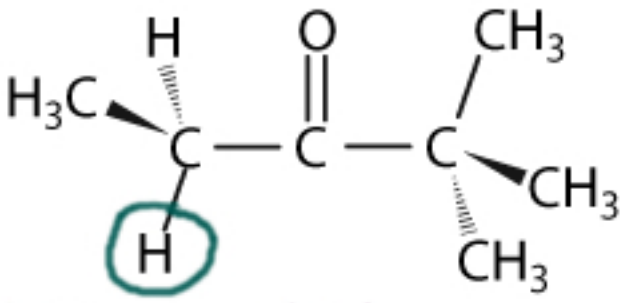
Acetoacetate



Acetoacetate and β hydroxybutyrate are ketone bodies

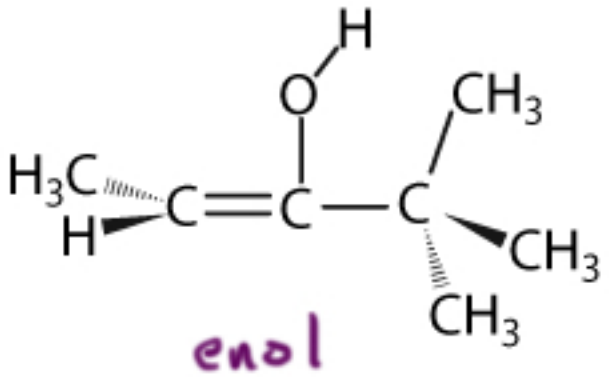
Tautomers - Constitutional isomers that interconvert

Keto Enol Tautomerism

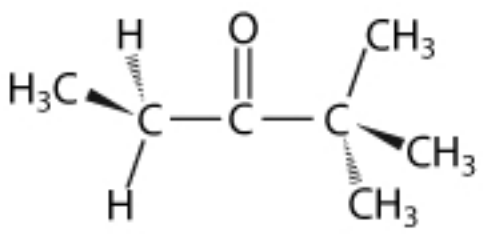


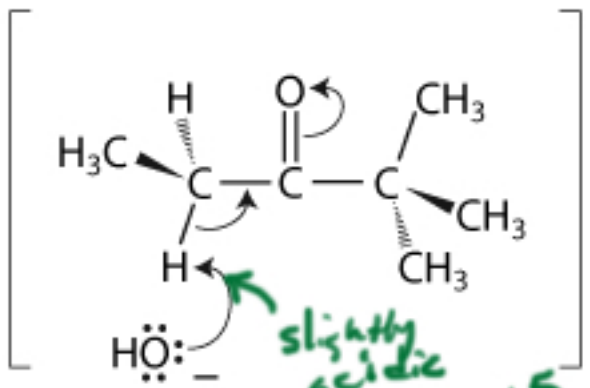
α hydrogen

aldehyde or ketone with α hydrogens



enol



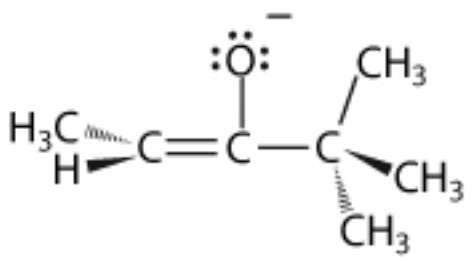


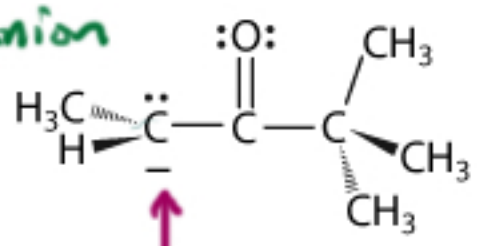
slightly acidic pKa ~ 15

$HA \rightleftharpoons A^- + H^+$

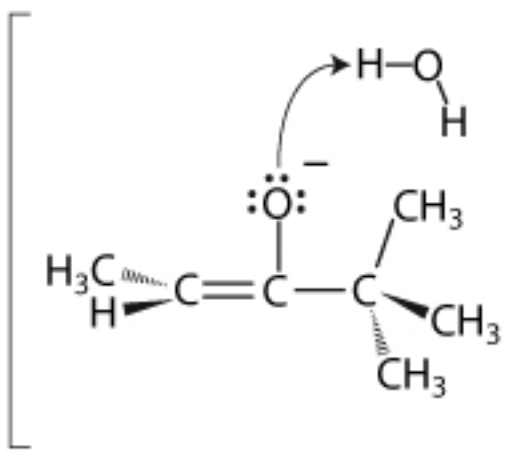
$K = e^{-\Delta G^\circ / RT}$

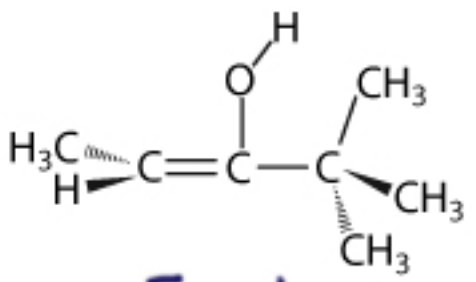
resonance stabilized enolate anion





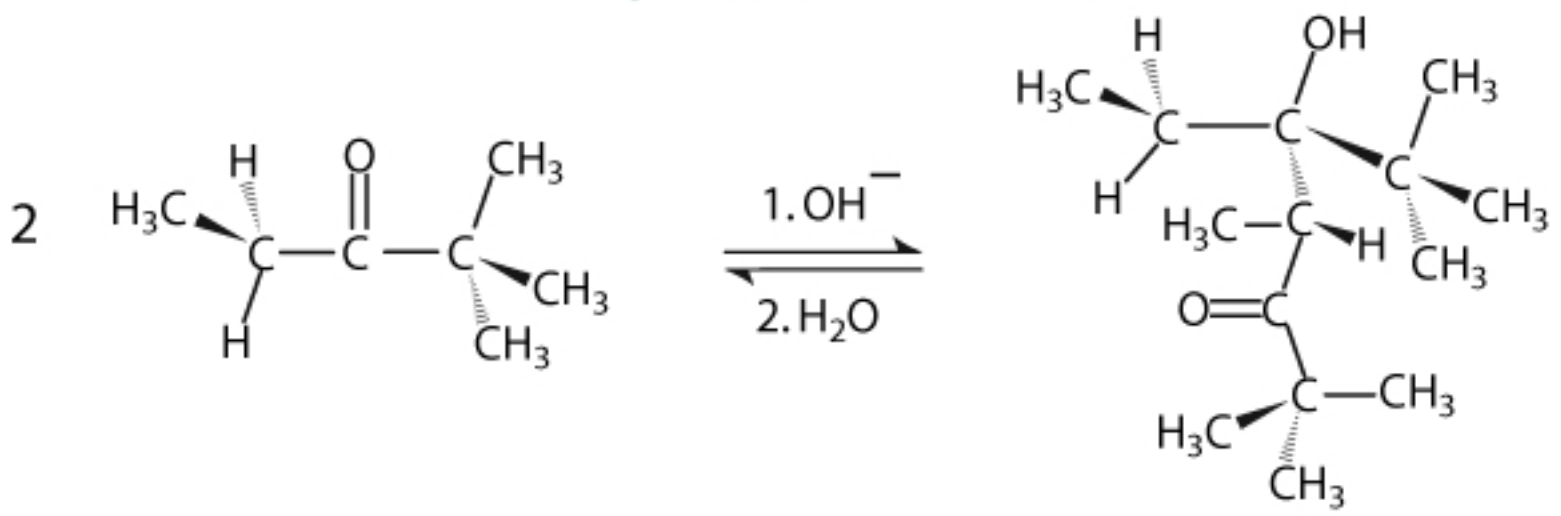
nucleophilic

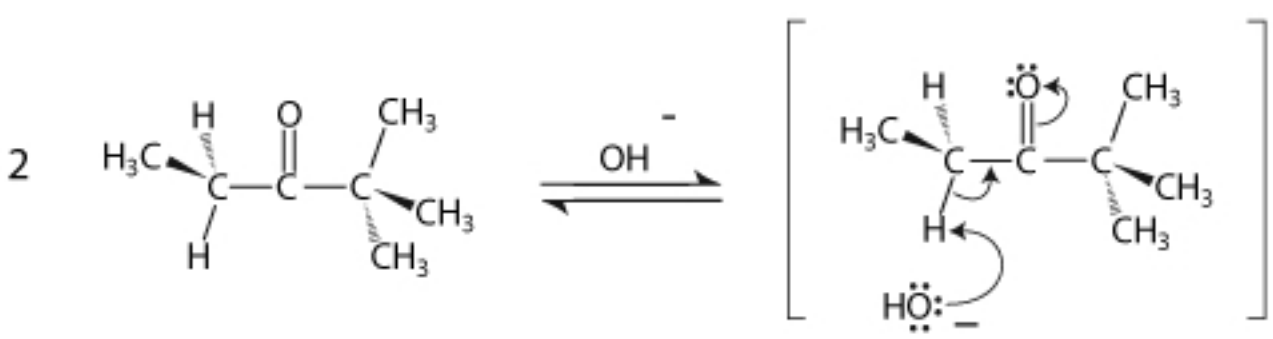




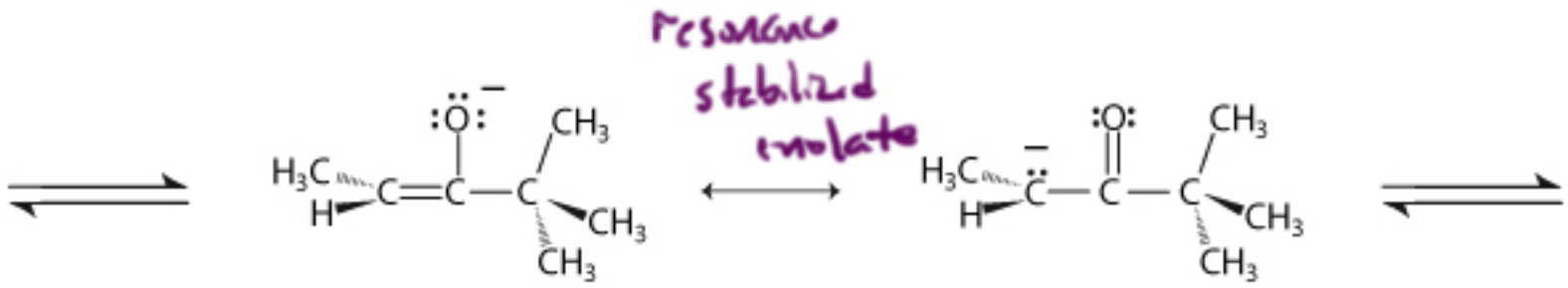
Enol

Aldol Addition

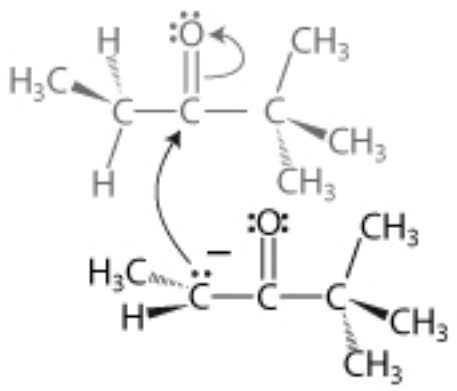


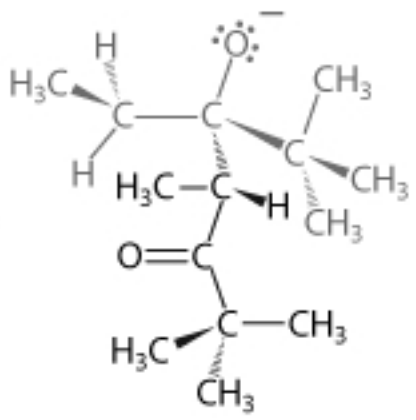


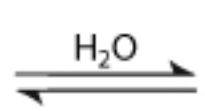
Base catalyzed enolate formation



the enolate of one attacking the carbonyl of another

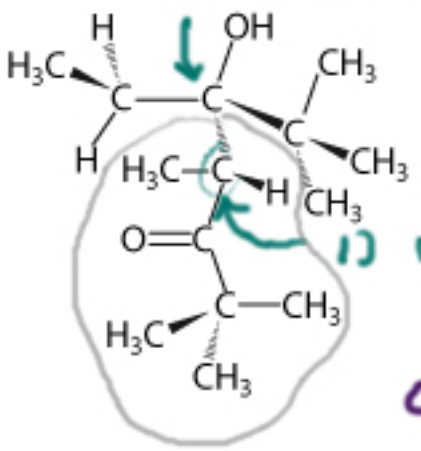


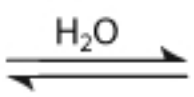




to work backwards

Find the carbon it attached

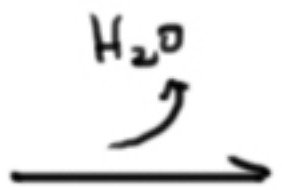




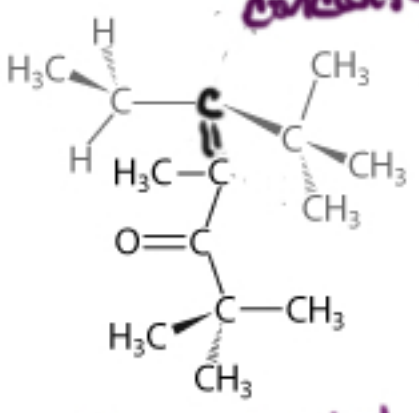
+ OH⁻

1) Find the original α carbon

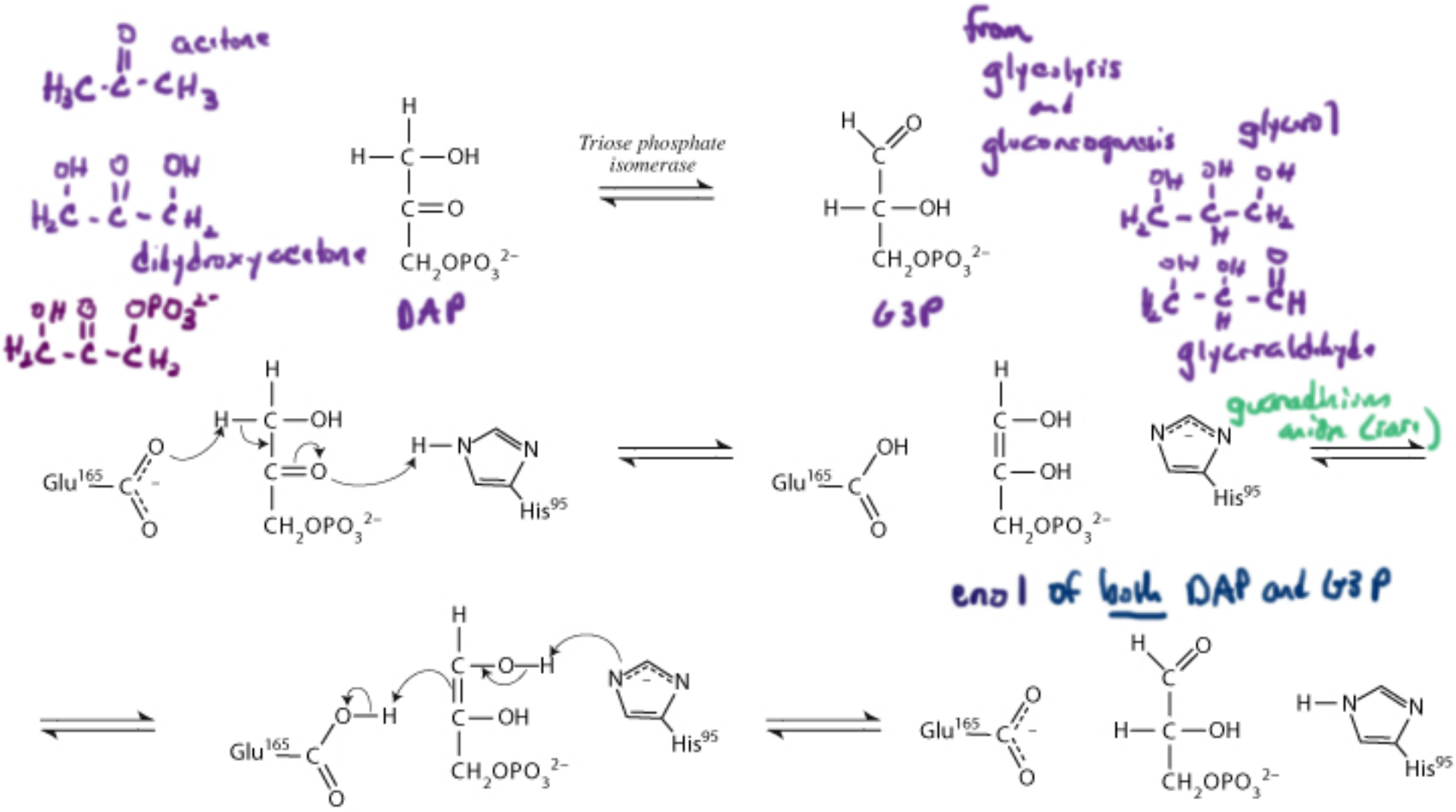
aldol addition product



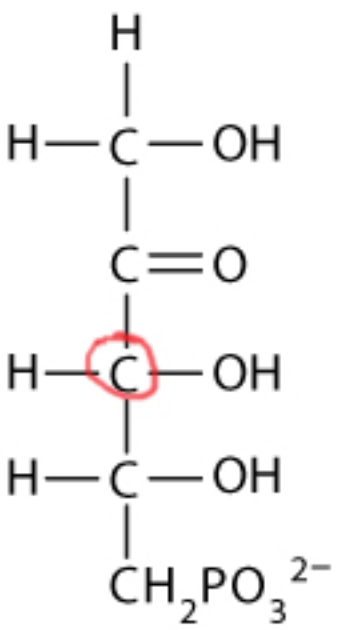
aldol condensation product



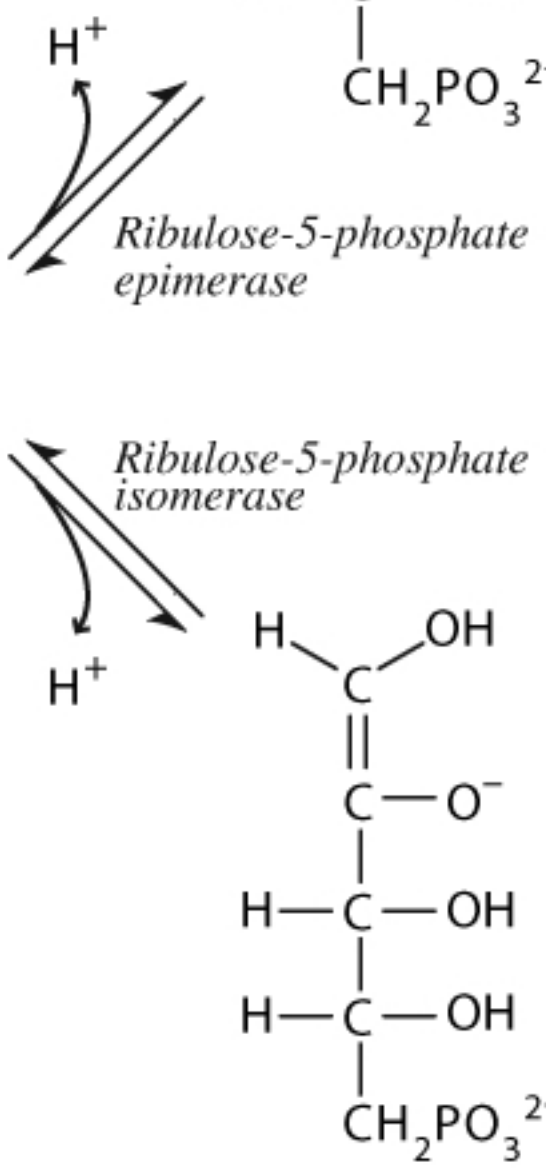
α,β unsaturated carbonyl compound


acetone
dihydroxyacetone
DAP
Triose phosphate isomerase
G3P
from glycolysis and gluconeogenesis
glycerol
glyceraldehyde
guanidinium anion (resn)
end of both DAP and G3P
Glu165
His95

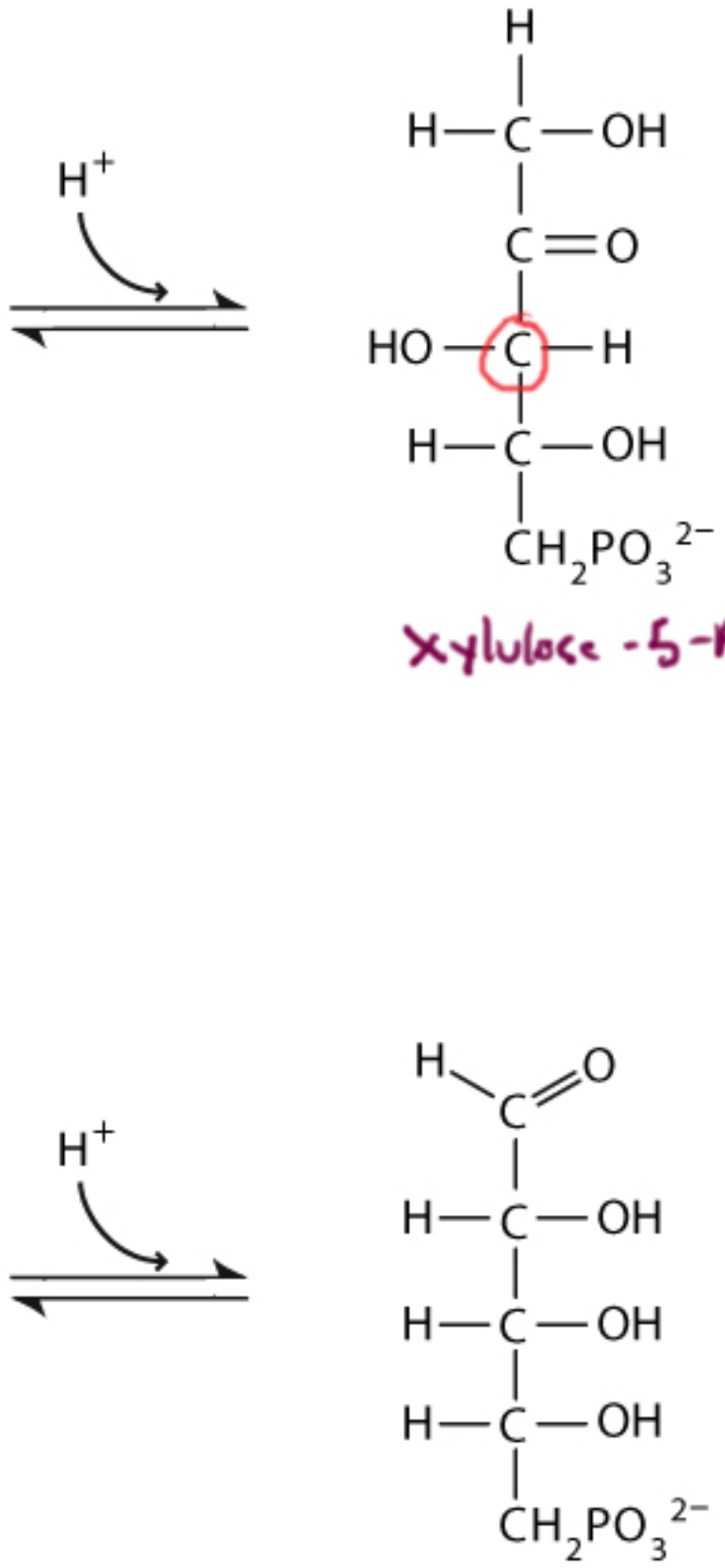
From pentose phosphate pathway (primary source of NADPH and ribose)



ribulose 5-P



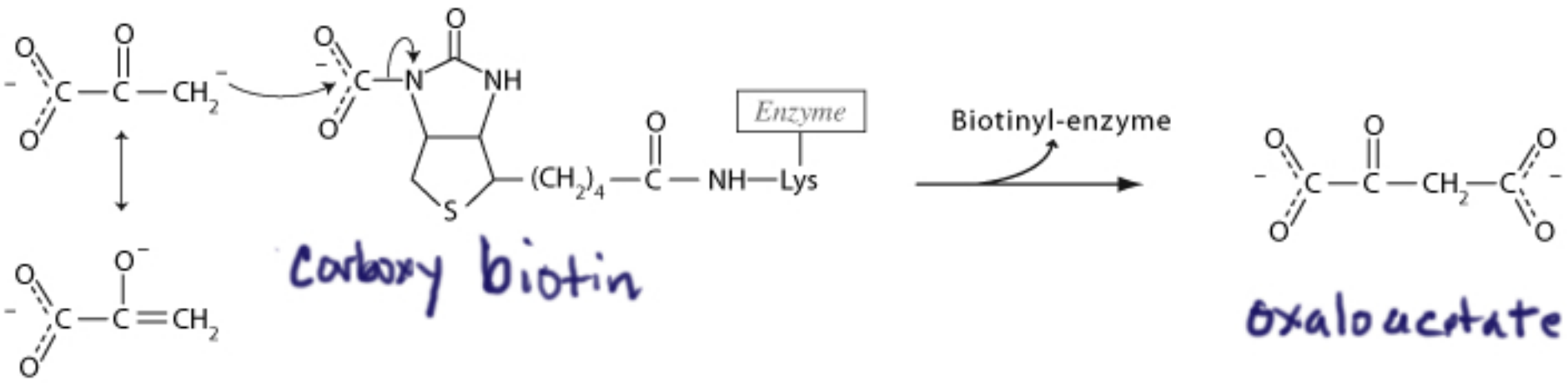
enol of both



Xylulose -5-P

Ribose 5-P

pyruvate carboxylase



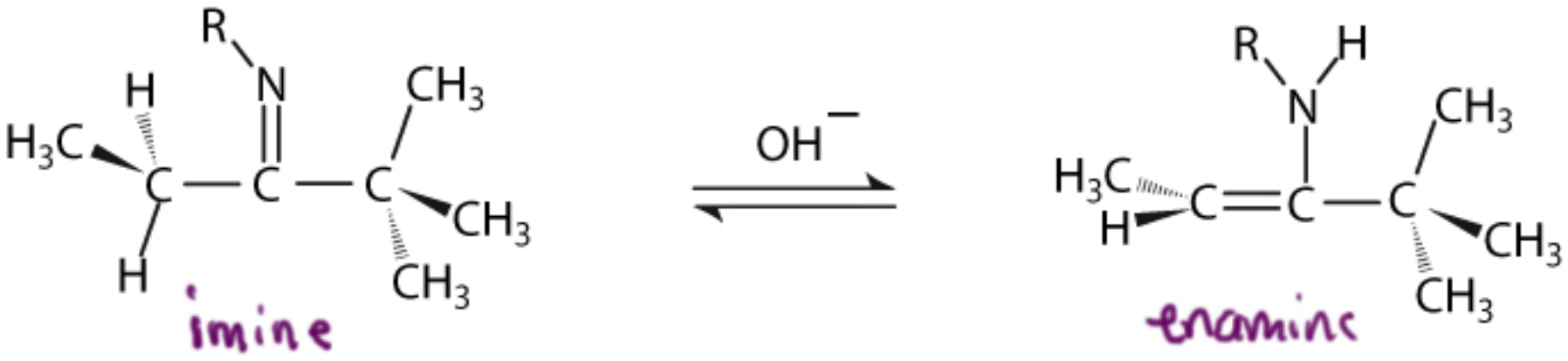
carboxy biotin

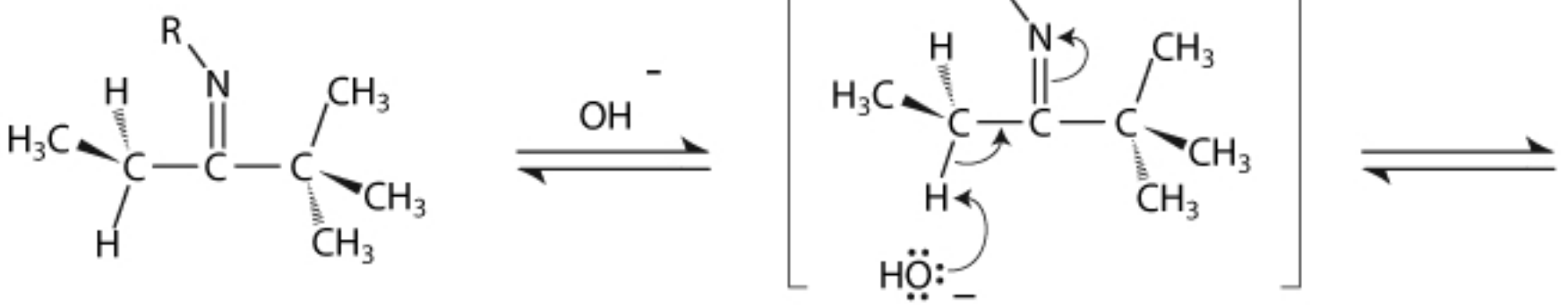
enolate of pyruvate

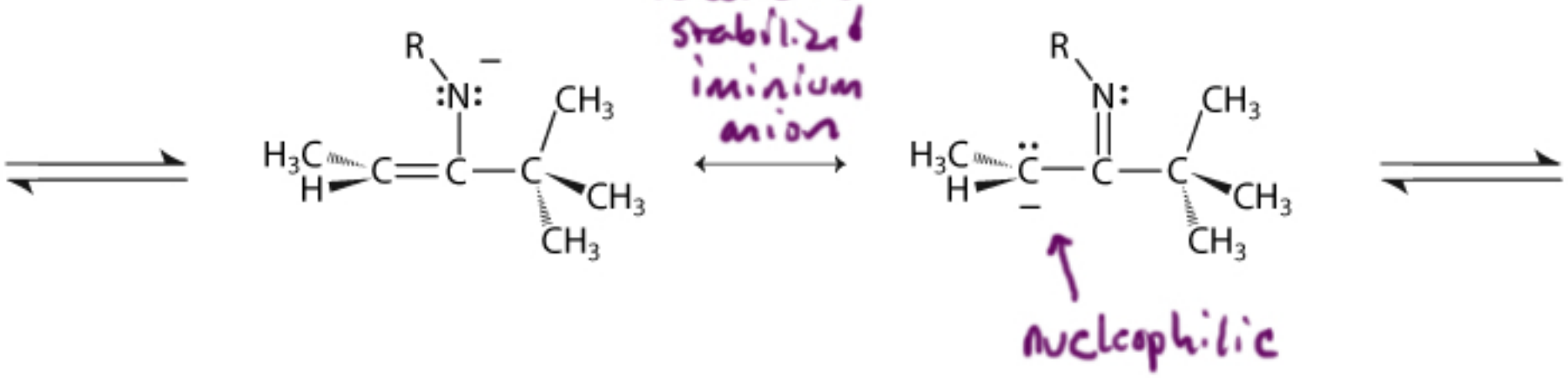
oxaloacetate

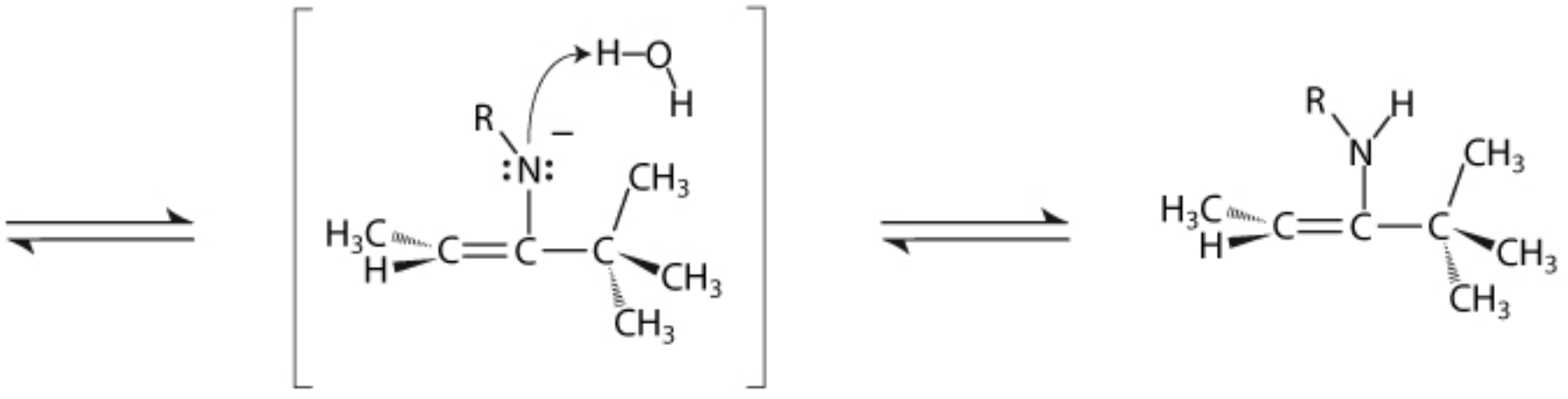
(biotin is a carboxyl donor)

imine enamine tautomerism

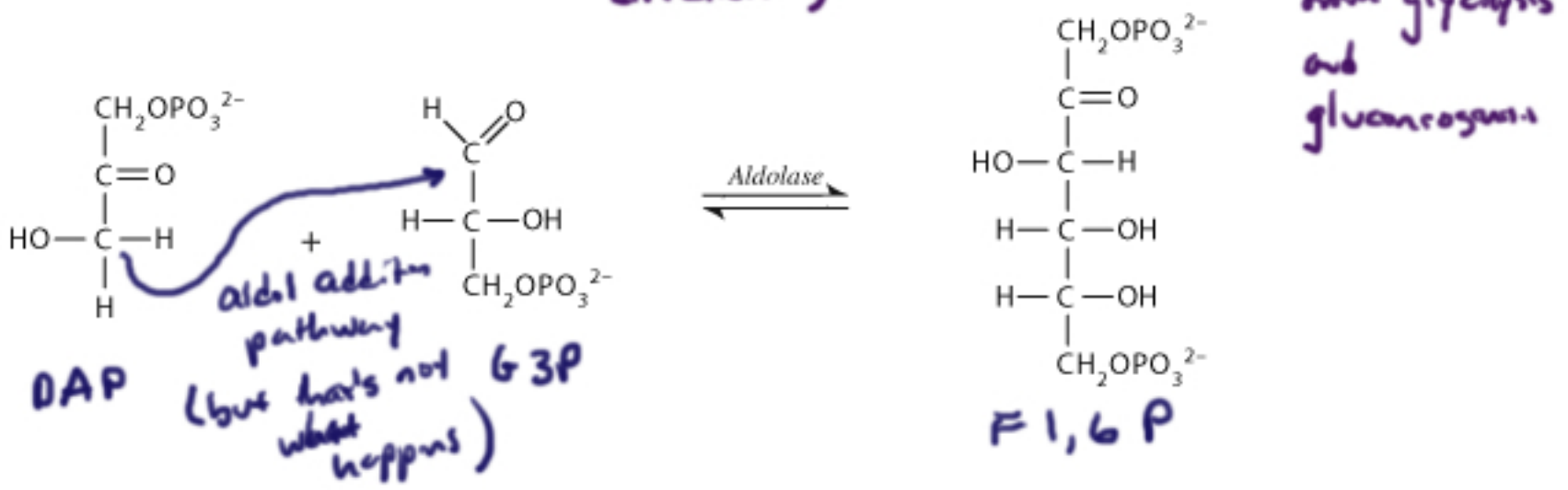


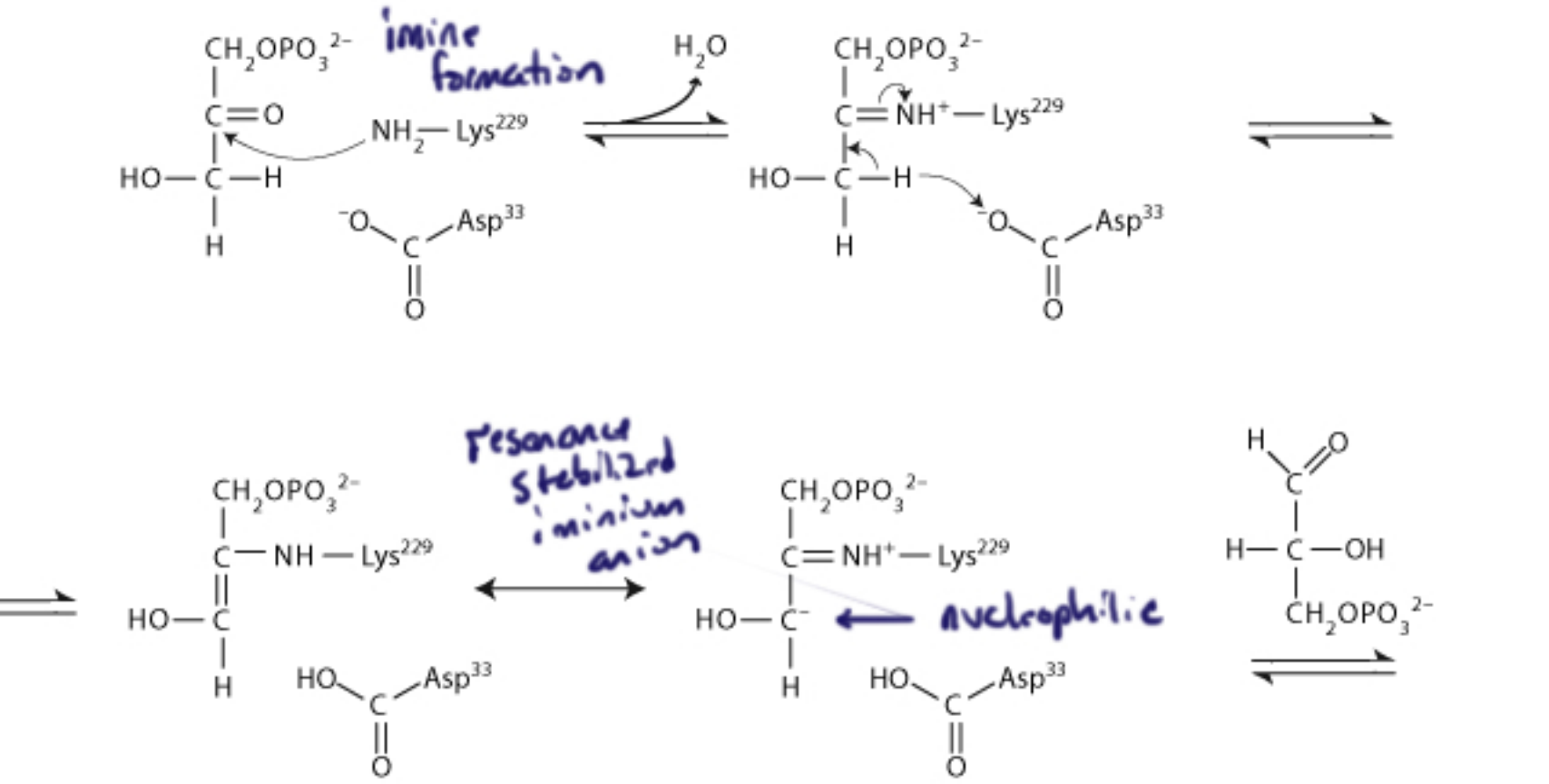


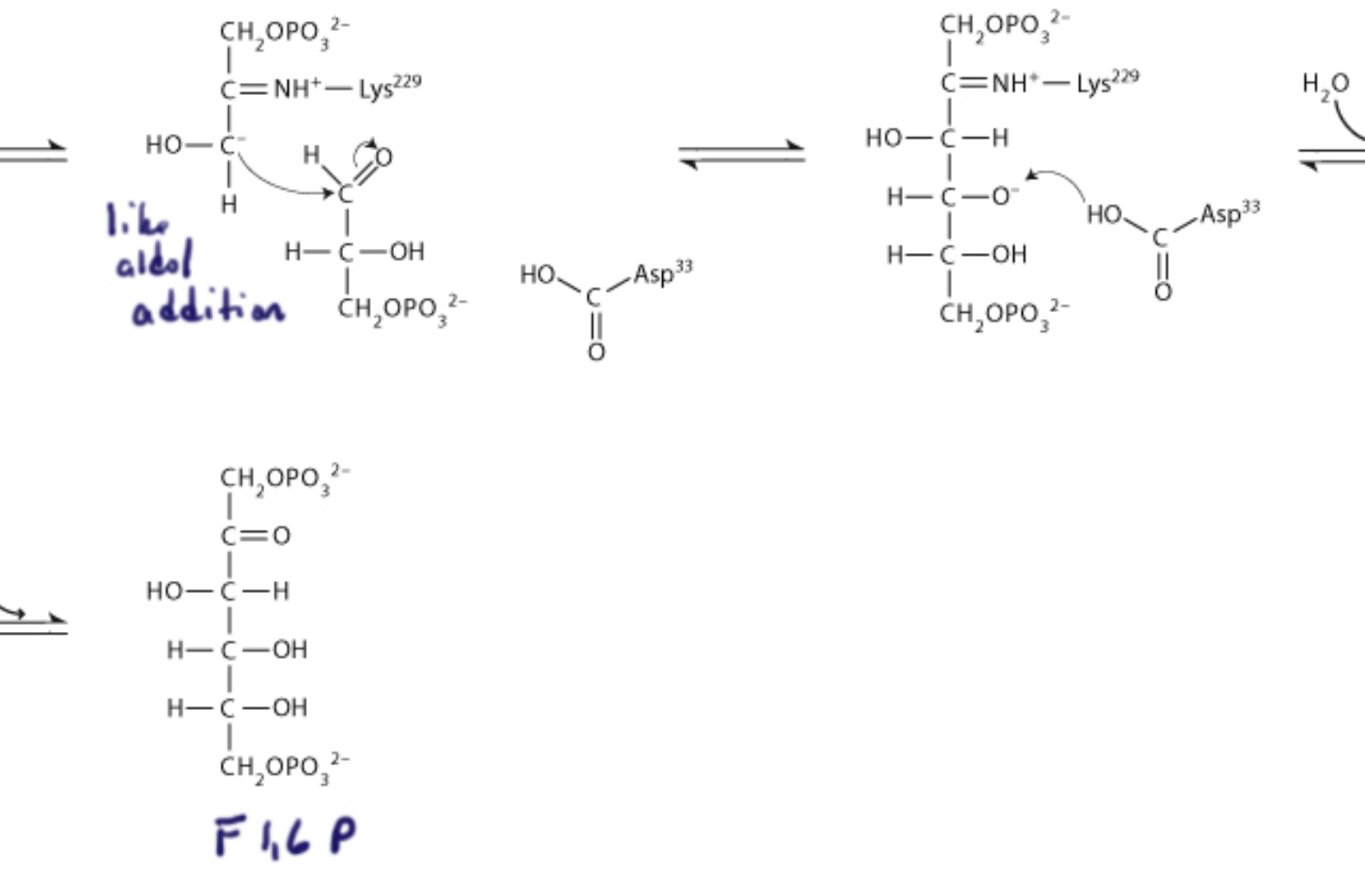




Aldolase (gluconeogenesis direction)



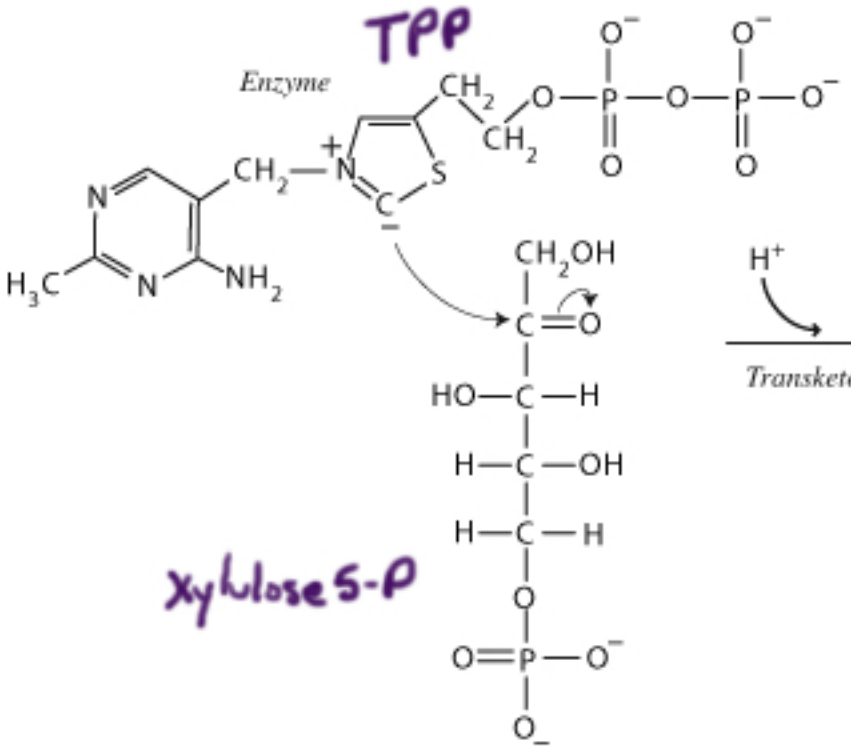




Transketolase (moves 2C)

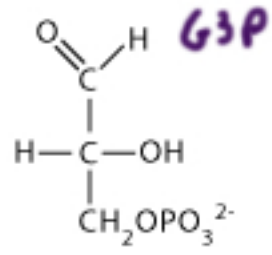
from PPP

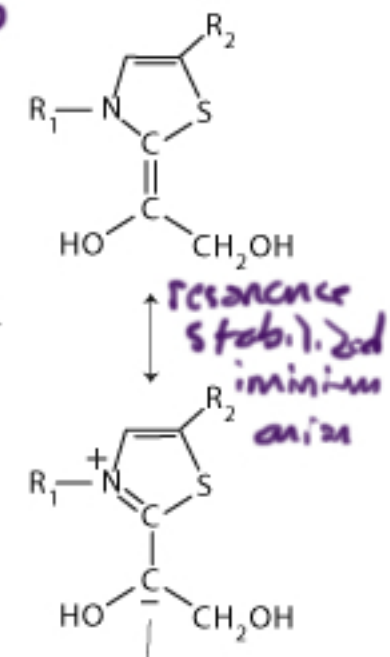
TPP



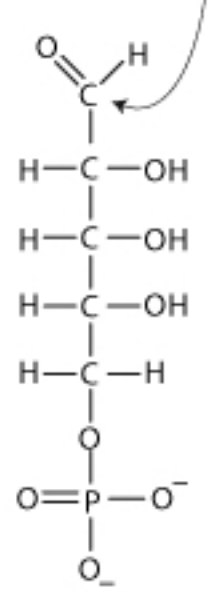
xylulose 5-P

G3P

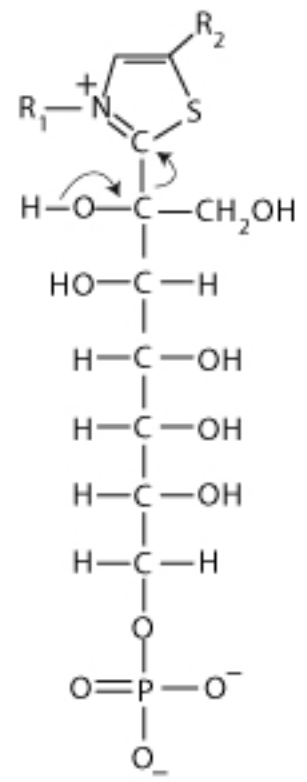




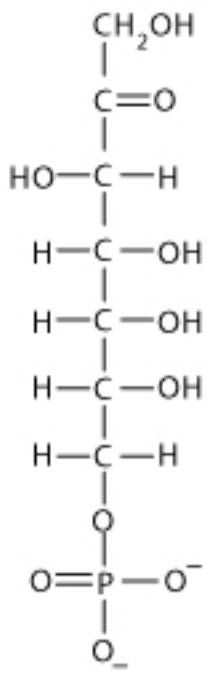
resonance stabilized iminium anion



like aldol addition



TPP



sed. heptulose 7-P

ribose 5-P

Transaldolase (moves 3C)