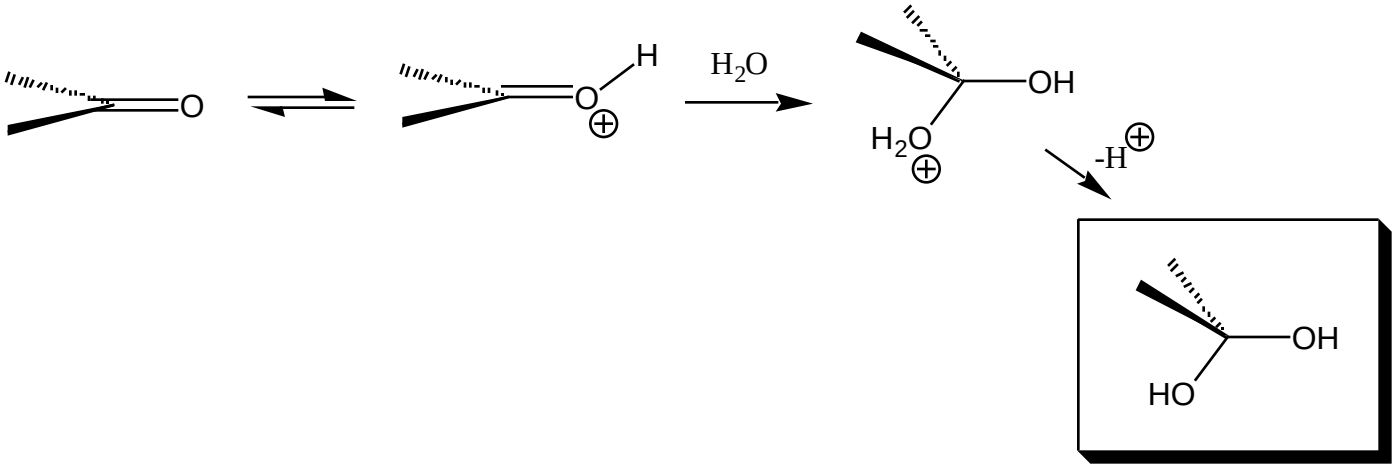
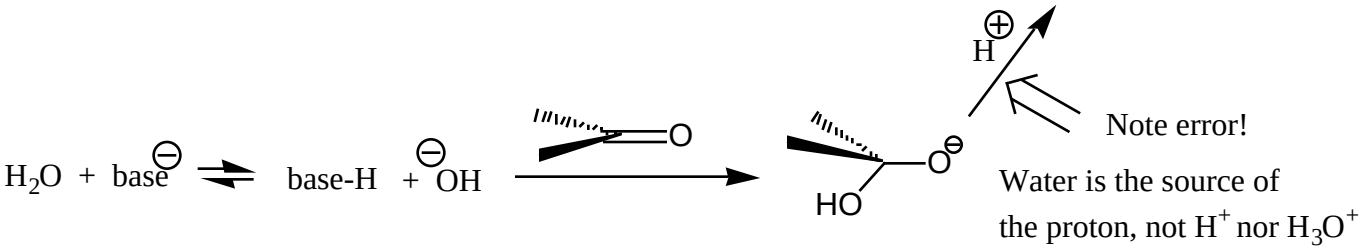
Chemistry 304B, Spring 1999 Lecture Notes 15
Reminder: turn in exam regrading request by Monday noon, in my mailbox.

CORRECTION:

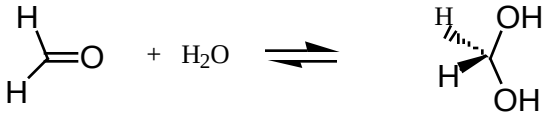


Catalysis by base:

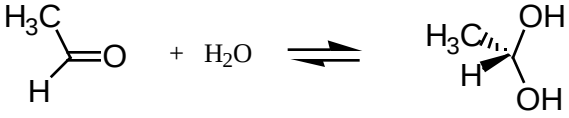


Cannot have acid (H^+) and base in the same medium (unless you use an enzyme...later)

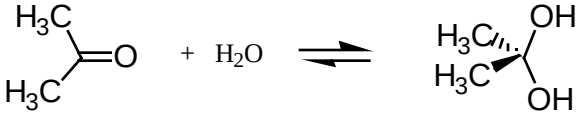
Important feature: Addition of water (and other weak nucleophiles) is easily reversible, low barriers



K_{eq} 2.3×10^3

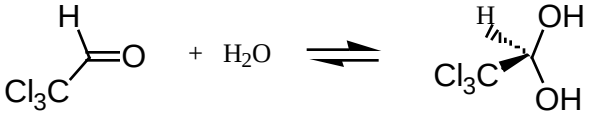


K_{eq} 1.06

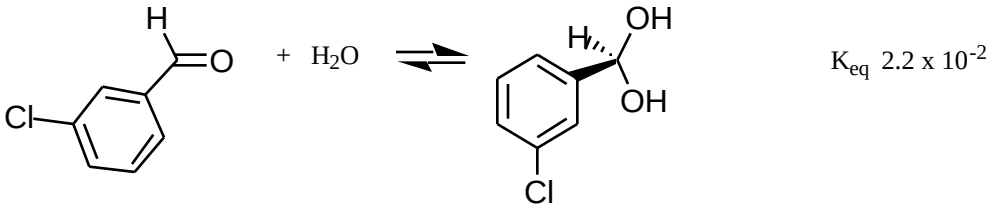


K_{eq} 2×10^{-3}

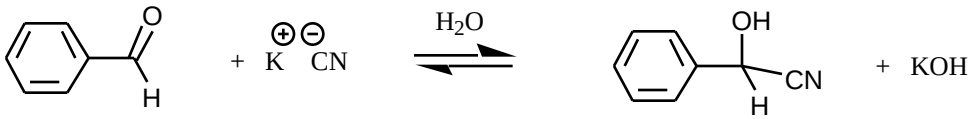
less stable product?
more stable reactant?



K_{eq} 2.8×10^4

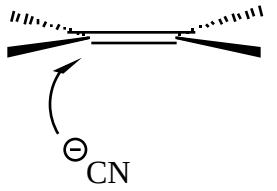


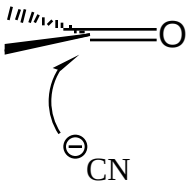
Variations: Cyanide Anion

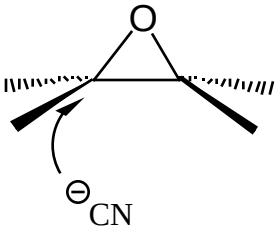


a cyanohydrin

Why does it add this way and not the reverse? why does an alkene not add nucleophiles as well?

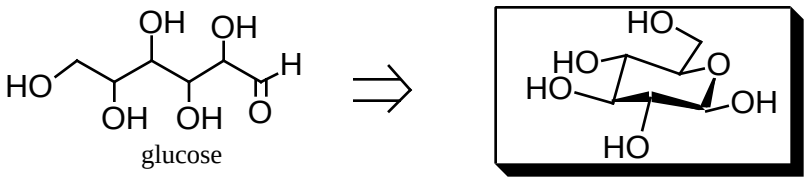




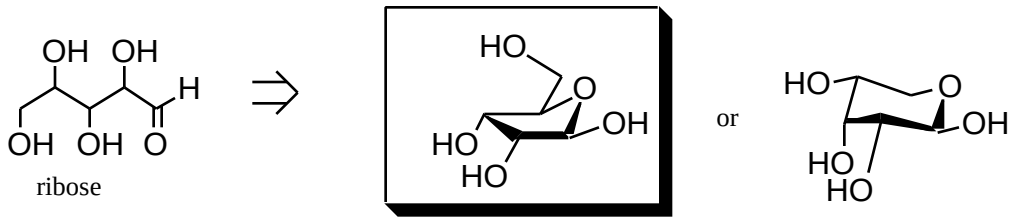


Further reactions after the addition:

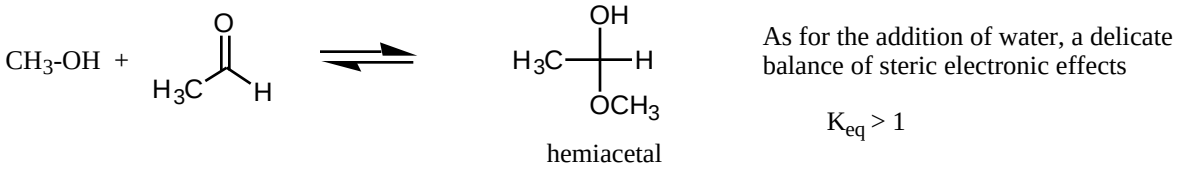
A. Acetals and hemiacetals



glucose



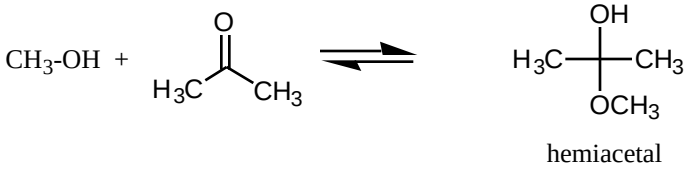
General reaction:



As for the addition of water, a delicate balance of steric electronic effects

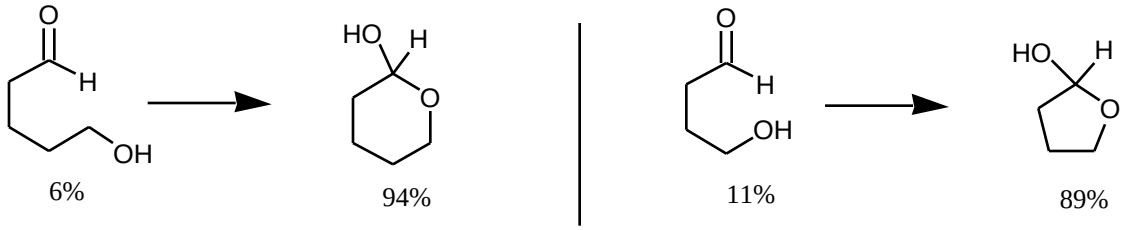
$K_{eq} > 1$

one hydroxy and one alkoxy on a carbon)

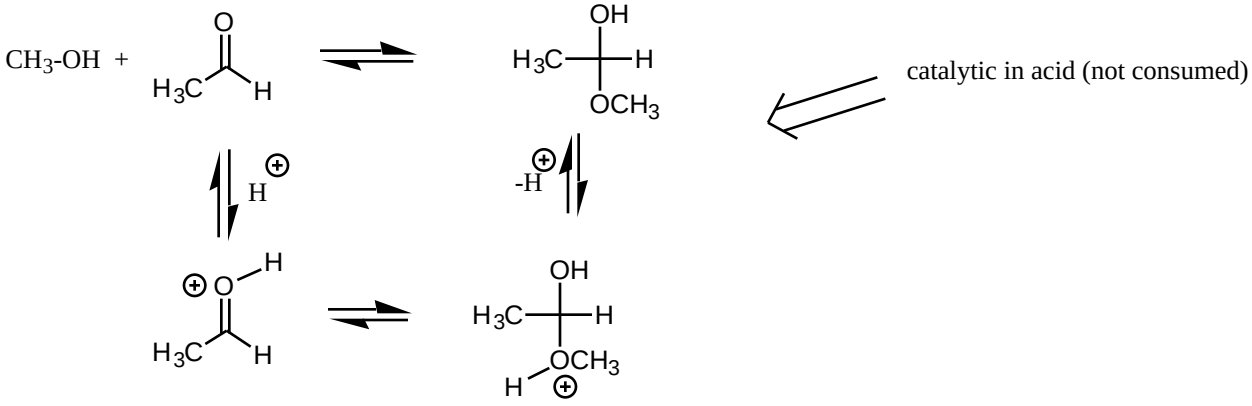


$K_{eq} < 1$

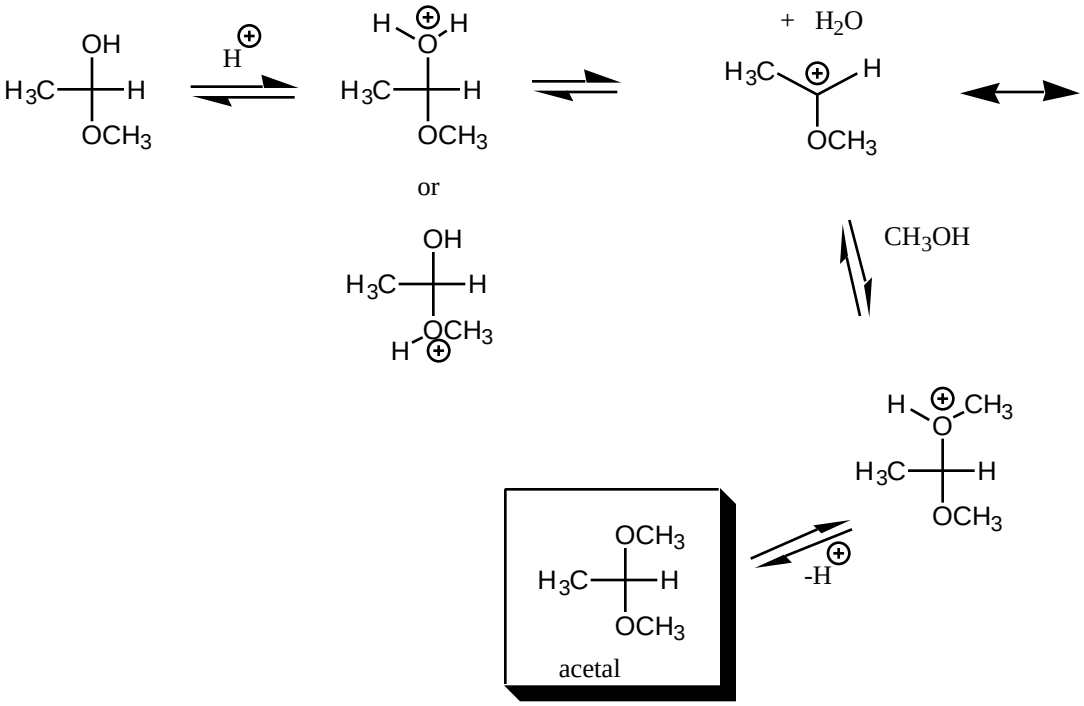
one hydroxy and one alkoxy on a carbon)



Hemiacetal formation in Acid:



Further reaction in acid:

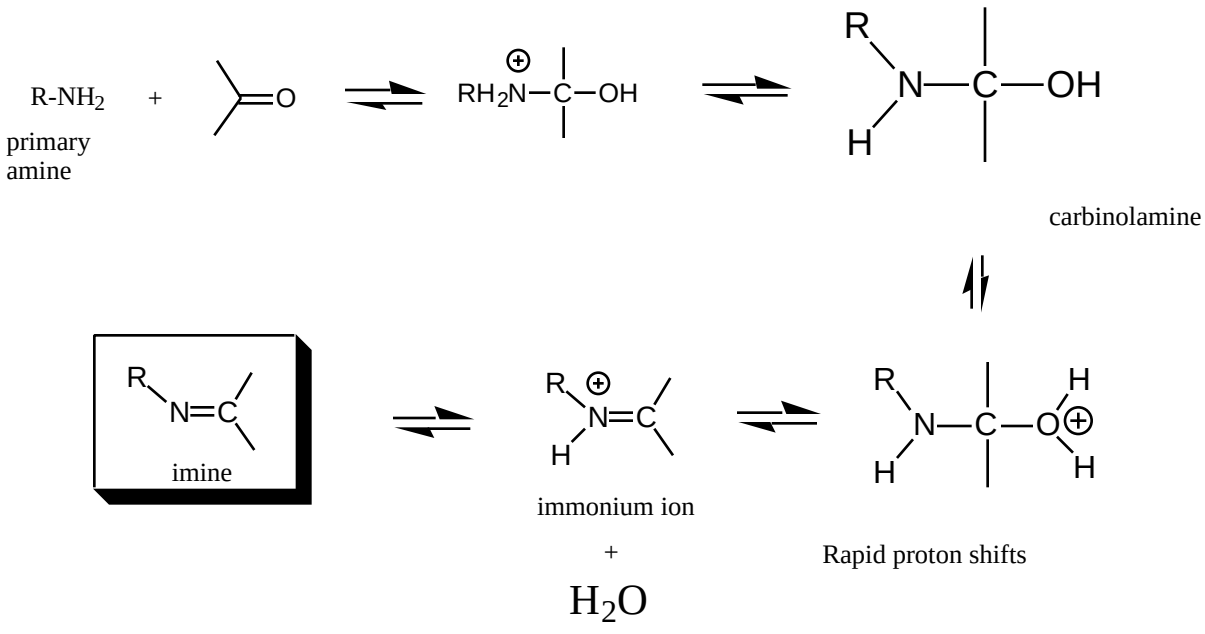


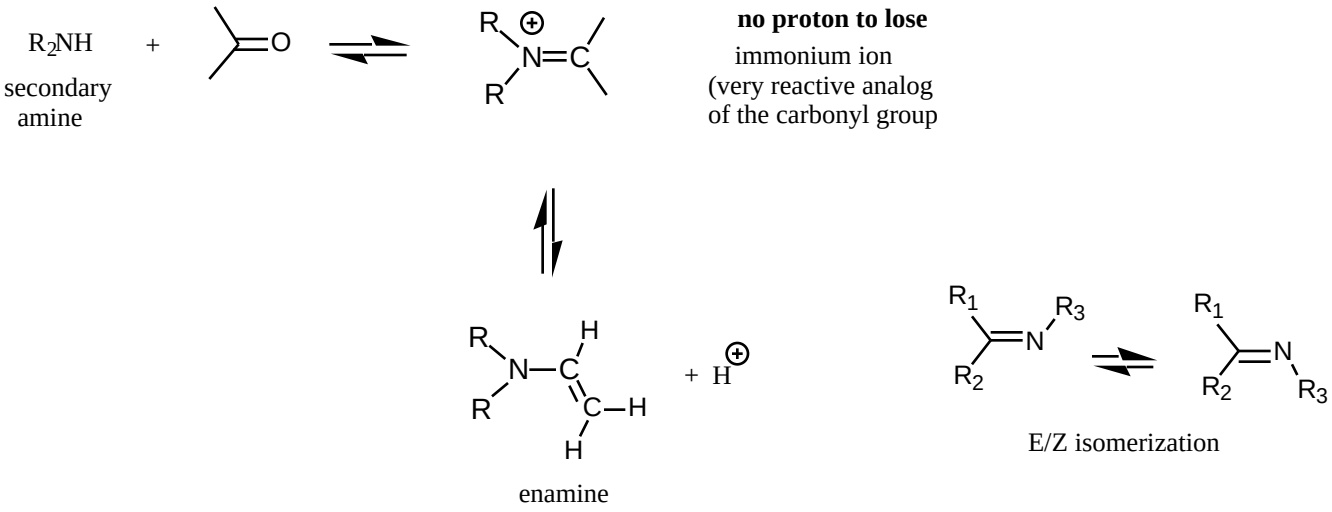
Hydrate: Unstable in both acid and base (write mechanisms)

Hemiacetal: unstable in both acid and base (write mechanisms)

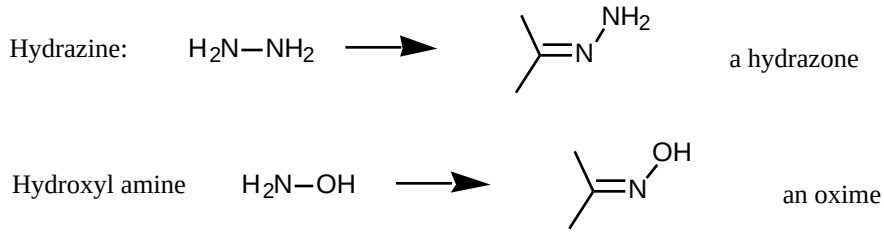
Acetal: Unstable in acid (induced ionization: S_N1)
but stable in base (tertiary, no S_N2)

<u>Nitrogen as the nucleophile:</u>





Variations on a theme: <u>ammonia analogs</u> (p 783)



Hydrazine is a more powerful nucleophile than ammonia---