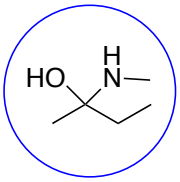
Formation of Cyanohydrins, Imines, Enamines

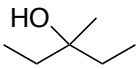
from chapter(s) _____ in the recommended text

A. Introduction

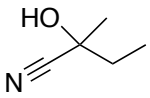
B. Tetrahedral Intermediates And Beyond



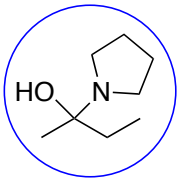
methylamine



EtMgX



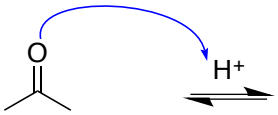
HCN



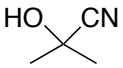
pyrrolidine

C. With HCN

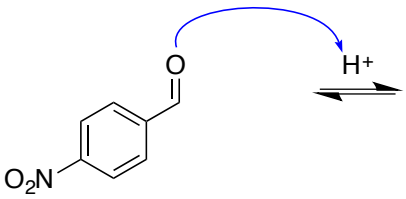
weak



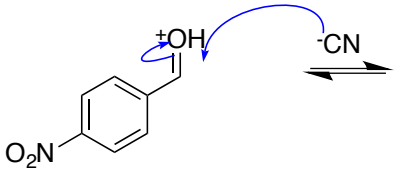
protonated carbonyl



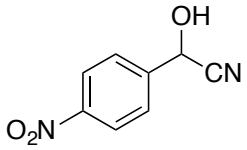
cyanohydrin adduct



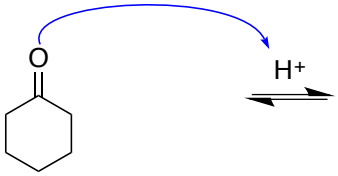
4-nitrobenzaldehyde



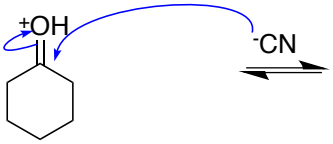
protonated carbonyl

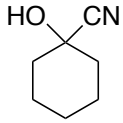


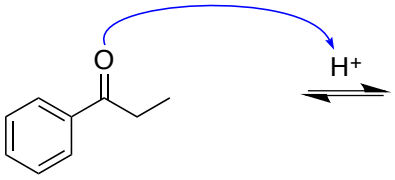
cyanohydrin adduct



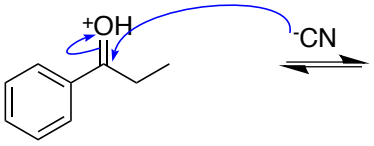
cyclohexanone

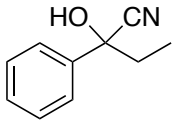






phenylethanone



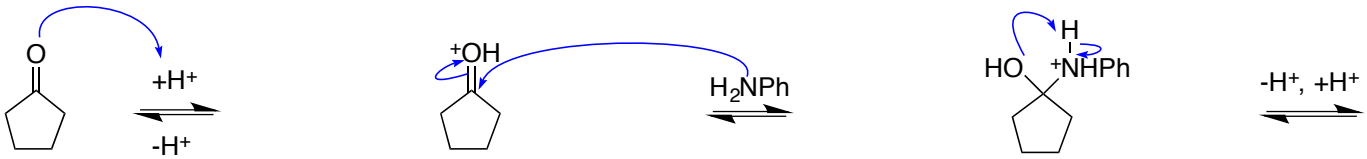


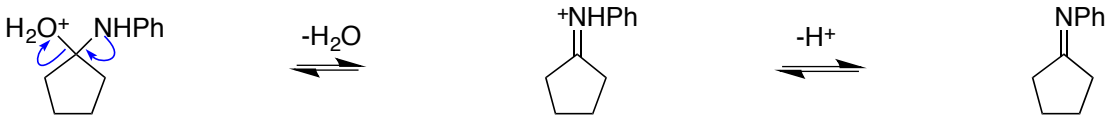
D. Condensations Of Aldehydes Or Ketones With H_2N-R Or H_2N-X

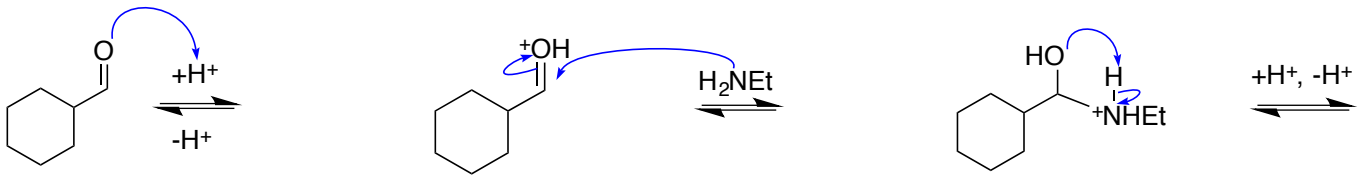
Primary Amines Form Imines

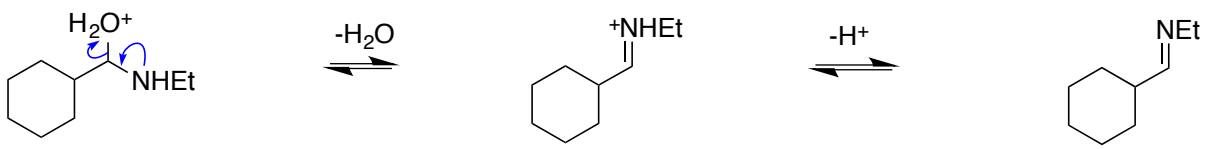
(*loose* water)

.

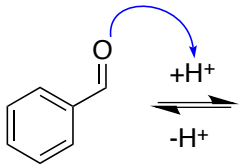


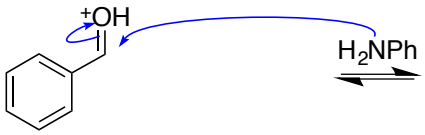


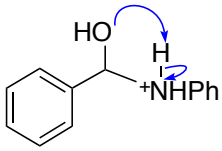


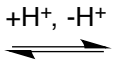


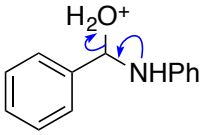
because: at this pH, the carbonyl will be protonated leading to activation of carbonyl group, facilitating the nucleophilic addition of amines. If the pH is lower than 4.5, most of the amine will be protonated making it non-nucleophilic, slowing the rate of reaction.

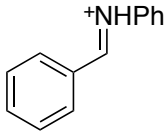


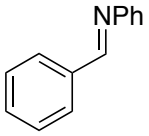








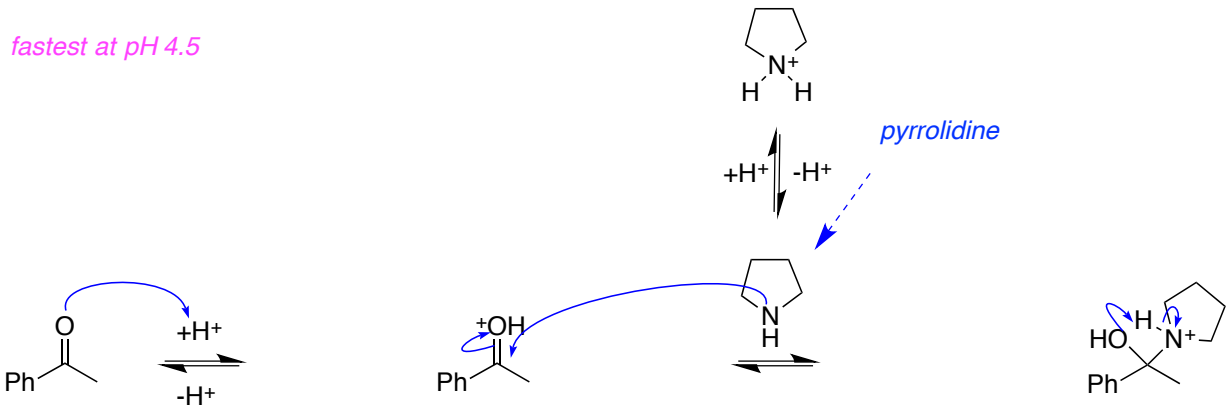


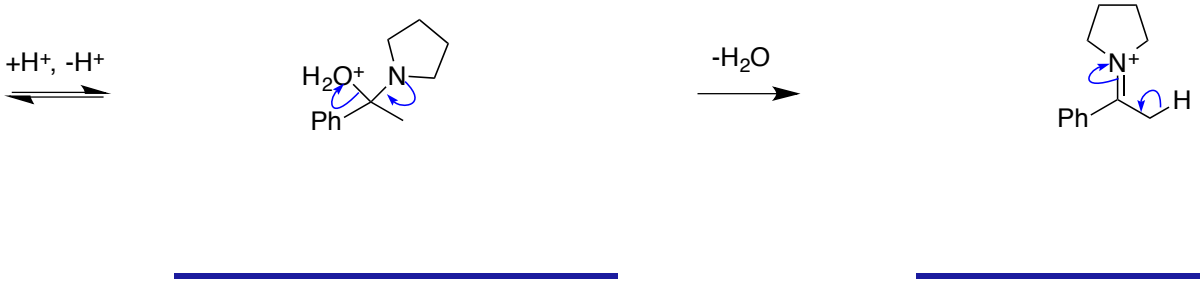


Secondary Amines Form Iminium Ions Then Enamines

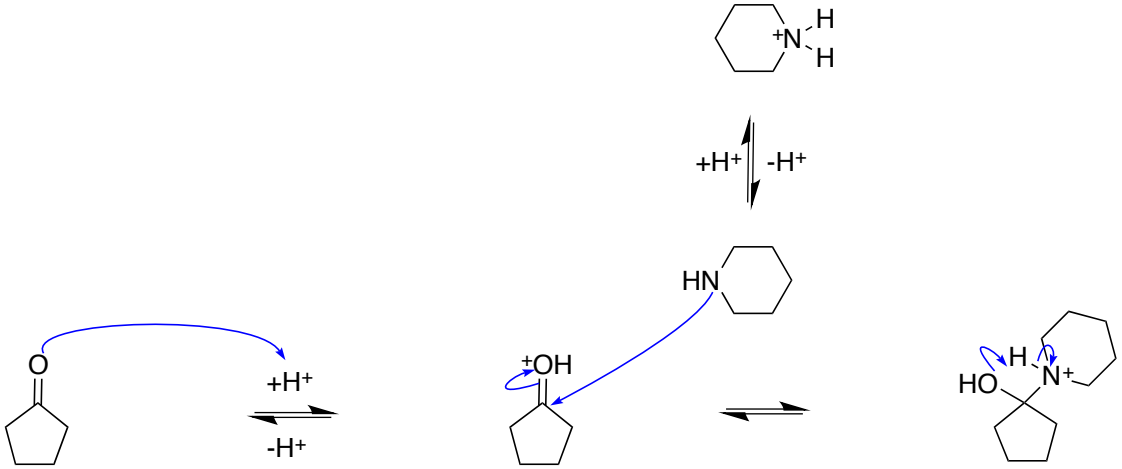
α ✗carbon.

are *reversible*.



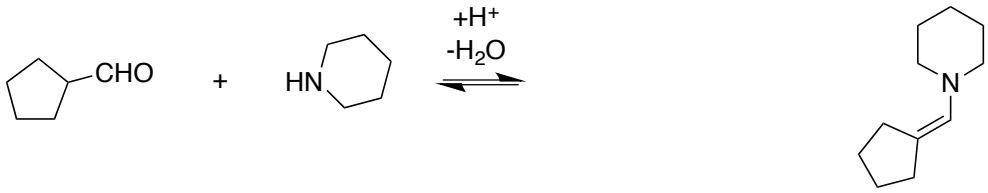


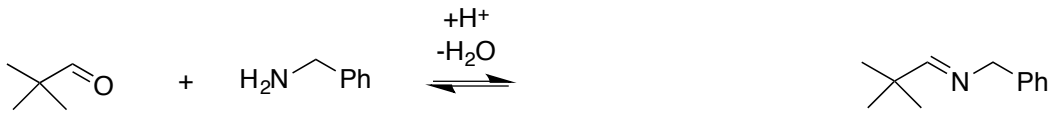
piperidine

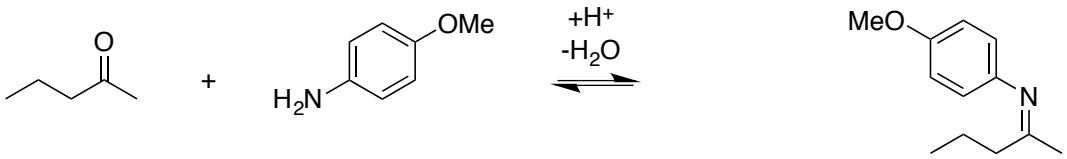


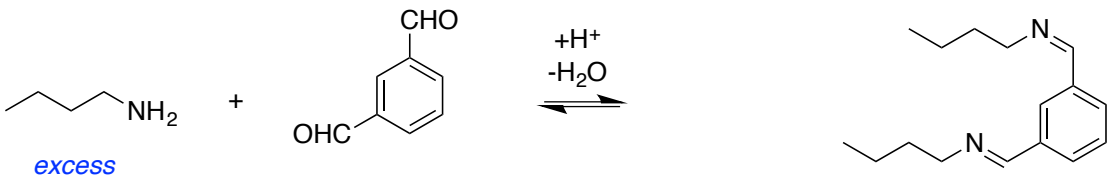
cyclopentanone

do hydrolyze

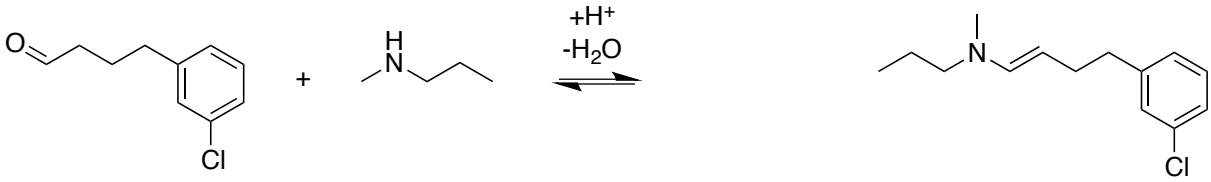

CHO
+
HN
+H+
-H2O
N


O
+
H2N
Ph
+H+
-H2O
N
Ph


O
+
OMe
H2N
+H+
-H2O
MeO
N


NH2
+
CHO
OHC
+H+
-H2O
N
N

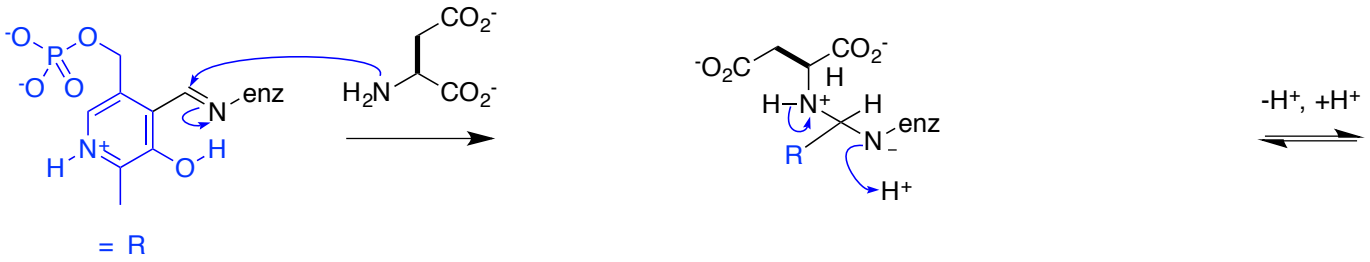
excess



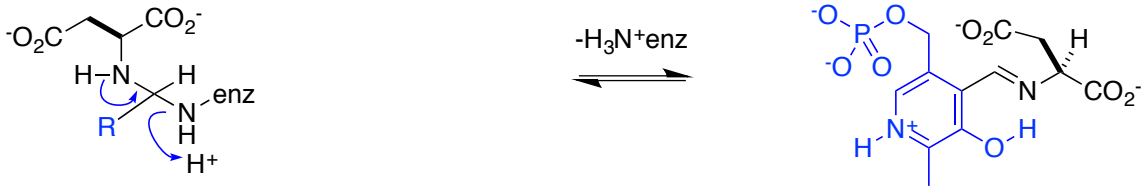
is:

Primary amines have two protons; one can be transferred to OH group then loss of water and another is removed to neutralize iminium to form imines. On the other hand, secondary amines have only one proton involved in dehydration step but no proton left to neutralize iminium ion. So the mechanism must involve to loosing a proton from the α-carbon to neutralize iminium ion thus forming enamines.

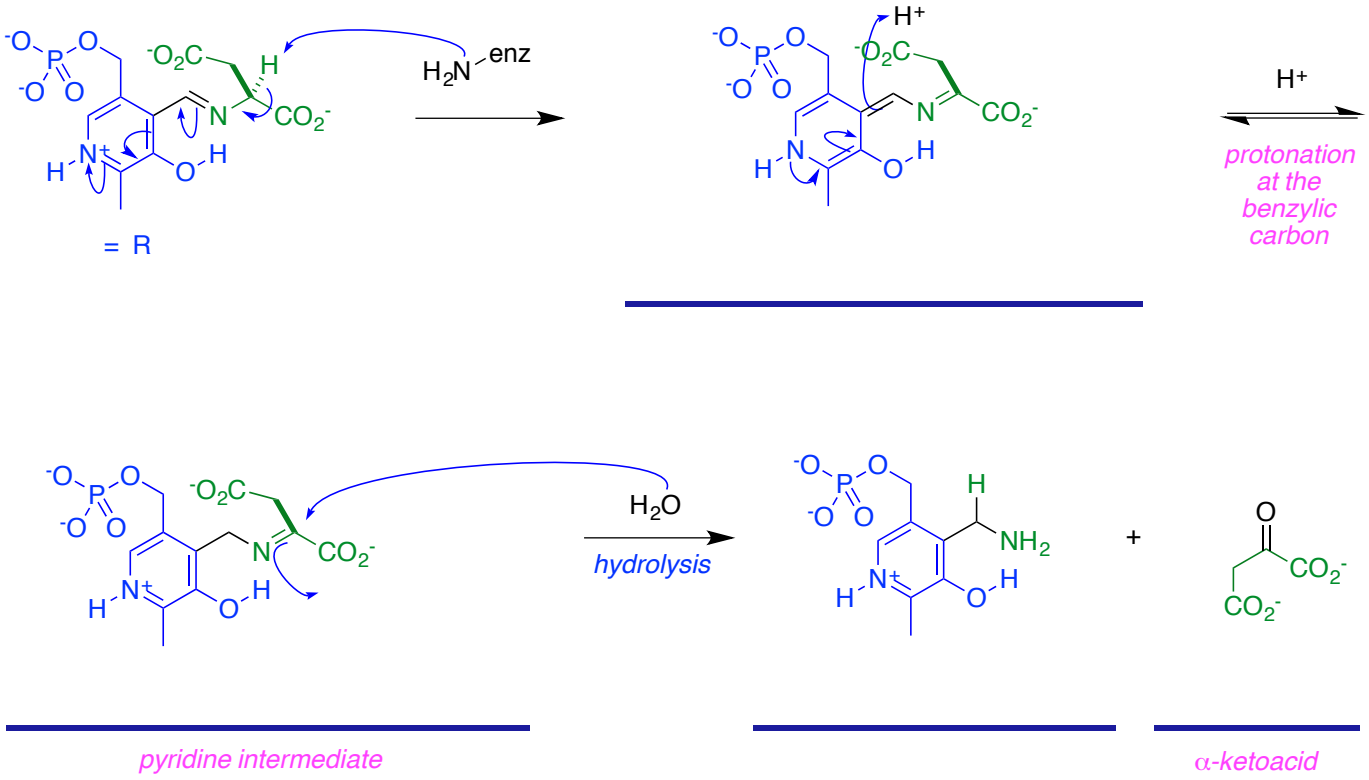
E. Transamination



tetrahedral intermediate



tetrahedral intermediate *imine products*



oxidation of

amine
degrade one and form another.