

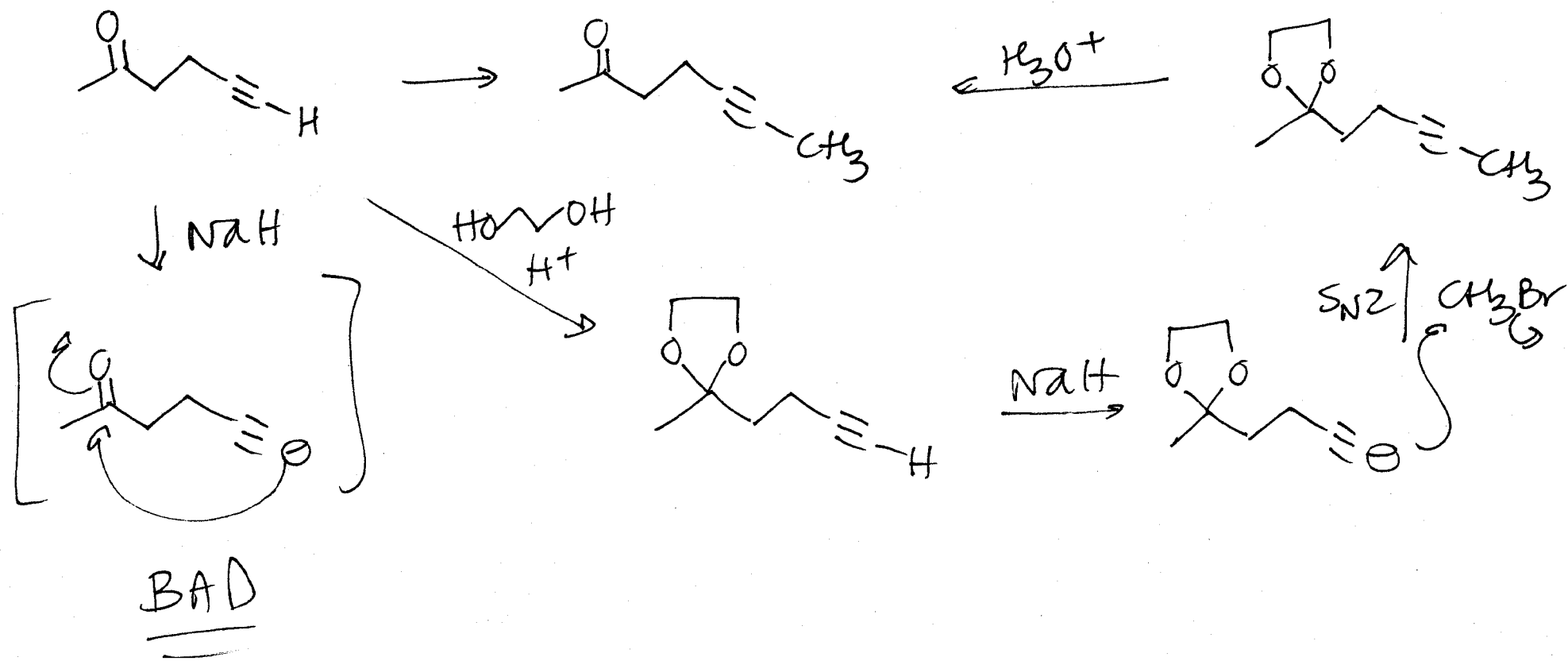
Alcohols as nucleophiles

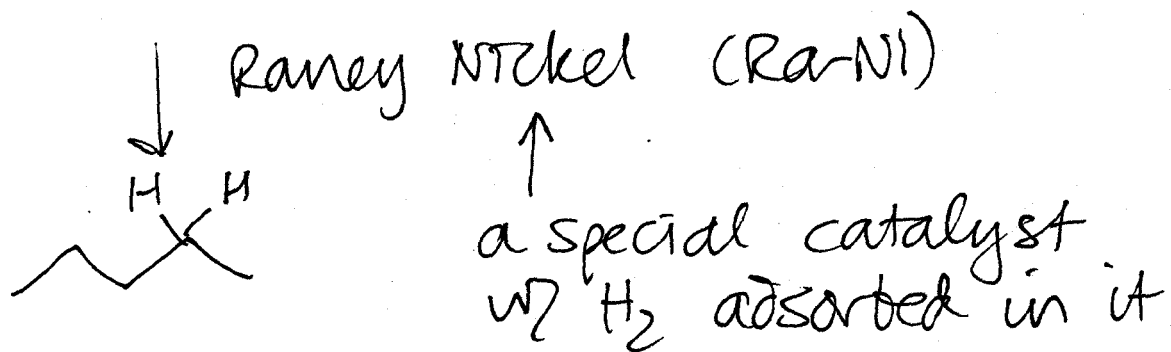
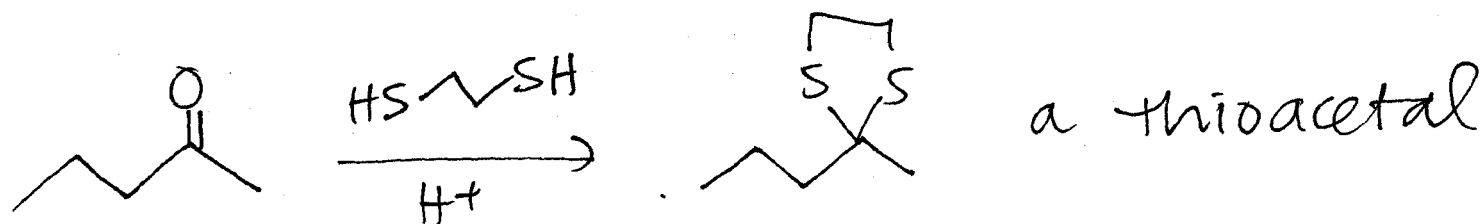
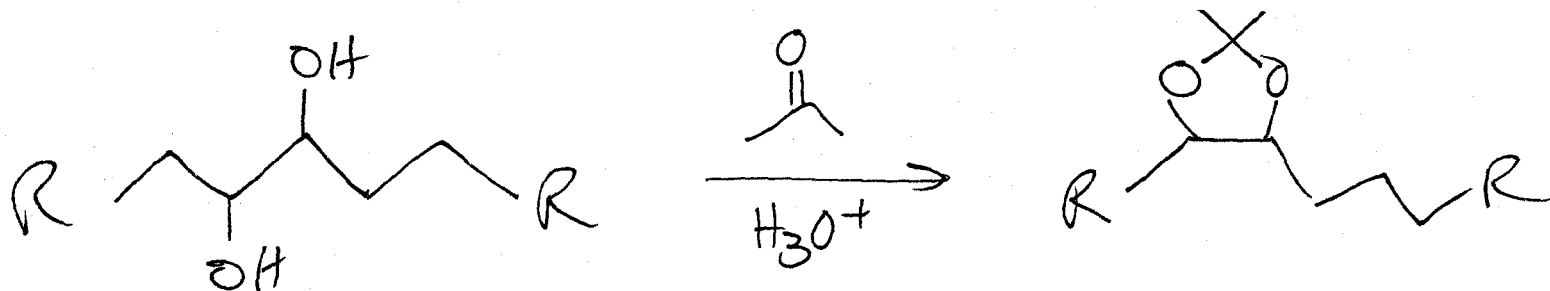
In base: adds one equiv. \rightarrow hemiacetal (unstable)

In acid: adds two equiv. \rightarrow acetal (v. stable)

Acetals are ethers - unreactive in presence of base, strong Nu, ox agents, etc.

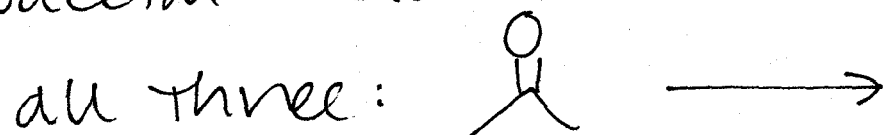
easily hydrolyzed back to parent C=O w/ H_3O^+



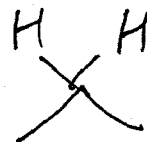


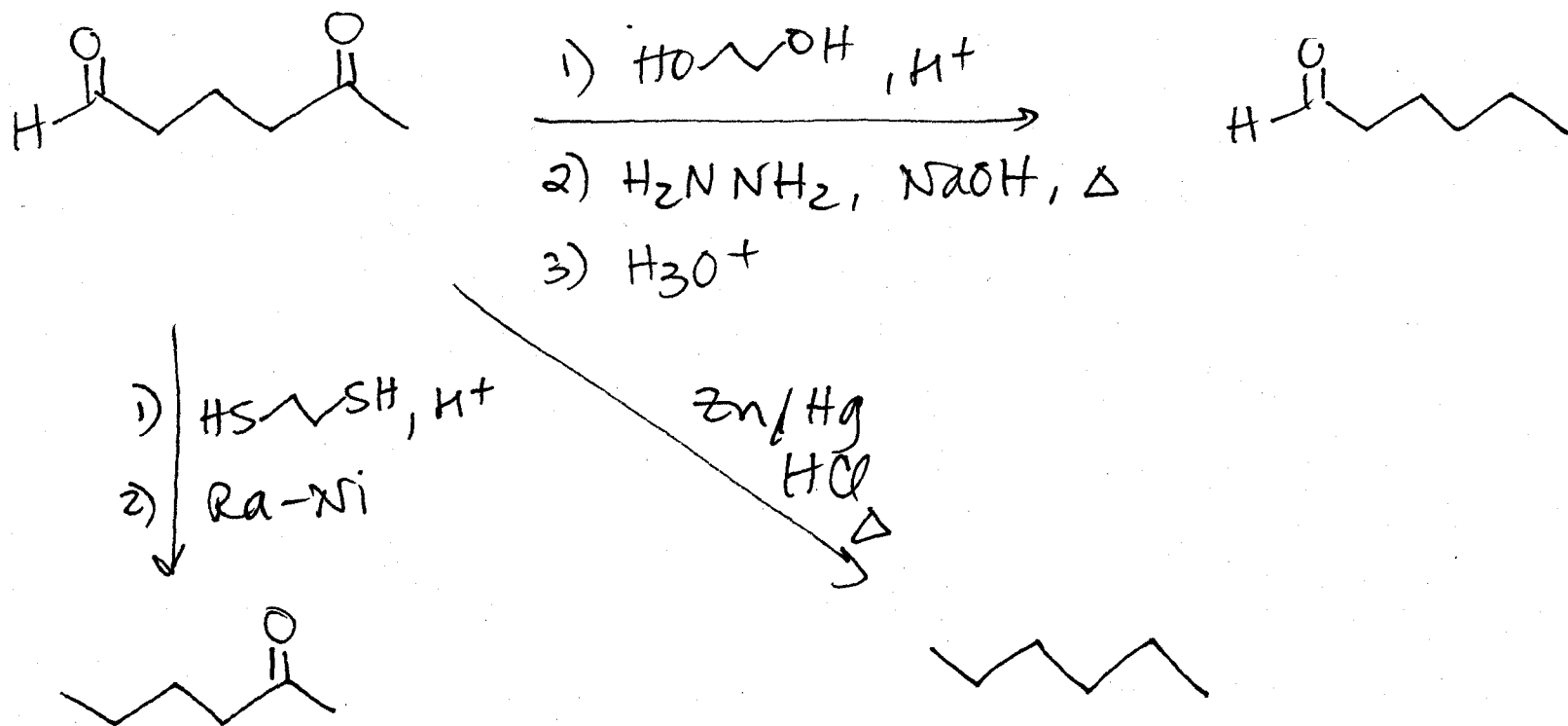
Reductive cleavage
of C-S bond

Clemmensen - strong acid
Wolff-Kishner - strong base
thioacetal - close to neutral

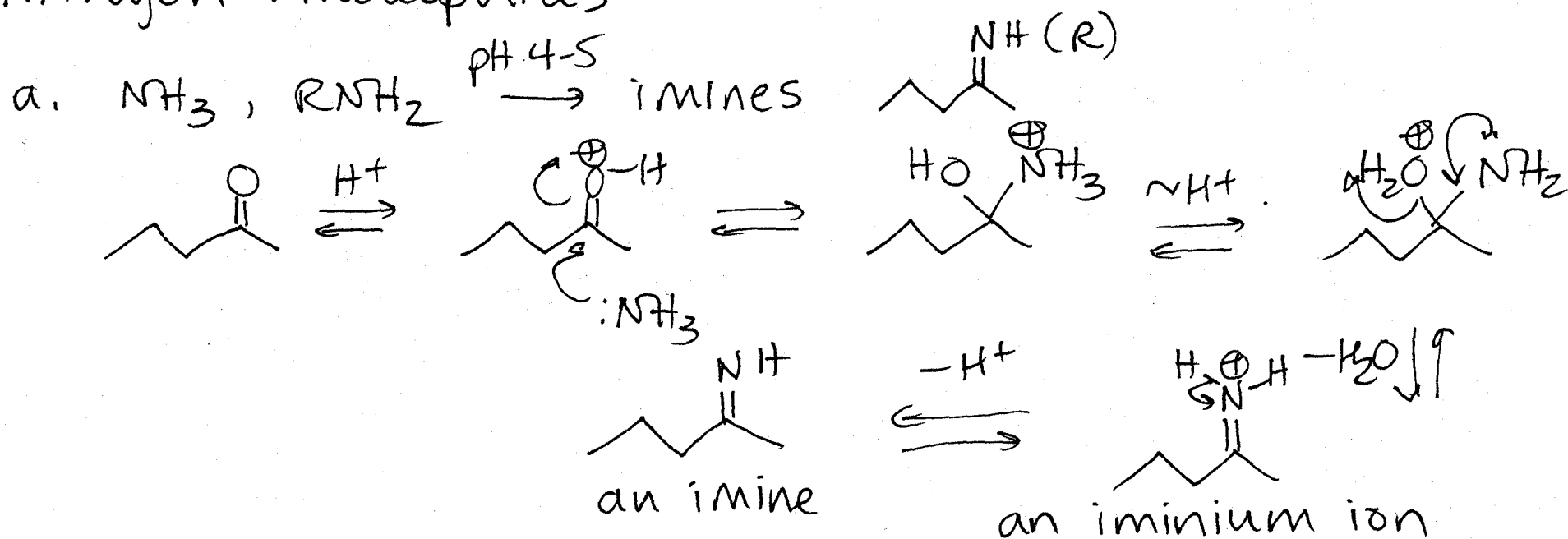


aldehyde +
ketone only

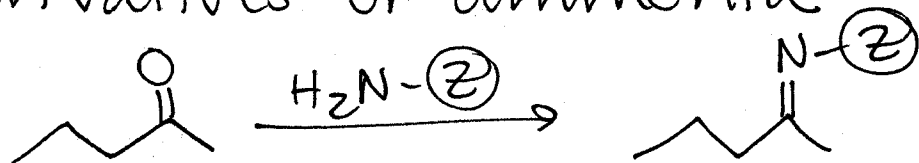




Nitrogen nucleophiles



b. Derivatives of ammonia $\text{H}_2\text{N}-\textcircled{Z}$

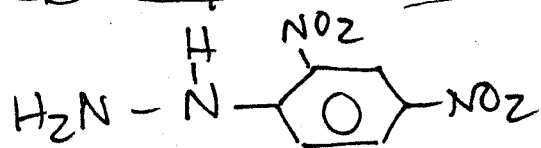


1. Hydroxylamine ($z = \text{OH}$) \rightarrow oxime CCCC(=NOH)C

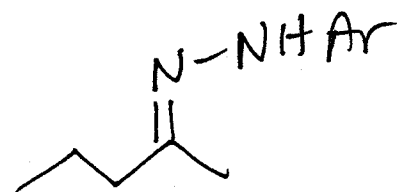
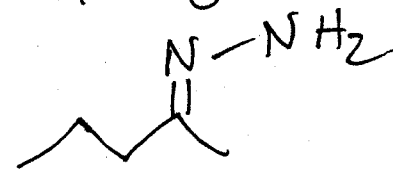
2. a hydrazine $\text{H}_2\text{N}-\text{NH}_2$

We usually use 2,4-DNP

~~2,4-DNP~~ 2,4-dinitrophenylhydrazine

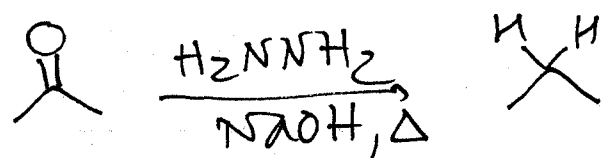


\rightarrow a hydrazone

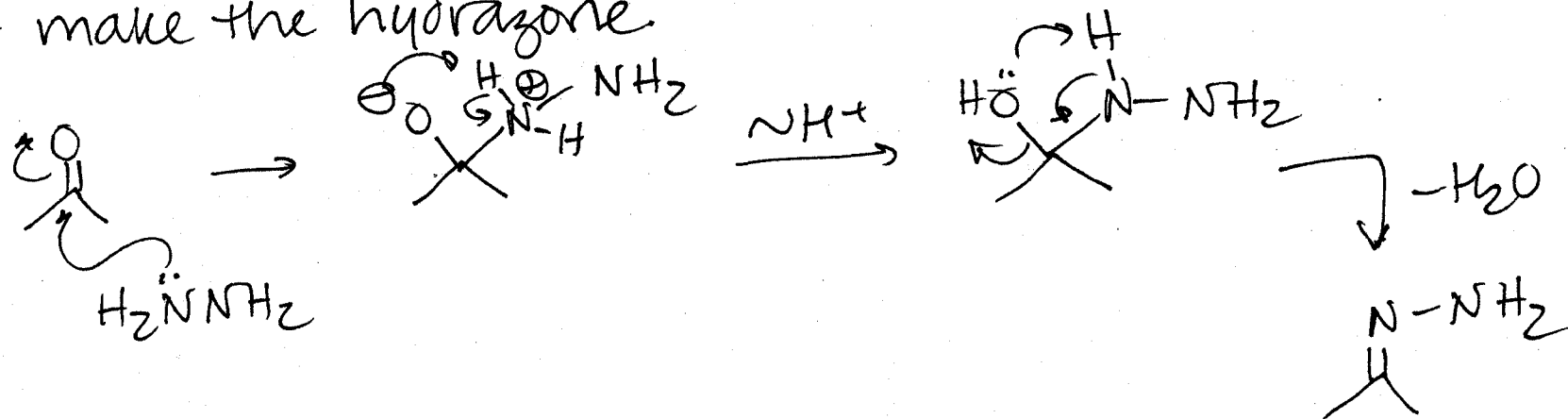


\uparrow
an excellent
functional group
test - reacts v.
quickly w/ aldehydes
+ ketones \rightarrow ppt.

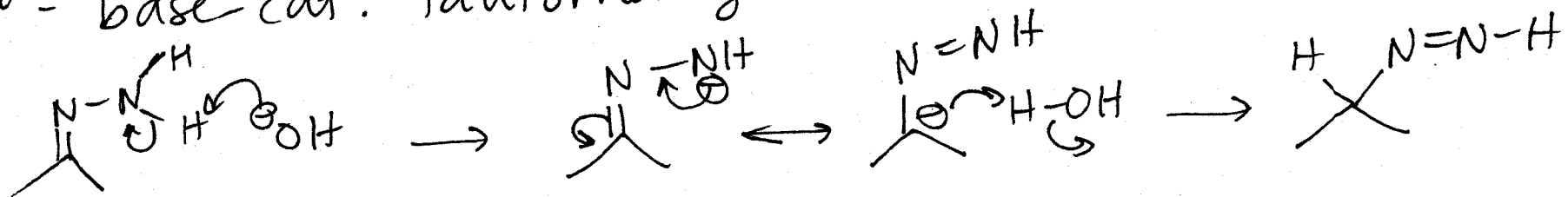
mechanism of Wolff-Kishner reduction:



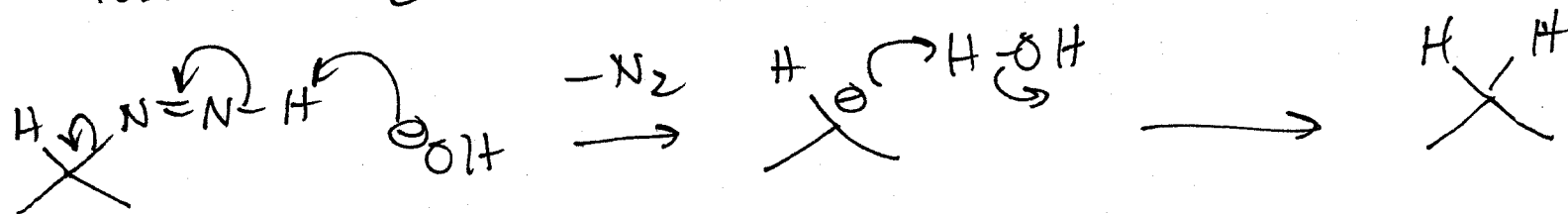
1st - make the hydrazone.



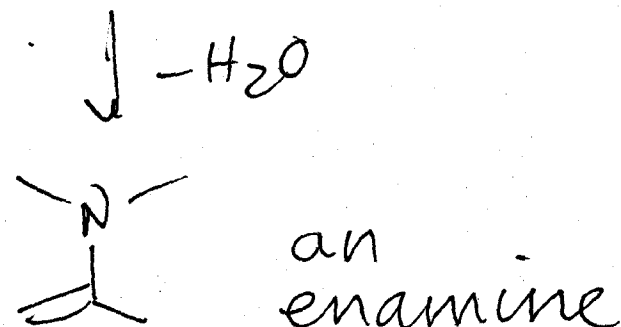
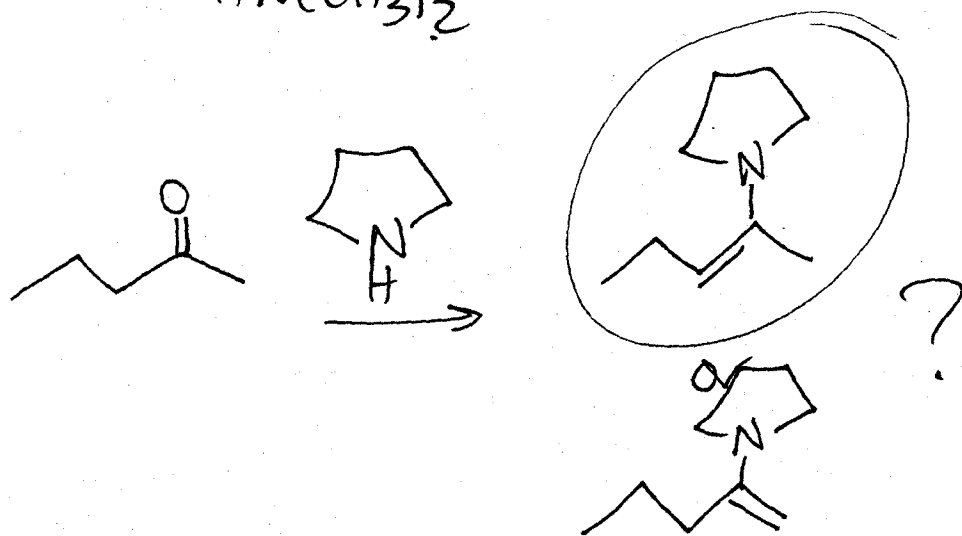
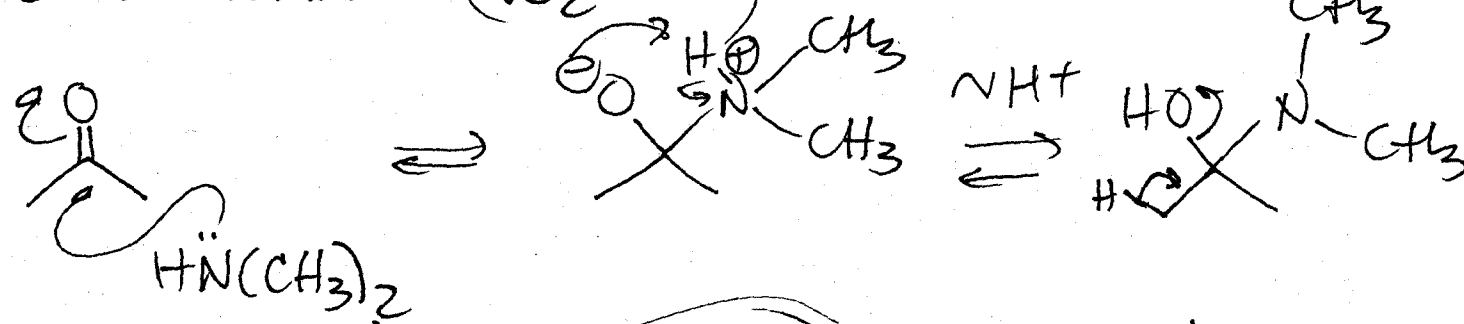
2nd - base cat. tautomerization



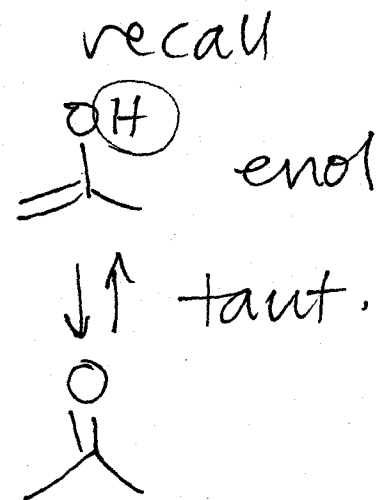
3rd - loss of N_2 ($\text{N}\equiv\text{N}$)



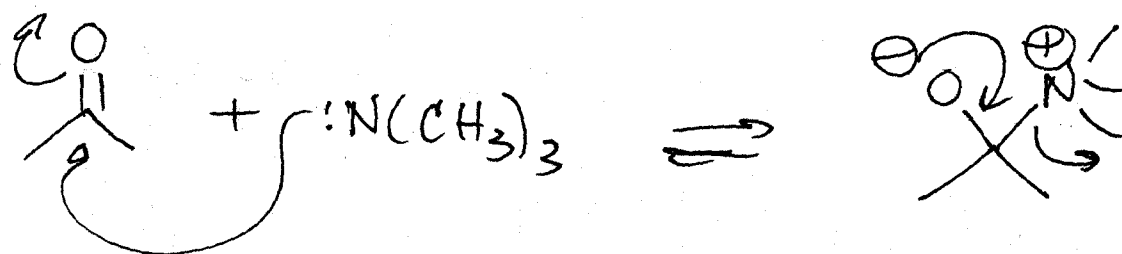
c. 2° amines (R_2NH)



* When more than one possible enamine - always make the thermodynamic one (more highly substituted)



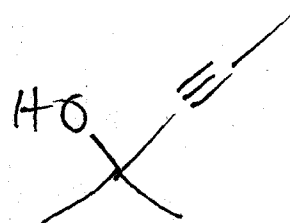
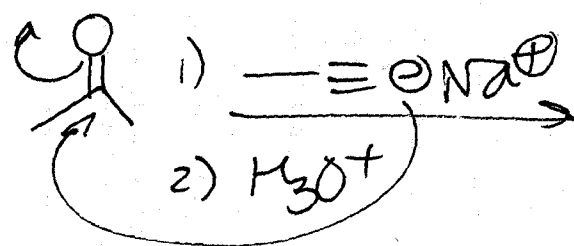
d. 3° amines (R_3N)



stuck @
zwitterion -
rxn reverses.

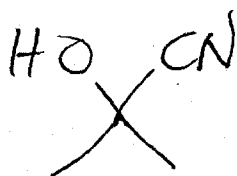
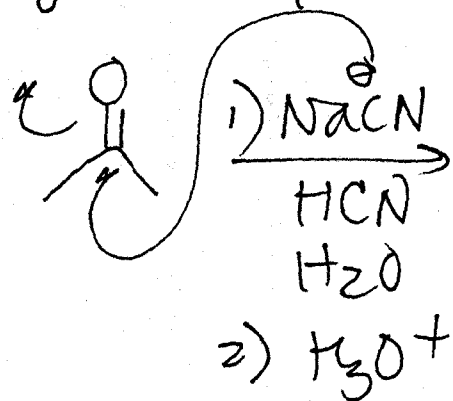
other random nucleophiles

a. acetylene anions



(propargyl
alcohols)

b. cyanohydrins



a cyanohydrin