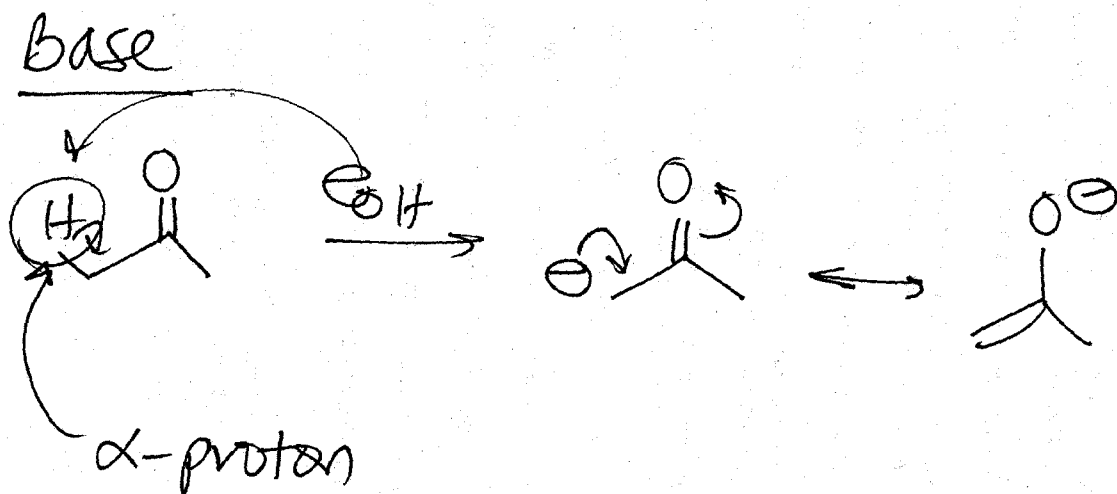
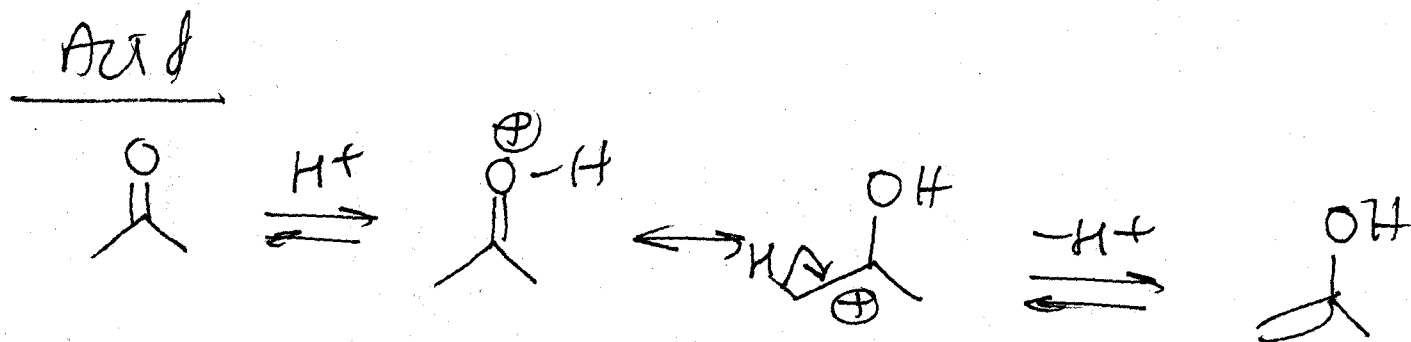
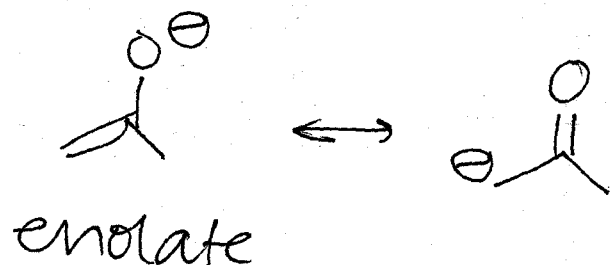
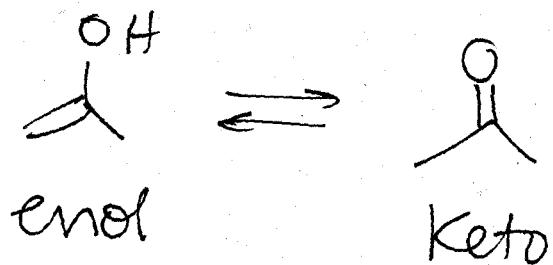


Chapter 18 - Enolates

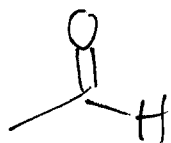


α -proton

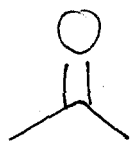
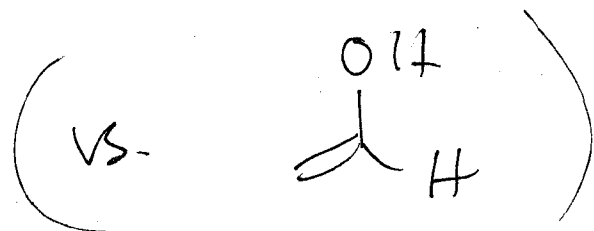
pKa 19-20

(expected 40-50 for
H on sp^3 C)

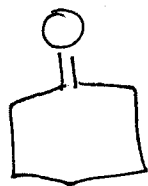
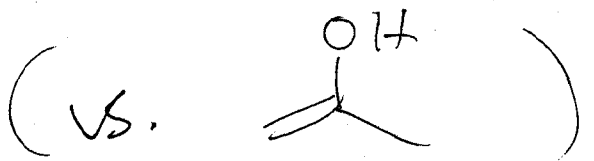
Keto vs. Enol



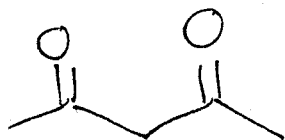
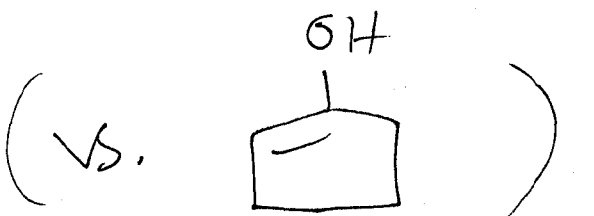
~ 100% Keto



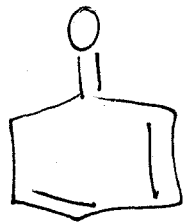
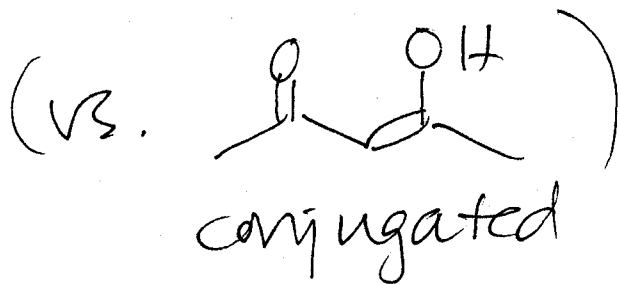
> 99% Keto



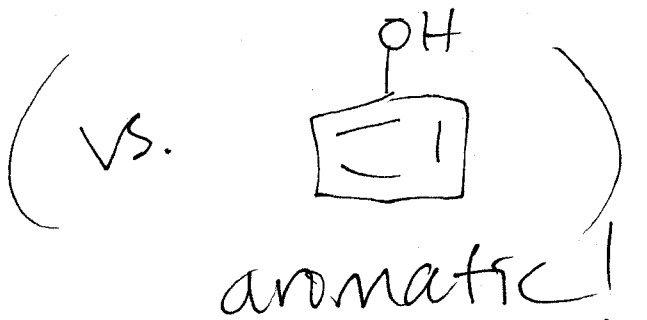
98.8% Keto



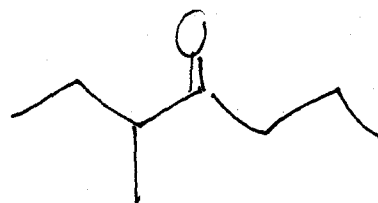
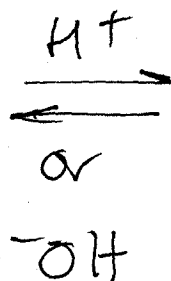
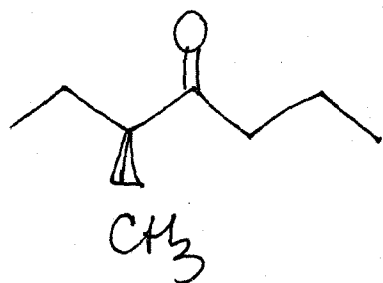
24% Keto



~ 0% Keto

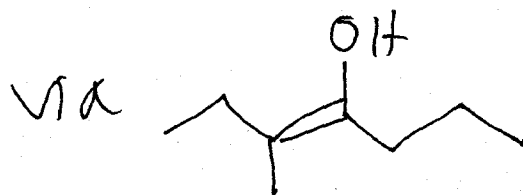


Enolization Causes Racemization



racemic

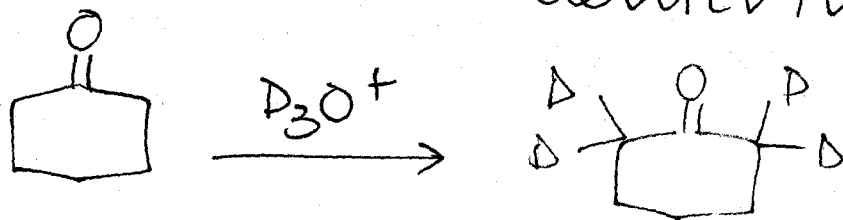
If there is a
stereocenter at
the α -carbon



Why are we interested in enols/enolates?

* They are another source of
nucleophilic carbon

Enol/enolate + deuterium



unknown C_4H_8O

SODAR = 1

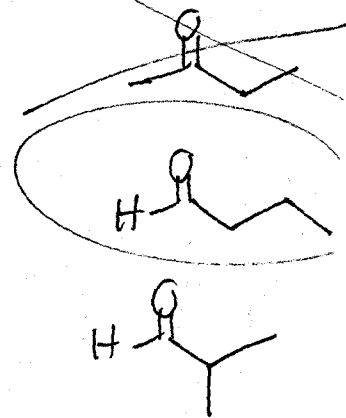
+ 2,4-DNP

aldehyde or ketone

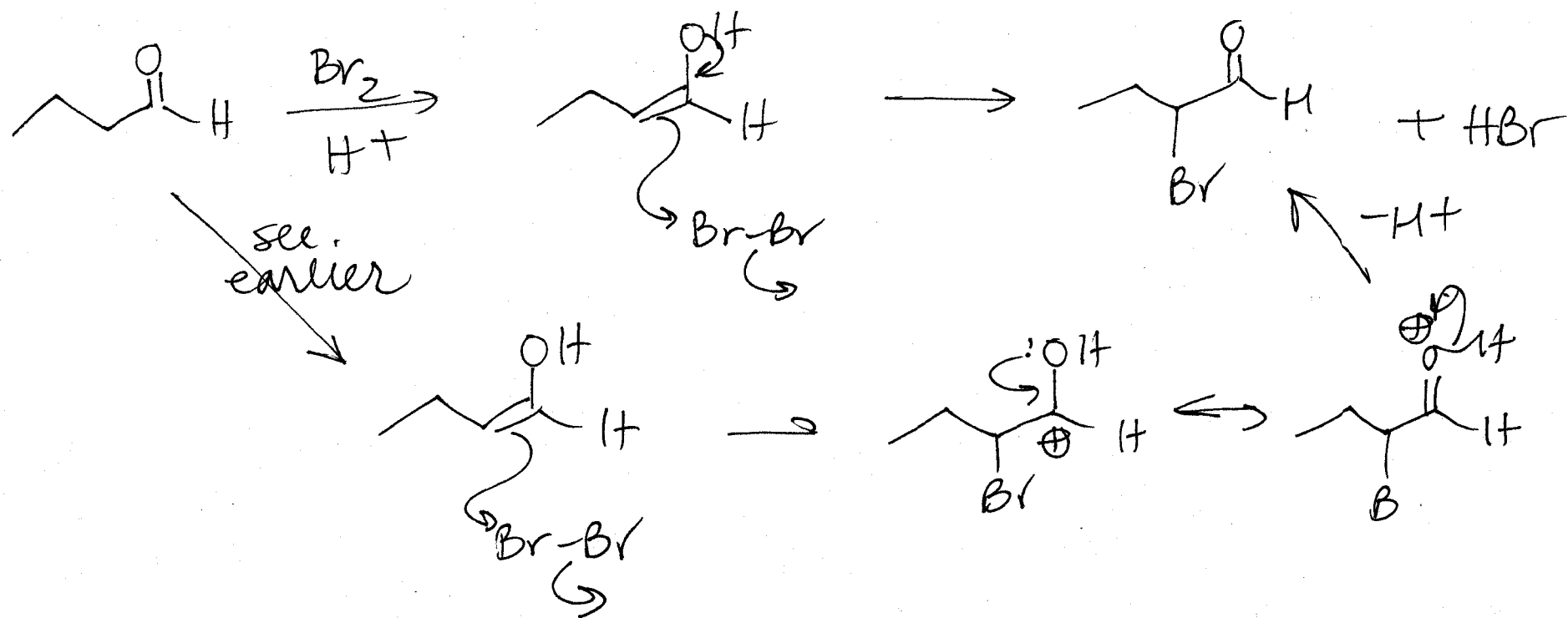
+ tollens

aldehyde

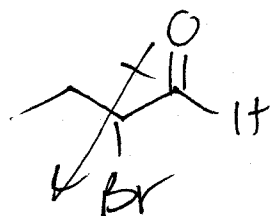
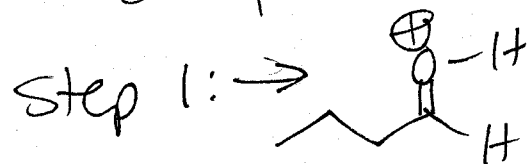
takes up 2 equiv. of
D in the presence
of D_2O/D^+



Enol/enolate + halogens

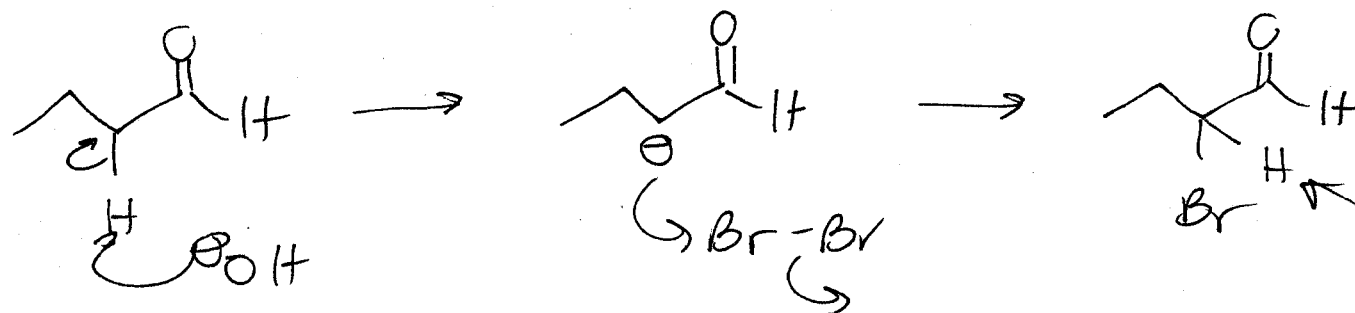


Done in acid to increase amt. of enol present
Also - easy to stop after the add'n of one halogen.



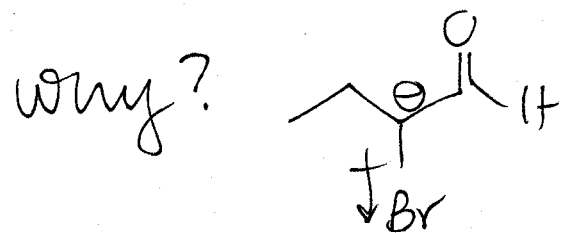
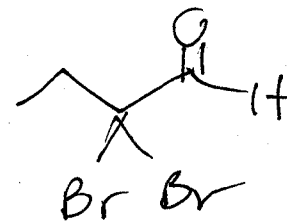
e^- withdrawing effects of the Br make it harder to protonate the C=O .

what about in base?



this proton is now even more acidic.

+ the rxn goes on.



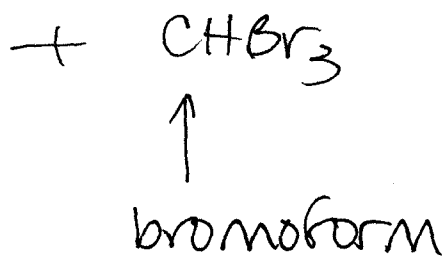
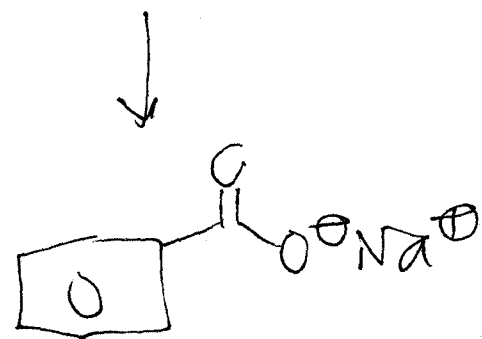
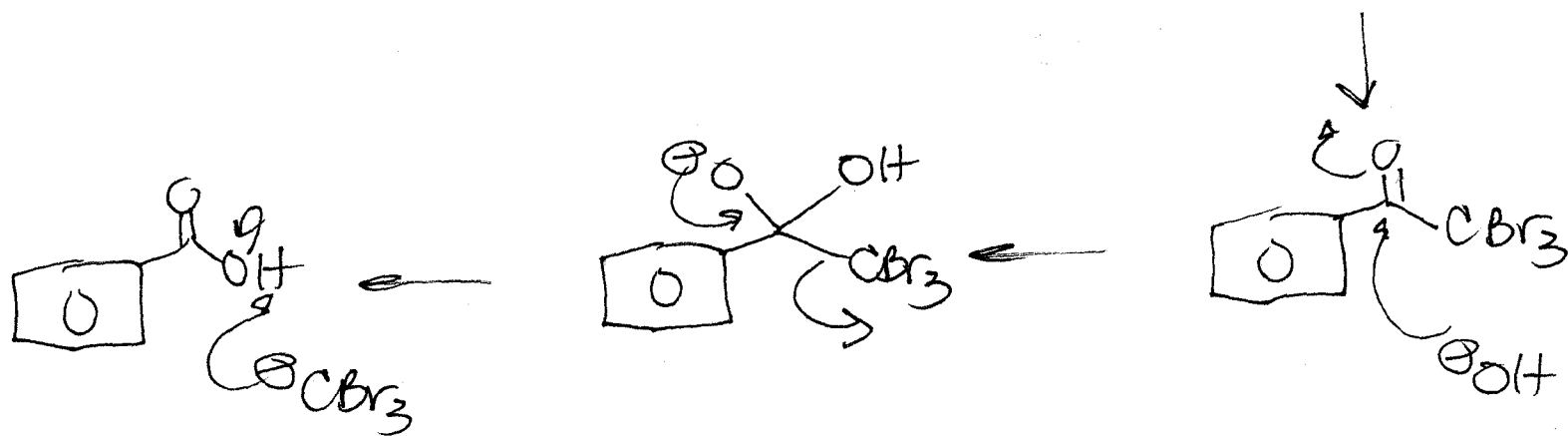
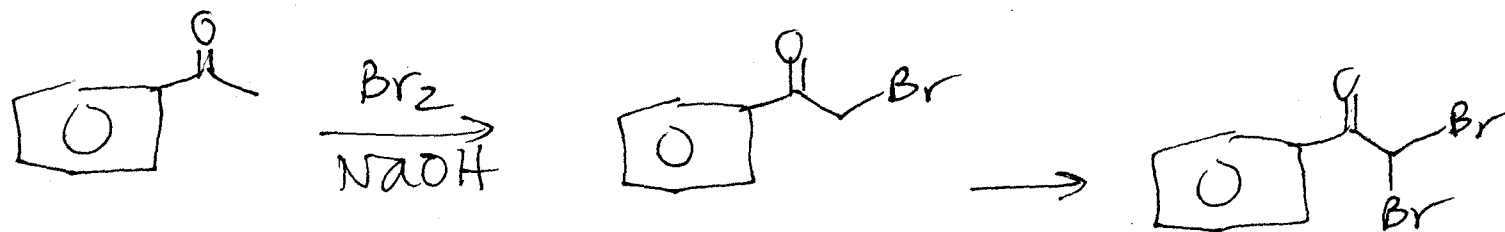
anion is stabilized by the e^- withdrawing Br

this is not usually what we want to happen.

however - we can take advantage of this.

* haloform rxn.

Halofarm only works on $\text{CH}_3\text{C}(=\text{O})\text{R}$ (methyl carbonyl)



CHCl_3
 chloroform

CHI_3
 iodoform
 yellow ppt.