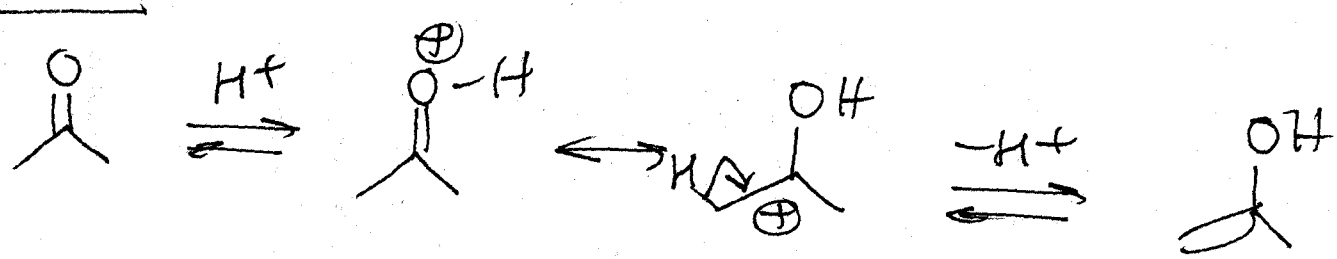
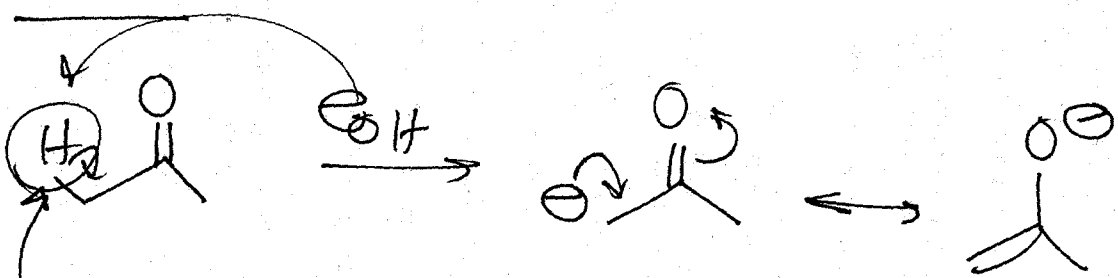
Chapter 18 – Enolates

Acid



Base

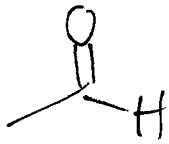


α-proton

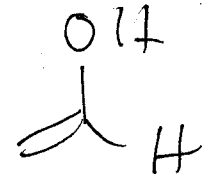
pka 19-20

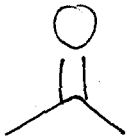
(expected 40-50 for H on sp^3 C)

Keto vs. Enol

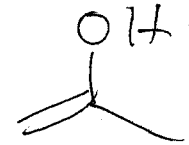


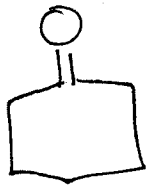
~100% keto

(vs. )



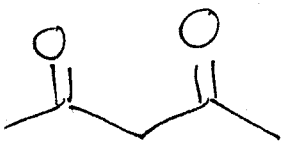
> 99% keto

(vs. )

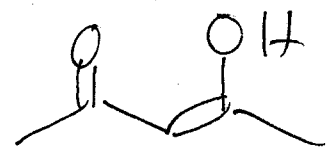


98.8% keto

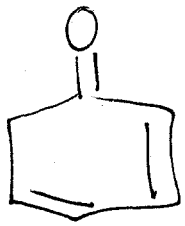
(vs. )



24% keto

(vs. )

conjugated

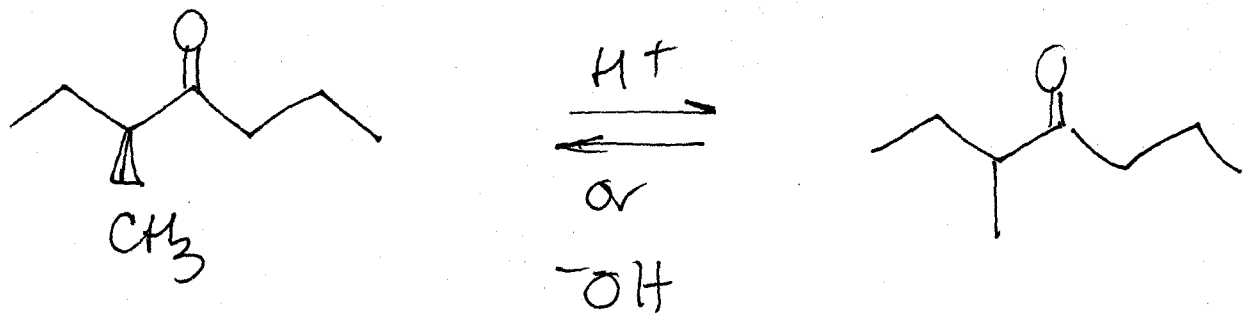


~0% keto

(vs. )

aromatic!

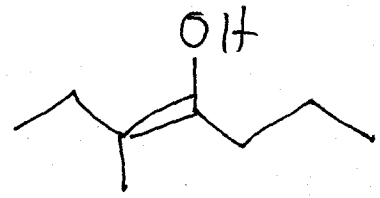
Enolization causes Racemization



If there is a stereocenter at the α-carbon

racemic

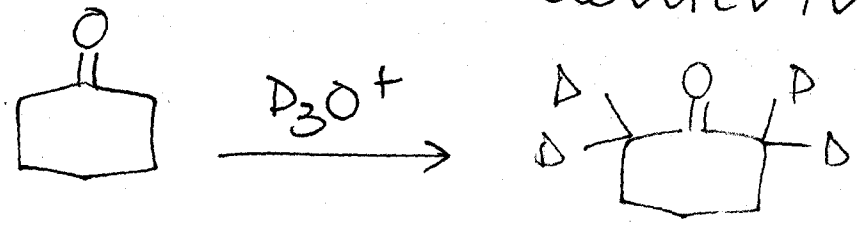
via



Why are we interested in enols/enolates?

* They are another source of nucleophilic carbon

Enol / enolate + deuterium



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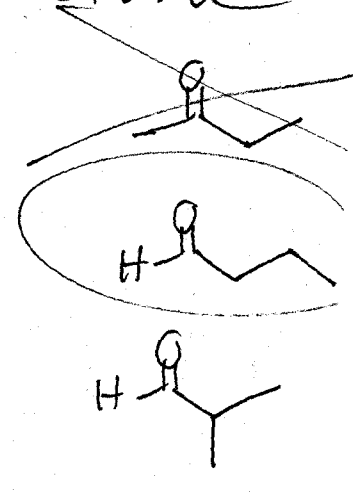
unknown C_4H_8O

SODAR = 1

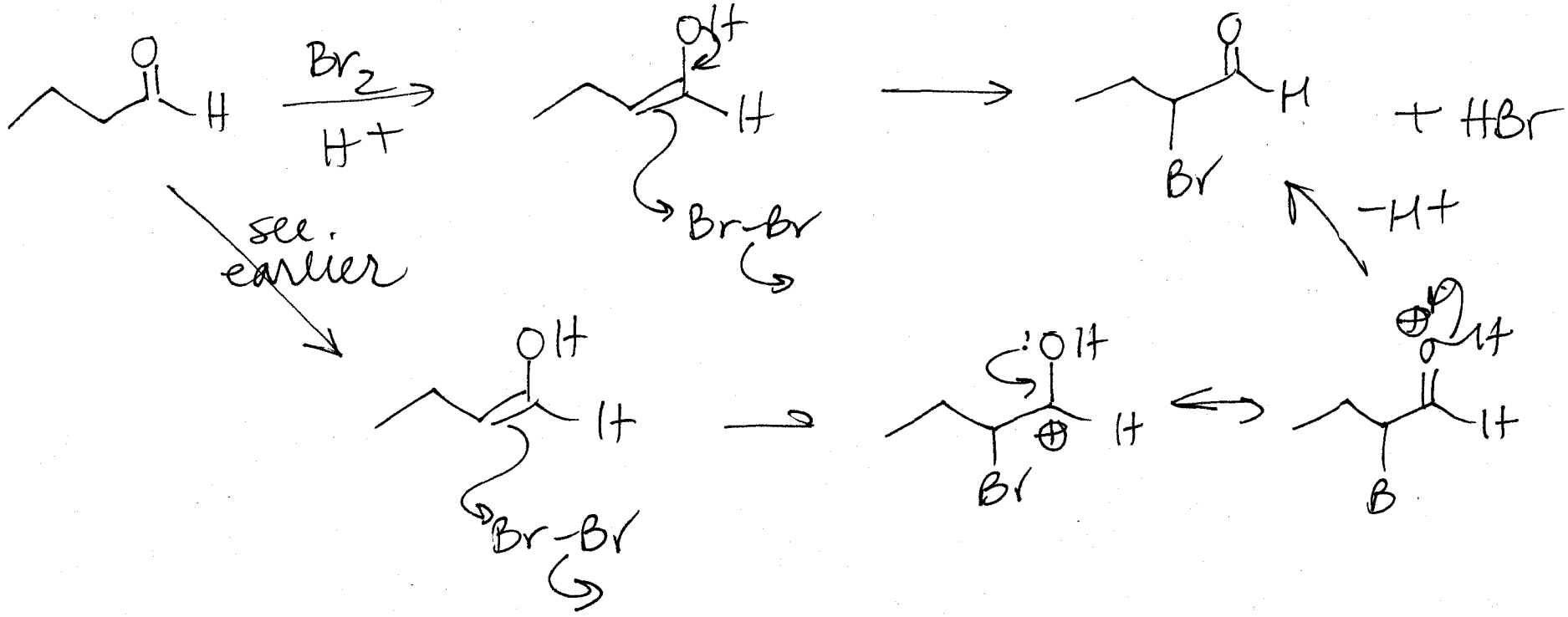
+ 2,4-DNP aldehyde or ketone

+ Tollens aldehyde



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

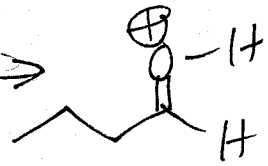
Enol / enolate + halogens

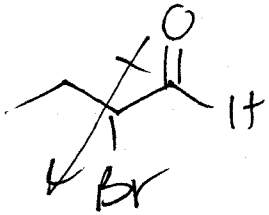


Done in acid to increase amt. of enol present

Also - easy to stop after the add'n of one halogen.

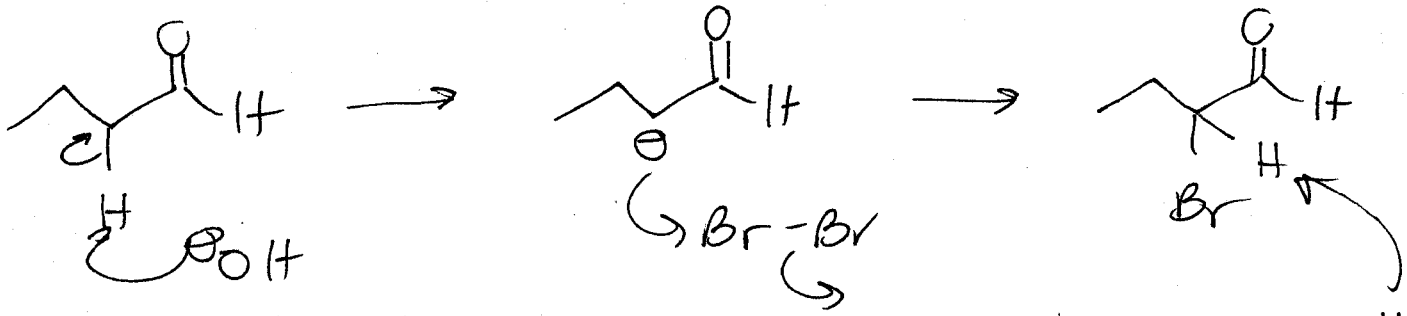
Step 1: →





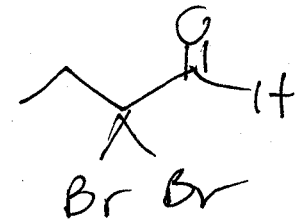
e⁻ withdrawing effects of the Br make it harder to protonate the C=O.

what about in base?

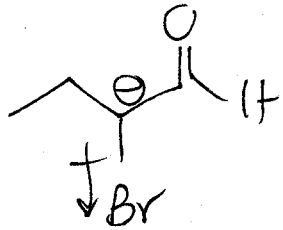


this proton is now even more acidic.

+ the rxn goes on.



why?

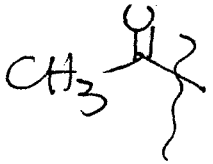


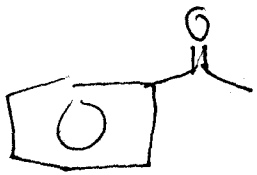
anion is stabilized by the e⁻ withdrawing Br

this is not usually what we want to happen.

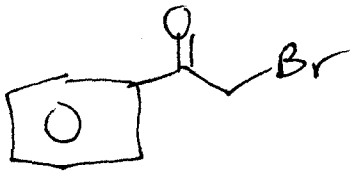
however - we can take advantage of this.

* Haloform rxn.

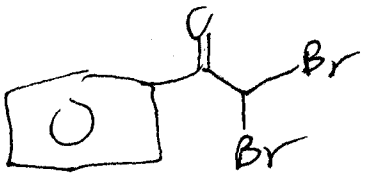
Haloform only works on CH_3  (methyl carbonyl)

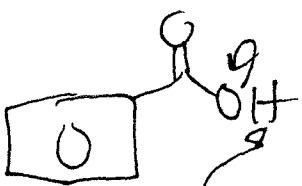


$\xrightarrow[NaOH]{Br_2}$

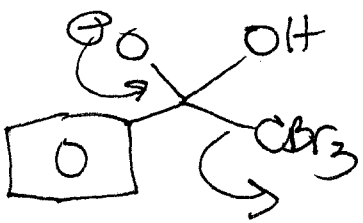


$\longrightarrow$

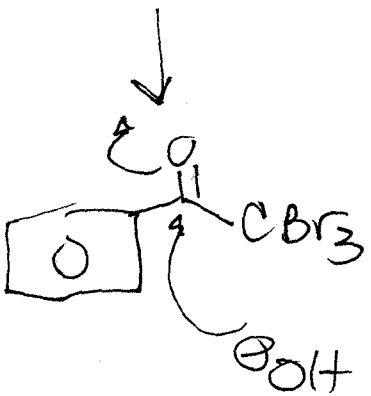




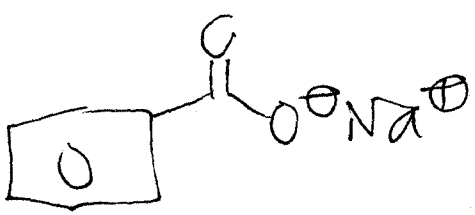
$\longleftarrow$



$\longleftarrow$



$\downarrow$



oxidized the ketone

$+ \quad CHBr_3$

$\uparrow$

bromoform

$CHCl_3$

chloroform

CHI_3

iodoform

yellow ppt.