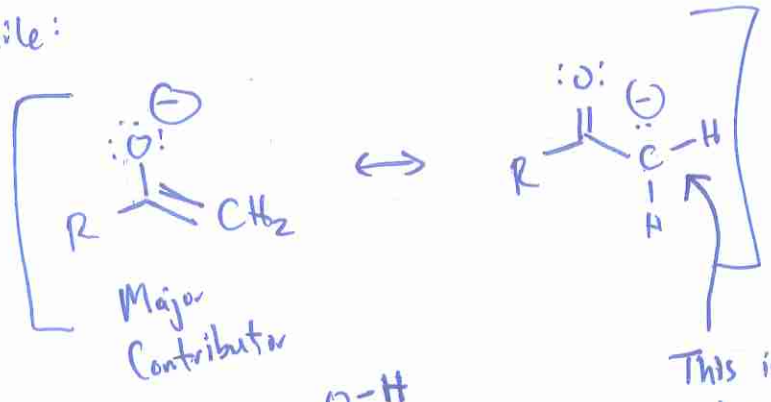
MTW

Mon 4/3/2017

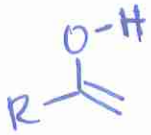
New Nucleophile:

-ate → negatively charged

Enolate:

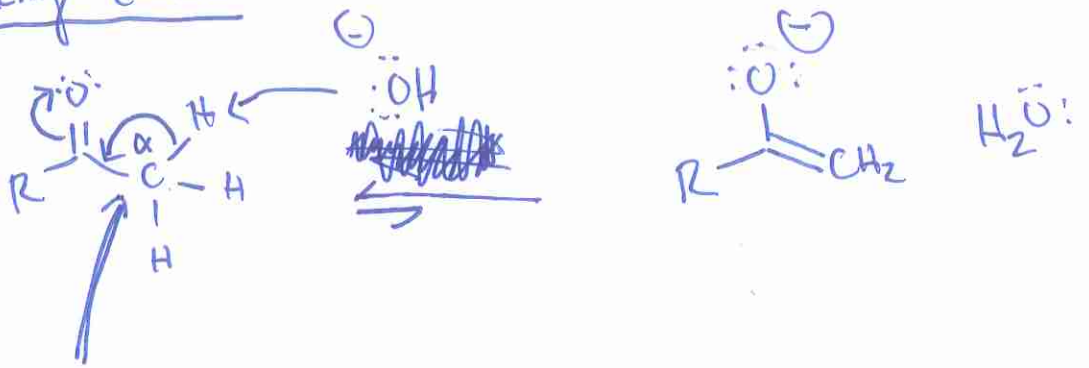


Remember Enol:



↳ Also a nucleophile → recall C=C is a nucleophile

Making Enolates:



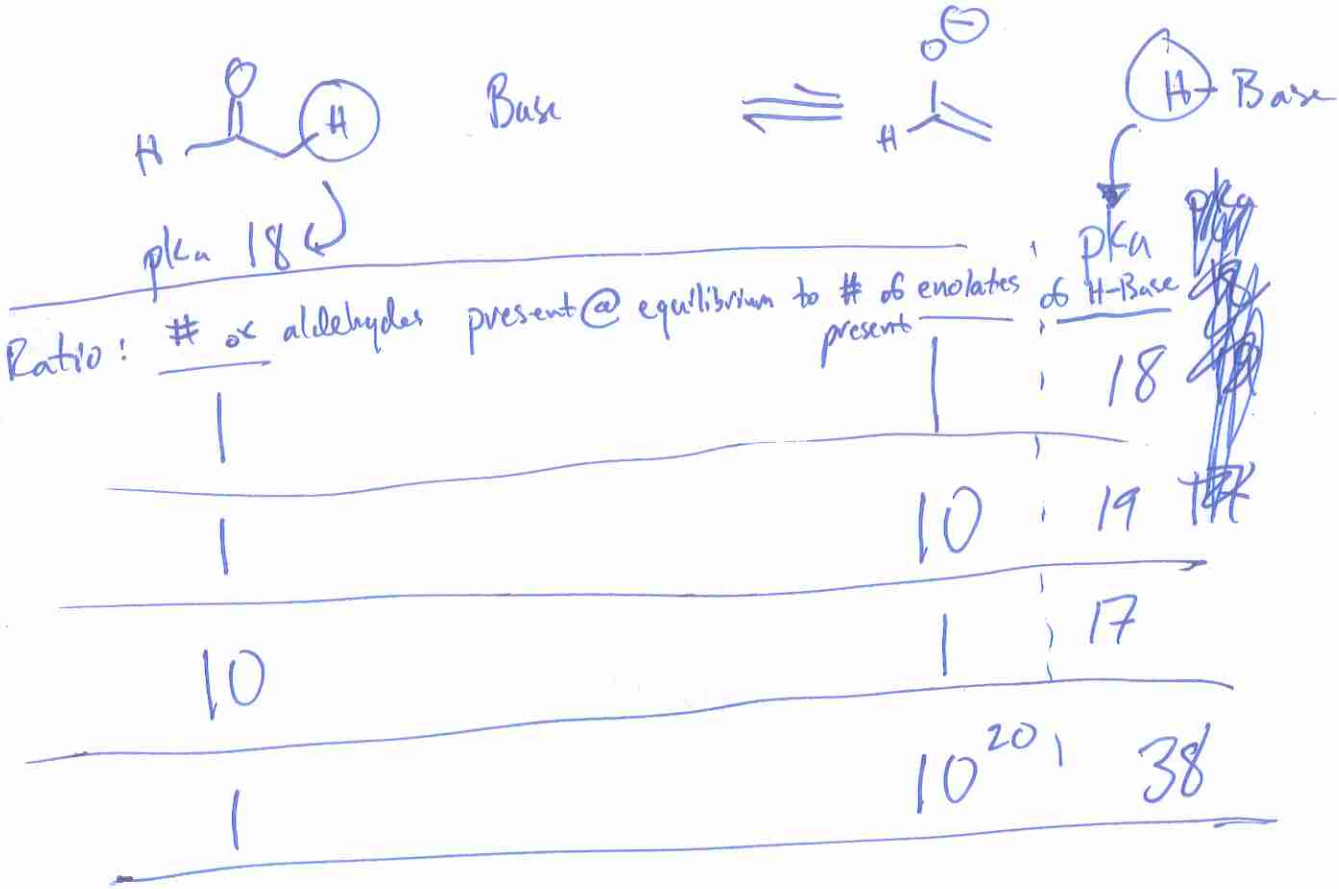
- α-Carbon
- H-atoms attached are called α-Protons

How do Enolates make bonds

$E^{\oplus}$ ≡ Electrophile

Nucleophilic C-atom

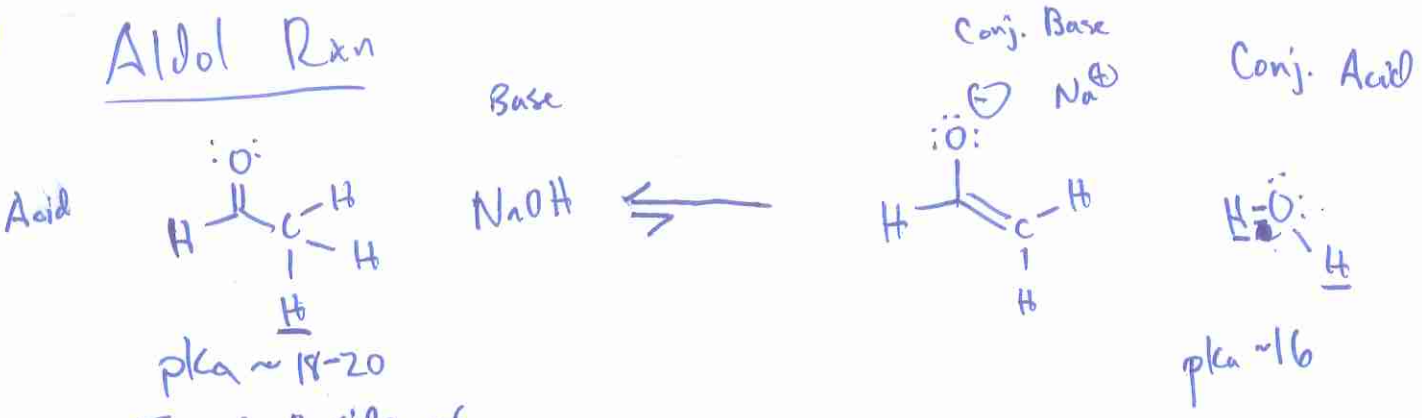
In our class the O-atom is not the ~~exact~~ nucleophilic atom, the C-atom is



- Hold Aldehyde pka constant at 18.
- Than determine populations of Aldehyde vs. Enolate for various Bases whose conjugate acids (H-Base) are shown on the right side

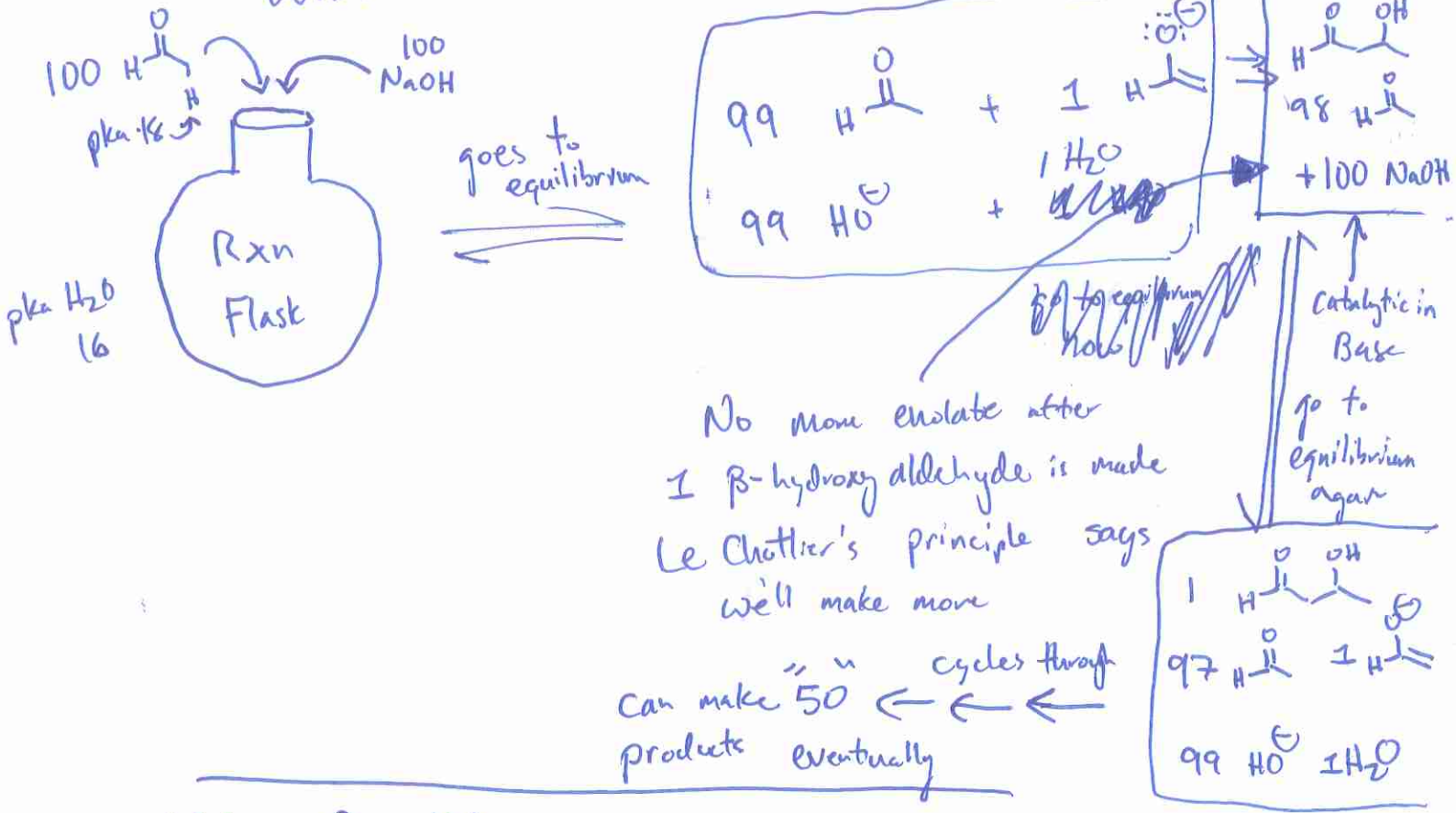
(2)

Aldol Rxn



Favored side of equilibrium → weaker acid favored at Equilibrium (higher pka)

What does this mean:



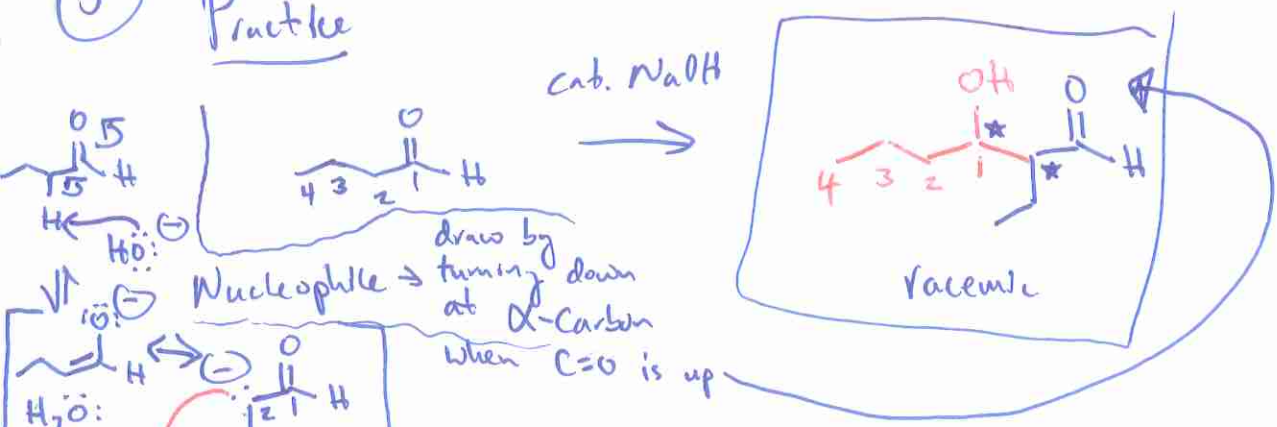
No more enolate after 1 β-hydroxy aldehyde is made

Le Chatlier's principle says we'll make more

Can make 50 " " cycles through products eventually

Notice for aldols you can use $NaOCH_3$, $NaOEt$, and $NaOR$ as a base

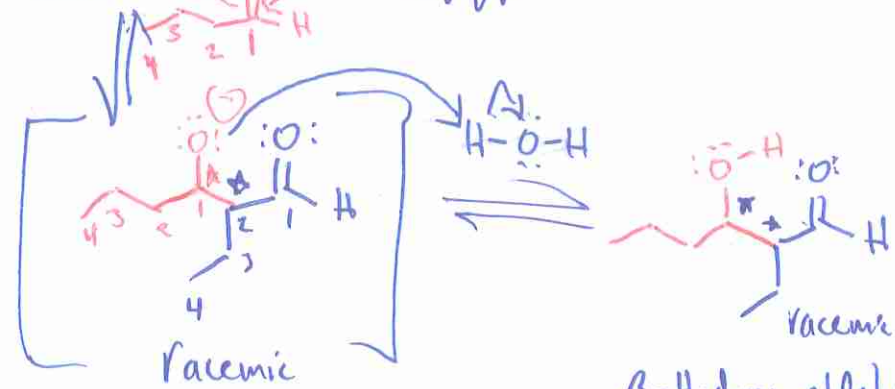
(3) Practice



Nucleophile → draw by turning down at α-Carbon when C=O is up

Make a Bond

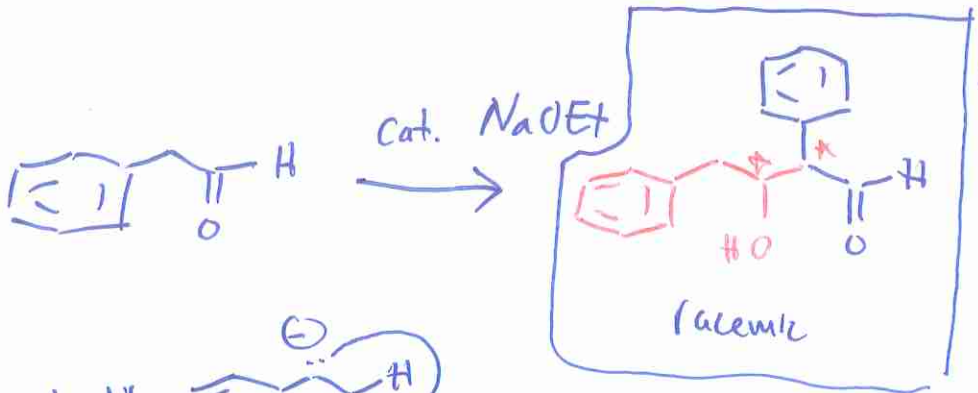
Electrophile

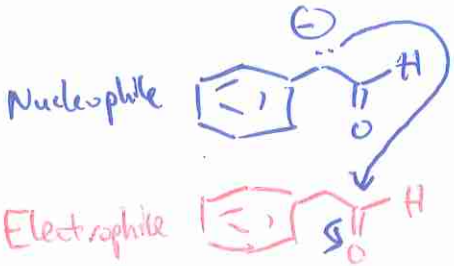


β-Hydroxy aldehyde

Drawing tip:

Nucleophile → turn up at α-Carbon when C=O points down



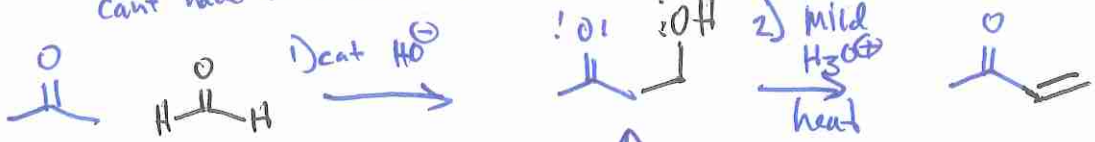


(4)

- Aldol rxn is favored for Aldehydes:

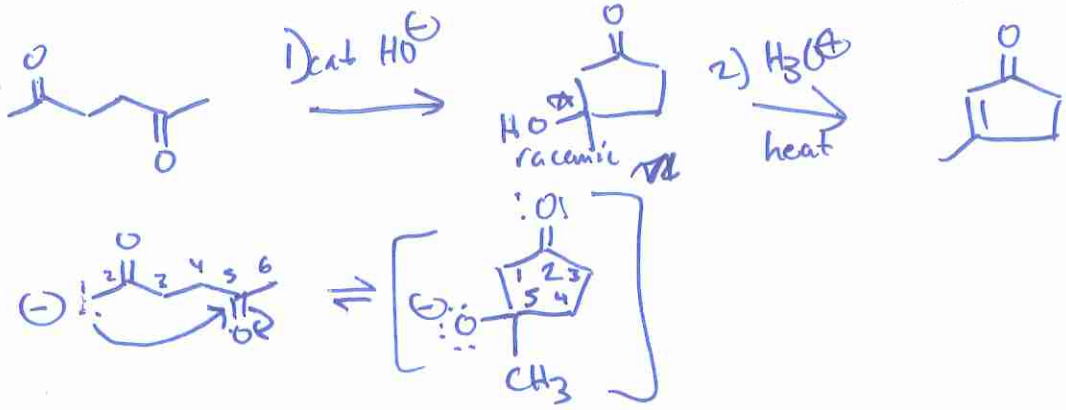
- Not favored for two ketones (exception - below!)

- Crossed Aldol can be favorable
  - 1 aldehyde & 1 ketone
    - can't have α-H atoms → it can't form an enolate



Think 100% yield is possible

- Cyclic Aldols w/ ketones → only way for two ketones to partake in an aldol where a good yield is possible
  (5 or 6 membered ring forms)

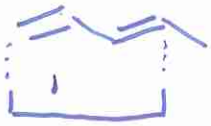


(5) Aldol Dehydration → see Mechanism Packet

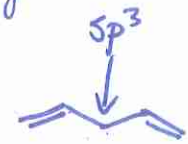
Golden Rule of Chemistry #7

Delocalization of π-$e^{\ominus}$ density over a large volume is stabilizing

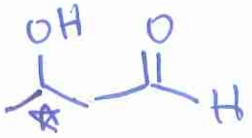
↳ Alternating single-double bonds → called conjugation



- all sp^2 Carbons
- Stable
- conjugated

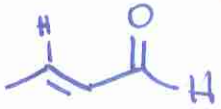


- Not all sp^2 are adjacent
- Not conjugated!



racemic

$H_3O^{\oplus}$
heat →



Trans (E) Product Only forms

E isomer doesn't form due to bad sterics

all sp^2 atoms "touch"

⇓

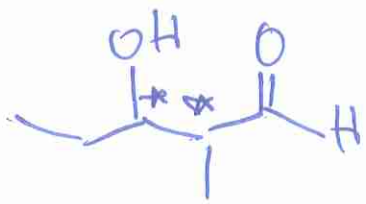
much more Stable than other dehydration product

↓

Not conjugated 

(doesn't form)

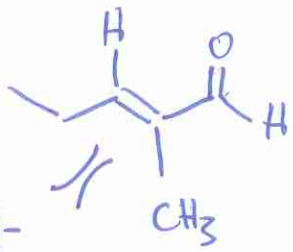
(c)



racemic

$H_3O^{\oplus}$

heat

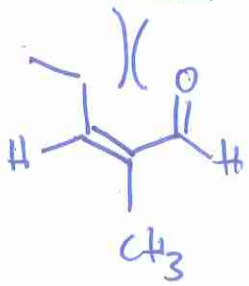


Methyl-carbonyl clash

(E)

vs

ethyl-carbonyl clash



(Z)

⇓

NOT obvious which is more stable → you get a mixture

⇓

Write E, Z mixture for cases where its not obvious

↳ exception is