Alpha-halogenation

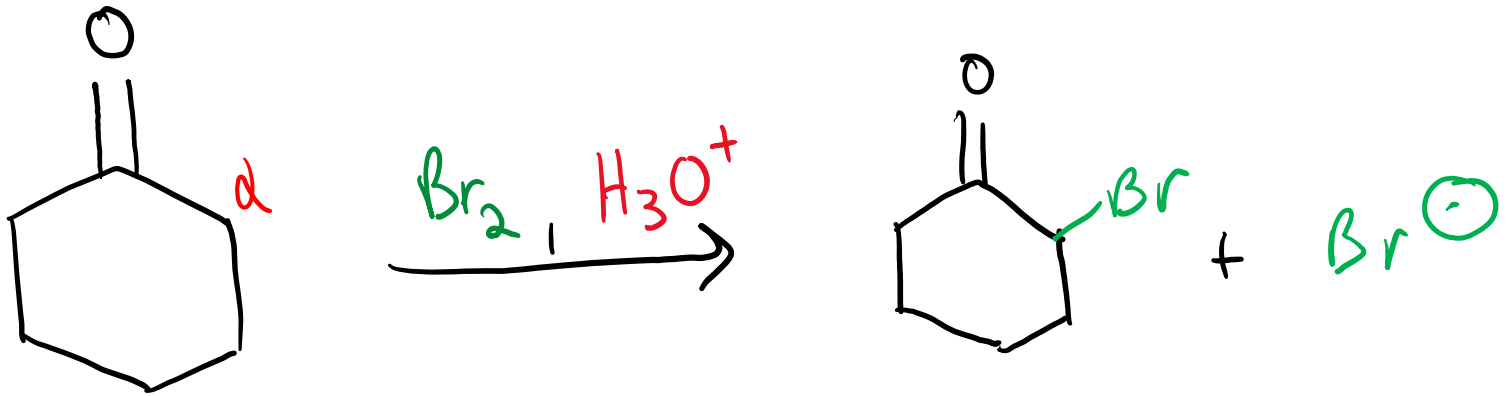
Aldol Reactions

3/17/2022

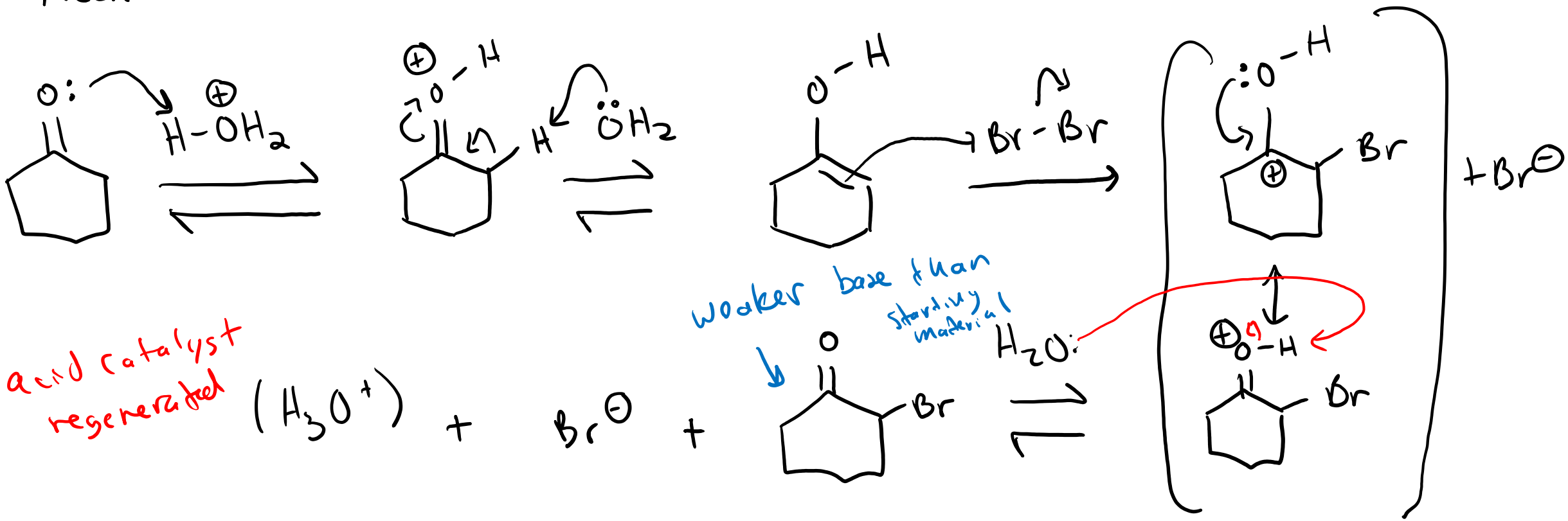
Alpha-halogenation: Acidic Conditions

(21.2)

In acidic conditions:



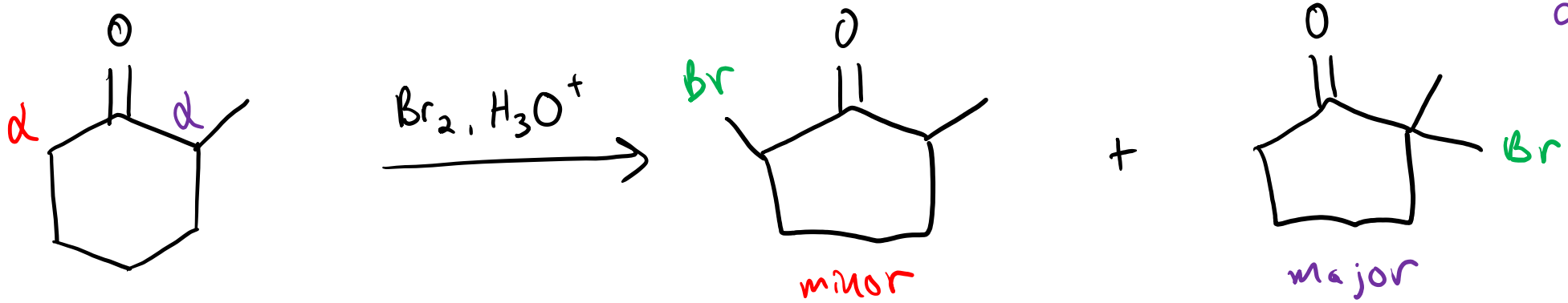
Mechanism:

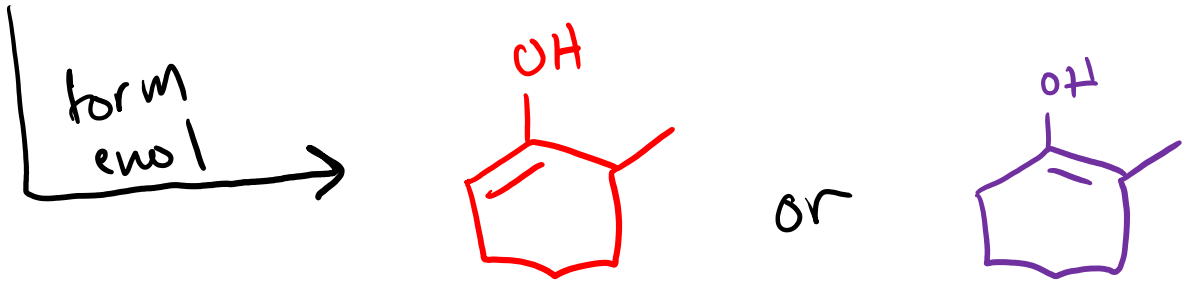


acid catalyst regenerated (H_3O^+) + $Br^\ominus$ +

Alpha-halogenation: Regioselectivity

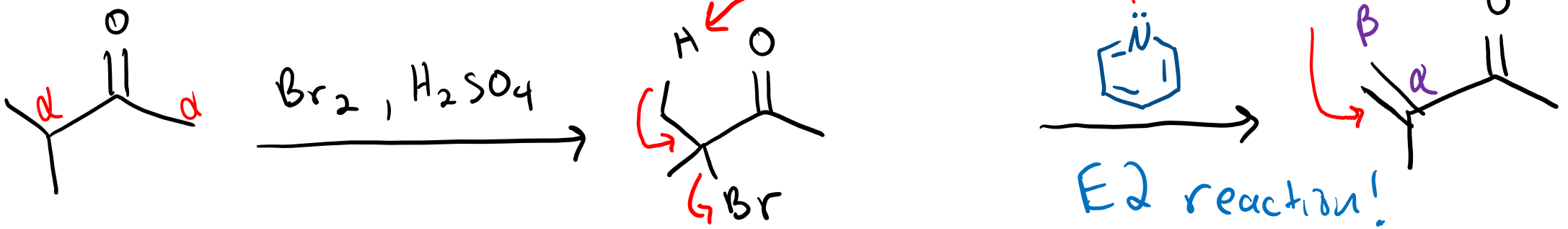
Br goes to more substituted α carbon





more substituted alkene → more stable enol → major product

Halogenation product can react with a base to form α-β unsaturated ketone

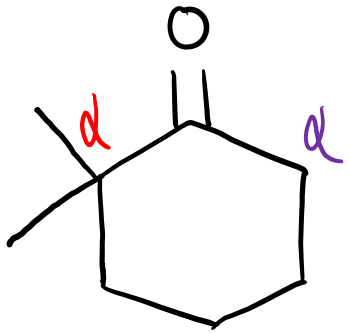


E2 reaction!

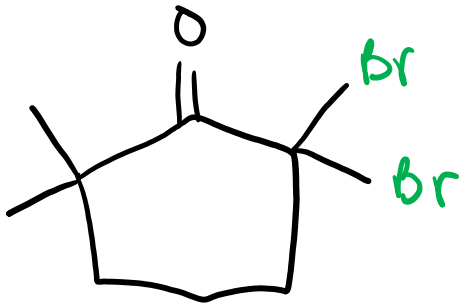
Alpha-halogenation: Basic Conditions

only used when 1 α-carbon has no H's

no α-H's



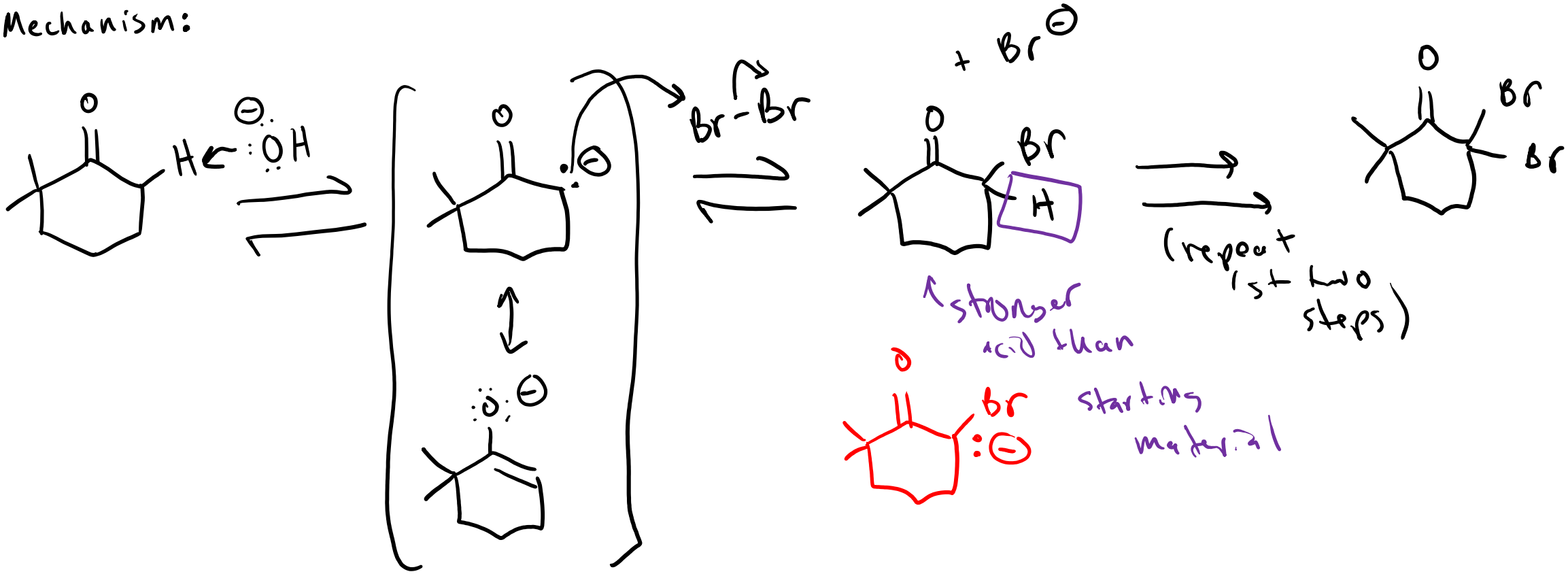
excess Br_2, NaOH



can't stop @ 1 Br in basic conditions!

all α-H's get brominated.

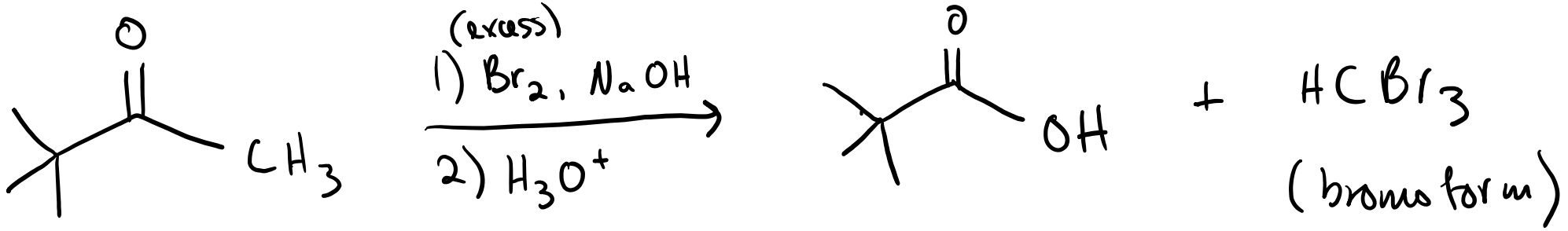
Mechanism:



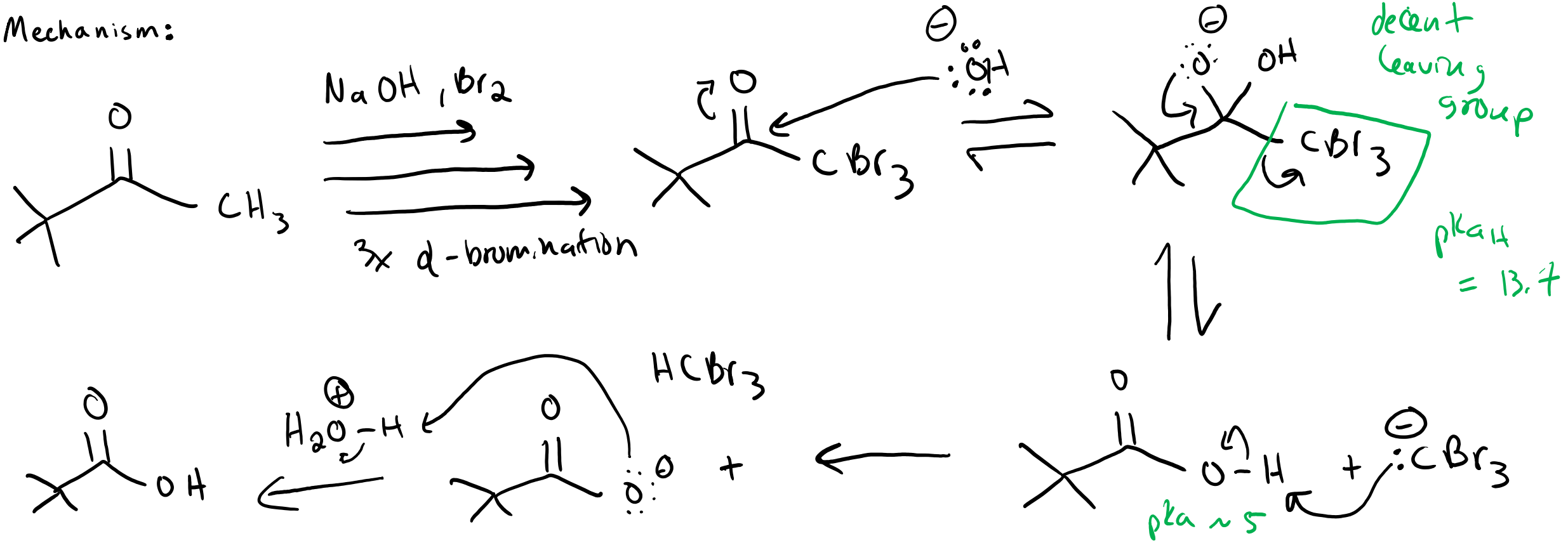
Haloform Reaction

HCX_3 X = halogen

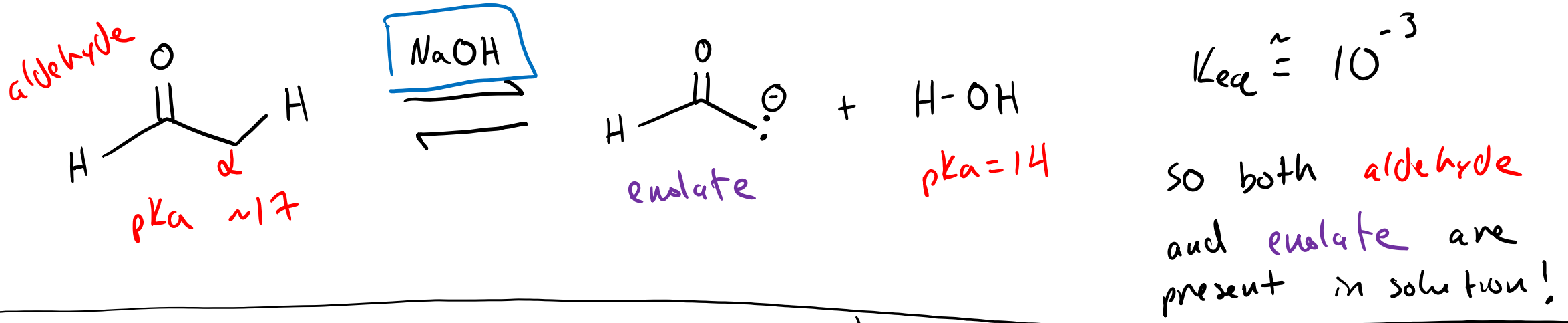
$HCCl_3$: chloroform

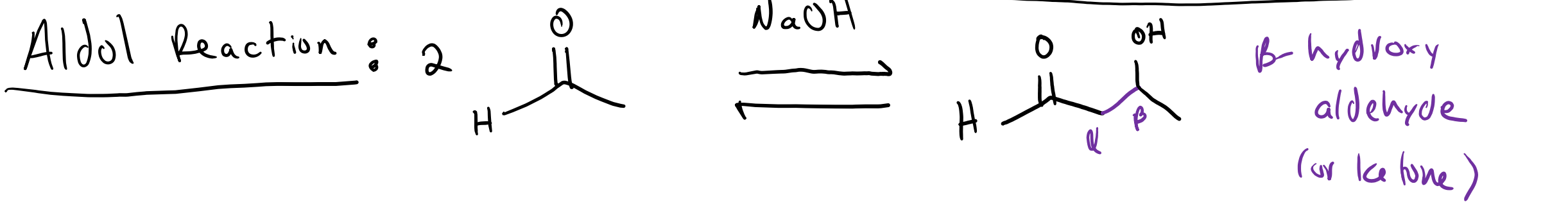


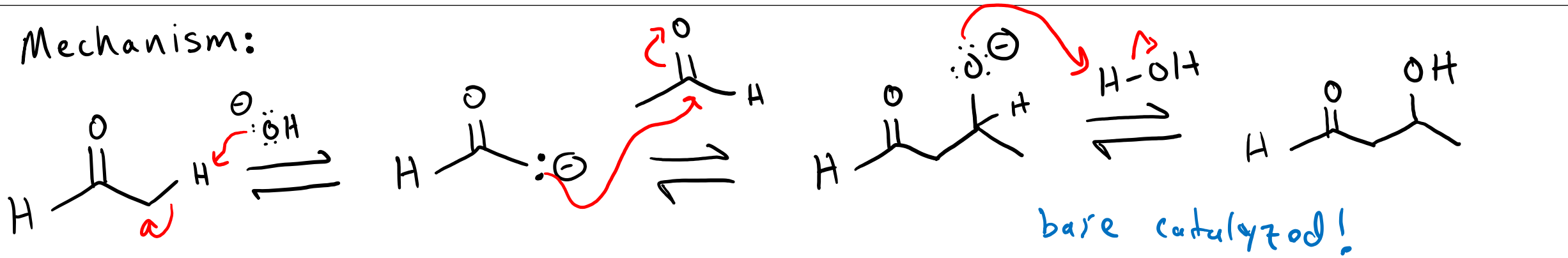
Mechanism:



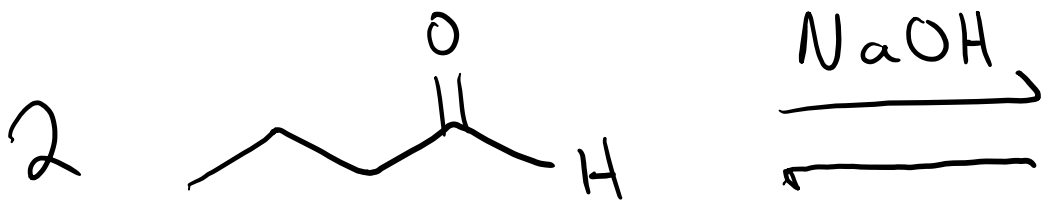
Reversibly Deprotonating Alpha-Carbons & the Aldol Reaction (20.3)

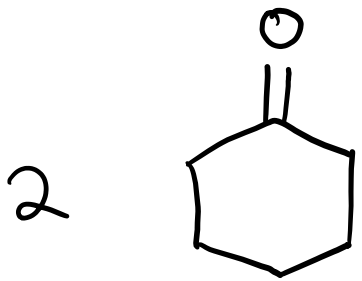






Aldol Reaction: Equilibrium Position & Retro-Aldol

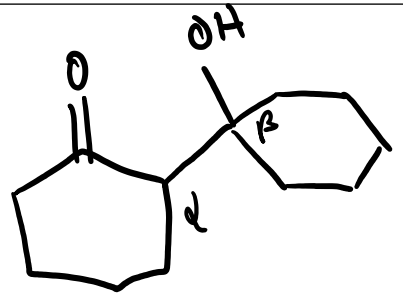




80 %

NaOH

base catalyst cannot affect equilibrium position

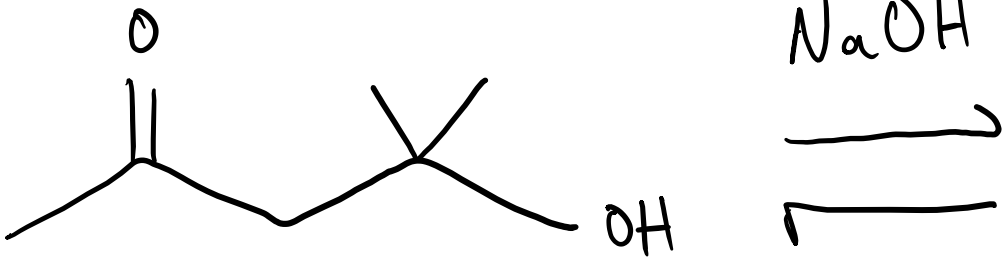


20 %

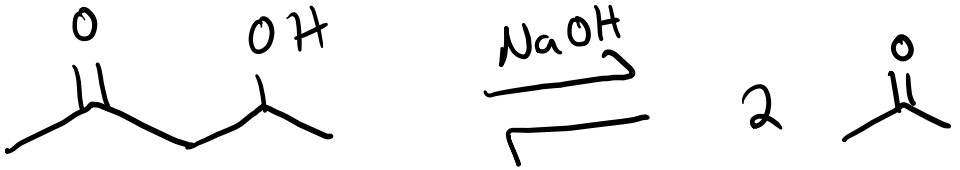
Ketone favors reactant!

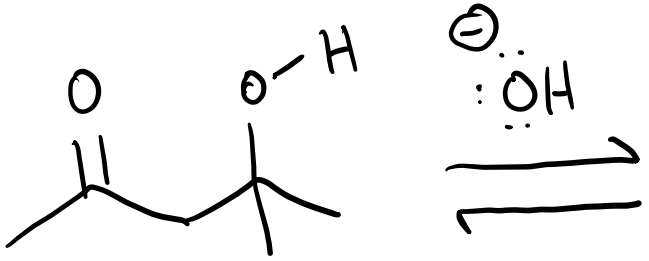
Can use to our advantage:

"Retro-Aldol" rxn.



Retro-Aldol: Mechanism





Examples: