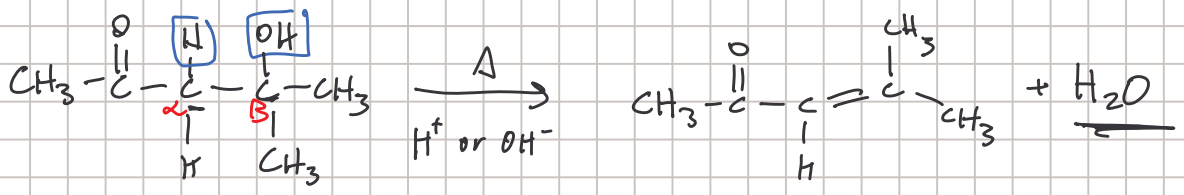
Ch 22

Note Title 4/24/2006

Wittig report due tomorrow

Dehydration of Aldol products



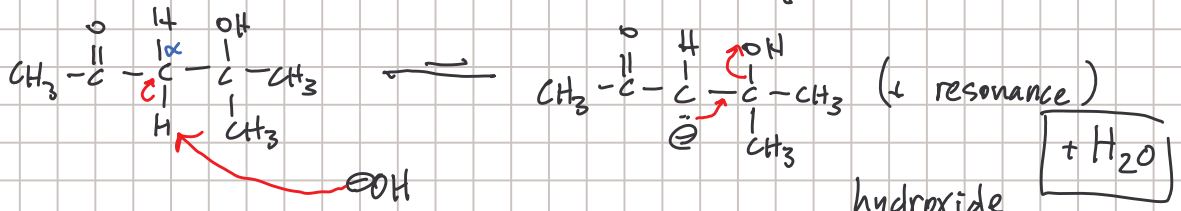
Aldol pdt

α, β-unsaturated ketone
aka enone

acid-cat = normal dehydration mech

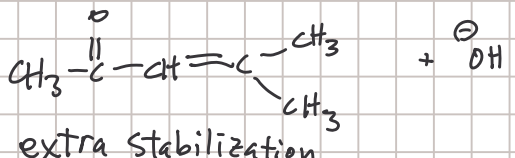
1) protonation of -OH
2) loss of H_2O
3) elimination of adjacent H

base-cat dehydration:



hydroxide leaves!!

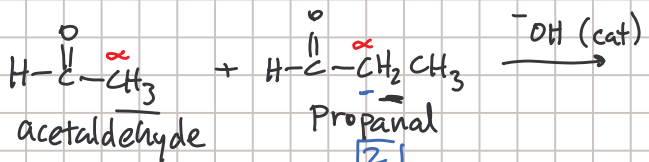
and high temperatures
will boil water away



extra stabilization
b/c of conjugation
makes up for bad leaving group

Crossed Aldol condensations: Condensing 2 different compounds

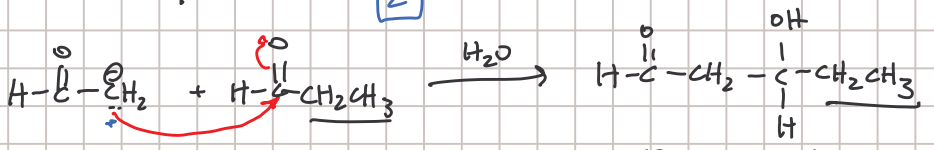
Can be very messy



1 acetaldehyde

Propanal 2

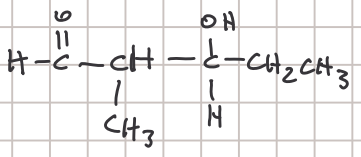
4 different products



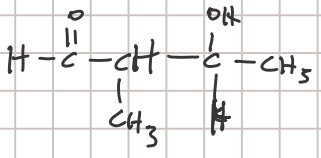
1 + 2

1 + 1

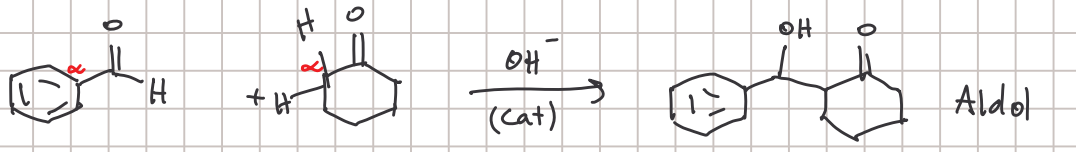
to combat this, choose reactants so only 1 has α Hydrogens.



2 + 2



2 + 1



Aldol

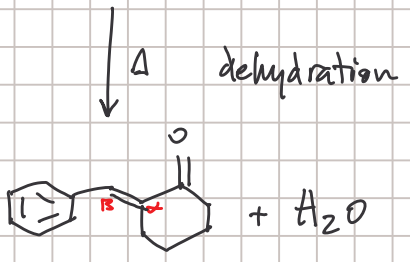
benzaldehyde

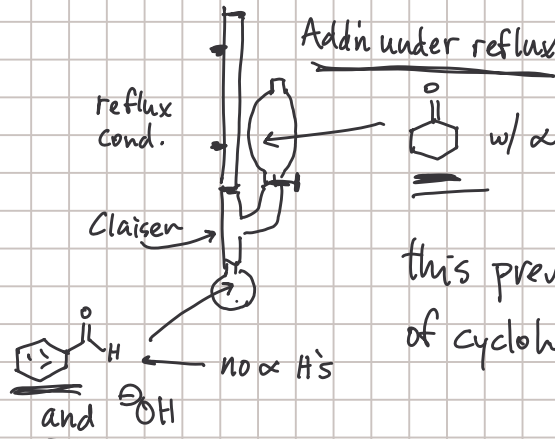
no α H's

cyclohexanone

4 equivalent α H's

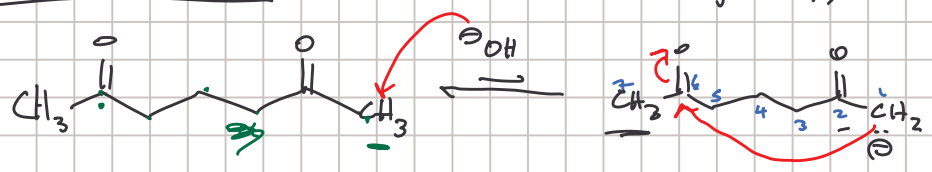
forms enolate

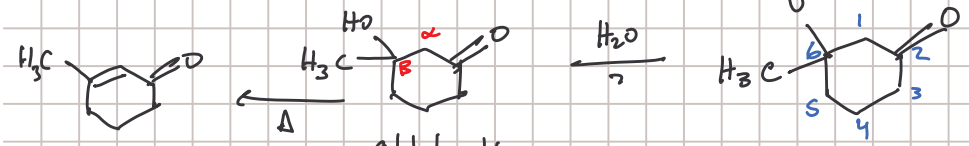




this prevents self-condensation of cyclohexanone

Aldol cyclizations (5 or 6-membered rings only)





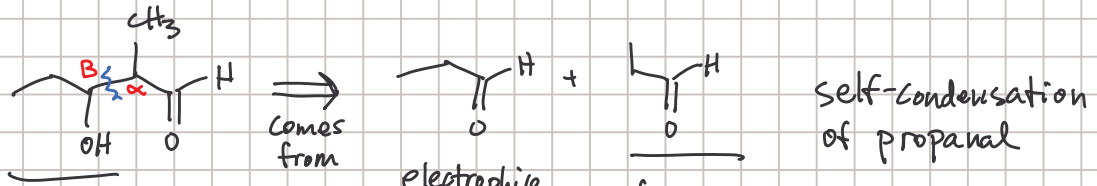
+ H_2O

enone

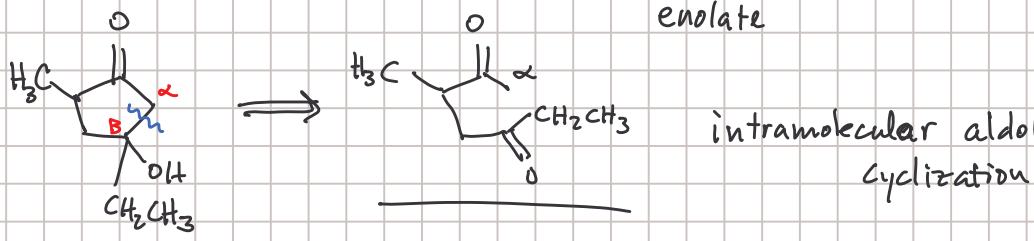
aldol pdt

Planning aldol syntheses

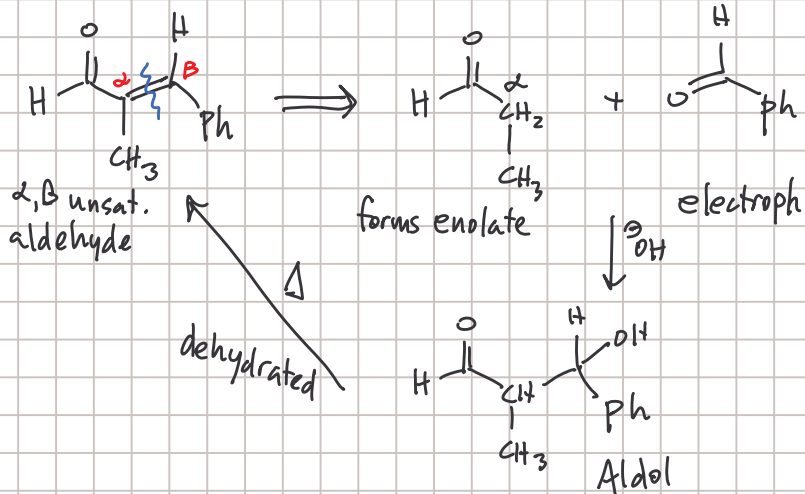
retrosynthetically break α, β bond



self-condensation of propanal



intramolecular aldol cyclization



α,β unsat. aldehyde

dehydrated

forms enolate

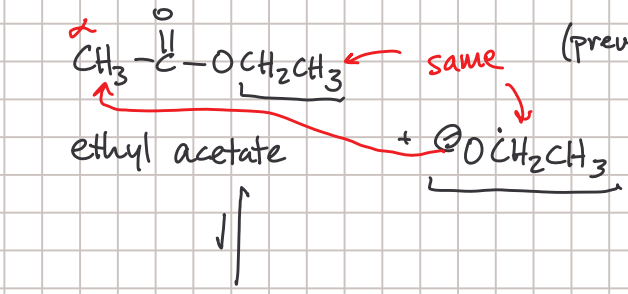
electrophile

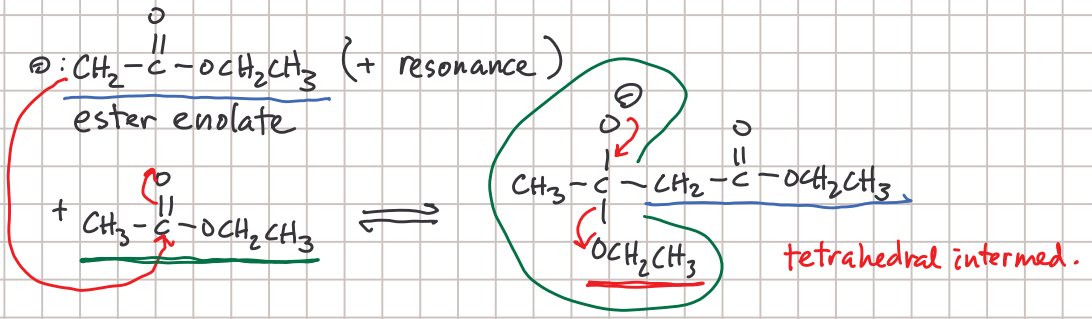
Aldol

Claisen condensation

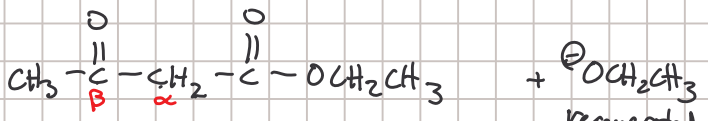
enolate + ester (as electrophile)

(prevents hydrolysis or ester exchange)



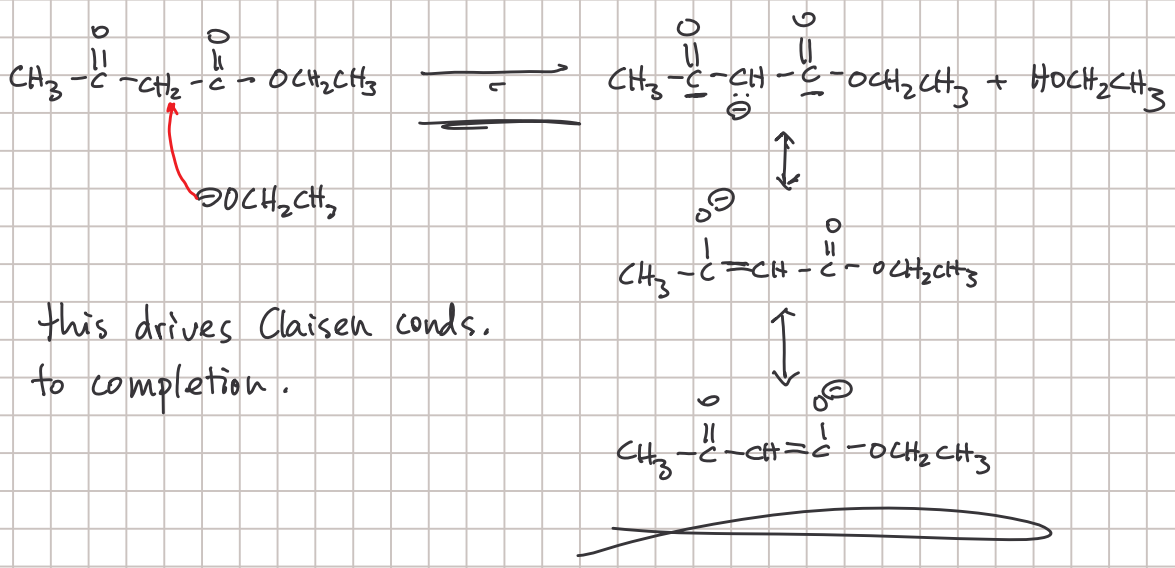


add'n/elim mechanism



β-ketoester

β-ketoesters have very acidic α H's (extra resonance stabilization)



this drives Claisen conds. to completion.