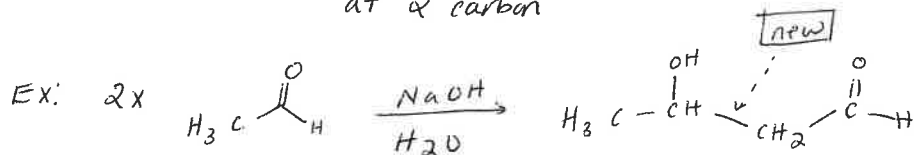


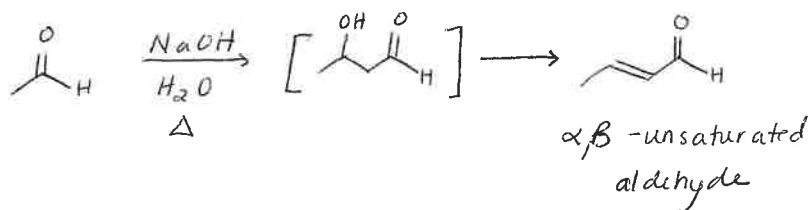
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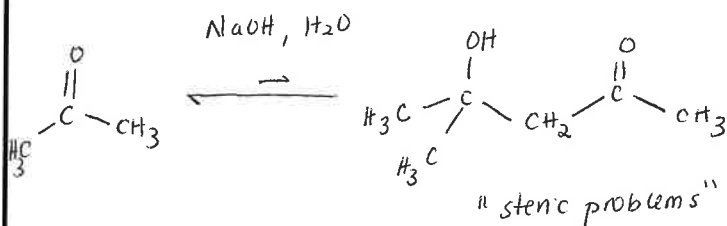
Recall: Aldol Rxn: combine electrophilicity at carbonyl carbon with nucleophilicity at α carbon



Harsher conditions can cause a further rxn - dehydration:



Note: all steps are reversible, for ketones, equilibrium disfavors the aldol product

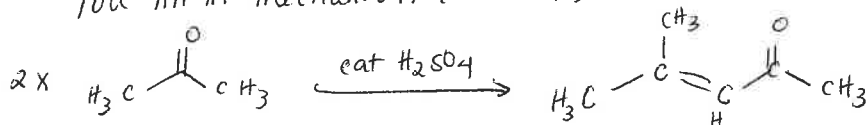


Aldol rxns can occur under acidic conditions...

Now, nucleophile = enol

electrophile = protonated carbonyl

You fill in mechanism (see text)



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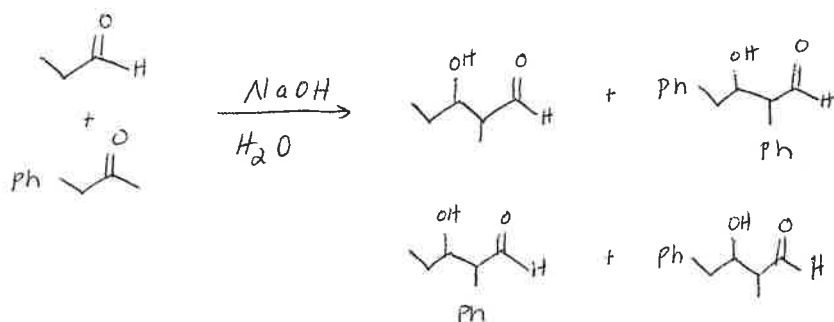
Aldol under acidic conditions

- Note: 1) Dehydration very common under acidic conditions
 2) thus, even ketone aldol rxns proceeds

Crossed aldol?

(distinct reactants as nucleophile + electrophile?)

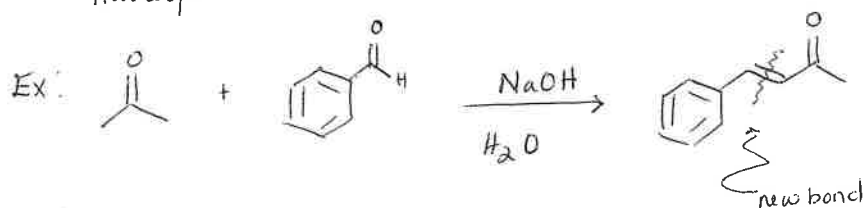
often, crossed aldol gives product mixture (not useful from preparative perspective)



(not even considering all of the stereoisomers!)

Special cases - product control in crossed aldol:

ketone + aldehyde lacking α H's
 ↓
 nucleophile electrophile



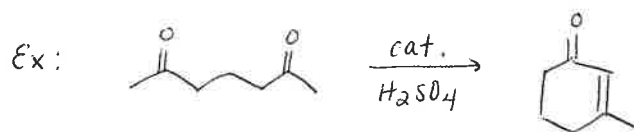
- Note: 1) aldehyde cannot serve as nucleophile because no α H's
 2) ketone self-rxn is unfavorable!

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Another special case - intramolecular aldol (ring formation)

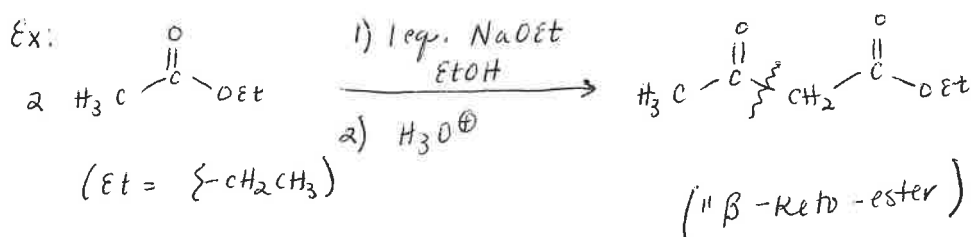
Esp. 5- and 6- membered rings.



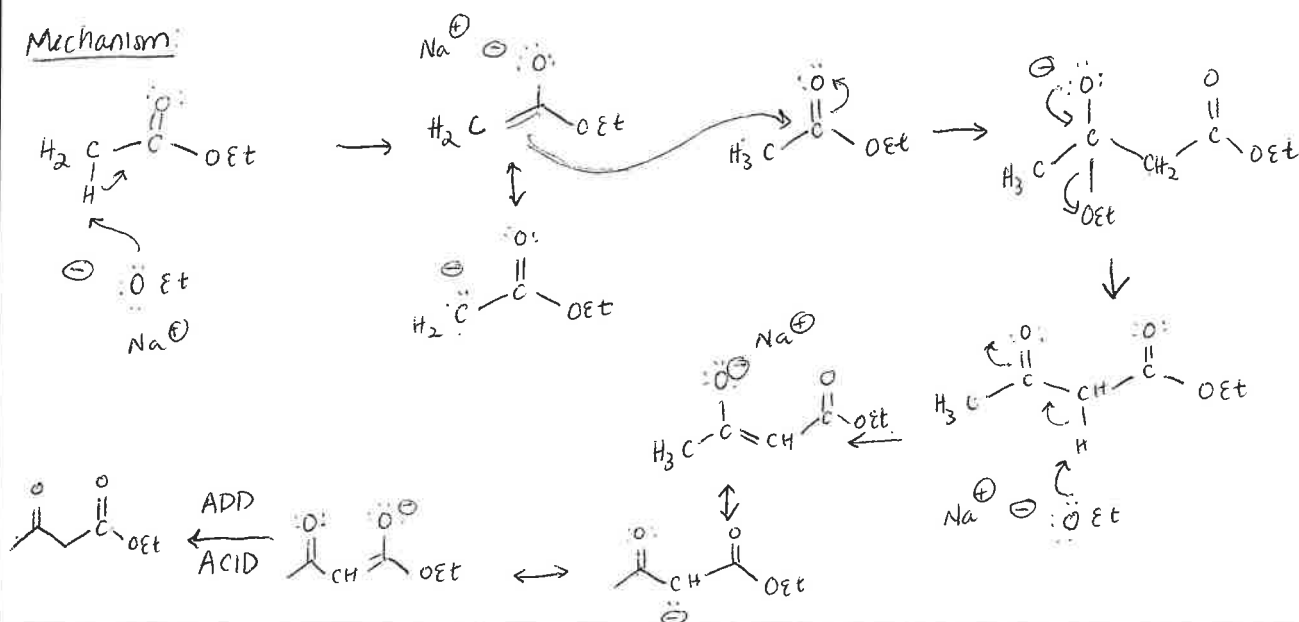
Section § 22.4 D - on synthesis

Claisen Condensation

Rxns of esters; analogies to aldol condensation.



Mechanism:



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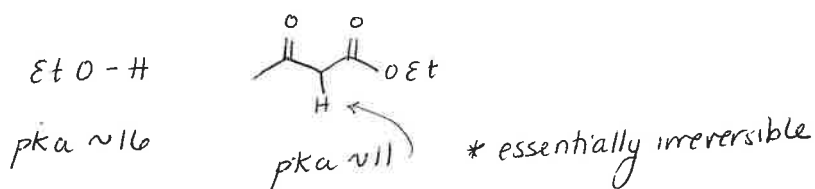
Note relationship:



Note: until the deprotonation of β -keto ester, all steps are reversible

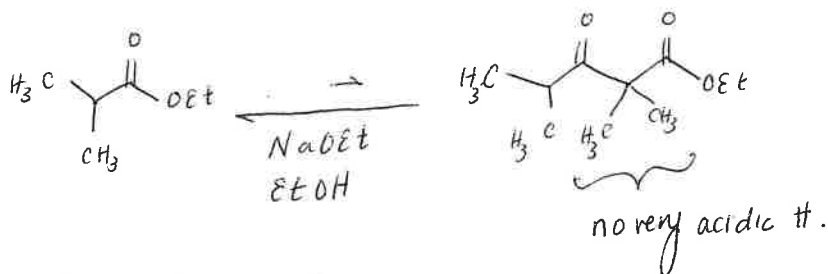
- starting esters are favored
- final deprotonation drives process

Consider:



Note: Rxn consumes one equiv. of NaOEt

- Also for cases in which β -keto ester lacks "very acidic H's", no Claisen condensation



You fill in reverse mechanism:

Appropriate diesters can form nngs:

