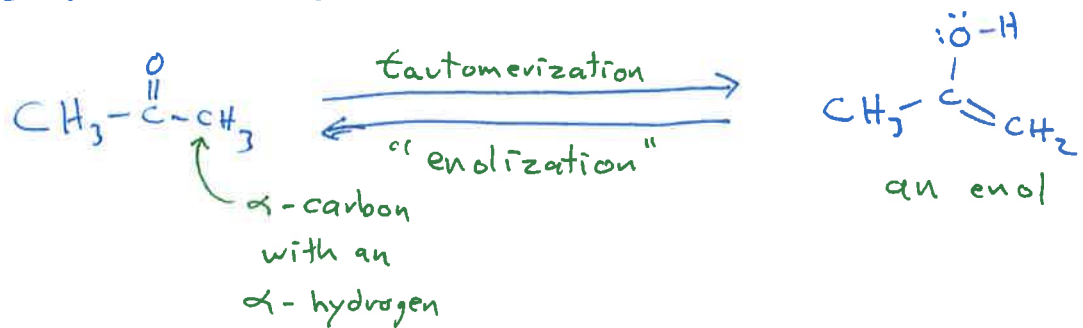
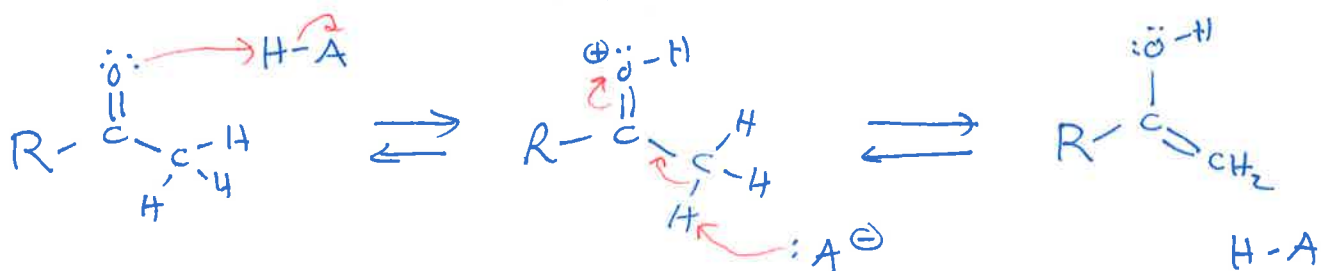


Enols and Enolates

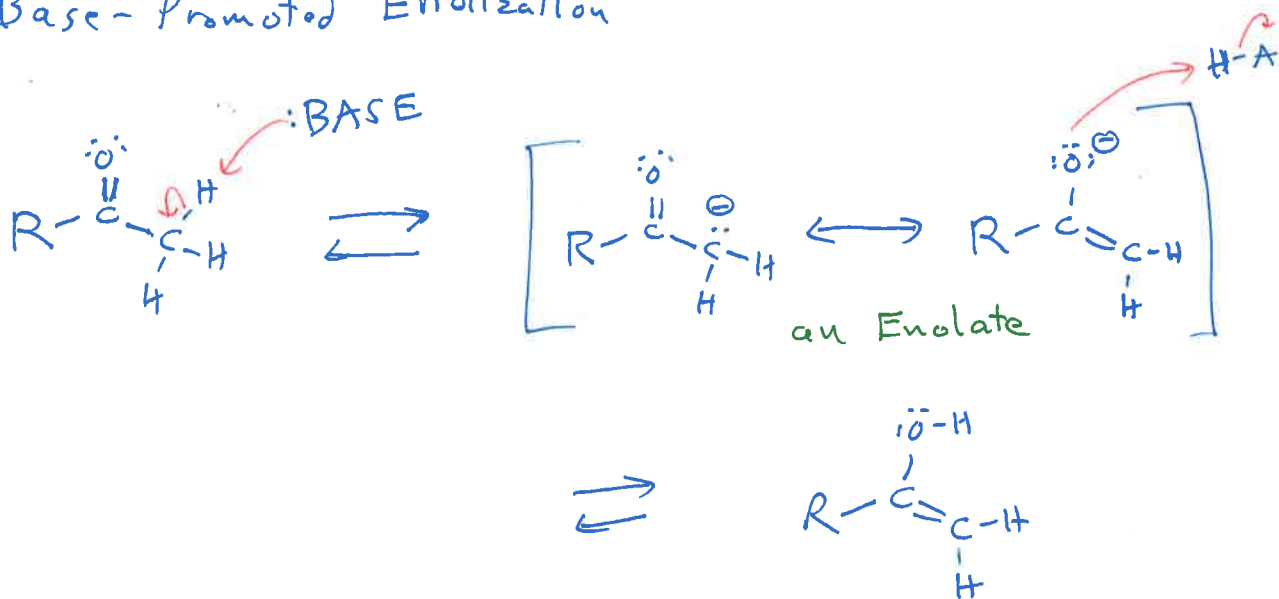


- enolization requires a carbonyl with an α -hydrogen
- most enols are unstable
 - carbonyl tautomer is preferred

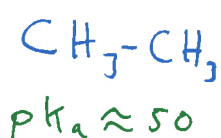
Acid-Promoted Enolization



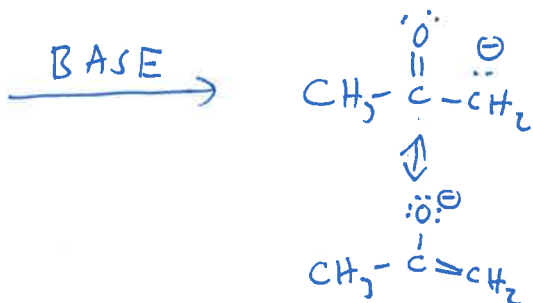
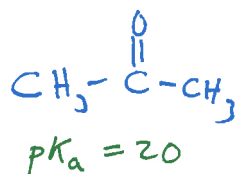
Base-Promoted Enolization



Acidities of Carbon Acids

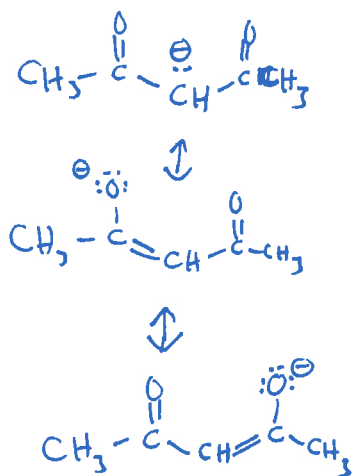
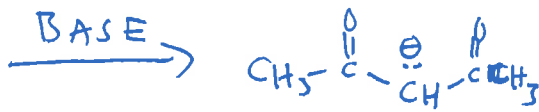
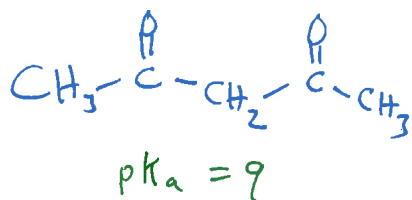


- No common bases are strong enough



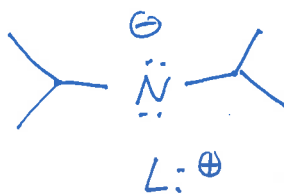
- BASE = $\ominus\text{OR}$ about 0.001% enolization

- BASE = LDA about 100% enolization



- Most good bases ($\ominus\text{OR}$, etc.) ~ 100% enolization

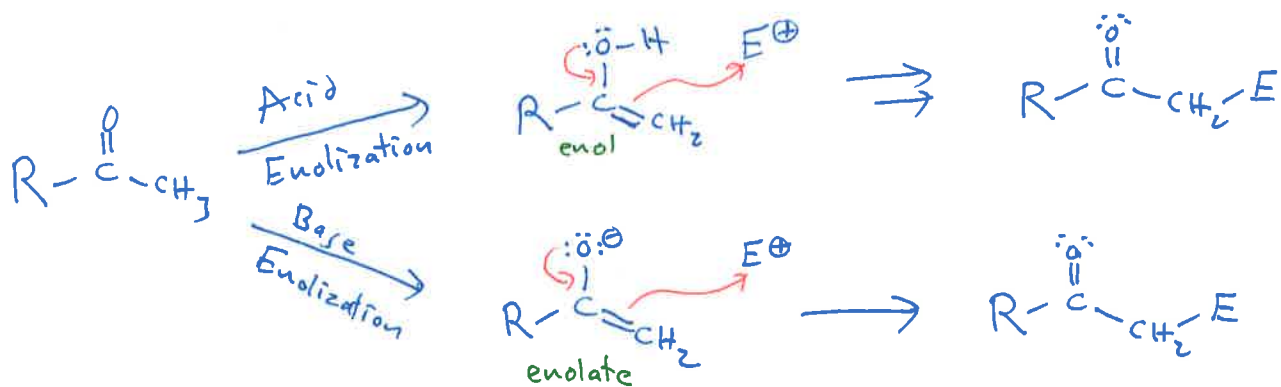
LDA



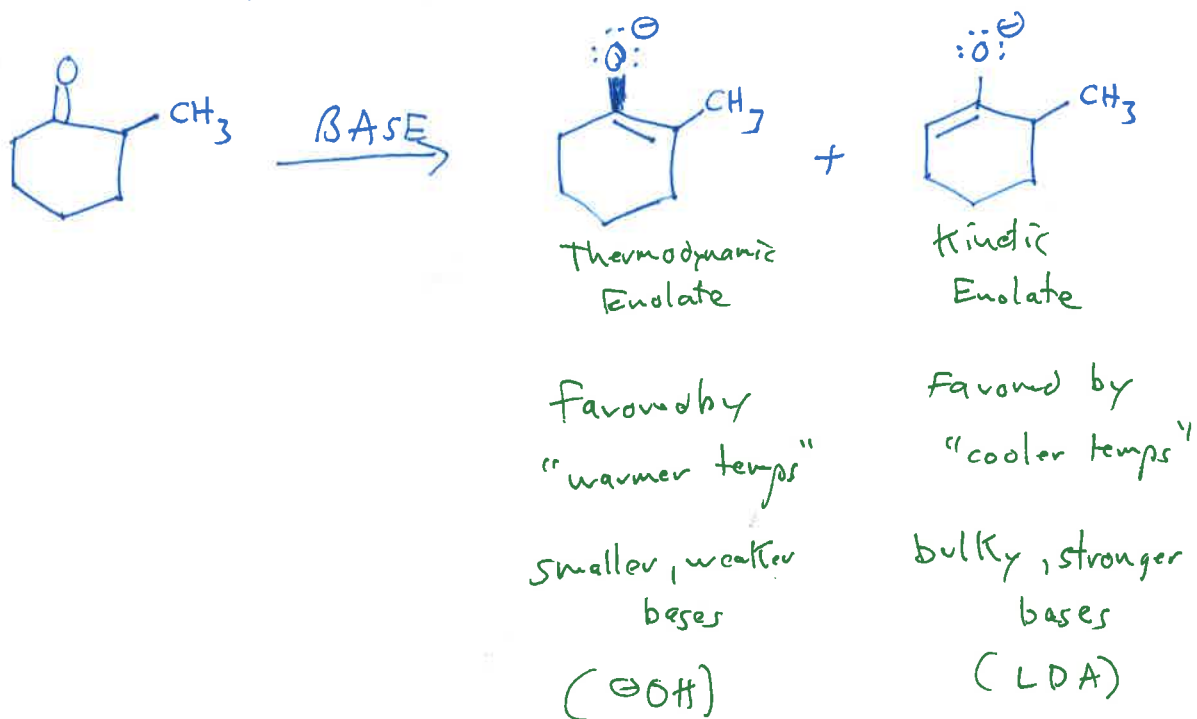
L^+

lithium diisopropylamide

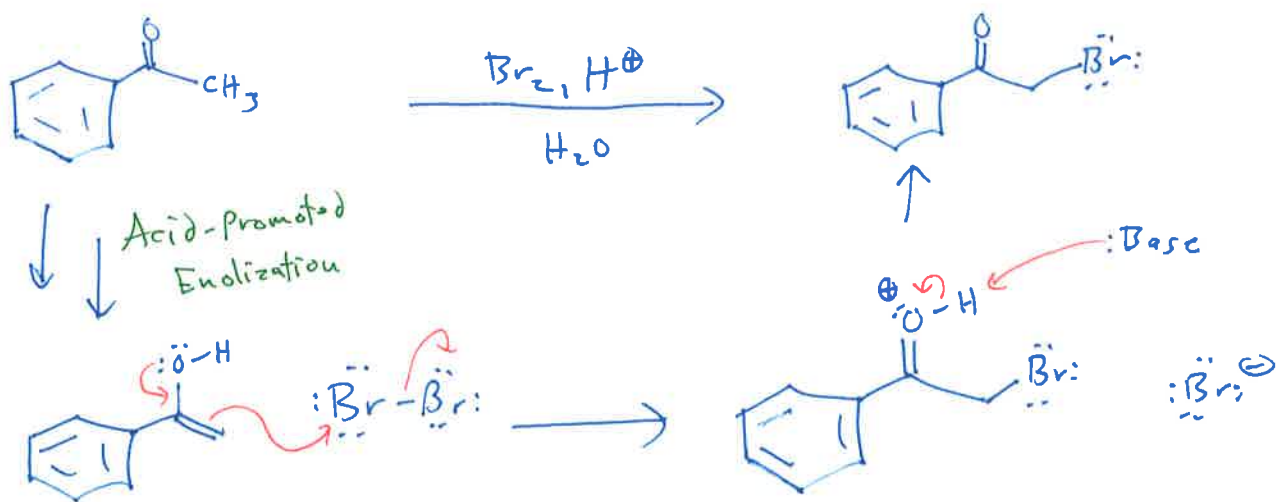
Reactivity of Enols and Enolates



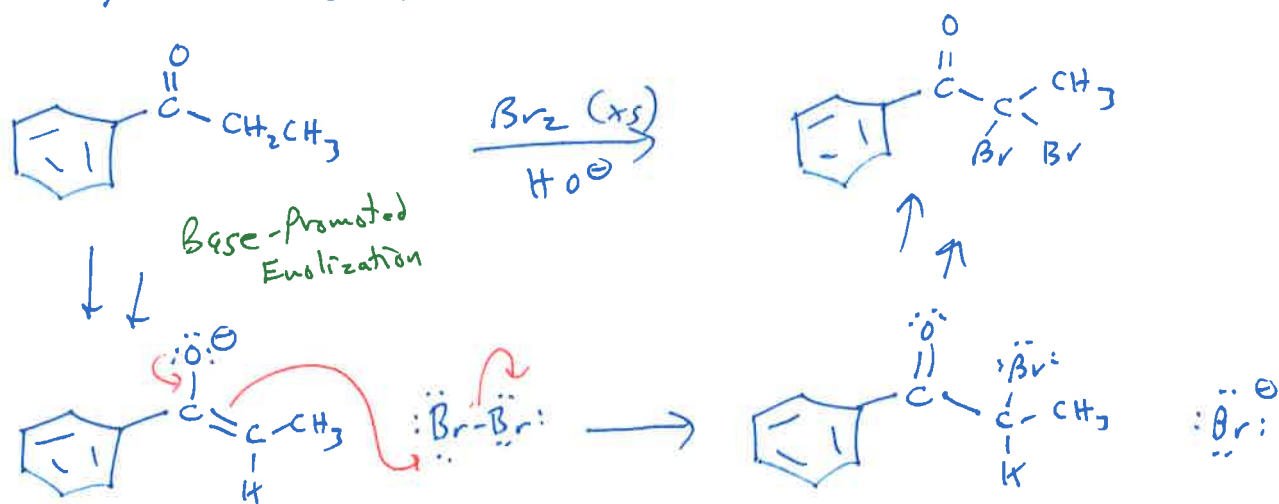
Regioselectivity of enolization



α -Halogenation (Acid-Promoted)



α -Halogenation (Base-Promoted)

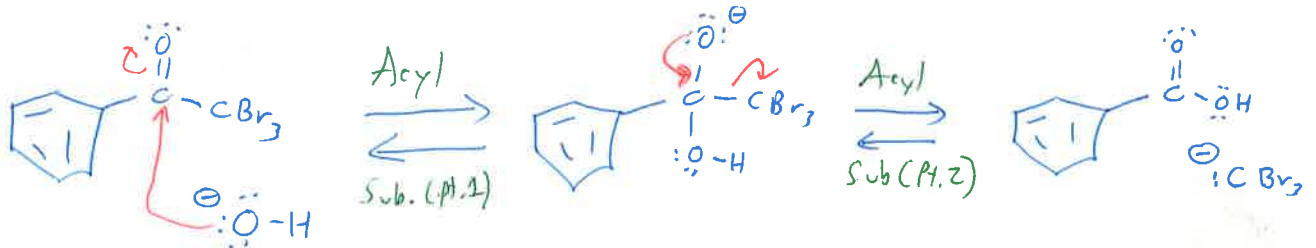


- typically replaces all α -hydrogens
- "exhaustive" halogenation

Haloform Reaction

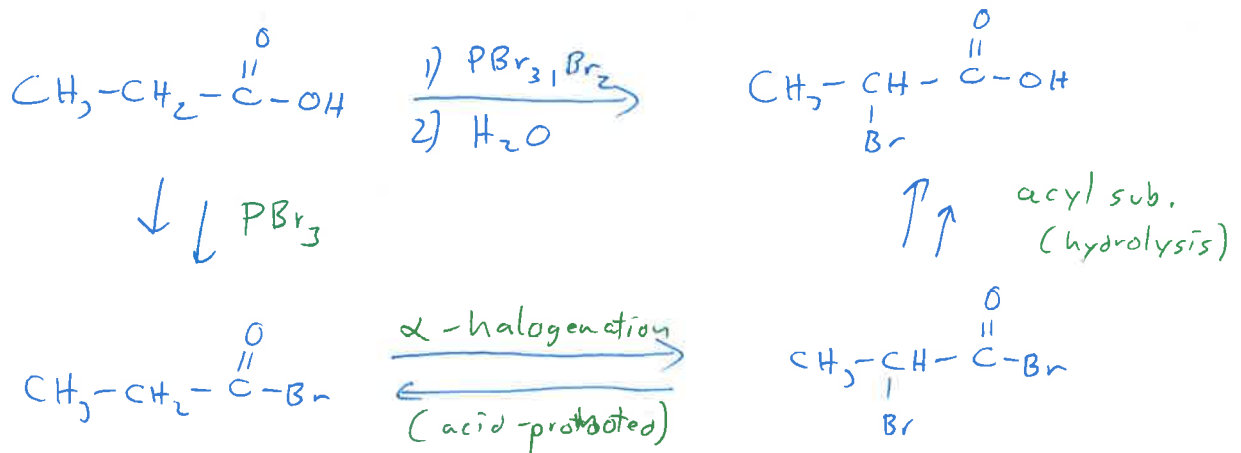


Base-promoted
α-halogenation

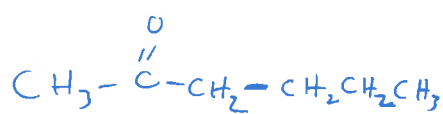
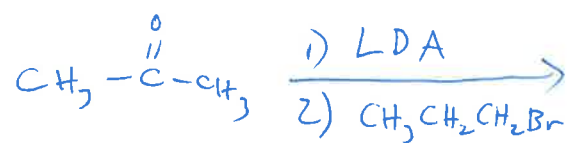


- only occurs on methyl ketones

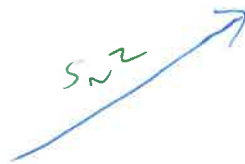
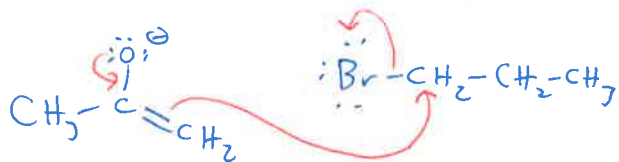
Hell-Volhard-Zelinski Reaction



Alkylation

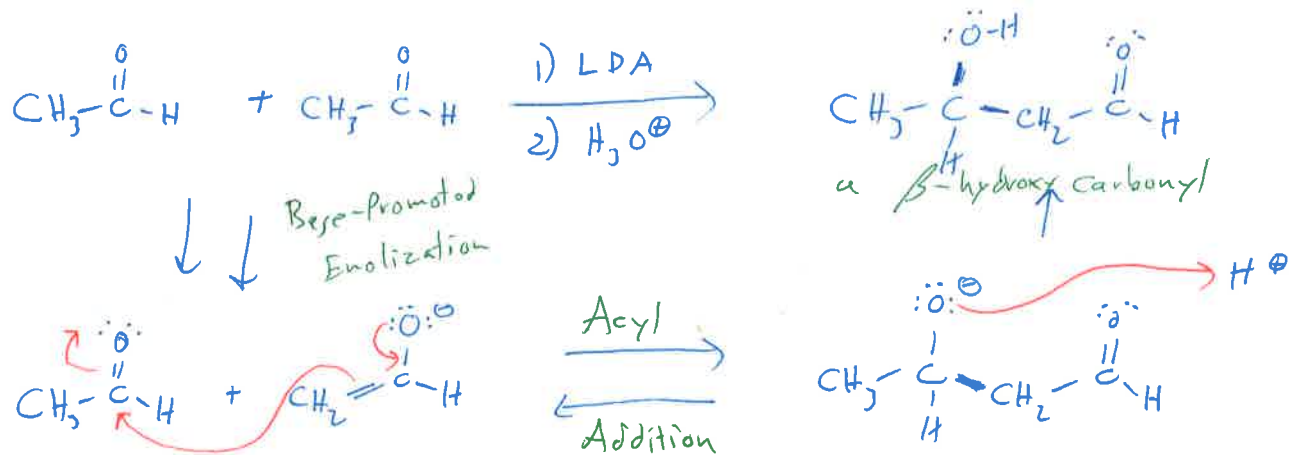


↓ ↓ Base-promoted
Enolization

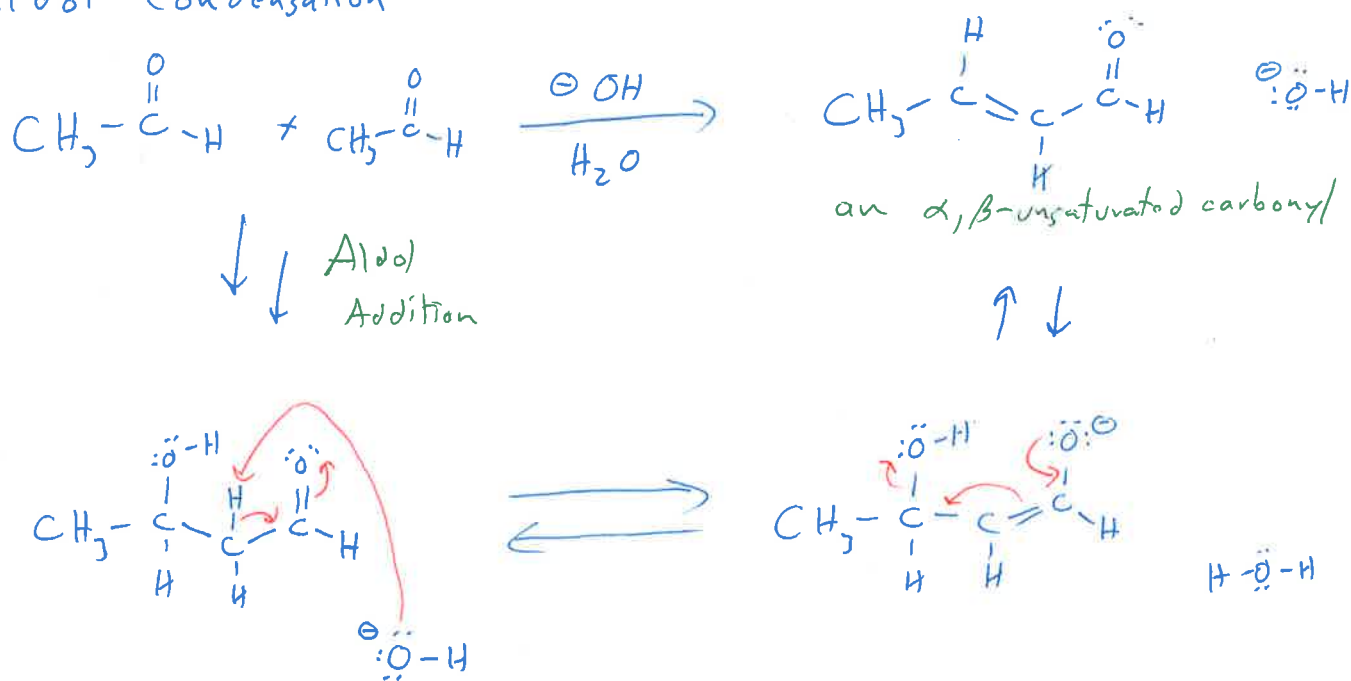


— must use "Kinetic" base

Aldol Addition



Aldol Condensation



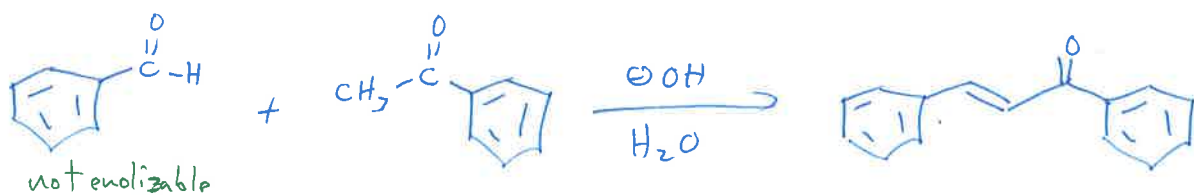
- typically preferred by "Thermodynamic" conditions
- also preferred when π -systems can be tied together

Mixed Aldol

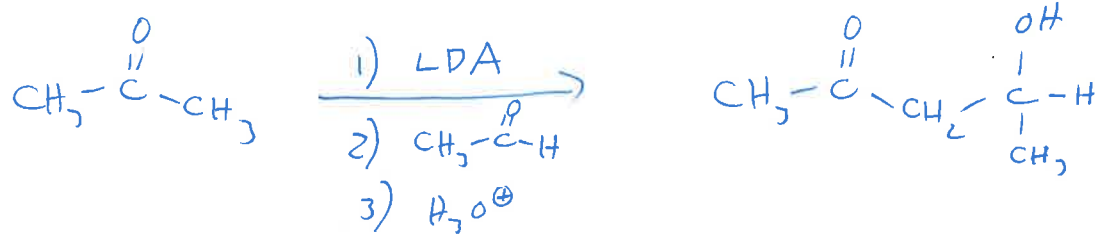


- both carbonyls are enolizable

— Solutions...

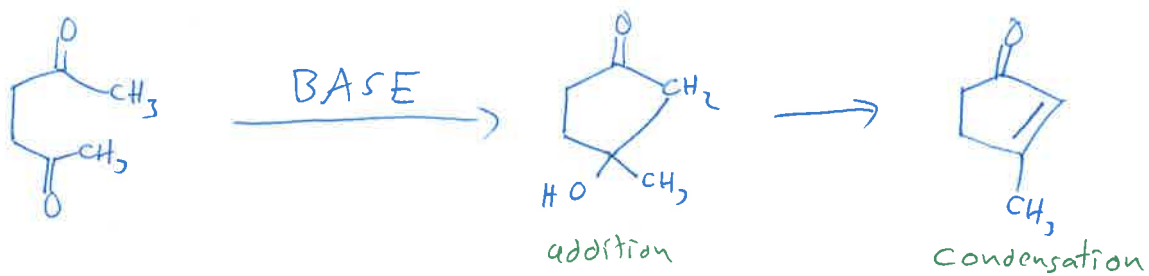


- use only one enolizable carbonyl



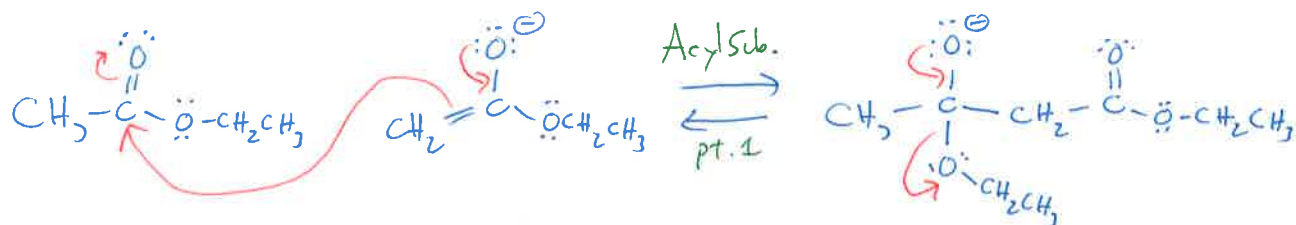
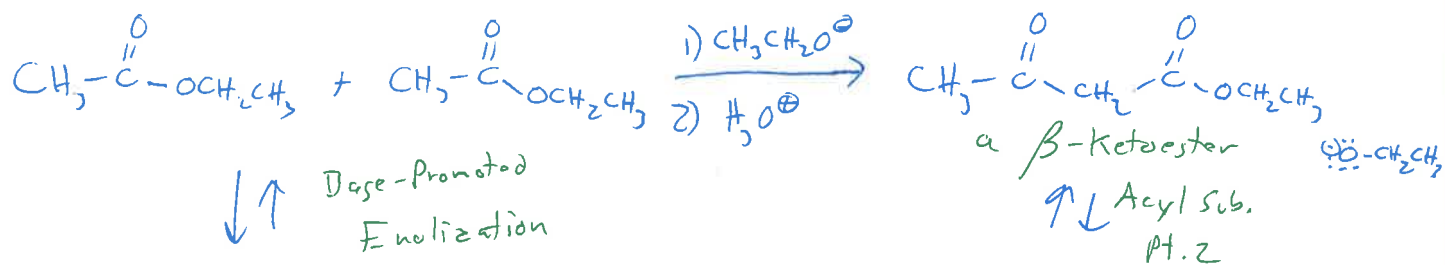
- pretreat one carbonyl with a kinetic base (LDA)

Intramolecular Aldol



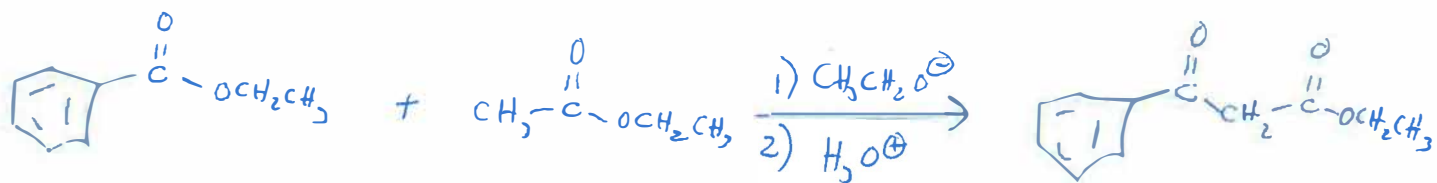
- formation of 5 or 6 atom rings is preferred

Claisen Condensation



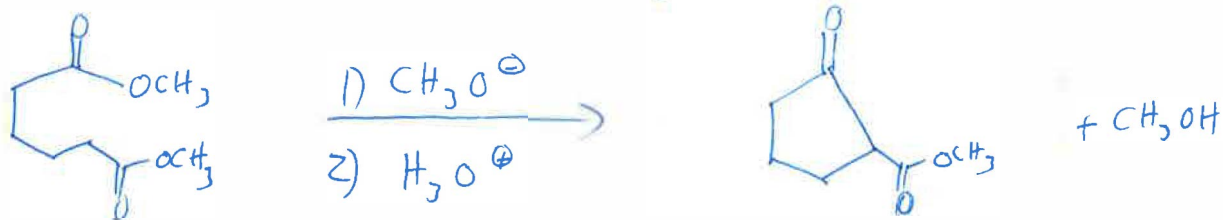
— match the base to the L.G.

Mixed Claisen

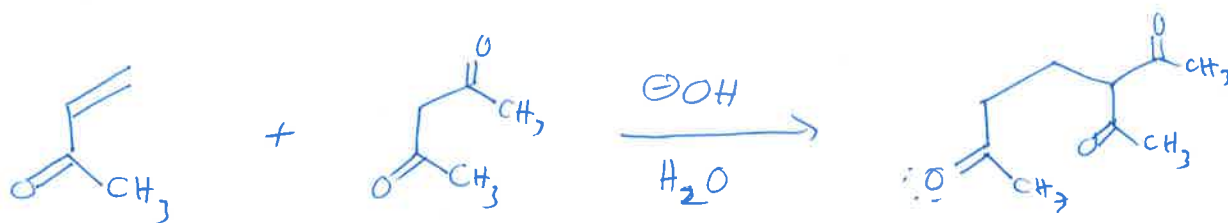


- Use only one enolizable ester
- or
- pretreat one ester with LDA

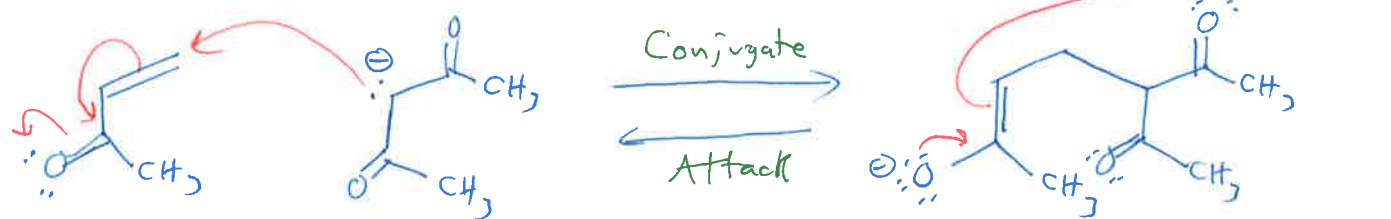
Intramolecular Claisen (Dieckmann Cyclization)



Michael Addition

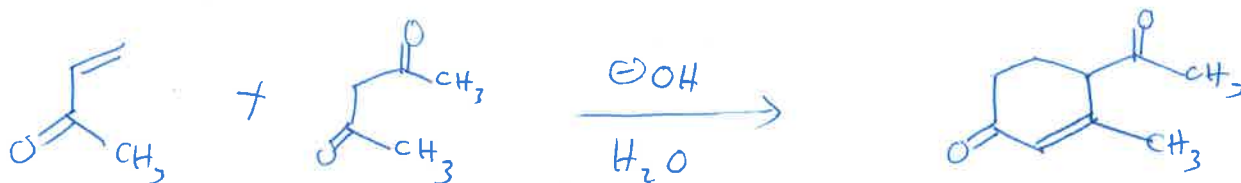


Base-promoted
Enolization

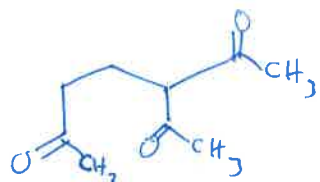


- conjugate attack to an α, β -unsaturated carbonyl with an enolate nucleophile
- gives a 1,5-dicarbonyl

Robinson Annulation



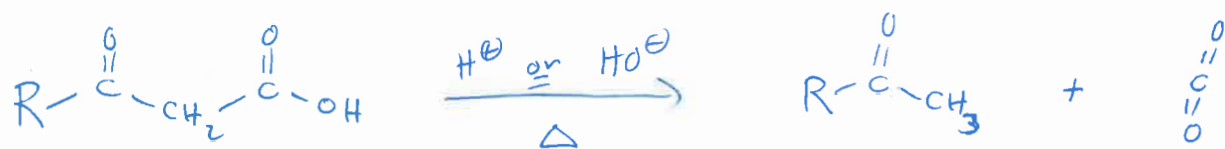
Michael Addition
Intramolecular Aldol Condensation



endize here
(other side of the α,β -unsaturated carbonyl)

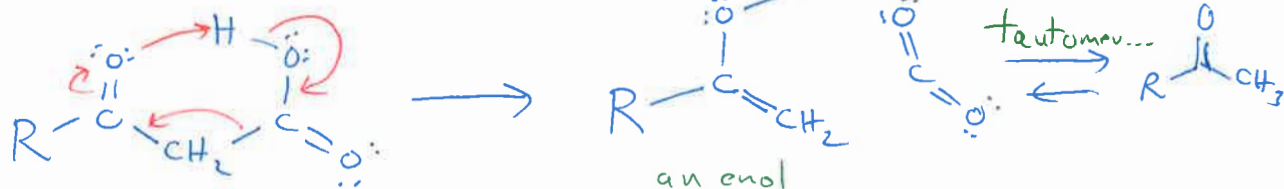
- makes cyclohexenones

Decarboxylation

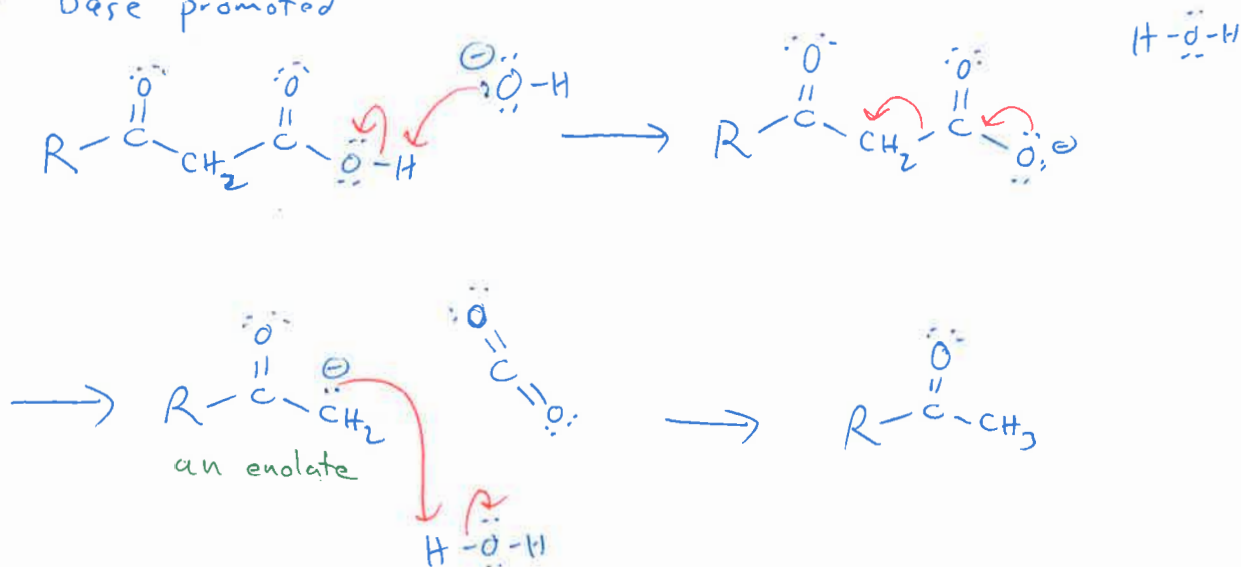


— requires a carbonyl β -to the carboxylic acid

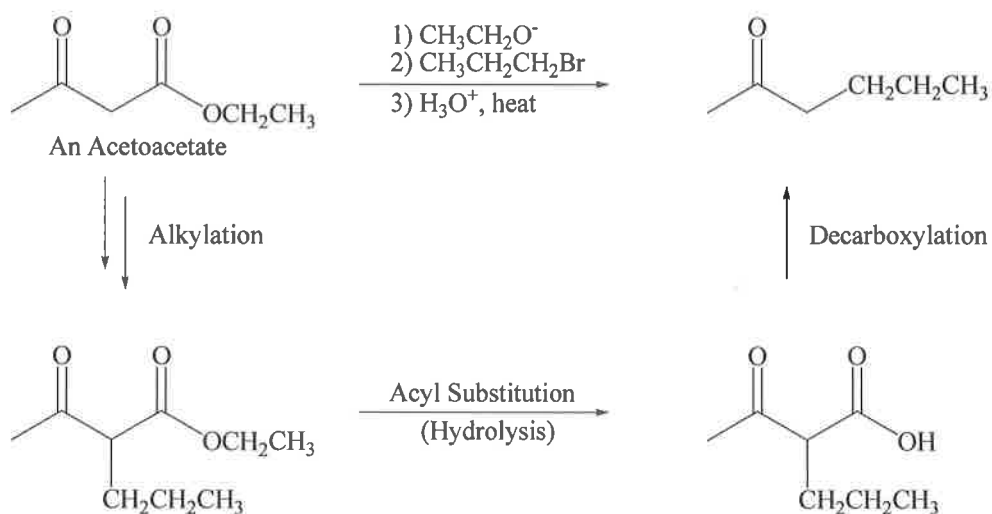
— acid promoted



— base promoted

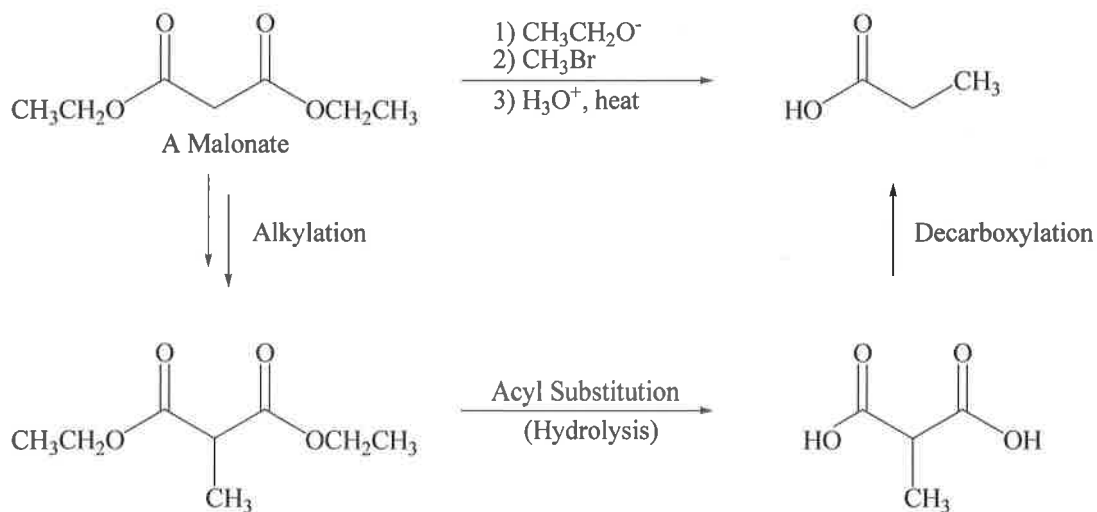


Acetoacetate Synthesis



- Makes ketones

Malonic Ester Synthesis



- Makes Carboxylic acids