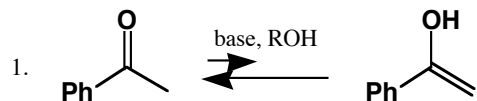


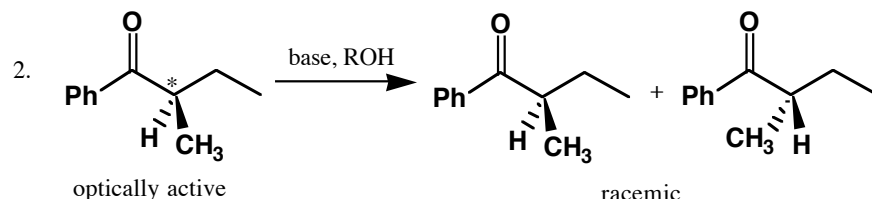
PROTON as ELECTROPHILE



-Base-catalyzed keto-enol equilibrium

-know mech (either direction)

-know impact of substituents on enol concentration



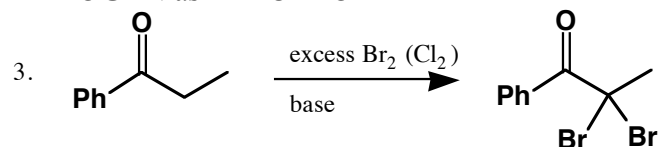
optically active

racemic

-Racemization of α -chiral optically active carbonyls

-Mech

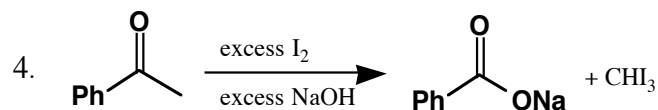
HALOGEN as ELECTROPHILE



-Base catalyzed halogenation

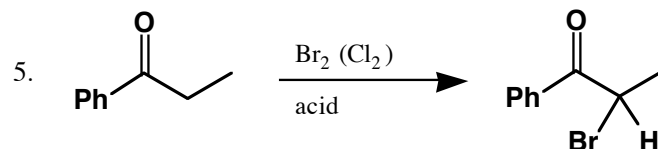
-with excess halogen, all α -hydrogens get replaced

-Mech



-Iodoform reaction.

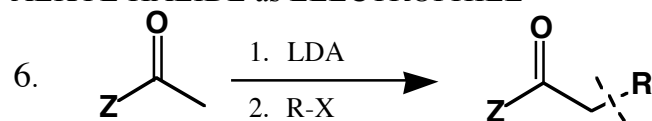
-chemical test for methyl ketones



-Acid-catalyzed halogenation

-can achieve selective mono-halogenation

ALKYL HALIDE as ELECTROPHILE



-Enolate alkylation

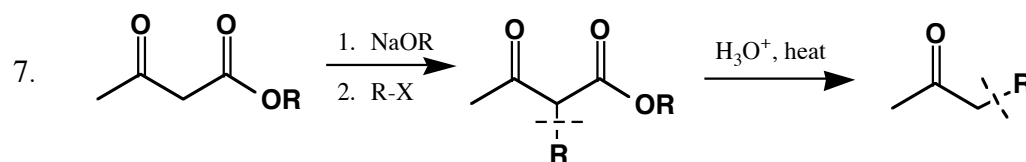
-strong LDA base required to completely deprotonate carbonyl

-Mech

-Ketones, Esters, Amides, Aldehydes: doesn't matter which kind of carbonyl

-unsymmetrical ketones give isomer problems

-S_N2 alkylation restricts R-X to active ones



-Enolate alkylation of 1,3-ketoester

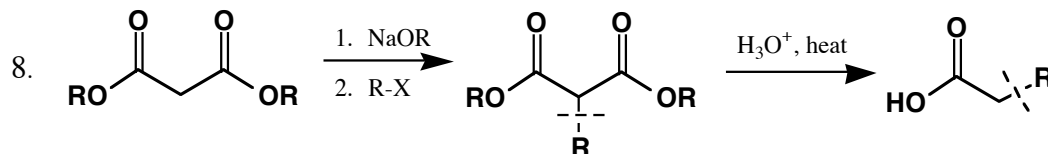
-alkoxide base strong enough to completely generate enolate

-Mech for alkylation

-S_N2 alkylation restricts R-X

-position of alkylation is unambiguous

-acid-catalyzed hydrolysis/decarboxylation



-Enolate alkylation of 1,3-diester

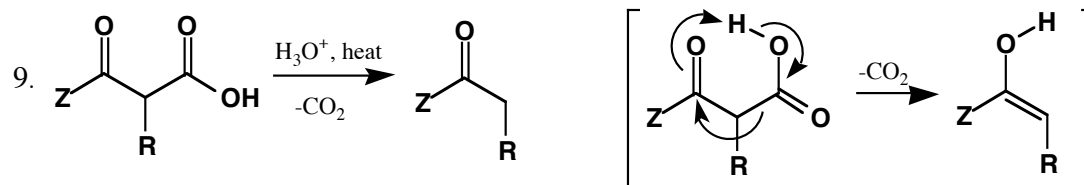
-alkoxide base strong enough to completely generate enolate

-Mech for alkylation

-S_N2 alkylation restricts R-X

-acid catalyzed hydrolysis/decarboxylation

-Final product is an ACID (Diester → Acid)



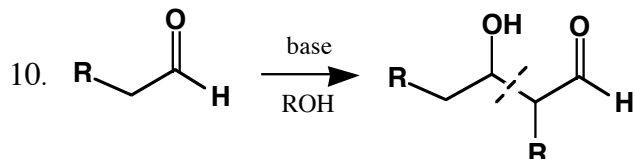
-decarboxylation of a 1,3-carboxylic acid

-“Z” can be anything so that you end with a ketone, aldehyde, or acid at the end

-know the mechanism for the decarboxylation, and acid-catalyzed enol to carbonyl isomerization

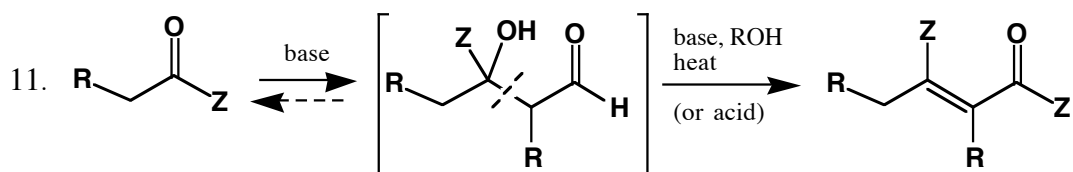
-rate will be impacted by stability of the enol intermediate

ALDEHYDE/KETONE as ELECTROPHILE



-Aldol Reaction

-Mech



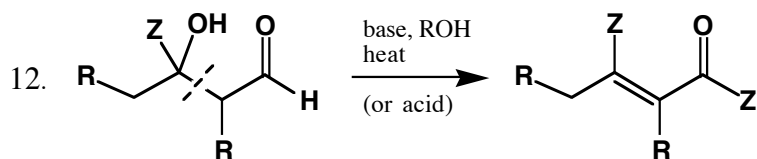
-Aldol Condensation

-Ketones as well as Aldehydes can be used

-In ketone case, unfavorable aldol equilibrium is still drawn off to enone

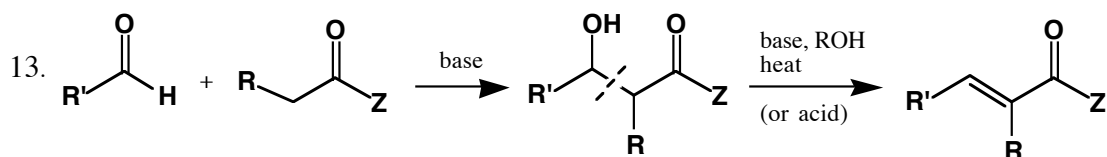
-In Aldehyde case, can stop at aldol if you don't heat

-Mech



-Aldol dehydration

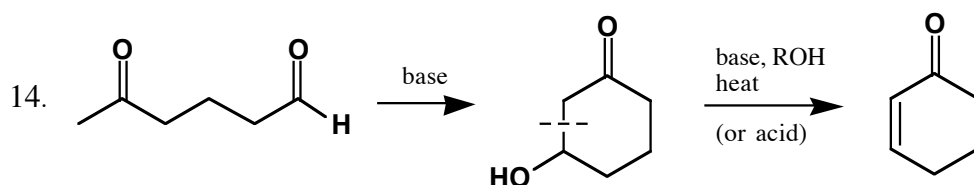
-Mech under basic conditions



-Crossed Aldol (2 different carbonyls)

-Many variations, but there must be some differentiation so that one acts selectively as the enolate and the other as the electrophile

-Mech



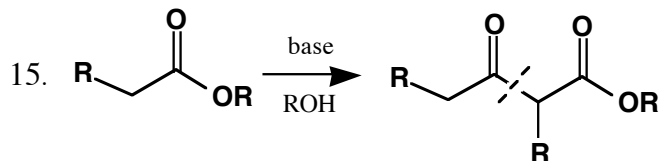
-Intramolecular aldol

-Mech

-many variations

-Normally only good for 5, 6-membered rings

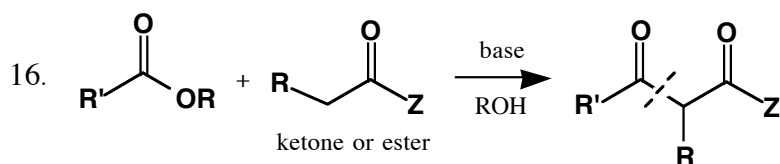
ESTER as ELECTROPHILE



-Claisen Reaction

-Mech

-Produces 1,3-ketoester



-Crossed Claisen

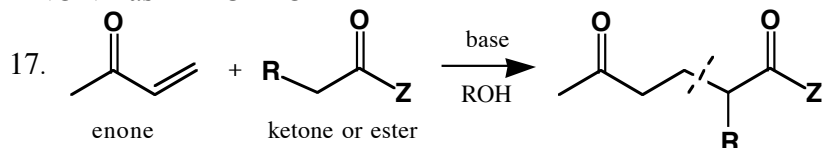
-May include cyclic Claisen reactions

-If the "enolate" carbonyl is a ketone, get a 1,3-diketone

-If the "enolate" carbonyl is an ester, get a 1,3-ketoester

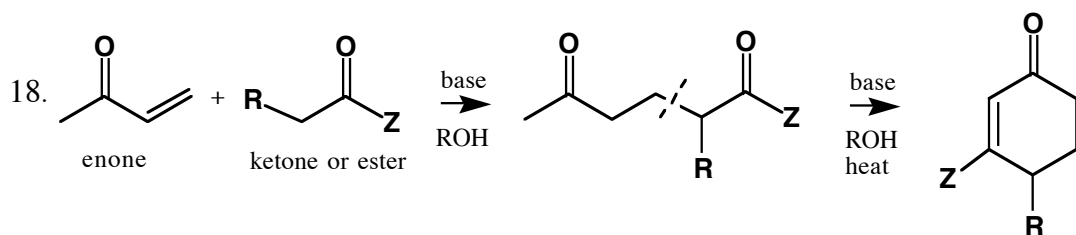
-Mech

ENONE as ELECTROPHILE



-Mech

-"Michael Addition"

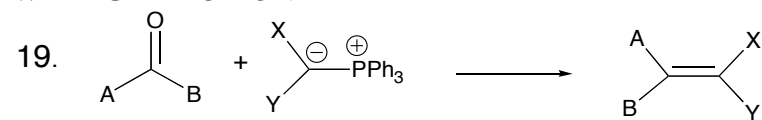


-"Robinson Annulation"

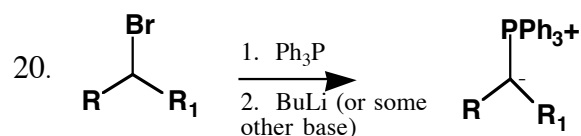
-Mech

-Michael addition gives 1,5-dicarbonyl, then intramolecular aldol reaction-dehydration

WITTIG REACTION



-Mech



-Mech