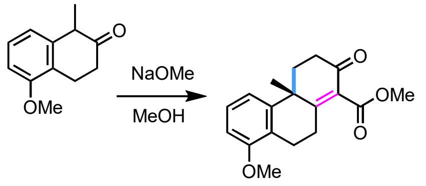
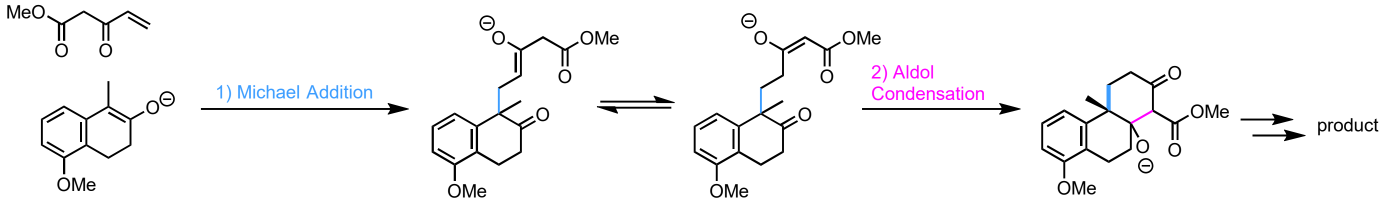
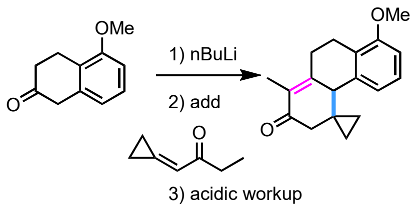
Complex Enolates A - Robinson Annulation under Basic Conditions



this one is a Robinson Annulation, so 1) Michael Addition and 2) Aldol Condensation

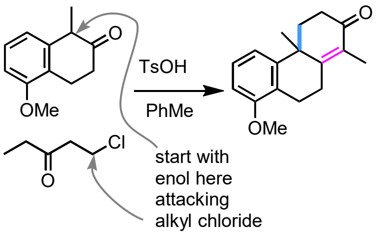


Complex Enolates B - Robinson Annulation under Basic Conditions



this one is a Robinson Annulation, so 1) Michael Addition and 2) Aldol Condensation

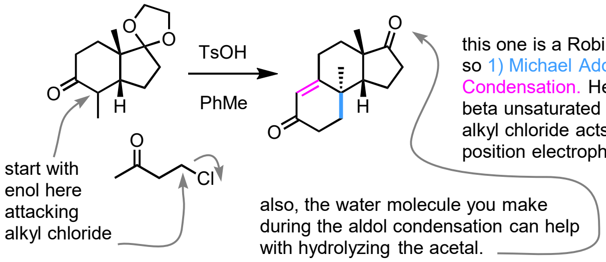
Complex Enolates C - Robinson Annulation under Acidic Conditions



start with enol here attacking alkyl chloride

this one is a Robinson Annulation, so 1) Michael Addition and 2) Aldol Condensation. Here there's no alpha-beta unsaturated carbonyl, but the alkyl chloride acts to make the beta position electrophilic

Complex Enolates D - Robinson Annulation under acidic conditions and acetal hydrolysis

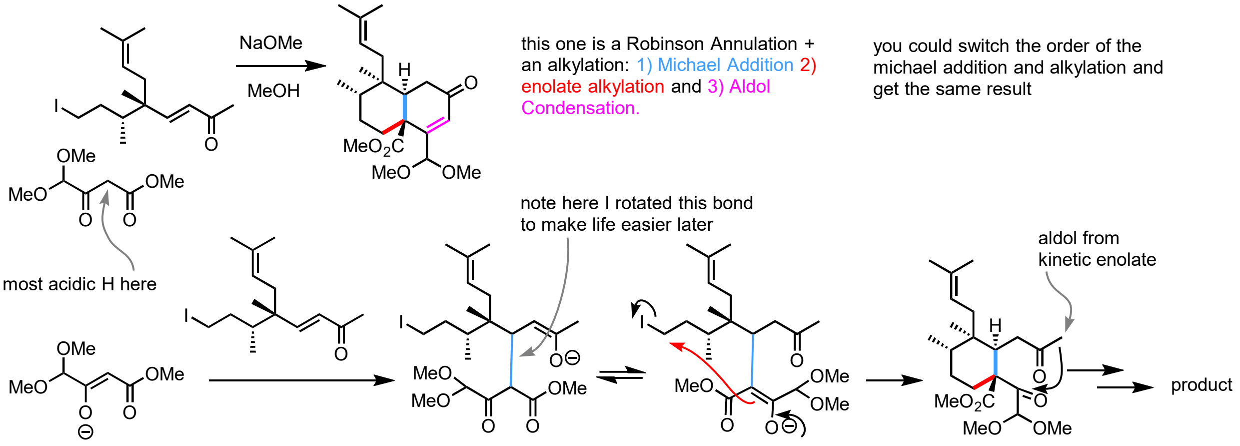


start with enol here attacking alkyl chloride

this one is a Robinson Annulation, so 1) Michael Addition and 2) Aldol Condensation. Here there's no alpha-beta unsaturated carbonyl, but the alkyl chloride acts to make the beta position electrophilic

also, the water molecule you make during the aldol condensation can help with hydrolyzing the acetal.

Complex Enolates E - Robinson Annulation + Alkylation



this one is a Robinson Annulation + an alkylation: 1) Michael Addition 2) enolate alkylation and 3) Aldol Condensation.

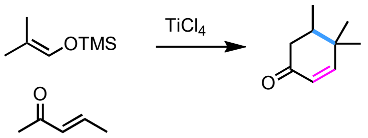
you could switch the order of the michael addition and alkylation and get the same result

most acidic H here

note here I rotated this bond to make life easier later

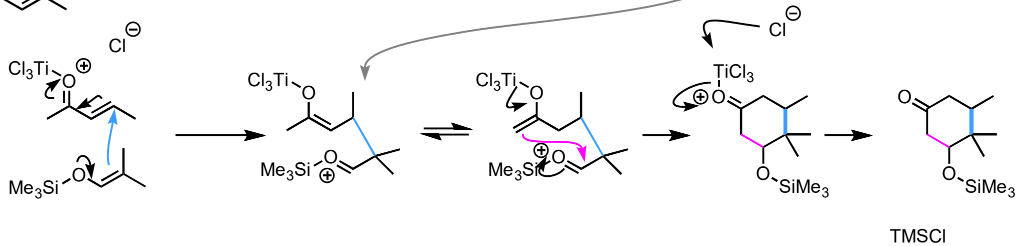
aldol from kinetic enolate

Complex Enolates F - Robinson Annulation with silyl enol ether

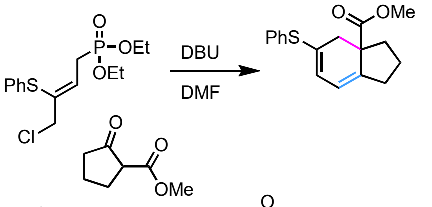


this one is a Robinson Annulation, so 1) Michael Addition and 2) Aldol Condensation

the way I've done the mechanism here, we would require an aq. acidic workup to get the condensation to take place. alternatively, you could desilylate earlier, and end up with TiCl3 in your product, which would also be removed by aq. workup

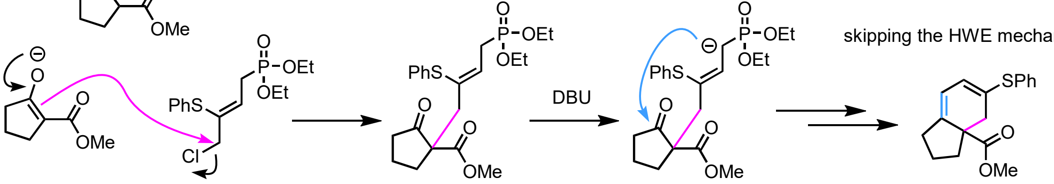


Complex Enolates G - Robinson Annulation with silyl enol ether

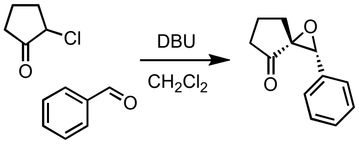


this one has both an HWE olefination and enolate alkylation I think the alkylation might happen first only because the pKa of the beta-dicarbonyl is so low

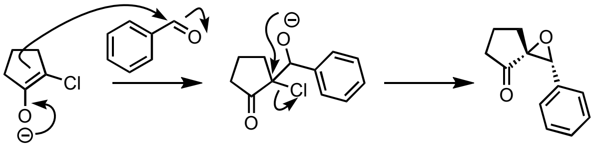
skipping the HWE mechanism here



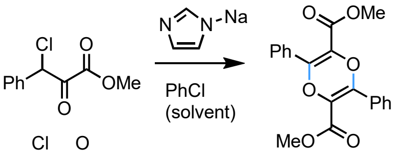
Complex Enolates H - Darzens Reaction



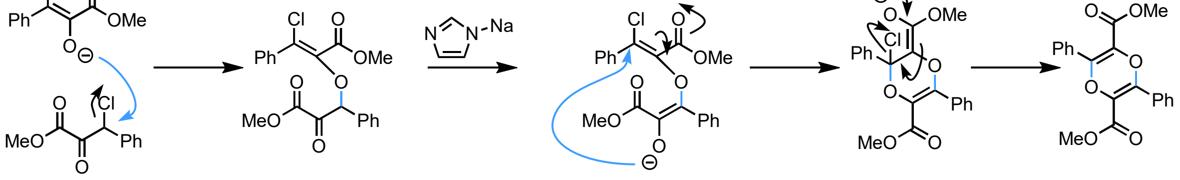
alpha halo carbonyls in enolate additions to other carbonyls typically are set up to form an epoxide



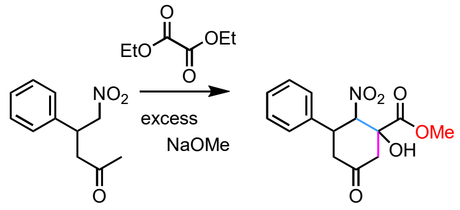
Complex Enolates I - a dimerization reaction with O-alkylation



dimerization = two of the same molecules react together, you can really view this as having some elements of a Michael Addition



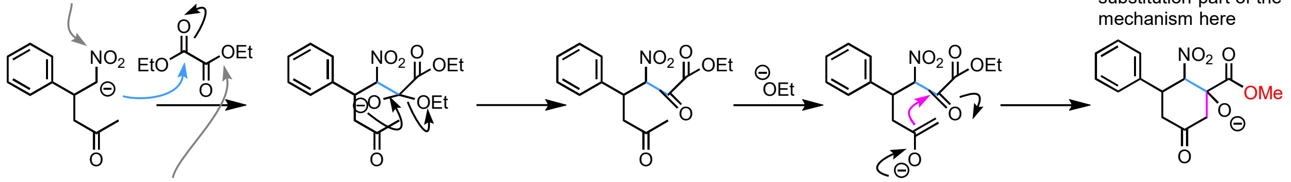
Complex Enolates J - Claisen + Aldol + Carbonyl Substitution



here we do a nitro-Claisen condensation, a Aldol addition, and finally a transesterification

(not necessarily in this order... particularly the transesterification can happen at any point)

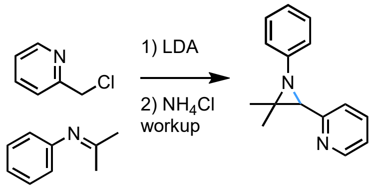
nitroalkanes (pKa = 16 ish) are a little more acidic than ketones (pKa = 20ish)



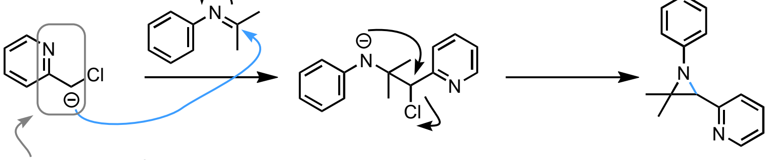
the excess NaOMe could transesterify these OEts at any point

I skipped the carbonyl substitution part of the mechanism here

Complex Enolates K - a pseudo enolate example

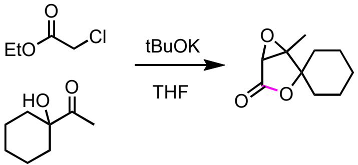


this one is tricky because the instinct is to make an aza-enolate. however that doesn't get you very far, so then we realize we should deprotonate the pyridine instead.

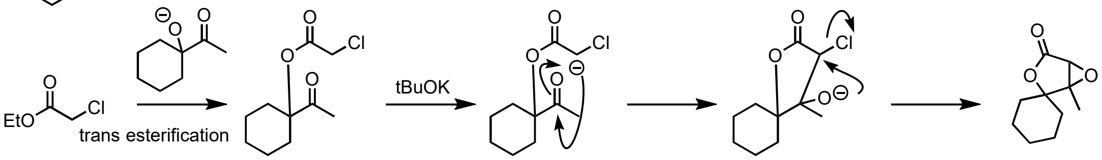


note this part kind of looks like an enolate!

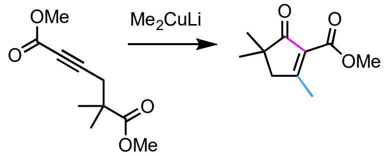
Complex Enolates L - Darzens + transesterification



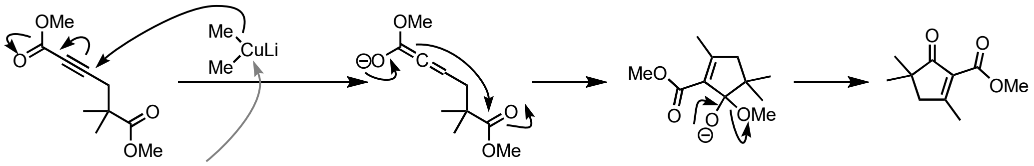
here we get an epoxide via Darzens reaction and a transesterification to make the second new ring. this theoretically might happen in either order



Complex Enolates M - Michael + Claisen

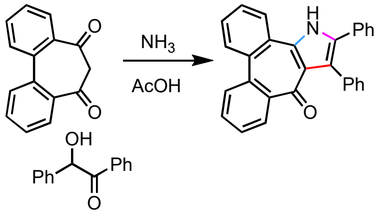


the Michael addition leads to an enolate that can then do the intramolecular Claisen (aka Dieckmann cyclization)



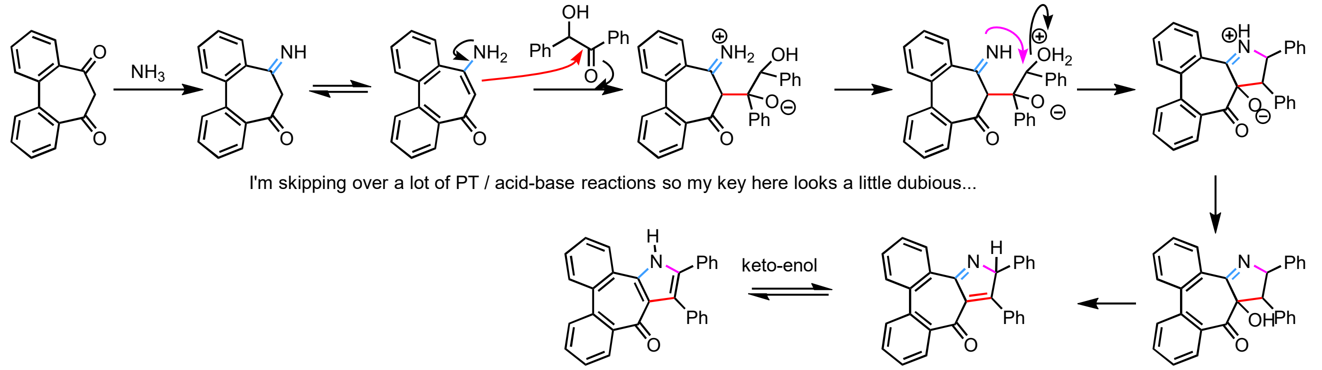
the Gilman reagent always adds 1,4

Complex Enolates N - imine/aza-enolate formation and aldols



here there's imine formation which gets to an azaenolate that can do an aldol condensation, and furthermore do N-alkylation

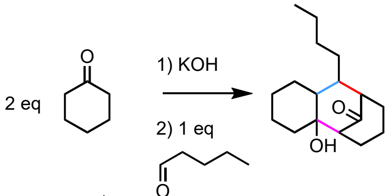
note that keto-enol aromatization reorganizes the double bonds, which is why the aldol condensation appears to create a single bond.



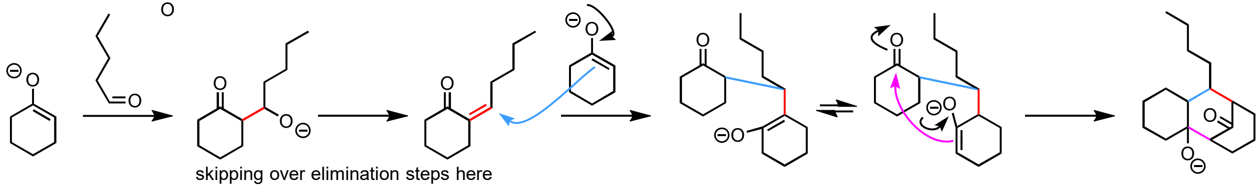
I'm skipping over a lot of PT / acid-base reactions so my key here looks a little dubious...

either E1cb or E1 elimination would be OK here

Complex Enolates O - crossed aldol condensation, Michael addition, and aldol addition,

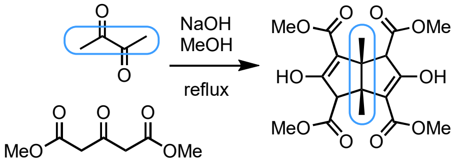


whoa that's a lot going on here, and it doesn't seem to make sense if we isolate step 1 and 2, so here's what I think is happening: 1) aldol condensation, 2) michael addition, 3) aldol addition

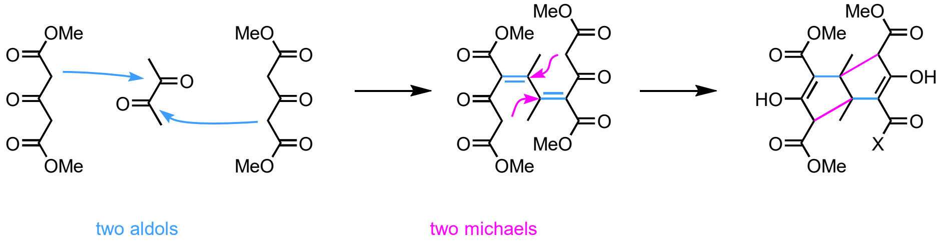


skipping over elimination steps here

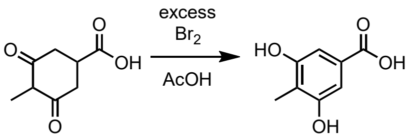
Complex Enolates P - aldols + michaels



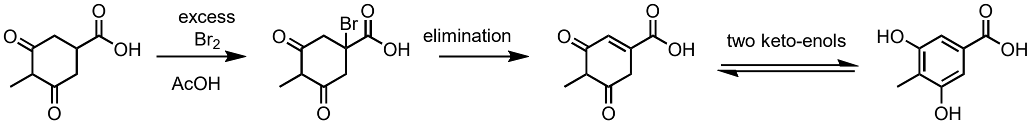
looks like a lot but this is just a bunch of aldol condensations then michael additions



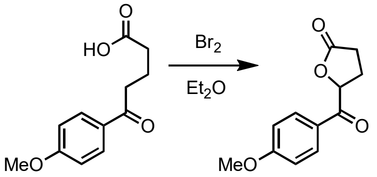
Complex Enolates Q - enolate halogenation then keto-enol



I'd argue to brominate one of the tertiary positions because those will be the thermodynamic enols formed, and they are also a little better for elimination in an E1-ish mechanism



Complex Enolates R - enolate halogenation then intramolecular SN2



we'll enolize the ketone, then halogenate it, then the carboxylic acid OH can SN2 on the alpha-bromo ketone.