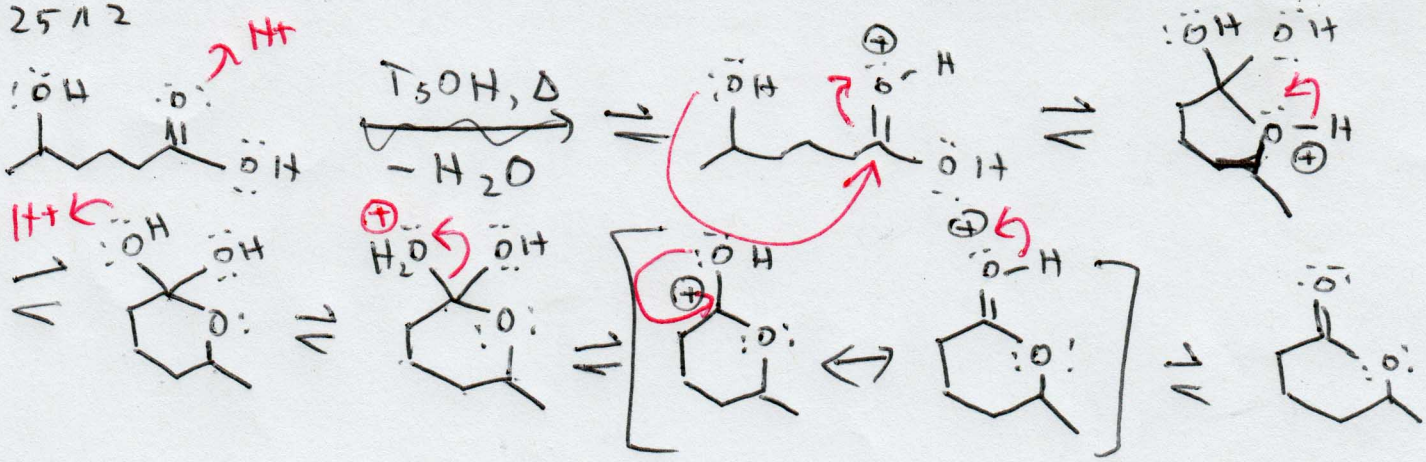
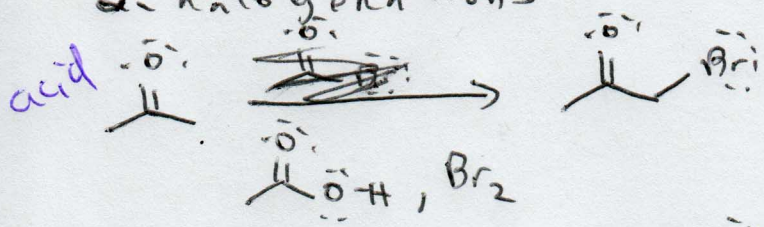
4/25/12



→ Insert α-acidity lecture here

→ Mixed aldol theory is a lab topic

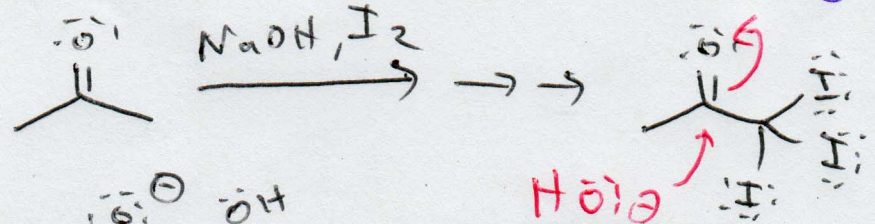
α-halogenations



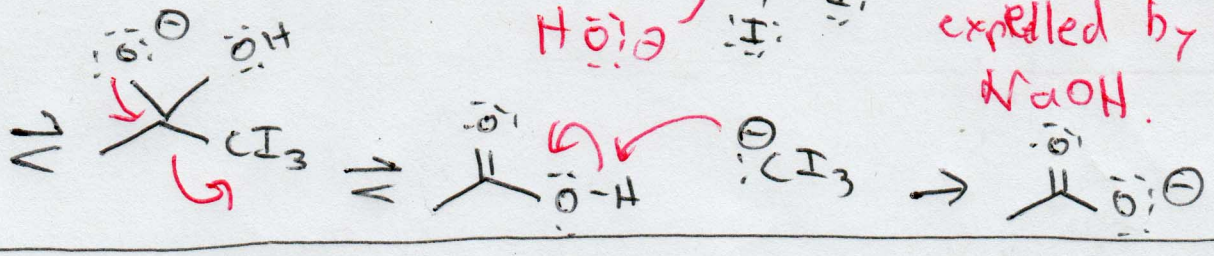
Under acidic conditions, halogenation only occurs once

Only two halogenations occur since only two α-hydrogens are present

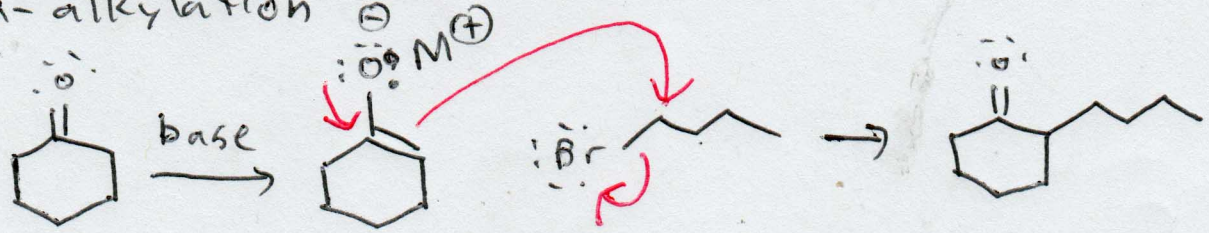
The haloform rxn is a special case of α-halogenation involving methyl ketones (R R = alkyl)

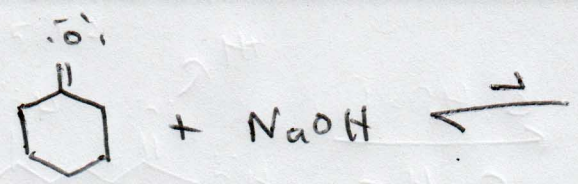


HCX_3 is acidic enough that its conjugate can be expelled by attack of NaOH.



α-alkylation



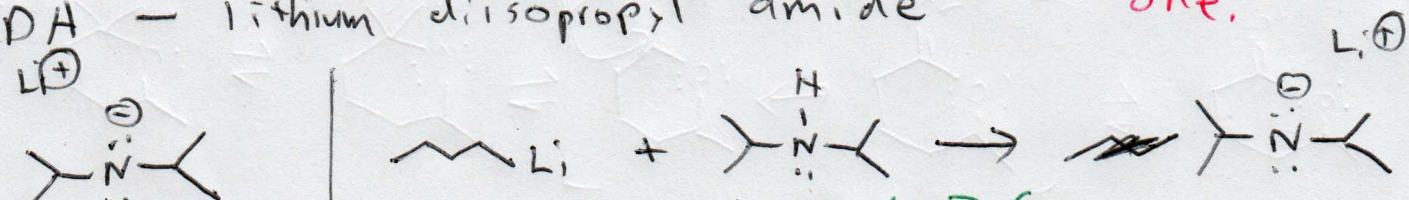


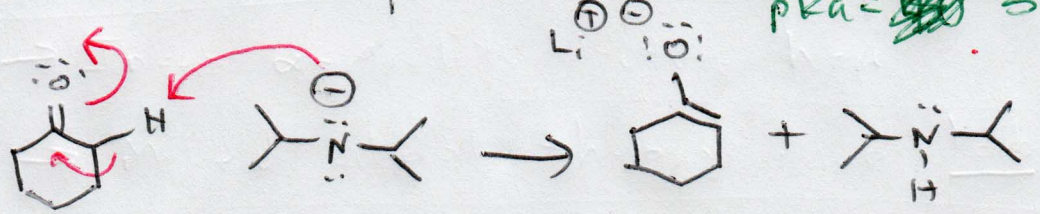
pka = 19

pka = 16

Unfavorable since a weaker acid is converted into a stronger one.

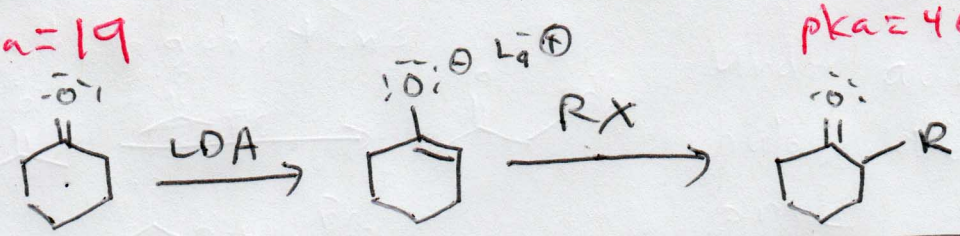
LDA — lithium diisopropyl amide



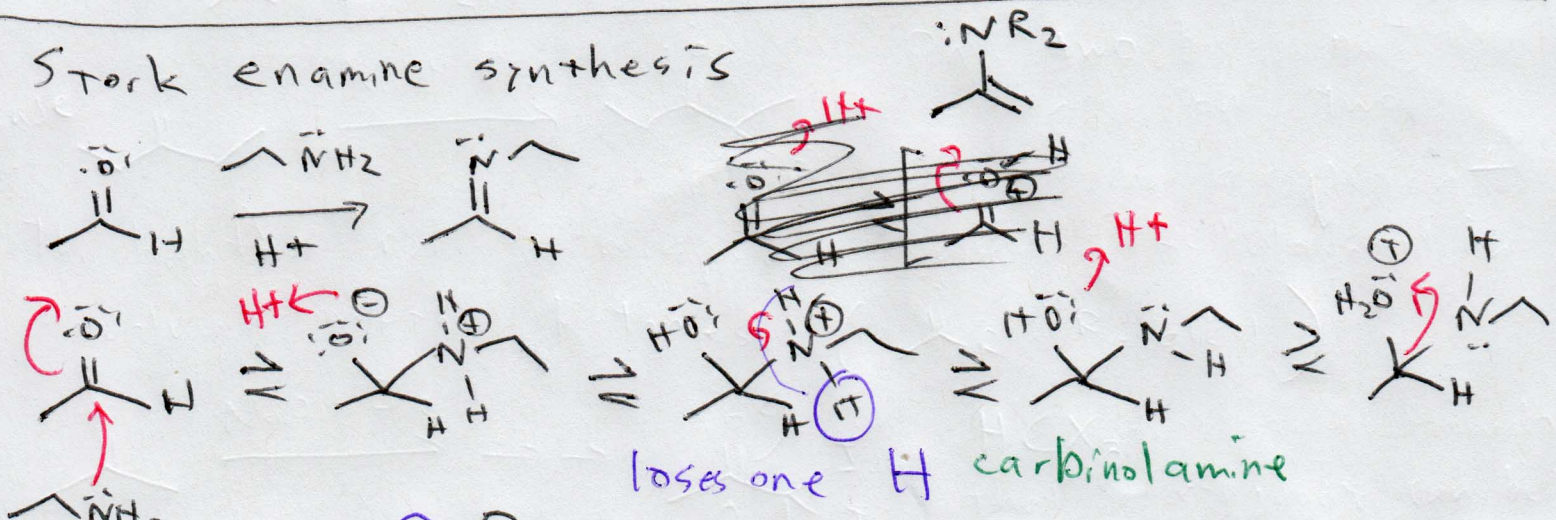


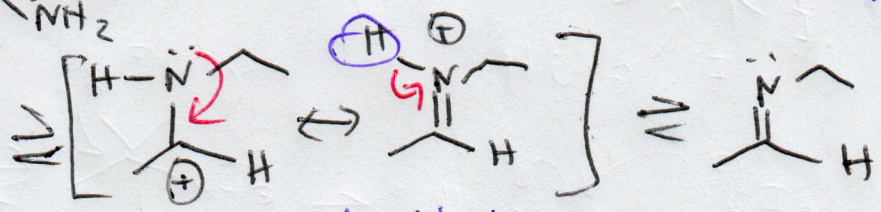
pka = 19

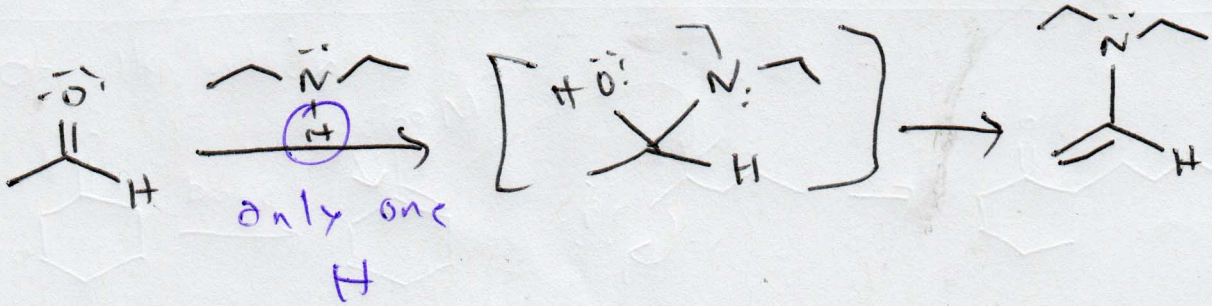
pka = 40

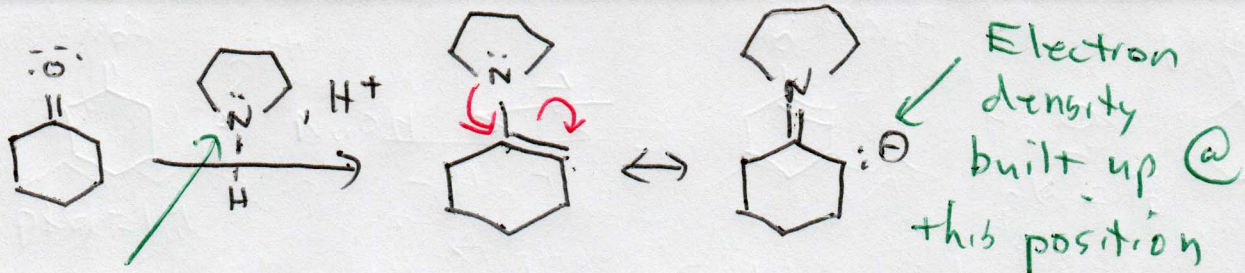


Stork enamine synthesis

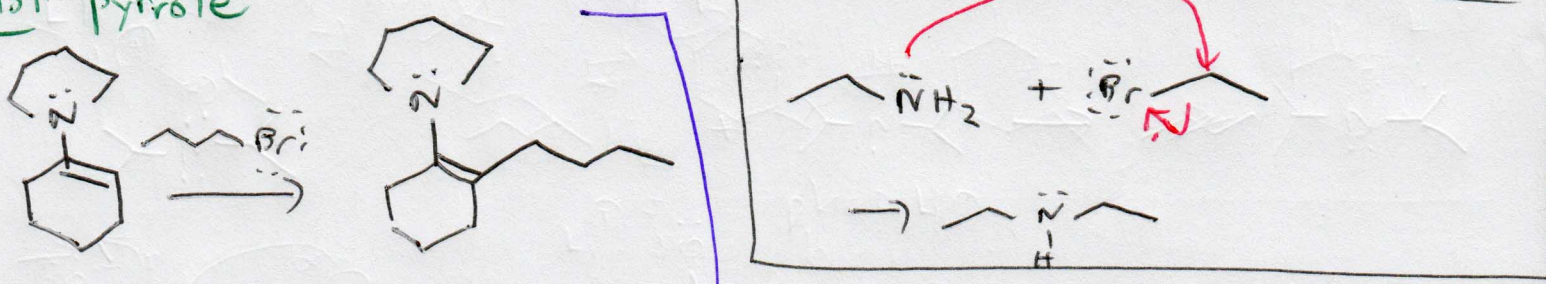


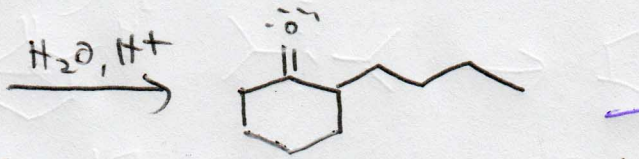






not pyrrole

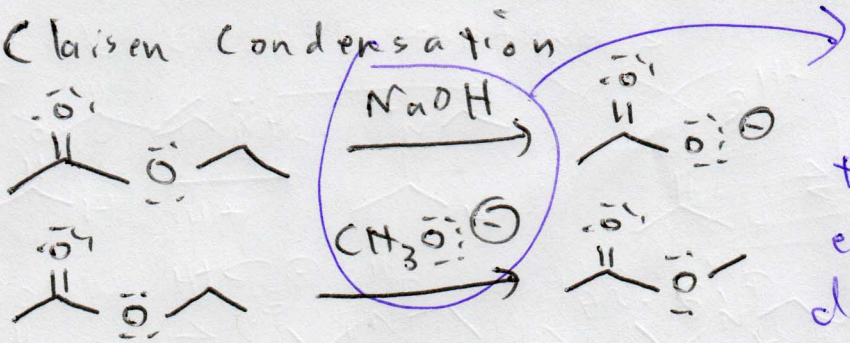




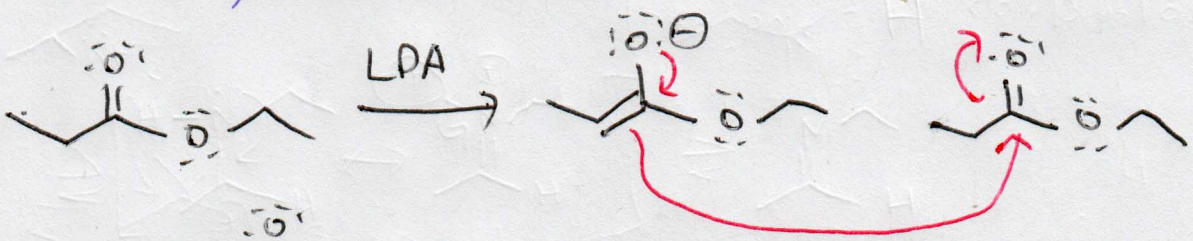
What is the mechanism?

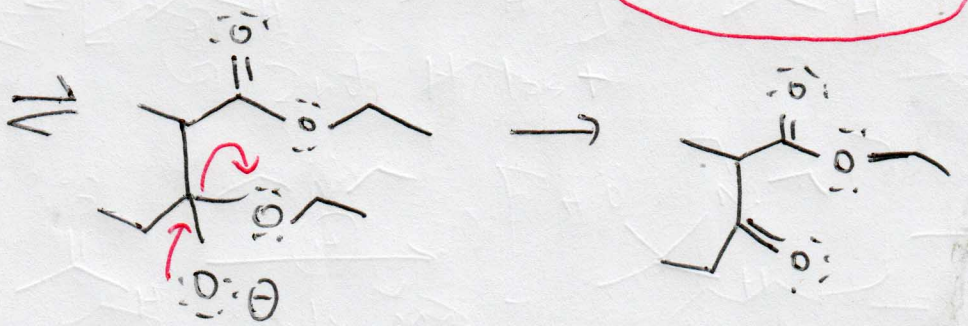
The Stork enamine synthesis is useful because no strong bases are used, which can allow more sensitive substrates to be used in alkylation reactions.

Claisen Condensation



Cannot be used to α-deprotonate because they are not strong enough bases and, depending on the type of ester, will cause saponification or transesterification.





β-keto ester