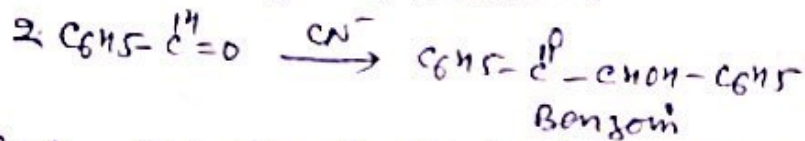
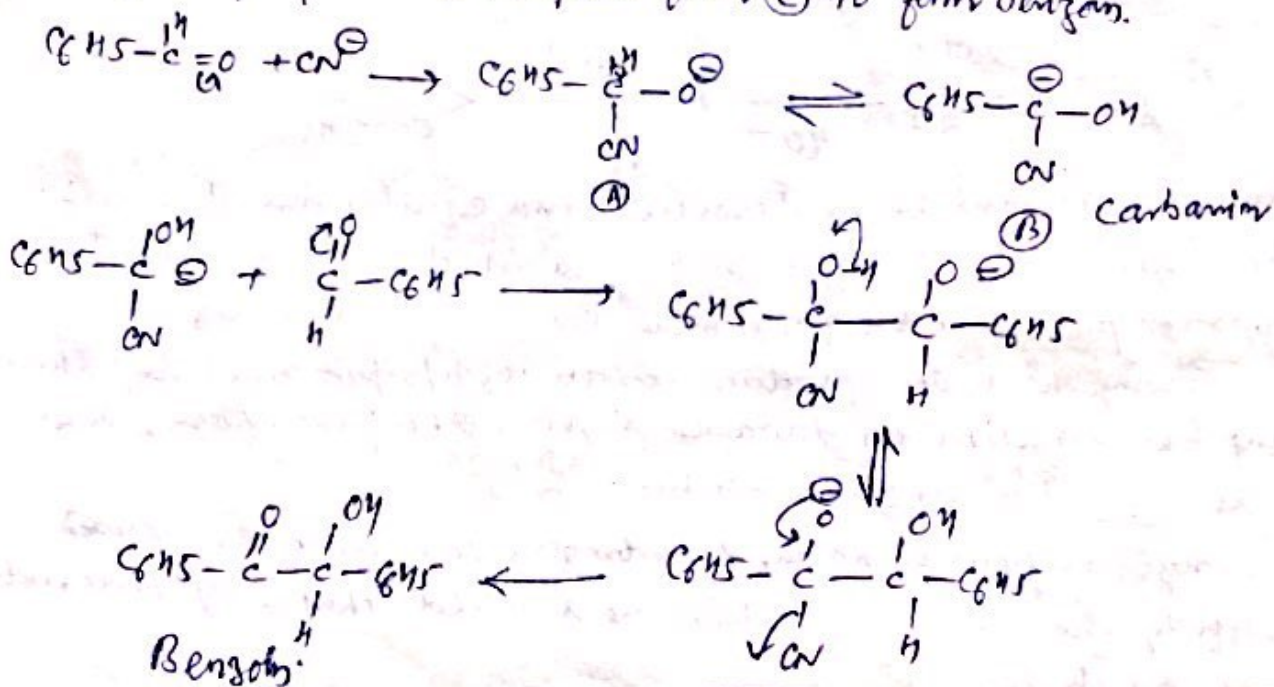


3/ Benzoin Condensation

The self condensation of aromatic aldehydes (having no α -hydrogens) in presence of cyanide ion as a catalyst to α -hydroxy ketone (Benzoin) is called Benzoin Condensation.



Mech. Cyanide ion attacks carbonyl group to give (A). Cyanide group due to its electron withdrawing nature makes aldehyde hydrogen more acidic to get (A) into (B). The anion (B) attacks another aldehyde carbon for the fusion. The deprotonation - protonation steps form (C) and finally cyanide ion departs from (C) to form benzoin.

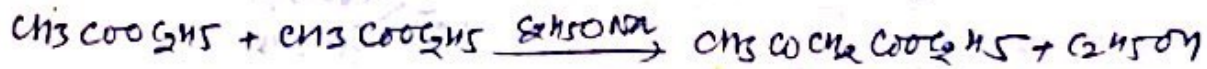


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4/ Claisen Condensation

The base catalyzed condensation of an ester containing α hydrogen atom with another molecule of the same or different ester to give β -keto ester is called Claisen Condensation.

The well known example is the condensation of two molecules of ethyl acetate in presence of Sodium Ethoxide to give ethyl aceto acetate

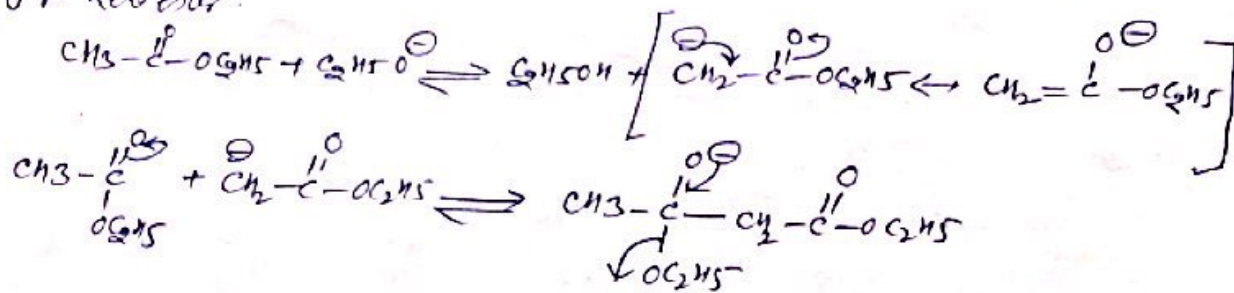


The base commonly used is Sodium alkoxide. Corresponding to the OR of the ester function to avoid ester interchange, which leads to mixed ester from transesterification.

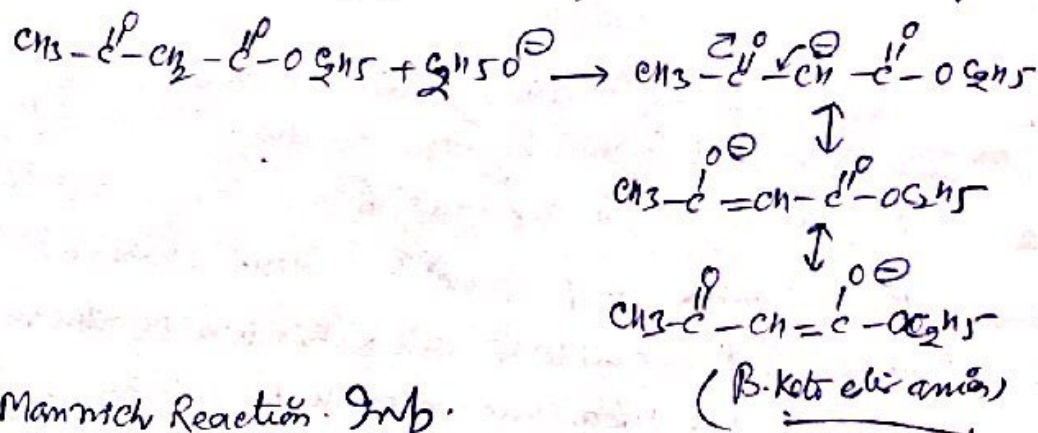
(Claisen Condensation)

(17)

Mechanism: As in aldol condensation, Base removes proton of ester to convert it into carbanion which is resonance stabilized. This anion behaves as a strong nucleophile and attacks another molecule of ester. Elimination of alkoxide ion in the next step leads to the formation of β -keto ester.

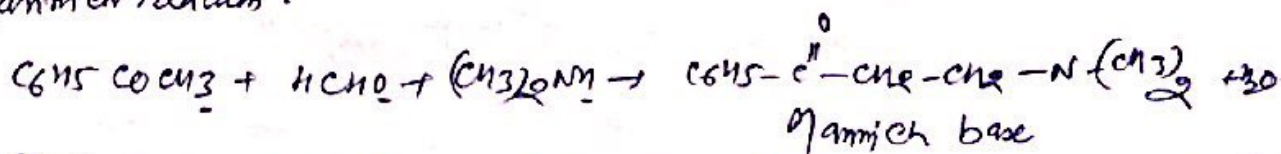


Since these steps are reversible, the success of Claisen condensation depends upon the removal of the final product from the reaction site and thus forcing the equilibrium to the right. Usually this is done by converting the product ester into an enolate anion, which is stabilized by resonance.



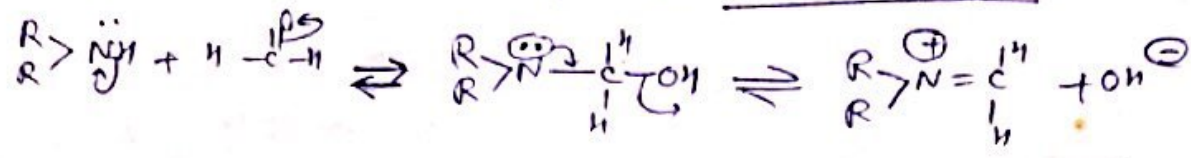
Mannich Reaction: Imp.

The reaction of an active methylene compound (ketones, nitroalkanes, β -keto ester, β -cyano acids etc) with formaldehyde and an amine to form β -amino carbonyl compound (Mannich base) is known as Mannich reaction.

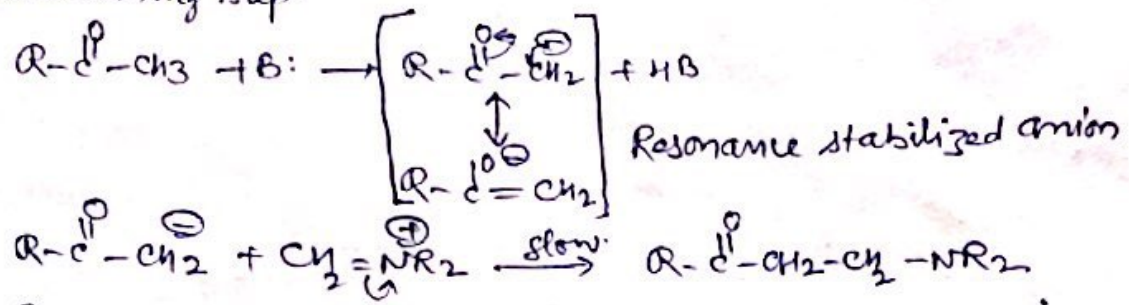


It is a convenient method for introducing a carbon atom in enolizable ketones.

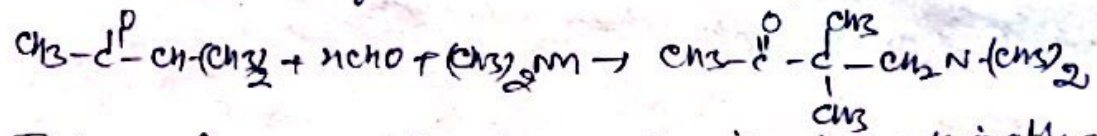
Mech. It is believed that in the first step of the reaction, the amine and formaldehyde condense to form the iminium salt. (18)



The iminium salt is then attacked by the enolate anion of the active methylene compound in the rate determining step:



Since the ease of enol formation increases by the presence of alkyl substituents, unsymmetrical ketones react predominantly at the more highly substituted alpha position.



The use of ammonia and primary amines is undesirable as the first formed Mannich base still carries hydrogen on the nitrogen atom and may thus participate in the further reaction.

A no. of cyclic products have been prepared via double Mannich condensation. An important example is the Robinson's synthesis of Tropicine, which also makes use of succinaldehyde in place of formaldehyde-oxen.

