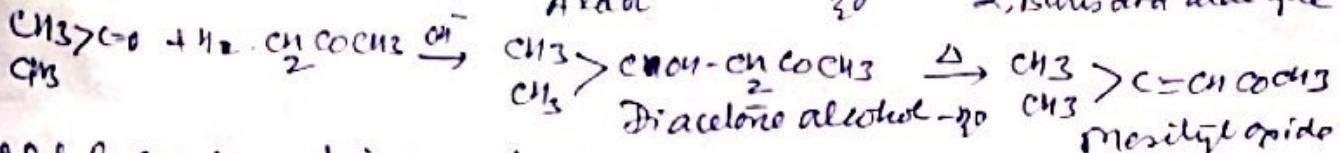
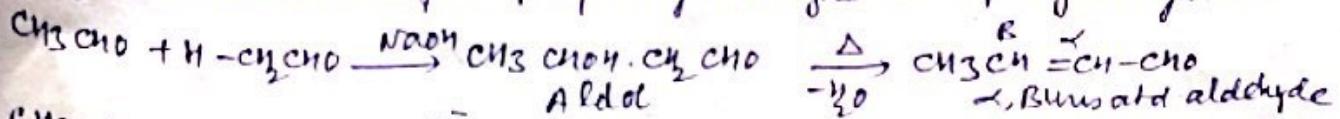


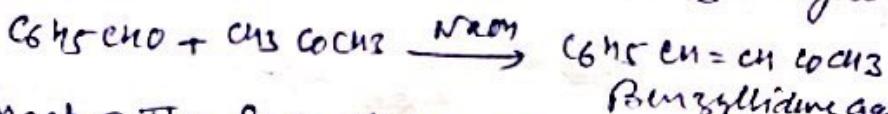
By - P.K. Sharma
11-2008

Mechanism of Condensation Reactions | IV Lect. on Addition to C-hetero bonds (13)

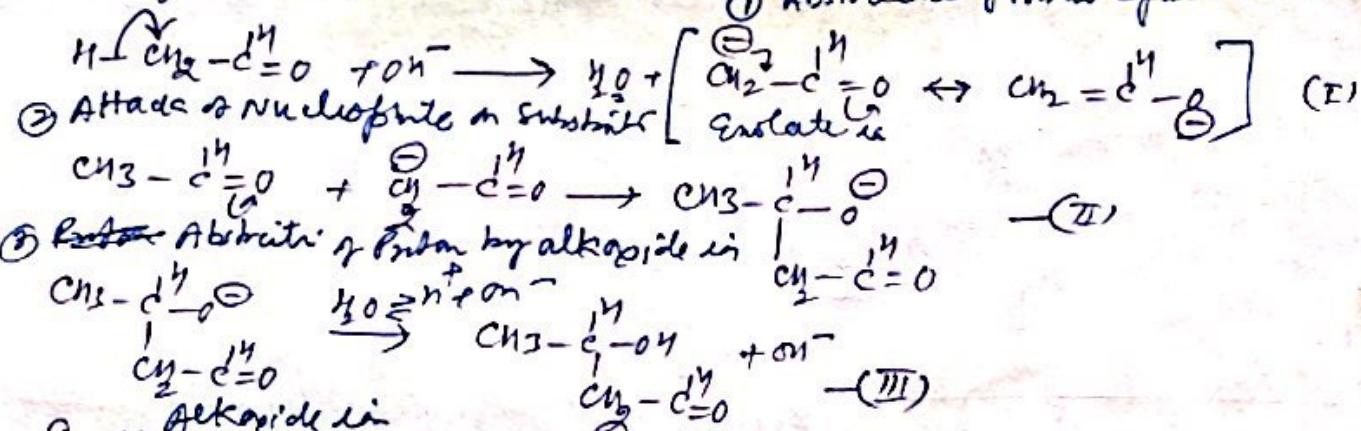
① Aldol Condensation Aldehydes and ketones having α -hydrogen atoms undergo condensation to form β -hydroxy aldehyde or a β -hydroxy ketone.



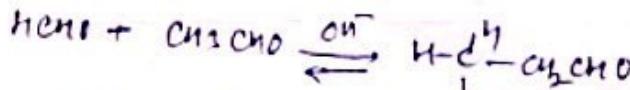
Aldol condensation can also take place between an aldehyde and a ketone. This is known as Grossed aldol condensation (Claisen-Schmidt reaction). The carbonyl group of ketone has less additive power than aldehyde, when aldehyde condenses with a ketone it serves as a substrate for the ketone. Similarly an aldehyde that has no α -hydrogen may undergo condensation with enolisable ketone e.g. condensation between benzaldehyde and acetone



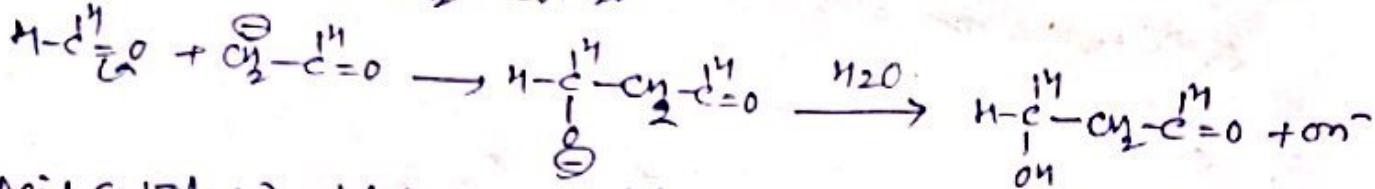
Mech. ① The first step of the reaction is the formation of enolate ion by interaction with base - ② Abstractn of proton by base



In the second step the carbanion attacks the 2nd molecule of aldehyde or ketone (as the case may be) to form aldol. A kinetic study of the aldol condensation between acetaldehyde and formaldehyde has shown that the concentration of formaldehyde does not affect the rate of reaction. It follows that the rate determining step of the reaction involves only acetaldehyde and as soon as its anion is formed it attacks rapidly the carbonyl carbon of the formaldehyde.

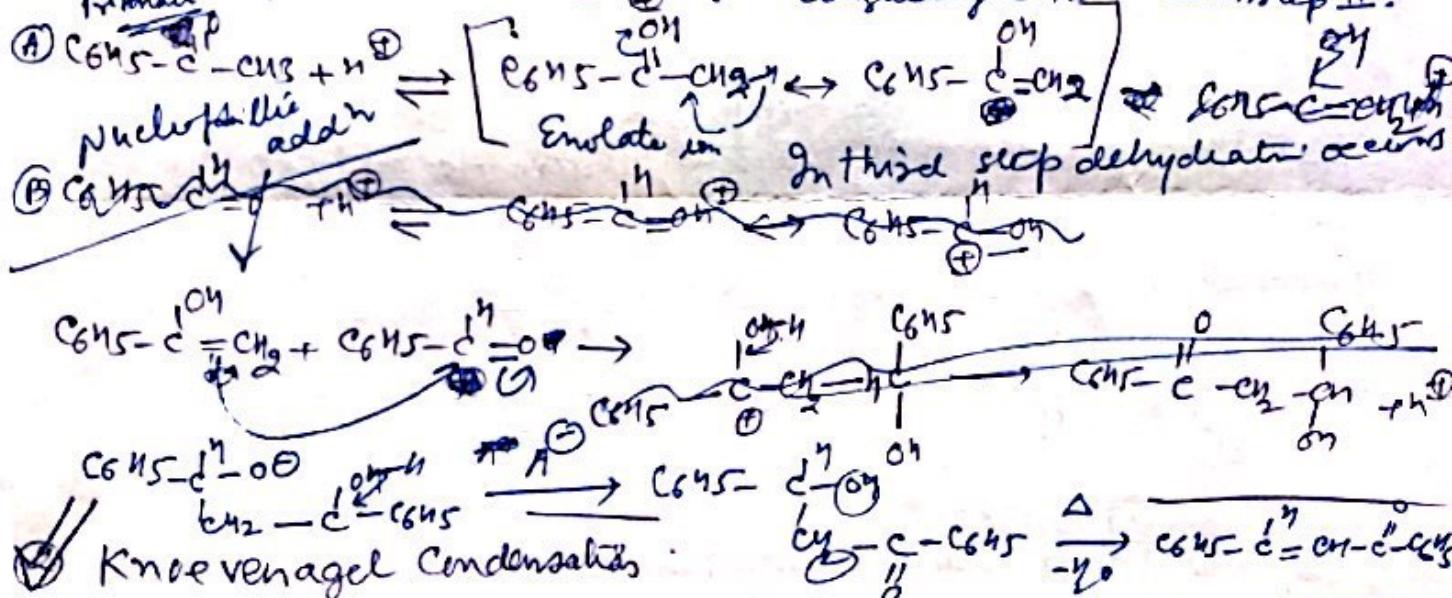


$$\text{Rate} \propto [\text{CH}_3\text{CHO}] [\text{OH}^-]$$

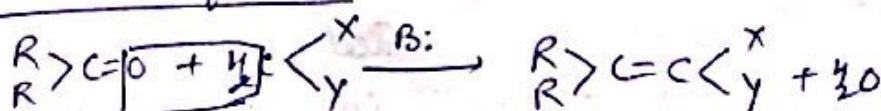


Acid catalyzed aldol condensation (Claisen-Schmidt Reaktion)

Aldol condensations are also catalysed by acids. The reaction of benzaldehyde with acetophenone in presence of acid was found to be first order in both the reactants. It appears that acid catalyzes the conversion of acetophenone into enol form, which then reacts with the protonated benzaldehyde. This enolate ion acts as nucleophile for protonation of benzaldehyde molecule in step II.



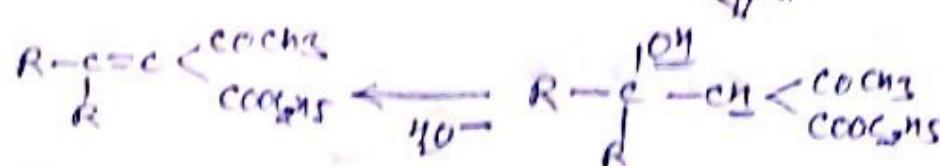
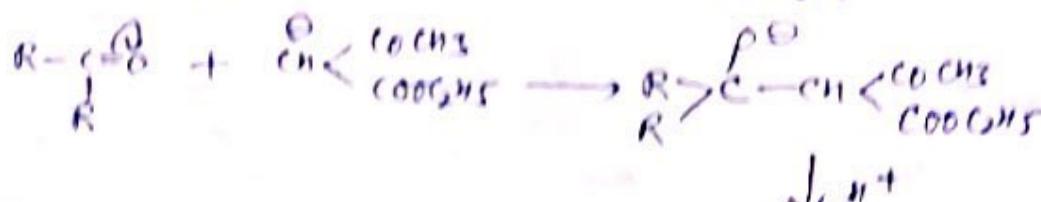
Base catalysed condensation between an aldehyde or ketone and any compound having reactive methylene group (malonic ester) is known as Knoevenagel condensation. Sometimes decarbonylation also occurs during the condensation, then it is known as Doebner modification.



The basic catalyst employed is usually an amine. The function of the base is only abstraction of proton from active methylene compd.

(Knoevenagel - contd.)

Mechanism It occurs in following steps (i) base removes a proton from reactant methylene group before carbonyl (ii) the resonance stabilized carbocation, then attacks the carbonyl group of aldehyde or ketone, (iii) subsequent protonation of the anion followed by dehydrogenation yields the product.

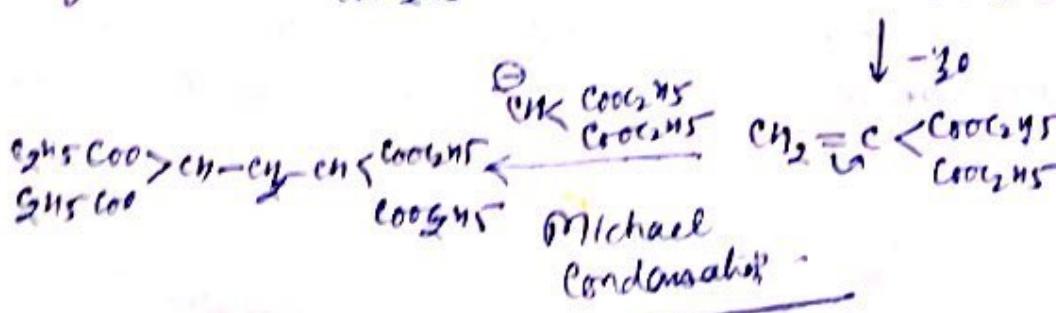


Knoevenagel reaction being reversible and equilibrium favouring towards reactants, the yield is not satisfactory. Cope introduced an improved procedure by performing the reaction in benzene and removing the water, produced as an azeotropic mixture, thus shifting the equilibrium towards right. This, therefore, now known as Cope-Knoevenagel reaction.

Carbonyl compounds having 2 hydrogens can also be condensed successfully since basic conditions are so mild that self condensate occurs rarely.

Knoevenagel reaction is more useful with aromatic aldehydes, since with aliphatic aldehydes the product obtained undergoes Michael-

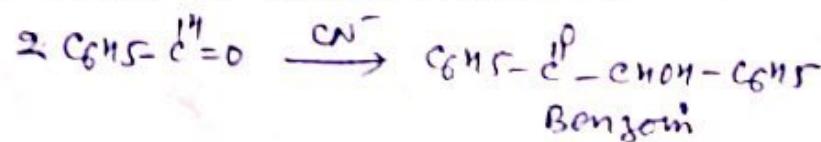
Condensation



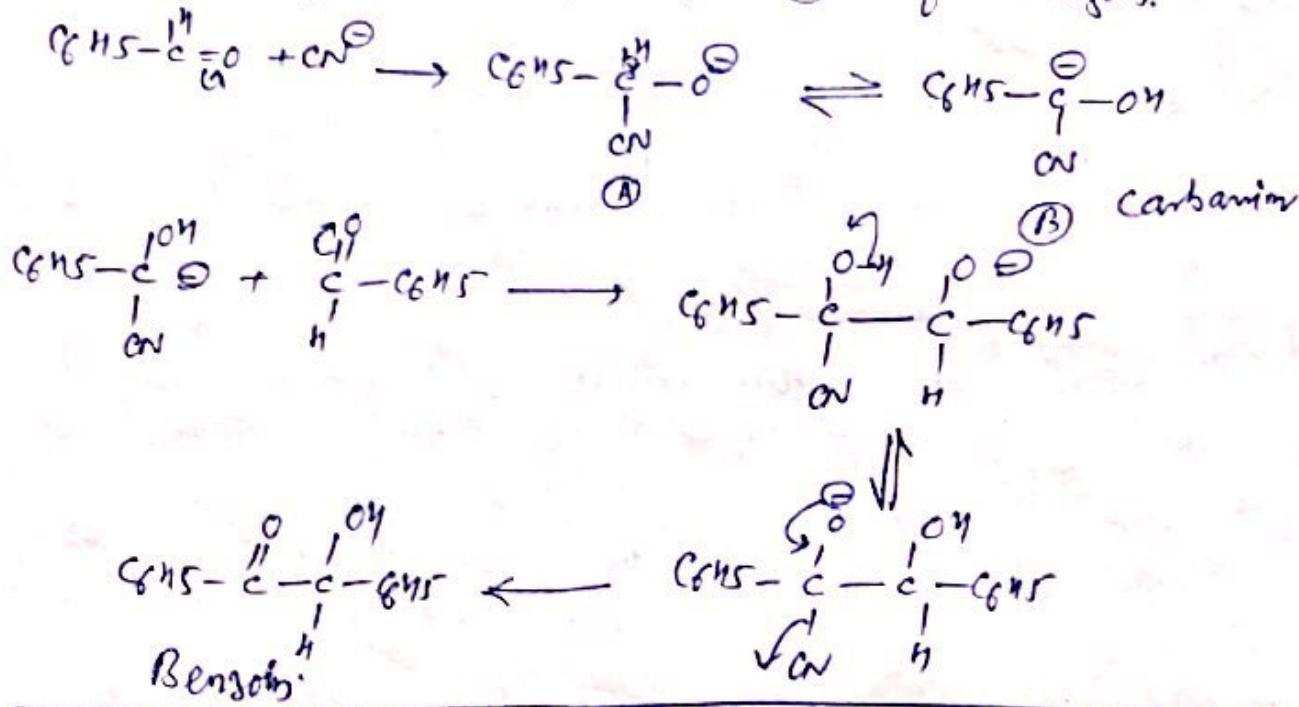
Benzoin Condensation

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



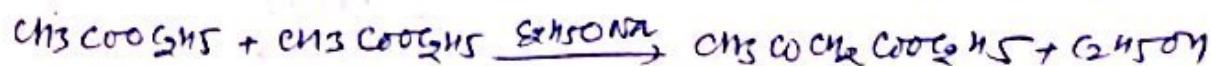
Mech. Cyanide ion attacks carbonyl group to give (A). Cy anilide group due to its electron-withdrawing nature makes aldehydic hydrogen more acidic to get (A) into (B). The anion (B) attacks another aldehyde carbon for the fusion. The deprotonation - protonation step form ion (C) and finally cyanide ion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



M.Sc. II Sem. Ith Lect: by P.K. Shinde. H-200D - Name Reactions

④ Claisen Condensation: The base catalysed condensation of an ester containing a 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 esters from trans-esterification.