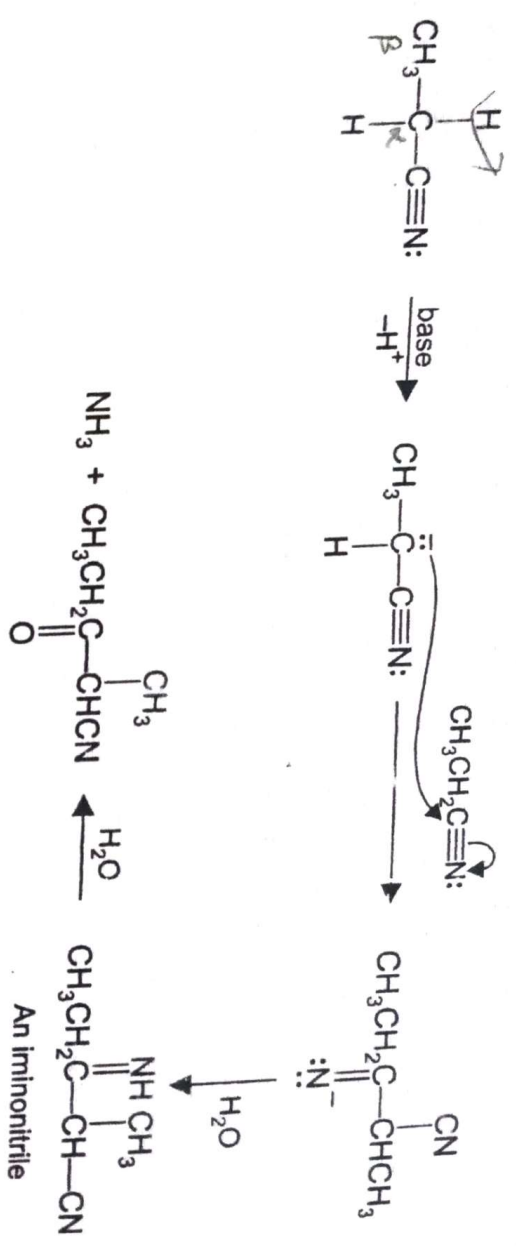


(P) The Thorpe Nitrile Condensation

In the Thorpe reaction, the α -carbon of one nitrile molecule (a carbanion source) adds to the CN carbon (acceptor site) of another molecule. The C=NH bond that results can be hydrolyzed to get β -keto nitriles (Scheme 6.37).

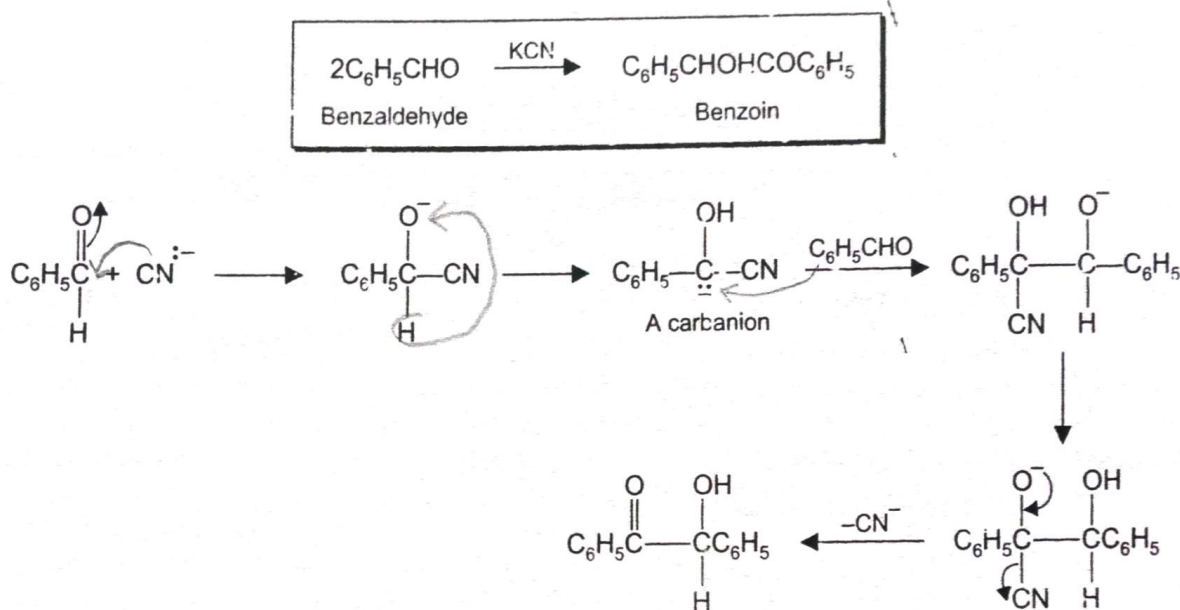


SCHEME 6.37

(Q) The Benzoin Condensation

This reaction is the cyanide ion catalysed intermolecular condensation of an aromatic aldehyde to give an acyloin. The condensation of benzaldehyde gives benzoin (Scheme 6.37a). The aromatic aldehydes do not form cyanohydrins, but the cyanide addition product, by base abstraction of a proton gives a carbanion. This reacts with a second molecule of the aldehyde. Thus benzoin condensation involves the reaction of two molecules of aldehyde (normally aromatic) in the presence of cyanide ion to give a benzoin (an α -hydroxyketone) which is also called an acyloin.

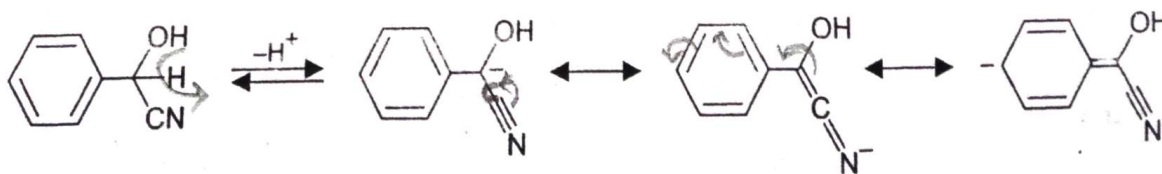
In benzoin condensation (recall that benzoin condensation resembles an aldol and Cannizzaro processes) cyanide ion is needed for the success of the reaction, however, it is regenerated at the end of the reaction (Scheme 6.37a).



Mechanism of the benzoin condensation

SCHEME 6.37a

The success of the reaction is due to the cyanide ion. Firstly it is a reactive nucleophile and secondly it has the capacity to delocalize the negative charge on the carbanion. Thus the carbanion formation is assisted. Moreover, with aromatic aldehydes (unlike aliphatic aldehydes) the negative charge of the carbanion is further delocalized on the aromatic ring (Scheme 6.37b) and this factor provides the extra driving force for the reaction.



SCHEME 6.37b