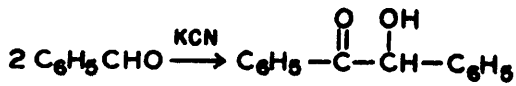
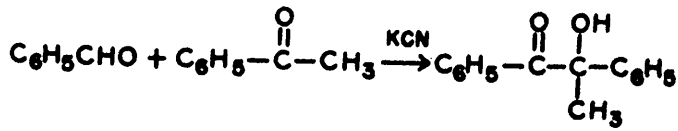
Condensations of Aldehydes and Ketones Catalyzed by Potassium Cyanide

ERNEST M. HODNETT and WILLIAM W. ROSS, Oklahoma A. and M. College, Stillwater

Many aromatic aldehydes may be condensed in aqueous alcoholic solutions of sodium or potassium cyanide with the formation of benzoin or its derivatives:



Ketones are not known to take part in this benzoin condensation, but it seemed possible that under proper conditions they might react as follows:



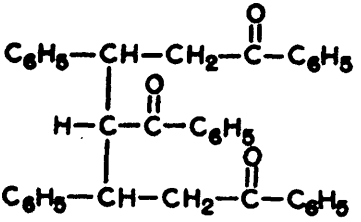
These compounds might have estrogenic activity, or at least would be valuable intermediates for the production of other compounds. The purpose of this investigation was to study condensations between aldehydes and ketones which might be catalyzed by potassium cyanide, with particular emphasis on the search for benzoin-type compounds.

Aldehydes chosen for study in this reaction were benzaldehyde because of the ease with which it undergoes the benzoin condensation, and 4-dimethylaminobenzaldehyde because it always acts as a hydrogen donor in benzoin condensations with other aldehydes. Ketones chosen for study were acetophenone because of its small number of α-hydrogen atoms, and benzophenone because of its lack of α-hydrogen atoms.

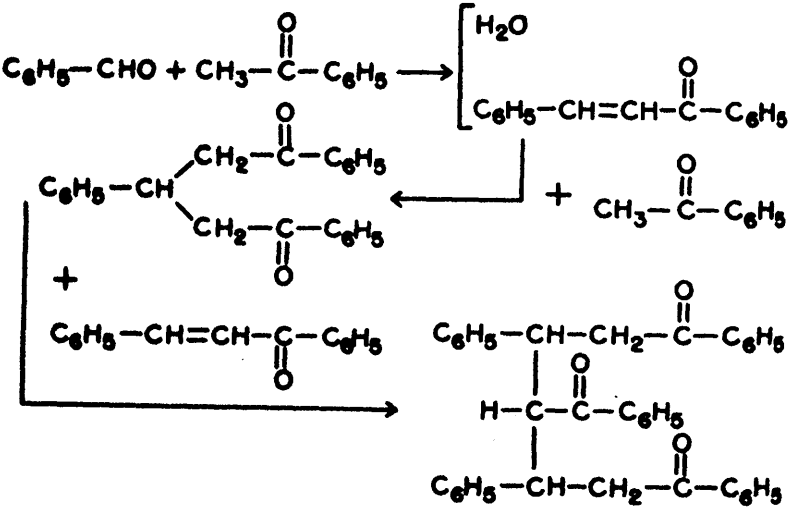
Experimental

Thirty grams (0.25 mole) of acetophenone, 10 gm. (0.15 mole) of potassium cyanide, 100 ml. of ethyl alcohol, and 25 ml. of water were placed in a flask and heated. While the mixture was refluxing, 26.5 gm. (0.25 mole) of benzaldehyde was added during 15 minutes. The solution became yellow, then orange, then red, and a white solid began to form on the walls of the flask. The mixture was cooled, acidified under a hood, and filtered. The white solid (12.5 gm.) was recrystallized from glacial acetic acid.

This white solid melts at 255-6° C., has a molecular weight (by the Rast camphor method) of 495, contains no nitrogen, and gives a precipitate with 2, 4-dinitrophenylhydrazine. The same compound was produced by the reaction of chalcone and acetophenone in the presence of potassium cyanide. Further investigation and consultation of the literature indicated that the compound is dibenzaltriacetophenone, melting point, 254° C:



Kostanecki and Rossbach (1) found that the reaction of acetophenone and benzaldehyde in the presence of sodium hydroxide produced dibenzaltriacetophenone and postulated the following mechanism for its formation:



Thirty grams (0.25 mole) of acetophenone, 6 gm. (0.09 mole) of potassium cyanide, and 200 ml. of ethyl alcohol were heated under reflux while 37 gm. (0.25 mole) of 4-dimethylaminobenzaldehyde was added. After refluxing for one hour, the mixture was cooled, acidified, and extracted with ether. Evaporation of the ether gave a red oil which was recrystallized from dilute alcohol. The yellow-orange solid (10.5 gm.) melts at 110-2° C. and was identified as 4-dimethylaminochalcone.

Benzophenone (0.1 mole), potassium cyanide (0.076 mole), alcohol (100 ml.), and water (5 ml.) were refluxed while benzaldehyde (0.1 mole) was added. When the mixture was cooled after one hour of refluxing, 18 gm. of a white solid precipitated. This solid was separated into two compounds by fractional crystallization. These compounds were identified as benzophenone and benzoin.

Discussion

Aldehydes and ketones react in the presence of potassium cyanide, but the base-catalyzed aldol condensation occurs in preference to the benzoin-type condensation. Since potassium cyanide is the salt of a weak acid and a strong base, its solutions are highly basic. Under these basic conditions aldol condensations occur if the compounds have α-hydrogen atoms, and chalcones are formed by dehydration. In the case of benzophenone which has no α-hydrogen atoms, the benzaldehyde condenses with itself and the benzophenone is recovered unchanged.

LITERATURE CITED

1. Kostanecki, St. V. and G. Rossbach. 1896. Ueber die Einwurkung von Benzaldehyd aud Acteophenon. Ber. deut. Chem. Ges. *29*: 1488.