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**SHORT
COMMUNICATIONS**

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New Condensation of Potassium Diphenylketyl and Its Dianion with Aniline*

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We found formerly that metal ketyls and dianions of benzophenone were capable of radical-anion substitution [1-4], and K-derivatives also participated in radical-anion disproportionation [5-7].

In continuation of these studies we investigated reactions between K-ketyl (**Ia**) and K-dianion (**Ib**) of benzophenone with aniline (**II**) and instead of radical-anion diphenyloxymethylation providing the corresponding substitution products we observed a condensation resulting in diphenylmethineaniline (**III**) in relatively high yield (70 and 44% respectively).

The reaction takes place in a solvating medium (in tetrahydrofuran) at room temperature and is accompanied by hydrogen liberation. As side reactions should be mentioned the reduction to benzhydrol (**IV**) and the cleavage with formation of benzoic acid (**V**).

The lower yield of the final product with dianion **Ib** rules out its presence as an intermediate form generated by disproportionation in the reaction of radical-anion **Ia** [8].

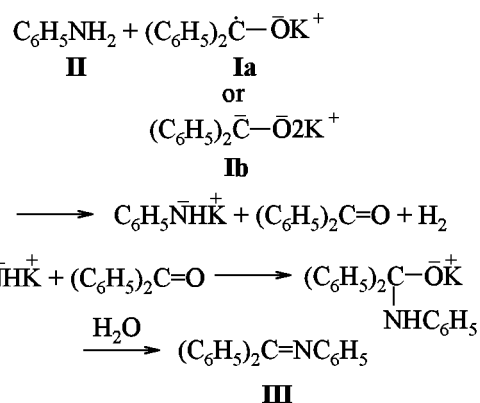
The first stage of the reaction consists in aniline metallation where aniline plays the role of NH-acid, and the benzophenone radical-anion is the base providing an active electron in one-electron transfer process [9] resulting in the observed release of hydrogen. Such transfer occurred in aniline reaction even with a less active metal, sodium [10], and also in a model reaction when we treated aniline with potassium under the conditions in question.

Radical-anions are particular bifunctional bases: firstly, as donors of weakly bound active electron [9], and secondly, as proton acceptors [11, 12]. However benzophenone-potassium ketyl hardly behaved in this system and under these conditions as proton acceptor:

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the final product of this base-acid reaction, benzohydrol (**IV**), formed in trace amounts. Moreover, this process is not characteristic even for benzophenone dianion which alongside an alkoxide basic site has a more active carbanion site.

Obviously in the key stage of C-N bond formation participate both anilide-anion and benzophenone. This is confirmed by the fact that this stage is common for the condensation mechanism of carbonyl compounds with amines catalyzed by bases [13], and by carrying out reaction of separately prepared potassium anilide with benzophenone under identical conditions and obtaining anil **III** in high yield (83%).



The discovered condensation may serve for development of a novel and sufficiently effective synthetic procedure for Schiff bases (especially with aromatic ketones and amines) that is distinguished by the use instead of weakly active ketones [14] a lot more reactive stable ketyls or dianions. The latter ensures considerably milder reaction conditions (room temperature, no catalyst) and sufficient yields of the target products.

Reaction of benzophenone-potassium ketyl (Ia) with aniline (II). To a solution of benzophenone-potassium ketyl prepared from 4.55 g (0.025 mol) of benzophenone (**I**) and 1 g (0.025 mol) of finely cut

potassium in 80 ml of anhydrous THF in a stream of purified dry nitrogen was added 4.6 g (0.05 mol) of amine **II** dissolved in 20 ml of THF. The color of the reaction mixture changed from blue to dark brown, and hydrogen evolution was observed. After 24 h water was poured to the reaction mixture, the separated yellow precipitate was filtered off. We obtained 3.5 g of diphenylmethineaniline (**III**). R_f 0.62 (TLC, Al_2O_3 of **II** activity grade, eluent benzene-hexane, 1:1, development in iodine vapor), mp 117°C (from acetone) [14]. The mixed sample with authentic diphenylmethineaniline prepared by procedure [14] melted without depression of the melting point. From the water-tetrahydrofuran mixture by extraction with ether was additionally separated 1 g of azomethine **III**, overall yield 70%. From the ether mother liquor was isolated 0.8 g (18%) of benzophenone. From the water solution after acidifying with dilute (1:1) hydrochloric acid we isolated 0.6 g (20%) of benzoic acid (**V**), mp 121°C.

Reaction of benzophenone-potassium dianion (Ib) with aniline (II). Benzophenone-potassium dianion was prepared from 4.55 g (0.025 mol) of benzophenone (**I**) and 2 g (0.05 mol) of finely cut potassium in 80 ml of anhydrous THF in a tightly stoppered flask. After complete dissolution of the metal (in two weeks) to the violet solution obtained in a stream of purified dry nitrogen was added 4.65 g (0.05 mol) of amine **II** dissolved in THF. Further work-up was carried out as described for the reaction with ketyl (**Ia**). We obtained 1.9 g (44%) of diphenylmethineaniline (**III**), 0.7 g (15%) of benzophenone (**I**), 33% of benzoic acid (**V**), and 5% of benzhydrol (**IV**).

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