

# Reactions of Aniline with Alkali Metal Diphenylketyls and Dianions Derived from Benzophenone and Michler's Ketone

D. A. Turaeva and Yu. V. Kurbatov

Alisher Navoi Samarkand State University, Universitetskii bul'var 15, Samarkand, 703004 Uzbekistan

Received March 15, 2004

**Abstract**—Potassium diphenylketyl and benzophenone dianion react with aniline to afford *N*-(diphenylmethylene)aniline. Under analogous conditions, the corresponding sodium and lithium derivatives undergo disproportionation with formation of triphenylmethanol, benzoic acid, and diphenylmethanol. The condensation of potassium and sodium bis(4-dimethylaminophenyl)ketyls and salts with Michler's ketone dianion leads to formation of *N*-[bis(4-dimethylaminophenyl)methylene]aniline, while lithium bis(4-dimethylaminophenyl)ketyl and Michler's ketone dilithium salt are reduced to bis(4-dimethylaminophenyl)methanol.

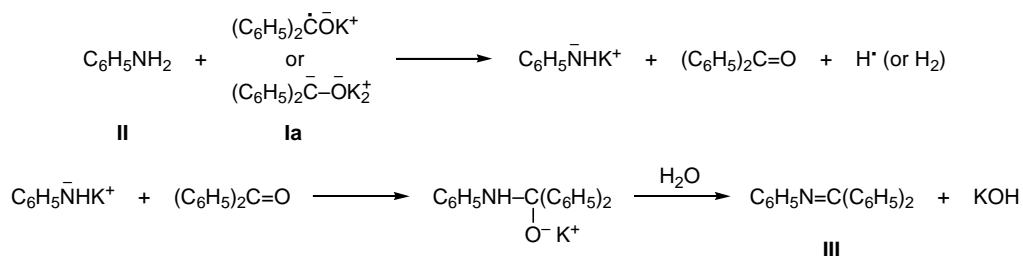
We previously found that metal diphenylketyls and metal salts with benzophenone dianion can be involved not only in radical anion diphenyloxymethylation [1] but also in reductive condensation with formation of triphenylmethane [2, 3] and that the corresponding potassium derivatives are capable of undergoing radical anion disproportionation [4]. The present work continues our studies on the reactivity of these compounds; in particular, we examined their reactions with aniline. We briefly reported in [5] that the reaction of potassium diphenylketyl (**Ia**) with aniline (**II**) leads to formation of up to 70% of *N*-(diphenylmethylene)aniline (**III**) (Scheme 1). The condensation is accompanied by cleavage of the C–C bond in **Ia** to give benzoic acid (**IV**) as by-product.

In the reactions with aniline of sodium and lithium diphenylketyls **Ib** and **Ic**, the process takes a different pathway. In the case of sodium derivative **Ib**, the main direction is disproportionation leading to triphenylmethanol (**V**) and benzoic acid (**IV**). The reaction of **Ic**

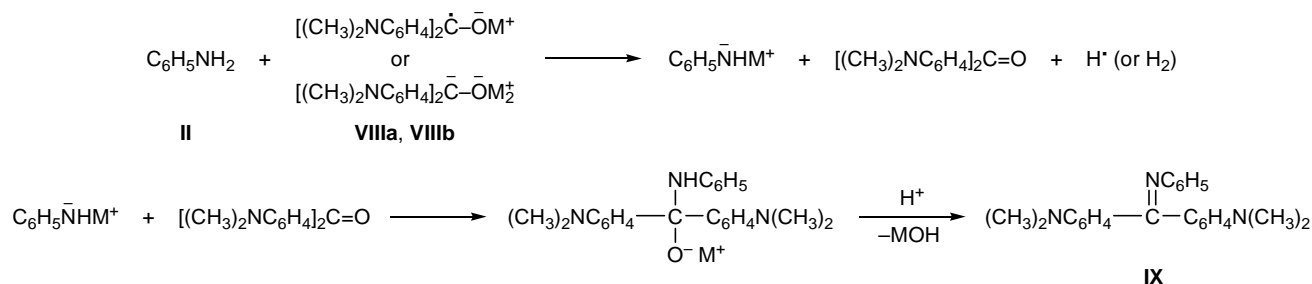
with aniline gave diphenylmethanol (**VI**), 1,2,2,2-triphenylethanone (**VII**), and benzoic acid (**IV**). Aniline (**II**) is not consumed in these reactions; presumably, it acts as a redox catalyst, for no disproportionation occurs in the absence of aniline [6]. The observed sharp differences in the reactivity of metal diphenylketyls **Ia–Ic** should originate from their structure, primarily from the fact that potassium diphenylketyl in a contact ion pair, like the metal itself, is a stronger electron donor, which favors metalation of aniline in the first stage of the condensation. By contrast, derivatives of less active metals, such as lithium and sodium, which give rise to loose (or nearly loose) ion pairs, undergo transformations other than condensation.

In order to compare the reactivities and condensation mechanisms we examined analogous reactions of benzophenone dianions with aniline (**II**). Here, the results also depended on the alkali metal nature. For example, benzophenone dipotassium salt, like potassium diphenylketyl, reacted with aniline to give Schiff

Scheme 1.



Scheme 2.



VIII, M = Na (a), K (b).

base **III** but in a lower yield (44%). This rules out participation of benzophenone dianion (as a possible reactive species formed via disproportionation) in the reaction with potassium diphenylketyl [7].

A more probable is nucleophilic condensation mechanism involving anilide ion and benzophenone as reactive species. In the first stage, acid–base interaction between the amine as an NH acid with benzophenone radical anion as a base (electron donor), following one-electron transfer pattern [8], leads to liberation of hydrogen which is observed experimentally. Analogous electron transfer occurs in the reaction of aniline even with a less active metal, sodium [9], as well as in the model reaction of aniline with potassium, which was performed under similar conditions.

Radical anions act as difunctional bases, i.e., donors of a weakly bound active electron [8] and acceptors of a proton [10, 11]. However, in the examined systems metal diphenylketyls almost do not act as proton acceptors at their alkoxide center: the final product of such acid–base interaction, diphenylmethanol (**VI**), is formed only in a small amount. Moreover, this process is not typical even of benzophenone dianion which possesses both alkoxide basic center and more active carbanionic center. In the second stage, anilide ion reacts with benzophenone to give a new C–N bond. This stage is general for base-catalyzed condensations of carbonyl compounds with amines [12]. In addition, the reaction of preliminarily prepared potassium anilide with benzophenone under analogous conditions resulted in formation of 83% of Schiff base **III**. The reactions of aniline with benzophenone disodium and dilithium salts followed a similar pattern; differences were observed only in the product yields.

Among the examined processes, the condensation of potassium diphenylketyl with aniline attracts specific attention. This reaction can be used as a basis for the development of a novel and fairly efficient procedure for the synthesis of Schiff bases, specifically

from aromatic ketones and amines. This procedure is advantageous, for it utilizes reactive stable ketyls and dianions instead of weakly reactive ketones [13]. In addition, the synthesis is performed under considerably milder conditions (room temperature, no catalyst required), and the yields of the target products are sufficiently high.

In the reactions of aniline with radical anions and dianions derived from Michler's ketone and sodium or potassium (compounds **VIIIa**, **VIIIb**), the condensation occurs more readily. As a result, the corresponding Schiff base, *N*-[bis(4-dimethylaminophenyl)methylene]aniline (**IX**) is formed in a high yield (58–70%; Scheme 2). The reaction with potassium derivative **VIIIa** is accompanied by side reduction with formation of bis(4-dimethylaminophenyl)methanol (**X**) and disproportionation to give Crystal Violet (**XI**). The latter was also formed in other reactions with potassium salts of aromatic ketone radical anions [1].

Lithium 4,4'-bis(dimethylamino)diphenylketyl and the corresponding dilithium salt turned out to be the least reactive toward aniline: in these cases, no condensation occurred. The reactions resulted in formation of a small amount (7%) of bis(4-dimethylaminophenyl)methanol (**X**). A probable reason is the low basicity of lithium 4,4'-bis(dimethylamino)diphenylketyl which is incapable of metalating aniline in the first stage of the process.

The condensation described in the present communication extends the potential for simple syntheses of Schiff bases, in particular of *N*-[bis(4-dimethylaminophenyl)methylene]aniline.

## EXPERIMENTAL

The reagents and solvents were thoroughly dried and distilled just before use. The products were identified by TLC using the following systems: Al<sub>2</sub>O<sub>3</sub>,

benzene–hexane–chloroform, 6:1:30 (A); Al<sub>2</sub>O<sub>3</sub>, chloroform (B); spots were visualized by treatment with iodine vapor.

**Reaction of potassium diphenyl ketyl (Ia) with aniline (II).** A solution of 4.6 g (50 mmol) of aniline (II) in 20 ml of THF was added to a solution of potassium diphenylketyl prepared from 4.55 g (25 mmol) of benzophenone and 1 g (0.025 mol) of potassium (cut in small pieces) in 80 ml of anhydrous THF in a stream of dry purified nitrogen. The originally blue mixture turned dark brown, and evolution of hydrogen was observed. After 24 h, the mixture was treated with water, and the precipitate was filtered off. Yield of *N*-(diphenylmethylene)aniline (III) 3.5 g; yellow crystals, mp 117°C (from acetone) [14], *R*<sub>f</sub> 0.97 (A); no depression of the melting point was observed on mixing with an authentic sample prepared by the procedure described in [13]. The filtrate was treated with diethyl ether to isolate an additional portion of Schiff base III, 1 g, mp 117°C [14]; overall yield 70%. From the ether mother liquor we isolated 0.8 g (18%) of benzophenone, mp 47°C; published data [14]: mp 48–49°C. The aqueous phase was acidified with dilute (1:1) hydrochloric acid and extracted with diethyl ether to isolate 0.6 g (20%) of benzoic acid (IV), mp 121°C [14].

**The reaction of sodium diphenylketyl (Ib) with aniline (II)** was carried out as described above for potassium derivative Ia. After addition of aniline, the reaction mixture changed from blue to black. The mixture was decomposed with water and extracted in succession with hexane and diethyl ether. From the hexane extract we obtained 7.15 g of an oily material which was treated with 10% hydrochloric acid until acid reaction and extracted with diethyl ether. Yield of triphenylmethanol (V) 1.9 g (30%), mp 158°C; published data [14]: mp 161°C. From the mother liquor we isolated 1 g (22%) of benzophenone with mp 45–47°C (48°C [14]). The acidic aqueous phase was made alkaline (pH 9) by adding potassium carbonate and was extracted with diethyl ether. Yield of aniline 4.1 g (90%), *R*<sub>f</sub> 0.82 (A). From the acidic aqueous solution we isolated 0.5 g (7%) of benzoic acid (IV) with mp 120°C [14].

**The reaction of lithium diphenylketyl (Ic) with aniline (II)** was carried out as described above for sodium derivative Ib. From the reaction mixture we isolated 18% of alcohol VI, mp 65°C (from benzene–heptane, 1:1), 90% of aniline, *R*<sub>f</sub> 0.82 (A), 10% of 1,2,2,2-tetraphenylethanone (VII), mp 185°C (186°C

[14]), 33% of benzophenone, mp 45–47°C, and 7% of benzoic acid (IV), mp 120°C.

**Reactions of benzophenone dipotassium, disodium, and dilithium salts with aniline (II).** Benzophenone salts were prepared from 4.55 g (25 mmol) of benzophenone and 50 mmol of the corresponding alkali metal (cut in small pieces) in 100 ml of THF (the mixture was kept in a hermetically closed vessel until it became homogeneous). After two weeks, a solution of 4.65 g (50 mmol) of aniline in THF was added in a stream of nitrogen to the resulting violet solution of benzophenone dipotassium salt. The mixture was then treated as described above for reactions of aniline with compounds Ia and Ib. In the reaction with benzophenone dipotassium salt we isolated 1.9 g (44%) of Schiff base III, mp 116°C, 1.8 g (39%) of aniline, *R*<sub>f</sub> 0.82 (A), 0.2 g (5%) of alcohol VI, mp 65°C, 0.7 g (15%) of benzophenone, mp 47°C, and 0.1 g (33%) of benzoic acid (IV), mp 120°C. In the reaction with benzophenone dipotassium salt we isolated 4 g (44%) of 1,2,2,2-tetraphenylethanone (VII), mp 185°C, 3.9 g (80%) of aniline, *R*<sub>f</sub> 0.82 (A); and 0.5 g (16%) of benzoic acid (IV), mp 120°C. In the reaction with benzophenone dilithium salt we isolated 2.3 g (55%) of alcohol VI, mp 95°C, 2 g (22%) of 1,2,2,2-tetraphenylethanone (VII), mp 185°C, 0.4 g (13%) of benzoic acid (IV), mp 120°C, and 4 g (90%) of aniline, *R*<sub>f</sub> 0.82 (A).

**Reaction of sodium bis(4-dimethylaminophenyl)-ketyl (VIIIa) with aniline (II).** A solution of 2.3 g (25 mmol) of aniline in 20 ml of THF was added to solution of sodium bis(4-dimethylaminophenyl)ketyl (VIIIa) prepared from 6.7 g (25 mmol) of Michler's ketone and 0.57 g (25 mmol) of sodium (cut in small pieces) in 80 ml of anhydrous THF in a stream of dry purified nitrogen. The originally blue solution turned brown, and evolution of hydrogen was observed. The mixture was treated with water, and the greenish–yellow precipitate was filtered off to obtain 4.1 g of a mixture of Michler's ketone, *R*<sub>f</sub> 0.86 (B) and *N*-[bis(4-dimethylaminophenyl)methylene]aniline (IX), *R*<sub>f</sub> 0.42 (B). A 0.5-g of this mixture was dissolved in chloroform, and the solution was applied to a column charged with aluminum oxide. The column was eluted with chloroform to isolate two fractions, orange and yellow. From the first fraction we isolated 0.4 g of *N*-[bis(4-dimethylaminophenyl)methylene]aniline (IX) as bright orange crystals with mp 185–187°C (from acetone); the product showed no depression of the melting point on mixing with an authentic sample prepared by the procedure described in [13]. Evaporation

of the second fraction gave 0.1 g of Michler's ketone. The aqueous tetrahydrofuran solution was extracted with hexane to isolate an additional amount of compound **IX**, 2.5 g; overall yield 5.0 g (70%).

**Reaction of potassium bis(4-dimethylamino-phenyl)ketyl (VIIIb) with aniline (II).** The reaction was carried out as described above for sodium derivative **VIIIa**. After addition of aniline, the originally blue solution turned brown, and vigorous evolution of hydrogen was observed. After 24 h, the mixture was treated with water and extracted in succession with hexane and benzene. Evaporation of the hexane extract gave 2.5 g of a mixture of compound **IX**,  $R_f$  0.42 (B) and bis(4-dimethylaminophenyl)methanol (**X**),  $R_f$  0.59 (B). A 0.5-g portion of this mixture was subjected to column chromatography (see the preceding procedure) to isolate 0.4 g of compound **IX**, mp 185–187°C (from acetone),  $R_f$  0.42 (B), overall yield 2.0 g (58%), 0.07 g of alcohol **X**, mp 88–90°C (published data [14]: mp 90°C), and 0.03 g of Crystal Violet (**XI**),  $R_f$  0.1 (B). From the benzene extract we isolated traces of Schiff base **IX**, overall yield 0.95 g (35%), and 0.6 g of alcohol **X**, mp 95°C; published data [14]: mp 96°C.

**The reaction of lithium bis(4-dimethylamino-phenyl)ketyl (VIIIc) with aniline (II)** was performed as described above for sodium derivative **VIIIa**. We isolated 0.2 g (2%) of alcohol **X**, mp 95°C, 5.7 g (85%) of Michler's ketone (**VIII**), mp 173°C (174°C [14]),  $R_f$  0.86 (B), and 1.9 g (87%) of aniline,  $R_f$  0.82 (B).

**Reactions of 4,4'-bis(dimethylamino)benzophenone disodium, dipotassium, and dilithium salts with aniline (II).** 4,4'-Bis(dimethylamino)benzophenone disodium, dipotassium, and dilithium salts were prepared from 2.68 g (10 mmol) of Michler's ketone (**VIII**) and 20 mmol of the corresponding alkali metal (cut in small pieces) in 100 ml of THF; the mixture was kept in a hermetically closed flask until it became homogeneous. After two weeks, a solution of 0.93 g (10 mmol) of aniline in THF was added in a stream of nitrogen to the resulting dark violet solution. The mixture was then treated as described above for the reactions of compounds **VIIIa** and **VIIIb** with aniline. In the reaction with 4,4'-bis(dimethylamino)benzophenone disodium salt, we isolated 2.58 g (30%) of compound **IX**, mp 185–187°C (from acetone),  $R_f$  0.42 (B), and 0.5 g of alcohol **X**, mp 95°C. In the reaction with

4,4'-bis(dimethylamino)benzophenone dipotassium salt, we isolated 1.1 g (37%) of Schiff base **IX**, mp 185–187°C (from acetone),  $R_f$  0.42 (B), 0.1 g (2.6%) of Crystal Violet (**XI**),  $R_f$  0.1 (B), and 0.5 g (18%) of alcohol **X**, mp 95°C. In the reaction with 4,4'-bis(dimethylamino)benzophenone dilithium salt, we isolated 0.2 g (2%) of alcohol **X**, mp 185–187°C,  $R_f$  0.42,\* 5.7 g (85%) of Michler's ketone (**VIII**), mp 173°C, and 1.9 g (87%) of aniline,  $R_f$  0.82 (B).

## REFERENCES

1. Kurbatova, A.S., Kurbatov, Yu.V., and Niyazova, D.A., *Zh. Org. Khim.*, 1990, vol. 26, p. 649.
2. Turaeva, D.A., Kurbatov, Yu.V., and Muratova, G., Book of Abstracts, *12th Int. Conf. on Organic Synthesis*, Venezia, Italy, 1998, p. 390.
3. Turaeva, D.A. and Kurbatov, Yu.V., *Russ. J. Org. Chem.*, 1999, vol. 35, p. 1092.
4. Turaeva, D.A., Kurbatova, A.S., and Kurbatov, Yu.V., Book of Abstracts, *10th IUPAC Symp. on Organometallic Chemistry Directed towards Organic Synthesis*, Versailles, France, 1999, p. 490.
5. Turaeva, D.A. and Kurbatov, Yu.V., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 1691.
6. Turaeva, D.A., *Cand. Sci. (Chem.) Dissertation*, Moscow, 1988.
7. Bachmann, V.E., *J. Am. Chem. Soc.*, 1933, vol. 55, p. 2827.
8. Okhlobystin, O.Yu., *Perenos elektrona v organicheskikh reaktsiyakh* (Electron Transfer in Organic Reactions), Rostov-on-Don: Rostov. Gos. Univ., 1974, p. 48.
9. Foerst, W., *Newer Methods of Preparative Organic Chemistry*, New York: Academic, 1963, p. 246.
10. Mendkovich, A.S. and Gul'tyai, V.P., *Teoreticheskie osnovy khimii organicheskikh anion-radikalov* (Principles of the Chemistry of Organic Radical Anions), Moscow: Nauka, 1990, p. 69.
11. Todres, Z.V., *Ion-radikaly v organicheskom sinteze* (Radical Ions in Organic Synthesis), Moscow: Khimiya, 1986, p. 20.
12. Denisov, E.T., *Kinetika gomogenykh khimicheskikh reaktsii* (Kinetics of Homogeneous Chemical Reactions), Moscow: Vysshaya Shkola, 1978, p. 127.
13. Billman, J.H. and Tai, K.M., *J. Org. Chem.*, 1958, vol. 23, p. 535.
14. *Spravochnik khimika* (Chemist's Handbook), Nikol'skii, B.P., Ed., Moscow: Khimiya, 1965, vol. 2, p. 476.

\* As in Russian original.—*Publisher*.