Reduction of p-Nitrosodiethylaniline by Means of Activated Zinc Dust and Ammonium Chloride

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Some reducing agents for preparation of *N*, *N*-diethyl-*p*-phenylenediamine from *p*-nitrosodiethylaniline have been reported, e. g., hydrochloric acid and stannous chloride[1], hydrochloric acid and zinc[2], and hydrochloric acid and iron[3]. Electrolytic reduction[4] and catalytic reduction[5] with Urushibara nickel are also favorable methods for the preparation. It has been found by the present authors that the reduction can be achieved very easily in methanol or ethanol by means of ammonium chloride and zinc dust activated with mercuric chloride. Reduction of nitrobenzene to phenylhydroxylamine with zinc dust and aqueous ammonium chloride is noted, but no application of this reducing agent in non-aqueous media has been reported. For the reduction of *p*-nitrosodiethylaniline, zinc dust and ammonium chloride are not effective either in water or in methanol or ethanol, but, by using zinc dust activated with mercuric chloride, the reduction takes place very smoothly in methanol or ethanol.

The procedure of this reaction is very simple. In a three-necked flask (500 cc.), fitted with a reflux condenser, a stirrer, and a dropping funnel, 40 g. (0.615 atom) of zinc dust and 50 g. (0.28 mole) of *p*-nitrosodiethylaniline are taken, and 300 cc. of methanol and 0.1 g. of mercuric chloride are added. The mixture is heated with stirring until *p*-nitrosodiethylaniline is completely dissolved and an active ebullition takes place. Then heating is stopped and 5 g. of ammonium chloride in 20 cc. of water is added drop by drop into the mixture. An active reaction occurs, and methanol boils owing to the heat of the reaction. Addition of the ammonium chloride solution is controlled so as to keep the methanol boiling gently without applying heat. After the addition of ammonium chloride, the mixture is again heated and refluxed until the original dark brown color turns pale yellow. The change of color indicates the completion of reduction of the nitroso compound to the amino compound. The solution is filtered, and the residue washed with 100 cc. of hot methanol. The filtrate and the washing are combined and evaporated in nitrogen. The residual dark oil is distilled under a reduced pressure to yield 35 g. (75.6 % of the theory) of *N*, *N*-diethyl-*p*-phenylenediamine boiling at 139～140°C/10 mm.Hg, or at 216.5°C/760 mm.Hg. Anal., N, 16.98%.

For a smooth reaction and a good yield, it is necessary to use purified *p*-nitrosodiethylaniline melting at 83～84°C, because resinous impurities in crude *p*-nitrosodiethylaniline decrease the yield of the reduction and mask the color change

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[1] Gattermann, "Die Praxis des Organischen Chemikers", W. de Gruyter, Berlin (1940), p. 315.

[2] G. Wurster, *Ber.*, **12**, 523, 530 (1878).

[3] **FIAT No. 1313** Vol. 1, p. 29, 175, 229 (1948).

[4] S. Kikuchi and K. Honda, *Seisan-Kenkyu*, **2**, 267 (1950).

[5] R. Uehara, unpublished data.

to indicate the end point of the reaction. *N, N*-dimethyl-*p*-phenylenediamine can be obtained from *p*-nitrosodimethylaniline in the same way.

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