CCXCIII.—*The Reduction of Nitro-compounds in Pyridine Solution.*

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The reduction of solid nitro-compounds with hydrogen sulphide or ammonium sulphide is generally carried out in alcoholic or aqueous-alcoholic solution; when, however, the nitro-compound is very sparingly soluble in these solvents the method is often unsatisfactory. This was found to be so with 2 : 4-dinitromethylaniline and as we required a considerable quantity of 4-nitro-2-aminomethylaniline in connexion with other work we investigated the reduction in other solvents. The most suitable was pyridine. A solution of the nitro-compound in this solvent with hydrogen sulphide in the presence or absence of ammonia or piperidine gave excellent yields of the reduction products.

EXPERIMENTAL.

Five methods were tried : (1) The action of hydrogen sulphide on a solution of the nitro-compound in pyridine containing a little water at 100°; (2) similar to (1), except that slightly more than the calculated amount of concentrated aqueous ammonia was added to the pyridine; (3) as in (2), the ammonia being replaced by an equivalent amount of piperidine; (4) the action of the theoretical amount of ammonium sulphide in the cold on a solution or suspension of the nitro-compound in cold pyridine; (5) as in (4), the ammonia being replaced by piperidine. The best method was found to depend on the particular nitro-compound.

2 : 4-*Dinitromethylaniline.*—Kehrmann and Messinger (*J. pr. Chem.*, 1892, **46**, 573) and Pinnow and Koch (*Ber.*, 1897, **30**, 2851) describe the reduction with alcoholic ammonium sulphide at 50°.

Methods (2) and (3) gave a better yield and a cleaner product than method (1), and methods (4) and (5) were unsatisfactory. The dinitromethylaniline (5 g.) was added to a mixture of pyridine (50 c.c.) and aqueous ammonia (5 c.c.; *d* 0·880) and the suspension was saturated with hydrogen sulphide and then warmed to 100°, a slow current of the gas being passed for 2 hours; a deep red solution was then obtained. As much of the pyridine as possible was removed on the water-bath under reduced pressure, and the residue shaken with water (100 c.c.). After some time the red solid obtained was washed with water and extracted repeatedly with small quantities of boiling 2*N*-hydrochloric acid; the extracts were concentrated to 100 c.c., cooled to 0°, and made alkaline with ammonia. The precipitated base after crystallisation from hot water gave a 60% yield of 4-nitro-2-aminomethylaniline.

2 : 5-*Dinitroaniline*, 2 : 5-*Dinitro*-p-*toluidine*, *and* 3 : 5-*Dinitro*-p-*toluidine*.—The reduction of these compounds by method (2) gave good yields of 4-nitro-*m*-phenylenediamine and 5-nitro-2 : 4-tolylenediamine, previously prepared by the nitration, followed by hydrolysis, of diacetyl-*m*-phenylenediamine (Barbaglia, *Ber.*, 1874, **7**, 1259) and of diacetyl-2 : 4-tolylenediamine (Ladenberg, *Ber.*, 1875, **8**, 211); and of 5-nitro-3 : 4-tolylenediamine, previously obtained by reduction of 3 : 5-dinitro-*p*-toluidine with alcoholic sodium sulphide (Lindemann and Krause, *J. pr. Chem.*, 1927, **115**, 256).

4 : 6-*Dinitromethyl*-m-*toluidine*.—Attempts to reduce this compound with alcoholic ammonium sulphide gave poor yields. Methods (1), (2), and (3) were unsatisfactory, but good results were obtained by methods (4) and (5). A slight excess of the calculated amount of concentrated aqueous ammonia (5 c.c.) was added to pyridine (35 c.c.), half the mixture was saturated with hydrogen sulphide, and the other half added. This solution was at once added to a solution of 4 : 6-dinitromethyl-*m*-toluidine (3 g.) in pyridine (20 c.c.), and the mixture immediately cooled in ice and vigorously stirred. After an hour the pyridine was removed in a vacuum at as low a temperature as possible, and the base purified through the hydrochloride as with 4-nitro-2-aminomethylaniline. After crystallising from hot water or dilute alcohol, 6-*nitro*-4-*aminomethyl*-m-*toluidine* was obtained in dark red needles, m. p. 180° (Found: N, 23·3. $C_8H_{11}O_2N_3$ requires N, 23·2%). The amino-group must be in the ortho-position to the methylamino-group, since on treatment with nitrous acid the compound gave 5-*nitro*-1 : 6-*dimethyl*-1 : 2 : 3-*benztriazole*, which separated from alcohol in light brown needles, m. p. 203° (Found: N, 29·3. $C_8H_8O_2N_4$ requires N, 29·2%).

m-*Dinitrobenzene and* α-*Nitronaphthalene*.—Method (1) was used.

A solution of *m*-dinitrobenzene (5 g.) in pyridine (48 c.c.) and water (2 c.c.) was heated on the water-bath and hydrogen sulphide slowly passed through during 4 hours. Removal of the pyridine as before, extraction with hydrochloric acid, neutralisation with ammonia, and extraction with ether gave, after crystallisation, a 67% yield of *m*-nitroaniline. α-Naphthylamine was obtained in a similar way from α-nitronaphthalene, but method (2) gave a better yield (76%).

2 : 4 : 6-*Trinitrotoluene.*—The reduction of 2 : 4 : 6-trinitrotoluene with hydrogen sulphide presents special difficulties owing to side reactions occurring between the trinitrotoluene and the alcohol, used as solvent, in the presence of alkalis. Under various conditions the following reduction products have been obtained : 6-nitro-2 : 4-diaminotoluene (Tiemann, *Ber.*, 1870, **3**, 217), 2 : 6-dinitro-4-aminotoluene (Holleman and Böeseken, *Rec. trav. chim.*, 1897, **16**, 425), 2 : 4-dinitro-6-aminotoluene and 2 : 6-dinitro-4-hydroxylaminotoluene (Anschütz and Zimmermann, *Ber.*, 1915, **48**, 152; Cohen and Dakin, J., 1905, **87**, 1257). It was hoped that the use of pyridine would prevent the side reactions, but this was only partly achieved.

Hydrogen sulphide was passed through a hot mixture of pyridine (25 c.c.) and piperidine (2 c.c.), and trinitrotoluene (5 g.) in pyridine (25 c.c.) added during an hour. The heating was continued, hydrogen sulphide still being passed, for a further 1½ hours. Removal of the solvent under reduced pressure, extraction with hydrochloric acid, and neutralisation of the extracts gave an orange precipitate which, after crystallisation from benzene and light petroleum, was found to be 6-nitro-2 : 4-diaminotoluene, m. p. 130—131° (Found : N, 25·2. Calc. : N, 25·1%). A further quantity was obtained by extracting the neutralised solution with ether.

A solution of piperidine (5·6 g.) in pyridine (25 c.c.) was saturated with hydrogen sulphide, cooled to 0°, and added slowly to a well-cooled solution of trinitrotoluene (5 g.) in pyridine (25 c.c.). After the mixture had been kept for 30 minutes at 0°, the product was poured into water, and the black tarry mass extracted repeatedly with boiling 2*N*-hydrochloric acid. When the extracts were made alkaline with ammonia, a precipitate was obtained which, after crystallising from benzene and light petroleum, consisted of 2 : 6-dinitro-4-aminotoluene, m. p. 171°, as shown by comparison with an authentic specimen. The yield was poor (about 20%), but was somewhat better than that obtained by the use of alcoholic ammonium sulphide.

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