CCVI.—*The Action of Nitrous Acid on 3-Nitro- and 4-Nitro-dimethylaniline and the So-called β-3 : 4-Dinitrodimethylaniline.*

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SWANN'S α- and β-modifications of 3 : 4-dinitrodimethylaniline (J., 1920, **117**, 1) have been examined. The α-form, m. p. 176°, is the actual 3 : 4-dinitrodimethylaniline. The β-form, m. p. 154°, is a mixture of 3 : 4-dinitrodimethylaniline (needles) and a small quantity of 2 : 4 : 5-trinitrodimethylaniline (rhombs) which is separable by fractional crystallisation from alcohol. Microscopic examination

reveals the two crystalline forms. The analysis for nitrogen given by Swann is not a criterion of purity, as the presence of even 10% of the trinitro-compound scarcely affects the percentage. If the preparation of the β-form is attempted at a temperature initially higher (30°) than that employed by Swann (20°), the impurity becomes 2 : 4 : 5-trinitromonomethylaniline, m. p. 199°, which is even less soluble in alcohol than 2 : 4 : 5-trinitrodimethylaniline.

Nitrous acid reacts with 3-nitrodimethylaniline to form mainly 3 : 4-dinitrodimethylaniline (compare Kauffmann and Beisswenger, *Ber.*, 1904, **37**, 2615, Anm., K., Privatmitt.) under conditions under which it acts as a nitrating agent, whereas under other conditions *N*-nitrosation takes place with displacement of a methyl group and formation of *N*-nitroso-3-nitromonomethylaniline.

Nitrous acid fails to react with 4-nitrodimethylaniline under the above conditions, but it does so with 4-nitrosodimethylaniline hydrochloride to form *N*-nitroso-4-nitromonomethylaniline.

EXPERIMENTAL.

3 : 4-Dinitrodimethylaniline (Swann's α-form, *loc. cit.*) was obtained by the action of 20% nitric acid on 3-nitrodimethylaniline and also by the following method. 3-Nitrodimethylaniline (1 g.), suspended in a solution of sodium nitrite (1 g.) in water (30 c.c.), was treated gradually (with stirring) with concentrated hydrochloric acid (5 c.c.). It slowly dissolved, and 3 : 4-dinitrodimethylaniline separated gradually in fine orange-yellow needles, m. p (after recrystallisation from alcohol) and mixed m. p. (with Swann's α-form) 176°.

When 3-nitrodimethylaniline (1 g.), dissolved in 50% aqueous hydrochloric acid (100 c.c.), was treated portionwise during 30 minutes with powdered sodium nitrite (0·6 g.), bright yellow needles of *N*-nitroso-3-nitromonomethylaniline separated, m. p. 68° (Found : N, 23·4. Calc. : N, 23·2%). Hydrolysis of the product with boiling concentrated hydrochloric acid gave 3-nitromonomethylaniline, m. p. 65° (Found : N, 18·7. Calc. : N, 18·4%).

The So-called β-3 : 4-*Dinitrodimethylaniline.*—Prepared by Swann's method, this melted at 154° after one recrystallisation from alcohol. By treatment with insufficient alcohol for complete solution, it was separated into 3 : 4-dinitrodimethylaniline, m. p. and mixed m. p. 176°, and the less soluble 2 : 4 : 5-trinitrodimethylaniline, which formed orange-red rhombs, m. p. 196° (van Romburgh, *Rec. trav. chim.*, 1887, **6**, 253, describes it as cinnabar-red crystals, m. p. 196°) (Found : N, 22·1. Calc. : N, 21·9%).

Action of Nitrous Acid on 4-*Nitrosodimethylaniline Hydrochloride.*—The hydrochloride (5 g.) was mixed with sodium nitrite (5 g.)

and treated with 10% hydrochloric acid (100 c.c.). After 2 hours the liquid was filtered; it slowly deposited yellow needles of *N*-nitroso-4-nitromonomethylaniline, m. p. 100° (Found : N, 23·3. Calc. : N, 23·2%), which on boiling with concentrated hydrochloric acid or even on crystallising from boiling alcohol were converted into yellow-brown needles, with a violet lustre, of 4-nitromonomethylaniline, m. p. 152°.

Alternatively, when a mixture of 4-nitrosodimethylaniline hydrochloride (1 g.), sodium nitrite (1 g.), concentrated hydrochloric acid (5 c.c.), and water (30 c.c.) was kept for 2 days, *N*-nitroso-4-nitromonomethylaniline separated in yellow needles, m. p. 100°.

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