202. *The Four Dinitrodimethyl-*p*-anisidines.*

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2 : 6- and 3 : 5-*Dinitrodimethyl-*p*-anisidine* are easily obtained by direct dinitration of dimethyl-*p*-anisidine in concentrated and in moderately dilute sulphuric acid respectively. The former has been synthesised from 2 : 6-dinitro-*p*-anisidine, and the latter from 4-*chloro*-3 : 5-*dinitroanisole*.

2 : 5-*Dinitrodimethyl*-p-*anisidine* is produced by the action of nitrous acid on 2-nitrodimethyl-*p*-anisidine and by the dimethylation of 2 : 5-dinitro-*p*-anisidine.

2 : 3- and 2 : 5-Dinitrodimethyl-*p*-anisidine are formed in the ratio of about 4 : 1 during the nitration of 3-nitrodimethyl-*p*-anisidine in concentrated sulphuric acid. The constitution of the former follows from its reduction to 2 : 3-*diaminodimethyl*-p-*anisidine*, which is then condensed with benzil.

Solutions of all four dinitro-compounds in hydrochloric acid, light petroleum, carbon tetrachloride, and non-ionising solvents generally, are yellow, whereas those in alcohol and in phenol are deep red. The dinitro-compounds do not form picrates (contrast the mononitrodimethyl-*p*-anisidines; Hodgson and Crook, J., 1932, 1814).

When 3 : 5-dinitrodimethyl-*p*-anisidine is heated with a mixture of dilute nitric acid and sodium nitrite, or when 3-nitrodimethyl-*p*-anisidine is too violently nitrated, one methyl group is expelled and colourless 3 : 5-*dinitro*-N-*nitrosomethyl*-p-*anisidine* is formed. Removal of the nitroso-group from this compound gives 3 : 5-*dinitromonomethyl*-p-*anisidine*, which has also been prepared by the action of methylamine on 4-chloro-3 : 5-dinitroanisole.

Experimental.

2 : 3-*Dinitrodimethyl*-p-*anisidine*.—3-Nitrodimethyl-*p*-anisidine (5 g.), dissolved in concentrated sulphuric acid (20 c.c.), was nitrated with a mixture of 5 c.c. of nitric acid (*d* 1·5) and 15 c.c. of concentrated sulphuric acid at 0—5°; after 10 minutes, the whole was poured on ice, the resulting solution just neutralised with aqueous sodium hydroxide, and the precipitate (4 g., mainly 2 : 3-*dinitrodimethyl*-p-*anisidine*) immediately filtered off, washed, dissolved in concentrated hydrochloric acid, and fractionally precipitated with water. The earlier fractions, consisting of the 2 : 3-dinitro-compound, crystallised from carbon tetrachloride in long, slender, scarlet parallelepipeds, m. p. 130° (Found : N, 17·6. $C_9H_{11}O_5N_3$ requires N, 17·4%), almost insoluble in cold water and sparingly soluble in hot water and in light petroleum.

The filtrate from the neutralised nitration mixture slowly deposited 2 : 5-*dinitrodimethyl*-p-*anisidine* (1 g.), which crystallised from alcohol in very deep red plates, m. p. and mixed m. p. with an authentic specimen (below) 137° (Found : N, 17·5%).

5-*Dimethylamino*-8-*methoxy*-2 : 3-*diphenylquinoxaline*.—2 : 3-Dinitrodimethyl-*p*-anisidine (0·5 g.) was dissolved in acetic acid (6 c.c.) and heated with zinc (1 g.) and concentrated hydrochloric acid (1 c.c.) for 15 minutes on the water-bath, and the filtered solution was then similarly heated for 3 hours with benzil (0·5 g.) in acetic acid (6 c.c.). The product was precipitated by water, redissolved in concentrated hydrochloric acid to remove benzil, reprecipitated by water, and crystallised from aqueous alcohol, giving pale yellow needles, m. p. 233° (decomp.) (Found : C, 77·5; H, 5·6; N, 12·0. $C_{23}H_{21}ON_3$ requires C, 77·7; H, 5·9; N, 11·8%).

2 : 5-*Dinitrodimethyl*-p-*anisidine*.—(*a*) A solution of 2-nitrodimethyl-*p*-anisidine (5 g.) in concentrated sulphuric acid (5 c.c.) and water (15 c.c.) was treated with one of nitric acid (10 c.c.; *d* 1·4) and water (15 c.c.) at room temperature (the reaction being very slow between 0° and 15°), the mixture, after being kept for 15 minutes at 20°, was made alkaline with aqueous sodium hydroxide, and the precipitate of the 2 : 5-dinitro-compound was washed and crystallised thrice from alcohol, giving large, very deep red plates with a greenish lustre, m. p. 137° (Found : N, 17·5%). This compound is more soluble in hot water and dilute acids than the 2 : 3-isomeride.

(*b*) 2-Nitrodimethyl-*p*-anisidine (5 g.) was nitrated with nitrous acid (Hodgson and Kershaw, J., 1930, 279), the yield of 2 : 5-dinitrodimethyl-*p*-anisidine being practically quantitative.

(*c*) 2 : 5-Dinitro-*p*-anisidine (5 g.) and methyl sulphate (20 c.c.) were heated at 160—165° for 15 minutes, the mixture cooled and made alkaline with aqueous sodium hydroxide, and the precipitate of 2 : 5-dinitrodimethyl-*p*-anisidine washed and crystallised from alcohol; deep red plates, m. p. and mixed m. p.'s with the products from (*a*) and (*b*) 137° (Found : N, 17·5%).

2 : 6-*Dinitrodimethyl*-p-*anisidine*.—(*a*) Dimethyl-*p*-anisidine (4 g.), dissolved in concentrated sulphuric acid (20 c.c.), was treated gradually with nitric acid (2·2 c.c.; *d* 1·5) in concentrated sulphuric acid (20 c.c.) at 0—5°, the mixture being immediately poured on ice and made alkaline with sodium hydroxide, and the precipitated 2 : 6-*dinitro*-derivative (6 g.) washed and crystallised from alcohol; long yellow needles, m. p. 151°, were obtained (Found : N, 17·5. $C_9H_{11}O_5N_3$ requires N, 17·4%).

(*b*) Better than Meldola and Stevens's method (J., 1905, **87**, 1204) of preparing 2 : 6-dinitro-*p*-anisidine is the initial preparation of 2 : 6-dinitro-*p*-acetamidoanisole (Reverdin and Bucky,

Ber., **1906**, **39**, 2690) and its subsequent hydrolysis. The anisidine, dimethylated as in (*c*) above, gave long yellow needles, m. p. and mixed m. p. with the product from (*a*) 151° (Found: N, 17·6%).

3 : 5-*Dinitrodimethyl*-p-*anisidine*.—(*a*) Dimethyl-*p*-anisidine (1·5 g.), dissolved in concentrated sulphuric acid (7 c.c.) and water (15 c.c.), was treated gradually at 0—5° with nitric acid (5 c.c.; *d* 1·4) in water (10 c.c.); the mixture was kept for 30 minutes in ice-water and then allowed to attain room temperature slowly. The precipitate (1·5 g.) which separated was steam-distilled; **3 : 5-*dinitrodimethyl*-p-*anisidine*** (0·5 g.), which passed over, crystallised from alcohol in very long, orange-yellow needles, m. p. **90°** (Found: N, 17·5. $C_9H_{11}O_5N_3$ requires N, 17·4%). The flask liquor, on cooling, deposited non-steam-volatile **3 : 5-*dinitro*-N-*nitrosomethyl*-p-*anisidine*** (0·3 g.), which crystallised from water, alcohol, carbon tetrachloride, or light petroleum in almost colourless needles, m. p. 113° (Found: N, 22·1. $C_8H_8O_6N_4$ requires N, 21·9%), and gave Liebermann's nitrosoamine reaction (green ⟶ red ⟶ blue).

When the nitration was carried out in a more concentrated mixed acid, or when the temperature was allowed to rise, the reaction became violent and only the *N*-nitroso-compound was formed.

(*b*) **3 : 5-Dinitro-*p*-toluenesulphonyl-*p*-anisidine** (Reverdin, *Ber.*, **1909**, **42**, 1524) was hydrolysed by treatment with concentrated sulphuric acid at 30°, and the product isolated and converted by the Sandmeyer reaction into **4-*chloro*-3 : 5-*dinitroanisole***, which crystallised from alcohol in pale yellow, hexagonal plates, m. p. 123° (Found: N, 12·2; Cl, 15·1. $C_7H_5O_5N_2Cl$ requires N, 12·0; Cl, 15·3%). This product (4 g.) was refluxed for 4 hours on the water-bath with dimethylamine (5 g.) in alcohol (20 c.c.); **3 : 5-dinitrodimethyl-*p*-anisidine**, isolated by steam distillation, crystallised from alcohol in long orange-yellow needles, m. p. and mixed m. p. with (*a*) 90° (Found: N, 17·6%).

Removal of the Nitroso-group from **3 : 5-*Dinitro*-N-*nitrosomethyl*-p-*anisidine*.**—This was effected by treatment with urea and sulphuric acid (Macmillan and Reade, J., 1929, 586); the **3 : 5-*dinitromonomethyl*-p-*anisidine*** formed was slowly volatile in steam, and crystallised from alcohol in brilliant crimson needles, m. p. 130° (Found: N, 18·7. $C_8H_9O_5N_3$ requires N, 18·5%), identical with a synthetic preparation obtained by refluxing together for 4 hours on the water-bath a mixture of 4-chloro-3 : 5-dinitroanisole (4 g.), methylamine hydrochloride (6 g.), and sodium acetate (5 g.), cooling the mixture, precipitating the product with water, dissolving the amine portion thereof in concentrated hydrochloric acid, reprecipitating it from the filtered solution by water, and crystallising it as described above (Found: N, 18·6%).

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