17. *The Tetrazotisation of* 1 : 5- *and* 1 : 8-*Naphthylenediamines and the Tetranitration of* 1 : 5- *and* 1 : 8-*Di*-p-*toluenesulphonamidonaphthalenes.*

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1 : 8-Naphthylenediamine is tetrazotised completely by the nitrosylsulphuric–glacial acetic acid method. 1 : 5- and 1 : 8-Di-*p*-toluenesulphonamidonaphthalenes are readily tetranitrated by nitric acid in acetic acid solution.

Whereas the tetrazotisation of 1 : 5-naphthylenediamine proceeds normally by the direct method, the process referred to in Beilstein XIII, p. 205, where sodium nitrite in concentrated hydrochloric acid is employed, is most unsatisfactory. The nitrosylsulphuric–glacial acetic acid method of Hodgson and Walker (*J.*, 1933, 1620), however, efficiently tetrazotised 1 : 8-naphthylenediamine as shown by the subsequent Sandmeyer reactions which afforded satisfactory yields of 1 : 8-dichloro-, 1 : 8-dibromo-, and 1 : 8-di-iodo-naphthalenes.

The remarkable facilitation of dinitration by the toluenesulphonamido-group (cf. Bell, *J.*, 1928, 2771; 1931, 2338; Hodgson and Walker, *J.*, 1934, 180) is further exemplified and amplified in the di-*p*-toluenesulphonyl derivatives of 1 : 5- and 1 : 8-naphthylenediamines, which are readily tetranitrated in nitric acid–glacial acetic acid solution. The ease of tetranitration is noteworthy and is the first example of its kind. The resulting tetranitro-compounds are readily hydrolysed by concentrated sulphuric acid to 2 : 4 : 6 : 8-*tetranitro*-1 : 5- and 2 : 4 : 5 : 7-*tetranitro*-1 : 8-*naphthylenediamines*.

The 1 : 5- and 1 : 8-dihalogeno-compounds mentioned in the experimental part have been prepared for the first time from the diamines, with the exception of 1 : 8-dichloronaphthalene, for which the recorded method of preparation in Beilstein (*loc. cit.*) is very unsatisfactory.

Experimental.

Tetrazotisation of 1 : 5-*Naphthylenediamine*.—A partial suspension of the diamine (6 g.) in sulphuric acid (10 c.c., *d* 1·84) and water (150 c.c.) was treated at 0° with one of sodium nitrite (6 g.) in water (50 c.c.), and after complete tetrazotisation had taken place urea (1 g.) was added to remove excess of nitrous acid. The filtered solution was divided into three equal parts which were added severally to solutions of (*a*) cuprous chloride (5 g.) in hydrochloric acid (150 c.c., *d* 1·18), (*b*) cuprous bromide (5 g.) in hydrobromic acid (75 c.c., *d* 1·7) and water (75 c.c.), and (*c*) potassium iodide (10 g.) in water (100 c.c.). The products isolated were from (*a*) 1 : 5-dichloronaphthalene (1·8 g.), from (*b*) 1 : 5-dibromonaphthalene (1·8 g.), and from (*c*) 1 : 5-*di-iodonaphthalene* (2·4 g.), which crystallised from glacial acetic acid in pale fawn needles, m. p. 147° (Found : I, 67·0. $C_{10}H_6I_2$ requires I, 66·8%).

Tetrazotisation of 1 : 8-*Naphthylenediamine*.—A solution of the diamine (6 g.) in glacial acetic acid (50 c.c.) was stirred at 0° into a solution of sodium nitrite (6 g.) in sulphuric acid (50 c.c., *d* 1·84). After 1 hour the mixture was poured into water (50 c.c.) and mixed with chopped ice (50 g.), and urea (1 g.) was added to remove excess of nitrous acid. The solution was filtered, divided into three equal parts, and treated exactly as for tetrazotised 1 : 5-naphthylenediamine. From (*a*), (*b*), and (*c*) were obtained 1 : 8-dichloronaphthalene (1 g.), 1 : 8-dibromonaphthalene (1·5 g.), and 1 : 8-di-iodonaphthalene (1·8 g.) respectively.

Coupling of Tetrazotised 1 : 5-*Naphthylenediamine*.—The diamine (4 g.) was tetrazotised as above, and the solution after neutralisation with calcium carbonate and filtration was divided into 2 equal parts, which were stirred respectively into (*a*) a solution of β-naphthol (4 g.) in water (100 c.c.) containing sodium hydroxide (3 g.), and (*b*) a solution of β-naphthylamine (4 g.) in ethyl alcohol (100 c.c.) and pyridine (50 c.c.) to which sodium acetate (2 g.) in water (20 c.c.) was subsequently added. From (*a*), 1 : 5-*naphthalenebisazo-β-naphthol* separated in almost quantitative yield and crystallised from nitrobenzene in dark red needles, m. p. > 300° (Found : N, 12·3. $C_{30}H_{20}O_2N_4$ requires N, 12·0%), which gave a deep blue colour with concentrated sulphuric acid; from (*b*), 1 : 5-*naphthalenebisazo-β-naphthylamine* was precipitated in almost quantitative amount and crystallised from nitrobenzene in scarlet plates with a green fluorescence, m. p. 284° (Found : N, 18·4. $C_{30}H_{22}N_6$ requires N, 18·0%), which gave a brilliant dark green colour with concentrated sulphuric acid.

Nitration of 1 : 5-*Di*-m-*nitrobenzenesulphonamido- and* 1 : 5-*Di*-p-*toluenesulphonamido-naphthalene*.—The sulphonamide (10 g.) in glacial acetic acid (100 c.c.) was treated dropwise below 45° with a solution of nitric acid (6·5 g., *d* 1·42; 20% excess) in glacial acetic acid (10 c.c.) containing sodium nitrite (0·1 g.). An induction period of *ca.* 2—10 minutes was observed, when the sodium nitrite was omitted, before crystallisation of the tetranitrated products from the solution began; the product was separated (yield *ca.* 8 g.) and then recrystallised from solution in pyridine by careful addition of water. The 2 : 4 : 6 : 8-*tetranitro*-1 : 5-*di*-m-*nitrobenzenesulphonamide* separated from aqueous pyridine in yellow needles, m. p. 263° (decomp.; darkened at 250°) (Found : N, 16·1. $C_{22}H_{12}O_{16}N_8S_2$ requires N, 15·8%). The 2 : 4 : 6 : 8-*tetranitro*-1 : 5-*di*-p-*toluenesulphonamide* separated in yellow needles from aqueous pyridine or better from glacial acetic acid in which it is only moderately soluble, m. p. 257° (decomp.; darkened at 224°) (Found : N, 13·3. $C_{24}H_{18}O_{12}N_6S_2$ requires N, 13·0%).

Nitration of 1 : 8-*Di*-p-*toluenesulphonamidonaphthalene*.—The sulphonamide (10 g.) in glacial acetic acid (50 c.c.) was cautiously nitrated by the dropwise addition of nitric acid (6·5 c.c., *d* 1·42) in glacial acetic acid (6·5 c.c.) containing sodium nitrite (0·1 g.) below 45°. The nitration mixture was kept cool externally by ice for 2 hours, after which the separated 2 : 4 : 5 : 7-*tetranitro*-1 : 8-*di*-p-*toluenesulphonamide* (7·5 g.) was removed and dried; it crystallised from glacial acetic acid, in which it is very soluble, in large yellow rhombs, m. p. 194° (decomp.) (Found : N, 13·3. $C_{24}H_{18}O_{12}N_6S_2$ requires N, 13·0%).

The above tetranitro-1 : 5- and -1 : 8-di-*p*-toluenesulphonamides were readily hydrolysed by intimate admixture with sulphuric acid (100 c.c., *d* 1·84) at 20° and subsequent heating in the water-bath at 45° for 1 hour, after which the mixture was poured on ice and the precipitate of the tetranitronaphthylenediamine removed and dried. 2 : 4 : 6 : 8-*Tetranitro*-1 : 5-*naphthylenediamine* crystallised from nitrobenzene in red plates and from phenol in red pyramids, m. p. 295° (with explosive decomp.) (Found : N, 25·2. $C_{10}H_6O_8N_6$ requires N, 24·85%). 2 : 4 : 5 : 7-*Tetranitro*-1 : 8-*naphthylenediamine* crystallised from nitrobenzene in orange plates, m. p. 260° (decomp.) (Found : N, 25·2%). 4 : 6 : 7 : 9-*Tetranitrodimethyldihydroperimidine* separated from acetone in orange-yellow plates, m. p. 280° (decomp.) (Found : N, 22·5. $C_{13}H_{10}O_8N_6$ requires N, 22·2%).

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