164. *Some Derivatives of 5-Nitro-2-naphthylamine with a Note on its Preparation.*

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From a review of existing methods, it would appear that the most serviceable method for the preparation of 5-nitro-2-naphthylamine is the reduction of 1 : 6-dinitronaphthalene by alkaline hydrosulphide. 5-Nitro-*m*-nitrobenzenesulphon-2-naphthalide is nitrated further only by excess of nitric acid (*d* 1·5) to give 1 : 5-dinitro-*m*-nitrobenzenesulphon-2-naphthalide, a compound which monobrominates, probably to 3-bromo-1 : 5-dinitro-*m*-nitrobenzenesulphon-2-naphthalide. The 2-bromo-5-nitronaphthalene now described completes the set of bromonitronaphthalenes.

Of the methods extant for the preparation of 5-nitro-2-naphthylamine, several involve the simultaneous production of the isomeric 8-nitro-2-naphthylamine. For example, the procedures described by Friedländer and Szymanski (*Ber.*, 1892, **25**, 2076), Morgan and Chazan (*J. Soc. Chem. Ind.*, 1922, **41**, 1T, 61T), and Morgan and Jones (*ibid.*, 1923, **42**, 341T) are based on the addition of β-naphthylamine nitrate to concentrated sulphuric acid at $< -5°$, with the subsequent tedious separation of the two bases by fractional crystallisation of their hydrochlorides, sulphates, or oxalates. The solubilities, however, of the free bases or their salts in various solvents are so similar, that separation is difficult. The proportions in which the isomerides occur are difficult to determine, since the diagram of the mixed m. p.s is indefinite over a wide range, but from the experimental fact that 5-nitro-2-naphthylamine is relatively much easier to obtain in greater yield and higher purity than the 8-nitro-isomeride, it would appear to preponderate in the mixture.

Hodgson and Crook's method (*J.*, 1936, 1844), which depends on the nitration of phthalo-β-naphthylimide, is superior from the manipulative point of view, since the higher temperature employed enables more rapid nitration, and a method of hydrolysis of the mixed phthalo-5- and -8-nitronaphthylimides by ethanol–hydrochloric acid (cf. Hey and Lawton, *J.*, 1940, 381) is now described, as an alternative to that by aqueous ammonia under pressure.

It is concluded that the most serviceable method for the preparation of pure 5-nitro-2-naphthylamine in good yield involves the deamination of 1 : 6-dinitro-2-naphthylamine (Hodgson and Turner, *J.*, 1943, 318), and the reduction of 6-nitro-group of the 1 : 6-nitronaphthalene by the aqueous sodium sulphide–sodium hydrogen carbonate–methanol procedure of Hodgson and Birtwell (*J.*, 1944, 75) (cf. also, improvements by Hodgson and Ward, *J.*, 1945, 590, 663, 794; 1948, 242).

The 2-bromo-5-nitronaphthalene, prepared from the 5-nitro-2-naphthylamine by the Sandmeyer reaction, together with the 1-bromo-7-nitronaphthalene (Hodgson and Dean, *J.*, 1950, 818) complete the set of bromonitronaphthalenes.

The further nitration of 5-nitro-*m*-nitrobenzenesulphon-2-naphthalide gives 1 : 5-dinitro-*m*-nitrobenzenesulphon-2-naphthalide, independently of whether the calculated amount or an excess of nitric acid (*d* 1·5) is used, whereas (cf. p. 820) the action of excess of nitric acid (*d* 1·5) on 7-nitro-*m*-nitrobenzenesulphon-2-naphthalide is to give 1 : 5(?) : 7-trinitro-*m*-nitrobenzenesulphon-2-naphthalide. The 1 : 5-dinitro-compound gives a monobromo-derivative to which the structure 3-bromo-1 : 5-dinitro-*m*-nitrobenzenesulphon-2-naphthalide is assigned by analogy with the results of Consden and Kenyon (*J.*, 1935, 1595).

EXPERIMENTAL.

Acid Hydrolysis of the Mixture of Phthalo-5- and -8-nitro-2-naphthylimides.—The mixture (95 g.) was heated under reflux with ethanol (750 c.c.) and hydrochloric acid (225 c.c.; *d* 1·2) for 8 hours, a further quantity of hydrochloric acid (20 c.c.) being added at hourly intervals. At the end of this period, a considerable amount of an orange solid was undissolved; it was filtered off and again heated under reflux as before for 8 hours, but even then an appreciable amount still remained undissolved. The two filtrates were combined, cooled, and stirred into iced water, and the mixture of bases precipitated by ammonia (32 g.; m. p. 70—80°) and dried. Ethanol–sulphuric acid attacked the mixed phthalimides more rapidly, but side reactions led to a decreased yield of the mixed bases.

5-*Nitro*-m-*nitrobenzenesulphon*-2-*naphthalide*.—5-Nitro-2-naphthylamine (10 g.) and *m*-nitrobenzenesulphonyl chloride (15 g.) were intimately ground together in a mortar, the mixture heated under reflux for 3 hours with pyridine (30 c.c.), and the solution cooled to 0° and stirred into iced 15% hydrochloric acid (200 c.c.). The resulting *naphthalide* was dissolved in boiling 70% acetic acid (charcoal), and the filtered solution allowed to crystallise (16·2 g.; 81·6%); it recrystallised from hot glacial acetic acid in brown micro-crystals, m. p. 171° (Found: N, 11·4. $C_{16}H_{11}O_6N_3S$ requires N, 11·2%).

Mononitration of 5-*Nitro*-m-*nitrobenzenesulphon*-2-*naphthalide*.—The powdered compound (5 g.) was boiled with glacial acetic acid (25 c.c.), the temperature allowed to fall to 50°, and a crystal of sodium nitrite added followed by the dropwise addition with stirring of 2 c.c. of a solution of nitric acid (5·6 c.c.; *d* 1·5) in glacial acetic acid (14·4 c.c.); the temperature rose to 60°, after which it was raised to 75° for 5 minutes, and the mixture kept for 5 hours at room temperature. Glacial acetic acid (20 c.c.) was then added, and the precipitate (5 g.) filtered off, washed with glacial acetic acid and ether, and dried at 100°. The 1 : 5-*dinitro*-m-*nitrobenzenesulphon*-2-*naphthalide* crystallised from glacial acetic acid in pale yellow needles, m. p. 216° (Found: N, 13·6. $C_{16}H_{10}O_8N_4S$ requires N, 13·4%). Excess of nitric acid (*d* 1·5) afforded the same product. This compound (1 g.) was hydrolysed by sulphuric acid (*d* 1·84) at 50° for 15 minutes and gave 1 : 5-dinitro-2-naphthylamine, which crystallised from glacial acetic acid in golden brown needles, m. p. 193° (Bell, *J.*, 1929, 2784, gives m. p. 191°), and, when diazotised by Hodgson and Walker's method (*J.*, 1933, 1620) and subsequently treated by the cuprous oxide–methanol procedure (cf. Hodgson and Turner, *J.*, 1942, 748; 1943, 86), it gave 1 : 5-dinitronaphthalene which crystallised from ethylene dichloride in yellow plates, m. p. and mixed m. p. with an authentic specimen, 216°.

Reaction of 1 : 5-*Dinitro*-m-*nitrobenzenesulphon*-2-*naphthalide with Bromine*.—A solution of the naphthalide (5 g.) in pyridine (15 c.c.) was stirred and bromine (0·6 c.c.) added dropwise below 20°, the mixture kept overnight, then cooled to 5° and stirred into iced 15% hydrochloric acid (100 c.c.). The reddish-brown precipitate (5 g.) of 3-*bromo*-1 : 5-*dinitro*-m-*nitrobenzenesulphon*-2-*naphthalide* was washed with water and dried at 100°; it crystallised from glacial acetic acid in golden-yellow micro-needles, m. p. 234° (Found: N, 11·5; Br, 16·0. $C_{16}H_9O_8N_4BrS$ requires N, 11·3; Br, 16·1%).

2-*Bromo*-5-*nitronaphthalene*.—A solution of 5-nitro-2-naphthylamine (2 g.) in sulphuric acid (5 c.c.; *d* 1·84) at 10° was stirred with one of sodium nitrite (1 g.) in sulphuric acid (5 c.c.; *d* 1·84) at <20°, and, when diazotisation was complete, the mixture was stirred into a solution of cuprous bromide (2·5 g.) in hydrobromic acid (25 c.c.; *d* 1·7). After reaction had ceased the mixture was poured into iced water, the precipitate of 2-*bromo*-5-*nitronaphthalene* filtered off, washed with water, 2% aqueous sodium carbonate, and water, and dried at 40°. It crystallised from ethanol (charcoal) in light brown rods, m. p. 98—99° (Found: N, 5·6; Br, 31·6. $C_{10}H_6O_2NBr$ requires N, 5·5; Br, 31·7%).

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