85. *The Monoreduction of Dinitronaphthalenes in Acid Solution and of* 1 : 5- *and* 1 : 6-*Dinitronaphthalene by Aqueous Sodium Sulphide.*

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Improvements in the methods for the monoreduction of dinitronaphthalenes in acid and in alkaline environment are described.

A solution of stannous chloride in glacial acetic acid–hydrogen chloride can be advantageously used for the monoreduction of the α-nitro-group in αβ-dinitronaphthalenes. 1 : 6-Dinitronaphthalene is thus much more efficiently reduced to 6-nitro-1-naphthylamine than by Vĕsely and Dvorăk's process (*Bull. Soc. chim.*, 1923, **33**, 319). From 1 : 3-dinitronaphthalene, a mixture of 3-nitro-1- and 4-nitro-2-naphthylamine is obtained, the former greatly predominating (cf. Vĕselý and Dvorăk, *loc. cit.*). 1 : 5- and 1 : 8-Dinitronaphthalenes, however, are reduced to the corresponding diamines whether an excess or a deficit of the reducing agent is used. Aqueous sodium sulphide reduces 1 : 6-dinitronaphthalene to 5-nitro-2-naphthylamine and 1 : 5-dinitronaphthalene to 5-nitro-1-naphthylamine.

Experimental.

Preparation of the Reducing Agent.—A current of hydrogen chloride was passed through stannous chloride crystals (64 g.) in hot glacial acetic acid (140 c.c.) and continued while the clear solution was cooled to 0°. This then contained the correct amount of reducing agent for 20 g. of a dinitronaphthalene.

Monoreduction of 1 : 6-*Dinitronaphthalene.*—A solution of the compound (20 g.) in hot glacial acetic acid (160 c.c.) was rapidly chilled, and the fine suspension treated during 45 minutes below 30° with the reducing agent; stirring was continued for 2 hours, and the mixture kept overnight. The pasty product was mixed with water (20 c.c.), heated to 60—70°, and distilled at 65° under reduced pressure to remove most of the acetic acid, the 6-nitro-1-naphthylamine stannichloride washed out with water (150 c.c.) and basified below 25° with 20% aqueous sodium hydroxide (450—550 c.c.), and the orange-red mixture of 6-nitro-1-naphthylamine and unchanged 1 : 6-dinitronaphthalene washed with water and dried in a vacuum. The small quantity of 1 : 6-naphthylenediamine also formed remained in the filtrate from the basification mixture and was extracted therefrom by chloroform. The orange-red precipitate was worked up either (*a*) by three extractions (300, 100, and 50 c.c.) with boiling ether, and passage of hydrogen chloride through the extract to precipitate 6-nitro-1-naphthylamine hydrochloride (10·5—11 g.), the unchanged 1 : 6-dinitronaphthalene (6 g.) being recovered from the ether-insoluble residue and the filtrate; or (*b*) by repeated extraction with boiling 10% hydrochloric acid until the extract gave no precipitate on addition of ammonia, the combined extracts being then basified with ammonia at 0°. Yield of 6-nitro-1-naphthylamine by (*a*) or (*b*), *ca.* 7·2 g. (*ca.* 60%); it crystallised from chloroform in bright orange-red needles, and from aqueous alcohol in deep red needles, m. p. 167·5° (Found : N, 15·0. Calc. : N, 14·9%).

Reduction of 1 : 3-*Dinitronaphthalene.*—The crude basified mixture of 3-nitro-1- and 4-nitro-2-naphthylamine obtained from 1 : 3-dinitronaphthalene (20 g.) was ether-extracted (500 c.c.), and on passage of hydrogen chloride the extract afforded a precipitate of mixed hydrochlorides (11·9 g.); the filtrate therefrom yielded 1 : 3-dinitronaphthalene

(4·1 g.). After basification, the mixed nitroamines (7·6 g.) were dissolved in hot hydrochloric acid (50 c.c. of acid, *d* 1·16, and 320 c.c. of water), the solution boiled with charcoal for a few minutes and filtered, the filtrate chilled in ice, and the crystalline precipitate of 3-nitro-1-naphthylamine hydrochloride removed and basified to give almost pure 3-nitro-1-naphthylamine (5·85 g., m. p. 131°), which had m. p. 137° after crystallisation from dilute alcohol. The acid filtrate on basification yielded the remainder of the mixed amines (1·75 g., m. p. 75°).

Improved Monoreduction of 1 : 5-*Dinitronaphthalene by Sodium Sulphide.*—Finely powdered 1 : 5-dinitronaphthalene (25 g.), wetted with alcohol (10 c.c.) (it tends to float on water), was stirred with hot water (450 c.c.), and then treated at 95° during 15 minutes with a solution of crystallised sodium sulphide (27·5 g.) in water (50 c.c.) (Hodgson and Walker, J., 1933, 1346). The water-washed residue of 5-nitro-1-naphthylamine was repeatedly extracted with hot 7% hydrochloric acid (total, 3 l.), and the extract basified at 0° with ammonia to give 5-nitro-1-naphthylamine (13 g., 60·5% yield; Hodgson and Walker, *loc. cit.*, give 36%), which crystallised from ligroin in red needles, m. p. 119°.

Monoreduction of 1 : 6-*Dinitronaphthalene by Sodium Sulphide.*—1 : 6-Dinitronaphthalene (3 g.), suspended in a boiling mixture of alcohol (20 c.c.) and water (15 c.c.), was treated with a solution of crystallised sodium sulphide (5·25 g.; 1·6 g.-mol. per g.-mol. of nitro-compound) in the minimum amount of water; after 30 minutes' refluxing, 5-nitro-2-naphthylamine (1·7 g.) separated on cooling; it crystallised from hot aqueous alcohol in small red needles, m. p. and mixed m. p. with an authentic specimen, 146° (Hodgson and Crook, J., 1936, 1844, give m. p. 145—146°) (Found : N, 15·0. Calc. : N, 14·9%).

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