30. *The Monoreduction of* 1 : 3-*Dinitronaphthalene and the Separation of* 3-*Nitro*-1-*naphthylamine and* 4-*Nitro*-2-*naphthylamine.*

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The monoreduction of 1 : 3-dinitronaphthalene by sodium sulphide is described, and a new technique devised for the separation of the resulting mixture of 3-nitro-1-naphthylamine and 4-nitro-2-naphthylamine based on their different rates of acetylation. Some reactions of the very stable 3-nitronaphthalene-1-diazonium chloride are recorded.

THE preparation of 3-nitro-1-naphthylamine and of 4-nitro-2-naphthylamine was first accomplished by Vesely and Dvorăk (*Bull. Soc. chim.*, 1923, **33**, 319), who monoreduced 1 : 3-dinitronaphthalene, (*a*) by hydrogen sulphide passed into an alcoholic ammonia suspension, and (*b*) by alcoholic stannous chloride. Procedure (*a*) has now been found to give yields of the mixed amines which never exceed 60%, and Vesely and Dvorăk's separation procedure not only is tedious but affords 4-nitro-2-naphthylamine in amount only sufficient for its identification.

The present study of the sodium sulphide monoreduction of 1 : 3-dinitronaphthalene has revealed the necessity for the exclusion of sodium hydroxide and the prevention of a rise in pH in the reduction medium. For this purpose various combinations of sodium sulphide with sodium bicarbonate and with boric acid in aqueous alcohol have been tried. Sodium bicarbonate proved to be the best reagent for addition to the sodium sulphide, and excess of methyl alcohol enabled the reaction to be conducted at the minimum temperature for securing maximum purity and appearance of the reduction product. Ethyl alcohol was somewhat inferior in this respect.

Based on the data of many trials, a method has been devised by which the mixed amines have been obtained in yields exceeding 85%. This method involves slightly less than the equivalent amount of sodium bicarbonate necessary to convert all the sodium sulphide into sodium hydrosulphide according to the equation $Na_2S + NaHCO_3 \rightleftharpoons Na_2CO_3 + NaSH$, and since sodium carbonate is almost insoluble in methyl alcohol, this equilibrium will be very much in favour of NaSH. The amount of sodium sulphide employed must not greatly exceed the theoretical requirement for monoreduction, otherwise the reaction may go beyond this stage. Monoreduction of 1 : 3-dinitronaphthalene by sodium sulphide alone, in either aqueous or alcoholic suspension, gave an insoluble tar in the former and a very small yield of mixed amines in the latter case; a 75% yield was obtained, however, by reduction with hydrogen sulphide in pyridine solution. Ammonium sulphide (sodium sulphide with ammonium chloride) was less reactive than the bicarbonate mixture with sodium sulphide, and also involved considerable precipitation of sulphur.

No method is yet available for the preparation of 4-nitro-2-naphthylamine in quantity, but a simple procedure is now described for the separation of the mixed amines of the present reduction, which is based on the preferential acetylation of the 4-nitro-2-naphthylamine when the solution of the mixed amines in glacial acetic acid is treated with insufficient acetic anhydride for complete acetylation (cf. the similar separation of α- and β-naphthylamines; Hodgson and Elliott, *J. Soc. Dyers and Col.*, 1938, **56**, 264). This stronger basic character of β-naphthylamine and its derivatives was also manifested by the greater stability of the sulphate of 4-nitro-2-naphthylamine towards hydrolysis when compared with the α-isomeride.

Attempted separation of the mixed amines by fractional precipitation with alkali from their solution in dilute hydrochloric acid always resulted in mixtures, and, in like manner, their solution in benzene or nitrobenzene, when treated with hydrogen chloride, always afforded a mixture of hydrochlorides; also, no separation could be effected based on the differential solubilities in weak acids such as oxalic, phosphoric, or citric. Further, the formyl derivatives of the mixed amines could not be separated satisfactorily by fractional crystallisation.

Like all the other nitro-2-naphthylamines, whether homo- or hetero-nuclear, 4-nitro-2-naphthylamine is red, whereas 3-nitro-1-naphthylamine, like the other two homonuclear 1-amino-isomerides, is yellow.

The very stable 3-nitronaphthalene-1-diazonium chloride is only sparingly soluble in hydrochloric acid and can be separated therefrom in solid form, as likewise can its stable *zinc chloride double salt.* 4-Chloro- and 4-cyano-2-nitronaphthalene have been prepared from the diazonium hydrochloride.

EXPERIMENTAL.

Monoreduction of 1 : 3-*Dinitronaphthalene.*—To a suspension of 1 : 3-dinitronaphthalene (11 g.) in boiling methyl alcohol (200 c.c.), in a bolt-head flask fitted with a reflux condenser, mechanical stirrer, and dropping-funnel, a preheated solution of crystallised sodium sulphide (19 g.) and sodium bicarbonate (6 g.) in water (50 c.c.) was added during 20 minutes. Excess of sodium sulphide was tested for by ferrous sulphate paper during the addition. On cooling (externally by ice-water) to 0°, almost pure 3-nitro-1-naphthylamine crystallised together with a little sodium carbonate; it was collected, and washed with a small amount of methyl alcohol and then with cold water. Yield, 4·4 g.; m. p. 132—133° (Vesely and Dvorăk, *loc. cit.*, give m. p. 136—137° for the pure product). The alcoholic mother-liquor was diluted with ice-water (700 g.) and after 1 hour the precipitated mixed amines (3·8 g.) were collected. Total yield of monoamines, 8·2 g. (87%).

Separation of 4-*Nitro*-2-*naphthylamine from* 3-*Nitro*-1-*naphthylamine.*—The mixed amines (3 g.), dissolved in glacial acetic acid (15 c.c.) containing a pinch of sodium acetate, were shaken in the cold with a 10% solution of acetic anhydride in glacial acetic acid (6 c.c.); the mixture was then warmed slowly and finally heated at *ca.* 70° for 30 minutes to complete the reaction. After cooling, the precipitate of 4-nitroaceto-2-naphthalide (0·9 g., m. p. 238—240°) was collected, a further 2 c.c. of the 10% acetic anhydride–acetic acid mixture added to the filtrate, and the procedure repeated, a mixture of acetylated amines (0·5 g., m. p. 210—230°) separating; excess of acetic anhydride then precipitated pure 3-nitroaceto-1-naphthalide from the previous filtrate (1 g., m. p. 254—258°). The 4-nitroaceto-2-naphthalide crystallised from alcohol in greenish-yellow rectangular plates, m. p. 241° (Veselý and Dvorăk, *loc. cit.*, give m. p. 237—238°) (Found : N, 12·3. Calc. : N, 12·2%). The 3-nitroaceto-1-naphthalide crystallised from alcohol in greenish-yellow needles, m. p. 259° (Veselý and Dvorăk, *loc. cit.*, give m. p. 255°) (Found : N, 12·3%). 4-Nitro-2-naphthylamine was obtained when the acetyl derivative (0·2 g.) was refluxed for 1 hour with a mixture of 50% sulphuric acid (4 c.c.) and alcohol (4 c.c.); after filtration and cooling, the sulphate of the base was precipitated by addition of an equal volume of water, and then basified by dilute aqueous ammonia. The 4-nitro-2-naphthylamine obtained (m. p. 95°) crystallised from 50% aqueous alcohol in red needles, m. p. 97° (Veselý and Dvorăk, *loc. cit.*, give m. p. 95°). 3-Nitro-1-naphthylamine was likewise obtained when the acetyl derivative (0·5 g.) was refluxed for 1—1½ hours with 50% sulphuric acid (10 c.c.) and alcohol (10 c.c.); complete dissolution occurred, and, on cooling, the sulphate was precipitated without the necessity of subsequent dilution; it was collected and basified with ammonia; the 3-nitro-1-naphthylamine (0·3 g.), m. p. 135°, then crystallised from 50% alcohol in orange-yellow needles, m. p. 137° (Veselý and Dvorăk, *loc. cit.*, give m. p. 136—137°).

3-*Nitroformo*-1-*naphthalide* was obtained when 3-nitro-1-naphthylamine (0·2 g.) was refluxed for 30 minutes with 90% formic acid (5 c.c.); the solution, on cooling, deposited it in greenish-yellow needles, m. p. 216° (Found: N, 13·1. $C_{11}H_8O_3N_2$ requires N, 13·0%).

4-*Nitroformo*-2-*naphthalide*, similarly prepared, crystallised from alcohol in bright lemon-yellow needles, m. p. 205° (Found: N, 13·2%).

Reduction of 1 : 3-*Dinitronaphthalene in Pyridine Suspension by Hydrogen Sulphide.*—The nitro-compound (2·2 g.) was suspended in pyridine (10 c.c.), and treated with hydrogen sulphide for 10 minutes; the mixture was refluxed and then again treated with the gas, the operations being repeated until no further increase in weight occurred. The reaction mixture was poured into water, the pyridine removed by steam-distillation, and the residual liquor acidified with hydrochloric acid, boiled, and filtered hot; the free base was precipitated from the cooled filtrate by ammonia or preferably by sodium acetate. Yield of mixed amines, 1·4 g. (75%).

The Diazotisation of 3-*Nitro*-1-*naphthylamine.*—The hydrochloride of the amine [2·2 g., m. p. 226° (decomp.)] was dissolved in boiling 6% hydrochloric acid (75 c.c.), and the solution rapidly chilled during vigorous agitation to produce a finely divided precipitate, which was then stirred at 15—20° with a solution of sodium nitrite (0·8 g.) in water (10 c.c.) until a clear solution of the diazonium salt was obtained (10—15 minutes). With less acid, or more concentrated hydrochloric acid, the very stable 3-nitronaphthalene-1-diazonium chloride separated, and could be dried without decomposition. When the above diazo-solution was treated with zinc chloride (2 g.), a crystalline precipitate of the *zinc chloride double salt* separated and was collected and dried. Yield, 2·5 g. (83%) (Found: Cl, 23·2. $C_{20}H_{12}O_4N_6Cl_4Zn$ requires Cl, 23·4%). When boiled with alcohol it gave 2-nitronaphthalene, m. p. and mixed m. p. 79°. When the above diazo-solution or the zinc compound was submitted to the Sandmeyer reaction, 1-chloro-3-nitronaphthalene was obtained, which crystallised from aqueous pyridine in brownish-yellow needles, m. p. 129·5° (Hodgson and Elliott, J., 1935, 1850, give dark brown micro-crystals from 90% formic acid, m. p. 127°) (Found: Cl, 17·0. Calc.: Cl, 17·1%).

4-*Nitro*-4-*cyanonaphthalene.*—3-Nitro-1-naphthylamine hydrochloride (2·2 g.) was diazotised as above, and the filtered solution added to one of crystallised copper sulphate (5·0 g.) and potassium cyanide (5·5 g.) in water (20 c.c.) at 50—60° and kept for 30 minutes at this temperature. The brownish-white precipitate was then collected, washed with cold water, dried, and extracted with boiling alcohol (70 c.c.). The filtered extract, on cooling, deposited a red solid (0·5 g., m. p. 160—165°), probably an azo-compound, and the filtrate therefrom gave an almost white precipitate (0·6 g.) on dilution with water. Steam-distillation of this product afforded 2-*nitro*-4-*cyanonaphthalene*, which was only slowly volatile in steam and crystallised from dilute alcohol in cream-coloured micro-needles, m. p. 163° (Found: N, 14·2. $C_{11}H_6O_2N_2$ requires N, 14·1%). When the double nickel potassium cyanide was used, decomposition only occurred slowly and the red solid (1·7 g.) was the main product, although a small amount of 2-nitro-4-cyanonaphthalene was obtained by steam-distillation.

The authors thank I.C.I. (Dyestuffs) Ltd. for various gifts.

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[*Received, October* 13*th*, 1943.]