157. *The Preparation of 7-Nitro-2-naphthylamine and of 3 : 6-Dinitronaphthalic Anhydride.*

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7-Nitro-2-naphthylamine is obtained from 2 : 7-dinitronaphthalene by mono-reduction with sodium sulphide–sodium bicarbonate in aqueous methyl alcohol; it is yellow-orange in colour and thus differs from all the other nitro-2-naphthylamines which are scarlet to orange. An improved procedure is given for the preparation of 3 : 6-dinitronaphthalic anhydride.

Since the work of Vesely and Dvorák (*Bull. Soc. chim.*, 1923, **33**, 319) all but two of the nitronaphthylamines have been obtained, and of these the 3-nitro-2-naphthylamine has already been prepared by Hodgson and Turner (*J.*, 1943, 635). The one remaining, 7-*nitro*-2-*naphthylamine*, has now been isolated by the mono-reduction of 2 : 7-dinitronaphthalene (Rule and Brown, *J.*, 1934, 171). All previous nitro-2-naphthylamines whether homo- or hetero-nuclear have all been red or orange-red in colour, but 7-nitro-2-naphthylamine is brilliant yellow-orange and its structure should in consequence be similar to the structures of the three homonuclear 2-, 3-, and 4-nitro-1-naphthylamines which are yellow or yellow-orange. Since the greatest electronic strain must be present in the structures of these yellow-orange compounds it has been assumed that the Erlenmeyer structure with its restraining central double bond makes the greatest contribution to their resultant resonating structures (cf. Hodgson and Turner, *J. Soc. Dyers and Col.*, 1943, **59**, 218; Hodgson and Hathway, *Trans. Faraday Soc.*, 1945, **41**, 115). That 7-nitro-2-naphthylamine should be yellow would appear to follow also from the circumstance that the amino- and nitro-groups will have the minimum of influence on each other since they are situated in different rings which, if connected by the double bond postulated in the Erlenmeyer formula, will be virtually separated from each other (cf. Lewis and Calvin, *Chem. Rev.*, 1939, **25**, 305); in any event, the compound cannot resonate into any of the six canonical naphthaquinone structures (cf. Pauling, "Nature of the Chemical Bond," Cornell, 1940, 152).

The dinitration of naphthalic anhydride has been reported previously by Anselm and Zuckmayer (*Ber.*, 1899, **32**, 3284) and by Francesconi and Bargellini (*Gazzetta*, 1902, **32** (2), 94); neither of these authors oriented their product which was identified as 3 : 6-dinitronaphthalic anhydride by Rule and Brown (*loc. cit.*). Details of a method based on that of Anselm and Zuckmayer (*loc. cit.*) are now given to secure an 85% yield of 3 : 6-dinitronaphthalic anhydride (m. p. 214°); this compares favourably with the 67% yield of a less pure product (m. p. 208—210°) reported by Rule and Brown using the method of Francesconi and Bargellini (*loc. cit.*) and confirmed by us. A more detailed decarboxylation procedure than that recorded by Rule and Brown for the preparation of 2 : 7-dinitronaphthalene is also included. It will be noted that the dinitration of naphthalic anhydride in 3 : 6-positions is analogous with the dinitration of 1 : 8-ditronaphthalene to give 1 : 3 : 6 : 8-tetranitronaphthalene (cf. Hodgson, Ward, and Whitehurst, this vol., p. 454).

The further nitrated compound of m. p. >266° (decomp.) reported by Francesconi and Bargellini (*loc. cit.*) is now found to be a tetranitronaphthalene.

Experimental.

Nitration of Naphthalic Anhydride.—A solution of naphthalic anhydride (50 g., m. p. 272—274°) in sulphuric acid (200 c.c., *d* 1·84) is cooled to 0° and then treated dropwise with one of nitric acid (40 c.c., *d* 1·5) in sulphuric acid (50 c.c., *d* 1·84) so that the temperature does not exceed 40°. The nitration is completed by heating the mixture at 55° for 1 hour, but should the temperature rise above 60° oxidation commences and continues with increasing vigour. After cooling to 0°, the nitration mixture is stirred gently into ice-water (5 l.), the cream flocculent precipitate separated and washed with water until the filtrate is almost colourless; water-soluble yellow material is thereby removed. The crude 3 : 6-dinitronaphthalic anhydride (61 g., 85% yield) crystallises from boiling toluene or xylene in colourless needles, m. p. 214° (Found : N, 10·0. Calc. : N, 9·7%), which are practically insoluble in boiling water.

Formation of a Tetranitronaphthalene.—A solution of 3 : 6-dinitronaphthalic anhydride (10 g.) in the minimum quantity of boiling nitric acid (*d* 1·42) when boiled for 1 minute, cooled to 0°, and filtered through asbestos gave a residue of a tetranitronaphthalene (0·2 g.) which when washed with cold nitric acid (*d* 1·42) and water was only sparingly soluble in boiling toluene, acetone, and alcohol but crystallised from glacial acetic acid in colourless needles, decomp. above 295° (Found : N, 18·3. $C_{10}H_4O_8N_4$ requires N, 18·1%). It gave no particular colour when stirred with acetone followed by 10% aqueous potassium hydroxide, but dissolved in boiling aqueous 10% sodium carbonate to a yellow solution which afforded a colourless precipitate on acidification, m. p. >310° (decomp.). The new tetranitronaphthalene gave with cold sodium sulphite solution a red colour similar to that given by 1 : 3 : 6 : 8-tetranitronaphthalene (m. p. 207°) and rapidly dissolved in the hot sulphite to a violet solution from which a colourless precipitate was given by hydrochloric acid, exactly like the behaviour of the 1 : 3 : 6 : 8-isomeride. The filtrate from the boiling nitric acid above gave only unchanged 3 : 6-dinitronaphthalic anhydride (8·5 g.) when poured into ice-water. Boiling nitric acid (*d*, 1·52) has little or no effect on 3 : 6-dinitronaphthalic anhydride.

2 : 7-Dinitronaphthalene was obtained when a solution of 3 : 6-dinitronaphthalic anhydride (20 g.) in dry boiling quinoline (40 c.c.) was treated cautiously with copper bronze (15 g.) during 15 minutes, the mixture cooled to room temperature, ether (200 c.c.) added, filtered, and the residue extracted four times with ether (total of 800 c.c.). The filtered ether extract was shaken twice with 15% hydrochloric acid (100 c.c.) to remove the quinoline present, washed with cold saturated aqueous sodium carbonate (25 c.c.) and with water (100 c.c.). The crude residue, remaining after distilling away the ether, crystallised from boiling glacial acetic acid to give pure 2 : 7-dinitronaphthalene, m. p. 234° (Rule and Brown, *loc. cit.*, give m. p. 234°) (Found : N, 12·8. Calc. : N, 12·8%), which gave an intense red colour in acetone with 10% aqueous potassium hydroxide only when heated and was not attacked by boiling aqueous sodium sulphite.

7-*Nitro*-2-*naphthylamine* was prepared by adding dropwise during 20 minutes a solution of sodium sulphide crystals (6 g.) and sodium bicarbonate (2 g.) in water (15 c.c.) to a well-stirred suspension of 2 : 7-dinitronaphthalene (3 g.) in boiling methyl alcohol (50 c.c.). Reduction was slow, but the solution became violet immediately (due to the formation of a small amount of a sulphur dye which dyed cotton to a bluish-green shade). A slight excess of sulphide was found present at the end of the reduction period, when the mixture was cooled to 20° and ice added followed by water (1 l.). After keeping for 1 hour, the solid matter was separated and extracted thoroughly with a total of 300 c.c. of 8% hydrochloric acid. The extract was treated at 0° with ammonia until just alkaline; the orange-yellow precipitate of crude 7-nitro-2-naphthylamine (2·1 g., 80%), m. p. 182—184°, separated. After washing with water and drying, it was crystallised from ethanol (charcoal) and obtained in brilliant orange-yellow parallelepipeds, m. p. 184·5° (Found: N, 15·1. $C_{10}H_8O_2N_2$ requires N, 14·9%), which were readily soluble in cold formic and acetic acids, acetone, and pyridine.

7-*Nitro*-2-*naphthylamine hydrochloride* separated from a hot hydrochloric solution of the base in colourless plates, m. p. 259° (decomp.) (Found: N, 12·6. $C_{10}H_9O_2N_2Cl$ requires N, 12·5%).

7-*Nitro*-2-*formonaphthalide* was obtained when the amine (0·05 g.) was refluxed for 1 hour in 90% formic acid (2 c.c.); it separated from the solution on cooling in greenish-yellow needles which crystallised from 50% aqueous alcohol in lemon-yellow needles, m. p. 188·5° (Found: N, 13·3. $C_{11}H_8O_3N_2$ requires N, 13·0%).

7-*Nitro*-2-*acetonaphthalide* was formed when a solution of the amine (0·1 g.) in cold pyridine was shaken for 5 minutes with a slight excess of acetyl chloride, the solution heated to 50° and cooled. The compound separated in yellow crystals which crystallised from 50% aqueous ethyl alcohol in yellow plates, m. p. 221° (Found: N, 12·4. $C_{12}H_{10}O_3N_2$ requires N, 12·2%).

7-*Nitro*-2-*naphthylamine picrate* was prepared when boiling solutions of the amine (0·1 g.) and picric acid (0·12 g.) in the minimum quantities of ethyl alcohol were mixed; it separated in yellow needles, m. p. 203° (Found: N, 17·0. $C_{16}H_{11}O_9N_5$ requires N, 16·8%).

7-*Nitro*-2-*naphthaleneazo*-β-*naphthol*, formed by diazotisation of the amine and coupling with β-naphthol by the usual methods, crystallised from glacial acetic acid in small needles, m. p. 225·1° (Found: N, 12·5. $C_{20}H_{13}O_3N_3$ requires N, 12·2%), which gave a violet colour with concentrated sulphuric acid.

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