148. *The Mononitration of α-Naphthol and of α-Naphthyl Methyl Ether, and the Monoreduction of 2 : 4-Dinitro-α-naphthol.*

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PICTET and v. KRIJANOWSKI (*Chem. Zentr.*, 1903, II, 1109) state that the reaction between diacetylorthonitric acid and α-naphthol gives 2-nitro-1-naphthol and α-naphthaquinone, whereas in a table published by Bell (J., 1933, 286) the initial nitration of α-naphthol is recorded as occurring at position 4. Since α-naphthol under a variety of nitration conditions, even including a deficiency of nitric acid, affords 2 : 4-dinitro-1-naphthol, we repeated the work of the former authors and obtained a 34% yield of 2-nitro-1-naphthol but no α-naphthaquinone. When α-naphthyl acetate was used instead of α-naphthol, the yield of 2-nitro-1-naphthol was 45%; the acetate, however, was very prone to dinitration.

Pictet and v. Krijanowski (*loc. cit.*) also state that the mononitration of α-naphthyl methyl ether gives 2-nitro-1-naphthyl methyl ether, whereas Bell's table records a mixture of the 2- and the 4-isomeride. Actually the bulk of the product is 4-nitro-1-naphthyl methyl ether, and the presence of the 2-nitro-compound has not been detected, a result to be anticipated from the electronic theory, since the inductive electron-attracting ($-I$) effect of the methoxyl group would favour nitration in the more remote 4-position (compare also Ingold, *Ann. Reports*, 1928, **25**, 122; Hodgson and Clay, J., 1929, 2776).

Further nitration of both 2- and 4-nitro-1-naphthyl methyl ether gives almost entirely 2 : 4-dinitro-1-naphthyl methyl ether; no 4 : 5-dinitro-1-naphthyl methyl ether was detected (compare Bell's table).

2 : 4-Dinitro-1-naphthol is reduced almost quantitatively by stannous chloride in alcoholic hydrochloric acid to 2-*nitro*-4-*amino*-1-*naphthol*, but the composition of the mixture of nitroamines obtained by similar reduction of 2 : 4-dinitro-1-naphthyl methyl ether indicates an approach towards electropositive equality of the nitro-groups in this compound.

Diazotisation of 2-nitro-4-amino-1-naphthol under ordinary conditions gives a stable 2-*nitro*-4-*diazonaphthalene* 1-*oxide*, which couples with β-naphthol in acetic acid solution only on addition of hydrochloric acid.

Owing to salt formation, the aceto-4-halogeno-2-nitro-1-naphthalides are very resistant to hydrolysis by caustic alkalis. They are, however, gradually converted by boiling hydrochloric acid into the amines, which are readily transformed by boiling alkalis into the 4-halogeno-2-nitro-1-naphthols.

On halogenation, 2-nitro-4-amino-1-naphthol readily forms 3-halogeno-2-nitro-4-amino-1-naphthols, the homonuclear constitution being established by oxidation to phthalic anhydride, and by the synthesis of 3-*bromo*-2-*nitro*-4-*amino*-1-*naphthol* from authentic 2-bromo-4-nitro-1-naphthylamine (Hodgson and Elliott, J., 1934, 1706).

EXPERIMENTAL.

Nitration of α-Naphthol.—A solution of α-naphthol (5 g.) in acetic anhydride (20 c.c.) was treated gradually, below 7° during 1½ hours, with diacetylorthonitric acid (7 c.c.) in acetic anhydride (10 c.c.). The dark mixture was poured on ice (see below), and the black precipitate (8 g.) repeatedly extracted with 2% aqueous sodium carbonate; the filtered extracts, on acidification, afforded only 2-nitro-1-naphthol (2·2 g.).

Nitration of α-Naphthyl Acetate.—The acetate (6·5 g.), treated exactly as above, gave a product free from blackening, which yielded 3·0 g. of 2-nitro-1-naphthol by the alkali extraction. When, however, the reaction mixture was kept for 3 hours, crystals appeared, which were identified as 2 : 4-dinitro-1-naphthol (m. p. 138°). Cautious addition of ice increased the precipitation to 2·5 g., but the mother-liquor when poured on ice gave much unchanged α-naphthyl acetate. Tetranitromethane did not react with α-naphthyl acetate either in methyl-alcoholic or in glacial acetic acid solution.

Nitration of α-Naphthyl Methyl Ether.—The ether (10 g.), dissolved in acetic anhydride (20 c.c.), was treated gradually at 3—5° during 3 hours with a solution of diacetylorthonitric acid (15 c.c.) in acetic anhydride (10 c.c.); the mixture was kept over-night, diluted with water (60 c.c.), and again kept over-night. The precipitate (12·5 g.), after two crystallisations from alcohol, formed long yellow needles, m. p. 85°, identical with authentic 4-nitro-1-naphthyl methyl ether (Found: N, 7·0. Calc. for $C_{11}H_9O_3N$: N, 6·9%); the m. p. was depressed by 2-nitro-1-naphthyl methyl ether (m. p. 80°. Cf. Clemo, Cockburn, and Spence, J., 1931, 1271).

Methylation of 4-*Nitro*-1-*naphthol.*—4-Nitro-1-naphthylamine (20 g.) was boiled (5 hours) with 10% aqueous sodium hydroxide (200 c.c.), and the cooled solution acidified to precipitate 4-nitro-1-naphthol. This naphthol (10 g.) was ground with potassium carbonate (10 g.), and the mixture heated (1 hour) on the water-bath with methyl sulphate (10 c.c.). After extraction with aqueous sodium carbonate, the insoluble 4-nitro-1-naphthyl methyl ether crystallised from alcohol as above, m. p. 85° (Found: N, 7·1%).

Reduction of 4-*Nitro*-1-*naphthyl Methyl Ether*.—The ether (9 g., obtained by either of the methods described above) was heated on the water-bath with 50% aqueous acetic acid (100 c.c.), iron filings (10 g.) added gradually, and the heating continued for 2 hours. The liquid was filtered hot, cooled, and shaken with acetic anhydride (10 c.c.); 4-acetamido-1-naphthyl methyl ether, which separated, crystallised from alcohol in lustrous pearly-white needles, m. p. 187° (Woroshzow, *Chem. Zentr.*, 1911, I, 650, gives m. p. 180—181°) (Found: N, 6·7, 6·6. Calc.: N, 6·5%). This ether (1 g.), dissolved in acetic anhydride (2 c.c.), was nitrated with a mixture of diacetylorthonitric acid (1·5 c.c.) and acetic anhydride at 18—20°; 3-*nitro*-4-*acetamido*-1-*naphthyl methyl ether*, which separated over-night, crystallised from alcohol in yellow needles, m. p. 246° (Found: N, 11·0. $C_{13}H_{12}O_4N_2$ requires N, 10·8%).

Nitration of 2- *and* 4-*Nitro*-1-*naphthyl Methyl Ether*.—Either compound (5 g.), suspended in acetic anhydride (20 c.c.), was treated gradually with diacetylorthonitric acid (10 c.c.), the temperature rising to *ca.* 70°. The product, twice crystallised from alcohol, gave cream-coloured needles of 2 : 4-dinitro-1-naphthyl methyl ether, m. p. 95° (Ullmann and Bruck, *Ber.*, 1908, **41**, 3938, describe yellow needles from methyl alcohol, m. p. 87°) (Found: N, 11·3, 11·4. Calc.: N, 11·3%). Demethylation with concentrated sulphuric acid gave 2 : 4-dinitro-1-naphthol.

Monoreduction of 2 : 4-*Dinitro*-1-*naphthol*.—The naphthol (5 g.), suspended in concentrated hydrochloric acid (20 c.c.) and alcohol (10 c.c.), was stirred for 1 hour during the addition below 30° of a solution of crystallised stannous chloride (15 g.) and alcohol (20 c.c.). After 12 hours, the *hydrochloride* of 2-*nitro*-4-*amino*-1-*naphthol* separated in pale yellow needles (5 g.; 98% yield), m. p. 175° (decomp.) after recrystallisation from alcoholic hydrochloric acid (Found: Cl, 14·6. $C_{10}H_8O_3N_2,HCl$ requires Cl, 14·8%). Hydrolysis with water produced 2-*nitro*-4-*amino*-1-*naphthol*, which crystallised from alcohol in iridescent maroon needles, m. p. 160° (decomp.) (Found: N, 13·9. $C_{10}H_8O_3N_2$ requires N, 13·7%), gave an intensely red sodium salt, and was converted on deamination into 2-nitro-1-naphthol. 2-Nitro-4-acetamido-1-naphthol crystallised from glacial acetic acid in yellow-orange needles, m. p. 250° (decomp.) (Found: N, 11·6. Calc.: N, 11·4%) (Panizzon-Favre, *Gazzetta*, 1924, **54**, 826, gives m. p. 238°), and 2-*nitro*-4-*acetamido*-1-*naphthyl methyl ether* in stellate clusters of buff needles, m. p. 214° (Found: N, 10·9. $C_{13}H_{12}O_4N_2$ requires N, 10·8%). 2-*Nitro*-4-*benzamido*-1-*naphthol* crystallised from alcohol in orange needles, m. p. 230° (decomp.) (Found: N, 9·3. $C_{17}H_{12}O_4N_2$ requires N, 9·1%).

2-*Nitro*-4-*diazonaphthalene* 1-*oxide* was prepared by suspending the hydrochloride of 2-nitro-4-amino-1-naphthol (4·3 g.) in concentrated hydrochloric acid (30 c.c.; *d* 1·16) and water (30 c.c.), and adding 20% aqueous sodium nitrite with stirring until it was just in permanent excess. The diazo-oxide, collected after 12 hours, crystallised from alcohol or 80% acetic acid in pale yellow needles, m. p. 163° (decomp.) (Found: N, 19·8. $C_{10}H_5O_3N_3$ requires N, 19·5%). From it, by the Sandmeyer process, were prepared 4-*chloro*-2-*nitro*-1-*naphthol*, yellow needles from 70% alcohol, m. p. 155° (Found: Cl, 15·7. $C_{10}H_6O_3NCl$ requires Cl, 15·9%), 4-bromo-2-nitro-1-naphthol, yellow needles from 80% alcohol, m. p. 144° (Biedermann and Remmers, *Ber.*, 1874, **7**, 539, give m. p. 142°) (Found: Br, 29·7. Calc.: Br, 29·8%), and 4-iodo-2-nitro-1-naphthol, yellow needles from 80% alcohol, m. p. 152° (Meldola and Streatfeild, J., 1895, **67**, 913, give m. p. 150°) (Found: I, 40·2. Calc.: I, 40·3%). In each case the compound reddens prior to fusion.

Other Reactions of 2-*Nitro*-4-*diazonaphthalene* 1-*Oxide*.—(a) Coupling with β-naphthol requires the presence of mineral acid; 2-*nitro*-1-*hydroxynaphthalene*-4-*azo*-β-*naphthol* crystallised from glacial acetic acid in iridescent, deep red plates, m. p. 233° (decomp.) (Found: N, 11·9. $C_{20}H_{13}O_4N_3$ requires N, 11·7%), which gave a blue-violet colour with concentrated sulphuric acid, gradually changing through blue to green; the sodium salt was deep red, almost black.

(b) Decomposition by potassium xanthate and hydrolysis of the resulting xanthate to a mercaptan, gave on oxidation by alkali ferricyanide, 3 : 3′-*dinitro*-4 : 4′-*dihydroxydinaphthyl disulphide*, which crystallised from glacial acetic acid in pale yellow micro-needles, m. p. 197° (decomp.) (Found: S, 14·6. $C_{20}H_{12}O_6N_2S_2$ requires S, 14·5%).

(c) Decomposition by dilute sulphuric acid on the boiling water-bath gave mainly 2-nitro-1-naphthol.

Reactions of 2-*Nitro*-4-*amino*-1-*naphthol*.—(a) *Nitration*. The base (1 g.) was stirred with 10% aqueous nitric acid (20 c.c.) at room temperature until it dissolved. 2 : 3-*Dinitro*-4-*amino*-1-*naphthol*, collected after 12 hours, crystallised from 80% acetic acid in pale orange needles, m. p. 130° (Found : N, 17·0. $C_{10}H_7O_5N_3$ requires N, 16·9%), and gave a red-orange potassium salt.

(b) *Chlorination.* The base in cold chloroform was treated with chlorine until the red colour disappeared; the *hydrochloride* of 3-*chloro*-2-*nitro*-4-*amino*-1-*naphthol* separated in cream-coloured needles, which decomposed on heating (Found : Cl, 25·6. $C_{10}H_7O_3N_2Cl,HCl$ requires Cl, 25·8%); 3-*chloro*-2-*nitro*-4-*amino*-1-*naphthol* crystallised from alcohol in yellow needles, m. p. 120° (Found : Cl, 14·8. $C_{10}H_7O_3N_2Cl$ requires Cl, 14·9%).

(c) *Bromination.* When the base (1 g.) in chloroform (30 c.c.) was stirred with bromine (0·5 c.c.) in chloroform (10 c.c.), 3-*bromo*-2-*nitro*-4-*amino*-1-*naphthol* separated; it crystallised from alcohol in pale orange needles, m. p. 123° (Found : Br, 28·1. $C_{10}H_7O_3N_2Br$ requires Br, 28·3%). In dry chloroform, the unstable hydrobromide of the base separated, but was readily hydrolysed by atmospheric moisture. The constitution was established as follows : 2-bromo-4-nitro-1-naphthylamine (10·5 g.), suspended in 50% aqueous acetic acid (100 c.c.), was heated on the water-bath during the gradual addition (2 hours) of iron filings (10 g.). After dilution with hot water (100 c.c.), the liquid was filtered hot, cooled, and shaken with acetic anhydride. 2-*Bromo*-4-*acetamido*-1-*naphthylamine*, which separated, crystallised from water in colourless needles, m. p. 230° (Found : Br, 28·7. $C_{12}H_{11}ON_2Br$ requires Br, 28·7%), and on nitration in acetic acid solution gave 2-*bromo*-3-*nitro*-4-*acetamido*-1-*naphthylamine*; this crystallised from water in cream-coloured needles, m. p. 300° (Found : Br, 24·7. $C_{12}H_{10}O_3N_3Br$ requires Br, 24·7%), and when boiled with 10% aqueous sodium hydroxide gave 3-bromo-2-nitro-4-amino-1-naphthol.

(d) *Iodination.* The base (1 g.) in chloroform (30 c.c.) was shaken with iodine (1·5 g.) in chloroform (10 c.c.), either with or without mercuric oxide. An orange product, m. p. 195°, was precipitated; the filtrate, on concentration, deposited 3-*iodo*-2-*nitro*-4-*amino*-1-*naphthol* in pale orange needles, m. p. 138° (Found : I, 38·3. $C_{10}H_7O_3N_2I$ requires I, 38·5%).

The authors thank Imperial Chemical Industries, Ltd. (Dyestuffs Group) for various gifts.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, February* 26*th*, 1935.]