163. *Some* 1 : 7- *and* 1 : 2 : 7-*Derivatives of Naphthalene.*

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7-Bromo-1- and 8-bromo-2-naphthylamine, 1-bromo-7- and 7-bromo-1-nitronaphthalene, 1 : 7-dibromonaphthalene, the 2-halogeno-1 : 7-dinitronaphthalenes, and 7-nitronaphthalene-2 : 1-diazo-oxide, and the nitration of 7-nitro-*m*-nitrobenzenesulphon-2-naphthalide are described. The nitration of 1 : 7-dinitro-*m*-nitrobenzenesulphon-2-naphthalide occurs in the naphthalene nucleus as shown by hydrolysis of the nitration product to 1 : 5(?) : 7-trinitro-2-naphthylamine. The last compound does not form a picrate or deaminate readily.

1 : 7-DINITRO-2-NAPHTHYLAMINE is readily diazotised by Hodgson and Walker's method (*J.*, 1933, 1620), and 2-chloro-, 2-bromo-, and 2-iodo-1 : 7-dinitronaphthalene are obtained by subsequent Sandmeyer reactions. Special conditions are necessary for the preparation of 7-nitronaphthalene-2 : 1-diazo-oxide.

Nitration of 1 : 7-dinitro-*m*-nitrobenzenesulphon-2-naphthalide occurs in the naphthalene nucleus and not in the side chain, as is shown by hydrolysis of the trinitrated product to a 1 : *x* : 7-trinitro-2-naphthylamine, where *x* has not been determined but on all analogy should be the 5-position. 1 : 5(?) : 7-Trinitro-2-naphthylamine would not form a picrate, owing either to steric or more probably to the much enfeebled basic character of the 2-amino-group. Similarly, 1 : 7-dinitro-2-naphthylamine is inert towards *m*-nitrobenzenesulphonyl chloride. Attempts to deaminate the trinitro-compound by the cuprous oxide–methanol procedure, described for 1 : 7-dinitro-2-naphthylamine, were unsuccessful.

EXPERIMENTAL.

Improvements in the Preparation of 2 : 7-*Dinitronaphthalene.*—Using a modification of Hodgson and Ward's method (*J.*, 1945, 590), 3 : 6-dinitronaphthalic anhydride (20 g.) is added during *ca.* 4 minutes to boiling dry quinoline (40 c.c.) containing copper bronze (5 g.) in suspension, and then more copper bronze (5 g.) is added and boiling continued for a total period of 15 minutes. Synthetic quinoline affords a cleaner product in somewhat better yield (34%) than does coal-tar quinoline (about 23%).

Preparation of Some 1 : 7-*Derivatives of Naphthalene.*—8-*Bromo*-2-*naphthylamine.* A solution of 1-bromo-7-nitro-2-naphthylamine (2·3 g.) (Hodgson and Ward, *J.*, 1947, 327) in sulphuric acid (5 c.c.; *d* 1·84) was added to one of sodium nitrite (1 g.) in sulphuric acid (5 c.c.; *d* 1·84), the whole was stirred into glacial acetic acid (20 c.c.) at $<$20°, and stirring was continued for 30 minutes. The mixture was then added gradually to a stirred suspension of cuprous oxide (4 g.) in methanol (70 c.c.) at 55°, and the stirring continued until the solution had cooled to room temperature, whereupon the whole was poured on ice and kept overnight. The precipitate was filtered off, washed with water, 2% aqueous sodium carbonate, and again with water, and then extracted with boiling ethanol (charcoal). The extract was filtered and allowed to evaporate, whereupon 1-*bromo*-7-*nitronaphthalene* separated (1·25 g., 58% yield); it recrystallised from ethanol in orange plates, m. p. 135° (Found : N, 5·7; Br, 31·6. $C_{10}H_6O_2NBr$ requires N, 5·5; Br, 31·7%). 1-Bromo-7-nitronaphthalene (1 g.) was reduced by being heated under reflux for 3 hours with a mixture of iron powder (pin dust) (3·0 g.), ferrous sulphate (0·5 g.), and water (30 c.c.); the solid was filtered off, washed with cold water, dried, and extracted with boiling ethanol (charcoal), and the filtered extract allowed to evaporate, whereupon 8-*bromo*-2-*naphthylamine* (0·4 g.) separated and was recrystallised from ethanol; it formed pale brown rods, m. p. 74° (Found : N, 6·5; Br, 35·9. $C_{10}H_8NBr$ requires N, 6·3; Br, 36·0%).

1 : 7-*Dibromonaphthalene.* A fine suspension of 7-*bromo*-1-*naphthylamine hydrobromide* [(Found : Br, 52·6. $C_{10}H_9NBr_2$ requires Br, 52·8%), obtained as colourless needles when 7-bromo-1-naphthylamine (2·0 g.) was dissolved in hot hydrobromic acid (2·5 c.c.; *d* 1·7) and water (15 c.c.), and the solution chilled to 0°] was diazotised at 0° by the addition of sodium nitrite (1 g.) in the minimum amount of water. After 20 minutes, the clear solution was stirred into one of cuprous bromide (4 g.) in hydrobromic acid (10 c.c.; *d* 1·7) at 60° and stirring continued until room temperature was attained; the mixture was poured on to ice and kept overnight. The latter was then filtered off, washed with water, 2% aqueous sodium carbonate, and finally with water, and extracted with boiling ethanol (charcoal). The extract was allowed to crystallise, and the crystals (0·15 g.) were recrystallised from ethanol, 1 : 7-*dibromonaphthalene* being obtained in colourless needles, m. p. 61° (Found : Br, 55·7. $C_{10}H_6Br_2$ requires Br, 55·9%).

7-Bromo-1-nitronaphthalene (5·7 g) was obtained from 8-nitro-2-naphthylamine (10 g.) by the same procedure as above, and crystallised from ethanol in small pale yellow needles, m p 107° (Salkind and Filinov, *J Gen. Chem. Russia*, 1934, **4**, 979, give m. p. 110—111°) which could not be raised by repeated crystallisation (Found : N, 5·6; Br, 31·5. Calc. for $C_{10}H_6O_2NBr$: N, 5·5; Br, 31·7%). *Brit. Abs.*, 1935, 204, incorrectly describe this compound as 2-bromo-7-nitronaphthalene.

7-*Bromo*-1-*naphthylamine.* Finely powdered 7-bromo-1-nitronaphthalene (4 g.) was heated under reflux for 3 hours with iron powder (pin dust) (12 g.), crystallised ferrous sulphate (2 g.), and water (100 c.c.), the mixture was filtered cold, and the residue washed with cold water, dried, and extracted with boiling ethanol. The extract, after being boiled with animal charcoal, was filtered, and the filtrate allowed to evaporate slowly, but crystallisation was unsatisfactory. The solid obtained was dissolved in hot 5% hydrochloric acid, and, from the cooling solution, 7-*bromo*-1-*naphthylamine hydrochloride* (3·2 g.) separated in white gleaming plates, m. p. 250° (Found : HCl, 14·0. $C_{10}H_8NBr,HCl$ requires HCl, 14·1%), which darkened on exposure to light. Basification with ammonia afforded pure 7-*bromo*-1-*naphthylamine* (2·8 g.), which crystallised from ethanol in colourless needles, m. p. 52° (Found : Br, 35·8. $C_{10}H_8NBr$ requires Br, 36·0%), that became mauve-brown in air.

Preparation of Some 1 : 2 : 7-*Derivatives of Naphthalene.*—*The* 2-*halogeno*-1 : 7-*dinitronaphthalenes.* 1 : 7-Dinitrotoluene-*p*-sulphon-2-naphthalide (2·3 g.; m. p. 171°; cf. Hodgson and Ward, *J.*, 1947, 1060, who give m. p. 165—166°) was hydrolysed by dissolution in sulphuric acid (5 c.c.; *d* 1·84) and heating at 40° for 5 minutes, a solution of sodium nitrite (1 g.) in sulphuric acid (5 c.c.; *d* 1·84) was added, and the mixture was stirred dropwise into glacial acetic acid (20 c.c.) at $<$20°. After a further 30 minutes' stirring the solution was divided into three equal portions which were dealt with separately as follows : (*a*) was stirred into a solution of cuprous chloride (2·5 g.) in hydrochloric acid (25 c.c.; *d* 1·18), and, when evolution of nitrogen had ceased, the thick dark mixture was poured into iced water, and the pale yellow precipitate (0·45 g.) was kept overnight, then filtered off, and washed with water (500 c.c.), 2% aqueous sodium carbonate (150 c.c.), and water (500 c.c.), dried at 70°, and extracted with boiling ethanol (charcoal); on evaporation, the filtered extract afforded 2-*chloro*-1 : 7-*dinitronaphthalene* (0·2 g.), which recrystallised from ethanol in pale brown needles, m. p. 161° (Found Cl, 13·9. $C_{10}H_5O_4N_2Cl$ requires Cl, 14·0%) : (*b*) was poured into a solution of cuprous bromide (2·5 g.) in hydrobromic acid (25 c.c. *d* 1·7), and then dealt with as in (*a*); the crude 2-*bromo*-1 : 7-*dinitronaphthalene* (0·6 g.) obtained crystallised from ethanol in yellow micro-needles (0·25 g.), m. p. 149° raised by sublimation to 155—156° (Found : Br, 27·0. $C_{10}H_5O_4N_2Br$ requires Br, 26·9% : (*c*) was stirred into a solution of potassium iodide (5 g.) in an amount of water insufficient for complete dissolution; the mixture was kept until reaction had ceased, then stirred into iced water and left overnight; the red precipitate (0·6 g.) was removed, washed with water (500 c.c.) and aqueous sodium thiosulphate (10 g. of solid in 500 c.c. of water), and dried at 70°; extraction as for (*a*) and (*b*) gave 2-*iodo*-1 : 7-*dinitronaphthalene*, which crystallised from ethanol in reddish-fawn rods, m.p. 163°, which sublimed to very pale fawn needles, m. p. 166° (Found: I, 36·7. $C_{10}H_5O_4N_2I$ requires I, 3·69%).

7-*Nitronaphthalene*-2 : 1-*diazo-oxide*. When a solution of 1 : 7-dinitro-2-naphthylamine (0·5 g.) in sulphuric acid (4 c.c.; *d* 1·84) was treated at <10° with one of sodium nitrite (1 g.) in sulphuric acid (5 c.c.; *d* 1·84) and the mixture stirred into a suspension of copper carbonate (3 g.) in glacial acetic acid (25 c.c.) there was an immediate precipitation of 7-*nitronaphthalene*-2 : 1-*diazo-oxide* (0·45 g.), which was filtered off, washed three times with water (100 c.c.) and dried at 50°; it separated from ethanol in clusters of pale yellow sword-like crystals (Found: N, 19·8. $C_{10}H_5O_3N_3$ requires N, 19·5%) which darkened on exposure to light, decomposed at *ca.* 160°, and coupled with alkaline β-naphthol. When a solution of the above diazonium sulphate was stirred into glacial acetic acid (18 c.c.) at <20° and the mixture poured into iced water (300 c.c.), only slight precipitation occurred (0·05 g.).

7-*Nitro*-m-*nitrobenzenesulphon*-2-*naphthalide*. 7-Nitro-2-naphthylamine (6 g.) was intimately ground with *m*-nitrobenzenesulphonyl chloride (75 g.) and the mixture heated under reflux with pyridine (25 c.c.) for 3 hours. The solution was cooled to 0° and then stirred dropwise into 15% aqueous hydrochloric acid (200 c.c.); the precipitate of 7-nitro-*m*-nitrobenzenesulphon-2-naphthalide (9·1 g.) was filtered off, washed with water, sucked as dry as possible on the Büchner funnel, and crystallised twice from 70% acetic acid (charcoal). It was obtained in clusters of golden needles, m. p. 212—213° (Found: N, 11·4; S, 8·5. $C_{16}H_{11}O_6N_3S$ requires N, 11·2; S, 8·6%).

The Nitration of 7-*Nitro*-m-*nitrobenzenesulphon*-2-*naphthalide*.—(a) *With an equimolecular amount of nitric acid in glacial acetic acid.* The naphthalide (2 g.) was boiled with glacial acetic acid (15 c.c.), the mixture cooled 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 (4·4 c.c.; *d* 1·5) in glacial acetic acid (35·6 c.c.). The temperature was then raised and kept at 80° for 5 minutes. 3 Hours later, glacial acetic acid (15 c.c.) was added at 15° with stirring, and next morning the suspension was filtered, and the solid 1 : 7-*dinitro*-m-*nitrobenzenesulphon*-2-*naphthalide* (1·7 g.) washed with glacial acetic acid and ether, and dried; it crystallised from glacial acetic acid (charcoal), in which it is sparingly soluble, in yellow micro-needles, m. p. 246—247° (decomp.) (Found: N, 13·3. S, 7·8. $C_{16}H_{10}O_8N_4S$ requires N, 13·4; S, 7·7%).

(b) *With 5-fold excess of nitric acid in glacial acetic acid.* With the same procedure as above but with 10 c.c. of nitrating reagent, the yield of 1 : 7-dinitro-*m*-nitrobenzenesulphon-2-naphthalide was practically unchanged (1·8 g.; m. p. 246—247°). Hydrolysis occurred when the naphthalide (1 g.) was stirred into sulphuric acid (50 c.c.; *d* 1·84) and slow dissolution completed by heating to 70°. The clear solution was kept overnight; it was filtered on to ice, and the 1 : 7-dinitro-2-naphthylamine which precipitated was crystallised from glacial acetic acid (charcoal); it formed golden yellow needles, m. p. and mixed m. p. with an authentic specimen, 248—249°.

(c) *With nitric acid* (d 1·5). The powdered naphthalide (2·8 g.) was added portionwise during 15 minutes to nitric acid (15 c.c.; *d* 1·5), initially below 5°, and the temperature not allowed to exceed 20°; it was raised to 35° when complete dissolution had occurred. After 3 hours the solution was cooled to 0°, glacial acetic acid (15 c.c.) was added, and overnight 1 : 5(?) : 7-*trinitro*-m-*nitrobenzenesulphon*-2-*naphthalide* separated in yellow micro-needles, m. p. 248° (decomp.); it recrystallised from glacial acetic acid in pale yellow, matted, silk-like needles, m. p. 262° (decomp.) (Found: N, 14·9; S, 7·27. $C_{16}H_9O_{10}N_5S$ requires N, 15·1; S, 6·9%). When this was hydrolysed, as described above for the dinitro-compound, 1 : 5(?) : 7-*trinitro*-2-*naphthylamine* was obtained, which crystallised from glacial acetic acid (charcoal) in golden yellow needles, m. p. 291—292° (Found: N, 19·9. $C_{10}H_6O_6N_4$ requires N, 20·1%), which would not form a picrate. Attempts to deaminate this compound were unsuccessful.

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