431. *Salt Formation of Homonuclear Naphthalene Derivatives.*

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The marked difference in basic character of 2- and 4-nitro-1-naphthylamine (Hodgson and Walker, J., 1923, **123**, 1205) suggested an investigation of the influence of further homonuclear substitution. It has been found that, whereas the hydrohalides of 4-nitro-1-naphthylamine are stable in air, though readily hydrolysed by trituration with water, the 2-halogeno-4-nitro-1-naphthylamines only form salts with hydrogen halides in nitrobenzene or similar media, and atmospheric moisture, as with the salts of 2-nitro-1-naphthylamine, immediately produces hydrolysis; 2-bromo-4-nitro-1-naphthylamine hydrobromide appears to be the most stable salt of the series.

The salts of the 4-halogeno-2-nitro-1-naphthylamines are even more unstable than those of 2-nitro-1-naphthylamine, as would be anticipated, whereas the salts of the 3-halogeno-1-naphthylamines are relatively very stable and require a minimum strength of 5% aqueous sodium hydroxide for their decomposition. When the last-mentioned amines are prepared by reduction of the 3-halogeno-1-nitronaphthalenes with stannous chloride and aqueous-alcoholic hydrochloric acid, their hydrochlorides crystallise from the reduction medium and tin double salts do not separate; whereas similar reduction of the 1-halogeno-3-nitronaphthalenes produces very stable tin double salts, which are hydrolysed by 2% aqueous sodium hydroxide. The β-naphthylamine derivatives would thus appear to be more basic than their α-isomerides, as is the case with the unsubstituted α- and β-naphthylamines, indicating a negative inductive (— *I*) effect of the unsubstituted nucleus.

The 2-halogeno-1 : 4-naphthylenediamines form only monohydrochlorides by the standard method, and only *NN'*-diacetyl or -dibenzoyl derivatives on acylation.

2-Chloro- and 2-bromo-4-nitro-1-naphthylamine are readily acetylated by the ordinary acetic anhydride method, but not the 2-iodo-analogue. 4-Nitro-1-naphthylamine is readily mercurated (Hodgson and Elliott, J., 1934, 1705), but 4-nitroaceto-1-naphthalide does not react with mercuric acetate in boiling glacial acetic acid solution.

The 4-halogeno-1 : 2-naphthylenediamines form only monohydrochlorides and are only monoacetylated when boiled with acetic anhydride, the 2-amino-group in each case being reactive. The latter fact was established by the preparation of the isomeric 4-halogeno-2-aminoaceto-1-naphthalides, which, when treated with acetic anhydride, gave the corresponding *NN'*-diacetyl-1 : 2-naphthylenediamines. The 4-halogeno-2-aminoaceto-1-naphthalides readily formed tin double salts. On reduction with alcoholic stannous chloride, 4-nitro-1-naphthylamine gave 1 : 4-naphthylenediamine dihydrochloride and 2-nitro-1-naphthylamine gave 1 : 2-naphthylenediamine monohydrochloride, whereas 1 : 5- and 1 : 8-dinitronaphthalene both gave tin double salts, $[C_{10}H_6(\overset{++}{NH_3})_2]Sn\overset{--}{Cl_6}$.

The 1 : 2-naphthylenediamines were much more readily oxidised than the 1 : 4-isomerides, *e.g.*, 4-chloro-1 : 2-naphthylenediamine was transformed by exposure to the atmosphere into 4-chloro-1 : 2-naphthaquinone within 20 minutes.

Experimental.

Preparation of the 4-Halogeno-2-naphthylamines.—2-Nitroaceto-1-naphthalide (20 g.) (prepared by partial hydrolysis of Lellmann and Remy's double compound; Hodgson and Walker, J., 1933, 1205), dissolved in glacial acetic acid (60 c.c.), was treated at 100° with chlorine for 30 minutes. 4-*Chloro*-2-*nitroaceto*-1-*naphthalide* (11 g.) crystallised from the solution on cooling; recrystallised from glacial acetic acid, it formed colourless feathery clusters of needles, m. p. 219° (Found : Cl, 13·4. $C_{12}H_9O_3N_2Cl$ requires Cl, 13·4%). It (10 g.) was refluxed for 6 hours with a mixture of dilute sulphuric acid (100 c.c. of 50%) and alcohol (100 c.c.), and 4-*chloro*-2-*nitro*-1-*naphthylamine* (8·4 g.) was filtered from the hot liquor, washed with bold water, dried, and crystallised from nitrobenzene or ethylene dichloride, forming orange needles, m. p. 202° (Found : Cl, 15·7. $C_{10}H_7O_2N_2Cl$ requires Cl, 15·9%). A hot solution of this compound (5 g.) in glacial acetic acid (50 c.c.) was chilled, and the suspension stirred into a solution of sodium nitrite (15 g.) in concentrated sulphuric acid (60 c.c.) below 20°; the mixture was poured into alcohol (150 c.c.) and heated on the water-bath until the volatile products had been expelled (90 minutes). The insoluble matter was washed with cold water, and the residue crystallised from alcohol or 90% formic acid, giving dark brown micro-needles of 1-*chloro*-3-*nitronaphthalene*, m. p. 127° (Found: Cl, 17·0. $C_{10}H_6O_2NCl$ requires Cl, 17·1%). This compound (4 g.) was intimately ground with hydrated stannous chloride (35 g.), and the mixture cautiously heated with concentrated hydrochloric acid (35 c.c.) and alcohol (5 c.c.); a vigorous reaction suddenly supervened with almost complete dissolution of the solids. 4-*Chloro*-2-*naphthylamine stannichloride* crystallised from the filtered cooled solution in large, light brown, lustrous plates [Found: Cl, 41·0. $(C_{10}H_8NCl,HCl)_2SnCl_4$ requires Cl, 41·2%]. On treatment with 2% aqueous sodium hydroxide at 50° it gave 4-*chloro*-2-*naphthylamine*, which crystallised from benzene or light petroleum in colourless needles, m. p. 68° (Found: Cl, 19·9. $C_{10}H_8NCl$ requires Cl, 20·0%).

4-*Bromo*-2-*naphthylamine*. In cold dry nitrobenzene, 2-nitro-1-naphthylamine (5 g. in 60 c.c.) was treated with bromine (1 c.c. in 10 c.c.). 4-Bromo-2-nitro-1-naphthylamine hydrobromide was formed, but decomposed as the reaction proceeded, giving the insoluble free base; this was washed successively with nitrobenzene and benzene, and crystallised from nitrobenzene, forming orange-brown needles, m. p. 197° (Meldola, J., 1885, **47**, 500, gives m. p. 197). Deamination by the standard process described above yielded 1-bromo-3-nitronaphthalene, which crystallised from 90% formic acid in pale yellow needles, m. p. 131° (Meldola, *loc. cit.*, gives m. p. 130—131°) (Found: Br, 31·7. Calc.: Br, 31·75%). Reduction by the above-described alcoholic stannous chloride method afforded buff-brown micro-needles of a *stannichloride*, which was recrystallised from concentrated hydrochloric acid [Found: Cl + Br, 47·7. $(C_{10}H_8NBr,HCl)_2SnCl_4$ requires Cl + Br, 47·9%]; decomposition of this with 2% aqueous sodium hydroxide at 40° gave 4-bromo-2-naphthylamine, which crystallised from 90% formic acid in colourless needles, m. p. 72° (Meldola, *loc. cit.*, gives m. p. 71·5°) (Found: Br, 36·0. Calc.: Br, 36·0%); the *acetyl* derivative crystallised from glacial acetic acid in colourless needles, m. p. 186·5° (Found: Br, 30·2. $C_{12}H_{10}ONBr$ requires Br, 30·3%).

2-*Nitro*-1-*naphthylamine* 4-*Mercuriacetate*.—When solutions of 2-nitro-1-naphthylamine (10 g. in 150 c.c.) and mercuric acetate (17·5 g. in 50 c.c.) in boiling glacial acetic acid were mixed, the *mercuriacetate* was precipitated as a powder, which crystallised from glacial acetic acid in orange-red needles, m. p. 242° (Found: Hg, 44·7. $C_{12}H_{10}O_4N_2Hg$ requires Hg, 44·9%). The *mercurichloride* formed brown needles, m. p. 289° (Found: Hg, 47·3. $C_{10}H_7O_2N_2ClHg$ requires Hg, 47·5%); the *mercuribromide*, red-brown needles, m. p. 248° (Found: Hg, 43·0. $C_{10}H_7O_2N_2BrHg$ requires Hg, 42·95%); the *mercuri-iodide*, deep scarlet needles, m. p. 237° (Found: Hg, 38·9. $C_{10}H_7O_2N_2IHg$ requires Hg, 39·0%); and the *mercurihydroxide*, scarlet needles, m. p. above 360° (decomp.) (Found: Hg, 49·5. $C_{10}H_8O_3N_2Hg$ requires Hg, 49·6%).

Treatment of the mercuriacetate in glacial acetic acid solution with chlorine and with bromine gave 4-chloro- and 4-bromo-2-nitro-1-naphthylamine respectively.

4-*Iodo*-2-*nitro*-1-*naphthylamine*.—2-Nitro-1-naphthylamine 4-mercuriacetate (50 g.) was added to a solution at 90° of 10% aqueous potassium iodide (500 c.c.) containing iodine (28·5 g.), the suspension boiled for 5 minutes, sufficient sodium thiosulphate added to destroy the residual iodine, and the precipitate of 4-iodo-2-nitro-1-naphthylamine removed from the hot solution, washed successively with boiling aqueous potassium iodide and boiling water, dried (44 g.), and crystallised from alcohol or nitrobenzene; it formed long golden-brown needles, m. p. 195·5° (Cumming and Howie, J., 1931, 3176, give m. p. 192—193°) (Found: I, 40·4. Calc.: I, 40·4%). Deamination by the standard process afforded 1-iodo-3-nitronaphthalene, which crystallised from alcohol or 90% formic acid in light orange plates, m. p. 146—147° (Cumming and Howie, *loc. cit.*, describe orange-yellow needles, m. p. 147°) (Found: I, 42·4. Calc.: I, 42·5%). Reduction by alcoholic stannous chloride gave light brown needles of 4-*iodo*-2-*naphthylamine stannichloride* [Found: Cl + I, 53·3. $(C_{10}H_8NI,HCl)_2SnCl_4$ requires Cl + I, 53·5%]. 4-*Iodo*-2-*naphthylamine*, obtained from this by means of 2% aqueous sodium hydroxide at 50°, crystallised from alcohol in brown needles, m. p. 76° (Found: I, 47·1. $C_{10}H_8NI$ requires I, 47·2%). The *acetyl* derivative, m. p. 201° (Found: I, 40·6. $C_{12}H_{10}ONI$ requires I, 40·8%), and the *benzoyl* derivative, m. p. 145° (Found: I, 33·9. $C_{17}H_{12}ONI$ requires I, 34·0%), both crystallised from glacial acetic acid in colourless needles.

2-*Chloro*-1 : 4-*naphthylenediamine and Derivatives*.—An intimate mixture of 2-chloro-4-nitro-1-naphthylamine (8 g.) and hydrated stannous chloride (64 g.) was suspended in alcohol (20 c.c.) and concentrated hydrochloric acid (60 c.c.), and carefully heated. After 5 minutes' boiling, 25 c.c. of concentrated hydrochloric acid were added; on cooling, 2-*chloro*-1 : 4-*naphthylenediamine monohydrochloride* separated in colourless needles, which were washed with and recrystallised from concentrated hydrochloric acid (Found: Cl, 30·7. $C_{10}H_9N_2Cl,HCl$ requires

Cl, 31·0%). Diazotisation of this hydrochloride in dilute hydrochloric acid proceeded normally at first, the solution giving a coupling with β-naphthol within 1 minute, but subsequently the diazo-solution deposited a deep purple powder, m. p. above 360° (decomp.) (Found: Cl, 5·6%).

2-*Chloro*-1 : 4-*naphthylenediamine* was obtained by the gradual dissolution of the hydrochloride (10 g.) in water (500 c.c.) at 90°, rapid addition of 20% aqueous sodium hydroxide (20 c.c.), and immediate chilling with vigorous stirring, a precaution which prevented superficial oxidation of the diamine. The colourless plates were recrystallised from hot water or 5% aqueous acetic acid and obtained in faintly green plates, m. p. 114° (Found: Cl, 18·4. $C_{10}H_9N_2Cl$ requires Cl, 18·4%). The diamine was readily oxidised by 2% alkaline potassium permanganate to give 2-chloro-1 : 4-naphthaquinone, which crystallised from water or alcohol in yellowish needles, m. p. 117° (Clève, *Ber.*, 1890, **23**, 955, gives m. p. 117°) (Found: Cl, 18·2. Calc.: Cl, 18·4%), and was volatile in steam.

Acetylation of the diamine with acetic anhydride alone (very violent reaction) or with this reagent in water or 5%, 20%, 40%, or 50% aqueous acetic acid always gave 2-*chloro*-NN′-*diacetyl*-1 : 4-*naphthylenediamine*, which crystallised from glacial acetic acid in colourless needles, m. p. 314° (Found: Cl, 12·8. $C_{14}H_{13}O_2N_2Cl$ requires Cl, 12·8%).

2-*Chloro*-NN′-*dibenzoyl*-1 : 4-*naphthylenediamine*, obtained from the diamine (2 g.), benzoyl chloride (10 c.c.) and 20% aqueous sodium hydroxide (20 c.c.), crystallised from alcohol in cream needles, m. p. 255° (Found: Cl, 8·7. $C_{24}H_{17}O_2N_2Cl$ requires Cl, 8·8%).

2-*Chloro*-1-N-*acetyl*-1 : 4-*naphthylenediamine*. 2-Chloro-4-nitroaceto-1-naphthalide (4 g.) (Hodgson and Elliott, *loc. cit.*), hydrated stannous chloride (40 g.), concentrated hydrochloric acid (30 c.c.) and alcohol (10 c.c.) gave, by the process already described, 2-*chloro*-1-N-*acetyl*-1 : 4-*naphthylenediamine stannichloride* in cream needles [Found: Cl, 35·3. $(C_{12}H_{11}ON_2Cl,HCl)_2SnCl_4$ requires Cl, 35·4%]. An aqueous solution of this salt (1 g. in 30 c.c.), treated with 20% aqueous sodium hydroxide (3 c.c.) at 60° and chilled as rapidly as possible, precipitated 2-*chloro*-1-N-*acetyl*-1 : 4-*naphthylenediamine*, which crystallised from water or 50% aqueous acetic acid in pinkish prisms, m. p. 215° (Found: Cl, 15·0. $C_{12}H_{11}ON_2Cl$ requires Cl, 15·1%).

2-*Bromo*-1 : 4-*naphthylenediamine and Derivatives.*—Reduction (as above) of 2-bromo-4-nitro-1-naphthylamine (Hodgson and Elliott, *loc. cit.*) afforded almost colourless needles of 2-*bromo*-1 : 4-*naphthylenediamine stannichloride* (Found: Cl + Br, 51·5. $C_{10}H_9N_2Br,2HCl,SnCl_4$ requires Cl + Br, 51·3%), which was converted by boiling concentrated hydrochloric acid into 2-*bromo*-1 : 4-*naphthylenediamine monohydrochloride*; this crystallised from the acid in colourless needles (Found: Cl + Br, 42·0. $C_{10}H_9N_2Br,HCl$ requires Cl + Br, 42·2%). Treatment of either salt with 5% aqueous sodium hydroxide at 90°, followed by rapid cooling, afforded 2-*bromo*-1 : 4-*naphthylenediamine*, which crystallised from hot water in greenish-yellow needles (slowly oxidised by air), m. p. 110° (Found: Br, 33·7. $C_{10}H_9N_2Br$ requires Br, 33·7%). The *diacetyl* derivative crystallised from glacial acetic acid in colourless needles, m. p. 318° (Found: Br, 24·8. $C_{14}H_{13}O_2N_2Br$ requires Br, 24·9%), and the *dibenzoyl* derivative from alcohol in needles, m. p. 259° (Found: Br, 17·9. $C_{24}H_{17}O_2N_2Br$ requires Br, 18·0%). Oxidation of the base gave 2-bromo-1 : 4-naphthaquinone, which crystallised from alcohol in yellow needles, m. p. 130° (Liebermann and Schlossberg, *Ber.*, 1899, **32**, 549, 2097, give m. p. **130°**) (Found: Br, 33·6. Calc.: Br, 33·7%).

2-*Bromo*-1-N-*acetyl*-1 : 4-*naphthylenediamine*. 2-*Bromo*-4-*nitroaceto*-1-*naphthalide*, prepared by boiling a solution of 2-bromo-4-nitro-1-naphthylamine (5 g.) (Hodgson and Elliott, *loc. cit.*) in glacial acetic acid (50 c.c.) with acetic anhydride (5 c.c.) for 3 minutes, and precipitated by water, crystallised from glacial acetic acid in pale green, feathery needles, m. p. 239° (Found: Br, 25·8. $C_{12}H_9O_3N_2Br$ requires Br, 25·9%). Its deep red solution in boiling 20% aqueous sodium hydroxide gave, on acidification with hydrochloric acid, 2-*bromo*-4-*nitro*-1-*naphthol*, which crystallised from alcohol in pale yellow needles, m. p. 236° (Found: Br, 29·8. $C_{10}H_6O_3NBr$ requires Br, 29·8%). Reduction of the naphthalide (as above) afforded 2-*bromo*-1-N-*acetyl*-1 : 4-*naphthylenediamine stannichloride*, which crystallised from concentrated hydrochloric acid in faintly pink needles [Found: Cl + Br, 41·7. $(C_{12}H_{11}ON_2Br,HCl)_2SnCl_4$ requires Cl + Br, 41·8%]. Treatment of this with 5% aqueous sodium hydroxide gave 2-*bromo*-1-N-*acetyl*-1 : 4-*naphthylenediamine*, which crystallised from 50% aqueous acetic acid in very light brown needles, m. p. 217° (Found: Br, 28·6. $C_{12}H_{11}ON_2Br$ requires Br, 28·7%), rapidly oxidised by air.

2-*Iodo*-1 : 4-*naphthylenediamine and Derivatives.*—Reduction (as above) of 2-iodo-4-nitro-1-naphthylamine (Hodgson and Elliott, *loc. cit.*) gave 2-*iodo*-1 : 4-*naphthylenediamine monohydrochloride*, which crystallised from concentrated hydrochloric acid in colourless needles (Found:

Cl + I, 50·6. $C_{10}H_9N_2I,HCl$ requires Cl + I, 50·7%) and on treatment with hot 5% aqueous sodium hydroxide afforded 2-*iodo*-1 : 4-*naphthylenediamine*, which crystallised from hot water in small, greenish-white needles, m. p. 119° (Found : I, 44·6. $C_{10}H_9N_2I$ requires I, 44·7%), slowly oxidised in air. Oxidation by alkaline 2% potassium permanganate solution produced 2-*iodo*-1 : 4-*naphthaquinone*, which crystallised from alcohol in yellow needles, m. p. 120° (Found : I, 44·5. $C_{10}H_5O_2I$ requires I, 44·7%). Acetylation, as above, of the diamine always afforded 2-*iodo*-NN′-*diacetyl*-1 : 4-*naphthylenediamine*, which crystallised from glacial acetic acid in pinkish plates, m. p. 322° (Found : I, 34·2. $C_{14}H_{13}O_2N_2I$ requires I, 34·5%). 2-*Iodo*-NN′-*dibenzoyl*-1 : 4-*naphthylenediamine* crystallised from alcohol in faintly purple needles, m. p. 262° (Found : I, 25·6. $C_{24}H_{17}O_2N_2I$ requires I, 25·8%).

2-*Iodo*-1-N-*acetyl*-1 : 4-*naphthylenediamine*. Since 2-iodo-4-nitro-1-naphthylamine could not be acetylated and 4-nitroaceto-1-naphthalide could not be mercurated, the desired compound was prepared as follows : 4-Nitro-1-naphthylamine 2-mercuriacetate (10 g.) (Hodgson and Elliott, *loc. cit.*) was heated with acetic anhydride (60 c.c.) for 6 minutes and the chrome-yellow precipitate was removed from the cooled solution, washed successively with acetic anhydride and acetic acid, and crystallised from glacial acetic acid, giving mustard-yellow needles of 4-*nitroaceto*-1-*naphthalide* 2-*mercuriacetate*, m. p. 270° (Found : Hg, 40·9. $C_{14}H_{12}O_5N_2Hg$ requires Hg, 41·1%). This mercuriacetate (10 g.) was boiled with a solution of iodine (5·7 g.) in aqueous potassium iodide for 5 minutes, the excess of iodine destroyed by sodium thiosulphate, and the 2-*iodo*-4-*nitroaceto*-1-*naphthalide* filtered off and crystallised from glacial acetic acid, forming greenish-yellow needles, m. p. 222° (Found : I, 35·5. $C_{12}H_9O_3N_2I$ requires I, 35·7%). Its blood-red solution in boiling 20% aqueous sodium hydroxide, on acidification with hydrochloric acid, gave 2-*iodo*-4-*nitro*-1-*naphthol*, which crystallised from alcohol in yellow-white needles, m. p. 229° (Found : I, 40·2. $C_{10}H_6O_3NI$ requires I, 40·3%).

Reduction of 2-iodo-4-nitroaceto-1-naphthalide by the stannous chloride process, gave 2-*iodo*-1-N-*acetyl*-1 : 4-*naphthylenediamine stannichloride*, which crystallised from concentrated hydrochloric acid in cream-coloured needles [Found : Cl + I, 47·3. $(C_{12}H_{11}ON_2I,HCl)_2SnCl_4$ requires Cl + I, 47·4%]. This, on treatment with warm 5% aqueous sodium hydroxide, afforded 2-*iodo*-1-N-*acetyl*-1 : 4-*naphthylenediamine*, which crystallised from glacial acetic acid in colourless needles, m. p. 235° (Found : I, 38·7. $C_{12}H_{11}ON_2I$ requires I, 38·9%).

4-*Chloro*-1 : 2-*naphthylenediamine and Derivatives.*—4-Chloro-2-nitro-1-naphthylamine, reduced by the stannous chloride process, gave 4-*chloro*-1 : 2-*naphthylenediamine monohydrochloride*, which crystallised from concentrated hydrochloric acid in very light brown plates (Found : Cl, 30·9. $C_{10}H_9N_2Cl,HCl$ requires Cl, 31·0%). Treatment with 2% aqueous sodium hydroxide at 60° gave 4-*chloro*-1 : 2-*naphthylenediamine*, which formed pinkish needles, m. p. 95°, from hot water (Found : Cl, 18·3. $C_{10}H_9N_2Cl$ requires Cl, 18·4%). Acetylation was effected by gently warming the diamine (3 g.) with acetic anhydride (10 c.c.) until reaction occurred (35—40°), cooling, pouring into cold water (100 c.c.), and keeping for 15 minutes; the precipitate crystallised from glacial acetic acid in brownish needles, m. p. 235° (Found : Cl, 15·0. $C_{12}H_{11}ON_2Cl$ requires Cl, 15·1%), of a monoacetylated derivative. On theoretical grounds the acetyl group should preferentially enter the 2-amino-group, and actually the product has been identified as 4-*chloro*-2-N-*acetyl*-1 : 2-*naphthylenediamine* by the following preparation of 4-*chloro*-1-N-*acetyl*-1 : 2-*naphthylenediamine* : 4-Chloro-2-nitroaceto-1-naphthalide, reduced by the stannous chloride process, gave 4-*chloro*-1-N-*acetyl*-1 : 2-*naphthylenediamine stannichloride* [Found : Cl, 35·2. $(C_{12}H_{11}ON_2Cl,HCl)_2SnCl_4$ requires Cl, 35·4%]. 4-Chloro-1-*N*-acetyl-1 : 2-naphthylenediamine, obtained from this by means of 5% aqueous sodium hydroxide, crystallised from hot water in cream-coloured needles, m. p. 243° (Found : Cl, 15·0%), depressed to 224° by the 2-*N*-acetyl isomeride. Boiling acetic anhydride converted 4-chloro-1-*N*-acetyl-1 : 2-naphthylenediamine into the *diacetyl* derivative [cream needles from glacial acetic acid, m. p. 174° (Found : Cl, 12·7. $C_{14}H_{13}O_2N_2Cl$ requires Cl, 12·8%)], but had no action on the 2-*N*-acetyl isomeride.

Air-oxidation of the 4-chloro-1 : 2-naphthylenediamine was so rapid that within 20 minutes of isolation it was converted into 4-*chloro*-1 : 2-*naphthaquinone*, which crystallised from alcohol in maroon needles, m. p. 188° (Found : Cl, 18·3. $C_{10}H_5O_2Cl$ requires Cl, 18·4%).

4-*Bromo*-1 : 2-*naphthylenediamine and Derivatives.*—From the solution obtained by the standard stannous chloride reduction of 4-bromo-2-nitro-1-naphthylamine (Hodgson and Elliott, *loc. cit.*), 4-*bromo*-1 : 2-*naphthylenediamine monohydrochloride* separated; it crystallised from hydrochloric acid in colourless needles (Found : Cl + Br, 42·0. $C_{10}H_9N_2Br,HCl$ requires Cl + Br, 42·2%).

Treatment of the hydrochloride with 5% aqueous sodium hydroxide at 90°, followed by rapid cooling, yielded 4-*bromo*-1 : 2-*naphthylenediamine*, which crystallised from hot water or 10% aqueous acetic acid in cream-coloured micro-plates, m. p. 97° (Found : Br, 33·6. $C_{10}H_9N_2Br$ requires Br, 33·7%). Acetylation of the diamine with boiling acetic anhydride gave only 4-*bromo*-2-N-*acetyl*-1 : 2-*naphthylenediamine*, which crystallised from glacial acetic acid in colourless needles, m. p. 225° (Found : Br, 28·4. $C_{12}H_{11}ON_2Br$ requires Br, 28·7%).

Bromine (0·65 c.c.) in glacial acetic acid (36 c.c.) was added drop by drop to a vigorously stirred solution of 2-nitroaceto-1-naphthalide (6 g.) in glacial acetic acid (36 c.c.) above 45°. On cooling, 4-*bromo*-2-*nitroaceto*-1-*naphthalide* separated; it crystallised from glacial acetic acid in pale greenish, feathery needles, m. p. 239° (Found : Br, 25·8. $C_{12}H_9O_3N_2Br$ requires Br, 25·9%). Reduction by the above stannous chloride process afforded 4-*bromo*-1-N-*acetyl*-1 : 2-*naphthylenediamine stannichloride*, which crystallised from hot concentrated hydrochloric acid (in which it is very soluble), on cooling, in colourless needles [Found : Cl + Br, 41·7. $(C_{12}H_{11}ON_2Br,HCl)_2SnCl_4$ requires Cl + Br, 41·8%]. 4-*Bromo*-1-N-*acetyl*-1 : 2-*naphthylenediamine* crystallised from hot water in colourless plates, m. p. 248° (Found : Br, 28·5. $C_{12}H_{11}ON_2Br$ requires Br, 28·7%), and 217° when mixed with 4-bromo-2-*N*-acetyl-1 : 2-naphthylenediamine. Boiling acetic anhydride converted the 1-*N*-acetyl compound into 4-*bromo*-NN'-*diacetyl*-1 : 2-*naphthylenediamine* [brownish needles, m. p. 225°, from glacial acetic acid (Found : Br, 24·7. $C_{14}H_{13}O_2N_2Br$ requires Br, 24·9%)], but did not attack the 2-*N*-acetyl isomeride.

4-*Iodo*-1 : 2-*naphthylenediamine and Derivatives*.—The following compounds were prepared from 4-iodo-2-nitro-1-naphthylamine (Hodgson and Elliott, *loc. cit.*) by the methods used for the bromo-analogues. 4-*Iodo*-1 : 2-*naphthylenediamine monohydrochloride*, pale brownish needles from concentrated hydrochloric acid (Found : Cl + I, 50·5. $C_{10}H_9N_2I,HCl$ requires Cl + I, 50·7%). 4-*Iodo*-1 : 2-*naphthylenediamine*, purplish prisms, m. p. 98°, from hot water (Found : I, 44·4. $C_{10}H_9N_2I$ requires I, 44·7%). 4-*Iodo*-2-N-*acetyl*-1 : 2-*naphthylenediamine*, colourless needles from glacial acetic acid, m. p. 238° (Found : I, 38·7. $C_{12}H_{11}ON_2I$ requires I, 38·9%); 4-*iodo*-1-N-*acetyl*-1 : 2-*naphthylenediamine*, colourless plates from hot water, m. p. 271° (Found : I, 38·8%); mixed m. p. 231°. 4-*Iodo*-NN'-*diacetyl*-1 : 2-*naphthylenediamine*, colourless needles, m. p. 167°, from glacial acetic acid (Found : I, 34·4. $C_{14}H_{13}O_2N_2I$ requires I, 34·5%). 4-*Iodo*-1-N-*acetyl*-1 : 2-*naphthylenediamine stannichloride*, colourless needles from concentrated hydrochloric acid [Found : Cl + I, 47·3. $(C_{12}H_{11}ON_2I,HCl)_2SnCl_4$ requires Cl + I, 47·4%]. As initial materials, 4-iodoaceto-1-naphthalide, and 4-iodo-2-nitroaceto-1-naphthalide were prepared by Meldola's methods (*loc. cit.*).

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