47. *Substitution Reactions of the Naphthylenediamines. Part III. The Bromination of* 1 : 5- *and* 1 : 8-*Naphthylenediamines and Related Compounds.*

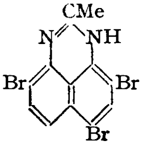
By J. S. Whitehurst.

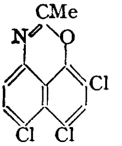
Bromination of 1 : 8-naphthylenediamine in glacial acetic acid gave first 2 : 4 : 7-tribromo-1 : 8-naphthylenediamine and then 4 : 7 : 9(or 4 : 6 : 9)-tribromo-2-methylperimidine dibromide. 2-Methylperimidine on bromination yielded a monobromo-2-methylperimidine, a dibromo-compound, and a dibromide of the latter, and on nitration a dinitro-compound. Although 1 : 5-naphthylenediamine and bromine produced substances of high molecular weight, the diacetyl derivative readily gave 1 : 5-diacetamido-4 : 8-dibromonaphthalene. 1 : 8-Dibenzamidonaphthalene, under similar conditions, lost a benzoyl group and was converted into a brominated 2-phenylperimidine, identical with the bromination product of 2-phenylperimidine itself

1 : 8-Naphthylenediamine, on treatment with excess of bromine in hot glacial acetic acid solution, gave, in high yield, a tribromo-2-methylperimidine dibromide, the *peri*-diamine groups having been involved in ring closure with one molecule of acetic acid. It was thought desirable to establish, not only the constitution of this substance, but also the approximate course of the reaction—whether, for instance, ring closure had occurred before or after the introduction of any of the bromine atoms. It was found that 1 : 8-naphthylenediamine was not substantially converted into 2-methylperimidine by hot glacial acetic acid, and that 2-methylperimidine, brominated under conditions similar to those employed for the diamine, gave a dibromo-2-methylperimidine dibromide. Furthermore, by use of only three molecular proportions of bromine in glacial acetic acid, 1 : 8-naphthylenediamine yielded a tribromo-diamine. Clearly, ring closure occurs after the entry of all three bromine atoms.

Tetrazotisation of the tribromo-diamine proved difficult, and the tribromonaphthalene obtained by deamination with ethanol was accompanied by a *peri*-triazine derivative. The melting point of the former was gradually raised to 95—96°. Attempts to increase the yield by deamination with hypophosphorous acid were unsuccessful. Obviously, unless anomalous *meta*-substitution has occurred, the bromine atoms in the tribromo-1 : 8-naphthylenediamine must be in either the 2 : 4 : 5- or the 2 : 4 : 7-positions, and therefore this tribromonaphthalene is either the 1 : 3 : 8- or the 1 : 3 : 6-compound. The former is yet unknown, but the latter was prepared by Claus and Jäck (*J. pr. Chem.*, 1898, **57**, 18) from 1 : 3 : 6-tribromo-2-naphthylamine, the constitution of which was established by Franzen and Stauble (*ibid.*, 1920, **101**, 59) [cf. Fries and Schimmelschmidt, *Annalen*, 1930, **484**, 248 (Note 1), 250 (Note 1)]. 1 : 3 : 6-Tribromo-2-naphthylamine has been obtained from 1-bromo-2-naphthylamine, by bromination in chloroform (Claus and Philipson, *J. pr. Chem.*, 1891, **43**, 56); from 2-toluene-*p*-sulphonamidonaphthalene, by bromination first in chloroform (which produces the 1 : 6-derivative) and then in pyridine, followed by hydrolysis (Bell, *J.*, 1932, 2732); and from benzylidene-2-naphthylamine, by repeated bromination and rearrangement of the products (Franzen and Aaslund, *J. pr. Chem.*, 1917, **95**, 160). Of these methods, that of Bell appeared the most promising. This author gives few experimental details for the preparation of 1 : 6-dibromo-2-toluene-*p*-sulphonamidonaphthalene and under the conditions employed by us it was found that the major product was

1 : 6-dibromo-2-naphthylamine hydrobromide, obviously formed by hydrolysis of the initially formed sulphonamide. Also, contrary to the statement of Claus and Philipson (*loc. cit.*), the bromination of 1-bromo-2-naphthylamine in chloroform did not proceed further than the formation of the same dibromonaphthylamine hydrobromide. However, 1 : 6-dibromo-2-naphthylamine on being rapidly treated with excess of bromine in hot chloroform produced 1 : 3 : 6-tribromo-2-naphthylamine hydrobromide, the formation of this compound being noteworthy in that Claus *et al.* (*loc. cit.*) failed to detect any basic properties of the amine. Diazotisation in sulphuric acid–glacial acetic acid, followed by deamination with ethanol, afforded, in good yield, 1 : 3 : 6-tribromonaphthalene, m. p. 100—101°, undepressed on admixture with the substance, m. p. 95—96°, prepared earlier. Microscopical examination of the two specimens under polarised light revealed their identity. Hence it was concluded that 1 : 8-naphthylenediamine had undergone bromination to yield 2 : 4 : 7-tribromo-1 : 8-naphthylenediamine and 4 : 7 : 9(or 4 : 6 : 9)-tribromo-2-methylperimidine (I). The two structures which can be written for the latter are probably identical, as this is almost certainly a case of hydrogen-bond mesomerism (cf. Hunter, *J.*, 1945, 806, for similar cases).


(I.)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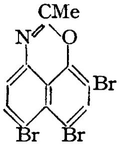
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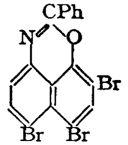
(IV.)

These results may be compared with those of Fichter *et al.* (*Ber.*, 1906, **39**, 3331; 1909, **42**, 4748) on the halogenation of 8-acetamido-1-naphthol and 8-benzamido-1-naphthol. Chlorination of the former in acetone yielded (II), and bromination in glacial acetic acid was reported to give the dibromide of (III). Under similar conditions, 8-benzamido-1-naphthol and bromine produced (IV). However, in none of these compounds was the orientation of the halogen atoms proved, and it was unfortunate that the halogenation of 8-amino-1-naphthol itself in glacial acetic acid was not reported.

When less bromine was used, 2-methylperimidine yielded a monobromo-compound, m. p. 181°, and a dibromo-compound, m. p. 217—219° (decomp.), and, as electrophilic substitution would be expected to occur in the naphthalene nucleus *ortho* and *para* to the nitrogen atoms, the former is either 4(9)- or 6(7)-bromo-2-methylperimidine. Hodgson and Hathway (*J.*, 1945, 543) have described 6(7)-bromo-2-methylperimidine (m. p. 131°), but attempts to repeat their work proved abortive. The possible nuclear-substituted dibromo-2-methylperimidines would seem to be the 4 : 6-, 7 : 9-, 4 : 7-, 6 : 9-, 6 : 7-, and 4 : 9-compounds, but of these the 4 : 6- and 7 : 9-structures are probably resonance forms of the same substance, and similar considerations apply to the 4 : 7- and 6 : 9-compounds. At any rate, the separate existence of tautomers in these pairs would be unrealisable under ordinary conditions. Hodgson and Crook (*J.*, 1936, 1338) have described 7 : 9-dibromo-2-methylperimidine, and this work was amply confirmed as far as the preparation of the stannichloride of the desired product, but the liberation of the latter proved extraordinarily difficult and the green solution obtained in the presence of ether or benzene furnished a dark green substance, m. p. *ca.* 150—160°. In these circumstances no conclusions could be drawn concerning the structures of these brominated 2-methylperimidines. On the other hand, after 1 : 8-naphthylenediamine had been treated in benzene with acetyl chloride, bromination of the basified product in acetic acid furnished 4 : 6(7) : 9-tribromo-2-methylperimidine, identical with a specimen made from 2 : 4 : 7-tribromo-1 : 8-naphthylenediamine and acetic anhydride. As 2-methylperimidine has been found to undergo bromination only so far as a dibromo-compound this must mean that the reaction product of 1 : 8-naphthylenediamine and acetyl chloride must contain either 8-acetamido-1-naphthylamine or unchanged 1 : 8-naphthylenediamine. None of the latter was detected.

The nitration of 2-methylperimidine in glacial acetic acid was parallel to that of bromination. After the initial separation of 2-methylperimidine nitrate, a dinitro-compound was formed. 1 : 5-Diacetamidonaphthalene, on nitration either in glacial acetic acid or in fuming nitric acid, gave yellow amorphous substances which proved intractable, but on bromination it gave a dibromo-derivative apparently identical with 1 : 5-diacetamido-4 : 8-dibromonaphthalene. Hence the bromination of 1 : 5-diacetamidonaphthalene occurs in the same sense as that of 1 : 5-ditoluene-*p*-sulphonamidonaphthalene (cf. Part II, preceding paper). Many fruitless attempts were made to prepare 1 : 8-diacetamidonaphthalene. Reaction of the diamine with acetic anhydride in aqueous alcoholic potassium hydroxide gave a blue solution containing unchanged diamine. In other media the only isolable product was 2-methylperimidine. 1 : 8-Dibenzamidonaphthalene, on bromination in glacial acetic acid, was converted into a compound $C_{17}H_8N_2Br_6$, which is clearly a brominated 2-phenylperimidine. During this reaction, one benzoyl group has been hydrolysed and the other has undergone ring closure. 2-Phenylperimidine, brominated under similar conditions, gave the same compound. Its structure has not yet been settled.

The bromination of 1 : 5-naphthylenediamine took place in an entirely unexpected manner, and was studied in a variety of media including water, dilute hydrochloric acid, benzene, ethanol, chloroform, carbon tetrachloride, ethylene dichloride, glacial acetic acid, and pyridine. In the last two solvents, the addition of bromine immediately gave amorphous black precipitates; in other media, in particular chloroform and carbon tetrachloride, the products were indigo-coloured. Dilute sodium carbonate solution removed practically no hydrobromic acid from these precipitates, and as they were virtually insoluble in organic solvents, and decomposed gradually when heated to high temperatures, they must have contained compounds of high molecular weight. Analysis of two products, (A) and (B) (see Experimental Section), the former obtained by employing 0·1 mole of bromine in chloroform, the latter by using excess of bromine in glacial acetic acid, showed clearly that the maximum amount of bromine introduced into the naphthalene molecule corresponded to one atom. The difference in the behaviour of 1 : 5- and 1 : 8-naphthylenediamines towards bromine is probably due to 1 : 5-naphthaquinone structures being possible whereas 1 : 8-naphthaquinone structures are not (Vesely and Jakes, *Bull. Soc., chim.*, 1923, **33**, 955). Most likely 1 : 5-naphthylenediamine is converted initially into a monobromonaphthylenediamine, the bromine atom perhaps entering position 2 (cf. the bromination of 1 : 5-dihydroxynaphthalene; Wheeler and Ergle, *J. Amer. Chem. Soc.*, 1930, **52**, 4872; Carter, Race, and Rowe, *J.*, 1942, 236); this may be oxidised to a highly reactive 1 : 5-naphthaquinonedi-imine which combines with excess of naphthylenediamine to produce (A). Further action of bromine will give rise to (B). The formation of these substances may be analogous to that of the highly coloured substances obtained by Thompson (*J. Org. Chem.*, 1948, **13**, 371) from 1 : 5-dihydroxynaphthalene and chlorine in glacial acetic acid solution.

Another possible synthesis of halogeno-diamines, *viz.*, from mercuri-compounds, proved impracticable as both diamines reduced mercuric acetate to the mercurous salt. The latter was precipitated almost immediately on mixing of glacial acetic solutions of mercuric acetate and 1 : 5-naphthylenediamine. The fate of the latter was not investigated in detail, although it was found that an equivalent molar quantity of 1 : 5-dihydroxynaphthalene yielded the same amount of mercurous acetate. As 1 : 5-dihydroxynaphthalene is known to be oxidised to juglone (Bernsthen and Semper, *Ber.*, 1887, **20**, 939) it seems that this compound is also produced from the diamine. Although 1 : 8-naphthylenediamine was also oxidised by mercuric acetate in glacial acetic acid no separation of mercurous acetate occurred until ethanol was added to the solution. It seems probable, therefore, that the oxidation of this diamine takes a different course from that of the 1 : 5-isomer, a fact observed by Willstätter and Wheeler (*Ber.*, 1914, **47**, 2798) in contrast to the claim of Erdmann (*Annalen*, 1888, **247**, 358) in the case of the corresponding dihydroxynaphthalenes.

EXPERIMENTAL.

(M. p.s are uncorrected.)

Bromination of 1 : 5-*Naphthylenediamine.*—(*a*) *In chloroform.* The diamine (1 g.) in chloroform (150 c.c.) was treated with a 1% (v/v) solution of bromine in chloroform (3 c.c.) with vigorous stirring at 15°. The indigo-coloured precipitate was washed with chloroform (50 c.c. in all), dried, and extracted with warm (40°) 2% sodium carbonate solution (100 c.c.) and dried again (product A). (*b*) *In glacial acetic acid.* The diamine (1 g.) in glacial acetic acid (50 c.c.) was treated with a solution of bromine (1·2 c.c.) in glacial acetic acid (10 c.c.) with vigorous stirring at 15°. The almost black precipitate was washed with glacial acetic acid (20 c.c.), dried, extracted with sodium carbonate solution (100 c.c.) as above, and dried again (product B). Both products shrank at *ca.* 250°, but did not melt at 350°, and were insoluble in the usual solvents [Found (first values for A, second for B) : C, 62·4, 49·6; H, 4·6, 3·1; N, 14·7, 11·6; Br, 16·6, 33·8. Calc. for $C_{10}H_5Br\cdot(NH_2)$: C, 50·65; H, 3·8; N, 11·8; Br, 33·7. Calc. for $C_{10}H_6(NH_2)_2$: C, 75·9; H, 6·4; N, 17·7; Br, 0·0%].

Bromination of 1 : 5-*Diacetamidonaphthalene.*—The compound (1 g.) in glacial acetic acid (50 c.c.) was treated with a solution of bromine (0·8 c.c.) in glacial acetic acid (5 c.c.) at *ca.* 90° with stirring. The initially formed oil rapidly solidified and on crystallisation from hot nitrobenzene gave colourless needles of 1 : 5-diacetamido-4 : 8-dibromonaphthalene (0·7 g.) (Found : C, 42·7; H, 3·1; Br, 37·8. Calc. for $C_{14}H_{12}O_2N_2Br_2$: C, 42·0; H, 3·0; Br, 40·0%). The compound darkened at *ca.* 250° and decomposed continuously above this temperature without forming a sublimate.

Bromination of 1 : 8-*Dibenzamidonaphthalene*.—A solution of bromine in glacial acetic acid (2·5 c.c.; 10% v/v) was added to the compound (0·32 g.) in glacial acetic acid (100 c.c.) at 90°. On cooling, beautiful orange-coloured needles crystallised from the solution (0·29 g.). The *substance* was sparingly soluble in the usual solvents. It darkened at 200° and melted at 235—240° (decomp.) (Found : C, 28·7; H, 1·23; N, 3·7; Br, 66·7. $C_{17}H_8N_2Br_6$ requires C, 28·4; H, 1·1; N, 3·9; Br, 66·6%).

2-*Phenylperimidine*.—This compound was made according to the directions of Sachs (*Annalen*, 1909, **365**, 94), as well as by the following method : 1 : 8-Naphthylenediamine (1 g.) in boiling benzene (25 c.c.) was treated with benzoic anhydride (2 g.). After 2 hours the benzene was slowly distilled off and the resulting gum left with 10% sodium hydroxide solution for a further 2 hours at *ca.* 50°. The crystalline residue was collected and recrystallised from aqueous ethanol (charcoal). 2-Phenylperimidine formed orange yellow needles (0·8 g.; m. p. 187—188°).

Bromination of 2-*Phenylperimidine*.—The compound (0·35 g.) in glacial acetic acid (100 c.c.) was treated with a solution of bromine in glacial acetic acid (5·5 c.c.; 10% v/v) at 90—95°. The mustard-yellow precipitate (0·80 g.) was collected, washed with a little glacial acetic acid, and dried in a vacuum (Found : C, 28·9; H, 1·3; N, 3·6; Br, 64·6%). No depression of melting point, 235—240° (decomp.), was observed when it was mixed with the previous specimen.

2-*Methylperimidine*.—The compound was best made by treating 1 : 8-naphthylenediamine (2 g.) with acetic anhydride (20 c.c.). Much heat was evolved; the diamine dissolved and the solution rapidly set to a mass of yellow needles of 2-methylperimidine acetate (2·0 g.). When crystallised from acetic anhydride it had m. p. 144° (Found : C, 69·1; H, 5·9. Calc. for $C_{14}H_{14}O_2N_2$: C, 69·4; H, 5·8%) (Sachs, *loc. cit.*, gives m. p. 130—140°). It was very soluble in the usual organic solvents, but sparingly soluble in cold acetic anhydride. Addition of aqueous ammonia to the aqueous solution liberated 2-methylperimidine, which crystallised from ethanol in pale greenish-yellow needles, m. p. 215—216° (decomp.) (Found: N, 15·2. Calc. for $C_{12}H_{10}N_2$: N, 15·4%).

Nitration of 2-*Methylperimidine*.—The compound (1 g.) in glacial acetic acid (10 c.c.) was treated dropwise with nitric acid (2 c.c.; *d* 1·42). The initial precipitate of 2-methylperimidine nitrate gradually dissolved and the reaction was completed by gentle warming on the water-bath. After filtration, the solution was treated with ethanol, and the orange-brown precipitate (m. p. *ca.* 180—190°) collected and crystallised from aqueous acetic acid. The *dinitro*-2-*methylperimidine* formed orange-yellow needles, darkening at 200° and melting at 238—240° to a deep-red liquid (Found : C, 53·2; H, 2·9; N, 20·2. $C_{12}H_8O_4N_4$ requires C, 52·9; H, 2·9; N, 20·6%). The nitration medium contained material which stained the fingers an intense orange-red.

Bromination of 2-*Methylperimidine*.—(a) *The monobromo-compound.* A vigorously stirred solution of the substance (0·3 g.) in glacial acetic acid (50 c.c.) was treated cautiously at 85—90° with a solution of bromine in glacial acetic acid (1·35 c.c., 1·5 moles; 10% v/v). On cooling, colourless nodules of the *hydrobromide* separated (0·19 g.), decomposing at *ca.* 300° (Found : Br′, 22·7. $C_{12}H_{10}N_2Br_2$ requires Br′, 23·4%), from which the *monobromo*-2-*methylperimidine* was liberated with aqueous ammonia. It crystallised from benzene in rosettes of pale green needles, m. p. 181° (Found : C, 55·1; H, 3·6; Br, 29·8. $C_{12}H_9N_2Br$ requires C, 55·2; H, 3·5; Br, 30·6%).

(b) *The dibromo-compound.* 2-Methylperimidine (0·4 g.) in well-stirred glacial acetic acid (90 c.c.) was treated with bromine in glacial acetic acid (3·6 c.c., 3 moles; 10% v/v) at 90°. The colourless *hydrobromide* (0·67 g.), m. p. 256—260° (decomp.) (Found : Br′, 18·4. $C_{12}H_9N_2Br_3$ requires Br′, 19·0%), which separated from the orange-coloured solution was collected and treated with aqueous ammonia, and the *dibromo*-2-*methylperimidine* was crystallised from benzene. It formed pale greenish-yellow needles which darkened at 200° and melted (decomp.) at 218—219° (Found : C, 42·7; H, 2·8; Br, 47·9. $C_{12}H_8N_2Br_2$ requires C, 42·4; H, 2·4; Br, 47·0%). The acetic acid filtrate from the above bromination on being poured into water produced a vivid blue colour.

(c) *The dibromo-compound dibromide.* A well stirred solution of 2-methylperimidine (0·5 g.) in glacial acetic acid (125 c.c.) was treated at 90—95° with a solution of bromine in the same solvent (6 c.c., 4·5 moles, 10% v/v). After cooling, the mustard-yellow needles [1·30 g.; m. p. *ca.* 225° (decomp.)] were collected, and a portion was crystallised from glacial acetic acid (in which it was sparingly soluble). The *dibromide* formed long mustard-yellow needles, m. p. 247° (decomp.) after darkening at 244° (Found : C, 28·1; H, 1·9; N, 5·2; Br, 62·6. $C_{12}H_8N_2Br_4$ requires C, 28·8; H, 1·6; N, 5·6; Br, 63·9%).

Bromination of 1 : 8-*Naphthylenediamine*.—(a) 2 : 4 : 7-*Tribromo*-1 : 8-*naphthylenediamine*. A vigorously stirred solution of 1 : 8-naphthylenediamine (0·5 g.) in glacial acetic acid (200 c.c.) at 90° was rapidly treated with a solution of bromine in the same solvent (5 c.c.; 10% v/v). On cooling, the shining silvery platelets of the *monohydrobromide* were removed, washed with a little glacial acetic acid, and dried in a vacuum (1·02 g.; darkens at 240° but is not molten at 320°) (Found : Br′, 16·2. $C_{10}H_8N_2Br_4$ requires Br′, 16·80%). It was decomposed with warm aqueous ammonia, and the liberated *tribromo-diamine*, recrystallised from ethanol, formed colourless rosettes of needles, m. p. 137—138° (Found : C, 30·7; H, 1·7; N, 6·9; Br, 60·2. $C_{10}H_7N_2Br_3$ requires C, 30·4; H, 1·8; N, 7·1; Br, 60·7%).

(b) *The dibromide of* 4 : 6(7) : 9-*tribromo*-2-*methylperimidine*. A solution of bromine (1 c.c.) in glacial acetic acid (5 c.c.) was added to a well stirred solution of 1 : 8-naphthylenediamine (0·5 g.) in glacial acetic acid (150 c.c.) at 95°. The yellow crystalline precipitate (1·5 g.) was collected, washed with a little glacial acetic acid, and dried in a vacuum. It is sparingly soluble in glacial acetic acid, crystallising therefrom in pale yellow needles, shrinking at *ca.* 250° and decomposing above this temperature (Found : C, 25·4; H, 1·6; Br, 68·2. $C_{12}H_7N_2Br_5$ requires C, 24·9; H, 1·2; Br, 69·0%).

4 : 6(7) : 9-*Tribromo*-2-*methylperimidine* was prepared from 2 : 4 : 7-tribromo-1 : 8-naphthylenediamine and boiling acetic anhydride. Addition of water to the cooled solution followed by crystallisation of the precipitate from benzene furnished yellow needles of the compound, m. p. 217—218°

(decomp.) after becoming green at *ca*. 200° (Found : C, 34·7; H, 1·8; N, 7·0; Br, 57·0. $C_{12}H_7N_2Br_3$ requires C, 34·4; H, 1·7; N, 6·7; Br, 57·2%). It was moderately soluble in ethanol, benzene, or glacial acetic acid.

4 : 6(7) : 9-*Tribromo-2-phenylperimidine* was formed from 2 : 4 : 7-tribromo-1 : 8-naphthylenediamine and benzoyl chloride in benzene solution. After being on a water-bath for 2 hours, the faint white precipitate was removed, and the solution concentrated in a vacuum. 4 : 6(7) : 9-Tribromo-2-phenylperimidine separated from benzene in beautiful orange needles, darkening at 200° and melting (decomp.) at 215° (Found : C, 42·4; H, 1·9; Br, 50·1. $C_{17}H_9N_2Br_3$ requires C, 42·4; H, 1·9; Br, 49·9%). It was sparingly soluble in ethanol or glacial acetic acid.

1-*Bromo-2-naphthylamine*.—2-Acetonaphthalide (20 g.; m. p. 132°), prepared from 2-naphthylamine and acetic anhydride in benzene (Leonard and Boyd, *J. Org. Chem.*, 1946, **11**, 416; Ott and Levy, unpublished), was dissolved in the minimum amount of hot chloroform, and treated rapidly, with stirring, with a solution of bromine (12 c.c.) in chloroform (50 c.c.). The colourless precipitate of 1-bromo-2-acetonaphthalide hydrobromide [22 g.; m. p. 185—195° (decomp.)] (Franzen and Eidis, *J. pr. Chem.*, 1913, **88**, 760, give m. p. 180—190°) (Found : Br′, 22·7. Calc. for $C_{12}H_{11}ONBr_2$: Br′, 23·2%), was collected, dried, and decomposed with hot water. The resulting 1-bromo-2-acetonaphthalide, m. p. 138—139° (Lellmann and Schmidt, *Ber.*, 1887, **20**, 3154, and James and Judd, *J.*, 1914, 1433, give m. p. 140°), was added, in small portions, to boiling hydrochloric acid (500 c.c.; 15% w/v). After 15 minutes, the mixture was cooled and the crystalline 1-bromo-2-naphthylamine hydrochloride [9·5 g.; m. p. 225° (decomp.) after darkening at 200°] removed. Treatment with aqueous ammonia and crystallisation from aqueous ethanol yielded 1-bromo-2-naphthylamine, m. p. 63° (Franzen and Eidis, *loc. cit.*, give m. p. 63—64°) (Found : N, 6·0. Calc. for $C_{10}H_8NBr$: N, 6·3%).

1 : 3 : 6-*Tribromo-2-naphthylamine*.—1-Bromo-2-naphthylamine (2 g.) in hot chloroform (50 c.c.) was treated with bromine (1 c.c.) in chloroform (5 c.c.). The almost colourless precipitate of 1 : 6-*dibromo-2-naphthylamine hydrobromide* [2·4 g.; m. p. 264° (decomp.)] (Found : Br′, 20·5. $C_{10}H_8NBr_3$ requires Br′, 20·9%) was treated with dilute aqueous sodium carbonate, and a portion of the residue was crystallised from ethanol. 1 : 6-Dibromo-2-naphthylamine separated therefrom in colourless needles, m. p. 119—120° (Franzen and Eidis, *loc. cit.*, give m. p. 122—123°). The remainder was dissolved in hot chloroform (50 c.c.) and bromine (1 c.c.) in chloroform (5 c.c.) added in one portion. The purple-red solution rapidly deposited orange needles of 1 : 3 : 6-*tribromo-2-naphthylamine hydrobromide* [1·95 g.; m. p. 215—220° (decomp.)] (Found : Br′, 17·0. $C_{10}H_7NBr_4$ requires Br′, 17·35%), which after treatment with aqueous ammonia and crystallisation from ether (charcoal) furnished colourless very small needles of 1 : 3 : 6-tribromo-2-naphthylamine, m. p. 143° (Claus and Philipson, *J. pr. Chem.*, 1891, **43**, 56, also give m. p. 143°) (Found : Br, 62·5. Calc. for $C_{10}H_6NBr_3$: Br, 63·1%).

1 : 3 : 6-*Tribromonaphthalene*.—The purple solution of 1 : 3 : 6-tribromo-2-naphthylamine (0·5 g.) in sulphuric acid (8 c.c.; *d* 1·84) was treated with sodium nitrite (0·18 g.) dissolved in sulphuric acid (8 c.c.; *d* 1·84), and, at 0°, glacial acetic acid (25 c.c.) was added slowly. After 30 minutes the diazonium solution was poured into vigorously stirred absolute ethanol (150 c.c.) containing cuprous oxide (1 g.). After effervescence had ceased, the solution was decanted from precipitated inorganic matter, and evaporated on the water bath. Water (*ca*. 200 c.c.) was added and the colourless residue (0·4 g.; m. p. 90—95°) was crystallised twice from ethanol and once from ligroin. 1 : 3 : 6-Tribromonaphthalene separated in colourless acicular crystals, m. p. 100—101° (Claus and Jäck, *loc. cit.*, give m. p. 98°) (Found : C, 32·6; H, 1·3; Br, 65·7. Calc. for $C_{10}H_5Br_3$: C, 32·9; H, 1·4; Br, 65·7%).

Deamination of 2 : 4 : 7-*Tribromo*-1 : 8-*naphthylenediamine*.—The diamine (0·5 g.) in sulphuric acid (15 c.c.; *d* 1·84) was treated with a solution of sodium nitrite (0·6 g.) in sulphuric acid (5 c.c.; *d* 1·84) and at 0° glacial acetic acid (30 c.c.) was added. After 30 minutes, the purple solution was poured into warm (60°) well-stirred absolute ethanol (150 c.c.) containing cuprous oxide (1·5 g.). After filtration, ethyl acetate and excess of ethanol were boiled off on the water-bath, and water (200 c.c.) was added. The solution was placed in the ice-chest, and after 12 hours the solid was removed, dried (in a vacuum), and crystallised repeatedly from ethanol (charcoal). The less soluble fraction furnished 2 : 4 : 7-*tribromo-triazino*(4′ : 5′ : 6′-1 : 8*a* : 8)*naphthalene*, (0·07 g.), m. p. 216—218° (decomp.) (Found : N, 9·9. $C_{10}H_4N_3Br_3$ requires N, 10·3%); the more soluble material gave, in minute yield, slightly impure 1 : 3 : 6-tribromonaphthalene, m. p. 85—96° (Found : C, 34·1; H, 1·4; Br, 64·1%), undepressed on admixture with an authentic specimen. Examination of the two specimens by means of a polarising microscope showed that, as far as could be ascertained, they were identical.

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