46. *Substitution Reactions of the Naphthylenediamines. Part II. The Bromination of the Ditoluene*-p-*sulphonyl Derivatives of* 1 : 5- *and* 1 : 8-*Naphthylenediamines.*

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Bromination of the compounds named in the title has been studied under various conditions. 1 : 5-Ditoluene-*p*-sulphonamidonaphthalene has yielded a 4 : 8-dibromo-, and 1 : 8-ditoluene-*p*-sulphonamidonaphthalene a 4-monobromo-derivative. The constitution of these compounds has been established by unequivocal methods. Bromination of 1 : 5-dibromonaphthalene gives a tetrabromonaphthalene identical with that prepared by brominating 1 : 5- and 1 : 8-dinitronaphthalenes. This compound is not 1 : 4 : 5 : 8-tetrabromonaphthalene.

Nitration of the ditoluene-*p*-sulphonyl derivatives of 1 : 5- and 1 : 8-naphthylenediamines has been previously reported and in each case tetranitro-compounds are produced (Hodgson and Whitehurst, *J.*, 1947, 80). The present paper deal with the bromination and subsequent nitration of these compounds.

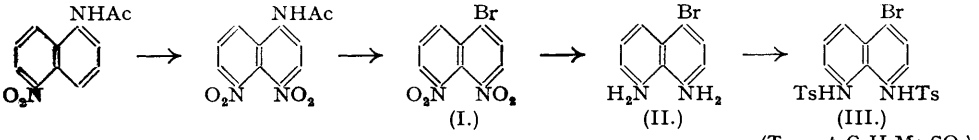
1 : 5-Ditoluene-*p*-sulphonamidonaphthalene did not undergo bromination in chloroform, but in glacial acetic acid it gave a dibromo-derivative, hydrolysed slowly by means of

concentrated sulphuric acid to a dibromonaphthylenediamine. Tetrazotisation and deamination of the latter furnished a dibromonaphthalene, having identical properties and giving no depression of melting point with an authentic specimen of 1 : 5-dibromonaphthalene, prepared unequivocally from 1 : 5-naphthylenediamine by the Sandmeyer reaction. Clearly, 1 : 5-ditoluene-*p*-sulphonamidonaphthalene undergoes bromination at the 4 : 8-positions. From the dibromonaphthylenediamine, by the usual methods, were prepared the corresponding 4 : 8-dibromo-1 : 5-dichloro-, 1 : 4 : 5 : 8-tetrabromo-, and 1 : 5-dibromo-4 : 8-di-iodonaphthalenes. The tetrabromonaphthalene thus obtained, m. p. 145°, was obviously not identical with that, m. p. 308°, described by Dhar (*J.*, 1920, 997) as the 1 : 4 : 5 : 8-compound, which had been made by the action of bromine on either 1 : 5- or 1 : 8-dinitronaphthalene. In view of this, it was decided to repeat Dhar's work.

It was found that either 1 : 5- or 1 : 8-dinitronaphthalene on being heated with two moles of bromine yielded a tetrabromonaphthalene, m. p. 231°. The best yield was obtained from 1 : 5-dinitronaphthalene and, even after prolonged heating, this compound still gave a good yield of the same tetrabromonaphthalene. Zalkind and Belikov (*Ber.*, 1931, **64**, 955) have reported a tetrabromonaphthalene, m. p. 235°, among the bromination products of 1 : 5-dibromonaphthalene and we confirmed their results; the tetrabromonaphthalene, m. p. 231°, gave no depression of melting point with that obtained previously. Dhar's formula rests on two postulates : first, that a bromine atom replaces a nitro-group, and as identical compounds are obtained from 1 : 5- and 1 : 8-dinitronaphthalenes three of the bromine atoms must be in the 1 : 4 : 5-positions, and secondly, that the remaining α-carbon atom is more readily attacked than any other. Neither assumption is necessarily correct. Zalkind and Belikov (*loc. cit.*) have established that the tribromonaphthalene obtained by brominating 1-bromonaphthalene is the 1 : 4 : 6-compound and, although, in their experiments, the bromination of 1 : 5-dibromonaphthalene was not arrested at the tribromo-stage, it is quite probable that 1 : 4 : 6-tribromonaphthalene is a precursor of the tetrabromonaphthalene described here, which may be 1 : 4 : 6 : 8-tetrabromonaphthalene.

Nitration of 4 : 8-dibromo-1 : 5-ditoluene-*p*-sulphonamidonaphthalene in glacial acetic acid gave 4-bromo-2 : 6 : 8-trinitro-1 : 5-ditoluene-*p*-sulphonamidonaphthalene, replacement of a bromine atom by a nitro-group having occurred. An attempted synthesis of this compound from 5-nitro-1-toluene-*p*-sulphonamidonaphthalene by bromination and subsequent reduction, toluenesulphonation, and nitration proved unsuccessful as the compound yielded a mixture of isomeric monobromo-derivatives from which the required 4-bromo-5-nitro-1-toluene-*p*-sulphonamidonaphthalene was isolated in too poor a yield for further work. It is an interesting comparison that 5-nitro-1-naphthylamine undergoes bromination in the 2-position in good yield (Hodgson and Turner, *J.*, 1942, 723).

Bromine reacted with 1 : 8-ditoluene-*p*-sulphonamidonaphthalene in chloroform or glacial acetic acid yielding, somewhat surprisingly, a monobromo-derivative, m. p. 208°. Hydrolysis of this compound could not be effected with sulphuric, hydrochloric, or phosphoric acid. Unless *meta*-substitution had occurred, the substance must have been either 2- or 4-bromo-1 : 8-ditoluene-*p*-sulphonamidonaphthalene, and according to Hodgson and Hathway (*J.*, 1945, 543) the latter (m. p. 225°) is preparable by the sequence of reactions :



(I.) (II.) (III.)

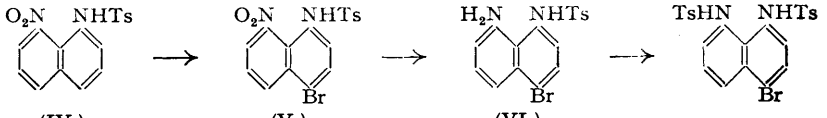
(Ts = *p*-$C_6H_4Me{\cdot}SO_2$)

As a means of obtaining (I) the synthesis is costly, and in our work the nitration of 1-bromonaphthalene (Merz and Weith, *Ber.*, 1882, **15**, 2708) was found to be more practicable. Reduction of (I) according to the directions of Hodgson and Hathway (*loc. cit.*) could not be achieved, but (I) did undergo reduction with stannous chloride in glacial acetic acid–hydrogen chloride, the stannichloride of (II) being obtained in fair yield. From it the hydrochloride and sulphate were prepared. An interesting feature of these salts is that the diamine behaves as a monoacidic base (cf. Hodgson and Hathway, *loc. cit.*, who give the normal formula for the sulphate). These findings were established not only by elementary analysis but also by conductometric and potentiometric titrations. Evaporation of ethereal or benzene solutions of the free diamine at reduced pressure under hydrogen gave pale green glassy solids which could not be induced to crystallise. Advent of moisture or air caused a fairly rapid coloration to

brown and then green, and an alcoholic solution of the diamine, even in the absence of oxygen, deposited a green amorphous powder stable on heating to 300°. The unstable nature of halogenonaphthylenediamines appears characteristic: for instance, 4 : 8-dibromo-1 : 5-naphthylenediamine explodes at 115°, and with hot ethanol is transformed into amorphous blue products; also, 4-chloro-1 : 8-naphthylenediamine (B.A.S.F., G.P. 122,475) is known only as its sulphate.

The action of toluene-*p*-sulphonyl chloride and sodium carbonate on a benzene solution of (II) (Hodgson and Hathway, *loc. cit.*) gave, in one experiment, a small amount (insufficient for analysis) of crystalline material, m. p. 215° (decomposing at 218°), which depressed the melting point of the bromination product of 1 : 8-ditoluene-*p*-sulphonamidonaphthalene. Owing to the minute yield and the fact that repetition often failed to produce anything but tar the method was abandoned. Other methods of acylating this diamine proved equally ineffective and attention was turned to alternative syntheses. A likely route to (III), *viz.*, from 4-bromo-8-nitro-1-naphthylamine by toluenesulphonation, reduction, and further action of toluene-*p*-sulphonyl chloride could not be achieved as the amine failed to react with toluene-*p*-sulphonyl chloride.

Finally the following method was adopted. 8-Nitro-1-toluene-*p*-sulphonamidonaphthalene (IV) underwent smooth bromination in glacial acetic acid, and the orientation of the bromine atom in the product (V) was proved by hydrolysis to 4-bromo-8-nitro-1-naphthylamine (Hodgson and Crook, *J.*, 1936, 1338). (V) on reduction gave (VI), and the latter was readily converted into 4-bromo-1 : 8-ditoluene-*p*-sulphonamidonaphthalene, identical with the bromination product of 1 : 8-ditoluene-*p*-sulphonamidonaphthalene.



(IV.) (V.) (VI.)

(Ts = *p*-$C_6H_4Me{\cdot}SO_2$)

Consden and Kenyon (*J.*, 1935, 1591) have shown that bromine reacts with 1-toluene-*p*-sulphonamidonaphthalene in chloroform, yielding 4-bromo-1-toluene-*p*-sulphonamidonaphthalene. As the toluenesulphonamido-groups in 1 : 8-ditoluene-*p*-sulphonamidonaphthalene are reinforcing each other as regards electrophilic substitution in the naphthalene nucleus, it might have been expected that under similar conditions dibromination would have occurred. The experimentally observed monbromination can thus be considered abnormal and perhaps savours of steric hindrance. Also, the bromination of 1 : 5- and 1 : 8-ditoluene-*p*-sulphonamidonaphthalenes in pyridine, which might have yielded polybromo-derivatives (cf. Consden and Kenyon, *loc. cit.*; Bell, *J.*, 1932, 2732), proved to be a complex reaction from which no pure products were isolated.

The nitration of 4-bromo-1 : 8-ditoluene-*p*-sulphonamidonaphthalene in glacial acetic acid proceeded normally, the product being 4-bromo-2 : 5 : 7-trinitro-1 : 8-ditoluene-*p*-sulphonamidonaphthalene. The latter underwent quantitative hydrolysis with concentrated sulphuric acid, yielding the corresponding diamine.

Experimental.

(All m. p.s are uncorrected.)

Bromination of 1 : 5-*Ditoluene*-p-*sulphonamidonaphthalene.*—The compound (10 g.), suspended in glacial acetic acid (300 c.c.), was treated with bromine (4 c.c.) in glacial acetic acid (20 c.c.) at 95° whilst being stirred. After 10 minutes the solution was cooled and the silvery needles collected (7·7 g.). Recrystallisation from nitrobenzene afforded colourless needles of 4 : 8-*dibromo*-1 : 5-*ditoluene*-p-*sulphonamidonaphthalene* (6·8 g.), m. p. 248° (decomp.) (Found: C, 46·3; H, 3·3; N, 4·8; Br, 24·9. $C_{24}H_{20}O_4N_2S_2Br_2$ requires C, 46·2; H, 3·2; N, 4·5; Br, 25·6%). The compound is readily soluble in aqueous alkalis, moderately soluble in pyridine, but sparingly soluble in the majority of organic solvents. A solution of the sulphonamide (5 g.) in sulphuric acid (50 c.c.; *d* 1·84) was kept for 24 hours and then poured on ice and water (*ca.* 300 g.). The pinkish-red solution was filtered and neutralised with aqueous ammonia at 0° (a temperature rise at this stage gives an uncrystallisable blue precipitate). The almost colourless precipitate was collected and dissolved in the minimum quantity of warm ethanol (charcoal; <60°), and the solution filtered. Cautious addition of water to the filtrate precipitated 4 : 8-*dibromo*-1 : 5-*naphthylenediamine* (0·4 g.) as long slender needles, decomposing explosively at 115° (Found: C, 37·0; H, 3·0; Br, 49·2. $C_{10}H_8N_2Br_2$ requires C, 38·0; H, 2·55; Br, 50·6%). The compound becomes blue, then purple, and finally black on storage, even in the dark. The addition of acetic anhydride (1 c.c.) to a solution of the amine (0·2 g.) in glacial acetic acid (1 c.c.) precipitated the *diacetyl* derivative (0·12 g.) which crystallised from warm nitrobenzene in colourless needles, darkening at 250° (Found: C, 42·8; H, 3·1; Br, 38·8. $C_{14}H_{12}O_2N_2Br_2$ requires C, 42·0; H, 3·0; Br, 40·0%).

Tetrazotisation and Coupling Reactions.—4 : 8-Dibromo-1 : 5-ditoluene-*p*-sulphonamidonaphthalene (10 g.) was stirred into sulphuric acid (60 c.c.; *d* 1·84) and after 36 hours the solution was poured on ice and water (300 g.) and filtered. Sodium nitrite (4 g.) in water (40 c.c.) was added at 0°, and after 5 minutes sufficient urea to destroy the excess of nitrous acid. The solution was then divided into four equal parts and the portions added severally at 0° to solutions of (*a*) cuprous chloride (10 g.) in hydrochloric acid (150 c.c.; *d* 1·18), (*b*) cuprous bromide (10 g.) in hydrobromic acid (150 c.c.; *d* 1·7), (*c*) potassium iodide (10 g.) in water (100 c.c.), and (*d*) 2-naphthol (5 g.) in 20% sodium hydroxide solution (200 c.c.). The products isolated were (*a*) 4 : 8-*dibromo*-1 : 5-*dichloronaphthalene* (0·65 g.) which after recrystallisation from aqueous acetic acid (charcoal) was obtained in colourless needles, m. p. 142° (Found : C, 34·6; H, 1·1; Halogen, 62·1. $C_{10}H_4Cl_2Br_2$ requires C, 33·8; H, 1·1; Halogen, 65·0%), (*b*) 1 : 4 : 5 : 8-*tetrabromonaphthalene* (0·67 g.), which separated from glacial acetic acid (charcoal) in colourless needles and prisms, m. p. 145° (Found : C, 27·8; H, 1·0; Br, 70·9. $C_{10}H_4Br_4$ requires C, 27·1; H, 0·9; Br, 72·0%), (*c*) 1 : 5-*dibromo*-4 : 8-*di-iodonaphthalene* (1·35 g.), which crystallised from glacial acetic acid (charcoal) in silvery plates, m. p. 148° (Found : C, 22·7; H, 0·8; Halogen, 74·8. $C_{10}H_4Br_2I_2$ requires C, 22·3; H, 0·75; Halogen, 76·9%), and (*d*) 4 : 8-*dibromo*-1 : 5-*naphthylene-bisazo*-2-*naphthol* (2·4 g.), which formed scarlet needles, m. p. 272° (decomp.), from nitrobenzene, and which imparted a beautiful blue colour to concentrated sulphuric acid (Found : N, 9·2. $C_{30}H_{18}O_2N_4Br_2$ requires N, 8·95%).

Deamination of 4 : 8-*Dibromo*-1 : 5-*naphthylenediamine.*—The sulphonamide (5 g.) was stirred into sulphuric acid (50 c.c.; *d* 1·84) and after 36 hours a solution of sodium nitrite (2 g.) in sulphuric acid (25 c.c.; *d* 1·84) was added. The solution was cooled to 0° and treated with glacial acetic acid (150 c.c.), after which it was added to vigorously stirred ethanol (300 c.c.; 100%) containing freshly prepared cuprous oxide (5 g.). When effervescence had ceased, the bulk of ethyl acetate and excess of ethanol were distilled off under reduced pressure, and water (*ca.* 500 c.c.) was added to the solution. After 24 hours, the solids were removed and extracted with boiling ethanol (charcoal), whereupon 1 : 5-dibromonaphthalene (0·35 g.) crystallised from the cold extract. After two recrystallisations from ethanol it had m. p. 130°, alone and mixed with an authentic specimen prepared from 1 : 5-naphthylenediamine (Found : C, 41·9; H, 2·4; Br, 54·3. Calc. for $C_{10}H_6Br_2$: C, 42·0; H, 2·1; Br, 55·9%).

Bromination of 1 : 5- *and* 1 : 8-*Dinitronaphthalenes.*—The directions given by Dhar (*loc. cit.*) were followed and the resulting compound was crystallised several times from benzene in each case. 1 : 5-Dinitronaphthalene (5 g.) yielded a tetrabromonaphthalene, m. p. 231° (0·95 g.); 1 : 8-dinitronaphthalene (5 g.) also yielded the same substance (0·37 g.) (Found : Br, 73·2. Calc. for $C_{10}H_4Br_4$: Br, 72·0%). Treatment of 1 : 5-dinitronaphthalene (5 g.) with bromine (2·5 c.c.) and a crystal of iodine at 220° for 18 hours also yielded the same compound (0·60 g.).

Bromination of 1 : 5-*Dibromonaphthalene.*—This compound was brominated in the absence of a solvent (cf. Zalkind and Belikov, *loc. cit.*) for comparison with the above. The compound (2 g.) was heated with bromine (2·4 g.) and a crystal of iodine in a sealed tube at 200° for 6 hours. The product was washed with warm water, dried, and crystallised repeatedly from benzene, yielding the same tetrabromonaphthalene, m. p. 231°, undepressed on admixture with either of the above specimens.

Nitration of 4 : 8-*Dibromo*-1 : 5-*ditoluene*-p-*sulphonamidonaphthalene.*—The substance (1 g.), suspended in glacial acetic acid (10 c.c.) containing sodium nitrite (0·05 g.), was treated in the cold with nitric acid (1·5 c.c.; *d* 1·52), and the mixture left overnight. The yellow residue (0·65 g.) was crystallised first from alcoholic pyridine and then from nitrobenzene. 4-*Bromo*-2 : 6 : 8-*trinitro*-1 : 5-*ditoluene*-p-*sulphonamidonaphthalene* was obtained in yellow needles, m. p. 245° (decomp.) (Found : C, 42·8; H, 2·6; N, 10·3; Br, 12·9. $C_{24}H_{18}O_{10}N_5BrS_2$ requires C, 42·35; H, 2·7; N, 10·3; Br, 11·75%). Hydrolysis was accomplished when the compound (0·5 g.) in sulphuric acid (5 c.c.; *d* 1·84) after being at 40° for 2 hours was poured into water. The precipitated 4-*bromo*-2 : 6 : 8-*trinitro*-1 : 5-*naphthylenediamine* (0·25 g., *ca.* 100%) when crystallised from nitrobenzene formed deep red needles with a purplish tinge, m. p. 258° (decomp.) (Found : C, 32·7; H, 1·6. $C_{10}H_6O_6N_5Br$ requires C, 32·3; H, 1·6%).

Bromination of 5-*Nitro*-1-*toluene*-p-*sulphonamidonaphthalene.*—The compound (1 g.), made according to the directions of Hodgson and Turner (*loc. cit.*), was treated in glacial acetic acid (30 c.c.) at 95° with a 10% (v/v) solution of bromine in the same solvent (3·5 c.c.). After 2 hours at this temperature the mixture was left overnight. The addition of water to this solution precipitated a colourless mixture of monobromo-compounds (0·77 g.), which was crystallised six times from aqueous acetic acid. 4-*Bromo*-5-*nitro*-1-*toluene*-p-*sulphonamidonaphthalene* was obtained in colourless needles (0·12 g.), m. p. 204° (Found : C, 48·7; H, 3·1; Br, 17·5. $C_{17}H_{13}O_4N_2BrS$ requires C, 48·5; H, 3·1; Br, 19·0%). Hydrolysis of the substance (0·10 g.) with sulphuric acid (3 c.c.; *d* 1·84) at 45° for 2 hours, and subsequent addition of ice (50 g.) followed by ammonia, gave the *amine* which crystallised from ethanol in orange needles (0·02 g.), m. p. 129·5° (Found : C, 45·2; H, 2·7. $C_{10}H_7O_2N_2Br$ requires C, 45·0; H, 2·6%). It gave a large depression of melting point when mixed with an authentic specimen of 2-bromo-5-nitro-1-naphthylamine prepared by the bromination of 5-nitro-1-naphthylamine, according to Hodgson and Turner (*loc. cit.*).

Bromination of 1 : 8-*Ditoluene*-p-*sulphonamidonaphthalene.*—(a) *In chloroform.* The substance (10 g.) in chloroform (200 c.c.) was treated with a solution of bromine (2·3 c.c.) in the same solvent (20 c.c.) at *ca.* 60°. The solution evolved much hydrogen bromide, and it was evaporated almost to dryness. Crystallisation of the residue (8·8 g.), first from toluene (charcoal) and then from glacial acetic acid, gave 4-*bromo*-1 : 8-*ditoluene*-p-*sulphonamidonaphthalene* as colourless fine needles (6·7 g.), m. p. 208° (Found : C, 52·9; H, 3·8; N, 5·0; Br, 15·2; S, 11·5. $C_{24}H_{21}O_4N_2BrS_2$ requires C, 52·8; H, 3·9; N, 5·1; Br, 14·65; S, 11·75%).

(b) *In glacial acetic acid.* The compound (2 g.), dissolved in the minimum quantity of glacial acetic acid (*ca.* 12 c.c.), was treated at *ca.* 80° with a solution of bromine in glacial acetic acid (6·5 c.c.; 10% v/v)

with stirring. The crystalline precipitate (1·2 g.) obtained on cooling was recrystallised from glacial acetic acid; 4-bromo-1 : 8-ditoluene-*p*-sulphonamidonaphthalene separated in long colourless needles (0·72 g.), m. p. 208°, alone and mixed with the previous specimen (Found : Br, 15·0%). It was soluble in the usual solvents. A solution of the compound (1 g.) in sulphuric acid (20 c.c.; *d* 1·84) was kept for 4 days at 20° and then poured on ice; the solution was filtered, rendered alkaline with aqueous ammonia, and extracted with ether, giving a pale yellowish-green solution in the latter, which after being dried and then saturated with dry hydrogen chloride furnished a minute amount of a colourless to grey *hydrochloride* (Found : Halogen, 45·5. $C_{10}H_{10}N_2ClBr$ requires Halogen, 42·2%). The free base, liberated with dilute aqueous ammonia, proved highly unstable.

4-*Bromo*-2 : 5 : 7-*trinitro*-1 : 8-*ditoluene*-p-*sulphonamidonaphthalene* was obtained when 4-bromo-1 : 8-ditoluene-*p*-sulphonamidonaphthalene (1 g.) in glacial acetic acid (5 c.c.) containing sodium nitrite (0·05 g.) was treated cautiously with nitric acid (0·5 c.c.; *d* 1·52) in glacial acetic acid (0·5 c.c.) below 60°. After 3 hours at 0°, the precipitated *compound* (0·65 g.) was collected, dried, and crystallised from glacial acetic acid. It formed clusters of yellow prisms and rhombs, m. p. 204° (decomp.) (Found : C, 43·1; H, 2·7; N, 10·6; Br, 11·6. $C_{24}H_{18}O_{10}N_5BrS_2$ requires C, 42·35; H, 2·7; N, 10·3; Br, 11·75%). When the substance in sulphuric acid [0·3 g. in 5 c.c. (*d* 1·84)] was kept at 40° for 1 hour and then poured into water, 4-*bromo*-2 : 5 : 7-*trinitro*-1 : 8-*naphthylenediamine* separated, and crystallisation from nitrobenzene gave needles, m. p. 268° (decomp.) (Found : C, 32·0; H, 1·9. $C_{10}H_6O_6N_5Br$ requires C, 32·3; H, 1·6%). On being crystallised from acetone it gave brown-red pyramids of 6-*bromo*-1 : 2-*dihydro*-2 : 2′-*dimethyl*-4 : 7 : 9-*trinitroperimidine*, m. p. 264° (Found : N, 17·4. $C_{13}H_{10}O_6N_5Br$ requires N, 17·0%).

1-*Bromo*-4 : 5-*dinitronaphthalene*.—The method of Hodgson and Hathway was replaced by a modification of that of Merz and Weith (*loc. cit.*). The 1-bromonaphthalene required was made by a method similar to that reported in *Org. Synth.* (Coll. Vol. I, 2nd edn., p. 121), but less bromine was used as it was found that naphthalene was a more tolerable impurity in the product than dibromonaphthalenes.

A solution of bromine (80 c.c.) in chloroform (200 c.c.) was led beneath the surface of a rapidly stirred solution of naphthalene (200 g.) in chloroform (300 c.c.) at *ca.* 40°. Hydrogen bromide was copiously evolved and after 24 hours at room temperature the bulk of the solvent was removed at reduced pressure. Finely powdered potassium hydroxide was then added to the resulting oil which thereupon assumed a clear yellow colour. After 6 hours at 50°, the oil was filtered and distilled in a current of air. At 150° some hydrogen bromide was evolved and the first runnings (at 230—240°) solidified to naphthalene. The second fraction (220 g.) was collected at 265—280° and redistilled. 1-Bromonaphthalene (190 g.) was obtained as a pale yellow oil, b. p. 272—273°/740 mm.

The substance (50 g.) was added dropwise to nitric acid [150 c.c. (*d* 1·52) + 75 c.c. (*d* 1·42)] at *ca.* 0—5°, and the mixture was then heated cautiously at *ca.* 80° for 30 minutes. After the mixture had been cooled to 0°, ice (*ca.* 500 g.) was added and the mixture was heated on the water-bath until no more brown fumes were evolved. The solid residue was crystallised three times from aqueous acetic acid; 1-bromo-4 : 5-dinitronaphthalene was thus obtained as long very pale yellow needles (15·4 g.), m. p. 168°, alone or mixed with a specimen prepared by the method of Hodgson and Hathway (*loc. cit.*) (Found : N, 9·7. Calc. for $C_{10}H_5O_4N_2Br$: N, 9·4%).

Reduction of 1-*Bromo*-4 : 5-*dinitronaphthalene*.—The compound (5 g.) in glacial acetic acid (150 c.c.) at 90° was treated with stannous chloride (25 g.) in glacial acetic acid (150 c.c.) previously saturated with dry hydrogen chloride. On cooling, the pale yellow needles of the bromodiamine *stannichloride* (4·7 g.) were collected (if crystallisation is delayed it is started by passing dry hydrogen chloride through the solution) (Found : N, 6·3; Halogen, 45·9; Sn, 13·7. $2C_{10}H_9N_2Br,H_2SnCl_6$ requires N, 6·9; Halogen, 46·1; Sn, 14·7%). The diamine liberated from the stannichloride with aqueous sodium carbonate (decomposition was slow and sodium hydroxide gave an inferior product) was extracted with ether, and from this solution the *monohydrochloride* (Found : Cl, 12·5. $C_{10}H_9N_2Br,HCl$ requires Cl, 13·0%) and the *sulphate* (Found : SO_4, 16·6. $2C_{10}H_9N_2Br,H_2SO_4$ requires SO_4, 16·8%) were made by adding ether containing hydrogen chloride and sulphuric acid respectively.

Bromination of 8-*Nitro*-1-*toluene*-p-*sulphonamidonaphthalene*.—The substance (4 g.) in glacial acetic acid (40 c.c.) was treated with a solution of bromine in glacial acetic acid (6·4 c.c.; 10% v/v) at 50° and, after cooling, the crystalline deposit (2·75 g.) was removed and recrystallised from glacial acetic acid (charcoal). 4-*Bromo*-8-*nitro*-1-*toluene*-p-*sulphonamidonaphthalene* separated therefrom in long colourless needles (2·01 g.), m. p. 225° (Found : C, 49·1; H, 3·5; Br, 18·9. $C_{17}H_{13}O_4N_2BrS$ requires C, 48·5; H, 3·1; Br, 19·0%). A solution of the compound (0·2 g.) in sulphuric acid (5 c.c.; *d* 1·84) was kept at 50° for 30 minutes and then poured on ice and water (50 g.). The precipitated crystalline amine sulphate was collected and treated with an excess of aqueous ammonia, and the residue crystallised from aqueous acetic acid. 4-Bromo-8-nitro-1-naphthylamine separated in fawn-red needles (0·06 g.), m. p. 115°, undepressed by a specimen obtained by the method of Hodgson and Crook (*loc. cit.*) (Found : N, 10·2. Calc. for $C_{10}H_7O_2N_2Br$: N, 10·5%).

1-*Amino*-5-*bromo*-8-*toluene*-p-*sulphonamidonaphthalene*.—4-Bromo-8-nitro-1-toluene-*p*-sulphonamidonaphthalene (1 g.) in glacial acetic acid (15 c.c.) was treated with a solution of stannous chloride (3 g.) in glacial acetic acid–dry hydrogen chloride (15 c.c.), and the solution was then evaporated almost to dryness on the water-bath at reduced pressure. The crystalline residue was then treated with aqueous sodium carbonate, and the solids were removed and extracted with hot ethanol, from which, after evaporation at reduced pressure and cautious addition of water, 1-*amino*-5-*bromo*-8-*toluene*-p-*sulphonamidonaphthalene* separated in colourless needles (0·24 g.), m. p. 193° (decomp.) (Found : C, 52·2; H, 4·2. $C_{17}H_{15}O_2N_2BrS$ requires C, 52·2; H, 3·9%). It appeared to be sparingly soluble in dilute sodium hydroxide solution, but was soluble in the usual organic solvents.

4-*Bromo*-1 : 8-*ditoluene*-p-*sulphonamidonaphthalene*.—The preceding compound (0·2 g.), toluene-*p*-sulphonyl chloride (0·1 g.), and pyridine (3 c.c.) were heated together at 95° for 30 minutes, and, after the mixture had cooled, dilute sulphuric acid was added. The solid was collected, washed, dried, and crystallised three times from chloroform. 4-Bromo-1 : 8-ditoluene-*p*-sulphonamidonaphthalene was obtained as fine felted needles (0·07 g.), m. p. 208°, undepressed on admixture with the bromination product of 1 : 8-ditoluene-*p*-sulphonamidonaphthalene.

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