453. *Stereochemical Aspects of Aromatic Substitution. Part I.* peri-*Derivatives of Naphthalene.*

By F. Bell, J. A. Gibson, and R. D. Wilson.

The influence of steric factors in substitution reactions of 2 : 7 dihydroxy- and 2 : 7-diamino-naphthalenes is discussed, and additional evidence obtained that one of the bromine atoms in dibromo-2 : 7-dihydroxynaphthalene is in position 6.

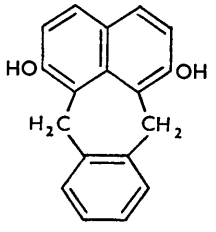
Although the influence of steric factors on the course of aromatic substitution has been frequently discussed few examples are known in which the structure of the final product can be definitely attributed to steric causes. Of particular interest would be the study of the substitution of compounds in which the product expected from normal orientation principles would be subject to considerable steric strain. For example, 2 : 7-diamino- and 2 : 7-dihydroxy-naphthalene would be expected to undergo halogenation in positions 1 : 8 in view of the well established reactivity of the 1-position in β-naphthylamine and β-naphthol compared with the inertness of the 3-position. Since, however, the distance between the carbon atoms in positions 1 : 8 is only 2·46 Å it would clearly be impossible to introduce two iodine atoms of covalent radius 1·33 Å in positions 1 : 8 without the iodine atoms' either departing from the plane of the naphthalene or undergoing a considerable lateral displacement, which would be opposed by the amino- or hydroxyl groups. Again, although bromine has a covalent radius of only 1·14 Å to this must be added the van der Waals envelope to obtain the effective size of the atom except in the direction of the bond. It is doubtful whether two bromine atoms could be accommodated in the 1 : 8-positions without distortions similar to those previously recognised by de Laszlo,[1] Sutton,[2] and Donaldson and Robertson [3] in certain naphthalene derivatives.

The literature relevant to this topic is slight. No experiments on the iodination of appropriate compounds have been recorded. Scholl, Seer, Weizenboch, and Ertl [4] state that bromination of 2 : 7-dihydroxynaphthalene, like chlorination,[5] yields the 1 : 8-derivative but this is controverted by Ioffe and Fedorova,[6] who give evidence that bromination yields successively the 3-bromo-, 3 : 6-dibromo-, and 1 : 3 : 6-tribromo-derivatives. They found that the mono- and the dibromo-derivative couple with two mols. of diazotised *p*-nitroaniline; so does the tribromo-derivative but this time with expulsion of one bromine atom. Fieser and Lothrop [7] had already shown that compound (I) would not couple with diazotised bases and had concluded that the 3 : 6-positions in a 2 : 7-dihydroxynaphthalene are inert as regards coupling.* Ioffe and Fedorova adopt this view and it appears, therefore, that bromination of 2 : 7-dihydroxynaphthalene follows a similar course to that of sulphonation.[10] These reactions might be regarded as analogous to 6-nitration in 2-acetonaphthalide.[11] Furthermore, Sunthanker and Gilman [12] have ascribed structure (II) to the acid obtained by carboxylation of the lithium derivative of 2 : 7-dimethoxynaphthalene because the phenol (III) derived from it couples with two mols. of diazotised sulphanilic acid. Their observation that neither acid (II) nor acid (III) could be dibrominated was taken to indicate the difficulty of disubstitution in positions 1 : 8.

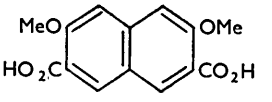
* Fieser's very general statement [8] beginning " Fieser and Lothrop investigated various 1 : 8-dialkyl derivatives of 2 : 7-dihydroxynaphthalene," although probably correct, cannot be supported from the literature. Indeed, simple 1 : 8-dialkyl-2 : 7-dihydroxynaphthalenes have only recently been described.[9]

[1] de Laszlo, *Trans. Faraday Soc.*, 1934, **30**, 892.
[2] Sutton, *J.*, 1949, 2312.
[3] Donaldson and Robertson, *J.*, 1955, 17.
[4] Scholl, Seer, Weizenboch, and Ertl, *Monatsh.*, 1921, **42**, 407.
[5] Clausius, *Ber.*, 1890, **23**, 526.
[6] Ioffe and Fedorova, *J. Gen. Chem.* (*U.S.S.R.*), 1936, **6**, 1079.
[7] Fieser and Lothrop, *J. Amer. Chem. Soc.*, 1935, **57**, 1459.
[8] In Gilman's " Organic Chemistry," Wiley, New York, 1947, Vol. I, p. 154.
[9] Buu-Hoï and Lavit, *J.*, 1955, 2776.
[10] A. G. Anilinfabrik, D.R.-P. 75,142.
[11] Veselý and Jakes, *Bull. Soc. chim. France*, 1923, **33**, 942.
[12] Sunthanker and Gilman, *J. Org. Chem.*, 1951, **16**, 8.

Adams, Miller, McGrew, and Anderson [13] on the other hand ignore completely the work of Ioffe and Fedorova and assume that entering groups always take up first position 1 and then position 8 in 2 : 7-dihydroxy- and 2 : 7-dimethoxy-naphthalene. They showed that the acid derived from bromo-2 : 7-dimethoxynaphthalene by metalation with lithium and subsequent carboxylation was identical with that obtained from 2 : 7-dihydroxynaphthalene by introduction of the aldehyde group, methylation, and subsequent oxidation; it was given structure (IV). From this acid they derived a number of supposedly *peri*-substituted naphthalenes, *e.g.*, (VI), which were regarded as potentially resolvable owing to restricted rotation of the groups in the 1 : 8-positions. If Ioffe and Fedorova are correct then Adams and his co-workers were attempting the resolution of compounds such as (V).



(I)



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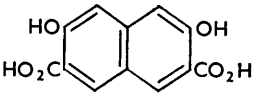

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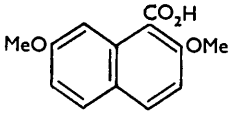

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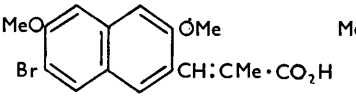
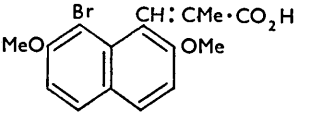
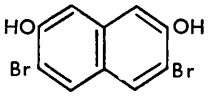


(V)



(VI)

It was first necessary to link the experiments of Ioffe and Fedorova with those of Adams *et al.* This was done by establishing the identity of mono- and di-brominated 2 : 7-dimethoxynaphthalenes with methylated mono- and di-bromo-2 : 7-dihydroxynaphthalenes. Additional evidence was now required with regard to the position of the bromine atoms, and strong confirmatory support for Ioffe and Fedorova's formula for dibromo-2 : 7-dihydroxynaphthalene (VII) was obtained by showing that the product obtained by its chlorination (VIII) was identical with that obtained by the bromination of Clausius's dichloro-2 : 7-dihydroxynaphthalene (IX).



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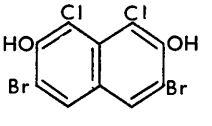

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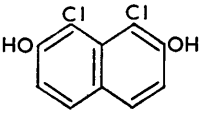

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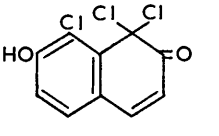
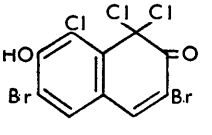


(X)



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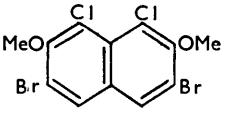
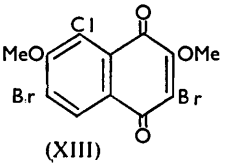


(XII)



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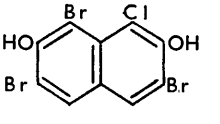


(XIV)

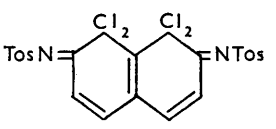
Dichlorination of 2 : 7-dihydroxynaphthalene gave rise not only to the phenol (IX), but to a trichloroquinone, regarded as (X), which could be easily reduced to (IX). Similarly chlorination of dibromo-2 : 7-dihydroxynaphthalene gave rise to a trichloroquinone, probably of structure (XI), since it can be smoothly reduced to the phenol (VIII). Methylation then gave a dimethyl ether regarded as (XII), which on oxidation with chromic acid

[13] Adams, Miller, McGrew, and Anderson, *J. Amer. Chem. Soc.*, 1942, **64**, 1795.

gave a bright yellow compound regarded as essentially 2 : 7-dibromo-5-chloro-3 : 6-dimethoxy-1 : 4-naphthaquinone (XIII), by analogy with the oxidation products obtained from 1-bromo-, 1 : 6-dibromo-, and 1 : 4-dichloro-2-methoxynaphthalenes.

Although Ioffe and Fedorova apparently found it necessary to employ a catalyst to cause bromine to enter tribromo-2 : 7-dihydroxynaphthalene to yield the tetrabromo-derivative, it is now found that this reaction proceeds with considerable ease.* Similarly one atom of chlorine enters to give most probably the compound (XIV). Further, dibromo-2 : 7-dimethoxynaphthalene gave a tetrabromo-derivative and 2 : 7-dimethoxynaphthaldehyde gave di- and tribromo-derivatives. It appears, therefore, that steric inhibition of substitution is slight and that out-of-plane movements allow fairly ready entry of bulky substituents into the 1 : 8-positions of naphthalene.

Next was examined the halogenation of 2 : 7-ditoluene-*p*-sulphonamidonaphthalene. Even with considerable excess of iodine or bromine only monosubstitution products were obtained. With chlorine, on the other hand, a tetrachloro-derivative was readily



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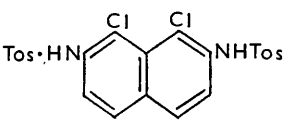
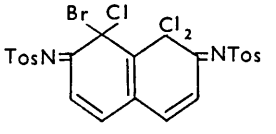


(XVI)



(XVII)

(Tos = *p* − $C_6H_4Me\cdot SO_2$)

produced, which is regarded as (XV) since it was easily reduced to a dichloro-derivative (XVI), which in turn was smoothly hydrolysed to a dichloro-base. In accordance with this view the above mentioned monobromo-derivative was readily converted by the action of chlorine into a monobromotrichloro-compound, regarded as (XVII), which could be reduced to the same dichloro-derivative. Similar compounds were not produced from 1 : 8- and 2 : 3-ditoluene-*p*-sulphonamidonaphthalenes, which gave normal substitution products.

Experimental

2 : 7-Dihydroxynaphthalene was prepared by Chakravarti and Pasupati's method.[14]

Monobromination of 2 : 7-*Dihydroxynaphthalene.*—The phenol (3 g.) in acetic acid (30 c.c.) was treated with bromine (3 g., carried in by carbon dioxide), and the resultant solution poured into water. The solution was partially evaporated, the product dried and dissolved in benzene, and the solution diluted with light petroleum. By crystallisation of the crop from aqueous ethanol the 3-bromo-compound was obtained in needles, m. p. 134—135° (Ioffe and Fedorova [6] give m. p. 135°).

Dibromination of 2 : 7-*Dihydroxynaphthalene.*—The product obtained as above but with 2 mols. of bromine, recrystallised from acetic acid to give the dibromo-derivative (VII), m. p. 153°.

2-*Bromo*-3 : 6-*dimethoxynaphthalene.*—This was obtained (*a*) by shaking a solution of the above monobromo-compound in sodium hydroxide with dimethyl sulphate, or (*b*) by introducing bromine (1 mol.) by means of dry carbon dioxide into a cold chloroform solution of 2 : 7-dimethoxynaphthalene. (Direct addition of the bromine to the chloroform solution resulted always in the production of appreciable amounts of the dibromo-derivative.) It crystallised from methanol in needles, m. p. 78° (Adams *et al.*[13] give m. p. 88°) (Found : C, 54·2; H, 4·0. Calc. for $C_{12}H_{11}O_2Br$: C, 53·9; H, 4·1%).

* It may be argued, therefore, that steric opposition to entry of a first halogen atom into position 1 of 2 : 7-dihydroxynaphthalene must be very slight indeed. Ioffe and Fedorova's monobromo-2 : 7-dihydroxynaphthalene might then be the 1-bromo-derivative if it is admitted that such a compound might couple with two mols. of diazotised *p*-nitroaniline. There is no unambiguous evidence against this possibility. Both Ioffe and Fedorova's dibromo-2 : 7-dihydroxynaphthalene and Clausius's dichloro-2 : 7-dihydroxynaphthalene would then be regarded as 1 : 6-dihalogenated compounds and both, on further halogenation, could yield 1 : 6-dibromo-3 : 8-dichloro-2 : 7-dihydroxynaphthalene, which would be an alternative structure for (VIII). The authors are indebted to the Referees for this suggestion.

[14] Chakravati and Pasupati, *J.*, 1937, 1860.

2 : 7-*Dibromo*-3 : 6-*dimethoxynaphthalene* was obtained (*a*) by methylation of dibromo-2 : 7-dihydroxynaphthalene (above) and (*b*) by bromination of 2 : 7-dimethoxynaphthalene. It crystallised from methanol in needles, m. p. 131° (Found : C, 42·0; H, 2·8. $C_{12}H_{10}O_2Br_2$ requires C, 41·6; H, 2·9%).

1 : 3 : 6-*Tribromo*-2 : 7-*dimethoxynaphthalene*, prepared by the methylation of 1 : 3 : 6-tribromo-2 : 7-dihydroxynaphthalene,[6] crystallised from methanol in needles, m. p. 173° (Found : C, 33·9; H, 2·1. $C_{12}H_9O_2Br_3$ requires C, 33·9; H, 2·1%).

1 : 3 : 6 : 8-*Tetrabromo*-2 : 7-*dimethoxynaphthalene*, readily obtained by the addition of bromine to a solution of the dibromo-derivative in acetic acid, crystallised from acetic acid in needles, m. p. 196° (Found : C, 28·6; H, 1·6. $C_{12}H_8O_2Br_4$ requires C, 28·9; H, 1·6%).

Dibromo-2 : 7-*dihydroxy*-1-*naphthaldehyde* was obtained by the addition of bromine (1 c.c.) in acetic acid (5 c.c.) to 2 : 7-dihydroxy-1-naphthaldehyde[13] (1 g.) in acetic acid (15 c.c.). After 2 hr. the precipitate was filtered off and recrystallised from acetic acid to give needles, m. p. 175° (decomp.) (Found : C, 38·2; H, 1·8. $C_{11}H_6O_3Br_2$ requires C, 38·1; H, 1·7%). By use of twice the above amount of bromine there could be isolated a *tribromo-derivative*, which formed needles, m. p. 178°, from acetic acid (Found : C, 31·2; H, 1·3. $C_{11}H_5O_3Br_3$ requires C, 31·1; H, 1·2%).

Chlorination of 2 : 7-*Dihydroxynaphthalene*.—(*a*) An attempt to repeat the preparation of 1 : 8-dichloro-2 : 7-dihydroxynaphthalene by the method of Clausius[5] failed. The final product, a very viscous, orange material, resisted efforts to crystallise it. (*b*) Dihydroxynaphthalene (2·3 g.) was added to sulphuryl chloride (5·7 g.) to form a paste, which, after 2 hr., was warmed in hot water for ½ hr. Volatile material was subsequently removed under diminished pressure. The residual yellowish-green solid was repeatedly recrystallised from acetic acid and finally gave 1 : 8-dichloro-2 : 7-dihydroxynaphthalene (IX) (0·2 g.) as needles, m. p. 188° (Clausius gives m. p. 192°). (*c*) The following procedure gave two products. Chlorine was passed into a solution of 2 : 7-dihydroxynaphthalene (1·38 g.) in acetic acid (12 c.c.) cooled by water. Chlorination was interrupted shortly after the first appearance of a pale yellow precipitate (A), which was filtered off. The filtrate was treated with more chlorine until, in all, there had been used 1·3 times the stoicheiometric weight required for production of the dichloro-derivative. A further precipitate (B) was thereby obtained. Recrystallisation of (A) from acetic acid gave light grey needles (0·28 g.), m. p. 189°, of 1 : 8-dichloro-2 : 7-dihydroxynaphthalene. Product (B) from acetic acid gave bright yellow crystals (0·45 g.), m. p. 182—183° (decomp.), regarded as 1 : 1 : 8-*trichloro*-1 : 2-*dihydro*-7-*hydroxy*-2-*oxonaphthalene* (X) (Found : C, 45·8; H, 2·2; Cl, 40·2. $C_{10}H_5O_2Cl_3$ requires C, 45·6; H, 1·9; Cl, 40·4%). When zinc dust was added to the yellow solution in acetic acid the colour was immediately discharged and 1 : 8-dichloro-2 : 7-dihydroxynaphthalene was produced.

3 : 6-*Dibromo*-1 : 8-*dichloro*-2 : 7-*dihydroxynaphthalene* (VIII).—(*a*) A solution of sulphuryl chloride (3·4 g.) in chloroform (7 c.c.) was poured into a solution of 2 : 7-dibromo-3 : 6-dihydroxynaphthalene (2·7 g.) in chloroform (55 c.c.). Next morning most of the chloroform was distilled off and the dark brown, sticky product repeatedly recrystallised from acetic acid and finally benzene to afford the *tetrahalogeno-compound* as needles, m. p. 204—205° (Found : C, 30·8; H, 1·3; Br, 40·7; Cl, 18·4. $C_{10}H_4O_2Cl_2Br_2$ requires C, 31·0; H, 1·0; Br, 41·3; Cl, 18·3%) (0·06 g.).

(*b*) Bromine (0·2 g.) in acetic acid (1 c.c.) was added to a solution of 1 : 8-dichloro-2 : 7-dihydroxynaphthalene (0·054 g.) in acetic acid (2 c.c.), and the mixture heated on a water-bath for ¼ hr. On cooling, there separated pale pink needles, m. p. 204°, alone or mixed with the compound prepared by method (*a*).

3 : 6-*Dibromo*-1 : 1 : 8-*trichloro*-1 : 2-*dihydro*-7-*hydroxy*-2-*oxonaphthalene* (XI) was obtained by passing chlorine (1·01 g.) into a cold solution of 2 : 7-dibromo-3 : 6-dihydroxynaphthalene (2·17 g.) in acetic acid (20 c.c.). The resultant yellow precipitate was dissolved in acetic acid, and the solution was cooled and filtered from a small crop, which yielded no definite compound. On concentration of the filtrate the *pentahalogeno-compound* was obtained as orange crystals (0·9 g.), m. p. 160—163°, which after recrystallisation from acetic acid formed platelets, m. p. 166° (Found : C, 27·9; H, 0·9; Halogen, 63·5. $C_{10}H_3O_2Cl_3Br_2$ requires C, 28·5; H, 0·7; Halogen, 63·2%).

The original mother-liquor, when poured into water, gave a sticky, deep yellow precipitate from which, after repeated recrystallisations from acetic acid, there was isolated 3 : 6-dibromo-1 : 8-dichloro-2 : 7-dihydroxynaphthalene (0·04 g.).

1 : 3 : 6-*Tribromo*-8-*chloro*-2 : 7-*dihydroxynaphthalene* (XIV) was obtained by passing chlorine (0·062 g.) into a solution of 1 : 3 : 6-tribromo-2 : 7-dihydroxynaphthalene[6] (0·22 g.) in acetic

acid (10 c.c.). The resultant precipitate (0·16 g.), m. p. 199°, after recrystallisation from acetic acid formed pink needles, m. p. 200° (Found ; C, 28·0; H, 1·2. $C_{10}H_4O_2ClBr_3$ requires C, 27·8; H, 0·9%). The mixed m. p. with 1 : 3 : 6-tribromo-2 : 7-dihydroxynaphthalene, m. p. 198—200°, was 174—183°.

3 : 6-*Dibromo*-1 : 8-*dichloro*-2 : 7-*dimethoxynaphthalene* (XII) prepared by shaking a solution of the corresponding dihydroxynaphthalene in sodium hydroxide with dimethyl sulphate, formed lustrous plates, m. p. 150° (Found : C, 35·1; H, 2·2. $C_{12}H_8O_2Cl_2Br_2$ requires C, 34·7; H, 1·9%). To this dimethoxy-compound (0·13 g.) in acetic acid (20 c.c.) was added chromium trioxide (0·47 g.) in water (1·5 c.c.). After 5 min. at 20° the product was poured into water (150 c.c.), and the yellow precipitate (0·06 g.; m. p. 152—153°) recrystallised twice from ethanol, to give impure 2 : 7-dibromo-5-chloro-3 : 6-dimethoxy-1 : 4-naphthaquinone (XIII) as orange-yellow needles, m. p. 157° (Found : C, 36·1; H, 1·9; Halogen, 48·5. Calc. for $C_{12}H_7O_4Br_2Cl$: C, 35·1; H, 1·7; Halogen, 47·6%). The reason for the poor analysis was not found; a new sample submitted to a different analyst furnished similar results.

Oxidation of Derivatives of 2-Methoxynaphthalene.—(a) 1-*Bromo*-2-*methoxynaphthalene*. Chromic acid (4 g.) in water (10 c.c.) was added to the compound (2 g.) in acetic acid (40 c.c.) kept at <55°. After 2 hr. the mixture was poured into water, and the precipitate purified by repeated crystallisation from benzene. 5-*Bromo*-6-*methoxy*-1 : 4-*naphthaquinone* was obtained in golden needles, m. p. 200° (Found : C, 49·0; H, 2·8. $C_{11}H_7O_3Br$ requires C, 49·5; H, 2·6%), which dissolved in sulphuric acid with a deep damson colour.

(b) 1 : 4-*Dichloro*-2-*methoxynaphthalene*. Chromic acid (8·3 g.) in water (21 c.c.) was added to the compound (2·5 g.) in acetic acid (83 c.c.) at 50°. After 3 hr. the mixture was poured into water, and the precipitate recrystallised from ethanol. 5 : 8-*Dichloro*-6-*methoxy*-1 : 4-*naphthaquinone* was obtained in yellow needles, m. p. 217° (Found : C, 51·5; H, 2·3; Cl, 28·6. $C_{11}H_6O_3Cl_2$ requires C, 51·4; H, 2·3; Cl, 27·6%).

(c) 1 : 6-*Dibromo*-2-*methoxynaphthalene*. Chromic acid (6 g.) in water (15 c.c.) was added to a suspension of the compound (3·8 g.) in acetic acid (76 c.c.) at 50°. Then the temperature was raised to 65° and the mixture allowed to cool during 2 hr. The yellow precipitate was filtered off and recrystallised from acetic acid, to give 2 : 5-*dibromo*-6-*methoxy*-1 : 4-*naphthaquinone* as golden-yellow needles, m. p. 203—205° (Found : C, 38·1; H, 1·6. $C_{11}H_6O_3Br_2$ requires C, 38·1; H, 1·7%). The filtrate was poured into water, and the precipitate recrystallised from acetic acid and then benzene, to give 6-*bromo*-2-*methoxy*-1 : 4-*naphthaquinone* as pale yellow needles, m. p. 222—224° (Found : C, 49·3; H, 2·5. $C_{11}H_7O_3Br$ requires C, 49·5; H, 2·6%).

2 : 7-*Diaminonaphthalene.*—2 : 7-Dihydroxynaphthalene (5 g.), saturated ammonium sulphite solution (40 c.c.), and aqueous ammonia (15 c.c., *d* 0·88) were heated together at 170—175° for 6 hr. The resultant solid was first extracted with sodium hydroxide solution, and the residue taken up in hydrochloric acid. On reprecipitation the diamine had m. p. 166—167° (3·5 g.). With toluene-*p*-sulphonyl chloride in pyridine it gave 2 : 7-*ditoluene*-p-*sulphonamidonaphthalene*, which formed needles, m. p. 198°, after repeated recrystallisation from ethanol (Found : C, 61·4; H, 5·2; N, 6·2. $C_{24}H_{22}O_4N_2S_2$ requires C, 61·8; H, 4·7; N, 6·0%).

Iodination of 2 : 7-*Ditoluene*-p-*sulphonamidonaphthalene.*—Iodine monochloride (1 g.) was added to the sulphonamide (0·75 g.) in pyridine, and the mixture boiled gently for 20 min. The precipitate obtained on addition of hydrochloric acid was repeatedly crystallised from acetic acid, to give x-*iodo*-2 : 7-*ditoluene*-p-*sulphonamidonaphthalene* as fawn needles, m. p. 186° (Found : I, 21·1. $C_{24}H_{21}O_4N_2S_2I$ requires I, 21·4%).

Bromination of 2 : 7-*Ditoluene*-p-*sulphonamidonaphthalene.*—Bromine (1·5 g.) in chloroform (10 c.c.) was added to a hot solution of the sulphonamide (1 g.) in chloroform (30 c.c.) and the mixture boiled for 2 hr. The crystalline deposit (1 g.) obtained on cooling was repeatedly recrystallised from acetic acid and gave x-*bromo*-2 : 7-*ditoluene*-p-*sulphonamidonaphthalene* as needles, m. p. 213° (Found : C, 52·9; H, 3·6. $C_{24}H_{21}O_4N_2S_2Br$ requires C, 52·8; H, 3·8%).

Chlorination of 2 : 7-*Ditoluene*-p-*sulphonamidonaphthalene.*—Excess of chlorine was passed into a boiling solution of the sulphonamide (2 g.) in chloroform (30 c.c.). The resultant dark solution was evaporated and the residue rubbed with light petroleum, yielding a cream-coloured powder. This on recrystallisation from acetic acid gave 1 : 1 : 8 : 8-*tetrachloro*-1 : 2 : 7 : 8-*tetrahydro*-2 : 7-*ditoluene*-p-*sulphonimidonaphthalene* (XV) as prisms, m. p. 193° (1·7 g.) (Found : C, 48·0; H, 3·6; Cl, 22·7. $C_{24}H_{18}O_4N_2S_2Cl_4$ requires C, 47·6; H, 3·0; Cl, 23·5%). On addition of zinc dust to a boiling solution of the tetrachloro-compound in acetic acid the solution became first deep-yellow and finally colourless. The filtered solution deposited needles, which after recrystallisation from acetic acid gave 1 : 8-*dichloro*-2 : 7-*ditoluene*-p-*sulphonamidonaphthalene*

(XVI) as needles, m. p. 219° (Found: Cl, 13·7. $C_{24}H_{20}O_4N_2S_2Cl_2$ requires Cl, 13·3%). Both these chloro-compounds were unchanged after treatment with bromine in chloroform.

1 : 8-*Dichloro*-2 : 7-*diaminonaphthalene*, obtained by dissolution of the above dichloro-derivative in cold sulphuric acid, crystallised from ethanol in slightly brown needles, m. p. 159° (Found: C, 53·3; H, 3·6. $C_{10}H_8N_2Cl_2$ requires C, 52·9; H, 3·5%).

Chlorination of Bromo-2 : 7-*ditoluene*-p-*sulphonamidonaphthalene*.—Chlorine (3 mols.) was led into a boiling solution of the compound (6·2 g.) in chloroform (200 c.c.). The orange-coloured solution was evaporated and the residue rubbed with light petroleum. The product was taken up in hot acetic acid and on cooling gave a crystalline deposit of the original compound (2·5 g.). The filtrate was poured into water, and the precipitate dried and boiled with a limited amount of ethanol, which removed more of the unchanged compound. The residue, after repeated recrystallisation from ethanol to remove considerable amounts of the 1 : 1 : 8 : 8-tetrachloro-compound (above), gave 1-*bromo*-1 : 8 : 8-*trichloro*-1 : 2 : 7 : 8-*tetrahydro*-2 : 7-*ditoluene*-p-*sulphonimidonaphthalene* (XVII) as needles, m. p. 177° (Found: C, 44·2; H, 3·0. $C_{24}H_{18}O_4N_2S_2BrCl_3$ requires C, 44·4; H, 2·8%). On treatment with zinc dust in boiling acetic acid solution this bromotrichloro-compound gave 1 : 8-dichloro-2 : 7-ditoluene-*p*-sulphonamidonaphthalene (above).

Bromination of 2 : 7-*Diaminonaphthalene*.—(*a*) Bromine (0·28 c.c.) in acetic acid (3·5 c.c.) was added to the diamine (0·81 g.) in acetic acid (16 c.c.). Immediate precipitation of a hydrobromide occurred. After 1 hr. this was filtered off and decomposed by sodium hydroxide, to give x-*bromo*-2 : 7-*diaminonaphthalene*, m. p. 135° after recrystallisation from ethanol (Found: C, 50·0; H, 3·7. $C_{10}H_9N_2Br$ requires C, 50·6; H, 3·8%). (*b*) Experiments as in (*a*) but with 2 or 3 mols. of bromine gave only brown amorphous powders.

Chlorination of 1 : 8-*Ditoluene*-p-*sulphonamidonaphthalene*.—Excess of chlorine was passed into a boiling solution of the compound [15] (2 g.) in chloroform (35 c.c.), and the resultant brown-coloured solution evaporated. The resinous product, on successive recrystallisation from acetic acid, ethanol and acetic acid, gave 2 : 4 : 7(?)-*trichloro*-1 : 8-*ditoluene*-p-*sulphonamidonaphthalene* as needles, m. p. 233° (Found: C, 50·5; H, 3·0. $C_{24}H_{19}O_4N_2S_2Cl_3$ requires C, 50·6; H, 3·3%). The suggested orientation is by analogy with the bromination of 1 : 8-diaminonaphthalene.[16]

2 : 3-*Ditoluene*-p-*sulphonamidonaphthalene*, prepared from the base, crystallised from acetic acid in needles, m. p. 193° (Found: C, 61·8; H, 4·6. $C_{24}H_{22}O_4N_2S_2$ requires C, 61·8; H, 4·7%). Excess of chlorine was passed into a solution of this compound (1·8 g.) in boiling chloroform (30 c.c.), and the solution allowed to cool. The crystalline deposit, m. p. 262—264°, was recrystallised from benzene and gave the *dichloro-derivative* in needles, m. p. 264° (1·5 g.) (Found: C, 54·4; H, 3·6. $C_{24}H_{20}O_4N_2S_2Cl_2$ requires C, 53·8; H, 3·7%).

One of the authors (R. D. W.) is indebted to Messrs. Scottish Oils, Ltd., for laboratory facilities for some of this work.

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[15] Hodgson and Whitehurst, *J.*, 1945, 202.
[16] Whitehurst, *J.*, 1951, 221.