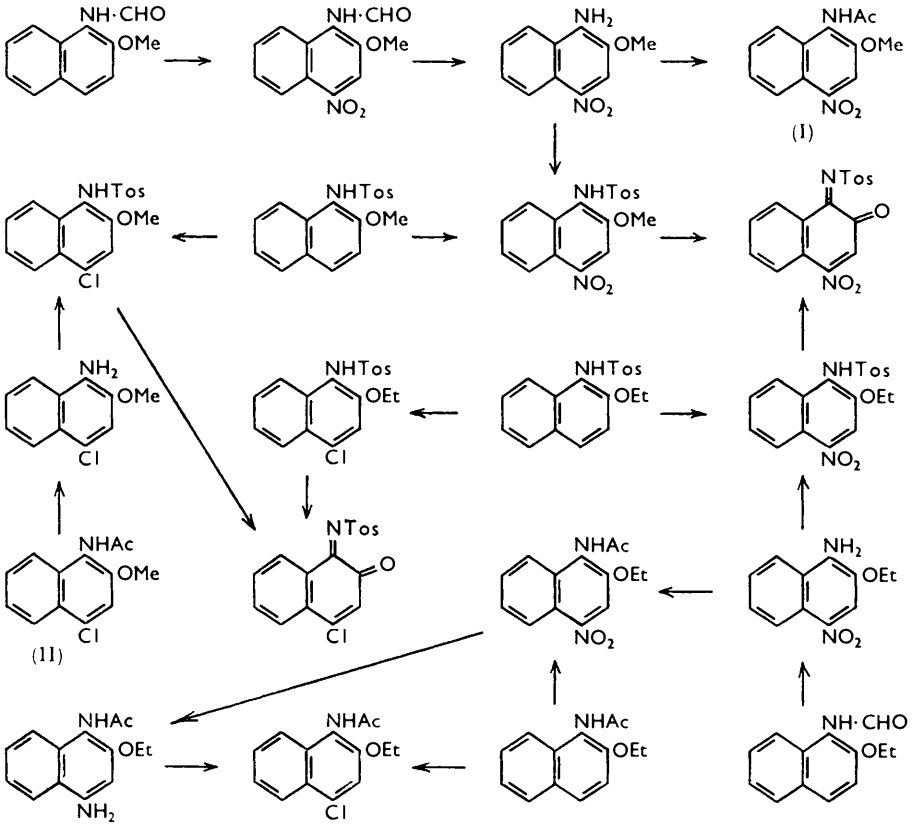
108. *Substitution Reactions with 2-Methoxy- and 2-Ethoxy-1-naphthylamines.*

By F. Bell.

Substitution experiments with the acetyl, formyl, and toluene-*p*-sulphonyl derivatives of 2-methoxy- and 2-ethoxy-1-naphthylamines show that, whereas chlorination and nitration proceed mainly, or even exclusively, in position 4, yet bromination may yield the 6-derivative as the main product.

A comparison is made with the results of substitution experiments with 2 : 6-xylidine.

Bradley and Robinson [1] showed that *N*-acetyl-2-methoxy-1-naphthylamine is nitrated at position 4, and Bell [2] showed that the same position is entered on chlorination. Davis [3] stated that both *N*-acetyl-2-methoxy- and -2-ethoxy-1-naphthylamine undergo bromination in position 6 exclusively. Other substitution products have been oriented only by analogy.



Scheme A. *Orientation of nitro-compounds based on* (I) *and of chloro-compounds based on* (II).
(Tos = $SO_2 \cdot C_7H_7$)

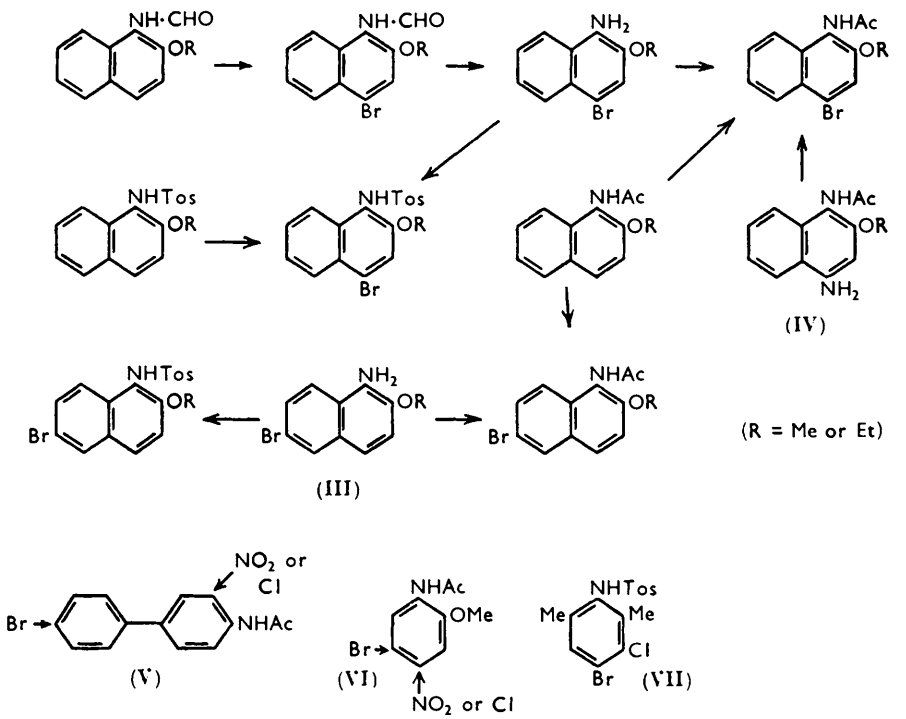
It was the present object to establish with certainty the structures of the already known substitution products and also to examine whether there really exists the marked

[1] Bradley and Robinson, *J.*, 1934, 1488.
[2] Bell, *J.*, 1954, 472.
[3] Davis, *Chem. News*, 1896, **74**, 302.

difference between nitration and chlorination on the one hand and bromination on the other which appears to emerge from the above experimental results.

The reactions set out in flow sheet (A) establish that nitration and chlorination of all derivatives examined occurs mainly or even exclusively in position 4. On the other hand, see flow sheet (B), the bromination of *N*-acetyl-2-methoxy-1-naphthylamine is complex; the main product was the 6-derivative accompanied by a small amount of the 4-derivative and another monobromo-compound not identical with the 3-derivative, which was synthesised from 3-bromo-1-nitro-2-naphthylamine.[4] Similarly, the bromination of *N*-acetyl-2-ethoxy-1-naphthylamine yielded the 6- and the 4-derivative, the latter in small amount. However, the bromination of 2-methoxy- and 2-ethoxy-*N*-formyl-1-naphthylamine yielded the 4-derivatives as the only readily isolable compounds.

Bromination of 2-ethoxy-*N*-toluene-*p*-sulphonyl-1-naphthylamine gave the 4-derivative as the main product accompanied by some 20% of the 6-derivative.



SCHEME B. *Orientation of bromo-compounds based on* (III) *and* (IV).

The results fall in line with the general observation that the products obtained on chlorination of an aromatic compound parallel those obtained on nitration, but bromination frequently follows a different course (V and VI are typical examples). A discordant observation is that of Wepster,[5] who has shown that *N*-toluene-*p*-sulphonyl-2 : 6-xylidine is nitrated at position 4, whereas, as is now shown, chlorination occurs at position 3 but bromination at position 4, the two monohalogen derivatives being in turn readily converted into the toluenesulphonamide (VII). Further, the acetamido-group in *N*-acetyl-2-methoxy-1-naphthylamine is perhaps not unsimilarly situated to that in 1-acetamido-2 : 6-xylidine and might be subjected to a similar suppression of resonance, if indeed such occurs.

[4] Consden and Kenyon, *J.*, 1935, 1593.
[5] Wepster, *Rec. Trav. chim.*, 1954, **73**, 814.

Experimental

Synthesis of N-*Acetyl*-3-*bromo*-2-*methoxy*-1-*naphthylamine.*—3-Bromo-1-nitro-2-naphthylamine [4] (5 g.) and a solution of sodium hydroxide (4 g.) in water (100 c.c.) were boiled under reflux for 6 hr. The filtered solution was acidified with hydrochloric acid, and the precipitate crystallised from a small bulk of ethanol to give 3-bromo-1-nitro-2-naphthol, yellow plates, m. p. 132° (without decomp.) (1·5 g.). From the mother-liquor was obtained material, m. p. *ca.* 180°, and this was boiled with benzene and then with chloroform to remove more soluble material. The residue on crystallisation from aqueous ethanol formed long, golden-yellow needles of 2 : 3-*dihydroxy*-1-*nitronaphthalene*, m. p. 210° (Found: C, 58·4; H, 3·1. $C_{10}H_7O_4N$ requires C, 58·5; H, 3·4%). 3-Bromo-1-nitro-2-naphthol can be purified by distillation in steam or by elution from alumina by ethyl acetate. It yielded a rather sparingly soluble sodium salt, which was not attacked by dimethyl sulphate. It was not methylated in xylene by dimethyl sulphate (K_2CO_3), but in ether with diazomethane methylation was smooth to give 3-*bromo*-2-*methoxy*-1-*nitronaphthalene*, which crystallised from methanol in silky, yellow needles, m. p. 83° (Found: C, 47·1; H, 3·0. $C_{11}H_8O_3NBr$ requires C, 46·8; H, 2·8%).

Stannous chloride (1 mol.) in concentrated hydrochloric acid was added to 3-bromo-2-methoxy-1-nitronaphthalene in boiling ethanol, and the solution concentrated. On being made alkaline with sodium hydroxide, the mixture rapidly became black and the base after extraction with ether and removal of the solvent was a black mass. It was dissolved in acetic anhydride and precipitated with water, and the dark, sticky product extracted with a small bulk of hot ethanol in order to remove most of the impurities. The residue, m. p. *ca.* 200°, was recrystallised first from acetic acid (charcoal) and then ethyl acetate to yield N-*acetyl*-3-*bromo*-2-*methoxy*-1-*naphthylamine* as a mass of fine needles, m. p. 210—213° (Found: C, 53·0; H, 4·1. $C_{13}H_{12}O_2NBr$ requires C, 53·1; H, 4·1%) (large depression with both 4-bromo- and the unoriented monobromo-isomer described below).

N-*Acetyl*-4-*bromo*-2-*methoxy*-1-*naphthylamine.*—*N*-Acetyl-4-amino-2-methoxy-1-naphthylamine [1] was diazotised in hydrobromic acid solution, and the filtered diazonium solution decomposed with copper powder. The precipitate was filtered off, and the *bromo-compound* removed from this by acetone. On recrystallisation from slightly aqueous acetic acid it formed needles, m. p. 211—213° (Found: C, 53·2; H, 4·0. $C_{13}H_{12}O_2NBr$ requires C, 53·1; H, 4·1%). A pure compound could not be isolated after treatment of this compound with bromine in acetic acid.

Bromination of N-*Acetyl*-2-*methoxy*-1-*naphthylamine.*—(*a*) Bromine (1 mol.) was added to a solution of the compound in chloroform, and the solution was then concentrated and diluted with light petroleum, and the resultant oil dissolved in acetic acid. The crop after further purification gave *N*-acetyl-6-bromo-2-methoxy-1-naphthylamine, m. p. 254°, in 20% yield.

(*b*) Addition of bromine (1 mol.) in acetic acid to the compound in warm acetic acid under various conditions gave highly impure products from which only the 6-bromo-derivative could be isolated in poor yield.

(*c*) After addition of *N*-bromosuccinimide (1 mol.) to a solution of the compound in pyridine the compound was recovered but in poor yield.

(*d*) Bromine (9 g.) in acetic acid (6 c.c.) was added to the compound (12 g.) in a mixture of acetic acid (60 c.c.) and acetic anhydride (6 c.c.) at room temperature. After a short time the mixture was heated to boiling and decomposed with a limited volume of water. The crop (7·8 g.) was essentially the 6-bromo-derivative with a small amount of the 4 : 6-dibromo-derivative (below). The filtrate on further dilution gave crystalline material, m. p. 180—197° (5·1 g.), which was separated by fractional crystallisation from acetic acid into the 4-bromo-derivative (above) and another *monobromo-derivative*, which formed prisms, m. p. 211—214° (Found: C, 54·1; H, 3·9%) greatly depressed on admixture with either the 3- or the 4-bromo-derivative. Chromium trioxide (2 g.) in the minimum of water was added to a hot solution of this compound (1 g.) in acetic acid (10 c.c.). The mixture was diluted with water, and the product recrystallised from acetic acid, to yield yellow needles of a *bromo*-2-*methoxy*-1 : 4-*naphthaquinone*, m. p. 190° (Found: C, 49·7; H, 2·8. $C_{11}H_7O_3Br$ requires C, 49·5; H, 2·6%), and an unidentified neutral compound, forming almost colourless plates, m. p. 176—178°.

Dr. D. M. W. Anderson, of Edinburgh University, has kindly provided the following report on the infrared spectra of the foregoing bromo-naphthalides:

" 3-Bromo: NH 3210; carbonyl 1665 vs, 1640 (sh), 1590 (all diffuse), 682 w, 728 m, 747 vs,

780 m, 805 w, 850 m cm.$^{-1}$. 4-Bromo: NH 3265; carbonyl 1660 vs, 1627 m, 1605 m (all sharp), 750 vs, 763 m, 793 w, 847 m, 900 m cm.$^{-1}$. 6-Bromo: NH 3260; carbonyl 1655 vs, 1635 (sh), 1596 m (all diffuse), 690 m, 800 vs, 815 vs, 880 vs, 900 m cm.$^{-1}$. (?)-Bromo: NH 3260 (broad); carbonyl 1660 (sh), 1650 vs (broad), 1622 m, 1603 m, 672 m, 755 m, 796 w, 830 vs, 937 m cm.$^{-1}$.

" Application of the principles of Cencelj and Hadži [6] and of Hawkins, Ward, and Whiffen [7] for substitution patterns leads to no precise conclusion regarding the structure of the last compound. The broad NH and carbonyl bands may indicate that these groups are involved in weak hydrogen-bonding effects and, if this is so, position 8 is indicated for the bromine."

Bromination of N-*Acetyl*-6-*bromo*-2-*methoxy*-1-*naphthylamine*.—Bromine (1 mol.) in acetic acid was added to a hot solution of the compound in acetic acid. On cooling, there separated a greenish deposit, which was washed with ammonia solution and then recrystallised from acetic acid to give the 4 : 6-*dibromo-derivative* as needles, m. p. 243° (Found: C, 42·6; H, 3·1. $C_{13}H_{11}O_2NBr_2$ requires C, 41·8; H, 3·0%). In appearance and solubility this compound closely resembles the 6-bromo-derivative, but the m. p. is depressed on admixture with it. It was recovered after treatment with ethanolic hydrogen chloride or potassium hydroxide. With hot 60% sulphuric acid it rapidly decomposed. Oxidation with chromium trioxide (as above) gave yellow needles, which suffered no depression in m. p. on admixture with 6-bromo-2-methoxy-1 : 4-naphthaquinone,[8] thereby establishing that the second bromine atom is in position 4.

Dr. D. M. W. Anderson had reported on the infrared spectrum of this compound: NH 3250; carbonyl 1663 vs, 1620 m, 1594 m (all sharp); 780, 815 vs, 838 m, 868 m, 903 s, 926 m, 978 s cm.$^{-1}$, and suggested that, owing to the striking similarity of the carbonyl region of this compound with that of the 4-isomer, the orientation would prove to be 4 : 6.

6-*Bromo*-2-*ethoxy*-N-*formylnaphthylamine*, prepared by boiling 6-bromo-2-ethoxy-1-naphthylamine with formic acid for 2 hr., crystallised from formic acid in needles, m. p. 229—231° (Found: C, 52·6; H, 3·9. $C_{13}H_{12}O_2NBr$ requires C, 53·1; H, 4·1%).

6-*Bromo*-2-*ethoxy*-N-*toluene*-p-*sulphonyl*-1-*naphthylamine*, prepared from the base and toluene-*p*-sulphonyl chloride in pyridine, crystallised from acetic acid in needles, m. p. 173° (Found: C, 54·7; H, 4·2. $C_{19}H_{18}O_3NSBr$ requires C, 54·3; H, 4·3%). Attempted further bromination either with *N*-bromosuccinimide in pyridine or with bromine in acetic acid led to dark, sticky products from which no definite compounds were isolated.

Bromination of 2-*Ethoxy*-N-*formyl*-1-*naphthylamine*.—Bromine (1 mol.) was added to a solution of the compound (2·9 g.) in warm chloroform. The very dark mixture was concentrated and diluted with light petroleum. A dark oil was precipitated which solidified (2·5 g.) when boiled with ethanol. After repeated recrystallisation from acetic acid or formic acid it gave 4-*bromo*-2-*ethoxy*-N-*formyl*-1-*naphthylamine* as fine needles, m. p. 202—204° (Found: C, 53·3; H, 4·3. $C_{13}H_{12}O_2NBr$ requires C, 53·1; H, 4·1%). Hydrochloric acid (4 c.c.) was added to a suspension of this compound (1 g.) in boiling ethanol (16 c.c.). A clear solution was rapidly obtained which on slight concentration gave needles of the base hydrochloride. The liberated base (m. p. 85° without further purification) gave N-*acetyl*-4-*bromo*-2-*ethoxy*-1-*naphthylamine*, needles, m. p. 187°, from ethanol or acetic acid (Found: C, 54·6; H, 4·3. $C_{14}H_{14}O_2NBr$ requires C, 54·5; H, 4·5%), and 4-*bromo*-2-*ethoxy*-N-*toluene*-p-*sulphonyl*-1-*naphthylamine*, rosettes, m. p. 149°, from acetic acid (Found: C, 53·8; H, 4·2. $C_{19}H_{18}O_3NSBr$ requires C, 54·3; H, 4·3%).

N-Acetyl-4-bromo-2-ethoxy-1-naphthylamine was alternatively prepared as follows. Sodium dithionite was added to a boiling suspension of *N*-acetyl-2-ethoxy-4-nitro-1-naphthylamine (2 g.) in water (20 c.c.) until the colour was discharged. The mixture was diluted with aqueous ammonia, and the product extracted with boiling ethanol. The amine, which separated in prisms, m. p. 197°, was diazotised in hydrobromic acid solution and decomposed with copper. The bromo-derivative was extracted from the product with a little acetone and purified by recrystallisation from acetic acid.

Bromination of N-*Formyl*-2-*methoxy*-1-*naphthylamine*.—The method employed for the ethoxy-analogue gave 4-*bromo*-1-*formyl*-2-*methoxy*-1-*naphthylamine*, which crystallised from acetic acid in a cotton-wool-like mass of needles, m. p. 204° (Found: C, 51·9; H, 3·2.

[6] Cencelj and Hadži, *Spectrochim. Acta*, 1955, **7**, 274.
[7] Hawkins, Ward, and Whiffen, *ibid.*, 1957, **10**, 105.
[8] Bell, Gibson, and Wilson, *J.*, 1956, 2339.

$C_{12}H_{10}O_2NBr$ requires C, 51·4; H, 3·6%). This compound was very readily hydrolysed by ethanolic hydrochloric acid to 4-*bromo*-2-*methoxy*-1-*naphthylamine*, which crystallised from methanol in plates, m. p. 68° (Found: C, 52·8; H, 3·8. $C_{11}H_{10}ONBr$ requires C, 52·4; H, 4·0%). This base with acetic anhydride gave an acetyl derivative, which underwent no depression in m. p. on admixture with synthetic *N*-acetyl-4-bromo-2-methoxy-1-naphthylamine, and with toluene-*p*-sulphonyl chloride gave a compound which underwent no change in m. p. on admixture with the compound [2] obtained by bromination of 2-methoxy-*N*-toluene-*p*-sulphonyl-1-naphthylamine. The latter is therefore the 4-bromo-derivative.

2-Ethoxy-1-naphthylamine with toluene-*p*-sulphonyl chloride in pyridine gave the N-*toluene*-p-*sulphonyl derivative*, needles, m. p. 147°, from acetic acid (Found: N, 3·6. $C_{19}H_{19}O_3NS$ requires N, 4·1%).

Bromination of 2-*Ethoxy*-N-*toluene*-p-*sulphonyl*-1-*naphthylamine.*—(*a*) Bromine (1 mol.) in chloroform was added to a warm suspension of the compound (3 g.) in chloroform (15 c.c.). The solution became very dark when boiled, and there was deposited a small amount of an unidentified hydrobromide (base, m. p. *ca.* 80°; acetyl derivative, m. p. 246—250°). The filtrate on dilution with light petroleum gave material which after repeated recrystallisation from acetic acid gave the 4-bromo-derivative, m. p. 149° (p. 522).

(*b*) *N*-Bromosuccinimide (1 mol.) was added to the compound in pyridine. The solution was decomposed by dilute hydrochloric acid to yield a dark oil, which was separated by decantation and dissolved in hot ethanol. The crop, after repeated recrystallisation, gave the 4-bromo-derivative.

(*c*) Bromine (1 mol.) in acetic acid was added to the compound (2 g.) in warm acetic acid (20 c.c.). After a short time the solution was poured into water, and the brown precipitate purified by crystallisation first from ethanol and then acetic acid. Both the 4-bromo- and the 6-bromo-derivative were isolated, the latter in about 20% yield after purification.

(*d*) Bromine (2 mol.) was used as in (*c*). On cooling, the mixture deposited crystals, m. p. *ca.* 190°, which after recrystallisation from acetic acid gave the 4 : 6-*dibromo-derivative* as needles, m. p. 195—196° (Found: C, 46·3; H, 3·4. $C_{19}H_{17}O_3NSBr_2$ requires C, 45·7; H, 3·4%). This dibromo-derivative was readily obtained by bromination of both 4- and 6-bromo-2-ethoxy-*N*-toluene-*p*-sulphonyl-1-naphthylamines.

Bromination of N-*Acetyl*-2-*ethoxy*-1-*naphthylamine.*—Addition of bromine (1 mol.) to a solution of the compound in chloroform or acetic acid–acetic anhydride (1 : 1) led to dark, complex mixtures from which by fractional crystallisation was isolated as the main product *N*-acetyl-6-bromo-2-ethoxy-1-naphthylamine, m. p. 252—254°, and a small amount of the 4-bromo-analogue (p. 522).

4-*Chloro*-2-*methoxy*-1-*naphthylamine* separated as the hydrochloride when *N*-acetyl-4-chloro-2-methoxy-1-naphthylamine [2] (2·5 g.) in ethanol (25 c.c.) was boiled with hydrochloric acid (10 c.c.). The hydrochloride was decomposed by aqueous ammonia to give the base, which crystallised from methanol in needles, m. p. 55° (Found: C, 63·6; H, 4·8. $C_{11}H_{10}ONCl$ requires C, 63·7; H, 4·8%), and with toluene-*p*-sulphonyl chloride in pyridine gave the *toluene*-p-*sulphonyl derivative*, needles (from acetic acid), m. p. 197° (Found: C, 59·3; H, 4·1. $C_{18}H_{16}O_3NSCl$ requires C, 59·7; H, 4·4%).

Chlorination of 2-*Methoxy*-N-*toluene*-p-*sulphonyl*-1-*naphthylamine.*—The compound in warm acetic acid was treated with chlorine (1 mol.). The crop (m. p. *ca.* 190°) obtained on cooling was recrystallised from acetic acid to give the 4-chloro-derivative, m. p. 197° (above), in about 50% yield.

Chlorination of 2-*Ethoxy*-N-*toluene*-p-*sulphonyl*-1-*naphthylamine.*—The compound with sulphuryl chloride (1 mol.) in chloroform gave the 4-*chloro-derivative*, which crystallised from acetic acid in needles, m. p. 147° (Found: C, 61·2; H, 4·4. $C_{19}H_{18}O_3NSCl$ requires C, 60·7; H, 4·8%).

Chlorination of N-*Acetyl*-2-*ethoxy*-1-*naphthylamine.*—Sulphuryl chloride (1 mol.) in chloroform was added dropwise to a solution of the compound in chloroform. The chloroform was removed on a steam-bath, and the dark residue taken up in hot ethanol. The crop, after several recrystallisations from ethanol, gave the 4-*chloro-derivative* as needles, m. p. 177° (Found: C, 64·2; H, 5·0. $C_{14}H_{14}O_2NCl$ requires C, 63·8; H, 5·3%). A suitable method for the hydrolysis of this compound was not found.

N-*Acetyl*-2-*ethoxy*-4-*nitro*-1-*naphthylamine.*—Concentrated nitric acid (1·7 c.c.) was added dropwise to a cooled suspension of *N*-acetyl-2-ethoxy-1-naphthylamine (5 g.) in acetic acid

(10 c.c.). After 2 hr., water was added, and the resulting plastic mass induced to solidify by rubbing it with warm ethanol. The product (1 g., m. p. 233—236°) gave the *4-nitro-derivative* as bright yellow needles, m. p. 234—236°, from acetic acid (Found: C, 61·5; H, 4·5. $C_{14}H_{14}O_4N_2$ requires C, 61·3; H, 5·1%). The yield was equally poor in other methods of nitration.

2-Ethoxy-4-nitro-1-naphthylamine.—This compound is mentioned in a patent [9] but no details of its preparation are given. 2-Ethoxy-*N*-formyl-1-naphthylamine (5 g.; m. p. 152°) was added slowly to a mixture of concentrated nitric acid (2·5 c.c.) and acetic acid (12·5 c.c.). After 2 hr. water was added to the pasty mass, and the product boiled with ethanol to yield the 4-nitro-derivative (2·5 g.), m. p. 211°. Potassium hydroxide (2 g. in a little water) was added to a boiling suspension of this nitro-compound (2·5 g.) in ethanol (50 c.c.). Hydrolysis was instantaneous. The clear solution was diluted with water, and on cooling 2-ethoxy-4-nitro-1-naphthylamine separated in bright red prisms, m. p. 152°. This base (1·5 g.) was left in pyridine with toluene-*p*-sulphonyl chloride (1·5 g.) for 24 hr., and the mixture then decomposed by excess of dilute hydrochloric acid. The sticky product was boiled successively with ethanol and ethyl acetate to remove unchanged base, and the residue recrystallised from acetic acid to give the N-*toluene*-p-*sulphonyl derivative* as yellow needles, m. p. 167—169° (Found: C, 59·6; H, 4·7. $C_{19}H_{18}O_5N_2S$ requires C, 59·1; H, 4·7%).

*Nitration of 2-Ethoxy-*N*-toluene-*p*-sulphonyl-1-naphthylamine.*—The compound (1 g.) was warmed on a steam-bath for about 2 hr. with a mixture of concentrated nitric acid (1 c.c.) and water (10 c.c.). The product on recrystallisation from acetic acid gave the pure 4-nitro-derivative (above).

The previously described [2] nitro-derivatives of *N*-formyl-2-methoxy- and 2-methoxy-*N*-toluene-*p*-sulphonyl-1-naphthylamine were shown to be 4-nitro-derivatives in the following way. The formamido-4-nitro-compound was rapidly and almost quantitatively converted into 2-methoxy-4-nitro-1-naphthylamine by addition of a slight excess of concentrated aqueous potassium hydroxide to its solution in boiling ethanol. This base in pyridine with toluene-*p*-sulphonyl chloride was slowly and partially converted into the toluene-*p*-sulphonyl derivative, which was readily separated from the base by its much lower solubility in ethyl acetate. It formed yellow needles, m. p. 199° alone or mixed with the product of nitration of 2-methoxy-*N*-toluene-*p*-sulphonyl-1-naphthylamine.

*Interaction of 2-Methoxy-*N*-toluene-*p*-sulphonyl-1-naphthylamine with Fuming Nitric Acid.*—Fuming nitric acid (2 c.c.) in acetic acid (2 c.c.) was added to a warm suspension of the compound (2 g.) in acetic acid (20 c.c.). Recrystallisation of the crystals from acetic acid gave *4-nitro-1 : 2-naphthaquinone 1-toluene-*p*-sulphonimide* in orange-red needles, m. p. 200° (decomp.) (Found: C, 57·6; H, 3·0. $C_{17}H_{12}O_5N_2S$ requires C, 57·3; H, 3·4%). The same compound was obtained by using either 2-ethoxy-*N*-toluene-*p*-sulphonyl-1-naphthylamine or 2-methoxy-4-nitro-*N*-toluene-*p*-sulphonyl-1-naphthylamine in the above experiment.

Oxidation of 2-methoxy-*N*-toluene-*p*-sulphonyl-1-naphthylamine with chromic acid in acetic acid gave 2-methoxy-1 : 4-naphthaquinone,[1] m. p. 184°, in fair yield.

*4-Chloro-1 : 2-naphthaquinone 1-toluene-*p*-sulphonimide*, obtained from either 4-chloro-2-ethoxy- or 4-chloro-2-methoxy-*N*-toluene-*p*-sulphonyl-1-naphthylamine by treatment with fuming nitric acid as above, formed bright red prisms, m. p. 220° (decomp.), from acetic acid (Found: C, 59·5; H, 3·5. $C_{17}H_{12}O_3NSCl$ requires C, 59·1; H, 3·5%) or long yellow needles from benzene.

6-Bromo-2-methoxy-*N*-toluene-*p*-sulphonyl-1-naphthylamine did not undergo smooth reaction with fuming nitric acid under the same conditions.

Bromination of N-*Toluene*-p-*sulphonyl-2 : 6-xylidine.*—*N*-Bromosuccinimide (1 mol.) was added to the compound in pyridine, and the resulting solution left for ½ hr. On decomposition with dilute hydrochloric acid the *4-bromo-derivative* was precipitated in almost theoretical yield. It formed needles, m. p. 149°, from acetic acid (Found: C, 50·7; H, 4·1. $C_{15}H_{16}O_2NSBr$ requires C, 50·9; H, 4·5%), and was hydrolysed during several days by concentrated sulphuric acid to give 4-bromo-2 : 6-xylidine, m. p. 47° (acetyl derivative, m. p. 195°). Bromination of *N*-toluene-*p*-sulphonyl-2 : 6-xylidine by bromine in chloroform gave a much less favourable result; the only solid product was 4-bromo-2 : 6-xylidine hydrobromide and most remained as an uncrystallisable oil.

[9] I. G. Farbenind., G.P. 491,022.

Chloro-*N*-toluene-*p*-sulphonyl-2 : 6-xylidine [10] was hydrolysed with concentrated sulphuric acid for several days to give an oily base which could not be solidified in ice and which gave an acetyl derivative, m. p. 146—147°. This agrees with 3-chloro-2 : 6-xylidine (liquid; acetyl derivative, m. p. 146—147°) and not 4-chloro-2 : 6-xylidine (m. p. 44—45°; acetyl derivative, m. p. 195°).[11]

*4-Bromo-3-chloro-*N*-toluene-*p*-sulphonyl-2 : 6-xylidine.*—(*a*) Excess of sulphuryl chloride was added to 4-bromo-*N*-toluene-*p*-sulphonyl-2 : 6-xylidine, and the excess removed on a steam-bath. The residual gum after repeated recrystallisation from acetic acid gave prisms identical with those obtained as below. (*b*) *N*-Bromosuccinimide (1 mol.) was added to 3-chloro-*N*-toluene-*p*-sulphonyl-2 : 6-xylidine dissolved in pyridine, and the mixture slightly warmed until solution resulted. Excess of dilute hydrochloric acid was added, and the precipitate recrystallised from acetic acid, giving *4-bromo-3-chloro-*N*-toluene-*p*-sulphonyl-2 : 6-xylidine* in prisms, m. p. 136° (Found: C, 46·8; H, 3·9. $C_{15}H_{15}O_2NSBrCl$ requires C, 46·3; H, 3·9%).

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[10] Bell, *J.*, 1955, 2382.
[11] Dadswell and Kenner, *J.*, 1927, 1105.