192. *The Mobility of Groups in 3-Chloro-4-nitro- and in 5-Chloro-2-nitro-diphenylsulphones.*

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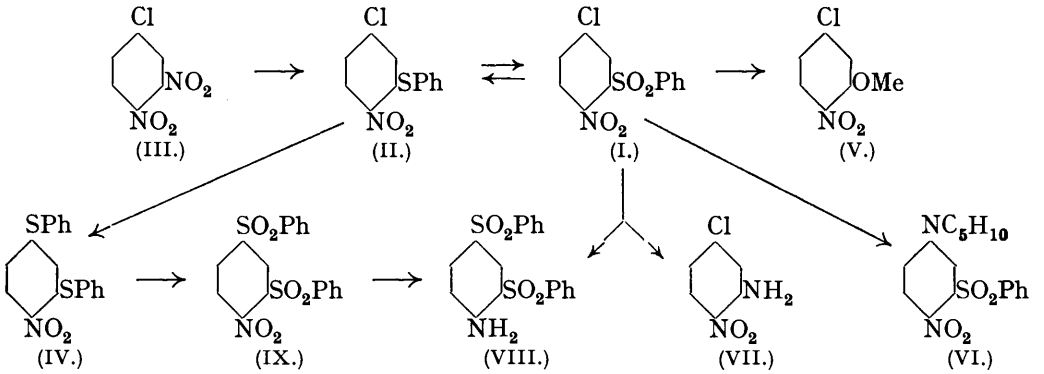
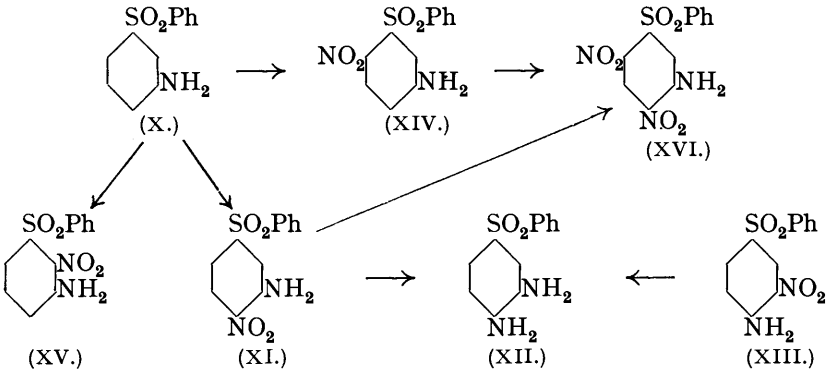
The reactions of these sulphones with various reagents have been examined and the results show that in most, but not all cases, replacement occurs at a centre *o* or *p* to the nitro-group. Incidental descriptions are given (*a*) of the homonuclear nitration products derived from 3-aminodiphenylsulphone and (*b*) of the reactivity of 2 : 4-*diphenylsulphonylnitrobenzene*.

THE sulphone types here under investigation contain potential anions, represented by the chlorine and sulphonyl substituents, in positions *o* or *p* to the nitro-group and, in providing thereby alternative outlets to the activating influence of the nitro-group, differ from the 2 : 4- and 4 : 2-chloronitrodiphenylsulphone types previously examined (Loudon and Robson, J., 1937, 242; Loudon and Shulman, J., 1938, 1618). It is hoped shortly to complete the series with a study of the vicinal isomers.

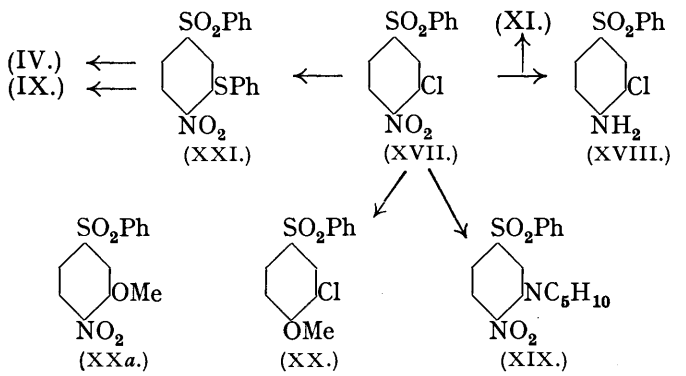


5-Chloro-2-nitrodiphenylsulphone (I) was obtained by oxidation of the *thio-ether* (II), which was formed, together with smaller quantities of the isomeric 4-chloro-2-nitrodiphenyl sulphide, by the action of thiophenol in presence of alkali on 3 : 4-dinitrochlorobenzene (III). With the mercaptide reagent in molecular proportion, (II) was regenerated from (I), whereas with excess of the reagent, the *bis-thio-ether* (IV) was formed from (I), (II), or (III). In reaction with sodium methoxide, (I) yielded 5-chloro-2-nitroanisole (V), and although this replacement of sulphonyl proceeds much more slowly than the reaction

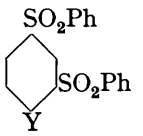
yielding (V) from (III) (Blanksma, *Rec. Trav. chim.*, 1902, **21**, 321), yet the alternative replacement of chlorine from (I) was not promoted, only traces of chloride ions being formed. On the other hand, the chlorine of (I) was rapidly replaced in reaction with piperidine, the *product* (VI) being obtained in good yield. At the high temperature (160°) required, the interaction of (I) with methyl-alcoholic ammonia was somewhat complicated and yielded a mixture of (VII) and (VIII). Apparently the sulphinate simultaneously formed with (VII) in the initial stage has reacted with unchanged (I) to give 2 : 4-*diphenylsulphonyl-nitrobenzene* (IX), from which the nitro-group is replaced (IX ⟶ VIII) by the further action of ammonia. The individual stages in the scheme (I) ⟶ (IX) ⟶ (VIII) were realised and (VIII) was also produced by reduction of (IX).

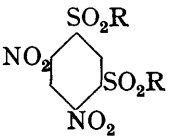


As a preliminary to the preparation of 3-chloro-4-nitrodiphenylsulphone an examination was made of the nitration products obtainable from the *acetyl* and p-*toluenesulphonyl* derivatives of 3-aminodiphenylsulphone (X). It has frequently been observed (Ullmann and Gross, *Ber.*, 1910, **43**, 2694; Bell, J., 1928, 2770) that the directive powers of these two acylamido-groups are very different and, in the present case also, a marked difference in the proportions of nuclear substitution products is observed. From both sources the required *amine* (XI) was obtained and its structure was proved by the fact that it yielded the same *diamine* (XII) and *quinoxaline* derivative as 3-nitro-4-aminodiphenylsulphone (XIII). Whereas, however, in the sulphonamide series the chief accompanying *isomer* was nitrated *para* to the amide group—the corresponding *amine* (XIV) was identified by conversion into (I)—the main *by-product* from the acetyl compound yielded on hydrolysis a different *amine*, to which, because of its relationship to vicinal compounds not described here, the structure (XV) is assigned. Despite the use of a very weak nitrating solution there was always produced from the sulphonyl derivative of (X) a quantity of dinitrated material and, since the same *product* was obtained by nitrating the sulphonamides of (XI) and (XIV), its structure corresponds to that given for the *amine* (XVI), which it yields when hydrolysed.



3-*Chloro*-4-*nitrodiphenylsulphone* (XVII) was obtained from the amine (XI) by the Sandmeyer process and, in reaction with methyl-alcoholic ammonia, was converted partly again into this amine and partly, by replacement of the nitro-group, into 3-*chloro*-4-*amino*-*diphenylsulphone* (XVIII), which was also formed when (XVII) was reduced. Corresponding to the chlorine replacement in the isomeric sulphone, piperidine with (XVII) gave the *piperidino*-compound (XIX). With sodium methoxide the nitro-group of (XVII) was replaced, yielding (XX), but, though the compound was not isolated, the production of chloride ions during the reaction indicated also the formation of (XX*a*). The formation of (XXI) from (XVII) by the action of alkaline thiophenol provided a notable exception to the preferred sulphonyl replacements observed with this reagent in other cases (*loc. cit.* and cf. I ⟶ II). The structure of (XXI) was confirmed by oxidising the compound to 2 : 4-diphenylsulphonylnitrobenzene (IX), from which it was again formed, accompanied by (XXII; Y = SPh), in reaction with the mercaptide. It is remarkable, in this connection, that by the action of ammonia, piperidine or sodium methoxide on (IX) only one *product* (XXII; Y = NH_2, NC_5H_{10}, or OMe)—formed by replacement of the nitro-group—could be isolated in each case. The reactions of (IX) correspond, therefore, with those of the 2 : 4-dinitro-1 : 5-diarylsulphonylbenzenes (XXIII) examined by Livingston and Loudon (J., 1937, 246), except that in the latter compounds, presumably because of the increased activation at the centres concerned, only the sulphonyl groups are replaced in reaction with mercaptides.

(XXII.) 



(XXIII.)

The results obtained show that the mobility of groups in these chloronitrodiphenylsulphones is largely but not completely controlled by the activating influence of the nitro-substituent. The conversion of 1 : 5-dichloro-2 : 4-dinitrobenzene into 1 : 2 : 4 : 5-tetraarylsulphonylbenzenes by the action of sulphinates (Livingston and Loudon, *loc. cit.*) finds its counterpart here in the formation of 1 : 2 : 4-*tri*-p-*tolylsulphonylbenzene* from sodium *p*-toluenesulphinate and 3 : 4-dinitrochlorobenzene, though the phenyl analogue is not so readily produced in this way.

Experimental.

5-*Chloro*-2-*nitrodiphenyl Sulphide* (II).—An aqueous-alcoholic solution containing sodium hydroxide and thiophenol in molecular proportion was added slowly to a cooled solution of 1-chloro-3 : 4-dinitrobenzene in alcohol. After several hours, the resulting precipitate was purified from acetic acid and formed yellow crystals, m. p. 127° (Found : N, 5·4. $C_{12}H_8O_2NClS$ requires N, 5·3%). The alcoholic mother-liquor, on dilution with water, gave 4-chloro-2-nitrodiphenyl sulphide, m. p. and mixed m. p. 86° after purification (Loudon and Shulman, *loc. cit.*), and also some phenyl disulphide. With a higher reaction temperature or a greater quantity of mercaptide there was produced 2 : 4-*diphenylthionitrobenzene* (IV), which, however, was best obtained from the mercaptide and (I) in hot alcoholic dioxan. It formed yellow plates, m. p. 120°, from acetic acid (Found : N, 4·25. $C_{18}H_{13}O_2NS_2$ requires N, 4·1%). The corresponding *bis-sulphone* (IX), obtained by oxidation with hydrogen peroxide in acetic acid, had m. p. 160° (Found : N, 3·6. $C_{18}H_{13}O_6NS_2$ requires N, 3·5%).

5-*Chloro*-2-*nitrodiphenylsulphone* (I) was obtained by oxidising (II). It formed fine needles or plates from acetic acid and had m. p. 186—187° (Found : N, 4·9. $C_{12}H_8O_4NClS$ requires N, 4·7%). The sulphide (II) was re-formed from (I) by the action of the mercaptide (1 mol.) in cold alcoholic dioxan. When heated for a few minutes with piperidine, (I) yielded 2-*nitro*-5-*piperidinodiphenylsulphone* (VI), golden-yellow needles, m. p. 192° (Found : N, 8·1. $C_{17}H_{18}O_4N_2S$ requires N, 8·1%). When a solution of the sulphone (I) and sodium methoxide in methyl-alcoholic dioxan was refluxed for 1 hour, the material which separated on cooling was unchanged (I), but the mother-liquor, on dilution with water, yielded 5-chloro-2-nitroanisole, m. p. and mixed m. p. 73—74° (Blanksma, *loc. cit.*).

Action of Methyl-alcoholic Ammonia on (I).—The materials were heated in a sealed tube at 160° for 6 hours. On cooling, the separated solid (A) was removed and the filtrate was distilled

in steam, yielding a yellow solid distillate which, after crystallisation from alcohol, was identified, m. p. and mixed m. p. 125°, as 5-chloro-2-nitroaniline (Laubenheimer, *Ber.*, 1876, **9**, 1826). The solid (A) was crystallised from acetic acid after refluxing with charcoal. It formed fine colourless needles of 2 : 4-*diphenylsulphonylaniline* (VIII), m. p. 203°, which were sparingly soluble in acids but could be diazotised in a sulphuric–acetic acid mixture and then coupled with β-naphthol (Found : C, 57·8; H, 4·2; N, 4·1. $C_{18}H_{15}O_4NS_2$ requires C, 57·9; H, 4·0; N, 3·75%). The same compound was also prepared by the action of alcoholic ammonia on 2 : 4-diphenylsulphonylnitrobenzene (IX) or, better, by reducing the latter with stannous chloride and dry hydrogen chloride in acetic acid (procedure, Heppenstall and Smiles, J., 1938, 899).

The following *p*-tolyl analogues of some of the above compounds were prepared by corresponding methods : 5-*chloro*-2-*nitro*-4′-*methyldiphenyl sulphide*, m. p. 127° (Found : N, 5·2. $C_{13}H_{10}O_2NClS$ requires N, 5·0%), accompanied by 4-chloro-3-nitro-4′-methyldiphenyl sulphide, m. p. 121° (Loudon and Robson, *loc. cit.*); 5-*chloro*-2-*nitro*-4′-*methyldiphenylsulphone*, m. p. 189° (Found : N, 4·8. $C_{13}H_{10}O_4NClS$ requires N, 4·5%); 2 : 4-*di*-p-*tolylthionitrobenzene*, m. p. 105° (Found : N, 4·0. $C_{20}H_{17}O_2NS_2$ requires N, 3·8%); 2 : 4-*di*-p-*tolylsulphonylnitrobenzene*, m. p. 158° (Found : N, 3·4. $C_{20}H_{17}O_6NS_2$ requires N, 3·25%); 2-*nitro*-5-*piperidino*-4′-*methyldiphenylsulphone*, m. p. 178° (Found : N, 7·9. $C_{18}H_{20}O_4N_2S$ requires N, 7·8%).

Nitro-derivatives of 3-*Aminodiphenylsulphone*.—3-p-*Toluenesulphonamidodiphenylsulphone*, m. p. 152°, was obtained from the action of *p*-toluenesulphonyl chloride on the amine (Heppenstall and Smiles, *loc. cit.*) dissolved in pyridine (Found : N, 3·8. $C_{19}H_{17}O_4NS_2$ requires N, 3·6%). It was nitrated by boiling for 20—30 minutes its solution in a nitrating mixture (10 c.c. per g.) made from acetic acid (100 c.c.) and nitric acid (3 c.c., *d* 1·4). On cooling, 4-*nitro*-3-p-*toluenesulphonamidodiphenylsulphone* (A) separated and was at once filtered off from the mother-liquor (B). The amide formed pale yellow crystals, m. p. 220°, from acetic acid (Found : N, 6·6. $C_{19}H_{16}O_6N_2S_2$ requires N, 6·5%) and, on hydrolysis with 80% sulphuric acid at 110°, yielded 4-*nitro*-3-*aminodiphenylsulphone* (XI), which had m. p. 185° after purification from acetic acid (Found : N, 11·1. $C_{12}H_{10}O_4N_2S$ requires N, 11·1%). Reduction of the amine (XI) or of 3-nitro-4-aminodiphenylsulphone (Loudon, J., 1936, 218) by means of alcoholic stannous chloride and hydrochloric acid yielded, in each case, 3 : 4-*diaminodiphenylsulphone* (XII), m. p. 126° (Found : N, 11·4. $C_{12}H_{12}O_2N_2S$ requires N, 11·3%), from which 6-*phenylsulphonyl*-2 : 3-*diphenylquinoxaline*, m. p. 196°, was obtained by reaction with benzil in the usual way (Found : N, 6·8. $C_{26}H_{18}O_2N_2S$ requires N, 6·6%).

The filtrate (B), on standing, deposited a second crop of crystals (C) melting indefinitely at 150°, and the filtrate from (C), after dilution with water and extraction of the resulting solid with a moderate amount of warm alcohol (extract D), gave a further quantity of (C) as a sparingly soluble residue. 2-*Nitro*-5-p-*toluenesulphonamidodiphenylsulphone* was obtained when the alcoholic extract (D) was cooled, after removal, where necessary, of a small initial deposit of (C). It melted at *ca.* 150°, markedly depressed by admixture with (C) and, after two crystallisations from acetic acid, formed rosettes of almost colourless crystals having a constant m. p. 152° (Found : N, 6·5. $C_{19}H_{16}O_6N_2S_2$ requires N, 6·5%). When hydrolysed with sulphuric acid, it yielded 2-*nitro*-5-*aminodiphenylsulphone* (XIV), which formed yellow needles, m. p. 235—236° (Found : N, 10·25. $C_{12}H_{10}O_4N_2S$ requires N, 10·1%), and gave 5-chloro-2-nitrodiphenylsulphone (I), identified by mixed m. p. and piperidino-derivative (VI), when submitted to the Sandmeyer reaction (Hodgson and Walker's procedure, J., 1933, 1620). 2 : 4-*Dinitro*-5-p-*toluenesulphonamidodiphenylsulphone* was obtained when the amides from fractions (A) and (D) were separately nitrated in an acetic–nitric acid mixture (1 : 1 by vol.), or when fraction (C) was crystallised from acetic acid. It formed colourless silky needles, m. p. 173° (Found : N, 8·7. $C_{19}H_{15}O_8N_3S_2$ requires N, 8·8%), and was hydrolysed to the corresponding *amine* (XVI), which formed long yellow needles, m. p. 241°, from acetic acid (Found : N, 12·85. $C_{12}H_9O_6N_3S$ requires N, 13·0%).

3-*Acetamidodiphenylsulphone* formed rosettes of needles, m. p. 143° (Found : N, 5·3. $C_{14}H_{13}O_3NS$ requires N, 5·1%). The amide (4 g.) was added with stirring to nitric acid (20 c.c., *d* 1·5) at 0°, the mixture poured into ice-water, and the gummy solid washed, dried in air, and dissolved in hot alcohol (20 c.c.), from which 4-*nitro*-3-*acetamidodiphenylsulphone* separated, on cooling, in small, pale yellow crystals, m. p. 154° (Found : N, 8·8. $C_{14}H_{12}O_5N_2S$ requires N, 8·75%), which were hydrolysed to the amine (XI) by sulphuric acid at 110°. The alcoholic mother-liquor from the acetyl compound yielded, on standing, 2-*nitro*-3-*acetamidodiphenylsulphone*, which crystallised from alcohol–acetic acid in colourless needles, m. p. 187° (Found : N, 8·5. $C_{14}H_{12}O_5N_2S$ requires N, 8·75%), and was hydrolysed to 2-*nitro*-3-*aminodiphenylsulphone*, m. p. 171° (Found : N, 10·3. $C_{12}H_{10}O_4N_2S$ requires N, 10·1%).

3-*Chloro*-4-*nitrodiphenylsulphone* (XVII) was prepared by the Sandmeyer reaction from the amine (XI) and had m. p. 133° (Found: N, 4·9. $C_{12}H_8O_4NClS$ requires N, 4·7%). When heated for a few minutes with piperidine, it yielded 4-*nitro*-3-*piperidinodiphenylsulphone* (XIX), m. p. 116° (Found: N, 8·2. $C_{17}H_{18}O_4N_2S$ requires N, 8·1%). 3-*Chloro*-4-*methoxydiphenylsulphone* (XX), almost colourless prisms, m. p. 111°, was formed (chloride ions were also detected) when the sulphone (XVII) was refluxed in a methyl-alcoholic–dioxan solution of sodium methoxide (Found: C, 55·0; H, 4·0. $C_{13}H_{11}O_3ClS$ requires C, 55·2; H, 3·9%).

3-*Chloro*-4-*aminodiphenylsulphone* (XVIII).—(a) The sulphone (XVII) was reduced with stannous chloride in an acetic acid solution of hydrochloric acid (cf. VIII); the resulting amine formed colourless crystals, m. p. 197°, from acetic acid (Found: C, 53·8; H, 3·7; N, 5·3. $C_{12}H_{10}O_2NClS$ requires C, 53·8; H, 3·7; N, 5·2%). (b) The sulphone (XVII) was heated with methyl-alcoholic ammonia in a sealed tube at 180° for 5 hours. After filtering from a small amount of resinous material, the clear solution was diluted with water; the resulting solid slowly crystallised (charcoal) from acetic acid as a mixture of pale yellow prisms and orange clusters, which were separated by hand. The light-coloured material was almost pure, having m. p. and mixed m. p. 195—196°, with the amine from (a); the orange solid, after repeated crystallisation from acetic acid, had m. p. 180—181°, raised to 184° by admixture with 4-nitro-3-aminodiphenylsulphone (XI).

4-*Nitro*-3-*phenylthiodiphenylsulphone* (XXI).—The sulphone (XVII) was warmed in aqueous-alcoholic solution with molecular proportions of sodium hydroxide and thiophenol. The oil which formed, slowly solidified and then crystallised from acetic acid in yellow needles or prisms, m. p. 166—167° (Found: N, 3·8. $C_{18}H_{13}O_4NS_2$ requires N, 3·8%). It gave (a) 2 : 4-diphenylthionitrobenzene (IV), m. p. and mixed m. p. 120°, when treated with the mercaptide reagent in aqueous-alcoholic dioxan, and (b) the corresponding bis-sulphone (IX), m. p. and mixed m. p. 159°, with hydrogen peroxide in acetic acid.

Reactions of 2 : 4-*Diphenylsulphonylnitrobenzene* (IX).—(a) For reaction with ammonia, see (1) above. (b) Heated with piperidine at 100°, it gave 1-*piperidino*-2 : 4-*diphenylsulphonylbenzene*, m. p. 156° (Found: N, 3·3. $C_{23}H_{23}O_4NS_2$ requires N, 3·2%). (c) A solution of (IX) in methyl-alcoholic dioxan containing sodium methoxide, refluxed for 30 minutes, yielded 2 : 4-*diphenylsulphonylanisole*, which crystallised from methyl alcohol in woolly needles, m. p. 176° (Found: C, 58·6; H, 4·0. $C_{19}H_{16}O_5S_2$ requires C, 58·7; H, 4·1%). (d) Molecular proportions of (IX), thiophenol, and sodium hydroxide were heated for a short time in alcoholic dioxan. The crystalline precipitate obtained consisted mainly of a colourless solid, mixed with some yellow material. The mixture was crystallised from much acetic acid and gave 2 : 4-*diphenylsulphonyldiphenyl sulphide* in long colourless needles, m. p. 221° (Found: S, 20·3. $C_{24}H_{18}O_4S_3$ requires S, 20·6%), which were oxidised to 1 : 2 : 4-*triphenylsulphonylbenzene*, m. p. 198° (Found: S, 18·95. $C_{24}H_{18}O_6S_3$ requires S, 19·3%). The combined mother-liquors from the mercaptide reaction and the crystallisation of the above sulphide yielded, on dilution and purification of the resulting solid, 4-nitro-3-phenylthiodiphenylsulphone (XXI), m. p. and mixed m. p. 166°

The following compounds were prepared by similar reactions from the *p*-tolyl analogue of (IX): 1-*piperidino*-2 : 4-*di*-p-*tolylsulphonylbenzene*, m. p. 163° (Found: N, 3·2. $C_{25}H_{27}O_4NS_2$ requires N, 3·0%); 2 : 4-*di*-p-*tolylsulphonyl*-4′-*methyldiphenyl sulphide*, m. p. 220° (Found: S, 18·6. $C_{27}H_{24}O_4S_3$ requires S, 18·9%); 1 : 2 : 4-*tri*-p-*tolylsulphonylbenzene*, m. p. 185° (Found: S, 17·5. $C_{27}H_{24}O_6S_3$ requires S, 17·8%), and 4-*nitro*-3-p-*tolylthio*-4′-*methyldiphenylsulphone*, m. p. 124° (Found: N, 3·65. $C_{20}H_{17}O_4NS_2$ requires N, 3·5%).

Action of Sodium p-*Toluenesulphinate on* 3 : 4-*Dinitrochlorobenzene*.—A solution of the nitro-compound in dioxan was added to an excess of the sulphinate dissolved in hot ethylene glycol and the resulting homogeneous solution was refluxed for 2½ hours. The solid which was obtained on cooling and dilution with water was washed with alcohol and fractionally crystallised from acetic acid. The first fraction, consisting of colourless needles, was identified, m. p. and mixed m. p. 183—185°, as 5-chloro-2-nitro-4′-methyldiphenylsulphone, and a second fraction, after further purification from acetic acid, melted at 182°, depressed by fraction I but raised to 184—185° by admixture with 1 : 2 : 4-tri-*p*-tolylsulphonylbenzene.

The author acknowledges his indebtedness to the Carnegie Trustee for the tenure of a Teaching Fellowship, and to the Chemical Society for a grant from the Research Fund. He also desires to thank Mr. J. M. L. Cameron, by whom the compounds were micro-analysed.

THE UNIVERSITY, GLASGOW. [*Received, March 31st*, 1939.]