612. *Reactions of Some Arenesulphonyl Chlorides.*

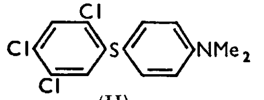
By W. V. FARRAR.

2,4,5-Trichlorobenzenesulphonyl chloride and some related compounds react with ammonia to give a mixture of the sulphonamide and the ammonium salt of the disulphonimide (I; X = H, R = $C_6H_2Cl_3$). Other nitrogenous bases also react in unexpected ways; thus phenylhydrazine gives the sulphinic acid and nitrogen, and cyclotetrathioimine gives novel compounds. The supposed biphenyl-2,2′-disulphonamide is shown to be the ammonium salt of biphenyl-2,2′-disulphonimide (V), and the supposed " trisarenesulphonyl amine oxides " are shown to be hydroxylamine derivatives (VI). Benzene-*o*-disulphonamide has been prepared and characterised. The reaction of some arenesulphonyl chlorides with sodium sulphite gives (in addition to the sulphinate) *S*-aryl thiosulphates (VII).

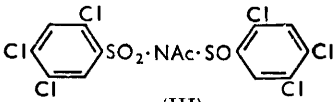
THE present investigation followed the discovery that the reaction of 2,4,5-trichlorobenzenesulphonyl chloride with ammonia gave, together with the expected sulphonamide, a large amount of the ammonium salt of the disulphonimide (I; R = 2,4,5-$Cl_3C_6H_2$, X = H). Other halogenoarenesulphonyl chlorides behaved similarly, and there is no doubt that a number of alleged sulphonamides,[1] described as having high and indefinite melting points, consist largely of ammonium salts of disulphonimides; the authentic sulphonamides melt quite sharply, and without decomposition, at lower temperatures.

$(RSO_2)_2NX$

(I)



(II)



(III)

In view of the unusual reactivity of these sulphonyl chlorides towards ammonia, the reactions of 2,4,5-trichlorobenzenesulphonyl chloride with other bases were briefly studied.

Reaction with methylamine alone gave the methyl-amide as sole product. The sodium salt of the methyl-amide, and the sulphonyl chloride, in boiling water, gave a minute yield of the methyl-imide, but a 30% yield was obtained from the sulphonyl chloride (2 mols.), methylamine (1 mol.), and aqueous sodium hydroxide (2 mols.). Similar results were obtained with aniline. This indicates that the disulphonimides are not formed by successive acylations of the ammonia or amine, as in the cases studied by Bell,[2] but from simultaneous reaction of two molecules of sulphonyl chloride with one of amine. A similar conclusion was reached by Thompson [3] from a study of the reactions of carboxylic chlorides under certain conditions. With 2,4,5-trichloroaniline in pyridine, the only crystalline product was the imide (I; R = X = 2,4,5-$Cl_3C_6H_2$) in poor yield.

Reaction with dimethylaniline gave a small amount of the sulphide (II), together with (unexpectedly) bis-2,4,5-trichlorophenyl trisulphide, and a dye resembling Crystal Violet. This evidently involves the intermediate formation of the sulphenyl chloride; these compounds are known to react with dimethylaniline to give compounds resembling (II). The normal reaction between arenesulphonyl chlorides and dimethylaniline gives the *N*-methylarenesulphonanilide, with elimination of a methyl group.[4]

Hydrazine gave the hydrazide in the normal way and more highly acylated compounds were not formed. Phenylhydrazine, however, acted simply as a reducing agent; nitrogen was evolved and phenylhydrazinium 2,4,5-trichlorobenzenesulphinate formed in over

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[1] Cf. (*a*) Huntress and Carten, *J. Amer. Chem. Soc.*, 1940, **62**, 511; (*b*) Langfürth, *Annalen*, 1878, **191**, 191; (*c*) Spiegelberg, *ibid.*, 1879, **197**, 284; (*d*) Boyle, *J.*, 1909, 1711.

[2] Bell, *J.*, 1929, 2787; 1930, 1071; 1931, 609; 1933, 1290.

[3] Thompson, *J. Amer. Chem. Soc.*, 1951, **73**, 5841.

[4] Bergel and Döring, *Ber.*, 1928, **61**, 844.

90% yield. Hydroxylamine gave a presumed hydroxamic acid which decomposed spontaneously, in contrast to benzenesulphonhydroxamic acid which is quite stable.[5]

Carboxyamides in pyridine were dehydrated to nitriles; the reaction is clean and almost quantitative. Reaction with thiourea was complex, giving bis-(2,4,5-trichlorophenyl) trisulphide. 2,4,5-Trichlorobenzenesulphonamide (in pyridine) gave a high yield of the pyridine salt of (I; X = H). Reaction with dibenzimide gave, surprisingly, tribenzoylamine; it is difficult to understand the mechanism of this reaction.

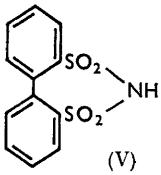
Disulphonimides did not react at all, and in no case could a compound of type $(RSO_2)_3N$ be obtained. Such compounds have since been described, however.[6] 2,4,5-Trichlorobenzenesulphonacetamide gave a small yield of the unusual compound (III).

Cyclotetrathioimine showed the sharpest difference between behaviour with " normal " sulphonyl chlorides (*e.g.*, benzenesulphonyl chloride) and with 2,4,5-trichlorobenzenesulphonyl chloride (and some related compounds). It did not react with the former in pyridine. 2,4,5-Trichlorobenzenesulphonyl chloride, however, readily gave a deep red solution from which red crystals, of composition $R_2N_2S_3$ ($R = 2,4,5\text{-}Cl_3C_6H_2$), were easily isolated. This compound is decomposed by warm dilute alkali to the diaryl disulphide, ammonia, and thiosulphate, and more slowly by sulphuric acid to the disulphide, ammonium sulphate, and sulphur dioxide. 2,5-Dichlorobenzenesulphonyl chloride gave an analogous product. These compounds are probably best represented by the group of formulæ (IV), similar to that ascribed [7] to the deep yellow compound $N_2S_3F_2$ (IV; R = F).

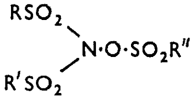
$$\text{(IV)}\quad R{-}\overset{+}{S}{=}N{-}S{-}\overset{-}{N}{-}S{-}R \qquad R{-}S{-}N{=}\overset{+}{S}{-}\overset{-}{N}{=}S{=}R \qquad R{-}S{-}\overset{-}{N}{-}\overset{+}{S}{=}N{-}S{-}R \qquad R{-}S{-}\overset{-}{N}{-}S{-}N{=}\overset{+}{S}{-}R$$

There are not many examples of the formation of disulphonimides by direct reaction of a sulphonyl chloride and ammonia. One such product [8] has properties quite different from those of other known disulphonimides, being readily cleaved by ammonia; the evidence given does not exclude its being a molecular compound of sulphonamide and sulphonyl chloride. Benzene-*o*-disulphonyl chloride gives the cyclic imide.[9] However, re-investigation of this reaction has shown that benzene-*o*-disulphonamide is formed in 10% yield. The very high melting point and low solubility of this substance led Holleman [9] to dismiss it as " mineral matter "; it has now been characterised as its water-soluble monoacetyl and diacetyl derivatives. Methylamine and benzene-*o*-disulphonyl chloride gave the methyl-imide and bismethyl-amide.

Biphenyl-2,2′-disulphonyl chloride reacts with ammonia to give the supposed 2,2′-disulphonamide.[10] This is now shown to be the ammonium salt of the heterocycle (V). The authentic disulphonamide was not isolated.



(V)



(VI)

$R{\cdot}S{\cdot}SO_3H$

(VII)

The failure of attempts to prepare compounds $(RSO_2)_3N$ directed attention to a class of substances, obtained by reaction of sulphinic acids with nitric acid, to which the formula $(RSO_2)_3NO$ has been assigned.[11] von Meyer [12] asserted that the product from toluene-*p*-sulphinic acid is tritoluene-*p*-sulphonylamine; this is certainly untrue (cf. ref. 6). It is

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[5] Piloty, *Ber.*, 1896, **29**, 1560.
[6] Steller and Hansmann, *Chem. Ber.*, 1957, **90**, 2728.
[7] Glemser and Wyszomirski, *Angew. Chem.*, 1957, **69**, 534.
[8] Hanby and Rydon, *J.*, 1946, 865.
[9] Holleman, *Rec. Trav. chim.*, 1921, **40**, 446.
[10] Limpricht, *Annalen*, 1891, **261**, 330.
[11] Beilstein, " Handbuch der organische Chemie," IV, 2; XI, 49, 108, 193.
[12] von Meyer, *J. prakt. Chem.*, 1901, **63**, 175.

likely that the compounds were trisarenesulphonyl hydroxylamines (VI), and this has been confirmed. An alternative synthesis [12] is from the bisarenesulphonhydroxamic acid and the sulphonyl chloride. A product was obtained from ditoluene-*p*-sulphonhydroxamic acid and benzenesulphonyl chloride which on reduction gave only ditoluene-*p*-sulphonimide (all reactions being practically quantitative). This shows that the benzenesulphonyl and toluene-*p*-sulphonyl groups do not occupy equivalent positions in the molecule, the structure of which is presumably (VI; $R = R' = p\text{-MeC}_6H_4$, $R'' = \text{Ph}$).

During the preparation of 2,4,5-trichlorobenzenesulphinic acid from the sulphonyl chloride and aqueous sodium sulphite, a by-product was always formed, which slowly precipitated bis-(2,4,5-trichlorophenyl) disulphide when the mixture was made alkaline. This was identified as sodium *S*-2,4,5-trichlorophenyl thiosulphate (as VII; $R = 2,4,5\text{-}Cl_3C_6H_2$) and isolated as its pyridine salt in 7% yield. It was identical with a sample made by Baumgarten's method [13] from 2,4,5-trichlorothiophenol and pyridine–sulphur trioxide. *p*-Chlorobenzenesulphonyl chloride similarly gave the thiosulphate (VII; $R = p\text{-ClC}_6H_4$) in 10% yield. With benzenesulphonyl chloride, toluene-*p*-sulphonyl chloride, and very concentrated aqueous sodium sulphite, the yields of *S*-aryl thiosulphate could be raised to approximately 50%. This synthesis of *S*-aryl thiosulphates is a valuable alternative to existing methods,[13,14] though it fails sometimes (*e.g.*, *m*-nitrobenzenesulphonyl chloride). The reaction may proceed through an intermediate, $ArSO_2{\cdot}SO_3Na$, which may decompose in two ways, (*a*) by hydrolysis to the sulphinate and sulphuric acid, or (*b*) by reduction with sulphite to give the thiosulphate (VII) and sodium sulphate. Attempts to isolate the intermediate have been unsuccessful.[15]

Reaction of benzenesulphonyl chloride with aqueous sodium thiosulphate gave benzenethiosulphonic acid ($PhSO_2{\cdot}SH$), isolated as aniline salt. This is also a new and convenient preparation.

EXPERIMENTAL

Arenesulphonyl Chlorides.—2,4,5-*Trichlorobenzenesulphonyl chloride.* 1,2,4-Trichlorobenzene (360 g.) was added during 2 hr. to chlorosulphonic acid (500 g.) stirred at 40°. After 3 hr. at 100°, the product was poured into ice-water (3 l.) and filtered. A solution of the wet solid in benzene (500 c.c.) was dried and distilled (230 g.; b. p. 138°/0·5 mm.; m. p. 66—68°). The analytical sample formed needles, m. p. 69°, from light petroleum (lit.,[1a] m. p. 31—34°) (Found: C, 25·9; H, 0·8. $C_6H_2O_2Cl_4S$ requires C, 25·7; H, 0·7%). The small non-distillable residue gave needles, m. p. 176°, of *bis*-2,4,5-*trichlorophenyl sulphone*, from acetic acid (Found: C, 34·0; H, 0·8. $C_{12}H_4O_2Cl_6S$ requires C, 33·7; H, 0·95%).

The following benzenesulphonyl chlorides were similarly prepared: 2,4,6-*trichloro*-, m. p. 49° (lit.,[1a] m. p. 35—40°) (Found: C, 26·0; H, 0·7. $C_6H_2O_2Cl_4S$ requires C, 25·7; H, 0·7%); 2,3,4-*trichloro*-, m. p. 50° (lit.,[1a] m. p. 64—65°, 65—66°) (Found: C, 26·0; H, 0·6%); 2,3,4,5-*tetrachloro*-, m. p. 76° (Found: C, 22·7; H, 0·6. $C_6HO_2Cl_5S$ requires C, 22·9; H, 0·3%); 2,3,5,6-*tetrachloro*-, m. p. 104° (Found: Cl, 56·4. $C_6HO_2Cl_5S$ requires Cl, 56·4%); and 4-*chloro*-2,5-*dimethoxy*-, m. p. 176° (from acetone) (Found: C, 35·6; H, 3·0. $C_8H_8O_4Cl_2S$ requires 35·4; H, 3·0%). The last three compounds were not distilled.

Pentachlorobenzenesulphonyl chloride. A suspension of pentachloroaniline (20 g.) in sulphuric acid (98%; 40 c.c.) was diazotised, diluted with ice, and filtered into a warm solution of sodium carbonate (90 g.) and potassium ethyl xanthate (10 g.) in water (1 l.). After 1 hr. at 100°, the yellowish solid was washed by decantation, covered with nitric acid (*d* 1·5), and warmed on the steam bath for 4 hr. After dilution and filtration (from mainly bispentachlorophenyl disulphide), the liquid was neutralised with sodium hydroxide; sodium pentachlorobenzenesulphonate formed plates (10 g. after recrystallisation from water). With phosphorus pentachloride for 2 hr. at 100° this gave the *sulphonyl chloride*, m. p. 75° (from light petroleum) (Found: C, 20·8; H, 0·0; Cl, 60·6. $C_6O_2Cl_6S$ requires C, 20·65; H, 0·0; Cl, 61·0%).

2,4,5-*Trichlorobenzylsulphonyl chloride.* 2,4,5-Trichlorobenzyl chloride (97 g.), sodium sulphite heptahydrate (106 g.), and water (300 c.c.) were refluxed 16 hr. On cooling, sodium

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[13] Baumgarten, *Ber.*, 1930, **63**, 1330.
[14] Lecher and Hardy, *J. Org. Chem.*, 1955, **20**, 475.
[15] Blomstrand, *Ber.*, 1870, **3**, 965.

trichlorobenzylsulphonate (104 g.) crystallised as needles. Reaction with phosphorus pentachloride gave the *sulphonyl chloride* as prisms, m. p. 78° (from light petroleum) (Found: C, 28·7; H, 1·3. $C_7H_4O_2Cl_4S$ requires C, 28·6; H, 1·3%).

Reaction of Sulphonyl Chlorides with Ammonia.—General method. The sulphonyl chloride, dissolved in 10 times its weight of benzene, was stirred and treated with gaseous ammonia until reaction was complete (usually about 10 hr.; sometimes it was necessary to filter off the voluminous precipitate after 2—3 hr., and to continue passage of ammonia into the filtrate). Only traces of material were left in solution. The total solid was extracted with warm acetone, which dissolved the sulphonamide. The residue was washed with water leaving the ammonium salt of the disulphonimide. The salts of these imides are generally very sparingly soluble in water, and it is difficult to obtain the free imides by acidifying these solutions. The free imides are best prepared by refluxing the ammonium salt with acetic anhydride; the salt slowly dissolves and the imide crystallises out either at the boiling point or on cooling. The imides are very stable both to acid and alkaline hydrolysis.

Arenesulphonamides.—The following benzenesulphonamides were prepared (all recrystallisations were from ethanol): 2,4,5-*trichloro*-, m. p. 195° (lit.,[1a] m. p. >200°) (Found: C, 27·6; H, 1·6%); 2,4,6-*trichloro*-, m. p. 179° [lit.,[1a] m. p. 210—212° (decomp.)] (Found: N, 5·4%); 2,3,4-*trichloro*-, m. p. 220° [lit.,[1a] m. p. 226—230° (decomp.)] (Found: N, 5·3. $C_6H_4O_2NCl_3S$ requires C, 27·6; H, 1·55; N, 5·4%); 2,3,5,6-*tetrachloro*-, m. p. 201° (Found: C, 24·9; H, 1·3%); 2,3,4,5-*tetrachloro*-, m. p. 206° (Found: C, 24·4; H, 4·9. $C_6H_3O_2NCl_4S$ requires C, 24·4; H, 1·05; N, 4·7%); *pentachloro*-, m. p. 233° (Found: C, 22·2; H, 0·8. $C_6H_2O_2NCl_5S$ requires C, 21·85; H, 0·6%); 2,4,5-*tribromo*-, m. p. 230—231° [lit., m. p. 223—224° (decomp.)] (Found: C, 18·6; H, 0·8. $C_6H_4O_2NBr_3S$ requires C, 18·3; H, 1·0%); 4-*chloro*-2,5-*dimethoxy*-, m. p. 208—210° (Found: C, 38·2; H, 3·9. $C_8H_{10}O_4NClS$ requires C, 38·2; H, 4·0%).

2,4,5-*Trichlorotoluene*-ω-*sulphonamide* had m. p. 196—197° (Found: C, 31·0; H, 2·2; N, 4·8. $C_7H_6O_2NCl_3S$ requires C, 30·6; H, 2·2; N, 5·1%).

Bis(arenesulphonyl)imides.—Figures in parentheses are approximate yields obtained for the "general method" described above. *Bis*-(3,4-*dichlorobenzenesulphon*)*imide* (5—10%), fluffy needles from benzene, had m. p. 204—206° (Found: C, 33·7; H, 1·9. $C_{12}H_7O_4NCl_4S_2$ requires C, 33·1; H, 1·6%); the 2,5-*isomer* (10%) formed prisms, m. p. 300—302° (decomp.), from acetic anhydride (Found: C, 33·7; H, 1·7%). *Bis*-(2,4,5-*trichlorobenzenesulphon*)*imide* (55%) had m. p. 286° (from benzene) (Found: C, 29·1; H, 0·9; N, 2·7, 2·9. $C_{12}H_5O_4NCl_6S_2$ requires C, 28·55; H, 1·0; N, 2·75%); the 2,4,6-*isomer* (50%) had m. p. 288—289° (Found: C, 28·9; H, 1·0%).

Bis-(2,3,5,6-*tetrachlorobenzenesulphon*)*imide* (20%) had m. p. 316—318° (Found: C, 25·4; H, 1·0. $C_{12}H_3O_4NCl_8S_2$ requires C, 25·15; H, 0·55%); the 2,3,4,5-*isomer* (25%) had m. p. 335—336° (decomp.) (Found: C, 25·5; H, 0·6%). *Bis*(*pentachlorobenzenesulphon*)*imide* (25%) had m. p. 335—340° (decomp.) (Found: C, 22·6; H, 0·3. $C_{12}HO_4NCl_{10}S_2$ requires C, 22·4; H, 0·15%). *Bis*-(2,4,5-*tribromobenzenesulphon*)*imide* (25%) had m. p. 308—309° (Found: C, 19·2; H, 0·4. $C_{12}H_5O_4NBr_6S_2$ requires C, 18·7; H, 0·65%). The last five compounds were crystallised from acetic anhydride. Analytical values for carbon were always high in this class of compound.

The following sulphonyl chlorides did not give a disulphonimide when treated with ammonia in benzene: 2,4-dichloro-, 2,3,4-trichloro-, 4-chloro-2,5-dimethoxy-benzenesulphonyl chloride; 2,4,5-trichlorotoluene-ω-sulphonyl chloride.

N-*Methyl*-2,4,5-*trichlorobenzenesulphonamide and* N-*Methylbis*-(2,4,5-*trichlorobenzenesulphon*)-*imide.*—2,4,5-Trichlorobenzenesulphonyl chloride (28 g.) was added to a stirred mixture of aqueous methylamine (27%; 6 c.c.), sodium hydroxide (4 g.), and water (100 c.c.) at 50—60°; an initial exothermic reaction soon moderated. After 2 hr. at 100°, the solution was diluted to 500 c.c., made alkaline with sodium hydroxide, and filtered hot. The insoluble nearly pure N-*methyl-imide* (8·0 g.), formed needles, m. p. 213—214°, from much ethanol (Found: C, 30·3; H, 1·3. $C_{13}H_7O_4NCl_6S_2$ requires C, 30·1; H, 1·35%). Acidification of the filtrate gave the *N-methyl-amide* (17 g.), needles, m. p. 136°, from ethanol (Found: C, 30·7; H, 2·5. $C_7H_6O_2NCl_3S$ requires C, 30·6; H, 2·2%). This compound could be obtained almost quantitatively from the sulphonyl chloride and 2 or more mols. of methylamine.

(2,4,5-*Trichlorobenzenesulphon*)*anilide and* N-*Phenylbis*-(2,4,5-*trichlorobenzenesulphon*)-*imide.*—Substitution of aniline (9·3 g.) for methylamine in the above reaction gave the alkali-insoluble N-*phenyl-imide* (2·0 g.), m. p. 238°, from much acetic acid (Found: C, 37·4; H, 1·6.

$C_{18}H_9O_4NCl_6S_2$ requires C, 37·25; H, 1·55%). Acidification of the alkaline filtrate gave the *anilide*, m. p. 159°, from ethanol (Found: C, 42·9; H, 2·3. $C_{12}H_8O_2NCl_3S$ requires C, 42·8; H, 2·4%).

N-2,4,5-*Trichlorophenylbis*-(2,4,5-*trichlorobenzenesulphon*)*imide* (I; R = X = 2,4,5-$Cl_3C_6H_2$). A solution of 2,4,5-trichlorobenzenesulphonyl chloride (7 g.) and 2,4,5-trichloroaniline (5 g.) in a mixture of benzene (100 c.c.) and pyridine (3 c.c.) was kept for 24 hr., and the product then extracted with water and with 2N-sodium hydroxide; the extract gave no precipitate on acidification. The benzene layer was evaporated and the resulting tar digested with ethanol; a solid (1·5 g.), m. p. 244° (from trichloroethylene), was obtained (Found: C, 31·7; H, 1·1; N, 2·3. $C_{18}H_6O_4NCl_9S_2$ requires C, 31·6; H, 0·9; N, 2·05%).

p-*Dimethylaminophenyl* 2,4,5-*Trichlorophenyl Sulphide*.—Dimethylaniline (25 g.) and 2,4,5-trichlorobenzenesulphonyl chloride (18 g.) were heated under reflux on the steam-bath for 1 hr. The resulting liquid was diluted with methanol (150 c.c.) and kept overnight. The colourless crystals (3—4 g.; m. p. 120—150°) were collected, digested with warm concentrated hydrochloric acid, and filtered. The insoluble material was bis-(2,4,5-trichlorophenyl) trisulphide (see below). Dilution of the filtrate precipitated the *dimethylaminophenyl trichlorophenyl sulphide* (II) (2—3 g.), glassy prisms (from light petroleum), m. p. 168—170° (Found: C, 50·6; H, 3·5; N, 4·8; S, 10·3. $C_{14}H_{12}NCl_3S$ requires C, 50·6; H, 3·6; N, 4·25; S, 9·6%).

2,4,5-*Trichlorobenzenesulphonylhydrazide*.—2,4,5-Trichlorobenzenesulphonyl chloride (14 g.), in benzene (80 c.c.), was shaken for 10 min. with 50% hydrazine hydrate (9 c.c.). The hydrazide (10·5 g.) was precipitated almost pure; it had m. p. 136° (decomp.), from benzene (Found: C, 26·3; H, 1·8; N, 10·5. $C_6H_5O_2N_2Cl_3S$ requires C, 26·15; H, 1·8; N, 10·15%). With more sulphonyl chloride this compound decomposed.

Reaction of 2,4,5-*Trichlorobenzenesulphonyl Chloride with Phenylhydrazine*.—Phenylhydrazine (17 g.) was added to the sulphonyl chloride (14 g.) in benzene (150 c.c.); a crystalline solid slowly separated with sluggish evolution of nitrogen. After 24 hr. the solid was collected, washed with benzene, and sparingly with methanol; the product (16 g.) had m. p. *ca.* 196° (decomp.). Its identity with phenylhydrazine 2,4,5-trichlorobenzenesulphinate was confirmed by direct comparison with material prepared from phenylhydrazine acetate and sodium 2,4,5-trichlorobenzenesulphinate in water.

Reaction of 2,4,5-*Trichlorobenzenesulphonyl Chloride with Hydroxylamine*.—Hydroxylamine hydrochloride (13 g.), in hot water (10 c.c.), was treated with a solution of sodium ethoxide [from sodium (4·25 g.)] in ethanol (100 c.c.). Sodium chloride was filtered off, and to the filtrate (at 0°) 2,4,5-trichlorobenzenesulphonyl chloride (16 g.) was added in portions. When the vigorous reaction was over, dilution with water gave a crystalline solid (11 g.), m. p. *ca.* 176° (decomp.). Attempts to recrystallise this resulted in decomposition, as did storage for 3 weeks. The residue consisted of 2,4,5-trichlorobenzenesulphonic acid with some bis-(2,4,5-trichlorobenzenesulphon)imide (*ca.* 2 g.). Reaction of 2,4,5-trichlorobenzenesulphinic acid with nitrous or nitric acid also failed to give the usual hydroxylamine derivatives.

Reaction of 2,4,5-*Trichlorobenzenesulphonyl Chloride with Thiourea*.—2,4,5-Trichlorobenzenesulphonyl chloride (14 g.) and thiourea (7·6 g.) in pyridine (40 c.c.) was kept overnight. Dilution with water gave *bis*-(2,4,5-*trichlorophenyl*) *trisulphide* (3 g., m. p. 150—155°) which after several recrystallisations from much acetic acid had m. p. 169° (Found: C, 31·3; H, 0·8; S, 21·1. $C_{12}H_4Cl_6S_3$ requires C, 31·3; H, 0·9; S, 21·0%).

Reaction of 2,4,5-*Trichlorobenzenesulphonyl Chloride with Dibenzimide*.—A mixture of dibenzimide (4·0 g.), 2,4,5-trichlorobenzenesulphonyl chloride (5·5 g.), and pyridine (20 c.c.) was heated at 100° for 24 hr. Dilution with water gave a brown solid which was digested with very dilute alkali; the residue was washed with methanol leaving tribenzoylamine (1 g.), m. p. 205—209°, raised to 210° by crystallisation from aqueous acetone (lit., m. p. 208°) (Found: C, 76·7; H, 4·6. Calc. for $C_{21}H_{15}O_3N$: C, 76·6; H, 4·6%).

Reaction of 2,4,5-*Trichlorobenzenesulphonyl Chloride with* 2,4,5-*Trichlorobenzenesulphonamide*.—Equimolecular quantities of these compounds, mixed in a small amount of pyridine, gave after 24 hr. an almost quantitative yield of the *pyridine salt* of the disulphonimide, as heavy prisms (from pyridine or acetic acid), m. p. 270—271° (Found: C, 35·0; H, 1·7; N, 4·5. $C_{17}H_{10}O_4N_2Cl_6S_2$ requires C, 35·0; H, 1·7; N, 4·8%).

N-*Acetyl*-N-(2,4,5-*trichlorobenzenesulphinyl*)-2,4,5-*trichlorobenzenesulphonamide* (III).—2,4,5-Trichlorobenzenesulphonamide (20 g.) was refluxed with acetic anhydride (50 c.c.) for 6 hr.

and then poured into water. The solid product formed felted needles (20·5 g.), m. p. 230—232°, from aqueous ethanol (Found: C, 31·8; H, 2·2. $C_8H_6O_3NCl_3S$ requires C, 31·75; H, 2·0%).

This N-*acetyl-sulphonamide* (20 g.), 2,4,5-trichlorobenzenesulphonyl chloride (20 g.) and pyridine (50 c.c.) were kept for 4 days, then diluted with water (300 c.c.). The residue was washed with cold acetone giving fawn-coloured microcrystals (3 g.); crystallisation from acetic acid then gave flat blades (2 g.), m. p. 227° (decomp.) (Found: C, 31·5, 31·8; H, 1·4, 1·4; N, 2·4; Cl, 40·3; S, 11·8. $C_{14}H_7O_4NCl_6S_2$ requires C, 31·7; H, 1·3; N, 2·6; Cl, 40·2; S, 12·0%). The structure was confirmed by hydrolysis with boiling dilute sodium hydroxide (2 hr.) which gave a mixture of the sodium salts of 2,4,5-trichlorobenzenesulphonamide and of 2,4,5-trichlorobenzenesulphinic acid. These were readily separated, and the amide and acid identified by mixed m. p.s.

Reaction of 2,4,5-*Trichlorobenzenesulphonyl Chloride with Cyclotetrathioimine.*—2,4,5-Trichlorobenzenesulphonyl chloride (12 g.) and cyclotetrathioimine (2 g.) were dissolved in dry pyridine (35 c.c.). After 1 hr., the solid was filtered off and washed with cold pyridine; after drying and crystallisation from trichloroethylene the *product* (IV; R = 2,4,5-$Cl_3C_6H_2$) (0·8 g.) formed orange-red needles, m. p. 209° (decomp.) (Found: C, 29·7; H, 1·0; N, 6·0; Cl, 43·6; S, 19·7. $C_{12}H_4N_2Cl_6S_3$ requires C, 29·7; H, 0·85; N, 5·8; Cl, 43·9; S, 19·8%). The pyridine filtrate contained mainly the pyridine and ammonium salts of bis-(2,4,5-trichlorobenzenesulphon)imide.

A similar experiment with 2,5-dichlorobenzenesulphonyl chloride gave the compound (IV; R = 2,5-$Cl_2C_6H_3$), m. p. 200° (decomp.), from trichloroethylene in about the same yield (Found: C, 34·8; H, 1·6; N, 7·0; Cl, 33·9; S, 22·9. $C_{12}H_6N_2Cl_4S_3$ requires C, 34·6; H, 1·5; N, 6·7; Cl, 34·1; S, 23·1%).

It is important during the working-up of these compounds to avoid the use of acetone, methanol, or ethanol; the products, of similar appearance and m. p., are then analytically different from the above, though the difference is apparently not due to solvation, since the compounds are still substantially free from oxygen.

2,4,5-Tribromobenzenesulphonyl chloride gave a sparingly soluble orange-red product, m. p. 214° (decomp.) from trichloroethylene. Analytical figures were only in approximate agreement with structure (IV), and the compound has not been more closely investigated (Found: C, 20·3; H, 0·6; N, 3·4; S, 11·6%).

Reaction of cyclotetrathioimine with 3,4-dichlorobenzenesulphonyl chloride in pyridine gave a deep red solution, but no satisfactory compound was isolated.

Benzene-o-*disulphonamide.*—Benzene-*o*-disulphonyl chloride (20 g.), in benzene (200 c.c.), was treated with a stream of ammonia gas for 1—2 hr. The solid was collected, freed from solvent, and triturated with cold water; the insoluble crude *disulphonamide* (2·6 g.) was eventually crystallised from 2-ethoxyethanol, forming heavy prisms, m. p. *ca.* 335—338° (decomp.) (Found: C, 31·0; H, 3·4; H, 11·8. $C_6H_8O_4N_2S_2$ requires C, 30·5; H, 3·4; N, 11·9%).

Acetylation. The disulphonamide (1·5 g.) when refluxed with acetic anhydride (10 c.c.) for 2 hr. gave unchanged starting material and the *monoacetyl derivative*, m. p. 230—232° (from water) (Found: C, 34·5; H, 3·7; N, 10·1. $C_8H_{10}O_5N_2S_2$ requires C, 34·5; H, 3·6; N, 10·1%). Extension of the reaction time to 16 hr. gave a tar, from which the water-soluble *diacetyl derivative* was isolated in about 70% yield; it formed prisms (from a little water) of a presumed hydrate of indefinite m. p., which became opaque on prolonged drying at 80°, and then had m. p. 193—195° (Found: C, 37·5; H, 4·1; N, 8·6. $C_{10}H_{12}O_6N_2S_2$ requires C, 37·5; H, 3·75; N, 8·75%).

Reaction of Benzene-o-*disulphonyl Chloride with Methylamine.*—Benzene-*o*-disulphonyl chloride (5 g.), in benzene (50 c.c.), was shaken for 1 hr. with excess of aqueous methylamine (30%). Benzene and methylamine were removed by steam-distillation, and the residue was made alkaline with sodium hydroxide. The insoluble *methyl-imide* (2·6 g.) formed plates, m. p. 179°, from acetic acid (Found: C, 36·3; H, 3·0. $C_7H_7O_4NS_2$ requires C, 36·05; H, 3·0%).

Acidification of the alkaline filtrate gave N-*methylbenzene*-o-*disulphonamide* (0·55 g.), as leaflets, m. p. 224°, from acetone (Found: C, 36·4; H, 4·6. $C_8H_{12}O_4N_2S_2$ requires C, 36·4; H, 4·6%).

Biphenyl-2,2′-*disulphonimide* (V).—Biphenyl-2,2′-disulphonyl chloride (8 g.) reacted slowly with aqueous-ethanolic ammonia. The resulting solution was evaporated to dryness, taken up in water, and acidified with a large excess of concentrated hydrochloric acid. The *imide* (V) crystallised from hydrochloric acid as sheaves of needles (5 g.), m. p. 250—251° (Found: C, 48·7; H, 3·2; N, 4·7. $C_{12}H_9O_4NS_2$ requires C, 48·8; H, 3·1; N, 4·75%). No disulphonamide was isolated.

O-*Benzenesulphonyl*-NN-*ditoluene*-p-*sulphonylhydroxylamine* (VI; R = R′ = MeC_6H_4, R″ = Ph).—*NN*-Ditoluene-*p*-sulphonylhydroxylamine (3·0 g.) in pyridine (10 c.c.) was treated at 0° with benzenesulphonyl chloride (2·0 g.), and the mixture kept at 0° for 40 min. Dilution with water gave the *hydroxylamine* (VI) (3·6 g.), m. p. 190—194°, raised to 198° by crystallisation from acetone (Found: N, 3·0. $C_{20}H_{19}O_7NS_3$ requires N, 2·9%).

Reduction. This compound (2·0 g.) was suspended in refluxing ethanol (70 c.c.)–acetic acid (10 c.c.); zinc dust was added until dissolution was complete. The filtered solution was concentrated to dryness, and the residue stirred with dilute hydrochloric acid, filtered, and washed, giving ditoluene-*p*-sulphonimide (1·25 g., 92%), m. p. 166—169°, not depressed bv an authentic sample.

Anilinium S-*Phenyl Thiosulphate.*—Benzenesulphonyl chloride (176·5 g.), sodium sulphite heptahydrate (650 g.), and water (600 c.c.) were heated at 100° for 5 hr. Next morning, the semi-solid mass was broken up, diluted slightly, and filtered. The filtrate was acidified and then extracted with ether; the extracts contained benzenesulphinic acid. The aqueous layer was treated with a solution of aniline (90 g.) in acetic acid; anilinium *S*-phenyl thiosulphate (VII; R = Ph) slowly crystallised (178 g.; m. p. *ca.* 160°). Recrystallisation from water gave fine hair-like needles, m. p. 182° (decomp.) (lit.,[14] gives m. p. 185°) (Found: C, 51·1; H, 4·8; N, 4·7; S, 22·9. Calc. for $C_6H_6O_3S_2,C_6H_7N$: C, 50·9; H, 4·6; N, 4·95; S, 22·6%).

The following *thiosulphates* were made similarly in the yields stated: p-*toluidinium* S-p-*tolyl* (40%), needles, m. p. 180° (decomp.), from water (Found: C, 54·2; H, 5·6. $C_7H_8O_3S_2,C_7H_9N$ requires C, 54·05; H, 5·5%); *anilinium* S-p-*chlorophenyl* (10%), prisms, m. p. 186° (decomp.), from water (Found: C, 45·4; H, 3·8; N, 4·6. $C_6H_5O_3S_2Cl,C_6H_7N$ requires C, 45·4; H, 3·8; N, 4·4%); and *pyridinium* S-2,4,5-*trichlorophenyl* (7%), plates, m. p. 192° (decomp.), from water (Found: C, 35·7; H, 2·0. $C_6H_3O_3S_2Cl_3,C_5H_5N$ requires C, 35·45; H, 2·15%). The main product in the last reaction was 2,4,5-*trichlorobenzenesulphinic acid*, isolated as its sparingly soluble sodium salt. The free sulphinic acid is best prepared from this by repeated crystallisation from dilute hydrochloric acid; it forms needles, m. p. 127° (Found: C, 29·5; H, 1·3; S, 13·6. $C_6H_3O_2Cl_3S$ requires C, 29·3; H, 1·2; S, 13·05%). This re-solidifies after melting, giving mainly *bis*-(2,4,5-*trichlorophenyl*) *disulphide*, flat needles, m. p. 147°, from acetone (Found: C, 34·0; H, 0·9; S, 15·2. $C_{12}H_4Cl_6S_2$ requires C, 34·3; H, 1·0; S, 15·05%).

Anilinium Benzenethiosulphonate.—A mixture of sodium thiosulphate (110 g.), water (50 c.c.), and benzenesulphonyl chloride (27 g.) was heated at 100° under reflux for 4 hr. Dilution left a pasty solid (5 g.), mainly diphenyl disulphide and sulphur. The aqueous portion was acidified, and treated with aniline (10 g.) in acetic acid, giving crystalline *anilinium benzenethiosulphonate* (20 g.); recrystallisation from water gave hair-like needles, m. p. 152° (decomp.) (Found: C, 53·8; N, 4·8; S, 24·3. $C_6H_6O_2S_2,C_6H_7N$ requires C, 53·9; H, 5·0; N, 5·2; S, 24·0%).

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