

103. *Trichloromethyl Sulphones and Related Compounds.**

By W. V. FARRAR.

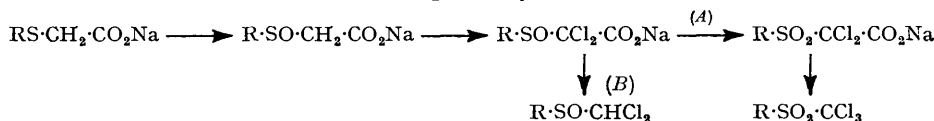
Sulphones, $R \cdot SO_2 \cdot CCl_3$, are readily formed by reaction of excess of aqueous sodium hypochlorite with salts of aryl- and arylalkyl-thioacetic acids $R \cdot S \cdot CH_2 \cdot CO_2H$. Hypobromite (but not hypoiodite) causes a similar reaction. Smaller amounts of hypochlorite gave dichloromethyl sulphoxides, $R \cdot SO \cdot CHCl_2$. Some related compounds and reactions are described.

ADDITION of sodium hypochlorite solution to an alkaline solution of a *S*-substituted mercaptoacetic acid, $R \cdot S \cdot CH_2 \cdot CO_2H$, causes precipitation of the corresponding trichloromethyl sulphone, $R \cdot SO_2 \cdot CCl_3$, usually crystalline, according to the reaction: $R \cdot S \cdot CH_2 \cdot CO_2Na + 5NaOCl \rightarrow R \cdot SO_2 \cdot CCl_3 + 2NaCl + 2NaOH + Na_2CO_3$. These sulphones, of which few have hitherto been described, thus become readily accessible. Hypobromites cause a similar reaction, giving tribromomethyl sulphones, but hypoiodites do not.

The products from a number of substituted mercaptoacetic acids are listed in Table 1. The sodium salts of the corresponding sulphonic acid are probably always formed as by-products, by direct oxidation ($R \cdot S \cdot CH_2 \cdot CO_2Na + 6NaOCl \rightarrow R \cdot SO_3Na + 2CO_2 + 6NaCl$) rather than by hydrolysis of the trichloromethyl sulphone, since the sulphones are rather stable to alkali. Two such acids were isolated and identified.

To obtain the maximum yield of sulphone, about 7 mols. of hypochlorite instead of the theoretical 5 mols. have to be used. The effect of smaller amounts of hypochlorite was studied systematically with *p*-chlorophenylthioacetic acid (Table 2). The first product isolated (when 2 mols. were used) was the sulphanylacetic acid *p*- $C_6H_4Cl \cdot SO \cdot CH_2 \cdot CO_2H$; as the amount of hypochlorite was increased, this acid was gradually replaced by the dichloromethyl sulphoxide *p*- $C_6H_4Cl \cdot SO \cdot CHCl_2$ (4—5 mols.), then by the trichloromethyl sulphone (6—7 mols.). Two other dichloromethyl sulphoxides were also prepared by this reaction in moderate yield. A similar reaction with smaller amounts of hypobromite could not be demonstrated in the one case tried; however, Claasz¹ recorded dibromomethyl *o*-nitrophenyl sulphoxide as formed on bromination of *o*-nitrophenylthioacetic acid in acetic acid.

The dichloromethyl sulphoxide is not, however, a genuine intermediate since it is unaffected by hypochlorite, even at 60°, and in solutions buffered with sodium hydrogen carbonate.² The course of the reaction is probably :



Generally, when hypochlorite is present in excess, reaction (A) is much faster than (B). One case was encountered, however (note 4 to Table 1), where even in presence of excess of hypochlorite the product was a mixture of sulphoxide and sulphone; here reactions (A) and (B) must have comparable velocities.

Dimorphism seems to be common among these sulphones and sulphoxides; several cases are noted in the Experimental section, in which the first and later preparations gave substances of different m. p.s. In each case a mixture of the two materials had the m. p. of the later ones.

As a special case of the reaction, thiobisacetic acid gives di(trichloromethyl) sulphone; rigorous control of pH is necessary to obtain a good yield (this case was independently discovered elsewhere³ during the course of the present work). The corresponding reaction with hypobromite gave, under neutral conditions, the expected hexabromo-sulphone, but

* Partly covered by B.P. 728,969.

¹ Claasz, *Ber.*, 1912, **45**, 1023.² Cf. Wood and Travis, *J. Amer. Chem. Soc.*, 1928, **50**, 1226.³ James, U.S.P. 2,628,982.

in alkali di(tribromomethyl) sulphoxide was obtained almost quantitatively. When the hypobromite contained free bromine, di(dibromomethyl) sulphone was formed; similarly, the reaction of thiobisacetic acid with chlorine gave di(dichloromethyl) sulphone.

By the action of hypobromite on proteins, Goldschmidt *et al.*⁴ isolated an unidentified substance, $C_2O_2Br_6S$, m. p. 134° , which is clearly di(tribromomethyl) sulphone. It may be formed, *via* thiobisacetic acid, by the oxidation of lanthionine $S[CH_2\cdot CH(NH_2)\cdot CO_2H]_2$, itself formed from cystine by the action of alkali.⁵ Goldschmidt *et al.* noted that their substance liberated iodine from sodium iodide in acetone, giving a compound, m. p. 164° , for which they gave no analyses; this has now been shown to be di(dibromomethyl) sulphone. It is a general reaction of highly chlorinated and brominated dimethyl sulphones that they are reduced by sodium iodide, one or more of their halogen atoms being replaced by hydrogen. Di(dibromomethyl) sulphone itself is further slowly reduced, giving bromomethyl dibromomethyl sulphone. Di(trichloromethyl) sulphone is reduced only to the pentachloro-compound. Di(tribromomethyl) sulphoxide is also reduced to the pentabromo-sulphoxide. The aryl trichloromethyl sulphones (and dichloromethyl sulphoxides) give only a slight colour of iodine after 1 hour's refluxing with sodium iodide in acetone.

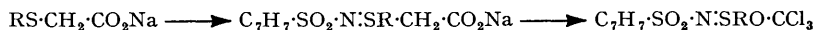
p-Chlorophenyl trichloromethyl sulphone is slowly hydrolysed by boiling dilute aqueous sodium hydroxide, giving sodium *p*-chlorobenzenesulphonate and chloride ions. Chloroform was not detected.

Aryl dichloromethyl sulphoxides react unexpectedly with cold concentrated sulphuric acid, after a short induction period, yielding hydrogen chloride and the diaryl disulphide in moderate yield.

Related Reactions.—The reaction of hypochlorite with sodium *p*-chlorophenylthio-methanesulphonate⁶ gave the salt (I). Evidently desulphonation, unlike decarboxylation, does not occur under these conditions.



An attempt was made to modify the synthesis of trichloromethyl sulphones so as to give a trichloromethyl sulphoximide, by the reaction, first of chloramine-T, then of hypochlorite, on an arylthioacetic acid:



When R was 2 : 4-dichlorophenyl, the only nitrogenous product isolated was the sulphimide (II), the final oxidation to sulphoximide not having occurred.

A compound of type (II) has probably been encountered previously, but not recognised. Clarke, Kenyon, and Phillips,⁷ by reaction between ethylthioacetic acid and chloramine-T, obtained a small yield of a substance whose formula appeared to be $C_{10}H_{12}O_4NCl_2S_2$, but did not propose a structure to fit this. If their chlorine analysis is wrong, however, the remaining figures agree well with those for the sulphimide (II; R = Et) (Found: C, 34.4; H, 3.7; N, 4.1; S, 18.2; Cl, 20.9. $C_{10}H_{12}O_2NCl_3S_2$ requires C, 34.45; H, 3.45; N, 3.95; S, 18.35; Cl, 30.6%).

Hypochlorite did not react with 1 : 3 : 5-trithian in alkali, but buffering with sodium hydrogen carbonate initiated an exothermic reaction, giving a substance $C_3O_4Cl_6S_3$, whose



infrared spectrum shows the presence of sulphone and the absence of sulphoxide groups, indicating that the formula is (IV) and not (III). Similar treatment of trithian trisulphoxide gave the known hexachloro-trisulphone.⁸

Related Compounds.—For comparison with trichloromethyl sulphones, two aryl

⁴ Goldschmidt, Wiberg, Nagel, and Martin, *Annalen*, 1927, **456**, 33.

⁵ Horn, Jones, Breese, and Ringel, *J. Biol. Chem.*, 1941, **138**, 141.

⁶ Barber, Cottrell, Fuller, and Green, *J. Appl. Chem.*, 1953, **3**, 253.

⁷ Clarke, Kenyon, and Phillips, *J.*, 1930, 1225.

⁸ Camps, *Ber.*, 1892, **25**, 247.

dichloromethyl sulphones were prepared by reaction of the corresponding sodium arene-sulphinates with chloroform. This reaction presented no difficulty, in spite of Otto and Otto's statement⁹ that sodium benzenesulphinate did not react with chloroform even at 160°. No trichloromethyl sulphone could be obtained, however, in the corresponding reaction with carbon tetrachloride.

Some attempts were also made to make α -disulphones $R \cdot SO_2 \cdot SO_2 \cdot CCl_3$. Di(trichloromethyl) disulphone was not produced by the permanganate oxidation of sodium trichloromethanesulphinate; instead, the product was hexachloroethane. Battagay and Kern¹⁰ who studied the action of metals on trichloromethanesulphonyl chloride (a reaction which would also be expected to give the above disulphone) obtained a volatile substance of m. p. ca. 180°; repetition of their work has shown this also to be impure hexachloroethane. A new carbon-carbon bond must therefore be formed, with loss of sulphur dioxide. The compound $p\text{-C}_6\text{H}_4\text{Cl} \cdot \text{SO}_2 \cdot \text{S} \cdot \text{CCl}_3$ (described¹¹ since the completion of this work) was recovered unchanged in attempts at its oxidation to the disulphone.

EXPERIMENTAL

Preparation of Trichloromethyl Sulphones.—General method. A solution (neutral or alkaline) of the substituted sodium mercaptoacetate was added rapidly to a stirred solution (8 equivs.)

TABLE 1. Sulphones, $R \cdot SO_2 \cdot CX_3$.

R	Yield (%)	M. p.	Description	Formula	Found (%)			Calculated (%)			Note
					C	H	Cl	C	H	Cl	
<i>Chlorides (X = Cl).</i>											
Ph	87	88°	Needles	$C_7H_5O_2Cl_3S$	32.7	2.1	—	32.4	1.95	—	1
$p\text{-C}_6\text{H}_4\text{Cl}$	82	146	Prisms	$C_7H_4O_2Cl_4S$	28.65	1.4	48.3	29.1	1.7	47.9	
2 : 4- $C_6H_3Cl_2$	68	98	"	$C_7H_3O_2Cl_5S$	25.8	1.0	—	25.6	0.95	—	2
2 : 5- $C_6H_3Cl_2$	65	111	"	"	—	—	54.7	—	—	54.05	3
2 : 4- $NO_2 \cdot C_6H_3Cl$	5	163	"	$C_7H_3O_2NCl_4S$	24.8	1.1	—	24.7	0.9	—	
$o\text{-C}_6H_4\text{Me}$	50	50	"	$C_8H_7O_2Cl_3S$	35.4	2.8	—	35.1	2.55	—	—
2 : 4- $C_6H_3\text{MeCl}$	55	100	"	$C_8H_6O_2Cl_3S$	31.5	1.9	—	31.2	2.0	—	
2 : 5 : 4- $C_{10}H_7\text{Me}_2\text{Cl}$	ca. 20	150—	Hexagonal tablets	$C_9H_8O_2Cl_4S$	33.7	2.5	—	33.55	2.5	—	4
$o\text{-NO}_2 \cdot C_6H_4$	83	112—	Pale yellow needles	$C_7H_4O_4NCl_3S$	28.0	1.1	34.7	27.6	1.3	34.95	5
$p\text{-NO}_2 \cdot C_6H_4$	75	174—	Pale yellow small needles	"	—	—	34.9	—	—	34.95	
2- $C_{10}H_7$	90	158—	Needles	$C_{11}H_7O_2Cl_3S$	—	—	34.1	—	—	34.4	
Ph $[\text{CH}_2]_2$	50	65	"	$C_9H_9O_2Cl_3S$	37.8	3.6	—	37.6	3.2	—	6
2-Benzothiazolyl	24	142—	Platelets	$C_8H_4O_2NCl_3S_2$	31.0	1.3	33.2	30.35	1.2	33.6	7
<i>Bromides (X = Br).</i>											
Ph	81	147	Needles	$C_7H_5O_2Br_3S$	21.6	1.5	—	21.4	1.3	—	8
2 : 4- $C_6H_3Cl_2$	90	132—	Heavy prisms	$C_7H_3O_2Cl_2Br_3S$	18.6	0.8	—	18.2	0.65	—	

Notes to Table 1. (1) Troeger and Muller¹² report m. p. 121.5° for an unidentified compound $C_7H_5O_2Cl_3S$, which from its method of preparation is certainly this sulphone. Sanna¹³ gives m. p. 121°; Böhme and Gran¹⁰ give m. p. 87°. (2) First obtained as needles, m. p. 88.5°. (3) Addition of sodium chloride to the filtrate from the sulphone gave sodium 2 : 5-dichlorobenzenesulphonate, platelets from ethanol (Found : Na, 9.1. Calc. for $C_6H_3O_2Cl_2SNa$: Na, 9.2%). (4) Accompanied by an approximately equal amount of the corresponding *dichloromethyl sulphoxide*, needles, m. p. 103—104° (Found : C, 39.5; H, 3.2. $C_6H_3OCl_2S$ requires C, 39.8; H, 3.3%), separated by fractional crystallisation from light petroleum, in which the sulphoxide is more soluble. (5) Indications of an unstable form, m. p. ca. 96°. The stable form (Found : N, 4.4; S, 10.8. $C_7H_4O_4NCl_3S$ requires N, 4.6; S, 10.5%) crystallised from benzene-light petroleum. (6) The starting material, phenethylthioacetic acid, was made according to Holmberg.¹⁵ The sulphone crystallised only on storage for about a week; recrystallisation was from light petroleum (b. p. 60—80°). (7) Addition of sodium chloride to the filtrate from sulphone gave sodium benzothiazole-2-sulphonate, platelets from ethanol. (8) Lit.,¹⁶ m. p. 145°.

⁹ Otto and Otto, *Ber.*, 1888, **21**, 1691.

¹⁰ Battagay and Kern, *Bull. Soc. chim. France*, 1927, **41**, 46.

¹¹ Lo, Wilson, and Croxall, *J. Amer. Chem. Soc.*, 1954, **76**, 1704.

¹² Troeger and Müller, *Arch. Pharm.*, 1914, **252**, 51.

¹³ Sanna, *Gazzetta*, 1942, **72**, 305.

¹⁴ Böhme and Gran, *Annalen*, 1953, **381**, 133.

¹⁵ Holmberg, *J. prakt. Chem.*, 1934, **141**, 93.

¹⁶ Troeger and Hille, *ibid.*, 1905, **71**, 128.

of sodium hypochlorite ("bleach liquor"; approx. 30% w/v of NaOCl, 12—13% "active chlorine"). External cooling was used if necessary to keep the temperature below about 45°. Precipitation of the sulphone usually began within a few minutes and was complete in 2—5 hr. *Compounds* made by this method are listed in Table 1; only one sulphone was grossly impure when precipitated (see note 4). Crystallisations, unless otherwise stated, were from ethanol or aqueous ethanol.

The bromine compounds were made by a similar method, by using an approx. 10% sodium hypobromite solution.

The following acids were vigorously oxidised by hypochlorite, but no neutral products could be isolated: mercaptoacetic acid, dithiobisacetic acid, phenylmethanebis(mercaptoacetic acid) (benzoic acid formed), methanetriss(mercaptoacetic acid), tri(carboxymethyl)amine, and di(carboxymethyl)thetin. *p*-Chlorophenylselenoacetic acid¹⁷ was oxidised by excess of hypochlorite to water-soluble substances; smaller amounts of hypochlorite gave di-*p*-chlorophenyl diselenide as the only neutral product. 2:4-Dichlorophenoxyacetic acid did not react with hypochlorite.

Reaction of p-Chlorophenylthioacetic Acid with Various Amounts of Hypochlorite.—To six solutions of *p*-chlorophenylthioacetic acid (10 g.) in 0.4*N*-sodium hydroxide (200 c.c.) were added, severally, 2, 3, 4, 5, 6, and 7 equivs. of sodium hypochlorite; the mixtures were then kept for 3 days at 20—25°. The solids which separated were filtered off; the filtrates were acidified, and the precipitated acid (if any) also examined. Results are summarised in Table 2. Of the

TABLE 2.

NaOCl (equivs.)	Neutral product	Acid product
2	0.5 g.; m. p. 65° (<i>A</i>)	7.0 g.; m. p. 125° (<i>B</i>)
3	3.4 g.; m. p. 65° (<i>A</i>)	3.0 g.; m. p. 125° (<i>B</i>)
4	3.9 g.; m. p. 65° (<i>A</i>)	2.0 g.; m. p. 120° * (<i>C</i>)
5	10.0 g.; m. p. 65° (<i>A</i>)	1.0 g.; m. p. 110—120° * (<i>C</i>)
6	7.0 g.; m. p. 130—140° (<i>D</i>)	2.0 g.; m. p. 60—110° * (<i>C</i>)
7	12.5 g.; m. p. 140° (<i>D</i>)	Nil

* With effervescence.

products, *A* is *p*-chlorophenyl dichloromethyl sulphoxide; *D* is the trichloromethyl sulphone (m. p. 146°); *B*, needles (from aqueous ethanol), m. p. 126—127°, is *p*-chlorophenylsulphinyl-acetic acid (Found: C, 43.5; H, 3.7. C₈H₇O₃ClS requires C, 43.9; H, 3.25). The acid (or mixture of acids) *C* was not identified; it decomposed on attempted recrystallisation.

Preparation of Dichloromethyl Sulphoxides.—A solution (neutral or alkaline) of the sodium salt of the substituted mercaptoacetic acid was mixed with sodium hypochlorite solution (approximately 5 equivs.) and set aside for 24 hr. The *dichloromethyl sulphoxide* was precipitated as an oil which crystallised on seeding or scratching. The products were the *phenyl*, hexagonal tablets (from benzene-light petroleum), m. p. 32—34° (30% yield) (Found: Cl, 34.5. C₇H₅OCl₂S requires Cl, 34.0%), *p*-chlorophenyl, m. p. 66° (from light petroleum) (80% yield) (Found: C, 34.6; H, 2.1; Cl, 43.2. C₇H₅OCl₃S requires C, 34.5; H, 2.1; Cl, 43.7%), and 2-naphthyl derivatives, needles (from aqueous ethanol), m. p. 89° (54% yield) (Found: Cl, 27.4. C₁₁H₈OCl₂S requires Cl, 27.4%). The second product was first obtained as needles, m. p. 59—60°, from aqueous ethanol.

Di(trichloromethyl) Sulphone.—A mixture of sodium sulphide nonahydrate (96 g.) and sodium chloroacetate (from 76 g. of chloroacetic acid) in water (500 c.c.) was refluxed for 1 hr., then made acid with hydrochloric acid to Congo-red and added dropwise to "bleach liquor" (1500 c.c.) with stirring. The temperature was not allowed to exceed 45°. The sulphone was precipitated as a lachrymatory oil, which crystallised (68.5 g.); it recrystallised from a small amount of light petroleum as prisms m. p. 37—38° (lit.¹⁸ m. p. 35.7—36.0°), but is otherwise very soluble in organic solvents. It is volatile in steam without much decomposition, but is rapidly hydrolysed by refluxing 2*N*-sodium hydroxide (Found: Cl, 70.8; S, 10.6. Calc. for C₂O₂Cl₆S: Cl, 70.75; S, 10.6%).

Di(dichloromethyl) Sulphone.—A solution of thiobisacetic acid, made as above, was stirred at 80° and treated with chlorine for 6 hr. The almost pure sulphone crystallised as needles, m. p. 104° (40 g.) (Found: C, 10.4; H, 0.9. Calc. for C₂H₂O₂Cl₄S: C, 10.35; H, 0.9%). Truce *et al.*¹⁸ report m. p. 103.8—104.5°.

¹⁷ Béhagel and Rollmann, *J. prakt. Chem.*, 1929, **123**, 329.

¹⁸ Truce, Birum, and McBee, *J. Amer. Chem. Soc.*, 1952, **74**, 3594.

Di(tribromomethyl) Sulphoxide and Sulphone.—(i) To a stirred solution of sodium hydroxide (64 g.) in water (1 l.), bromine (128 g.) was added dropwise at 10–25°. When reaction was complete, sodium hydrogen carbonate (20 g.) was added, followed gradually by thiobisacetic acid (15 g.) in water (150 c.c.). After 1 hr., the solid was collected, dried, and recrystallised from light petroleum, forming prisms, m. p. 134° (11 g.) (Found : Br, 84.1. Calc. for $C_2O_2Br_6S$: Br, 84.5%). Reported¹⁹ m. p.s are 132.5° and 134°. This substance has a characteristic “hypobromite” smell.

Addition of dilute sulphuric acid to the filtrate from the above sulphone gradually precipitated di(dibromomethyl) sulphone (20 g.), m. p. 160–162° (lit.,²⁰ m. p. 161°) forming prisms from chloroform (Found : Br, 77.4. Calc. for $C_2H_2O_2Br_4S$: Br, 78.0%). This sulphone is also formed when thiobisacetic acid reacts with hypobromite which contains excess of bromine.

(ii) When the reaction as described under (i) is carried out without addition of sodium hydrogen carbonate, the product (31 g.) is *di(tribromomethyl) sulphoxide*, plates (from ethanol), having a very characteristic smell, m. p. ca. 95–98° (decomp.) (Found : C, 4.1; H, 0.0; Br, 87.0, 86.7. C_2OBr_6S requires C, 4.35; H, 0.0; Br, 86.95%). When quantities of ca. 1 g. are heated alone above the m. p. they decompose with some violence, evolving vapours smelling of carbonyl chloride and leaving a residue of the sulphone.

Sodium Iodide Reactions.—*General method.* The substance, dissolved in acetone, was mixed with acetone containing an excess of sodium iodide. Iodine was liberated immediately, and the mixture was kept at room temperature until reaction appeared to be complete (2–24 hr.). Excess of aqueous sodium hydrogen sulphite was then added, and the resulting precipitate recrystallised. In this way, di(trichloromethyl) sulphone gave dichloromethyl trichloromethyl sulphone, m. p. 35° (lachrymatory) (Found : C, 9.2; H, 0.5; S, 12.3. Calc. for $C_2HO_2Cl_3S$: C, 9.05; H, 0.4; S, 12.0%). Truce *et al.*¹⁸ record m. p. 36.2–36.4°. Further reaction was very slow.

Di(tribromomethyl) sulphone gave di(dibromomethyl) sulphone, m. p. 160–162°. A further slow reaction occurred, giving *bromomethyl dibromomethyl sulphone*, m. p. 67° (needles from light petroleum) (Found : C, 7.6; H, 1.0; S, 9.7. $C_2H_2O_2Br_3S$ requires C, 7.25; H, 0.9; S, 9.65%). The hexabromo-sulphoxide gave *dibromomethyl tribromomethyl sulphoxide*, odourless prisms (from ethanol), m. p. 117° (Found : S, 7.0; Br, 83.9, 84.7. C_2HOBr_5S requires S, 6.8; Br, 84.55%).

Sodium Dichloro-p-chlorobenzenesulphonylmethanesulphonate (I).—Sodium *p*-chlorophenylthiomethanesulphonate⁶ (7 g.), in warm water (50 c.c.), was treated with “bleach liquor” (50 c.c.). The starting material was immediately salted out, then the temperature rose, with replacement of the original leaflets by needles (5.25 g.). The product recrystallised from a little hot water as prisms of *dihydrate* (Found : C, 21.6; H, 2.2; Cl, 26.6. $C_7H_4O_5Cl_3S_2Na, 2H_2O$ requires C, 21.15; H, 2.05; Cl, 26.8%).

S-2 : 4-Dichlorophenyl-S-trichloromethyl-N-toluene-p-sulphonylsulphimide (II; R = 2 : 4- $Cl_2C_6H_3$).—2 : 4-Dichlorophenylthioacetic acid (5 g.), in 2N-sodium hydroxide (100 c.c.), was treated with chloramine-T (tri-hydrate; 12 g.) in water (100 c.c.) and kept for 3 days : there was no visible change. Excess of “bleach liquor” (50 c.c.) was then added, and the resultant solid (8 g.) collected after 2 hr. This material seemed to consist of about equal amounts of the sulphimide and 2 : 4-dichlorophenyl trichloromethyl sulphone. Repeated crystallisation from benzene, in which the former compound is less soluble, gave the *sulphimide* (1.8 g.) as needles, m. p. 124° (decomp., after darkening above 120°) (Found : C, 36.0; H, 1.9; N, 3.1; Cl, 38.4. $C_{14}H_{10}O_2NCl_5S_2$ requires C, 36.05; H, 2.15; N, 3.0; Cl, 38.1%).

Hexachloro-1 : 3 : 5-trithian 1 : 1 : 3 : 3-Tetraoxide (IV).—Powdered trithian (20 g.) was added during 30 min. to a cooled, stirred mixture of “bleach liquor” (400 c.c.), water (400 c.c.), and sodium hydrogen carbonate (20 g.). After overnight stirring, the solid (38 g.) was collected, dried, and recrystallised twice from acetone, giving prisms (22 g.), m. p. 203–204° (decomp.) (Found : C, 8.7, 9.1; H, 0.2, 0.0; Cl, 52.4. $C_3O_4Cl_6S_3$ requires C, 8.8; H, 0.0; Cl, 52.1%). The mother-liquors probably contained di(trichloromethyl) sulphone. Decomposition of the tetraoxide at its m. p. caused the evolution of thiocarbonyl chloride (identified by its reaction with aniline to give diphenylthiourea). The tetraoxide liberates iodine from sodium iodide in acetone, but the product was not investigated.

Mr. M. St. C. Flett, who measured the infrared spectrum, reported : “A 5% solution in carbon tetrachloride showed bands at 1370–1410 and 1170–1190 cm^{-1} , fairly close to the

¹⁹ Reuterskiöld, *J. prakt. Chem.*, 1931, **129**, 121; ref. 4.

²⁰ Jönsson, *Svensk kem. Tidskr.*, 1922, **34**, 194.

positions characteristic of a sulphone group. There was no band near 1050 cm.^{-1} in the position characteristic of a sulphoxide group."

p-Chlorophenyl Dichloromethyl Sulphone.—A mixture of chlorobenzene-*p*-sulphinic acid (50 g.), chloroform (60 c.c.), and sodium hydroxide (30 g.) in water (450 c.c.) was refluxed for 10 hr. The product was extracted with chloroform : evaporation of the extracts gave 42 g. (57%) of crude sulphone. Acidification of the aqueous layer gave a 20% recovery of sulphinic acid. The sulphone formed prisms (from ethanol), m. p. 122° (Found : Cl, 40.7. $\text{C}_7\text{H}_5\text{O}_2\text{Cl}_2\text{S}$ requires Cl, 41.0%). Dichloromethyl *p*-tolyl sulphone, made in the same way, had m. p. 118° (lit., m. p. 114°).

IMPERIAL CHEMICAL INDUSTRIES LIMITED, DYESTUFFS DIVISION,
HEXAGON HOUSE, BLACKLEY, MANCHESTER 9.

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