XIII.—*Stereoisomerism of Disulphoxides and Related Substances. Part II. Derivatives of* 1 : 4-*Dithian.*

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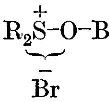
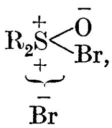
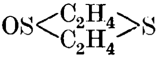
A detailed study of the reactions of the two dithian dioxides recently described (J., 1927, 1798) has provided further evidence that they are stereoisomeric. The two substances behave in an almost identical manner with a series of reagents. Each yields a *hydrochloride* (compare Fromm, *Annalen*, 1913, **396**, 75) and an unstable *hydrobromide*. Each is at once reduced by hydriodic acid and by phosphorus pentachloride, the latter reaction being highly exothermic. They yield crystalline *mercurichlorides* (compare the mercurichloride of a sulphoxide described by Zincke and Frohneberg, *Ber.*, 1909, **42**, 2729) and *bromides* sparingly soluble in water.

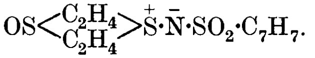
No compound of a sulphoxide with bromine has been described hitherto, yet there is no difficulty in formulating such a substance. The dibromide of a monosulphoxide might have either of the structures  $\underbrace{R_2\overset{+}{S}-O}_{\overset{-}{Br}}-Br$ and  $\underbrace{R_2\overset{+}{S}\,_{+}}_{\overset{-}{Br}}<^{\overset{-}{O}}_{Br}$, of which the former is perhaps the more probable (compare the case of dimethiodide formation, Bennett and Hock, J., 1927, 2496). With either structure, the conversion of the $\overset{-}{Br}$ ion into the $\overset{-}{Br_3}$ ion is to be expected in the presence of a large excess of bromine. A partial study of the system water–α-dithian dioxide–bromine shows the existence of a *tetrabromide* and a *hexabromide.* This is in agreement with the considerations advanced above.

The structure of a monosulphone of dithian (isomeric with the two dioxides) has been attributed in recent years to two distinct substances: by Helfrich and Reid (*J. Amer. Chem. Soc.*, 1920, **42**, 1215) to an amorphous product of the interaction of alkali sulphide and ββ′-dichlorodiethylsulphone, and by Fromm and Ungar (*Ber.*, 1923, **56**, 2286) to a substance of m. p. 200° obtained by reducing dithian trioxide (a sulphoxide sulphone). It seemed probable that the amorphous substance referred to was of high molecular weight and was related to dithian monosulphone in the same way as the "polymeric" ethylene sulphides are related to dithian (J., 1927, 1803). Confirmation of this view and of the structure of the true dithian sulphone has been obtained by repeating the experiment of Helfrich and Reid under conditions more favourable to ring closure. In this way, we obtained a crystalline monosulphone, m. p. 203°, identical with that of Fromm and Ungar. The amorphous substance of Helfrich and Reid is presumably a polyethylene polysulphide–sulphone of long open-chain structure.

The similar reaction between potassium sulphide and ββ′-dichlorodiethyl sulphoxide yielded *dithian monoxide*, ring closure taking place to the extent of 14·3% (as compared with 9·3% in the case of the sulphone; compare Cashmore and McCombie, J., 1923, **123**, 2884). The isolation of this monoxide, which we have also prepared in quantity by cautious oxidation of dithian, completes the list of possible oxidation products of dithian, namely, a monosulphoxide, a monosulphone, two stereoisomeric disulphoxides, a sulphoxide–sulphone and the disulphone.

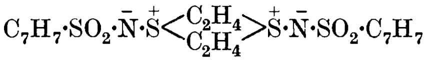
The groups $>\overset{+}{S}-\overset{-}{O}$, $>\overset{+}{S}-R\}\overset{-}{X}$ and $>\overset{+}{S}-\overset{-}{N}\cdot SO_2\cdot C_7H_7$, characteristic of sulphoxides, sulphonium salts and sulphilimines, respectively, are stereochemically analogous (Clarke, Kenyon, and

Phillips, J., 1927, 188). *cis-trans*-Isomerism is therefore to be expected in any compound in the molecule of which there are two of these groups, alike or different. In accordance with this view, we have now isolated pairs of isomeric *dithian monoxide methylsulphonium picrates* and *chloroplatinates*,  $OS<\substack{C_2H_4\\C_2H_4}>SMe\}X$, and two isomeric *dithian monoxide sulphilimines*,



$$OS<\substack{C_2H_4\\C_2H_4}>\overset{+}{S}\cdot\overset{-}{N}\cdot SO_2\cdot C_7H_7.$$

A re-examination of the bis-sulphilimine of dithian,



$$C_7H_7\cdot SO_2\cdot\overset{-}{N}\cdot\overset{+}{S}<\substack{C_2H_4\\C_2H_4}>\overset{+}{S}\cdot\overset{-}{N}\cdot SO_2\cdot C_7H_7$$

(Mann and Pope, J., 1922, **121**, 1052), has, moreover, shown that the substance described is a mixture, which we have separated into two crystalline isomerides.

EXPERIMENTAL.

Derivatives of α- *and* β-*Dithian Dioxides*.—Hydrogen chloride, passed into a solution of α-dithian dioxide in glacial acetic acid, throws down a sparingly soluble, white *monohydrochloride*, which loses hydrogen chloride on keeping (Found : Cl, 18·2. $C_4H_9O_2ClS_2$ requires Cl, 18·8%). A dihydrochloride was not detected when hydrogen chloride gas had been passed through the mixture for a further hour. β-Dithian dioxide reacts in the same way to yield a sparingly soluble *hydrochloride*.

With a solution of hydrogen bromide in glacial acetic acid, each of the dioxides yields an immediate white precipitate of a *hydrobromide*, which, however, becomes discoloured in a few minutes owing to reduction of the sulphoxide with liberation of bromine.

Addition of mercuric chloride to aqueous solutions of the α- and β-dioxides gives in each case a white, crystalline precipitate : α-*Dithian dioxide mercurichloride*, silvery plates from warm water (Found : Hg, 56·8, 57·4, 56·8. $C_4H_8O_2Cl_4S_2Hg_2$ requires Hg, 57·6%) ; β-*dithian dioxide mercurichloride*, which is more soluble than the preceding (Found : Hg, 56·7%).

Action of Bromine on the Dithian Dioxides.—Addition of bromine to the aqueous solutions of the α- and β-dithian dioxides yields in each case a crystalline *bromide* in orange or bright red crystals. These substances are very unstable in the air, the whole of the bromine being lost in a few minutes, the dioxide remaining behind. Determinations of the bromine content of specimens kept in an atmosphere saturated with bromine at laboratory temperature showed that even under these conditions the bromides are unstable. Parallel analyses were therefore made of the moist solid phase and of the mother-liquor, the composition of the solid being obtained by extrapolation in the usual manner. After a number of trials, the following method of analysis was adopted : to the specimen was added an excess of ammonia, and the solution allowed to evaporate to a constant weight at laboratory temperature in a vacuum over sulphuric acid. The bromine was determined in this mixture by Volhard's method. Subtraction of the corresponding weight of ammonium bromide from the total weight of residue gave the weight of dithian dioxide present.

The possibility that the solid might contain bromine in the form of hydrogen bromide (leaving free hypobromous acid in the mother-liquor) was disproved by comparative determinations of the combined bromine in the liquid by Volhard's method and of the volume of nitrogen evolved in a nitrometer on addition of ammonia.

The analyses of five pairs of samples are shown below :

	Moist solid.	Solution.	Dry solid (extrapolated).
(1)	Br, 25·1 ; X, 15·5	Br, 3·8 ; X, 7·8	Br, 68·6%
(2)	Br, 25·1 ; X, 10·8	Br, 6·0 ; X, 1·6	Br, 68·4%
(3)	Br, 24·8 ; X, 11·1	Br, 3·8 ; X, 6·2	Br, 76·6%
(4)	Br, 30·9 ; X, 10·3	Br, 3·5 ; X, 3·6	Br, 78·1%
(5)	Br, 28·0 ; X, 9·7	Br, 6·0 ; X, 7·8	Br, 76·8%

(X denotes α-dithian dioxide)

XBr_4 requires Br, 67·8%. XBr_6 requires Br, 76·0%.

Action of Potassium Sulphide on ββ′*-Dichlorodiethylsulphone.*—A mixture of potassium sulphide (from 14 g. of the hydroxide in a little water) with the sulphone (27 g.) in alcohol (1000 c.c.) was kept at laboratory temperature for 12 hours. The solid which had separated, consisting of potassium chloride and an amorphous substance similar to that described by Helfrich and Reid (*loc. cit.*), was removed by filtration, the solvent evaporated, and the residue crystallised from ethyl alcohol. This was identified as dithian monosulphone (2·0 g.), m. p. 203° (Found : C, 31·5; H, 5·4; *M*, cryoscopic in camphor, 163. Calc. : C, 31·5; H, 5·3%; *M*, 152). This sulphone is dimorphous, separating from glacial acetic acid in colourless needles with a straight extinction which slowly redissolve with deposition of more compact crystals. These are orthorhombic with $a : b : c = 0·854 : 1 : 0·696$. The following forms and mean angular values were observed with two crystals :

	m (110).	*b* (010).	*q* (011).
ϕ	0°0′	49°31′	49°31′
ρ	90°0′	90°0′	34°50′

The crystals were tabular with *m* large.

This sulphone is oxidised by hydrogen peroxide to the dithian trioxide, m. p. 279°, of Fromm and Ungar.

Action of Potassium Sulphide on ββ′-Dichlorodiethyl Sulphoxide.—A mixture of the sulphoxide (17·5 g.) and potassium sulphide (from 11 g. of the hydroxide) in ethyl alcohol (1000 c.c.) was kept for 12 hours at the ordinary temperature, and then evaporated. The residue was extracted with ethyl alcohol (30 c.c.) to separate the product from potassium chloride, and the extract, after evaporation, deposited crystals which, after draining on porous earthenware and recrystallisation from di-*n*-butyl ether, had m. p. 125° (yield, 0·75 g.). They were identified as *dithian monoxide*, of which a more convenient method of preparation is described below.

As the separation of this reaction product could hardly be made complete by the above method, the extent of ring closure was determined by weighing the product in the form of the more sparingly soluble dithian : the above experiment was repeated with 5·8 g. of the sulphoxide, the product reduced with an excess of zinc dust and hydrochloric acid, and the dithian removed in steam (dry weight 0·55 g. : 14·3% yield).

Oxidation of 1 : 4-*Dithian to a Monosulphoxide.*—To dithian (40 g.), dissolved in glacial acetic acid (1000 c.c.), hydrogen peroxide (5·67 g. in 500 c.c. of glacial acetic acid) was added drop by drop during 6 hours with constant stirring. After being kept for 12 hours, the mixture was distilled, the acetic acid carrying with it the unaltered dithian. The residue was evaporated several times with water to remove the remaining acetic acid. Extraction with ethyl alcohol (150 c.c.) left some dithian dioxide undissolved, and the monoxide crystallised from the solution (yield, 12·5 g.). It was recrystallised from di-*n*-butyl ether; m. p. 125° (Found : C, 35·25; H, 6·0. $C_4H_8OS_2$ requires C, 35·3; H, 5·9%). The substance is readily soluble in water and in all the common organic solvents. Crystals were obtained for goniometry by evaporation of the solution in water or in methyl formate. They belong to the monoclinic system, having $a : b : c = 1{\cdot}402 : 1 : 1{\cdot}878$ and $\beta = 61°20'$. The habit is a simple combination of *m* (110) and *c* (001), with *R* ($\bar{1}01$) occasionally appearing as a small triangular face truncating a corner of the crystal. The following mean angular values were obtained from two selected crystals :

	m (110).	*m′* ($1\bar{1}0$).	*c* (001).	*R* ($\bar{1}01$).
ϕ	0°	*101°46′	51°5′	230°55′
ρ	90°0′	90°0′	*28°40′	*44°26′

The substance yielded a *compound* with platinic chloride, a pale yellow powder (Found : Pt, 31·8. $C_8H_{16}O_2Cl_4S_4Pt$ requires Pt, 32·0%), and a *compound* with auric chloride, a deep orange powder (Found : Au, 45·0. $C_4H_8OCl_3S_2Au$ requires Au, 44·9%).

Isomeric Sulphonium Salts from Dithian Monoxide.—A mixture of dithian monoxide (10 g.), methyl iodide (35 g.), and ethyl alcohol (10 g.) was boiled under reflux for 8 hours and kept over-night and the sulphonium salts were then removed by filtration (17·7 g.). By crystallisation from 75% ethyl alcohol–water *α-dithian monoxide methylsulphonium iodide* was readily obtained pure (Found: I, 45·45. $C_5H_{11}OS_2I$ requires I, 45·7%). This substance is readily soluble in water and sparingly soluble in ethyl alcohol and other solvents. It separates from aqueous alcohol in feathery needles radiating from a point, or, when crystallised more slowly, in stout, monoclinic prisms. It decomposes on heating without melting. Sodium picrate in aqueous solution converts it into the corresponding *picrate*, m. p. 187° (Found: N, 11·2. $C_{11}H_{13}O_8N_3S_2$ requires N, 11·1%), which crystallises from warm water in bright yellow, monoclinic prisms or prismatic needles with an extinction angle of 36°.

The sulphonium iodide was also converted into a *chloroplatinate* (Found: Pt, 27·7. $C_{10}H_{22}O_2Cl_6S_4Pt$ requires Pt, 27·5%), crystallising in orange plates from water, in which it is sparingly soluble at the ordinary temperature.

The mother-liquors from the purification of the α-sulphonium iodide were concentrated and gave evidence of the presence of another iodide yielding a picrate of lower melting point (125—135°), but the second methiodide was not obtained pure, as it was very soluble and tended to dissociate during evaporation. A quantity (6 g.) of the crude methiodide was therefore dissolved in a little water, the equivalent of sodium picrate added, and the precipitate fractionally crystallised from hot water. In this way, the α-sulphonium picrate was quickly obtained pure (4·2 g.) and from the mother-liquor the isomeric *β-dithian monoxide methylsulphonium picrate* (1·0 g.), m. p. 137° (Found: N, 11·2%), was isolated. It is about three times as soluble in water as the α-isomeride, and crystallises in yellow, monoclinic plates or prisms with an extinction angle of 44°. A mixture of the α- and β-picrates melted at 125—170°. The picric acid was removed in ether from the acidified solution, and addition of platinic chloride and ethyl alcohol yielded the *chloroplatinate* as a pale buff precipitate soluble in water (Found: Pt, 28·0%).

Isolation of the Isomeric Sulphilimines of Dithian Monoxide.—Dithian monoxide (5 g.) and chloramine-T (18 g.) were dissolved together in the minimum quantity of cold water. The mixture, after standing for a few hours, was filtered and the precipitate fractionally crystallised from water. Two substances were found to be present in approximately equal proportions: *α-Dithian* *monoxide* S-p-*toluenesulphonylimine*, m. p. 230—234° (decomp.), which crystallises from water in colourless, flat needles with a straight extinction (Found : N, 4·5. $C_{11}H_{15}O_3NS_3$ requires N, 4·6%). β-*Dithian monoxide* S-p-*toluenesulphonylimine*, m. p. 176—177° (decomp.), which is about five times as soluble as the α-compound in hot water, and crystallises best from 80% ethyl alcohol–water (Found : N, 4·7%). The crystals from water are plates having an angle of 87° and an oblique extinction. A mixture of the two isomerides melted at 167—205°.

Both α- and β-isomerides yield dithian when boiled with zinc dust and dilute acid.

Isomeric Disulphilimines of Dithian.—A mixture of dithian (5 g.) in ethyl alcohol (100 c.c.) and chloramine-T (36 g.) in water (100 c.c.) was boiled under reflux for 3 hours and cooled, and the solid products were removed by filtration. Impurities such as sodium chloride and toluenesulphonamide were removed by two extractions with boiling water (50 c.c.). The residue (4·3 g.) had the properties described by Mann and Pope (*loc. cit.*), but it was separated into two isomerides by repeated extraction with boiling *cyclo*hexanol. The α-*dithianbis*-p-*toluenesulphonylimine* was thus left behind as a white powder insoluble in *cyclo*hexanol, but readily soluble in *m*-cresol. It decomposes at 250—255° (Found : N, 6·1. $C_{18}H_{22}O_4N_2S_4$ requires N, 6·1%). This substance separates from *m*-cresol–*cyclo*hexanol in minute, elongated plates with straight extinction which are frequently twinned, showing a clearly defined re-entrant angle at each end.

The hot *cyclo*hexanol extracts of the original mixture deposited, on cooling, β-*dithianbis*-p-*toluenesulphonylimine* in tufts of leaf-shaped plates radiating from a point, which decompose at 200—210° (Found : N, 6·1%). A mixture of these two isomerides decomposed at 200—235°.

We are indebted to the Chemical Society for assistance in the purchase of materials.

THE UNIVERSITY, SHEFFIELD. [*Received, November* 15*th*, 1927.]