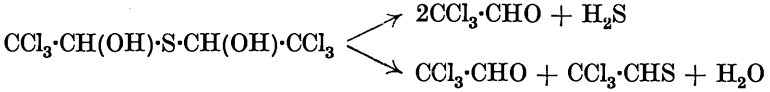
CCCXCIII.—*Compounds of the Thioparaldehyde Type Derived from Chloral.*

By Frederick Daniel Chattaway and Edwin Geoffrey Kellett.

Chloral forms two isomeric polymerides of the paraldehyde type (J., 1928, 2709). Two isomeric forms of trichloralimide, $(CCl_3{\cdot}CH{:}NH)_3$, in which the three oxygen atoms of the parachloral ring are replaced by imino-groups, are also known (Béhal and Choay, *Ann. Chim. Phys.*, 1892, **26**, 7, 34).

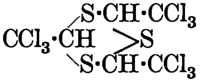
None of the corresponding thio-compounds, in which one or more of these oxygen atoms is replaced by sulphur, have hitherto been described.

A number of such thio-compounds are formed by the action of concentrated sulphuric acid on chloral sulphydrate, a solid addition product of two molecules of chloral with one molecule of hydrogen sulphide having the constitution $CCl_3{\cdot}CH(OH){\cdot}S{\cdot}CH(OH){\cdot}CCl_3$ (Hagemann, *Ber.*, 1872, **5**, 151; Wyss, *Ber.*, 1874, **7**, 80). Concentrated sulphuric acid apparently breaks down chloral sulphydrate in two ways, producing either chloral and hydrogen sulphide, or one molecule each of chloral, thiochloral, and water:

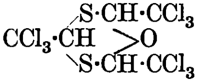


$$CCl_3{\cdot}CH(OH){\cdot}S{\cdot}CH(OH){\cdot}CCl_3 \begin{cases} \nearrow 2CCl_3{\cdot}CHO + H_2S \\ \searrow CCl_3{\cdot}CHO + CCl_3{\cdot}CHS + H_2O \end{cases}$$

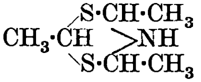
The thiochloral has not been isolated as such. To some extent it polymerises into *trithioparachloral* [2 : 4 : 6-*tristrichloromethyl*-1 : 3 : 5-*trithian*] (I); the remainder condenses with the free chloral present, in the ratio of two molecules of thiochloral to one molecule of chloral, forming *dithioparachloral* [2 : 4 : 6-*tristrichloromethyl*-cyclo-1 : 3 : 5-*oxadithia*-2 : 4 : 6-*trimethylene*] (II). Even in the presence of a large factitious excess of free chloral, no monothioparachloral is formed, the larger excess of chloral merely repressing the formation of trithioparachloral. Relative to this preferential formation of the dithioparaldehyde ring, it may be noted that thialdine (III) is readily formed by the action of excess of dry ammonia on trithioacetaldehyde, without any indication of a second sulphur atom being removed (Marckwald, *Ber.*, 1886, **19**, 1831).



(I.)



(II.)

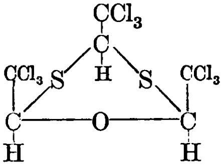


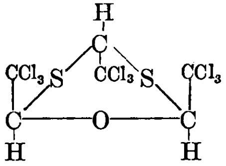
(III.)

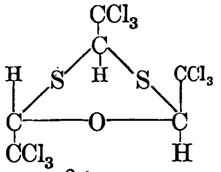
The ring structure of dithioparachloral appears to be of a type not previously prepared, since the "crystalline dithiotrioxymethylene,"

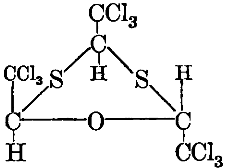
$2C_3H_6S_2O,H_2O$, reported by Rénard (*Ann. Chim. Phys.*, 1879, **17**, 307) can scarcely be accepted as a pure compound.

Although trithioparachloral may theoretically exist in two stereoisomeric forms, *cis*- and *trans*-, only a single form has been obtained. Similarly, dithioparachloral should exist in four stereoisomeric modifications, *viz.* (the oxygen atom being numbered as 1),


cis.


4-*trans*.

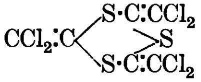

2-*trans*.


6-*trans*.

Of these possible modifications, both the *cis*- and the 4-*trans*- are symmetric, whilst the 2-*trans*- and the 6-*trans*- are asymmetric and, indeed, mirror-images of each other. A maximum number of three modifications separable by fractional crystallisation is therefore to be expected. Actually only two isomerides have been obtained.

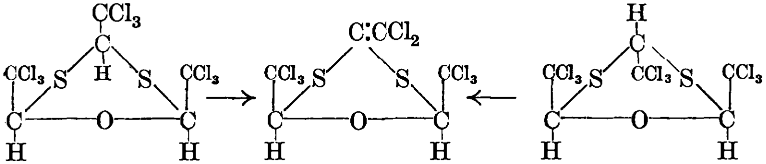
Thus in the cases both of trithioparachloral and of dithioparachloral there is one isomeride missing, and the same omission persists in their derivatives (see below).

It has been pointed out by Bennett and Hock (J., 1925, **127**, 2671) that chlorine atoms and bivalent sulphur atoms, when attached to adjacent carbon atoms, mutually affect one another's reactivity: the negative activity of the chlorine is accentuated, whilst the sulphur is rendered correspondingly inert, and very reluctant to assume a higher valency by oxidation or by addition of halogens or of alkyl halides. Owing to the presence of large groups of chlorine atoms, this effect is very strongly marked in the thioparachlorals. In trithioparachloral, the chlorine in each of the trichloromethyl groups is so reactive that, even in an alcoholic solution of potassium acetate, in which only very feebly alkaline conditions obtain, three molecules of hydrogen chloride are readily split off, giving 2 : 4 : 6-*trisdichloromethylene*-1 : 3 : 5-*trithian*,

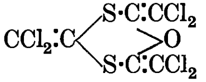


$$CCl_2{:}C\begin{cases} S\cdot C{:}CCl_2 \\ \qquad > S \\ S\cdot C{:}CCl_2 \end{cases}$$

(IV). In the dithioparachlorals, only the trichloromethyl group in the 4-position loses hydrogen chloride thus in the presence of alcoholic potassium acetate, the chlorine in this group (which is unique in that it is situated between two sulphur atoms) being more highly activated than the chlorine in the corresponding groups occupying the 2- and 6-positions. Each isomeride of dithioparachloral yields a corresponding form of 2 : 6-*bistrichloromethyl*-4-*dichloromethylene*cyclo-1 : 3 : 5-*oxadithia*-2 : 4 : 6-*trimethylene* (V). Since both *cis*- and 4-*trans*-dithioparachloral would give the same form of this compound, *viz.*, the *cis*-form, in which both of the trichloromethyl groups remaining intact are on the same side


cis- (V.) 4-*trans*-.

of the plane of the ring, it follows that one of the two dithioparachlorals now under consideration must be the racemic modification, consisting of 2-*trans*- and 6-*trans*-.

All three trichloromethyl groups in the dithioparachlorals are sufficiently activated to lose chlorine (as hydrogen chloride) even in the mildly alkaline conditions of a cold alcoholic suspension of potassium cyanide, giving 2 : 4 : 6-*trisdichloromethylene*cyclo-1 : 3 : 5-*oxadithia*-2 : 4 : 6-*trimethylene*,  $\mathrm{CCl_2{:}C}\Big\langle\substack{\mathrm{S\cdot C{:}CCl_2}\\ \\ \mathrm{S\cdot C{:}CCl_2}}\Big\rangle\mathrm{O}$ (VI). The possibility of stereoisomerism being thus eliminated, both isomeric dithioparachlorals give the same product, which is also obtained by the action of stronger alkalis.

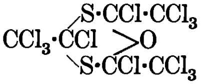
The inertness of the sulphur atoms in the thioparachlorals is similarly striking. They do not form additive compounds with halogens, nor do they give the addition compounds with mercuric chloride which characterise many organic sulphur compounds in which the sulphur is bivalent.

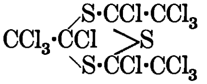
Trithioparachloral, on treatment with dry ammonia gas in dry alcohol, does not form a thialdine, but merely loses hydrogen chloride, yielding trisdichloromethylenetrithian (IV).

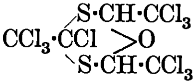
Neither trithioparachloral nor either of the dithioparachlorals is oxidised by 30% hydrogen peroxide under the conditions which Bell and Bennett (this vol., p. 17) found brought about the oxidation of other cyclic sulphur compounds, *e.g.*, trimethylene trisulphide [1 : 3 : 5-trithian]. Potassium permanganate in cold acetone oxidises them, but only with complete disruption of the molecule, accompanied by evolution of heat.

In such oxidations by potassium permanganate, if any one of the thioparachlorals is present in excess, it undergoes a secondary reaction with the hydrated manganese dioxide which is formed. This, acting as an extremely weak base, has the same effect as potassium acetate and brings about the removal of hydrogen chloride. This secondary reaction can be reproduced by refluxing any one of the thioparachlorals with freshly precipitated hydrated manganese dioxide suspended in alcohol.

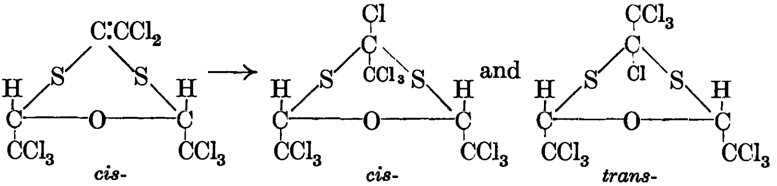
The unsaturated compounds described above, *viz.*, trisdichloromethylenetrithian, 2 : 4 : 6-trisdichloromethylene*cyclo*-1 : 3 : 5-oxadithia-2 : 4 : 6-trimethylene, and the two isomeric forms of 2 : 6-bistrichloromethyl-4-dichloromethylene*cyclo*-1 : 3 : 5-oxadithia-2 : 4 : 6-trimethylene, do not combine directly with bromine, but readily add on chlorine.

2 : 4 : 6-Trisdichloromethylene*cyclo*-1 : 3 : 5-oxadithia-2 : 4 : 6-trimethylene, by addition of six atoms of chlorine, gives 2 : 4 : 6-*trichloro*-2 : 4 : 6-*tristrichloromethyl*cyclo-1 : 3 : 5-*oxadithia*-2 : 4 : 6-*trimethylene*,  $\mathrm{CCl_3{\cdot}CCl}\begin{array}{l}\diagup\mathrm{S{\cdot}CCl{\cdot}CCl_3}\\ \quad>\mathrm{O}\\ \diagdown\mathrm{S{\cdot}CCl{\cdot}CCl_3}\end{array}$ (VII). In the saturated product (VII), as in the case of dithioparachloral itself, three stereoisomeric modifications are theoretically possible, but very careful fractionation has failed to furnish more than two.

Similarly, the addition of six atoms of chlorine to trisdichloromethylenetrithian yields 2 : 4 : 6-*trichloro*-2 : 4 : 6-*tristrichloromethyl*-1 : 3 : 5-*trithian*,  $\mathrm{CCl_3{\cdot}CCl}\begin{array}{l}\diagup\mathrm{S{\cdot}CCl{\cdot}CCl_3}\\ \quad>\mathrm{S}\\ \diagdown\mathrm{S{\cdot}CCl{\cdot}CCl_3}\end{array}$ (VIII), and in this case only a single pure compound has been obtained, instead of a mixture of the two theoretically possible isomerides.

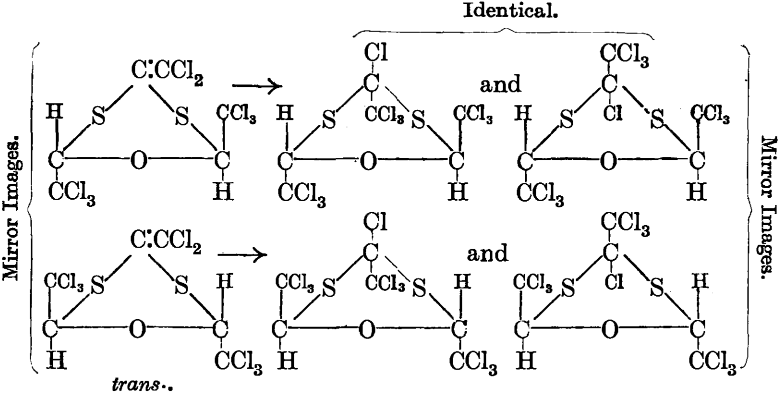
Both isomerides of (V) add on two atoms of chlorine, giving 4-*chloro*-2 : 4 : 6-*tristrichloromethyl*cyclo-1 : 3 : 5-*oxadithia*-2 : 4 : 6-*trimethylene*,  $\mathrm{CCl_3{\cdot}CCl}\begin{array}{l}\diagup\mathrm{S{\cdot}CH{\cdot}CCl_3}\\ \quad>\mathrm{O}\\ \diagdown\mathrm{S{\cdot}CH{\cdot}CCl_3}\end{array}$ (IX).

Of the two isomerides of the former compound (V), the *cis*-form should give a mixture of *cis*- and *trans*-isomerides by addition of two atoms of chlorine,

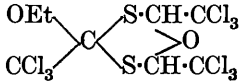
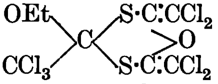


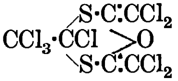
cis- *cis-* *trans-*

whereas the *trans*-form should give a racemic mixture, crystallising as a single compound :—



Actually, only a single pure compound has been obtained from each isomeride.

The two isomerides of 4-chloro-2 : 4 : 6-tristrichloromethyl*cyclo*-1 : 3 : 5-oxadithia-2 : 4 : 6-trimethylene, however, show a singular difference in reactivity of the single chlorine atom attached to carbon in a position α- to two sulphur atoms. When one isomeride is boiled with alcohol, this chlorine atom is replaced by an ethoxyl group, giving 4-*ethoxy*-2 : 4 : 6-*tristrichloromethyl*cyclo-1 : 3 : 5-*oxadithia*-2 : 4 : 6-*trimethylene*,  $\mathrm{\begin{matrix}OEt\\CCl_3\end{matrix}\!\!>\!C\!<\!\begin{matrix}S\cdot CH\cdot CCl_3\\S\cdot CH\cdot CCl_3\end{matrix}\!\!>\!O}$ (X); and similarly, by the action of cold sodium ethoxide in alcohol, it gives (by replacement of chlorine by ethoxyl in the 4-position and loss of hydrogen chloride from the 2- and 6-positions) 4-*ethoxy*-4-*trichloromethyl*-2 : 6-*bisdichloromethylene*cyclo-1 : 3 : 5-*oxadithia*-2 : 4 : 6-*trimethylene*,  $\mathrm{\begin{matrix}OEt\\CCl_3\end{matrix}\!\!>\!C\!<\!\begin{matrix}S\cdot C{:}CCl_2\\S\cdot C{:}CCl_2\end{matrix}\!\!>\!O}$ (XI).

In the other isomeride the chlorine is not thus reactive. The compound can be boiled with alcohol without change, and on treatment with cold sodium ethoxide loss of hydrogen chloride only occurs, giving 4-*chloro*-4-*trichloromethyl*-2 : 6-*bisdichloromethylene*-cyclo-1 : 3 : 5-*oxadithia*-2 : 4 : 6-*trimethylene*,  $\mathrm{CCl_3\cdot CCl\!<\!\begin{matrix}S\cdot C{:}CCl_2\\S\cdot C{:}CCl_2\end{matrix}\!\!>\!O}$ (XII).

EXPERIMENTAL.

Preparation of Chloral Sulphydrate.—A rapid stream of hydrogen sulphide was passed into a solution of 200 g. of chloral hydrate in 90 c.c. of water for 8 hours, separation of the sulphydrate in colourless leaflets beginning after about 2 hours. The solid product was washed with 250 c.c. of dilute hydrochloric acid and dried for 12 hours at 80° (yield, 100 g.); at a higher temperature some decomposition occurs.

The sulphydrate thus prepared is pure enough for use, since repeated crystallisation from chloroform does not appreciably raise its melting point. When pure and dry, it melts at 138—139°, not at 128° as recorded in the literature; and the diacetyl derivative, $CCl_3\cdot CHAc\cdot S\cdot CHAc\cdot CCl_3$, obtained from it by the action of acetic anhydride, melts at 84°, not at 78° as recorded.

Thorough drying is necessary, since in the absence of moisture the undesirable side reaction

$$CCl_3\cdot CH(OH)\cdot S\cdot CH(OH)\cdot CCl_3 \longrightarrow 2CCl_3\cdot CHO + H_2S$$

is repressed to a minimum, though not entirely inhibited.

*Preparation and Separation of Trithioparachloral and α- and β-Dithioparachloral.**—200 G. of chloral sulphydrate were added to a litre of concentrated sulphuric acid and kept for 24 hours at the ordinary temperature. (A large excess of sulphuric acid is desirable, in order to keep the chloral produced in the reaction in solution; this prevents to a considerable extent the formation of metachloral, which is only formed rapidly when a layer of chloral floats undissolved on the surface of the sulphuric acid.) Sulphur dioxide and free sulphur, resulting from the side reaction producing hydrogen sulphide, were liberated, the powdery sulphydrate disappeared, and a compact colourless solid was formed. This was separated, stirred with crushed ice, well washed with cold water, and crystallised twice from boiling alcohol (about 1 litre); the solution was yellow owing to the presence of free sulphur. The bulk of the α-dithioparachloral was thus extracted, since, although this is the less soluble, it is present in smaller amount than the β-modification.

The mother-liquors from these two crystallisations were evaporated, leaving a solid residue rich in α-dithioparachloral. This was recrystallised to constant melting point from high-boiling petroleum (yield, 11—12 g.).

The product obtained from the two alcohol recrystallisations of the original material was crystallised from alcohol about ten times, until pure trithioparachloral of constant m. p. separated (yield, 2—3 g.).

The mother-liquors from these crystallisations were evaporated, and the solid residue was extracted several times by boiling for a few seconds with a quantity of alcohol insufficient quite to dissolve it all, until the product crystallising from the extract had a constant m. p. Yield of β-dithioparachloral, 23—24 g.

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* As in the case of parachloral, etc. (*loc. cit.*), the prefixes α- and β- are used to indicate respectively the less and the more soluble of a pair of isomerides.

Trithioparachloral (I) crystallises from alcohol, in which it is only sparingly soluble, in colourless prisms, m. p. 181° (Found: C, 14·9; H, 0·95; Cl, 64·9; S, 19·7; *M*, cryoscopic in benzene, 466. $C_6H_3Cl_9S_3$ requires C, 14·7; H, 0·61; Cl, 65·1; S, 19·6%; *M*, 490).

α-*Dithioparachloral* (II) is moderately easily soluble in alcohol (about 2·8 g. dissolve in 100 c.c. of alcohol at 18°), but much less so in petroleum, from which it crystallises in plume-like clusters of slender colourless needles, m. p. 236° (Found: Cl, 67·1; S, 13·8; *M*, cryoscopic in benzene, 458. $C_6H_3OCl_9S_2$ requires C, 15·2; H, 0·65; Cl, 67·3; S, 13·7%; *M*, 474).

β-*Dithioparachloral* crystallises from alcohol (about 5·2 g. dissolve in 100 c.c. at 18°) in colourless slender prisms, m. p. 108°. It is readily soluble in petroleum (Found: C, 14·8; H, 0·9; Cl, 67·8; S, 14·0%; *M*, cryoscopic in benzene, 464).

All these compounds are very easily soluble in carbon disulphide or in acetone in the cold, and fairly readily soluble in most organic solvents, although not in water. The same applies to the derivatives described below.

The mixed product of the action of sulphuric acid on chloral sulphydrate, purified from free sulphur but not further separated, yielded on dry distillation a mixture of chloral, b. p. 98°, and trichloroethylene, b. p. 88°, leaving a residue of free sulphur. Sulphur and trichloroethylene thus appear as the decomposition products of thiochloral on distillation. This agrees with the result of Paternò and Oglialoro (*Ber.*, 1874, **7**, 81), who found that anhydrous chloral on heating with phosphorus pentasulphide yielded sulphur and trichloroethylene.

2 : 4 : 6-*Trisdichloromethylene*-1 : 3 : 5-*trithian* (IV).—An equivalent amount (3 mols.) of alcoholic sodium ethoxide was added to trithioparachloral dissolved in cold alcohol. Sodium chloride separated and the reaction was complete in a few minutes; water was then added. The *trithian*, which separated as a colourless solid, crystallised from alcohol, in which it was sparingly soluble, in plume-like clusters of slender needles, m. p. 126° (Found: Cl, 56·2; S, 25·1. $C_6Cl_6S_3$ requires Cl, 56·0; S, 25·3%).

In this reaction, as in those described below which involve abstraction of hydrogen chloride, the yield was practically quantitative.

2 : 4 : 6-*Trisdichloromethylene*cyclo-1 : 3 : 5-*oxadithia*-2 : 4 : 6-*trimethylene* (VI) was prepared, by a method similar to that described for (IV), from either α- or β-dithioparachloral. It crystallised from alcohol, in which it was sparingly soluble, in plumes of feathery colourless needles, m. p. 89° (Found: Cl, 58·2; S, 17·1. $C_6OCl_6S_2$ requires Cl, 58·3; S, 17·1%).

2 : 6-*Bistrichloromethyl*-4-*dichloromethylene*cyclo-1 : 3 : 5-*oxadithia*-

2 : 4 : 6-*trimethylene* (V).—*α-Form.* 10 G. of α-dithioparachloral were dissolved in 200 c.c. of hot alcohol, and 5 g. of powdered anhydrous potassium acetate added. (The reaction proceeds at the ordinary temperature, but is then slow.) The solution was boiled gently for an hour, filtered hot, and allowed to crystallise. α-2 : 6-*Bistrichloromethyl* - 4 - *dichloromethylene*cyclo - 1 : 3 : 5 - *oxadithia* - 2 : 4 : 6-*trimethylene* separated practically pure in slender colourless prisms, m. p. 97° (Found : Cl, 64·7; S, 14·6. $C_6H_2OCl_8S_2$ requires Cl, 64·8; S, 14·7%).

The isomeric β-*modification*, prepared by dissolving 10 g. of β-dithioparachloral in 150 c.c. of boiling alcohol and proceeding as above, crystallised from alcohol, in which it was somewhat sparingly soluble, in stout colourless prisms, m. p. 92° (Found : Cl, 64·5; S, 14·8%).

2 : 4 : 6 - *Trichloro* - 2 : 4 : 6 - *tristrichloromethyl* - 1 : 3 : 5 - *trithian* (VIII).—4 G. of trisdichloromethylenetrithian were suspended in 25 c.c. of cold glacial acetic acid and chlorine was bubbled through for 15 minutes; the solid had then gone completely into solution. The liquid was kept for 2 hours, and water was very slowly added. The *trithian* (VIII), which separated as a colourless solid, after being well washed with water, crystallised from alcohol in slender prisms, m. p. 175° (decomp.) (Found : Cl, 71·8. $C_6Cl_{12}S_3$ requires Cl, 71·8%).

The yield in this reaction, and in the other reactions described below which involve addition of chlorine, was about 70% of the theoretical. The addition compounds as a class are very readily soluble in all organic solvents except alcohol, in which they are moderately easily soluble.

2 : 4 : 6 - *Trichloro* - 2 : 4 : 6 - *tristrichloromethyl*cyclo - 1 : 3 : 5 - *oxa* - *dithia*-2 : 4 : 6-*trimethylene* (VII) was similarly prepared from (VI). A mixture of two isomerides was obtained, which were separated by fractional crystallisation from alcohol, the α-*modification* forming long colourless prisms, m. p. 175° (decomp.) (Found : Cl, 73·5; S, 11·0. $C_6OCl_{12}S_2$ requires Cl, 73·7; S, 11·1%), and the β-*modification* colourless needles, m. p. 157° (decomp.) (Found : Cl, 73·7; S, 11·0%).

Forty crystallisations in all were performed during this separation on a quantity of 30 g., but no trace of a third isomeride was found.

The 2 : 4 : 6-trichloro-compounds, on boiling with zinc dust in acetic acid, easily split off six atoms of chlorine and revert to the unsaturated compounds from which they are formed.

4-*Chloro*-2 : 4 : 6-*tristrichloromethyl*cyclo-1 : 3 : 5-*oxadithia*-2 : 4 : 6-*trimethylene.*—*α-Form* (IX). 8 G. of α-2 : 6-bistrichloromethyl-4-dichloromethylene*cyclo*-1 : 3 : 5-oxadithia-2 : 4 : 6-trimethylene, suspended in 15 c.c. of acetic acid, dissolved when chlorine was passed in for 15 minutes, but after 2 hours the mixture set almost solid again owing to the separation of the addition product. This was filtered off, and the mother-liquor precipitated in order that a second isomeride, if present, might not be overlooked. The *product*, however, crystallised from chloroform as a single pure compound in colourless small prisms, m. p. 136° (Found : Cl, 69·7. $C_6H_2OCl_{10}S_2$ requires Cl, 69·7%).

The isomeric β-*modification*, similarly prepared from β-2 : 6-bistrichloromethyl-4-dichloromethylene*cyclo*-1 : 3 : 5-oxadithia-2 : 4 : 6-trimethylene, crystallised from alcohol in colourless quadrilateral plates, apparently square, m. p. 98—99° (Found : Cl, 69·7%).

4-*Ethoxy*-2 : 4 : 6-*tristrichloromethyl*cyclo-1 : 3 : 5-*oxadithia*-2 : 4 : 6-*trimethylene* (X).—If it is attempted to crystallise α-4-chloro-2 : 4 : 6 - tristrichloromethyl*cyclo* - 1 : 3 : 5 - oxadithia - 2 : 4 : 6 - trimethylene from alcohol in the ordinary way, replacement of chlorine by ethoxyl occurs, and the *ethoxy*-compound crystallises in colourless rhombic plates, m. p. 137° (Found : C, 18·6; H, 1·35; Cl, 61·7. $C_8H_7O_2Cl_9S_2$ requires C, 19·1; H, 1·3; Cl, 61·6%).

4-*Ethoxy*-4-*trichloromethyl*-2 : 6-*bisdichloromethylene*cyclo-1 : 3 : 5-*oxadithia*-2 : 4 : 6-*trimethylene* (XI).—A solution of 1 g. of α-4-chloro-2 : 4 : 6 - tristrichloromethyl*cyclo* - 1 : 3 : 5 - oxadithia - 2 : 4 : 6 - trimethylene in 20 c.c. of cold alcohol was treated with alcoholic sodium ethoxide until it was permanently alkaline. The *product*, precipitated by addition of water, after being washed, crystallised from alcohol, in which it was moderately easily soluble, in large colourless prisms, m. p. 94° (Found : Cl, 56·0; S, 14·5. $C_8H_5O_2Cl_7S_2$ requires Cl, 55·8; S, 14·4%).

4-*Chloro*-4-*trichloromethyl*-2 : 6-*bisdichloromethylene*cyclo-1 : 3 : 5-*oxadithia*-2 : 4 : 6-*trimethylene* (XII) was obtained from β-4-chloro-2 : 4 : 6 - tristrichloromethyl*cyclo* - 1 : 3 : 5 - oxadithia - 2 : 4 : 6 - trimethylene by a procedure exactly similar to that described in the preceding preparation. It crystallised from alcohol, in which it was moderately easily soluble, in small colourless rhombohedra, m. p. 88° (Found : C, 16·5; H, negligible; Cl, 65·4; S, 14·0. $C_6OCl_8S_2$ requires C, 16·5; H, 0; Cl, 65·1; S, 14·0%).

The estimations of sulphur and of chlorine recorded in this research were carried out in a Parr ignition bomb, in which the compound for analysis is ignited for 50 seconds with sodium peroxide and potassium nitrate. A complete analysis can be carried out in this way in 2 hours. Estimations of chlorine made thus are fully as accurate as those obtained by the Carius method, and sulphur estimations definitely more trustworthy.

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