[CONTRIBUTION FROM THE QUEEN'S COLLEGE LABORATORY, OXFORD]

THE OXIDATION OF DITHIOPARACHLORAL

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Dithioparachloral (2,4,6-tris-trichloromethyl-1,3,5-oxadithiane) (I) does not form a stable sulfone but easily breaks down under the influence of oxidizing agents.

When, however, the inhibiting influence of the trichloromethyl groups on the adjacent sulfur atoms is diminished by loss of hydrogen chloride, oxidation of one sulfur atom can occur with formation of a stable, partly unsaturated monosulfone.

Thus when 2,6-bis-trichloromethyl-4-dichloromethylene-1,3,5-oxadithiane (II) is submitted to the action of hydrogen peroxide at the ordinary temperature, it is oxidized to a monosulfone (2,6-bis-trichloromethyl-4-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide (III).

If dithioparachloral (I) is dissolved in acetic acid and kept at 60° for some hours, small quantities of hydrogen peroxide being added from time to time, it is partly destructively oxidized, but to some extent the same unsaturated sulfone (III) is formed, showing that loss of hydrogen chloride is necessary either as a preliminary to, or as a consequence of, oxidation of the sulfur atom.

The sulfone group in this compound (III) exerts upon the neighboring chlorine atoms an even more potent[1] negative activating influence than does a bivalent sulfur atom, an influence equivalent indeed to that produced by two adjacent bivalent sulfur atoms,[1] since under the influence of alcoholic potassium acetate or aqueous caustic soda the compound loses hydrogen chloride from the 2-position, yielding 6-trichloromethyl-2,4-bis-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide (IV).

When dithioparachloral is subjected to the more powerful oxidizing action of chromic acid in hot acetic acid solution, complete destructive oxidation of the molecule occurs to a predominant extent, but an unsaturated disulfone (2,6-bis-dichloromethylene-1,3,5-oxadithiane-3,3,5,5-tetroxide (VI)) is also produced in small amount. In the formation of this compound, the introduction of two sulfone groups not only necessitates the removal of chlorine as hydrogen chloride from both the 2- and 6-position but also its removal by hydrolysis of the trichloromethyl group in the 4-position (V), loss of carbon dioxide subsequently occurring.

The two hydrogen atoms in the 4-position in (VI) show a positive activation like the hydrogen in the 2-position in (III), but, naturally, in an even more marked degree. The compound (VI) dissolves in aqueous sodium carbonate, and is recovered unchanged on acidification; while on chlorina-

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[1] Chattaway and Kellett, *J. Chem. Soc.*, 2909 (1929).

tion the two hydrogen atoms are replaced by chlorine, yielding 2,6-bis-dichloromethylene - 4,4 - dichloro - 1,3,5, - oxadithiane - 3,3,5,5 - tetroxide (VII), which does not dissolve in aqueous alkalies.

These reactions of the disulfone (VI) serve to explain the curious behavior on chlorination of the monosulfone (III) which, in warm solution, produces the same compound (IV) as is obtained by the action of alcoholic potassium acetate or of aqueous caustic soda. In this reaction, the activated hydrogen atom in the 2-position must first be substituted by chlorine, forming (VIII). In the $=CClCCl_3$ group of this compound, the α-chlorine atom is positively, and the β-atom negatively, activated, so that a molecule of chlorine splits off between these two positions, leaving the bis-unsaturated compound (IV).

On the same view, double bonds in positions adjacent to a sulfone group (as the 2- and 4-positions in (IV), and the 2- and 6-positions in (VI)) would not be expected to add on chlorine; and they are actually found not to do so.

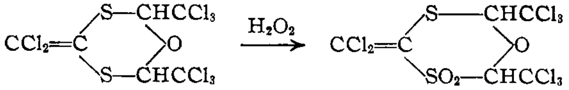
When the monosulfone (III) is treated with alcoholic caustic soda, the dichloromethylene group in the 4-position (which is subject to negative activation both by the sulfone group and the bivalent sulfur atom) is hydrolyzed; loss of hydrogen chloride also occurs from the 2- and 6-positions, yielding 2,6 - bis - dichloromethylene - 4 - carbethoxy - 1,3,5 - oxadithiane - 3,3 - dioxide (IX).

This compound, having a positively activated hydrogen atom in the 4-position, dissolves in aqueous caustic soda (not however, in sodium carbonate: it is therefore less acidic than the disulfone (VI)). On regulated chlorination, two atoms of chlorine are first added on—presumably to the double bond more remote from the sulfone group, giving 2-dichloromethylene - 6 - trichloromethyl - 6 - chloro - 4 - carbethoxy-1,3,5 - oxadithiane-3,3-dioxide (X), which is still soluble in aqueous alkali. On further chlorination, the acidic hydrogen atom is replaced by chlorine, giving 2 - dichloromethylene - 6 - trichloromethyl - 4,6 - dichloro - 4 - carbethoxy-1,3,5,-oxadithiane-3,3-dioxide (XI), which is not soluble in aqueous alkali.

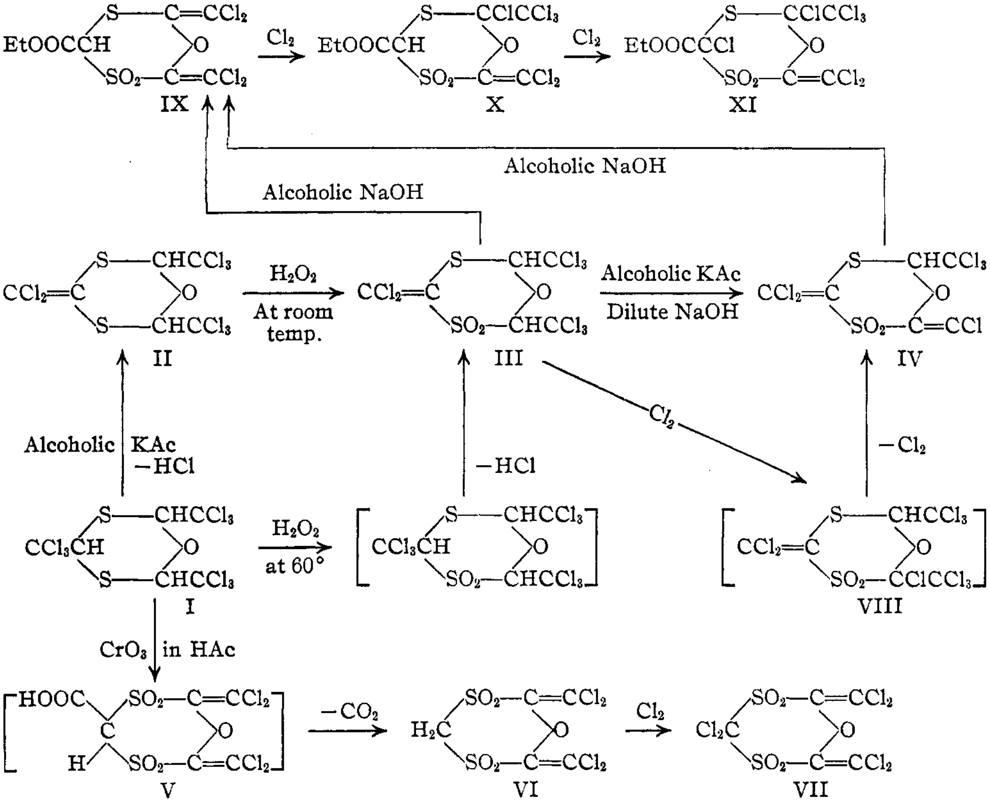
The reactions are represented in the scheme given.

Experimental

Oxidation of 2,6-Bis-trichloromethyl-4-dichloromethylene-1,3,5-oxadithiane to the Dioxide.—Eight grams of finely powdered β-2,6-bis-trichloromethyl-4-dichloromethylene-1,3,5-oxadithiane was suspended in 100 cc. of cold acetic acid and 10 cc. (excess) of 30% aqueous hydrogen peroxide added. The mixture was allowed to remain at the



II III

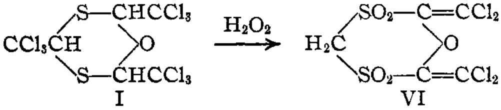


ordinary temperature for fourteen days, during which time the suspended solid passed into solution. The liquid was then diluted with water, and the 2,6-bis-trichloromethyl-4-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide, which separated as a colorless solid, crystallized from ligroin, in which it is somewhat sparingly soluble, and from which it separates in clusters of slender colorless prisms, m. p. 166–167°; yield, 7 g.

Anal. Calcd. for $C_6H_2O_3Cl_8S_2$: C, 15.3; Cl, 60.4; S, 13.6; mol. wt., 470. Found: C, 15.6; Cl, 60.8; S, 13.8; mol. wt., cryoscopic in benzene, 451.

This compound does not react with chlorine or bromine in the cold, nor is it reduced by tin in a boiling mixture of hydrochloric and acetic acids. After heating for thirty minutes at 100° with acetic anhydride and a little strong sulfuric acid, it crystallizes unchanged on cooling. It dissolves readily in cold strong sulfuric acid, and is recovered unchanged on pouring the solution over crushed ice.

Oxidation of Dithioparachloral to 2,6-Bis-dichloromethylene-1,3,5-oxadithiane-3,3,5,5-tetroxide.—Five grams of β-dithioparachloral was dissolved in 60 cc. of acetic acid at 100°; 10 g. of anhydrous chromic acid was added in small portions during one hour, after which heating was continued on the water-bath for another hour. Some



carbon dioxide was evolved during this process, and sulfate ion could be detected in the solution, showing that disruptive oxidation had occurred to some extent.

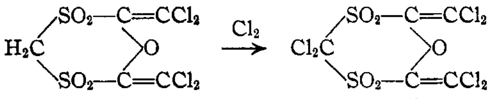
The reaction mixture was cooled and diluted with water, when the *tetroxide*, mixed with the dioxide (above) separated as a colorless solid. It was washed with aqueous sodium carbonate, which dissolves the tetroxide but not the dioxide; the filtrate was acidified with hydrochloric acid, and the tetroxide which again separated was crystallized from mixed chloroform and ligroin. It is only sparingly soluble in organic solvents, and separates as a felt of colorless silky needles, m. p. 185°; yield, 0.4–0.8 g.

Anal. Calcd. for $C_5H_2O_5Cl_4S_2$: Cl, 40.8; S, 18.4. Found: Cl, 40.5; S, 18.3.

The tetroxide may also be isolated by repeatedly recrystallizing the crude oxidation product from ligroin; showing that the bis-dichloromethylene structure arises in the actual oxidation process, and is not merely introduced by the use of the alkaline carbonate solvent in working up.

An identical product was similarly obtained from α-dithioparachloral.

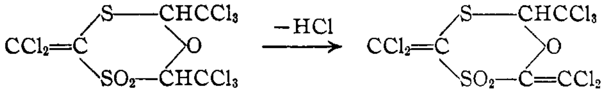
Chlorination of the Tetroxide.—Five grams of the tetroxide was dissolved in 4 cc. of warm acetic acid, and a rapid stream of chlorine passed through the solution for one hour. Hydrogen chloride was evolved during the chlorination. The solution was allowed to stand overnight, when 4,4-dichloro-2,6-bis-dichloromethylene-1,3,5-oxadithiane-3,3,5,5-tetroxide separated in large colorless rhombs, m. p. 143°. It is very readily soluble in acetic acid, and moderately easily soluble in alcohol, from which it is best recrystallized; it does not dissolve in cold aqueous caustic soda.



VI VII

Anal. Calcd. for $C_5O_5Cl_6S_2$: Cl, 51.1; S, 15.4. Found: Cl, 51.4; S, 15.5.

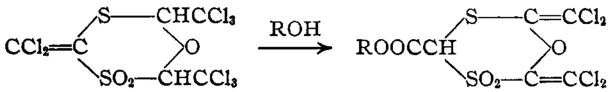
Preparation of 2,4-Bis-dichloromethylene-6-trichloromethyl-1,3,5-oxadithiane-3,3-dioxide.—One gram of the dioxide (III) was suspended in 20 cc. of 10% aqueous caustic soda, and warmed gently for a few minutes at 40–50°. After cooling and acidifying with hydrochloric acid, the solid was separated and crystallized from petroleum, in which it is somewhat sparingly soluble, and from which it separates as a felt of colorless needles, m. p. 148°.



Anal. Calcd. for $C_6HO_3Cl_7S_2$: Cl, 57.3. Found: Cl, 57.6.

The same compound was obtained by heating the dioxide with alcoholic potassium acetate, and also by chlorinating it in warm acetic acid solution; hydrogen chloride is evolved during the chlorination.

Hydrolysis of the Dioxide.—To obtain a clean workable product in these hydrolyses, the procedure given below must be followed with some care. It is especially essential to work in dilute solution.



Ethyl 2,6-Bis-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide-4-carboxylate.—Eight grams of the dioxide was dissolved in 800 cc. of cold ethyl alcohol, and aqueous caustic soda (10%) added until the mixture was permanently alkaline. It was then bright yellow in color; 350 cc. of water, followed by 100 cc. of strong hydrochloric acid, was then added. The solution became practically colorless and on diluting with about 3 liters of water, the *ester* separated as a flocculent precipitate. It was crystallized from ligroin (500 cc.), from which it separates in plume-like clusters of colorless needles, m. p. 112.5°; yield, 4 g.

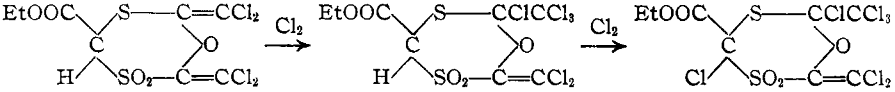
Anal. Calcd. for $C_8H_6O_5Cl_4S_2$: C, 24.9; H, 1.3; Cl, 36.6; S, 16.6. Found: C, 25.0; H, 1.9; Cl, 37.0; S, 16.8.

Methyl 2,6-Bis-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide-4-carboxylate.—This ester was similarly prepared by using methyl alcohol instead of ethyl alcohol as the solvent. It crystallizes from ligroin, in which it is sparingly soluble, in colorless needles, m. p. 126°.

Anal. Calcd. for $C_7H_4O_5Cl_4S_2$: Cl, 38.2; S, 17.2. Found: Cl, 38.5; S, 17.2.

The ethyl and methyl esters are somewhat unstable and turn brown on long exposure to air. Attempts to prepare the free carboxylic acid from them were unsuccessful. On heating with acids or alkalies, they are decomposed and tarry products formed. Similarly, when the hydrolysis of the dioxide was carried out in aqueous acetone instead of an alcohol with a view to obtaining the free acid directly, only an uncrystallizable tarry product was obtained.

Chlorination of the Ethyl Ester



IX X XI

First Stage.—One gram of the ethyl ester (IX) was suspended in 5 cc. of cold acetic acid, and a slow stream of chlorine bubbled through for half an hour. During this time the solid went into solution, and on allowing the mixture to stand for two hours, ethyl 6-chloro-6-trichloromethyl-2-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide-4-carboxylate crystallized out. This was filtered off and recrystallized from ligroin, in which it is moderately easily soluble, and from which it separates in slender colorless prisms, m. p. 151–152°.

Anal. Calcd. for $C_8H_6O_5Cl_6S_2$: Cl, 46.6. Found: Cl, 47.0.

This compound dissolves in aqueous alkalies, but decomposes rather rapidly in alkaline solution, and consequently separates in an impure brownish state on acidification. It is somewhat unstable, and even when kept in a sealed tube decomposes in time into a brown tarry mass.

Second Stage.—Two grams of the ester (IX) was suspended in 20 cc. of acetic acid and chlorinated as above. After the chlorine addition product had crystallized out, chlorine was again passed through. Hydrogen chloride was slowly evolved, and the crystals again went into solution. When all had dissolved, the solution was very gradually diluted by addition of cold water, when ethyl 4,6-dichloro-6-trichloromethyl-2-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide-4-carboxylate separated. It was recrystallized from alcohol, in which it is readily soluble, and from which it separates in colorless rhombic plates, m. p. 161.5°.

Anal. Calcd. for $C_8H_5O_5Cl_7S_2$: C, 19.4; H, 1.0; Cl, 50.2; S, 12.9; mol. wt. 493. Found: C, 19.8; H, 1.1; Cl, 50.5; S, 13.0; mol. wt., cryoscopic in benzene, 452.

This compound is insoluble in aqueous alkalies, and, unlike the compounds above, which contain the acidic hydrogen atom, it is perfectly stable at the ordinary temperature.

Summary

Dithioparachloral does not form stable sulfoxides or sulfones owing to the mutual influence of the chlorine and bivalent sulfur atoms. Oxidation only occurs when some of the chlorine is removed either by previous treatment or in the oxidation process itself.

On oxidation with hydrogen peroxide it yields 2,6-bis-trichloromethyl-4-dichloromethylene-1,3,5-oxadithiane-3,3-dioxide, and with hot chromic acid 2,6-bis-dichloromethylene-1,3,5-oxadithiane-3,3,5,5-tetroxide.

The behavior of these oxidation products toward alkaline reagents and on chlorination illustrates both the activating influence of bivalent sulfur and the alternating effect originating from sulfone groups.

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THE SUPPOSED ISOMER OF 1,3,5-TRITHIANE

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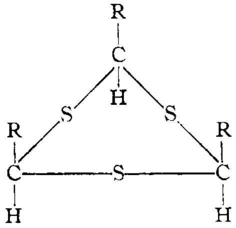
Accepting the view that the trithioaldehydes are 1,3,5-trithianes, strictly analogous in their isomerism to the paraldehydes, there can be no *cis–trans* isomerism of 1,3,5-trithiane itself.



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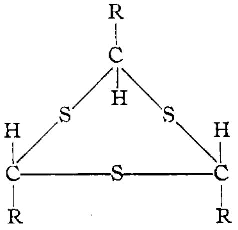
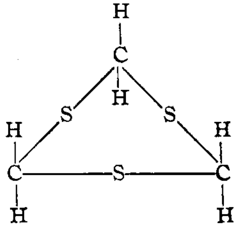


Trans



1,3,5-Trithiane

Hinsberg,[1] however, has stated that this compound, which melts at 216°, is converted under the influence of hydriodic acid (which converts α- into β-trithioacetaldehyde) into an isomeric modification which melts with decomposition at 247°. It is reconverted into the "stable form" on crystallization from benzene.

Fromm and Schultis,[2] and Bell and Bennett,[3] have since reëxamined this phenomenon without arriving at any satisfactory conclusion.

Since, however, by the action of other reducing agents upon 1,3,5-trithiane, a product of the same or only slightly lower m. p. (247°) is ob-

[1] Hinsberg, *J. prakt. Chem.*, **85**, 341 (1912).

[2] Fromm and Schultis, *Ber.*, **56**, 937 (1923).

[3] Bell and Bennett, *J. Chem. Soc.*, 19 (1929).