

### 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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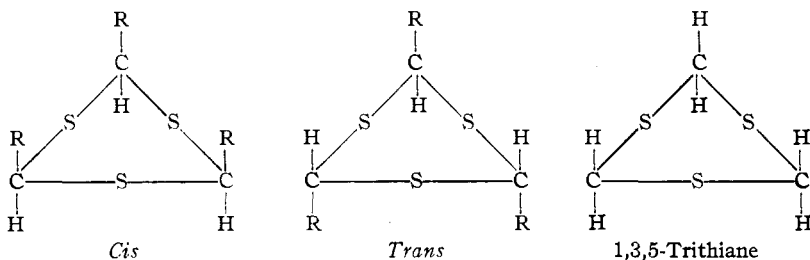
### THE SUPPOSED ISOMER OF 1,3,5-TRITHIANE

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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.



Hinsberg,<sup>1</sup> however, has stated that this compound, which melts at 216°, is converted under the influence of hydriodic acid (which converts  $\alpha$ - into  $\beta$ -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,<sup>2</sup> and Bell and Bennett,<sup>3</sup> have since reexamined 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-

<sup>1</sup> Hinsberg, *J. prakt. Chem.*, **85**, 341 (1912).

<sup>2</sup> Fromm and Schultis, *Ber.*, **56**, 937 (1923).

<sup>3</sup> Bell and Bennett, *J. Chem. Soc.*, 19 (1929).

tained and this compound on mild oxidation yields again the original material of m. p. 216,<sup>o</sup> it seems probable that the supposed higher-melting isomer is actually an unstable reduction product (or mixture of products) of 1,3,5-trithiane, and that the latter compound exists as the theory demands in only a single modification.

### Experimental

**The Alleged Isomerism of 1,3,5-Trithiane.**—When hydrogen sulfide is passed into a mixture of 1 volume of formalin with 2 volumes of strong hydrochloric acid, the colorless solid which separates (after washing with air-free water and drying *in vacuo*) melts at 247<sup>o</sup> (decomp.). After crystallization from any solvent, it melts at 216<sup>o</sup>; the same lowering of the melting point takes place on solution even at the ordinary temperature, since if the compound of m. p. 247<sup>o</sup> is dissolved in cold benzene and precipitated out with ligroin, the product melts at 216<sup>o</sup>. The compound of m. p. 247<sup>o</sup> is also converted into ordinary pure 1,3,5-trithiane, m. p. 216<sup>o</sup>, on exposure to air for about twenty-four hours, or on heating for more than a short time on the steam-bath, or on shaking for a minute with cold dilute aqueous hydrogen peroxide. The high-melting product can be obtained from normal 1,3,5-trithiane, m. p. 216<sup>o</sup>, not only (as Hinsberg found) by the action of hydriodic acid, but also by the action of other *reducing* agents, *e. g.*, stannous chloride, or metals and hydrochloric acid, reagents which do *not* effect steric inversion in the trithioacetaldehydes. The melting point is not perfectly constant, and may be as low as 243<sup>o</sup>, but there appears to be no reason to doubt that the same compound is present in each case.

If a weighed quantity of the freshly-prepared substance of m. p. 247<sup>o</sup> is shaken with a known amount of dilute aqueous hydrogen peroxide, filtered and washed, and the filtrate back-titrated against standard permanganate, an appreciable decrease in the amount of available oxygen present is observed; but no consistent analyses have been obtained by this method.

These observations appear to show that the compound, m. p. 247<sup>o</sup>, is of the nature of an unstable *reduction product* (or mixture of products) of 1,3,5-trithiane.

### Summary

The compound of m. p. 247<sup>o</sup>, which Hinsberg supposed to be isomeric with 1,3,5-trithiane, has not the properties of an *isomer* of the latter compound but rather those of an unstable *reduction product*.

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