

CLXXV.—*The Space Configuration of the Trithioacetaldehydes.*

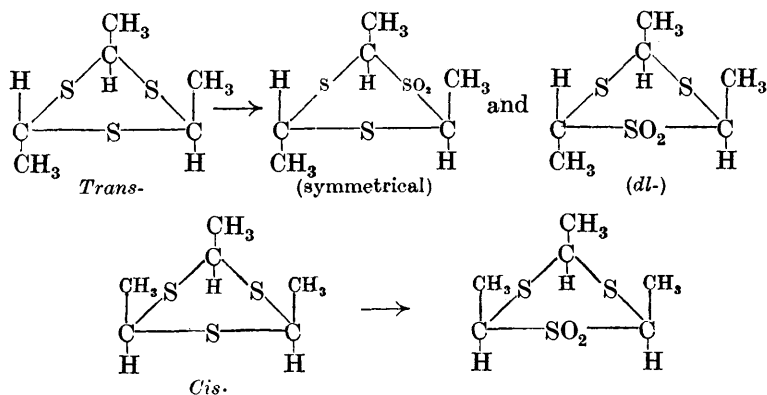
By FREDERICK DANIEL CHATTAWAY and EDWIN GEOFFREY
KELLETT.

RECENT work (Fromm and Engler, *Ber.*, 1925, **58**, 1916; Bell, Bennett, and Mann, J., 1929, 1462) has supported the earlier view of Baumann and Fromm (*Ber.*, 1889, **22**, 2600) that trithioacetaldehyde, $(\text{CH}_3\cdot\text{CH}\cdot\text{S})_3$, exists in two isomeric forms, the so-called α -trithioacetaldehyde, m. p. 101° , and β -trithioacetaldehyde, m. p. 126° , and that the supposed γ -form (Marckwald, *Ber.*, 1886, **19**, 1826; Polack and Thummel, *Ber.*, 1889, **22**, 2871; Mann and Pope, J., 1923, **123**, 1178) is a mixture of these two. Although it has been customary to regard the α -form as the *cis*-isomeride

(having all three methyl groups on the same side of the plane of the ring), there is no direct chemical evidence for this view. Baumann and Fromm regarded the β -form as *trans*- (*Ber.*, 1891, **24**, 1428) because it is the more stable isomeride, arguing by analogy with the hexahydrophthalic acids. Auwers and Ottens (*Ber.*, 1924, **57**, 439) support this view from comparisons of physical data.

The oxidation products of these two isomerides which have previously been described are anomalous in that both isomerides give one and the same trisulphone (Baumann and Fromm, *Ber.*, 1889, **22**, 2606; Lomnitz, *Ber.*, 1894, **27**, 1667) and one and the same disulphone (Baumann and Fromm, *Ber.*, 1893, **26**, 2074); while only one trisulphoxide of α -trithioacetaldehyde and one of the β -form have been obtained (Fromm and Engler, *loc. cit.*), though the stereoisomeric possibilities, having regard to the possible dispositions of the semipolar double bonds in relation to the plane of the ring (compare Bell and Bennett, *J.*, 1927, 1798), are much more numerous than this (six trisulphoxides of the *trans*-form, and four of the *cis*-form, may be predicted).

It is shown in the present paper that α -trithioacetaldehyde forms *two* isomeric *monosulphoxides*, and β -trithioacetaldehyde *one*. The maximum number theoretically possible is *two* from the *cis*-form and *four* from the *trans*-form. Each of the three monosulphoxides actually obtained has, however, been further oxidised to a distinct *monosulphone*. Hence, since α -trithioacetaldehyde yields two isomeric monosulphones, and the β -form only one, the α -form must have the *trans*-structure.



EXPERIMENTAL.

Oxidation of β -Trithioacetaldehyde to a Monosulphoxide.—10 G. of finely powdered β -trithioacetaldehyde, m. p. 126°, were suspended

in 100 c.c. of glacial acetic acid, and 6 c.c. of "perhydrol," dissolved in 150 c.c. of acetic acid, added during 8 hours, with vigorous shaking. (The reaction is rapid, since 15 minutes after addition of the last drop of "perhydrol" solution no free hydrogen peroxide could be detected in the reaction mixture by the perchromic acid test.) The clear solution thus obtained was diluted to 1500 c.c. with cold water and 220 g. of anhydrous sodium carbonate were added; it was then filtered, and the filtrate extracted with 400 c.c. of chloroform in eight portions. The extract was dried over calcium chloride and the chloroform evaporated, leaving 9.5 g. of crude product. On crystallisation from 20% aqueous alcohol (60 c.c.), this proved to be a single pure compound.

β-Trithioacetaldehyde monosulphoxide crystallises from alcohol, in which it is very readily soluble, in large, compact, colourless crystals of ill-defined shape, m. p. 118.5° (Found: S, 49.2. $C_6H_{12}OS_3$ requires S, 49.1%). It is moderately easily soluble in cold water, and readily soluble in all the usual organic solvents. On warming with zinc dust in dilute hydrochloric acid, it is reduced to *β*-trithioacetaldehyde.

Oxidation of β-Trithioacetaldehyde Monosulphoxide to a Monosulphone.—3 G. of potassium permanganate, dissolved in 300 c.c. of water, were added during 6 hours to a stirred solution of 5.6 g. of *β*-trithioacetaldehyde monosulphoxide in 750 c.c. of water containing 10 g. of magnesium sulphate. Each drop of permanganate was decolorised almost instantaneously. When all had been added, the precipitated manganese dioxide was dissolved by passing sulphur dioxide through the mixture. The resulting liquor, containing the product partly in suspension and partly in solution, was extracted with 120 c.c. of chloroform in eight portions. The extract was dried and evaporated, and the residue recrystallised from 50% aqueous alcohol (yield, 4 g.).

β-Trithioacetaldehyde monosulphone crystallises from alcohol, in which it is moderately easily soluble, in slender colourless prisms, m. p. 190° (Found: S, 45.6. $C_6H_{12}O_2S_3$ requires S, 45.3%). It is only sparingly soluble in cold water. It is not reduced by zinc in hydrochloric acid, nor by tin in a mixture of hot hydrochloric and acetic acids, nor by hydriodic acid in the cold. On boiling for some time with fresh, constant-boiling hydriodic acid, it is to some extent decomposed, hydrogen sulphide being liberated and tarry products formed; any crystallisable product recovered from this reaction, however, is the unchanged sulphone.

It may be noted (a) that *β*-trithioacetaldehyde is not oxidised by "perhydrol" in neutral acetone solution, (b) that, if it is attempted to oxidise *β*-trithioacetaldehyde directly to its lower oxidation

products with a limited amount of either neutral or acid permanganate, a complex mixture of products is formed, even though the process be protracted over several days, and (c) that, if it is attempted to oxidise β -trithioacetaldehyde monosulphoxide with a limited amount of acid permanganate, a complex mixture of products is again obtained.

Oxidation of α -Trithioacetaldehyde to a Pair of Isomeric Monosulphoxides.—10 G. of α -trithioacetaldehyde, m. p. 100° , were suspended in 75 c.c. of acetic acid and oxidised with "perhydrol" as above. Yield of crude product, 9.5 g. This was recrystallised from 20% aqueous alcohol (75 c.c. for the first operation) until it had a constant m. p. 136° (4.6 g.). The mother-liquors were concentrated on the water-bath and evaporated to dryness in a vacuum desiccator. The residue was extracted by rinsing it several times with quantities of 25 c.c. of water at 50° ; these extracts were evaporated to dryness and the residue was recrystallised from 10% aqueous alcohol until it had m. p. 93° (1 g.).

α -Trithioacetaldehyde α -monosulphoxide crystallises from 20% alcohol, in which it is readily soluble, in large, colourless, rhombic plates, m. p. 136° (Found: S, 49.4%). It is moderately easily soluble in cold water and very readily in organic solvents. It is reduced to α -trithioacetaldehyde by warming with zinc dust and dilute hydrochloric acid.

α -Trithioacetaldehyde β -monosulphoxide crystallises from 10% alcohol in slender colourless prisms, m. p. 93° (Found: S, 49.4%). Its solubilities are only slightly greater than those of the α -form, above. It is reduced by nascent hydrogen to α -trithioacetaldehyde.

Each of the three isomeric monosulphoxides lowers the m. p. of either of the others.

Oxidation of α -Trithioacetaldehyde to a Pair of Isomeric Monosulphones.—8.3 G. of α -trithioacetaldehyde were oxidised to the monosulphoxide stage, as above, with "perhydrol." To the solution in acetic acid, aqueous caustic potash was added until the mixture was just alkaline to phenolphthalein; the total volume of the solution was then about 1200 c.c. 20 G. of magnesium sulphate were dissolved in this, and 4.9 g. of potassium permanganate, dissolved in 500 c.c. of water, added with mechanical stirring during 9 hours. The resulting reaction mixture was worked up as described for β -trithioacetaldehyde monosulphone. Yield of crude product, 9.5 g. By fractional crystallisation from alcohol, two isomeric products were isolated.

α -Trithioacetaldehyde α -monosulphone is sparingly soluble in water, more readily in alcohol. It crystallises in two polymorphic forms. When a hot alcoholic solution is cooled, the labile form

separates as a felted mass of colourless needles. These, on standing in contact with the solvent for 24 hours at the ordinary temperature, dissolve, and the stable form separates as large, colourless, rhombic crystals. Both forms melt at 157.5° , transformation into the stable form occurring before melting (Found : S, 45.3%).

α -Trithioacetaldehyde β -monosulphone crystallises from alcohol, in which it is appreciably more soluble than the α -monosulphone, in slender colourless prisms, m. p. $115-116^{\circ}$ (Found : S, 45.1%).

These two isomerides are stable towards reducing agents in the same way as is β -trithioacetaldehyde monosulphone. They do not undergo stereoisomeric inversion under the influence of hydrogen iodide, iodine or acetyl chloride. The α -monosulphone corresponds to the α -monosulphoxide, since if the latter compound is oxidised with the appropriate amount of neutral permanganate, the α -monosulphone is obtained alone in practically quantitative yield.

THE QUEEN'S COLLEGE LABORATORY,
OXFORD.

[Received, April 12th, 1930.]
