CLXXXVII.—*The Isomeric Trithioacetaldehydes.*

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IN addition to the two trithioacetaldehydes  $\mathrm{MeHC}{<}\begin{smallmatrix}\mathrm{S{\cdot}CHMe}\\ \mathrm{S{\cdot}CHMe}\end{smallmatrix}{>}\mathrm{S}$ which have long been known and melt at 101° and 126°, respectively, a third form was described by Mann and Pope (J., 1923, **123**, 1178) melting at 80—81° and apparently identical with the γ-isomeride obtained previously by Marckwald (*Ber.*, 1886, **19**, 1826) and by Poleck and Thümmel (*Ber.*, 1889, **22**, 2871). This third (or γ-) form was considered to be a definite chemical individual, chiefly because it could be prepared by a variety of methods and had always the same sharp melting point, which it retained even when recrystallised repeatedly from various solvents or when sublimed. In view of the comments of Fromm and Engler (*Ber.*, 1925, **58**, 1916), and of the fact that stereochemical theory requires the existence of only two isomerides, we have re-examined the substance of m. p. 80—81° and find that it is in fact a mixture of the α- and the β-isomeride containing 40% of the latter. This proportion is different from that stated by Fromm and Engler and is identical with that of the eutectic mixture of the two compounds.

As the isomerides are readily interconvertible in the presence of catalysts, we regard physical evidence as the best proof of identity. The melting point of phenol already saturated with the "γ"-substance is no further depressed by the addition of the α- and the β-compound successively, so the supposed third isomeride must be a mixture of the other two. This is confirmed by direct microscopic examination. The melting points of series of mixtures of the "γ-" with the α- and the β-isomeride are all consistent with the former being a mixture of the composition stated.

The peculiar circumstances which cause this mixture to simulate so closely the behaviour of a single substance deserve special consideration, for such a case may well occur again with a pair of isomeric or closely related compounds. The α- and the β-trithioacetaldehyde differ only slightly in their solubilities in eight solvents examined by Suyver (*Rec. trav. chim.*, 1905, **24**, 377). Consequently, as the joint solubility curve of two substances in a solvent is closely related to the melting-point curve of their mixtures, it is intelligible, although at first sight surprising, that the proportion of these two stereoisomerides dissolved at the invariant point should be the same as that in their eutectic mixture. This accounts for the constancy and sharpness of melting point of the "γ"-product. As this mixture was frequently recrystallised from several solvents without change in composition, the position of the invariant point on the solubility curve must be practically independent of the individual solvent and of the temperature (over the range involved). The fact that such a mixture may also be sublimed without change of composition has been confirmed.

The isolation of this same mixture from a variety of reactions is no doubt due to the production by rapid reactions of the α- and the β-trithioacetaldehyde in approximately equal proportions (as is to be expected from considerations of probability), so that the solvent used for recrystallisation became saturated with both solids at the same time and the usual invariant mixture was isolated. Specimens of diethylidene trisulphide and αα′-diethoxydiethyl sulphide (J., 1923, **123**, 1172) kept sealed in the Cambridge laboratories for 6 years have slowly decomposed with production of trithioacetaldehydes. The former deposited needles of the β-isomeride only, the latter crystals of both the α- and the β-isomeride side by side. This difference may be explained by the presence in the diethylidene trisulphide of sub-analytical traces of a catalyst such as hydrogen chloride or a chlorosulphide which is absent (as would be expected from its mode of preparation) from the diethoxydiethyl sulphide. The equilibrium mixture *in solution* obtained by Suyver in presence of such catalysts as acids or alkyl halides contained about 90% of the β-isomeride.

A crystallographic examination shows that the α-trithioacetaldehyde crystallises in the monoclinic system, and the β-isomeride is orthorhombic.

EXPERIMENTAL.

Cryoscopic Observations with Phenol as Solvent.—The following values of depression of the freezing point of phenol were observed with a thermometer graduated in 0·1° :—

Δt for phenol saturated with "γ"-compound, 22·24° : after the further addition of 0·5 g. of β-isomeride, Δt 22·27°, and after the addition also of 0·5 g. of α-isomeride, Δt 22·34°, whereas a final addition of 0·5 g. of another solute (dithian) increased the depression to Δt 25·54°.

In the same way it was found that the addition of "γ"-substance to phenol already saturated with pure α- and β-isomerides caused no further depression of the freezing point. No interconversion of the isomerides could have been involved, since each of the three substances was separately kept in solution in phenol for 18 hours and recovered unchanged.

Melting Points of Mixtures of α-, β-, and "γ"-Trithioacetaldehydes.—The curve for mixtures of the α- and the β-isomeride was examined by Suyver, who observed the temperatures of initial solidification of mixtures. In order to economise material and to obtain comparable results the melting points of these α–β mixtures and also those of the "γ"-isomeride with the α- and the β-isomeride respectively were determined in capillary tubes heated in a mechanically stirred bath. The figures for the α–β mixtures were :

Weight % of *a*-	100	80	70	65	60	55	50	40	20	0
M. p.	101°	92°	86°	83°	80°	85·5°	91·5°	102°	116°	126°

These values give a curve similar to Suyver's with a simple eutectic at 60% of α-isomeride, but the melting points are up to 4° higher than those of Suyver. This must be due to the method of observation, for the thermometer was standardised and moreover a cooling curve of the eutectic mixture showed a single arrest at 76° (in agreement with Suyver) whereas the m. p. was consistently found to be 80°.

The figures for α–"γ" mixtures were :

Weight % of *a*-	100	79	61	38·5	21	5·3	0
M. p.	101°	97°	93°	88°	84°	81°	80°
	(101°	97·5°	94°	89°	84·5°	81°	80°)

and for the β–"γ" mixtures :

Weight % of *β*-	100	77·5	63	41	20	4·6	1·6	0
M. p.	126°	119·5°	114°	105°	92°	84°	81°	81°
	(126°	119·5°	114·5°	105°	94°	84°	81°	80°)

In each case the figures in parentheses are the melting points to be anticipated (from the α–β figures) on the assumption that the "γ"-substance has the eutectic composition of 60% of α-isomeride. This was also confirmed by the fact that no depression of melting point of the "γ"-substance was produced by adding 1% of either isomeride to it.

Direct Examination of the Trithioacetaldehydes.—The α-isomeride crystallises in the monoclinic system with *a* : *b* : *c* = 0·6907 : 1 : 0·8009 and axial angle β = 114° 44′. Crystals from acetone or ethyl alcohol were of tabular habit developed on *b*(010) and bounded by *m*(110) and *q*(011) with *c*(001) occasionally present. The following mean angular values were obtained by measurement of three selected crystals :

	b (010).	*m* (110).	*c* (001).	*q* (001).
φ	0° 0′	*57° 54′	90°	*29° 54′
ρ	90° 0′	90° 0′	*24° 44′	*42° 44′

Oblique extinctions were observed on the faces *b* and *m*, but the position of the optic axes was not detected.

The β-isomeride crystallises from various solvents in prismatic needles which rarely show any satisfactory terminal faces. Consequently one axial ratio remains uncertain. The substance is orthorhombic with $a : b : c = 0{\cdot}9217 : 1 : ?$. Crystals from acetone had *a*(100), *b*(010), and *m*(110) equally developed and elongated along the *c* axis. The form *n*(120) and the terminal face *c*(001) were present occasionally. The following mean angles were found :

	a (100).	*m* (110).	*n* (120).	*b* (010).	*c* (001).
ϕ	0° 0′	*42° 40′	62° 38′	90° 0′	All values
ρ	90° 0′	90° 0′	90° 0′	90° 0′	0° 3′

A straight extinction is visible on *a*. The position of the optic axes could not be found.

The "γ"-substance may, like the α- and β-forms, be crystallised from a variety of solvents without change of melting point. Slow crystallisation of acetone solutions, however, yielded sufficiently well-formed crystals for the selection of some which were identified as the α-isomeride (m. p. 101°). From a crop of crystals deposited slowly from benzene, on the other hand, needles could be separated which consisted of the nearly pure β-isomeride (m. p. 123°, not depressed by addition of pure β-form). When the "γ"-material was crystallised from ethyl alcohol on a microscope slide it was easy to distinguish blunt-ended needles with a straight extinction (β-isomeride) and opaque compact rhomb-shaped crystals (α-isomeride) : each was present in quantity.

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