CCCLXXXIV.—*Studies in the Penthian Series. Part III. Stereoisomeric Derivatives of Some Penthianols.*

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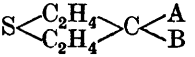
THE sulphoxide, the sulphilimine, and the alkylsulphonium salts derived from cyclic sulphides of the type  $\mathrm{S}{<}\begin{smallmatrix}C_2H_4\\C_2H_4\end{smallmatrix}{>}\mathrm{C}{<}\begin{smallmatrix}A\\B\end{smallmatrix}$ should according to stereochemical theory each occur in the *cis*- and *trans*-isomerides analogous to the dioxides, disulphilimines, sulphoxide-sulphilimines and sulphoxide-sulphonium salts of 1 : 4-dithian (Bell and Bennett, J., 1927, 1798; 1928, 86) and to the quaternary ammonium salts of 4-substituted piperidines (Mills, Parkin, and Ward, J., 1927, 2613).

Three penthianols of the required structure have been synthesised (see preceding paper) and the examination of their derivatives for the occurrence of stereoisomerism is now described.

Each of the three sulphides studied yielded on oxidation a mixture from which two stereoisomeric *sulphoxides* were isolated by fractional crystallisation. These isomerides are tabulated below :

	α-.	β-.
Phenylpenthianol oxides ...	M. p. 187·5° orthorhombic	M. p. 200° monoclinic
Benzylpenthianol oxides ...	M. p. 186° orthorhombic	M. p. 150·5—152·5° monoclinic
Penthianolcarboxylic acid oxides	M. p. 222° (decomp.)	M. p. 184° (decomp.)

The melting point of a mixture of the α- and β-forms is in each case lower than that of either. Complete crystallographic examination has been made of two of these pairs of isomerides.

The ease of separation of the stereoisomerides varied considerably, great difficulty being met with in the phenylpenthianol oxides, where the mixture contained approximately equal amounts of substances of almost equal solubilities. This separation was finally accomplished by hand-picking crystals which were well developed as a result of slow crystallisation : the two distinct substances were then separately purified.

The methylsulphonium salts and the sulphilimine of phenylpenthianol were also prepared. The *methylsulphonium picrate* was readily separated into an α-*isomeride*, m. p. 158°, and a more soluble β-*isomeride*, m. p. 148°, which yielded respectively the α- and β-*chloroplatinates*.

On the other hand, *phenylpenthianol*-p-*toluenesulphonylimine* was a beautifully crystalline substance of m. p. 217° and no second isomeride was isolated. From the mother-liquor of its preparation, however, besides *p*-toluenesulphonamide, a little phenylpenthianol β-oxide was obtained. This may have arisen by direct oxidation of the original sulphide, but it may also be an indication of hydrolysis of the sulphilimines. It must be concluded that if a second sulphilimine is formed it is either lost by hydrolysis or is present in too small a quantity to be detected.

With the exception of the uncertainty concerning the sulphilimine, the results of this study are in full accord with the requirements of stereochemical theory.

EXPERIMENTAL.

Oxidation of Phenylpenthianol to a Pair of Sulphoxides.—Hydrogen peroxide (1 mol.) was slowly added to a stirred solution of the phenylpenthianol in glacial acetic acid kept cool by cold water. After 12 hours, a crystal of sodium acetate was added, the bulk of the solvent removed in steam, the solution evaporated to dryness on the steam-bath, and the residue dried in a desiccator.

Crystallisation of the mixed sulphoxides from ethyl acetate yielded a small quantity of 4-*phenylpenthian*-4-*ol* α-*oxide*, which after further recrystallisation from ethyl acetate formed long thin plates, m. p. 187—187·5° (Found : C, 62·6; H, 6·7; *M*, in camphor, 237. $C_{11}H_{14}O_2S$ requires C, 62·8; H, 6·7%; *M*, 210).

The remainder of the oxidation product was fractionally crystallised from ethyl acetate, but separation was effected only after slow crystallisation; the plates and fine needles then formed could sometimes be separated by hand-picking. A quantity of the needles, which had a m. p. higher than that found for the α-oxide, was collected and recrystallised from ethyl acetate.

4-*Phenylpenthian*-4-*ol* β-*oxide* was thus obtained in flat needles, m. p. 199—200° (Found : C, 62·8; H, 7·0%; *M*, 227). A mixture of the α- and β-oxides melted at 152—154°, and one of the β-oxide with the sulphone (m. p. 197°) at 165—178°. The separation of the β-oxide also led to the isolation of more of the α-isomeride.

Crystallographic Properties of the α- *and* β-*Phenylpenthianol Oxides.*—The α-*oxide* crystallises in the orthorhombic system with $a : b : c = 0·9110 : 1 : 0·5650$. The following forms and mean angular values were observed with five crystals (from ethyl acetate) :

	b(010).	*m*(110).	*l*(210).	*h*(410).	*s*(023).	*q*(011).	*t*(053).
φ	0° 0′	*47° 40′	65° 29′	77° 20′	0° 0′	0° 0′	0° 0′
ρ	90° 0′	90° 0′	90° 0′	90° 0′	21° 28′	*29° 28′	43° 9′

The habit was usually tabular with *b* large, as in Fig. 1, but some crystals were of prismatic habit elongated along the *c*-axis with *b* small. The forms *h*, *t* and either *s* or *q* were often absent.

Straight extinctions were observed on *b* and on the prism faces, which confirms the symmetry. The position of the optic axes was not found.

The β-*oxide* is monoclinic with $a : b : c = 0·3877 : 1 : 0·4674$ and axial angle $\beta = 113° 11'$. The following forms and mean angular co-ordinates were determined with six crystals (from ethyl acetate) :

	b(010).	*k*(230).	*m*(110).	*l*(210).	*q*(011).	*u*(012).	*R*($\bar{1}$01).	*w*($\bar{2}$12).
φ ...	0° 0′	60° 20′	*70° 23′	29° 25′	43° 27′	*61° 24′	270°	255° 24′
ρ ...	90° 0′	90° 0′	90° 0′	90° 0′	31° 47′	*26° 0′	38° 36′	39° 38′

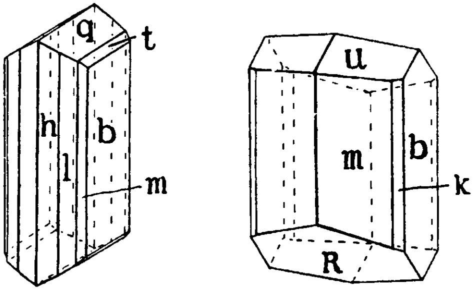
The usual habit is shown in Fig. 1; the forms *k*, *l*, *q*, and *w* were rarely observed. An oblique extinction found on *b* confirms the monoclinic symmetry.

Solubilities of the Phenylpenthianol Oxides and Proportions produced.—The determination of the solubilities of the isomerides in ethyl acetate supplied an explanation of the difficulty of separation by crystallisation. The solvent was saturated by stirring for 4 hours in a thermostat at 20·0°. The solubilities of the α- and the β-oxide are 0·422 g. and 0·475 g., respectively, per 100 g. of ethyl acetate The two oxides appear to be present in the oxidation product in approximately equal proportion.

Oxidation of Benzylpenthianol to a Pair of Sulphoxides.—The oxidation of benzylpenthianol (6·5 g.) by the method described above yielded a crude mixture of oxides (7 g.). Crystallisation from ethyl acetate gave 4-*benzylpenthian*-4-*ol* α-*oxide,* which separated from ethyl acetate in granular crystals (1·3 g.), m. p. 186° (Found: C, 64·2; H, 7·2; *M*, in camphor, 229. $C_{12}H_{16}O_2S$ requires C, 64·2; H, 7·2%; *M*, 224).

FIG. 1.

Phenylpenthianol oxides.



α- *β-Oxide.*

By fractional crystallisation of the remainder of the oxidation product, 4-*benzylpenthian*-4-*ol* β-*oxide* (0·75 g.) was isolated, which formed fine needles, m. p. 150·5—152·5°, from ethyl acetate (Found: C, 63·9; H, 7·2%; *M*, 222). Admixture of the α-oxide depressed the m. p. to 133—136°: a mixture with the corresponding sulphone melted at 135—136°.

Crystallographic Properties of α- *and* β-*Benzylpenthianol Oxides.*—The α-*oxide* is orthorhombic with $a : b : c = 0{\cdot}6072 : 1 : 0{\cdot}4194$. The following forms and mean angular values were observed with five crystals from ethyl acetate:

	a(100).	*m*(110).	*b*(010).	*c*(001).	*r*(101).	*d*(102).
ϕ	0° 0′	*31° 16′	90°	All values	0° 0′	0°
ρ	90° 0′	90° 0′	90° 0′	0° 0′	*34° 38′	18° 52′

The habit is shown in Fig. 2.

Straight extinctions were found on the faces *a*, *b*, and *c*. In convergent polarised light the central portion of a biaxial figure is seen through either *a* or *b*, the separation of the optic axes being so large that they lie just outside the field of view. One axis may be seen when the observation is made through the face *m*, the plane of the optic axes being parallel to *c*(001).

The β-*oxide* is monoclinic with $a : b : c = 1{\cdot}0738 : 1 : 0{\cdot}5505$ and axial angle $\beta = 92°\ 16'$. The forms and mean angles observed with four crystals from ethyl acetate were :

	$b(010)$.	$g(230)$.	$m(110)$.	$l(210)$.	$a(100)$.
ϕ	0° 0′	32° 24′	*42° 59′	61° 57′	90° 0′
ρ	90° 0′	90°	90°	90°	90°

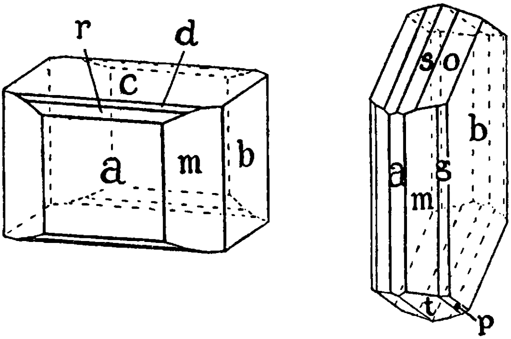
	$o(111)$.	$s(211)$.	$p(\bar{1}11)$.	$t(\bar{2}11)$.
ϕ	*45° 7′	62° 54′	221° 48′	241° 14′
ρ	*37° 57′	32° 5′	36° 10′	29° 4′

The habit is tabular with *b* large and more or less elongation along the *c* axis (Fig. 2). The forms *g*, *m*, *a*, and *p* were sometimes absent and $R(\bar{1}01)$ was found in one instance.

The extinction on *b* is at 44° with the edge *bm*.

FIG. 2.

Benzylpenthianol oxides.



α-Oxide. *β-Oxide.*

Solubilities of the Benzylpenthianol Oxides and Proportions produced.—The solubilities in ethyl acetate at 20·0° are α-oxide 0·297 g. and β-oxide 0·872 g. per 100 g. of solvent. The α- and β-oxides appear to have been formed approximately in the ratio of 2 : 3.

Oxidation of Penthianolcarboxylic Acid to a Pair of Sulphoxides.—The acid (7 g.), dissolved in glacial acetic acid, was oxidised by slow addition of hydrogen peroxide (1 mol.). The mixture was kept over-night, a crystal of sodium acetate added, and the solvent removed in the usual manner. The oxides were readily soluble in water or alcohol and sparingly soluble in benzene, acetone, or ethyl acetate. After several unsuccessful attempts the separation was effected by crystallisation from methyl ethyl ketone.

Penthian-4-*ol*-4-*carboxylic acid α-oxide* crystallised from water in monoclinic prisms, m. p. 222° (decomp.; bath preheated to 210°) (Found : S, 17·9. $C_6H_{10}O_4S$ requires S, 18·0%). The m. p. was depressed to 188—193° by admixture of the corresponding sulphone.

Penthian-4-ol-4-carboxylic acid β-oxide crystallised from water in rectangular plates with a straight extinction, m. p. 182—184° (decomp.) (Found: S, 17·8%). A mixture with the α-isomeride melted at 165—171° (decomp.).

The solubilities of the α- and β-isomerides in methyl ethyl ketone at 21·5° are 0·25 g. and 0·30 g., respectively, per 100 g. of solvent.

Stereoisomeric Sulphonium Salts of Phenylpenthianol.—Phenylpenthianol (5 g.) was boiled for 2 hours with an excess of methyl iodide (25 g.) in ethyl alcohol (10 c.c.). The pale yellow, crystalline precipitate (yield, 98%) was recrystallised from 90% alcohol, and 4-*phenyl*-1-*methylpenthian*-4-*olsulphonium α-iodide* obtained as colourless needles, m. p. 182·5° (decomp.) (Found: I, 37·7. $C_{12}H_{17}OIS$ requires I, 37·8%). The m. p. of this salt fell on further crystallisation. Examination of the mother-liquor from the original crop gave indications of the presence of a more soluble substance, but owing to its instability this could not be isolated in a state of purity.

The crude iodides (4 g.) were converted into picrates by the action of aqueous sodium picrate. The yellow oil which was precipitated solidified on scratching and was separated with little difficulty into two substances.

4-*Phenyl*-1-*methylpenthian*-4-*olsulphonium α-picrate* (2·75 g.) was isolated from the mixed picrates by repeated crystallisation from warm water. When crystallised from alcohol, it formed flat yellow needles, m. p. 158° (Found: N, 9·9. $C_{18}H_{19}O_8N_3S$ requires N, 9·6%). This picrate constituted more than half of the original mixture. It is readily soluble in hot water or alcohol, but sparingly soluble in the cold solvents. The conversion of the α-iodide, described above, into the pure α-picrate by means of sodium picrate shows these salts to have the same configuration.

The picrate was acidified with dilute hydrochloric acid, the picric acid removed in ether, and chloroplatinic acid added. The *α-chloroplatinate* was deposited in radiating clusters of prismatic needles, decomposing at 190—200° (Found: Pt, 23·4. $C_{24}H_{34}O_2Cl_6S_2Pt$ requires Pt, 23·6%).

The material in the mother-liquors from the isolation of the α-picrate, fractionally crystallised from ethyl alcohol, yielded the isomeric 4-*phenyl*-1-*methylpenthian*-4-*olsulphonium β-picrate* (0·5 g.), which crystallised from alcohol in fine needles, often forming sheaf-like bundles, m. p. 146—148° (Found: N, 10·0%). This substance is markedly more soluble in water and alcohol than its isomeride. The m. p. of a mixture with the α-picrate was 143—152°.

The β-picrate was converted as before into the *β-chloroplatinate*, which formed rectangular micro-plates decomposing at 165—194°

(Found: Pt, 23·9%). This substance is so soluble in water that it was necessary to keep the volume of the solutions used as small as possible in order to cause it to crystallise.

Isolation of the Sulphilimine of Phenylpenthianol.—A solution of "chloramine T" (12 g.) in water (65 c.c.) was filtered and added to phenylpenthianol (5 g. in 40 c.c. of alcohol). The mixture was heated on the steam-bath for ½ hour and cooled, and the precipitate collected. The crude substance had m. p. 206° and crystallisation from ethyl alcohol gave *4-phenylpenthian-4-ol-*1-p-*toluenesulphonylimine* in white lustrous plates, m. p. 217° (Found: N, 4·1. $C_{18}H_{21}O_3NS_2$ requires N, 3·8%). Further small quantities of this substance were isolated from the mother-liquors of its purification.

The main reaction liquor was examined for the possible presence of an isomeric sulphilimine. After the separation and identification of two crops of *p*-toluenesulphonamide, the collected mother-liquors were evaporated to dryness. Extraction of the residue with dibutyl ether yielded a little crystalline material, m. p. 182—187°, which contained no nitrogen and by slow crystallisation from ethyl acetate yielded crystals, m. p. 192—195°, of almost pure phenylpenthianol β-oxide (m. p. 199—200°): admixture of the latter raised the m. p. to 195—199°.

The phenylpenthianolsulphilimine, heated for 10 minutes with concentrated hydrochloric acid on the steam-bath and then diluted with water, yielded a little *p*-toluenesulphonamide. The other product of hydrolysis was not identified.

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