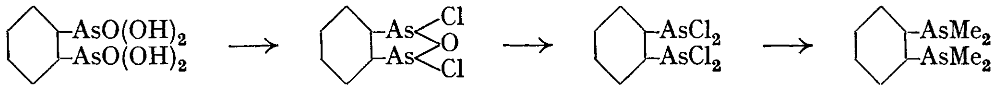
139. *The Synthesis of Ditertiary Arsines.* meso- *and Racemic Forms of Bis-4-covalent-arsenic Compounds.*

By Joseph Chatt and Frederick G. Mann.

Ditertiary arsines, in which the arsenic atoms are separated by only two carbon atoms, have been synthesised by two methods. In the first, *o*-aminophenylarsonic acid is converted into arsines of general formula *o*-$C_6H_4(AsR_2)_2$, and in the second, phenylarsonic acid is converted into arsines of formula $C_2H_4(AsPhR)_2$, R representing alkyl or aryl groups. The bis(arsonium picrate) $C_2H_4[AsMeBuPh{\cdot}O{\cdot}C_6H_2(NO_2)_3]_2$ has been isolated in two forms, the α of m. p. 113—115° and the β of m. p. 139·5—140·5°. The bis(arsine sulphide), $C_2H_4(BuPhAs{\rightarrow}S)_2$, has also been obtained in two forms, α m. p. 113—116°, β m. p. 121°; the α- is transformed into the β-form by heating alone or in organic solvents. Since both the above compounds contain two asymmetric 4-covalent arsenic atoms, one form in each case must be the *meso-* and the other the externally compensated isomeride.

For the investigation of a problem concerning the structure of bridged metallic compounds, ditertiary phosphines or arsines having the phosphorus or arsenic atoms separated by only two carbon atoms were required. Such compounds had apparently not been prepared and the difficulties in synthesising the phosphines were so great that we confined our attention to the arsines, for which two methods of preparation were worked out.

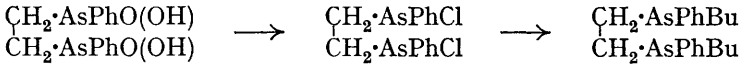
Kalb (*Annalen*, 1921, **423**, 74) prepared *o*-phenylenediarsonic acid (I) from *o*-aminophenylarsonic acid, and then, by the action of hydrochloric acid and sulphur dioxide, reduced the diarsonic acid to the cyclic diarsine oxychloride (II), but he could not convert this into the tetrachloride (III). We find, however, that the *tetrachloride* can be readily prepared by the action of warm thionyl chloride, and subsequently precipitated from the reaction mixture with *cyclo*hexane (strong heating with thionyl chloride causes rapid decomposition of the tetrachloride). The tetrachloride is extremely reactive, and on exposure to damp air soon evolves hydrogen chloride. When it is treated with excess of a Grignard reagent, the corresponding ditertiary arsine is readily obtained. In this way o-*phenylenebis*(*dimethylarsine*) (IV) and o-*phenylenebis*(*di*-n-*butylarsine*) have been prepared. These tetra-alkyl diarsines are liquid at room temperature: the former has a pronounced odour, but the latter is almost odourless. The bis(dimethylarsine) is readily oxidised on exposure to the air, but the butyl compound undergoes very little atmospheric oxidation even on long standing, and does not combine with sulphur even in boiling carbon disulphide



(I.) (II.) (III.) (IV.)

solution. *m*-Phenylenebis(dimethylarsine) has been similarly prepared from *m*-phenylenebis(dichlorarsine) by Steinkopf, Schmidt, and Penz (*J. pr. Chem.*, 1934, **141**, 301).

Similar ditertiary arsines, in which the arsenic atoms are separated by the two carbon atoms of an aliphatic group, were also required. Quick and Adams (*J. Amer. Chem. Soc.*, 1922, **44**, 805) found that ethylene dibromide, when boiled with phenyldichloroarsine and aqueous sodium hydroxide, gave ethylenebis(phenylarsonic acid) (V); this was obtained as an oil, and only after tedious purification was the crystalline arsonic acid isolated. By modifying the conditions of this reaction, we readily obtained the solid acid (V) in good yield. When an ice-cold solution of the arsonic acid in dilute hydrochloric acid containing a trace of potassium iodide is treated with sulphur dioxide, *ethylene*-αβ-*bis*(*phenylchloroarsine*) (VI) results. This compound is remarkably inert, compared with the tetrachloride (III): it is not appreciably hydrolysed by damp air, it can be recrystallised unchanged from hot alcohol, and when heated with aqueous sodium hydroxide it melts at first without decomposition and then only slowly undergoes hydrolysis. Hot hydrochloric acid, however, causes decomposition and formation of phenyldichloroarsine. When the dichloride (VI) is treated with excess of phenylmagnesium bromide, the crystalline *ethylene*-αβ-*bis*(*diphenylarsine*), $C_2H_4(AsPh_2)_2$, results. This general synthesis differs from that of the *o*-phenylene series, however, in that diarsines having asymmetric arsenic atoms can also be obtained, and the use, *e.g.*, of *n*-butylmagnesium bromide gives the liquid *ethylene*-αβ-*bis*(*phenyl*-n-*butylarsine*) (VII). Both these diarsines show the same comparative inertness towards addition of oxygen and sulphur as the *o*-phenylenebis(di-*n*-butylarsine) of type (IV).

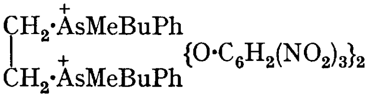


$$\begin{array}{l}CH_2\cdot AsPhO(OH)\\ CH_2\cdot AsPhO(OH)\end{array} \longrightarrow \begin{array}{l}CH_2\cdot AsPhCl\\ CH_2\cdot AsPhCl\end{array} \longrightarrow \begin{array}{l}CH_2\cdot AsPhBu\\ CH_2\cdot AsPhBu\end{array}$$

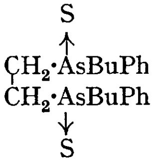
(V.) (VI.) (VII.)

The compound (VII) combines readily with methyl iodide to give the dimethiodide $C_2H_4(AsMeBuPhI)_2$, containing two similar asymmetric 4-covalent arsenic atoms. The extreme difficulty experienced in crystallising this compound indicated the probable presence of both *meso*- and racemic forms. It was therefore converted into the corresponding *ethylene*-αβ-*bis*(*phenylmethyl*-n-*butylarsonium picrate*) (VIII); this crystallised readily from alcohol, and repeated recrystallisation separated it into two isomeric forms, the more soluble α-form having m. p. 113—115°, and the β-form having m. p. 139·5—140·5°, a mixture of the two forms having m. p. 114—123°. No interconversion of the two forms in boiling alcoholic solution was detected. It is clear, therefore, that these compounds must represent *meso*- and racemic isomerides, and that one of them should therefore be resolvable into optically active forms. No attempt to do so has been made in view of the great difficulty of resolving dissymmetric arsonium salts and the comparative inaccessibility of the two pure picrates.

(VIII.)



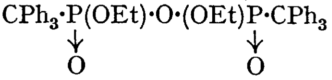
$$\begin{array}{l}CH_2\cdot\overset{+}{As}MeBuPh\\ |\\ CH_2\cdot\overset{+}{As}MeBuPh\end{array}\{O\cdot C_6H_2(NO_2)_3\}_2$$



$$\begin{array}{c}S\\ \uparrow\\ CH_2\cdot AsBuPh\\ CH_2\cdot AsBuPh\\ \downarrow\\ S\end{array}$$

(IX.)

When 2 mols. of bromine were added to ethylenebis(phenyl-*n*-butylarsine), and the resulting bis(arsine dibromide) was treated with sodium sulphide or hydrogen sulphide, *ethylene*-αβ-*bis*(*phenyl*-n-*butylarsine sulphide*) (IX) was obtained. Recrystallisation of this compound in turn from *cyclo*hexane and ether separated it into isomeric α- and β-*sulphides*, m. p. 113—116° and 121° respectively; a mixture of the two forms had m. p. 95—103°. It follows, again, that one of these forms must be the *meso*- and the other the racemic compound. The conversion of the α- into the β-sulphide which occurs when the α-sulphide is heated alone or in organic solvents illustrates the ready change of configuration which asymmetric 4-covalent arsenic atoms undergo. Both forms show an exceptional power of separating



$$CPh_3\cdot\underset{\substack{\downarrow\\ O}}{P}(OEt)\cdot O\cdot(OEt)\underset{\substack{\downarrow\\ O}}{P}\cdot CPh_3$$

(X.)

from organic solutions with solvent of crystallisation. A similar example of *meso*- and racemic isomerides was obtained by Hatt (J., 1933, 776), who separated ethyl triphenylmethylpyrophosphonate (X) into two forms, m. p. 222—223° and 228—231°. The higher-melting isomeride also showed a marked tendency to crystallise from organic solutions with solvent of crystallisation.

EXPERIMENTAL.

o-*Phenylenediarsine Tetrachloride* (III).—Thionyl chloride (8 c.c., 1·75 mols.) was cautiously added with efficient cooling to the powdered oxychloride (II; 20 g.), and the mixture heated on the water-bath with frequent shaking for 20 mins. In these conditions the thionyl chloride does not boil; direct heating with a flame causes decomposition. *cyclo*Hexane (50 c.c.) was then added, and the mixture cooled in ice-water with stirring. The tetrachloride which separated was collected, washed with *cyclo*hexane, and at once placed in a vacuum. This product (20 g.) was sufficiently pure for use in the next stage. A portion was, however, recrystallised from dioxan containing a small quantity of thionyl chloride: the heating was reduced to a minimum, and the temperature not allowed to rise above 60°. The *tetrachloride* with 2 mols. of dioxan of crystallisation separated as colourless plates, m. p. 76—86°; they were immediately placed in a vacuum (Found: C, 30·9; H, 3·8; Cl, 26·0. $C_6H_4Cl_4As_2,2C_4H_8O_2$ requires C, 30·9; H, 3·7; Cl, 26·1%).

o-*Phenylenebis*(*dimethylarsine*) (IV).—The tetrachloride (III) (18 g.) was shaken with ether (100 c.c.) and the clear solution was decanted from a small residue and slowly added to a cooled (ice-water) stirred Grignard reagent prepared from methyl iodide (41·5 g.; 6 mols.), magnesium (7 g.; 6 atoms), and ether (150 c.c.) in an atmosphere of nitrogen, a vigorous reaction ensuing. Stirring was continued for 1 hour at room temperature and the product was then hydrolysed by a solution of ammonium chloride (60 g.) in water (200 c.c.) with continued ice-cooling. When the magnesium hydroxide had dissolved, the ethereal layer was collected and dried (sodium sulphate), and the solvent distilled; the residue was distilled under reduced pressure in a hydrogen atmosphere, the *bis*(*dimethylarsine*) being obtained as a colourless liquid, b. p. 156°/20 mm. (Found: C, 41·8; H, 5·3. $C_{10}H_{16}As_2$ requires C, 41·9; H, 5·6%). Yield, 6 g.

o-*Phenylenebis*(*di*-n-*butylarsine*), similarly prepared, was obtained as a colourless liquid, b. p. 245—247°/20 mm., 168—172°/0·05 mm. (Found: C, 58·6; H, 8·6. $C_{22}H_{40}As_2$ requires C, 58·1; H, 8·9%). The yield, 16 g., was much higher than that of the methyl arsine, owing presumably to the greater resistance to oxidation.

Ethylene-αβ-*bis*(*phenylarsonic acid*) (V) was prepared by the following modification of Quick and Adams's method (*loc. cit.*). Phenyldichloroarsine (64 g., 2 mols.) and ethylene dibromide (27 g., 1 mol.) were in turn cautiously added to cold 10N-aqueous sodium hydroxide solution (120 c.c., 8 mols.) with vigorous stirring, and the mixture then boiled under reflux with continual stirring for 5 hours; at the end of each of the first two hours, more dibromide (7 and 5 c.c. respectively) was added. The mixture was cooled, and concentrated hydrochloric acid added until the colour of phenolphthalein was completely discharged. Sodium halide and all the unchanged phenylarsenoxide separated from the solution, and were removed. Concentrated hydrochloric acid was then cautiously added to the well-stirred solution until the latter was *just* acid to Congo-red paper, all the bis(phenylarsonic acid) thus being precipitated as fine white crystals (22 g.): rapid addition or excess of hydrochloric acid gave a sticky product difficult to manipulate. A small quantity, recrystallised from 50% aqueous alcohol, had m. p. 210—212°; Quick and Adams give 209—211° (Found: C, 42·6; H, 3·9. Calc. for $C_{14}H_{16}O_4As_2$: C, 42·2; H, 4·0%).

Ethylene-αβ-*bis*(*phenylchloroarsine*) (VI).—Concentrated hydrochloric acid (360 c.c.) was added to a suspension of the powdered phenylarsonic acid (36 g.) in water (540 c.c.), the mixture thoroughly shaken, and water (720 c.c.) at once added, giving an almost clear solution. This was filtered, and the filtrate chilled in ice. Potassium iodide (1 g.) dissolved in water (10 c.c.) was added, and sulphur dioxide passed through the solution for 1½ hours. The yellow oily product which separated finally became solid. After standing for 48 hours, the pale yellow crude *chloroarsine* (VI) was collected, washed with dilute hydrochloric acid, and dried (31 g.). This material after one recrystallisation from *cyclo*hexane (charcoal) was sufficiently pure for use in the next stage; further recrystallisation gave the pure compound as a colourless solid, m. p. 91—93° (Found: C, 41·3; H, 3·6. $C_{14}H_{14}Cl_2As_2$ requires C, 41·7; H, 3·5%).

Ethylene-αβ-*bis*(*phenyliodoarsine*).—A suspension of the powdered phenylarsonic acid (2 g.) in saturated aqueous potassium iodide (10 c.c.) was diluted with water (10 c.c.), followed by concentrated hydrochloric acid (1 c.c.), cooled in ice, and then sulphur dioxide passed through until the solution was decolorised. More hydrochloric acid (1 c.c.) was added, and passage of gas continued until the solid product, detached from the walls of the vessel and broken up, gave an iodine-free powder. Hydrochloric acid (6 c.c.) was again added, and ultimately much fine sulphur was precipitated. The mixture of the iodoarsine and the sulphur was collected, dried, and the iodoarsine extracted with warm benzene. Evaporation of the latter gave an oil which ultimately solidified; it was recrystallised from *cyclo*hexane, and the *iodoarsine* obtained as yellow crystals, m. p. 82° (Found: C, 28·2; H, 2·4. $C_{14}H_{14}I_2As_2$ requires C, 28·7; H, 2·4%).

Ethylene-αβ-bis(diphenylarsine).—A reaction occurs between the chloroarsine and ether at room temperature, giving a brown product, but not apparently at 0°: hence the use of the following benzene solution. A solution of the chloroarsine (20 g.) in benzene (120 c.c.) was added very slowly to a Grignard reagent prepared from magnesium (4·2 g.) and bromobenzene (27·6 g., 3·5 mols.) in ether (90 c.c.), the mixture being stirred and cooled throughout. It was kept for 15 minutes, boiled under reflux for 30 minutes, cooled, and hydrolysed with a solution of ammonium chloride (30 g.) in water (200 c.c.), followed by dilute hydrochloric acid (20 c.c.). The organic layer was collected and dried, and the solvent removed under reduced pressure below 100°; the warm liquid residue was poured into alcohol (100 c.c.) with stirring to precipitate the solid *bis(diphenylarsine)*, which on recrystallisation from alcohol gave colourless crystals, m. p. 99—102° (Found: C, 64·5; H, 5·0. $C_{26}H_{24}As_2$ requires C, 64·2; H, 5·0%). Yield, 15 g.

*Ethylene-αβ-bis(phenyl-*n*-butylarsine)* (VII).—Butyl bromide (24 g.) was substituted for bromobenzene in the above preparation. After hydrolysis, the dried organic layer was distilled as before, and the residue heated to 150° at 20 mm. pressure for 30 minutes. It was then finally distilled at greatly reduced pressure. The *phenylbutylarsine* was obtained as a colourless liquid, b. p. 184—188°/0·06 mm. (Found: C, 59·1; H, 6·9. $C_{22}H_{32}As_2$ requires C, 59·15; H, 7·2%). Yield 18 g. When distillation was attempted at 20 mm. pressure, decomposition of the arsine occurred at *ca.* 245°.

*α- and β-Forms of Ethylene-αβ-bis(phenylmethyl-*n*-butylarsonium picrate)* (VIII).—When the compound (VII) (20 g.) and methyl iodide (103 g., 16 mols.) were mixed in a flask fitted with a reflux condenser, the mixture rapidly became warm, and later a cloudy emulsion was formed. After 1 hour, when a quantity of a red syrup had separated, more methyl iodide (103 g.) was added, and the mixture was boiled under reflux for 1 hour, and then transferred to a basin. When cold, the excess of methyl iodide was decanted, and the residual syrup placed in a vacuum until it formed a hard, dry, glassy mass. This crude bis(methiodide) became sticky in damp air, and could not be satisfactorily crystallised from any of the usual solvents. It was therefore dissolved in a warm mixture of alcohol (200 c.c.) and water (120 c.c.), and this was vigorously stirred while an excess of a saturated solution of sodium picrate in aqueous alcohol (1 : 1 by vol.) was slowly added. (To prevent the arsonium picrate separating first as an oil, it is advisable to perform the preparation in dilute solution on a test-tube scale to obtain the solid picrate, and then to seed the main mixture with this material as the sodium picrate is added.) The crude yellow picrate was then collected, washed with alcohol and much water, and dried. Yield, 40 g. (theoretical, 44 g.).

The β-picrate. Ethyl alcohol proved the most satisfactory solvent for the separation of the two picrates, but even in it the difference in solubility of the two isomerides was not large. The dry mixed picrates (40 g.) were extracted six times with boiling alcohol (500 c.c. each time). Each boiling extract was filtered, and successive crops of picrate were collected from the cold filtrates: the six crops had m. p.'s 110—115°, 110—116°, 110—118°, 108—118°, 110—123°, 111—125°. The undissolved residue was then recrystallised from a large volume of alcohol, and a crop (8 g.) rich in the less soluble β-picrate and of m. p. 131—135° thus obtained. This was extracted twice more with boiling alcohol, the extracts giving two crops of m. p.'s 124—132° and 128—137°, whereas the undissolved residue, again recrystallised from much alcohol, gave a fraction of m. p. 138—140°. The latter was finally extracted once more with boiling alcohol, the filtrate depositing a fraction of m. p. 135—139°, and the undissolved residue was then twice recrystallised from alcohol, the pure *β-picrate* being thus obtained as bright yellow crystals, m. p. 139·5—140·5° (Found: C, 46·2; H, 4·3; N, 9·4. $C_{24}H_{38}As_2,2C_6H_2O_7N_3$ requires C, 46·3; H, 4·5; N, 9·1%).

The α-picrate. This was most satisfactorily isolated by uniting the crops which separated from the first four of the above extracts, boiling them with alcohol until only a small proportion remained undissolved, and then allowing the hot filtrate to cool spontaneously with stirring to 40°, the picrate which had then crystallised being collected: cooling to room temperature before filtration appeared to contaminate the product with traces of a more soluble impurity. The process was repeated with the fraction so obtained until yellow crystals of pure α-*picrate*, m. p. 113—115°, resulted (Found : C, 46·4; H, 4·2; N, 9·3%). A mixture of equal quantities of the α- and the β-picrate had m. p. 114—123°.

α- *and* β-*Forms of Ethylene*-αβ-*bis*(*phenyl*-n-*butylarsine sulphide*) (IX).—*The* β-*sulphide.* Bromine (3·6 g., 2 mols.) was cautiously added to a solution of ethylenebis(butylphenylarsine) (5 g.) in chloroform (100 c.c.). A few drops of water were added, and a stream of hydrogen sulphide, washed with water, was passed through the solution for 17 hours. (The presence of water appears to be essential to obtain a crude product rich in the β-sulphide. If the reagents are carefully dried, the product is largely α-sulphide.) Spontaneous evaporation gave an oil which was contaminated with hydrogen bromide but rapidly solidified in a vacuum : if complete solidification did not occur, the reaction was incomplete, and the product was redissolved in chloroform and again treated with hydrogen sulphide. The solid was twice extracted with boiling *cyclo*hexane (40 c.c.) and the undissolved residue then recrystallised from *cyclo*hexane (charcoal), a product of m. p. 108—115°, consisting mainly of the *cyclo*hexane addition derivative of the β-sulphide, being thus obtained. This product was twice recrystallised from ether, and the white crystals were then heated in a vacuum at 110° for 30 mins. to remove ether of crystallisation: the pure β-*sulphide*, m. p. 120·5—121·5°, was thus obtained (Found : C, 51·5; H, 6·2; *M*, ebullioscopic in 2·02% benzene solution, 512; in 2·06%, 485. $C_{22}H_{32}S_2As_2$ requires C, 51·7; H, 6·3%; *M*, 510). When the pure β-sulphide was recrystallised from *cyclo*hexane, white crystals of the *addition product* were obtained (Found : C, 53·85; H, 6·9; S, 12·0. $3C_{22}H_{32}S_2As_2,C_6H_{12}$ requires C, 53·5; H, 6·75; S, 11·9%); this was unaffected by prolonged exposure in a vacuum at room temperature; when slowly heated, however, it lost *cyclo*hexane, and the pure β-sulphide remaining had m. p. 120—121°, but the addition product melted immediately when plunged into a bath at 114°. When the partly purified product from the above preparation was repeatedly recrystallised from *cyclo*hexane, instead of from ether, the same pure addition product was ultimately obtained; recrystallisation from ether gave, however, the most rapid purification. A small quantity of the more soluble α-sulphide was isolated from the first *cyclo*hexane extraction liquor.

The α-*sulphide.* A solution of the arsine (3 g.) in chloroform (45 c.c.) was treated as before with bromine (0·7 c.c.). A mixture of powdered sodium sulphide nonahydrate (4·8 g., 3 mols.) and alcohol (250 c.c.) was warmed until a cloudy solution was obtained, and hydrogen sulphide passed through until the temperature had fallen to 25°. The chloroform solution was then added, and the mixture kept for at least 3 hours. The filtered solution was concentrated at 15 mm. pressure to about one-quarter of its original volume, and finally taken to dryness in a vacuum. The residue was extracted with cold water, dried, and then recrystallised from *cyclo*hexane (charcoal), a product of m. p. 88—92° and consisting chiefly of the *cyclo*hexane addition product of the α-sulphide being thus obtained. The isolation of the pure α-sulphide from this product was difficult, owing to the conversion α → β which occurs in hot solvents. It was finally achieved by rapidly extracting this product with insufficient hot *cyclo*hexane to give a complete solution, and then at once cooling the filtrate. The crystals so obtained were then extracted with sufficient boiling petrol (b. p. 60—80°) to dissolve about half the material; the filtrate was again rapidly cooled, and the product which separated was then finally recrystallised from *cyclo*hexane. White acicular crystals of the *addition product* of the pure α-sulphide and *cyclo*hexane, m. p. 87—89°, were thus obtained (Found : C, 52·7; H, 6·5; S, 12·2. $6C_{22}H_{32}S_2As_2,C_6H_{12}$ requires C, 52·65; H, 6·5; S, 12·2%).

This addition product was unaffected when heated at 60° in a stream of dry air at 15 mm. pressure for 6 hours (Found : C, 52·8; H, 6·6%). The *cyclo*hexane was therefore removed by recrystallising the product from ether, the white needles so obtained being then heated at 75°/15 mm. for 1 hour to eliminate ether of crystallisation; the pure α-*sulphide*, m. p. 113—116°, was thus obtained (Found : C, 51·7; H, 6·45%; *M*, ebullioscopic in 0·834% benzene solution, 480. The α-sulphide was recovered unchanged from the benzene solution and hence no appreciable conversion into the β-form had occurred during the determination). The pure β-sulphide was also isolated in small yield from the *cyclo*hexane residues from the above preparation.

Success in isolating the pure α-sulphide in the above preparation depends chiefly upon obtaining an initial product rich in the α-isomer, since if the β-form is present in appreciable quantities the separation of the α-sulphide becomes very difficult. It was found that if in the above preparation the alcoholic sodium sulphide solution was not saturated with hydrogen sulphide before use, a crude product containing an appreciably higher proportion of the β-sulphide was obtained.

A mixture of approximately equal quantities of the pure α- and β-sulphides had m. p. 95—103°. The α- was more soluble than the β-sulphide in all the organic solvents investigated.

Conversion of the α- into the β-sulphide. A sample of the pure α-sulphide was heated in a vacuum at 110° for 45 minutes, and then had m. p. 107—113°, owing to partial conversion into the β-sulphide. The latter was then isolated by recrystallising the mixture from ether and drying the product at 75°/15 mm. for 1 hour; an almost pure sample of the β-sulphide, m. p. 119—120°, was thus obtained. A mixture of this sample with some pure α-sulphide had m. p. 95—108°.

This thermal conversion of the α- into the β-sulphide at 110° may possibly occur to a slight extent during a determination of the m. p. of the former, and may account for the range of 3° in the m. p. of pure samples of the α-sulphide.

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