247. *Derivatives of* cyclo-2 : 5-*Dithia*-3 : 4-*dimethylenestibine.*

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In view of the recent publication of the preparation of derivatives of *cyclo*-2 : 5-dithia-3 : 4-dimethylenearsine (Cohen, King, and Strangeways, J., 1931, 3056) it seems advisable to publish a preliminary account of an investigation which was designed to discover a type of derivative containing an asymmetric antimony atom suitable for resolution.

When 1 : 2-dimercaptoethane (1 mol.) was added to a hydrochloric acid solution of antimony chloride (1 mol.), 1-*chloro*cyclo-2 : 5-*dithia*-3 : 4-*dimethylenestibine*, $\begin{matrix}CH_2\cdot S\\ CH_2\cdot S\end{matrix}\!\!>\!SbR$ (I; R = Cl), was deposited. Treatment with hydrogen peroxide gave the hydrated *oxychloride* as an amorphous precipitate. Both compounds were hydrolysed slowly by hot alkalis or acids.

Attempts were then made to surround the antimony by sulphur atoms. The chloride (I; R = Cl) and thiolacetic acid (or its disodium salt) in alcoholic solution gave no crystalline product, but in warm pyridine the *pyridine* salt of *cyclo*-2 : 5-dithia-3 : 4-dimethylenestibine-1-thiolacetic acid was formed. The acid itself could not be obtained pure.

m-Thiolbenzoic acid condensed with the chloride (I; R = Cl) on one occasion to give 1-m-*carboxyphenylthiol*cyclo-2 : 5-*dithia*-3 : 4-*dimethylenestibine* (I; R = $S\cdot C_6H_4\cdot CO_2H$), but in subsequent preparations an insoluble product was obtained instead.

Compounds containing a phenyl group attached to the antimony atom were obtained by the action of the corresponding phenyldi-iodostibines on the mercaptan. *p*-Tolyldichlorostibine (Hausen-

baumer, *Ber.*, 1898, **31**, 2914), easily obtained by the reduction of *p*-tolylstibonic acid with stannous chloride, condensed with 1 : 2-dimercaptoethane in methyl alcohol to give dimorphous 1-p-*tolyl*-cyclo-2 : 5-*dithia*-3 : 4-*dimethylenestibine* (I; R = *p*-C_7H_7).

All efforts to prepare *p*-carboxyphenylstibonic acid directly from *p*-aminobenzoic acid were in vain. The methyl ester, however, reacted readily, and the product was reduced with stannous chloride and hydrochloric acid to *p*-carbomethoxy(or *p*-carboxy)phenyldiiodostibine. This on treatment with methyl-alcoholic 1 : 2-dimercaptoethane yielded at first a crystalline compound the nature of which was not completely determined. When warmed with sodium carbonate solution, this dissolved, and dilute acids threw out the free *acid* (I; R = *p*-$C_6H_4{\cdot}CO_2H$). In subsequent preparations the free acid was obtained directly together with a trace of the first compound. The compound was readily convertible into the antimonic state, and it is thought that an analogous derivative from an unsymmetrical mercaptan, when converted into its oxide or sulphide, would be suitable for an attempted resolution.

EXPERIMENTAL.

1-*Chloro*cyclo-2 : 5-*dithia*-3 : 4-*dimethylenestibine* (I; R = Cl).—Antimony trichloride (7·5 g.) was dissolved in the minimum quantity of cold concentrated hydrochloric acid, 3·1 g. of 1 : 2-dimercaptoethane added, and the mixture heated on the water-bath for 15—20 minutes. The crystalline powder was collected and washed with water; a further 0·3 g. was deposited by the mother-liquor (total yield, 7·6 g.; 93%). The *substance* dissolved slowly in boiling alcohol and crystallised from hot benzene in needles, often several cm. long, m. p. 124° (Found: Sb, 48·5. $C_2H_4ClS_2Sb$ requires Sb, 48·6%). The crude product rapidly became yellowish-red in light, but the pure substance coloured only after prolonged exposure. When it was treated (0·7 g.) in boiling alcohol (20 c.c.) with a slight excess of perhydrol, a white *precipitate* immediately formed, which was washed with spirit (Found: Sb, 42·95. $C_2H_4OClS_2Sb,H_2O$ requires Sb, 42·85%).

Pyridine cyclo-2 : 5-*Dithia*-3 : 4-*dimethylenestibine*-1-*thiolacetate*.—The chloride (I; R = Cl) (2·5 g.) and thiolacetic acid (2·0 g.) were heated in pyridine (4 c.c.) on the water-bath for 2 hours and cold water was then slowly introduced until crystallisation commenced. The crystals were filtered off when cold and washed with water; further dilution of the mother-liquor gave a small additional yield (total, 2·5 g.); m. p. 101° (Found: Sb, 31·2. $C_4H_7O_2S_3Sb,C_5H_5N$ requires Sb, 31·6%). The substance could not be recrystallised satisfactorily.

Condensation of the Chloride (I; R = Cl) *with* m-*Thiolbenzoic Acid.*—A solution of the freshly prepared acid (0·30 g.) in rectified spirit (10 c.c.) containing 3·9 c.c. (2 mols.) of *N*-sodium hydroxide was added slowly to a solution of the chloride (0·43 g.) in boiling spirit (30 c.c.). The mixture was heated on the water-bath for a few minutes and poured into 100 c.c. of hot water (stage A). Addition of 2·5 c.c. of *N*-hydrochloric acid and cooling produced needles, which were washed with water and cold alcohol and dissolved in hot alcohol. The filtered solution was quickly cooled, freed from a small deposit of impurity, evaporated somewhat, and allowed to crystallise. The *product* was recrystallised from spirit and obtained as colourless, highly crystalline nodules. It was acidic (Found: Sb, 33·3. $C_9H_9O_2S_3Sb$ requires Sb, 33·2%).

In subsequent preparations a precipitate was obtained at the stage marked (A), *e.g.*, 0·35 g. from 0·41 g. of *m*-thiolbenzoic acid and 0·65 g. of the chloride (Found in two experiments: Sb, 53·2, 52·9. $C_2H_4S_2Sb{\cdot}OH$ requires Sb, 52·7%). It was hydrolysed by hot dilute sulphuric acid to 1 : 2-dimercaptoethane and antimony chloride.

p-*Tolyldichlorostibine.*—A solution of 32 g. of *p*-toluidine in 75 c.c. of hydrochloric acid and 150 c.c. of water was diazotised, and 45 g. of antimony oxide in 150 c.c. of hydrochloric acid and 50 c.c. of water added. The double salt was suspended in ice-water and treated with dilute sodium hydroxide solution, butyl alcohol being used to minimise frothing. After 12 hours, the filtered liquid was acidified and the precipitate produced was washed, nearly dried at 100°, and dissolved in 150 c.c. of warm hydrochloric acid. Water (100 c.c.) was added to remove coloured impurities, and the filtrate treated with ammonium chloride and hydrochloric acid. The double salt was washed with hydrochloric acid and decomposed by water (1 l.), and the precipitate dried. 10 G. of this *p*-tolylstibonic acid, dissolved in 30 c.c. of concentrated hydrochloric acid and 10 c.c. of water, were reduced with 10 g. of stannous chloride in 30 c.c. of acid. The *p*-tolyldichlorostibine, which crystallised, had m. p. 93·5° after two crystallisations from methyl alcohol containing a trace of hydrochloric acid.

1 - p - *Tolyl*cyclo - 2 : 5 - *dithia* - 3 : 4 - *dimethylenestibine* (I; R = *p*-C_7H_7).—*p*-Tolyldichlorostibine (9·0 g.) and 3·0 g. of 1 : 2-dimercaptoethane in 30 c.c. of methyl alcohol gave 6·0 g. of precipitate and a further 2·5 g. on standing (total yield, 88%). The *compound*, washed with methyl alcohol and recrystallised from light petroleum (b. p. 40—60°), was obtained as a mixture of long needles and small nodules, m. p. 90°. The former passed into the latter on standing with the mother-liquor. By seeding solutions with either form,

the compound was easily made to crystallise in that form alone (Found : Sb, 40·4. $C_9H_{11}S_2Sb$ requires Sb, 39·8%).

p-*Carboxy*(or *carbomethoxy*)*phenylstibonic Acid.*—Methyl *p*-aminobenzoate (7·5 g.) in hydrochloric acid (20 c.c.) and water (20 c.c.) was diazotised (sodium nitrite, 3·5 g.), and the filtered solution treated with antimony trioxide (7·0 g.) in hydrochloric acid (30 c.c.). The solid cake obtained was stirred in ice-cold water (1 l.) while a large excess of sodium hydroxide was slowly added. After 2—3 hours, the liquid was filtered, acidified, and refiltered. The dark brown powder (7·5 g.) obtained after drying was dissolved in a hot mixture of concentrated hydrochloric acid (25 c.c.) and methyl alcohol (25 c.c.) and water was slowly added until the material being precipitated lost its black colour. The tar was removed, and the acid (7·0 g.) precipitated from the filtrate by addition of water (1 l.).

p-*Carboxy*(or *carbomethoxy*)*phenyldi-iodostibine.*—6·0 G. of the above crude acid were dissolved in hydrochloric acid (18 c.c. with 6 c.c. of water) on the water-bath, and to the cooled, deep brick-red solution 5 g. of stannous chloride in 18 c.c. of hydrochloric acid were added. Tar was removed, now and after 12 hours, and to the filtrate potassium iodide solution was added until no more precipitate formed. This was oily at first but finally solidified; after being washed with water and dried in a vacuum, it sintered at 107° and melted at 120—132°. It could not be obtained pure.

Condensation with 1 : 2-*dimercaptoethane.* A solution of the crude di-iodide (5 g.) in boiling methyl alcohol (20—30 c.c.) was chilled, 1·0 g. of 1 : 2-dimercaptoethane added, and the white precipitate filtered off and recrystallised three or four times from glacial acetic acid; m. p. 138° (Found : C, 31·3; H, 2·9; Sb, 32·4. The methyl ester, $C_{10}H_{11}O_2S_2Sb$, requires C, 34·5; H, 3·2; Sb, 34·8%. Atomic ratios found, C : Sb : H = 10 : 1·02 : 11·1). Sufficient material for further work was not available. The compound was non-acidic, but dissolved in hot sodium carbonate solution to give the sodium salt of an *acid*, m. p. 199°, which could be precipitated by hydrochloric acid. This acid was obtained as the main product of the foregoing preparation in subsequent experiments (with a different sample of di-iodide) together with small quantities of the compound, m. p. 138°. It crystallised from acetic acid, being much less soluble than the previous compound [Found : Sb, 36·5; equiv. by titration with sodium hydroxide, 267 (at room temperature), 299 (at 0°), 236 (by heating with excess of sodium hydroxide on the water-bath for a few minutes, and back-titration with acid). $C_9H_9O_2S_2Sb$ requires Sb, 36·2%; equiv., 334]. An acetic acid solution reacted readily with 1 mol. of iodine and a microcrystalline precipitate, probably of the stibinic oxide (halogen-free), separated.

Treatment with iodine (1 mol.) in chloroform gave long needles, m. p. 164—170°, containing iodine, but satisfactory analytical figures could not be obtained.

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