

288. *The Configuration of Heterocyclic Antimony Compounds. Part IV.* Attempts to obtain 9-Stibiafluorene Oxides for Resolution Experiments.*

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The considerable optical stability of 9-stibiafluorenes led to the hope that oxides of such compounds could be similarly resolved, but they appeared to form dihydroxides which could not be dehydrated.

EARLIER Parts * describe the synthesis and optical resolution of substituted stibiafluorenes in which the antimony atom is trivalent, and we proposed to extend the work to the quadricovalent stibiafluorene oxides, since optical resolution of oxides of the type $abcMO$, where M is a member of Group VB, has been achieved only when M is nitrogen or phosphorus. Attempts to resolve arsine oxides have uniformly failed except for 2-carboxy-10-phenyl-phenoxarsine 10-oxide,¹ and the enantiomers of this oxide, $[\alpha]_D +36^\circ$ and -29° (in dilute ammonia), are readily racemised, in striking contrast to the marked optical stability of the unoxidised phenoxarsine. In commenting on this, Leslie suggested that the most probable cause was the hydration of the oxide to dihydroxide, a possibility which has been referred to more recently² where the failure to isolate enantiomers is ascribed to the possible conversion $(abcAs\cdot OH)X \longrightarrow abcAsO$ through the dihydroxide $abcAs(OH)_2$. The dihydroxides, if covalent, would be expected to possess the symmetrical trigonal bipyramidal configuration but, if ionic, would be tetrahedral and give a tetrahedral oxide.

The considerable optical stability of the 9-stibiafluorenes³ encouraged us to investigate the oxides of this type of molecule, particularly as in the synthesis of the unsymmetrically substituted compounds, the product of cyclisation of the 2-diphenylstibinic acid (I) was presumed to be the oxide (II), although this intermediate was usually reduced without characterisation to the corresponding stibiafluorene. Only in one case was the intermediate purified by crystallisation (from ethyl acetate), and then analysis indicated it to be the oxide (II; $R = H$, $R' = CO_2Et$)⁴. However, on examining the product of cyclisation of the acids (I; $R = OMe$, $R' = CO_2Et$; and I; $R = O\cdot CH_2CO_2Et$, $R' = Me$), it was found that the cyclic product was, in each case, the dihydroxide (III). These

* Part III, *J.*, 1955, 1662.

¹ Leslie, *J.*, 1939, 1050.

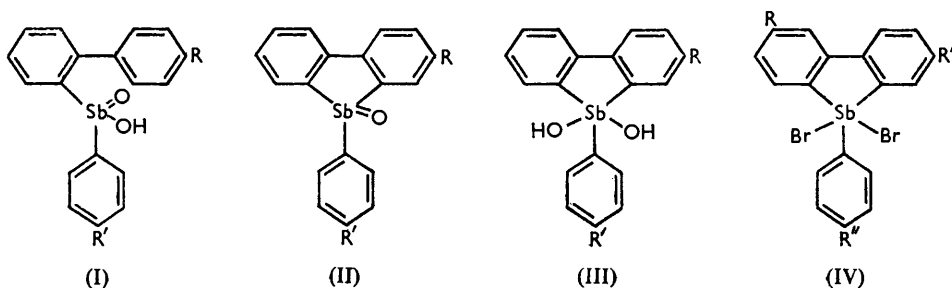
² Hart and Mann, *J.*, 1955, 4107.

³ (a) Campbell and Poller, *J.*, 1956, 1195; (b) Campbell and Morrill, *J.*, 1955, 1662.

⁴ Campbell, *J.*, 1952, 4448.

dihydroxides did not tend to lose water to form the oxides, despite prolonged heating at 100° under vacuum.

In an attempt to avoid the use of acetic anhydride which might encourage the retention of hydroxyl groups by acetylation, cyclisation was attempted with "polyphosphoric acid," a very successful reagent in the arsenic series;^{3a} but when the stibinic acid (I;



R = O·CH₂·CO₂Et, R' = Me) was so treated, extensive decomposition occurred and 4-diphenylloxyacetic acid, m. p. 190°, was the sole product identified.

Another method recommended for the preparation of stibinic oxides is treatment of stibine dibromides with alcoholic alkali,⁵ and this method was applied to 2-carboxy-9-*p*-tolyl-, 3-bromo-9-*p*-tolyl- and 3-bromo-9-*p*-ethoxycarbonylphenyl-9-stibiafluorene. The dibromides (IV) separated readily on addition of bromine to the stibiafluorenes in chloroform, carbon tetrachloride, or benzene, but possessed the property, which seems to be characteristic of stibine halides,⁶ of retaining solvent of crystallisation. Consistent analyses were obtained only when carbon tetrachloride was used for both preparation and recrystallisation. Treatment of the dibromides (IV; R = Br, R' = H, R'' = CO₂Et) and (IV; R = Br, R' = H, R'' = Me) with warm alcoholic alkali gave oxides which retained two molecules of water even after prolonged vacuum-drying at 100°. [The dibromide (IV; R = H, R' = CO₂H, R'' = Me) gave an insoluble product, m. p. >310° and apparently polymeric.]

As three of the five compounds investigated yield products of this composition it is tempting to suggest that these are solid complexes of the structure H⁺[Ar₃Sb(OH)₃]⁻, and the solubility of the compound from the dibromide (IV; R = Br, R' = H, R'' = Me) in dilute aqueous alkali supports the idea. Triphenylstibine dihydroxide, Pb₃Sb(OH)₂, also dissolves in dilute alkali and may form the same type of salt, Na⁺[Ph₃Sb(OH)₃]⁻, the corresponding complex acid losing water on isolation.

A final attempt to obtain an oxide by treatment of 2-carboxy-9-*p*-tolyl-9-stibiafluorene in glacial acetic acid with hydrogen peroxide again produced insoluble material, m. p. >310°, and when the (–)-isomer was used, complete racemisation occurred.

The tendency for the stibiafluorene oxides to form extremely stable hydrates is evidently shared by triarylstibine oxides in general. For example, triphenylstibine oxide has apparently never been isolated; the dihydroxide is stable up to its m. p., 212°. Further, the formulæ given for many such "oxides" show that, to comply with analysis, one and occasionally more than one molecule of water has to be included.⁸ In the stibiafluorene series this property is so pronounced that successful optical resolution of a member seems remote, for, even if a true oxide could be prepared, the process of resolution, involving salt formation and decomposition, would almost certainly convert the oxide into the hydrated form, and consequently no attempts have been made.

⁵ Christiansen, "Organic Derivatives of Antimony," Chem. Catalog Co., 1925, p. 38.

⁶ Worrall, *J. Amer. Chem. Soc.*, 1930, **52**, 2046; Campbell and White, *J.*, 1958, 1184.

⁷ May, *J.*, 1910, **97**, 1956.

⁸ Newton Friend, "Textbook of Inorganic Chemistry," Vol. XI, Part III (Goddard), Chas. Griffin, 1936, pp. 203–209.

EXPERIMENTAL

9-p-Ethoxycarbonylphenyl-2-methoxy-9-stibiafluorene 9-Dihydroxide.—*p*-Ethoxycarbonylphenyl-4'-methoxy-2-diphenylstibinic acid (7.5 g.) was cyclised as previously described^{3b} and the product (6.7 g.) was extracted with acetone. The insoluble residue (0.6 g.), m. p. 285—290° (decomp.), was the *dihydroxide* of the free acid (Found: C, 52.4; H, 4.0. $C_{26}H_{17}O_5Sb$ requires C, 52.3; H, 3.8%). The portion soluble in acetone was regained, crystallised from ethyl acetate-ethanol, and proved to be the *ester dihydroxide*, m. p. 185—188° (Found: C, 54.6; H, 4.3; Sb, 24.9. $C_{22}H_{21}O_5Sb$ requires C, 54.2; H, 4.3; Sb, 25.0%). This compound (0.5 g.) was hydrolysed by boiling with ethanolic potassium hydroxide (20 ml., 4%) for 0.5 hr. and the gelatinous precipitate obtained on acidifying the diluted solution was dried (0.35 g.) and found to be identical with the free acid obtained directly from the ring closure (Found: C, 51.9; H, 4.0%). Proof that the ester and acid were both ring compounds, and not the uncyclised stibinic acids which have the same molecular formulæ, was obtained by reduction to the corresponding stibiafluorenes, m. p. 147° and m. p. 231°, respectively. For comparison, the uncyclised stibinic acid was reduced under the same conditions and gave *p-ethoxycarbonylphenyl-4'-methoxy-2-diphenylstibinous chloride*, m. p. 96° (Found: C, 54.4; H, 4.0. $C_{22}H_{20}O_3ClSb$ requires C, 54.0; H, 4.1%).

2-Carboxymethoxy-9-p-tolyl-9-stibiafluorene 9-Dihydroxide.—Ring closure of the required stibinic acid (5 g.), as in the previous experiment, gave a mixture (4.5 g.) which on crystallisation gave fractions of indefinite m. p. ranging from 200° to 260°. Reduction proved that this material was largely the cyclic compound, as 2-ethoxycarbonylmethoxy-9-*p*-tolyl-9-stibiafluorene was obtained in 70% yield, m. p. 132—133°, alone or mixed with an authentic sample.^{3b} The crude product (3.3 g.) in ethanol (110 ml.) was boiled with 10% aqueous potassium hydroxide (33 ml.) for 0.5 hr., and the diluted solution acidified to Congo Red with dilute sulphuric acid. The dry product was purified by solution in aqueous sodium hydrogen carbonate and reprecipitation, as no suitable solvent could be found for crystallisation. After drying at 100°/15 mm. for prolonged periods, the acid had m. p. 276° (decomp.), and appeared to be the *dihydroxide monohydrate* (Found: C, 51.7; H, 4.7. $C_{21}H_{19}O_5Sb \cdot H_2O$ requires C, 51.4; H, 4.3%). Repetition of the ring closure gave a solid which, after crystallisation from ethanol-chloroform, proved to be the *ester dihydroxide*, m. p. 148—150° (decomp.) (Found: C, 54.5; H, 4.5. $C_{23}H_{23}O_5Sb$ requires C, 55.1; H, 4.6%). Hydrolysis of this ester gave an acid which was crystallised once from ethanol and had m. p. 276° (decomp.), but could not be recrystallised from the same solvent (Found: C, 51.7; H, 4.2%).

Attempted Cyclisation by Means of "Polyphosphoric Acid."—The stibinic acid (I; R = O-CH₂·CO₂Et, R' = Me) (1 g.) was added to polyphosphoric acid (5 g.), warmed to 160° for 3 min., cooled, and poured into water (100 ml.). The product (0.56 g.) was extracted with acetone (10 ml.), leaving a residue (0.2 g.) which contained antimony and had m. p. >330°, but was not further identified. The fraction soluble in acetone, after crystallisation from benzene, had m. p. 190—190.5° and was almost certainly 4-diphenylloxyacetic acid (m. p. 189—190°)⁹ (Found: C, 72.9; H, 5.4. Calc. for C₁₄H₁₂O₃: C, 73.7; H, 5.3%).

Stibiafluorene Dibromides (IV).—The stibiafluorene (0.5 g.) was dissolved in the minimum of carbon tetrachloride, cooled to 0°, and the calculated quantity of bromine added from a micro-pipette. The dibromide separated almost immediately (0.4—0.5 g.) and was recrystallised from carbon tetrachloride. The *dibromide* (IV; R = H, R' = CO₂H, R'' = Me) had m. p. 195° (decomp.) (Found: C, 34.4; H, 2.1. $C_{20}H_{15}O_2Br_2Sb \cdot CCl_4$ requires C, 34.9; H, 2.1%); (IV; R = Br, R' = H, R'' = Me) had m. p. 190°, with slight previous shrinkage (Found: C, 31.6; H, 2.2; Sb, 16.1. $C_{19}H_{14}Br_3Sb \cdot CCl_4$ requires C, 31.7; H, 1.9; Sb, 16.1%); and (IV; R = Br, R' = H, R'' = CO₂Et) had m. p. 188—189° again with previous shrinkage but no obvious decomposition (Found: C, 32.8; H, 2.0; Sb, 15.0. $C_{21}H_{16}O_2Br_3Sb \cdot CCl_4$ requires C, 32.4; H, 2.0; Sb, 14.9%). Analysis of these compounds by the modified Stepanow method¹⁰ gave weights of mixed silver halide representing only 70—90% of the calculated total, presumably because some loss of carbon tetrachloride occurred during decomposition. The *ester dibromide* (IV; R = Br, R' = H, R'' = CO₂Et) was recrystallised thrice from benzene and then had m. p. 194—195° (Found: C, 40.0; H, 2.7. $C_{21}H_{16}O_2Br_3Sb \cdot \frac{1}{2}C_6H_6$ requires C, 40.2; H, 2.6%). The same product was isolated directly when bromination was carried out in benzene.

⁹ Clark, "Semi-micro Quantitative Organic Analysis," Academic Press, 1943, p. 53.

¹⁰ Chem. Abs., 1946, 40, 1474.

Hydrated Stibiafluorene Oxides.—The dibromide (0.2—0.5 g.) was dissolved in 10% alcoholic sodium hydroxide (5 ml.) and warmed to 60° for 10 min., and the product isolated by acidification. In the case of (IV; R = H, R' = CO₂H, R'' = Me) the gelatinous precipitate obtained was purified by dissolution in aqueous sodium hydrogen carbonate and reprecipitation, and when dried *in vacuo* at 100° had m. p. >310° (Found: C, 44.4, 43.8; H, 3.5, 3.8. C₂₀H₁₇O₄Sb requires C, 54.2; H, 3.9%). The product from (IV; R = Br, R' = H, R'' = Me), after recrystallisation from ethyl acetate-ethanol, had m. p. 275—280° (Found: C, 46.1; H, 3.9. C₁₉H₁₆O₂BrSb,H₂O requires C, 46.0; H, 3.7%), and that from (IV; R = Br, R' = H, R'' = CO₂Et) had m. p. 302—304° (Found: C, 45.2; H, 3.4. C₂₁H₁₈O₄BrSb,H₂O requires C, 45.5; H, 3.6%).

Attempted Oxidation by Hydrogen Peroxide.—2-Carboxy-9-*p*-tolyl-9-stibiafluorene (0.1 g.) was dissolved in glacial acetic acid (3 ml.), and then hydrogen peroxide (100-vol.; 1 ml.) was added at room temperature. The precipitate which separated immediately was filtered off after 30 min. and when dried at 100° (vac.) had m. p. >310° (Found: C, 49.2; H, 3.4%). When this experiment was repeated with the (–)-isomer, [α]_D –245.7° (c 0.25 in pyridine), the precipitate obtained had m. p. >310°, [α]_D = 0° (c 0.285 in pyridine; *l* = 2).

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