605. *The Configuration of Heterocyclic Antimony Compounds. Part I. Preparation of 9-Stibiafluorenes and Optical Resolution of 2-Carboxy-9-p-tolyl-9-stibiafluorene.*

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The synthesis of substituted 9-stibiafluorenes by ring closure of 2-diphenylylarylstibonous acids is described. 2-Carboxy-9-*p*-tolyl-9-stibiafluorene has been resolved into (+)- and (−)-forms by means of (+)- and (−)-α-phenylethylamine and the optically active acids, $[\alpha]_D^{20}$ ±245°, are stable in pyridine at 20° but are racemised at 40°, though too slowly for accurate rate determination. The asymmetry of the molecule is due to one of two possible causes: either the stable pyramidal disposition of the three valency bonds of the antimony atom, if the tricyclic system is planar; or the twisted position of the two benzene rings in the tricyclic system, which deprives the molecule of any symmetry whether the bonds from antimony are pyramidal or planar.

The configuration of 3-covalent compounds of nitrogen, phosphorus, arsenic, and antimony is generally accepted as pyramidal. Sutherland, Lee, and Wu (*Trans. Faraday Soc.*, 1939, **35**, 1373) have determined the structural constants of phosphine and arsine using infra-red spectra. Their results show that the height of the pyramidal molecule increases, and the frequency of inversion decreases, from ammonia to arsine, and further that replacement of hydrogen by deuterium considerably lowers the frequency of inversion, that of PD_3 being reduced to one-thousandth of its value in PH_3, and that of AsD_3 to the comparatively low value of 30 per second. These authors suggest that the use of heavy organic radicals might reduce the speed of inversion of phosphorus and arsenic derivatives to such an extent that the optical resolution of asymmetric phosphines and arsines might become practicable. Although precise information is lacking, it is probable that the same considerations hold for stibine, and as antimony is a heavier atom it is likely that the frequency of inversion will be lower than that of arsine, though probably still too high for successful optical resolution of a simple stibine containing three different aryl groups. It was therefore decided to attempt the resolution of a heterocyclic stibine in which the inversion of the pyramidal configuration would be considerably inhibited.

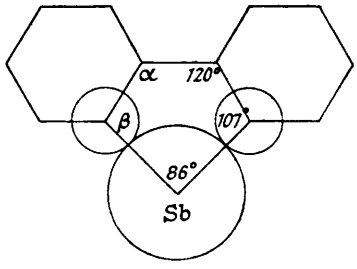
The only case of optical activity caused by the disposition of the valency bonds in a 3-covalent antimony compound is that of 10-*p*-carboxyphenyl-2-methylphenoxstibine (*J.*, 1947, 4) in which the molecule is folded about the O–Sb axis in the same way as in the phenoxarsines (Lesslie and Turner, *J.*, 1934, 1170; 1935, 1268; 1936, 730; 1938, 1001; 1949, 1183) and 5 : 10-di-*p*-tolyl-5 : 10-dihydroarsanthrene (Chatt and Mann, *J.*, 1940, 1184). Resolution of the phenoxstibine was effected by the use of strychnine, and the (+)- and (−)-acids, $[\alpha]_D$ ±77°, were stable in chloroform at 20°, but in experiments with quinine as resolving agent an apparently anomalous resolution produced an analytically pure acid, $[\alpha]_D$ −27°, which racemised slowly in chloroform at 20° with a half-life of 29 hours (unpublished results). The possible explanation of this result, that two causes of asymmetry were present, the first due to the folding of the molecule and the second due to the unstable pyramidal configuration of the tervalent antimony, was not further investigated because of the difficulties involved in the synthesis of the (±)-acid and because it seemed wiser to attempt the optical resolution of a cyclic antimony compound in which the unnecessary complication of the folded molecule was absent. The 9-stibiafluorenes (IV) were considered to be suitable for investigation.

Scale drawings of 9-stibiafluorenes, embodying the accepted dimensions for diphenyl, indicate that the antimony atom (radius 1·41 A.) can be accommodated between the two coaxial benzene rings and allow the tricyclic system to remain planar if the antimony bond angle is 86°, and the bonds from the 2- and 2′-carbon atoms of the diphenyl system are bent inwards making the angle 107° instead of 120° (see figure).

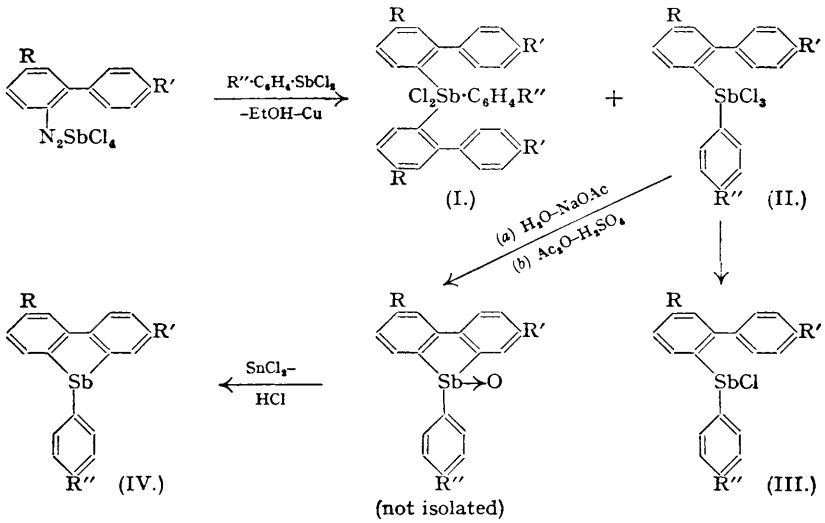
If the two benzene rings remain coplanar but not coaxial, *i.e.*, if the rings are bent away from each other and the angle α in the figure is increased from 120° to 122°, the antimony bond angle becomes 90° and the angle β is reduced to 103°. By comparison with molecules of known dimensions, these distortions of the valency angles do not seem improbable. The interbond angle in tervalent antimony compounds has been shown by electron diffraction to be about 100° in the trihalides and by *X*-ray studies to be 90° in valentinite, one of the forms of Sb_4O_6 (Wells, *Quart. Reviews*, 1948, **2**, 193). Further, it has been predicted on theoretical grounds (Stevenson, *J. Chem. Physics*, 1940, **8**, 285) that in stibine the angle should be 90° ± 1°, so that an antimony angle of 86° would probably only require two of the valency bonds to approach by 2°. Distortions of the external valency angles of the benzene-carbon atoms towards substituent atoms are known to occur. For instance, in phthalocyanine, fusion of the benzene ring with the five-membered nitrogenous ring reduces the external bond angles to 106·5° and 104° as shown by *X*-ray measurement (Robertson, *J.*, 1936, 1195), and investigation of diphenylene by both electron diffraction and *X*-ray methods has shown that it is indeed dibenz*cyclo*butadiene, so that the external angle must be 90° (*J. Amer. Chem. Soc.*, 1943, **65**, 1451; 1944, **66**, 2035).

There remains the possibility that the two benzene rings remain coaxial but not coplanar and accommodate the antimony atom with its normal bond angle by forming a twisted or " skew " molecule. To allow an antimony bond angle of 100°, 95° or 90°, the angle subtended between the two benzene rings must be 62°, 48·6°, or 31·2° respectively. This seems an improbable configuration as it involves bending the bonds from the 2- and the 2′-carbon atoms considerably out of the planes of the rings. However, if this twisted form is preferred the molecule is asymmetric whether antimony is planar or pyramidal, and a 9-stibiafluorene unsubstituted in the diphenyl residue should be capable of optical resolution. This possibility is under investigation.

The only stibiafluorenes known are those described by Morgan (*Proc. Roy. Soc.*, *A*, 1930, **127**, 1), and preliminary attempts were made to obtain 9-chloro-9-stibiafluorene (xenylenestibine chloride) by Morgan's method, and by the method used by Aeschlimann *et al.* (*J.*, 1925, 66) for the preparation of derivatives of the arsenic analogue of carbazole. As the yield of



diphenyl-2-stibonic acid from the usual Bart–Schmidt reaction on 2-aminodiphenyl was rarely more than 5%, this route proved unsuitable and the compounds were prepared according to the following scheme (cf. Bruker, *Chem. Abstr.*, 1949, **43**, 1737, 4647) :



Addition of a solution of diphenyl-2-diazonium chloride to *p*-tolylstibinous chloride in ethyl alcohol gave a yellow addition product (similar to that obtained with antimony trichloride), which decomposed on addition of a trace of copper powder to give a small quantity of the diarylstibine trichloride. Much better yields were obtained in the absence of aqueous acid. Addition of the antimony chloride double salt of diphenyl-2-diazonium chloride, filtered and washed with alcohol, to *p*-tolylstibinous chloride in alcohol in the presence of a trace of copper gave a readily separable mixture of a little di-2-diphenylyl-*p*-tolylstibine dichloride (I; R = R′ = H, R″ = Me) along with 30% of 2-diphenylyl-*p*-tolylstibine trichloride (II; R = R′ = H, R″ = Me). Ring closure of the latter could not be accomplished by heat but was effected by dehydration of the corresponding stibonous acid using acetic anhydride containing a little sulphuric acid (cf. Morgan, *Proc. Roy. Soc.*, *A*, 1933, **143**, 38). The cyclic oxide obtained was readily reduced in solution in acetone by stannous chloride in hydrochloric acid, giving 9-*p*-tolyl-9-stibiafluorene (IV; R = R′ = H, R″ = Me). When this series of reactions was carried out with 2-amino-5-bromodiphenyl and *p*-carbethoxyphenylstibinous chloride, 3-bromo-9-*p*-carbethoxyphenyl-9-stibiafluorene (IV; R = Br, R′ = H, R″ = CO_2Et) was obtained in 30—35% yield. Hydrolysis of this ester provided an acid but unfortunately the alkaloidal salts were too insoluble for attempted resolution. Finally 9-*p*-tolyl-9-stibiafluorene-2-carboxylic acid (IV; R = H, R′ = CO_2H, R″ = Me) was obtained from ethyl 2-aminodiphenyl-4′-carboxylate and *p*-tolylstibinous chloride. Alkaloidal salts of this acid also proved unsuitable for the resolution as they separated as sticky glasses or as mixtures of the free acid with the salt, and α-phenylethylamine was used as the resolving agent. Even the α-phenylethylamine salts tended to dissociate in alcohol but this difficulty was overcome by crystallising the salts from alcohol containing a little of the free base. When (−)-α-phenylethylamine was used the least soluble salt proved to be that of the (+)-acid and two recrystallisations of the first fraction gave pure (+)-acid–(−)-base, $[\alpha]_D^{19}$ +180·1°, m. p. 164—165°. The use of the (+)-base gave the enantiomeric salt, (−)-acid–(+)-base, $[\alpha]_D^{19}$ −179·2°, and the resolution of 8 g. of the (±)-acid with (+)-base allowed the isolation of the pure (−)-acid–(+)-base, $[\alpha]_{63}^{19}$ −180·1°, and (+)-acid–(+)-base, $[\alpha]_D^{19}$ +204·4°, m. p. 160—163°. Both diastereoisomeric salts crystallised as rosettes of fine needles and their melting points were too close to be of use in indicating the course of the resolution. Chloroform solutions of the salts were not optically stable and studies of the racemisation at 20° and at 40° showed abnormalities which have not yet been satisfactorily explained. The racemate isolated from solution was analytically pure. Isolation of the free acids was attempted initially by shaking the salts in chloroform solution with 4N-hydrochloric acid, the chloroform retaining no optically active product. When 2N-acid was used and the chloroform solution of the acid was examined

polarimetrically without removal of all the hydrogen chloride, rapid racemisation occurred and the half-life of the optically active acid at 20° was 30 minutes. By using 0·5N-hydrochloric acid and carefully washing and drying the chloroform, a solution of the acid having $[\alpha]_D^{20}$ −246·4° was obtained and this was optically stable at 20°. Removal of the solvent below 35° gave a specimen of the acid, very sparingly soluble in chloroform and having $[\alpha]_D^{20}$ −216° (in pyridine) which was later shown to be optically impure. The pure acids obtained by precipitation from an alcoholic solution of the salt by addition of excess 0·1N-hydrochloric acid had $[\alpha]_D^{20}$ ±245° in pyridine and were optically stable at 20° and racemised at 40°, but too slowly for accurate measurement of half-life.

Hydrochloric acid was found to be unique in catalysing the rapid racemisation observed in the initial efforts to obtain the (+)- and (−)-acids. The use of 4N-phosphoric or -sulphuric acid for the decomposition of the (−)-acid–(+)-α-phenylethylamine salt gave solutions of the acid in chloroform which showed no loss of optical activity at 20° unless, as frequently occurred, the sparingly soluble acid separated from solution. The solid acid isolated from such experiments showed slight racemisation when examined in pyridine ($[\alpha]_D^{20}$ −210° to −220°) but was analytically pure. On the other hand, the inactive product from the hydrochloric acid-induced racemisation contained chlorine, and results of carbon and hydrogen analyses were consistently low, indicating that addition of hydrochloric acid had occurred to some extent. Of the three acids used to decompose the optically active salt only hydrochloric is appreciably soluble in chloroform. This may permit the conversion of Sb^{III} into a compound $[R_3SbH]^+Cl^-$ (though no definite compounds of this type have been isolated) and the diminution in the diameter of Sb^+ may allow an initially "skew" molecule to become planar with consequent loss of optical activity. The conversion of Sb^{III} into Sb^V by the action of hydrochloric acid would probably involve a change from a pyramidal to a trigonal bipyramidal configuration in which the three Sb–C bonds would be planar, so that the racemisation may be explained on either postulate.

If the optical activity of this stibiafluorene is due to the stable pyramidal configuration of the bonds of tervalent antimony, and the two benzene rings in the molecule remain co-axial and coplanar, examination of the ultra-violet absorption spectrum might be expected to show the presence of the characteristic diphenyl band at 252 mμ. ($\varepsilon_{max.}$ = 17,000) (Cookson and Mann, *J.*, 1949, 2890). Dr. R. N. Haszeldine has examined the ultra-violet spectra of two of these compounds and finds that 9-*p*-tolyl-9-stibiafluorene has an absorption band, $\lambda_{max.}$ 285—287 mμ. ($\varepsilon_{max.}$ = 12,100), which may be the diphenyl band, reduced in intensity and shifted to longer wave-length, while ethyl 9-*p*-tolylstibiafluorene-2-carboxylate has two bands, one almost coincident with that of diphenyl, $\lambda_{max.}$ 252·5 mμ. ($\varepsilon_{max.}$ = 23,000) and a second at 301·5—302·5 mμ. ($\varepsilon_{max.}$ = 21,000). The former may be the diphenyl band but its intensity is very great and the significance of the major band at 301·5 mμ. is unknown. Ethyl diphenyl-4-carboxylate, examined for comparison, has $\lambda_{max.}$ 271—272 mμ. ($\varepsilon_{max.}$ = 21,000). The evidence for the presence of the diphenyl residue in the molecule is therefore indecisive, but it does not rule out a planar configuration for the tricyclic system as the two benzene rings though coplanar may not be coaxial.

A decision whether the asymmetry of 9-*p*-tolyl-9-stibiafluorene-2-carboxylic acid is due to the stable pyramidal configuration of tervalent antimony or to the twisting of the two benzene rings in the tricyclic system must await the results of further work now in progress. Resolution of symmetrically substituted 9-stibiafluorenes can only indicate a "skew" molecule, whereas non-resolution may indicate a planar tricyclic system and more precise information may be obtainable from *X*-ray examination of suitably substituted compounds.

Experimental.

(Carbon and hydrogen analyses are by Drs. Weiler and Strauss, Oxford. M. p.s are uncorrected.)

*2-Diphenylyl-*p*-tolylstibine Trichloride* (II; R = R′ = H, R″ = Me).—2-Aminodiphenyl was prepared from 2-nitrodiphenyl (Monsanto) by reduction with iron filings and acidulated water at 100° and had m. p. 48—50° (85—90% yield) after crystallisation from aqueous ethanol. 2-Aminodiphenyl (16·9 g., 0·1 mol.) in concentrated hydrochloric acid (25 c.c.) and water (80 c.c.) was diazotised with sodium nitrite (7 g.). The filtered diazonium solution was added to antimony oxide (16 g., 0·055 mol.) in concentrated hydrochloric acid (100 c.c.) at −10° and the precipitated double salt was filtered off, washed with ice-cold ethanol and added in small portions to *p*-tolylstibinous chloride (28 g., 0·1 mol.) in ethanol (120 c.c.). Evolution of nitrogen started on the addition of copper bronze (0·5 g.) and the temperature rose spontaneously to 30°. After all the double salt had been added (0·5 hour) the reaction mixture was warmed to 40°, cooled, and filtered from a crystalline deposit (3·5 g.) of *di-2-diphenylyl-*p*-tolylstibine dichloride* (I; R = R′ = H, R″ = Me) which crystallised from benzene in thick prisms, m. p. 228—230° (Found: C, 63·3; H, 4·4; Sb, 20·5. $C_{31}H_{25}Cl_2Sb$ requires C, 63·1; H, 4·2; Sb,

20·6%). The filtrate from (I) was reduced in volume to 60 c.c. and gave, on cooling, a second deposit of crystals (11·5 g.), m. p. 150—154°. One recrystallisation of this material from carbon tetrachloride gave pure 2-*diphenylyl*-p-*tolylstibine trichloride* (II; R = R′ = H, R″ = Me) (9·5 g.), m. p. 153—154° (Found: C, 48·1; H, 3·4; Sb, 25·6. $C_{19}H_{16}Cl_3Sb$ requires C, 48·3; H, 3·4; Sb, 25·8%). The filtrate from (II) was evaporated to small bulk, dissolved in carbon tetrachloride, and extracted with dilute hydrochloric acid to remove inorganic antimony. From the carbon tetrachloride extract, toluene, diphenyl, and a small quantity of (II) were obtained.

2-*Diphenylyl*-p-*tolylstibinous Chloride* (III; R = R′ = H, R″ = Me).—The trichloride (6·3 g.) was suspended in a mixture of ethanol (150 c.c.) and 3·5N-hydrochloric acid (30 c.c.), and stannous chloride (6 g.) was added. On warming of the mixture, a clear solution was obtained which clouded immediately and deposited 2-*diphenylyl*-p-*tolylstibinous chloride* as white needles, m. p. 94—95° (4·55 g.). A second fraction (0·55 g.) was obtained on addition of hydrochloric acid (50 c.c.) to the filtrate (Found: C, 56·8; H, 3·9; Sb, 30·3. $C_{19}H_{16}ClSb$ requires C, 56·85; H, 4·0; Sb, 30·3%). Reduction of (I; R = R′ = H, R″ = Me) (2 g.) occurred in ethanol (40 c.c.) containing aqueous ammonia (*d* 0·880; 3 c.c.) when hydrogen sulphide was passed into the hot mixture until a permanent yellow colour was obtained. When this solution was kept overnight (ice-chest) long needles separated, which, on recrystallisation from ethanol containing a little chloroform, gave *di*-2-*diphenylyl*-p-*tolylstibine* (1·5 g.), m. p. 130—131° (Found: C, 71·1; H, 4·7; Sb, 23·55. $C_{31}H_{25}Sb$ requires C, 71·7; H, 4·8; Sb, 23·45%).

5-*Bromo*-2-*diphenylyl*-p-*carbethoxyphenylstibine Trichloride*.—2-Amino-5-bromodiphenyl was prepared by the known method (*J.*, 1927, 89) and obtained in 67% overall yield with m. p. 56—58° after recrystallisation from light petroleum (b. p. 40—60°). The diazonium chloride–antimony chloride double salt from 2-amino-5-bromodiphenyl (24·8 g.) was added to *p*-carbethoxyphenylstibinous chloride (34 g., 0·1 mol.) (*J.*, 1947, 8) in ethanol (160 c.c.) containing copper bronze (0·5 g.). Evolution of nitrogen slowed down after 1 hour, the reaction was completed by heating to 50°, and the solid which had separated was filtered off. Crystallisation of this solid from ethyl acetate gave *di*-5-*bromo*-2-*diphenylyl*-p-*carbethoxyphenylstibine dichloride* (I; R = Br, R′ = H, R″ = CO_2Et) (5·1 g.), m. p. 214—215° (Found: C, 49·1; H, 3·2; Sb, 15·2. $C_{33}H_{25}O_2Cl_2Br_2Sb$ requires C, 49·2; H, 3·1; Sb, 15·1%). A second crop of crystals was obtained when the alcoholic filtrate was evaporated under reduced pressure and the residue (60 c.c.) was set aside overnight Recrystallisation of this crop from ethyl acetate gave 5-*bromo*-2-*diphenylyl*-p-*carbethoxyphenylstibine trichloride* (II; R = Br, R′ = H, R″ = CO_2Et), m. p. 164—165° (14·1 g.), as small nodules (Found: C, 41·8; H, 2·7; Sb, 19·8. $C_{21}H_{17}O_2Cl_3BrSb$ requires C, 41·4; H, 2·8; Sb, 20·0%).

The corresponding *p*-tolyl compounds were prepared in a similar way when the double salt from 2-amino-5-bromodiphenyl (0·1 mol.) was added to *p*-tolylstibinous chloride (0·1 mol.) in ethanol (300 c.c.). The use of less than this volume of alcohol resulted in the separation of the di- and tri-chlorides as a mixture from which the individuals were isolated only after numerous recrystallisations from ethyl acetate. *Di*-5-*bromo*-2-*diphenylyl*-p-*tolylstibine dichloride* (I; R = Br, R′ = H, R″ = Me) crystallises from benzene in small prisms, m. p. 240—241° (4·8 g.) (Found: C, 49·7; H, 3·4; Sb, 16·3. $C_{31}H_{23}Cl_2Br_2Sb$ requires C, 49·8; H, 3·1; Sb, 16·3%), and 5-*bromo*-2-*diphenylyl*-p-*tolylstibine trichloride*, m. p. 190—192° (II; R = Br, R′ = H, R″ = Me), separates from the same solvent as thick hexagonal plates (Found: C, 41·6; H, 2·8; Sb, 22·3. $C_{19}H_{15}Cl_3BrSb$ requires C, 41·4; H, 2·7; Sb, 22·1%). Reduction of (II; R = Br, R′ = H, R″ = CO_2Et) (3 g.) in acetone (25 c.c.) with stannous chloride (3 g.) in 3·5N-hydrochloric acid (20 c.c.) yields 5-*bromo*-2-*diphenylyl*-p-*carbethoxyphenylstibinous chloride* (2·25 g.) which separated from ethanol as thick needles, m. p. 108° (Found: C, 46·3; H, 3·0; Sb, 22·8. $C_{21}H_{17}O_2ClBrSb$ requires C, 46·8; H, 3·2; Sb, 22·6%). Similarly (II; R = Br, R′ = H, R″ = Me) yields 5-*bromo*-2-*diphenylyl*-p-*tolylstibinous chloride*, m. p. 140—141° (Found: C, 47·7; H, 3·5; Sb, 25·5. $C_{19}H_{15}ClBrSb$ requires C, 47·5; H, 3·2; Sb, 25·3%).

4′-*Chloromethyl*-2-*nitrodiphenyl*.—2-Nitrodiphenyl (100 g.) was dissolved in acetic acid (150 c.c.), zinc chloride (68 g.) and paraformaldehyde (45 g.) were added, and a vigorous stream of gaseous hydrogen chloride was passed in at room temperature until the mixture was saturated. When heated at 80—90° with a continuous slow stream of hydrogen chloride passing in, the reaction mixture became homogeneous after an hour, but had separated into two layers after 12 hours' heating. The cooled mixture was poured into water (2 l.), and the pale yellow oil was extracted with ether. The ethereal layer was washed thrice with 10% aqueous potassium carbonate, then with water, and dried (Na_2SO_4). After removal of the ether the residue partly crystallised. The crystals (25 g.) were filtered off and the residue was distilled, yielding a first fraction, b. p. 136—140°/0·3 mm., of *o*-nitrodiphenyl (37 g.) and a second fraction, b. p. 175—182°/0·3 mm. (28 g.), which crystallised. Recrystallisation of this fraction, along with the crystalline material obtained before distillation, from ethanol–acetone or acetic acid gave 4′-*chloromethyl*-2-*nitrodiphenyl*, m. p. 89°, as pale yellow elongated prisms (46 g.) (Found: C, 63·2; H, 3·7; N, 5·9. $C_{13}H_{10}O_2NCl$ requires C, 63·0; H, 4·1; N, 5·7%).

2-*Aminodiphenyl*-4′-*carboxylic Acid*.—4′-Chloromethyl-2-nitrodiphenyl (25 g., 0·1 mol.) was suspended in a solution of sodium dichromate (45 g., 0·15 mol.) in water (100 c.c.), and sulphuric acid (100 g.) was added dropwise. No apparent reaction occurred on addition of the acid, but warming on a water-bath caused oxidation which was vigorous for a short time and was completed by 4 hours' boiling under reflux. The cooled mixture was poured into water, and the precipitated acid was dissolved in 4·5N-sodium hydroxide and filtered from unchanged chloromethyl compound (1·0 g.). Addition of 3·5N-hydrochloric acid to the alkaline filtrate gave 4′-carboxy-2-nitrodiphenyl, m. p. 246—248° (22·7 g.). One crystallisation from acetic acid gave the pure acid, m. p. 250° (Grieve and Hey, *J.*, 1932, 1892). The crude acid (10 g.) was suspended in a solution of ferrous sulphate (140 g.) in water (120 c.c.), and aqueous ammonia (*d* 0·880; 60 c.c.) was added. The mixture was boiled for 20 minutes, very vigorous stirring being necessary to prevent bumping. After cooling, the mixture was filtered, the filtrate rejected, and the residue extracted with warm 10% sodium hydroxide solution. Acidification of this extract

precipitated a little nitro-acid which was filtered off, and addition of crystalline sodium acetate to the filtrate gave 2-aminodiphenyl-4′-carboxylic acid (5·7 g.), m. p. 179° after crystallisation from aqueous alcohol or benzene (Found: C, 73·6; H, 5·2; N, 7·3. $C_{13}H_{11}O_2N$ requires C, 73·2; H, 5·2; N, 6·6%). Acetylation of the sodium salt of the acid in 20% aqueous sodium hydroxide with acetic anhydride, followed by acidification with hydrochloric acid, gave 2-*acetamidodiphenyl-4′-carboxylic acid*, m. p. 253° (Found: C, 70·7; H, 5·4; N, 6·1. $C_{15}H_{13}O_3N$ requires C, 70·6; H, 5·1; N, 5·5%).

Di-(4′-carboxy-2-diphenylyl)stibinous Chloride.—2-Aminodiphenyl-4′-carboxylic acid (10·6 g., 0·05 mol.) was dissolved in concentrated hydrochloric acid (25 c.c.) and water (75 c.c.) and diazotised with sodium nitrite (3·5 g.). The diazonium salt crystallised out, was filtered off, dissolved in the minimum volume of ice-cold water, and added to a solution of antimony oxide (8 g.) in concentrated hydrochloric acid (75 c.c.). The double salt was filtered off, washed with ethanol, and decomposed in ethanol (200 c.c.) (25 c.c. of which had been saturated with hydrogen chloride gas) on addition of copper bronze (0·5 g.). The crude stibonic acid obtained on pouring the reaction mixture into water was filtered off, dissolved in concentrated hydrochloric acid, and reduced at 0° with stannous chloride. The stibinous chloride which separated when the solution was kept for an hour was dried on tile and recrystallised from carbon tetrachloride or benzene, and proved to be *di-(4′-carboxy-2-diphenylyl)stibinous chloride*, m. p. 169—170°, instead of the expected primary stibinous chloride (Found: C, 56·1; H, 3·55; Sb, 21·7. $C_{26}H_{18}O_4ClSb$ requires C, 56·6; H, 3·3; Sb, 22·1%).

Ethyl 2-Aminodiphenyl-4′-carboxylate.—Crude 2-nitrodiphenyl-4′-carboxylic acid was esterified by boiling it under reflux with ethanol containing hydrogen chloride, and the ester isolated by pouring the reaction mixture into dilute aqueous sodium carbonate. Recrystallisation from light petroleum (b. p. 40—60°) gave the *nitro*-ester as pale yellow prisms, m. p. 79—80° (Found: C, 66·6; H, 4·9; N, 4·95. $C_{15}H_{13}O_4N$ requires C, 66·4; H, 4·8; N, 5·2%). The crude nitro-ester (20 g.) was reduced with an equal weight of iron filings and acidulated water at 100° (2 hours) and extraction with hot ethanol gave *ethyl 2-aminodiphenyl-4′-carboxylate* (15·4 g., 86·5%), which crystallised from aqueous alcohol in needles, or from carbon tetrachloride in elongated prisms, m. p. 74° (Found: C, 74·9; H, 6·3; N, 5·8. $C_{15}H_{15}O_2N$ requires C, 74·7; H, 6·3; N, 5·8%). Attempts to replace the amino-group in the ester by SbO_3H_2 by the Bart–Schmidt reaction or by the modified method of decomposing the diazonium–antimony trichloride double salt in ethanol failed.

2-4′-*Carbethoxydiphenylyl-*p*-tolylstibine Trichloride* (II; R = H, R′ = CO_2Et, R″ = Me).—Despite the failure to obtain the monoarylstibonic acid, the diazonium–antimony chloride double salt from the base (0·1 mol.) reacted with *p*-tolylstibinous chloride (0·1 mol.) in ethanol (150 c.c.) (50 c.c. of which had been saturated with hydrogen chloride), yielding a mixture (22 g.) of the triaryl dichloride and diaryl trichloride. When the reaction was carried out in the absence of hydrogen chloride, partial hydrolysis or alcoholysis of the trichloride occurred and a compound with an indefinite melting point and varying antimony content was obtained. The mixture of di- and tri-chlorides was separated by boiling ethyl acetate in which the trichloride is soluble. The insoluble fraction (4 g.), recrystallised from benzene, gave *di-2-4′-carbethoxydiphenylyl-*p*-tolylstibine dichloride*, m. p. 251—252·5°, as squat prisms (Found: C, 60·7; H, 5·0; Sb, 16·7. $C_{37}H_{33}O_4Cl_2Sb$ requires C, 60·5; H, 4·5; Sb, 16·6%). 2-4′-*Carbethoxydiphenylyl-*p*-tolylstibine trichloride* (II; R = H; R′ = CO_2Et; R″ = Me) was obtained from ethyl acetate in elongated prisms (16·9 g., 31%), m. p. 151—152° (Found: C, 48·8; H, 3·5; Sb, 22·5. $C_{22}H_{20}O_2Cl_3Sb$ requires C, 48·5; H, 3·7; Sb, 22·4%). Reduction of this compound in acetone with stannous chloride in dilute hydrochloric acid gave 2-4′-*carbethoxydiphenylyl-*p*-tolylstibinous chloride*, which crystallised from ethanol in needles, m. p. 90—91° (Found: C, 55·8; H, 4·4; Sb, 25·9. $C_{22}H_{20}O_2ClSb$ requires C, 55·8; H, 4·3; Sb, 25·7%). The filtrate from the original separation of the di- and the tri-chloride was evaporated and the residue dissolved in carbon tetrachloride and extracted with 3N-hydrochloric acid. From the organic layer there was obtained 4′-*carbethoxydiphenylyl-2-stibinous chloride* (3·5 g.)., m. p. 155—156° (Found: C, 43·1; H, 3·4; Sb, 29·1. $C_{15}H_{13}O_2Cl_2Sb$ requires C, 43·1; H, 3·1; Sb, 29·1%), and a sticky oil, from which no further crystalline material could be obtained.

9-p-*Tolyl-9-stibiafluorene.*—Attempts to cyclise (II; R = R′ = H, R″ = Me) by heating it at 170—200°/0·1 mm. (cf. Morgan and Davies, *Proc. Roy. Soc.*, *A*, 1930, **127**, 1) or by heating it with aluminium chloride in benzene or in carbon disulphide failed. The stibinous chloride (III; R = R′ = H, R″ = Me) was regained unchanged after being kept at 100°/10^{-4} mm. for 1 hour. Heating (III) in benzene with aluminium trichloride (12 hours) gave a small yield of crystalline material, m. p. 174—190° (unchanged by further crystallisation from light petroleum or carbon tetrachloride), which may have resulted from condensation with the benzene used as solvent, but, as C, H, and Sb analyses were inconclusive, the material was not further investigated. Cyclisation was finally effected through the stibonous acid obtained from (II) in the following way. 2-Diphenylyl-*p*-tolylstibine trichloride (5 g.) was dissolved in a mixture of ethanol (100 c.c.) and acetone (50 c.c.) and added to crystalline sodium acetate (50 g.) in water (400 c.c.) and the whole set aside overnight. The flocculent white precipitate of the stibonous acid was filtered off and dried in a vacuum-desiccator for 48 hours. 2-Diphenylyl-*p*-tolylstibonous acid (4·7 g.) so obtained could not be satisfactorily crystallised and had an indefinite m. p. (>130°). This was dissolved in freshly distilled acetic anhydride (50 c.c.) containing concentrated sulphuric acid (2 c.c.), and the solution warmed to 90° and held at 90° for 10 minutes, cooled and poured on crushed ice. The precipitate obtained was filtered off after 2 hours, washed free from acetic acid, and found to be a mixture of the cyclic stibine oxide and unchanged stibonous acid. Isolation of the cyclic compound from the mixture while the antimony was in the quinquevalent state proved impracticable. The moist precipitate was dissolved in a mixture of acetone (50 c.c.) and 3·5N-hydrochloric acid (10 c.c.) and reduced by addition of stannous chloride (5 g.). The solution clouded immediately, and after 2 hours at 0° the crystals which had separated were filtered off and recrystallised from dry ethanol, giving 9-p-*tolyl-9-stibiafluorene* (IV; R = R′ = H, R″ = Me) (3 g.) as fine needles, m. p. 130° (Found: C, 62·0; H, 4·0; Sb, 33·5. $C_{19}H_{15}Sb$ requires C, 62·5; H, 4·1; Sb, 33·4%). Addition of 3·5N-hydrochloric acid (25 c.c.) to the filtrate from the reduction gave (III) (0·75 g.), m. p. 94°.

3-Bromo-9-p-carbethoxyphenyl-9-stibiafluorene (IV; R = Br, R′ = H, R″ = CO_2Et).—No ring closure occurred when 5-bromo-2-diphenylyl-*p*-carbethoxyphenylstibine trichloride (3 g.) was heated in benzene (50 c.c.) with aluminium chloride (1·3 g.) for 16 hours, but the ester was hydrolysed to the corresponding *acid*, m. p. 190—192° (Found: C, 39·3; H, 2·1. $C_{19}H_{13}O_2Cl_3BrSb$ requires C, 39·25; H, 2·25%). Reduction of this acid in acetone with stannous chloride in dilute hydrochloric acid gave *5-bromo-2-diphenylyl-p-carboxyphenylstibinous chloride*, m. p. 170°, after crystallisation from ethanol, from which it separated as rosettes of needles (Found: C, 44·6; H, 2·3. $C_{19}H_{13}O_2ClBrSb$ requires C, 44·7; H, 2·6%). The trichloride (II; R = Br, R′ = H, R″ = CO_2Et) (10 g.) was converted into the stibonous acid and hence into the stibiafluorene by the method described above for the preparation of (IV; R = R′ = H, R″ = Me) except that the cyclising medium consisted of freshly distilled acetic anhydride (100 c.c.) containing only 1 c.c. of concentrated sulphuric acid. Reduction of the cyclised product gave *3-bromo-9-p-carbethoxyphenyl-9-stibiafluorene* (6·8 g.) as thin plates, m. p. 157° after crystallisation from ethyl acetate (Found: C, 50·7; H, 3·0; Sb, 24·2. $C_{21}H_{16}O_2BrSb$ requires C, 50·2; H, 3·2; Sb, 24·25%). The monochloride III; R = Br, R′ = H, R″ = CO_2Et) (1·8 g.) was obtained by addition of excess of dilute hydrochloric acid to the filtrate from the reduction. The ester was hydrolysed by 5% alcoholic sodium hydroxide at the b. p. and on pouring the mixture into water the sodium salt separated. It crystallised from boiling water in shining plates. 3-Bromo-9-*p*-carboxyphenyl-9-stibiafluorene was obtained by pouring a hot solution of the sodium salt into dilute hydrochloric acid, and, after crystallisation from acetic acid, had m. p. 246—248° (Found: C, 48·2; H, 2·4; Sb, 25·8. $C_{19}H_{12}O_2BrSb$ requires C, 48·1; H, 2·55; Sb, 25·7%).

3-Bromo-9-p-tolyl-9-stibiafluorene (IV; R = Br, R′ = H, R″ = Me).—Similar treatment of the stibonous acid obtained from (II; R = Br, R′ = H, R″ = Me) (5 g.) gave *3-bromo-9-p-tolyl-9-stibiafluorene* (2 g.), which crystallised from ethyl acetate–ethanol in thick needles, m. p. 123—124° (Found: C, 51·1; H, 3·3; Sb, 27·1. $C_{19}H_{14}BrSb$ requires C, 51·4; H, 3·2; Sb, 27·4%). The monochloride, m. p. 140—141° (1·5 g.), was obtained on diluting the reduction medium with excess of hydrochloric acid.

2-Carbethoxy-9-p-tolyl-9-stibiafluorene (IV; R = H, R′ = CO_2Et, R″ = Me).—In this case, cyclisation of the stibonous acid required longer heating and careful temperature control and it was essential to cool the reaction mixture to 0° before its addition to ice, otherwise elimination of antimony occurred and ethyl diphenyl-4-carboxylate, m. p. 44—46°, was obtained. The dry stibonous acid from (II; R = H, R′ = CO_2Et, R″ = Me) (10 g.) was dissolved in acetic anhydride (100 c.c.) containing concentrated sulphuric acid (1 c.c.), and the mixture held at 90° for 3 hours, cooled to 0°, and poured on crushed ice. Reduction of the precipitated oxide in acetone (40 c.c.) containing 3·5N-hydrochloric acid (5 c.c.) with stannous chloride (10 g.) gave an immediate crystalline separation which was filtered after an hour at 0° and recrystallised from ethyl acetate, giving *2-carbethoxy-9-p-tolyl-9-stibiafluorene*, as rosettes of needles, m. p. 136—137° (5·8 g.) (Found: C, 60·45; H, 4·6; Sb, 27·9. $C_{22}H_{19}O_2Sb$ requires C, 60·4; H, 4·4 Sb, 27·9%). Hydrolysis with 5% alcoholic potassium hydroxide at the b. p. (0·75 hour) gave (±)-*2-carboxy-9-p-tolyl-9-stibiafluorene*, m. p. 208—209·5° (decomp.) after crystallisation from ethanol-chloroform or ethyl methyl ketone (Found: C, 58·8; H, 4·0; Sb, 29·6. $C_{20}H_{15}O_2Sb$ requires C, 58·7 H, 3·7; Sb, 29·8%).

Resolution of the (±)-Acid.—Alkaloidal salts of the acid proved unsuitable for optical resolution as they separated as glasses or as mixtures of the salt with free acid. Even the α-phenylethylamine salts used in the successful resolution tended to dissociate in solution in ethanol, allowing the sparingly soluble acid to separate, but satisfactory results were obtained when twice the calculated quantity of base was used in the initial preparation of the salt and a little free base was added in the recrystallisation of the various fractions. The most successful resolutions were carried out as follows. The acid (4·1 g., 0·01 mol.) was added to (−)-α-phenylethylamine (2·5 g., 0·02 mol.) in dry ethanol (40 c.c.) and warmed to complete dissolution, filtered, and set aside. Fractions of salt were filtered off at intervals and, when no further salt separated, the solution was distilled under reduced pressure until the volume was 15 c.c. and allowed to crystallise. A second resolution was carried out under the same conditions, but with (+)-α-phenylethylamine. The results are given in the following table.

Fraction.	Vol. of solution (c.c.).	Time of standing (hrs.).	Weight (g.).	$[\alpha]_D$.	M. p.
		(−)-α-*Phenylethylamine.*			
F1−	40	20	3·1	+ 35·6°	162°
F2−	40	24	0·85	− 65·9	150—155
F3−	15	20	1·00	− 38·5	162—167
		(+)-α-*Phenylethylamine.*			
F1+	40	22	3·2	− 43·6°	160—162
F2+	40	26	0·4	+107·6	158—160
F3+	40	48	0·5	+ 68·1	150—155
F4+	15	20	0·7	+ 20·0	164—167

Two recrystallisations of F1− from ethanol containing a few drops of (−)-base gave the optically pure (+)-*acid*–(−)-*base* (0·7 g.), m. p. 164—165°, $[\alpha]_D$ +180·1° (Found: C, 63·5; H, 5·1. $C_{28}H_{26}O_2NSb$ requires C, 63·4; H, 4·9%). Recrystallisation of F2 − from ethanol in the absence of (−)-base gave the (±)-acid *salt*, $[\alpha]_D$ −13·8° (Found: C, 63·6; H, 5·2%). Similarly two recrystallisations of F1+ from ethanol containing a little (+)-base gave the pure (−)-*acid*–(+)-*base* (0·5 g.), m. p. 163—165°, $[\alpha]_D$ −179·2° (Found: C, 63·5; H, 5·0%). Finally both diastereoisomerides were obtained optically pure in the resolution of 8·2 g. of (±)-acid with 6 g. of (+)-α-phenylethylamine in 70 c.c. of absolute ethanol (see next table).

Fraction.	Vol. of solution (c.c.).	Time of standing (hours).	Weight (g.).	$[\alpha]_D$.
X1	70	22	3·8	−134·2°
X2	70	25	2·2	+182·1
X3	70	48	1·1	−118·0
X4	20	20	1·9	+ 15·7
X5	10	220	0·9	+ 19·8

Pure (−)-acid–(+)-base (1·3 g.) was obtained from X1 after two recrystallisations and had $[\alpha]_D$ −180·5°, m. p. 164—165°, and one recrystallisation of X2 gave pure (+)-acid–(+)-base (1·4 g.), $[\alpha]_D$ +204·4°, m. p. 160—163° (Found: C, 62·8; H, 5·1%). A mixture of the two diastereoisomeric salts had m. p. 148—160°. Specific rotations of the salts (*c*, *ca.* 0·5) were measured in AnalaR chloroform in 2-dm. tubes at room temperature. These solutions were not optically stable but racemised slowly at 20°, reaching the specific rotation of the racemate in approx. 48 hours and at 40° in approx. 20 hours. Further study of this racemisation is necessary as it is apparently abnormal.

In an initial attempt to obtain the optically active acid, 0·1 g. of a slightly impure salt was dissolved in 20 c.c. of AnalaR chloroform at 20° ($[\alpha]_D$ −164·5°) and decomposed by extraction with 4N-hydrochloric acid (2 × 20 c.c.). After being washed and dried (Na_2SO_4), the chloroform solution was optically inactive. Decomposition of 0·1104 g. of the same salt with 40 c.c. of 2N-hydrochloric acid at 20° and polarimetric examination of the chloroform solution immediately without washing or drying gave α_D^{20} −1·60°, which fell to zero in 3½ hours (half-life period 30 minutes; *k*, 0·0995 minute^{-1}). The pure (−)-acid–(+)-base (0·1005 g.) was decomposed in chloroform with 0·5N-hydrochloric acid (2 × 20 c.c.) at 20° and the chloroform solution washed, dried, and made up to 20 c.c., giving α_D^{20} −1·91°, $[\alpha]_D^{20}$ −246·4° (if no loss of acid occurred during extraction). This solution was optically stable at 20° (overnight). At 40° racemisation started but could not be followed to completion because acid separated from solution after 3 hours. The optically pure acids were finally obtained by dissolution of the salts in absolute ethanol (0·1 g. in 20 c.c.) and precipitation with 0·1N-hydrochloric acid. The gelatinous precipitate of the acid was filtered off immediately, washed thoroughly, and dried *in vacuo*. The following table gives the properties of (+)- and (−)-2-*carboxy*-9-p-*tolyl*-9-*stibiafluorene*, m. p. 208° (decomp.).

Salt.	$[\alpha]_D^{20}$ salt (EtOH, *c*, 0·25).	$[\alpha]_D^{20}$ acid (pyridine, *c*, 0·25).	Found: C, %.	Found: H, %.	
(+)-A-(−)-B	+188·4°	+245·2°	58·3	3·9	Reqd.: C, 58·7; H, 3·7%
(+)-A-(+)-B	+201·5	+244·7	58·4	3·8	
(−)-A-(+)-B	−189·1	−245·7	58·4	3·7	

Solutions of the optically active acids in dilute alkalis (0·1N-potassium or sodium hydroxide or sodium hydrogen carbonate) were faintly opalescent so that satisfactory polarimetric readings were not possible. In pyridine (*c*, 0·25) the acids were optically stable at 20°, but at 40° very slow racemisation occurred. A solution (α_D^{20} +1·23°) of (+)-acid in pyridine, after 36 hours at 40°, had α_D^{20} +0·94°.

To investigate the acid-catalysed racemisation, the (−)-acid–(+)-base salt (0·1008 g.) was dissolved in AnalaR chloroform (20 c.c.) and shaken with 4N-sulphuric acid (2 × 20 c.c.). The chloroform solution, before being washed or dried, had α_D^{20} −2·30°, which remained unchanged for 2 hours. Thereafter solid acid began to separate and further readings were impossible. Similar treatment of the same salt (0·1057 g.) in AnalaR chloroform (20 c.c.) with 4N-phosphoric acid gave α_D^{20} −2·28° which remained unchanged for 1·5 hours; when the same solution was shaken with 5N-hydrochloric acid (40 c.c.) and examined after 5 minutes it had α_D^{20} −0·96° which fell to zero in 14 minutes. The chloroform solution of the inactive product was not washed with water, so as to avoid decomposition of any hydrogen chloride addition product, but it was dried (Na_2SO_4) and evaporated at 20°/10 mm. and the dry product was kept for 30 minutes at 10^{-3}—10^{-4} mm. This product and the specimen previously obtained when using 2N-hydrochloric acid had C, 55·8, 55·1; H, 4·5, 4·1%, respectively; $C_{20}H_{15}O_2Sb$ requires C, 58·7; H, 3·7, and $C_{20}H_{15}O_2Sb$,HCl requires C, 54·2; H, 3·6%. Both specimens contained chlorine (qualitative tests).

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