The Stereochemistry of Triarylstibines. Synthesis and Optical Resolution of p-*Carboxyphenyl-2-diphenylylphenylstibine.*

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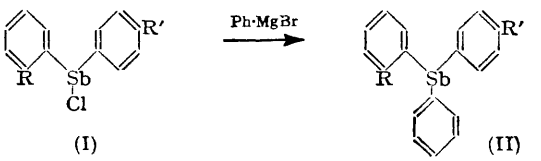
The synthesis of two stibines in which antimony is attached to three different aryl groups and the resolution of one of these, *p*-carboxyphenyl-2-diphenylylphenylstibine, into (+)- and (−)-forms, $[\alpha]_D^{20}$ ±47·0°, are described. The enantiomers are optically stable in toluene and in *p*-xylene at the boiling point. The optical stability of the stibine is contrasted with the lability of enantiomeric arylamines and possible reasons for the difference are discussed. The ultraviolet spectrum of 2-diphenylyl-*p*-tolylphenylstibine and of 9-*p*-tolyl-9-stibiafluorene are recorded and compared with that of triphenylstibine.

The considerable optical stability observed in the stibiafluorenes, compounds in which antimony occurs as a tervalent heteroatom in a five-membered ring (*J.*, 1955, 1662), suggested that it might prove possible to demonstrate optical activity in stibines in which the antimony atom was not held in a ring, but attached to three different groups. Substituted triarylstibines were considered the most promising material for such an attempt, but apparently no compound of this type, *e.g.*, (II), in which antimony is attached to three different aryl groups has been prepared. The most obvious route is the reaction of a Grignard reagent on an unsymmetrical diarylstibinous halide (I), and some information on this type of compound was available, for several members of the series had been obtained by the reduction of the diarylstibinic chlorides used in the synthesis of stibiafluorenes. However, all these diarylstibinous halides contained a 2-diphenylyl group (I;



(I) (II)

R = Ph) and were therefore considered unsuitable for the purpose, because of the possibility of restricted rotation. To avoid such complication, the introduction of a 4-diphenylyl group was attempted, but the interaction of diphenyl-4-diazonium antimony chloride with

p-ethoxycarbonylphenylstibonous chloride failed to give the expected product. Instead, a very insoluble compound was obtained, along with a considerable yield of diphenyl and ethyl benzoate. Disproportionation had apparently occurred, for reduction of the insoluble compound with stannous chloride gave di-4-diphenylylstibinous chloride, m. p. 200°. Similar attempts to introduce *p*-bromo- or *p*-chloro-phenyl groups also failed, and, as unsymmetrical stibinous chlorides were available from previous work, it was decided to investigate the reaction of a Grignard reagent on these, despite the structural disadvantages of the 2-diphenylyl group.

The reaction of phenylmagnesium bromide on the chloride (I; R = Ph, R′ = Me) gave the expected triarylstibine in good yield, although initially it was necessary to isolate it by conversion into the dibromide and subsequent reduction. When a crystalline specimen had been obtained, this process became unnecessary, because seeding sufficed. The corresponding reaction with the ester (I; R = Ph, R′ = CO_2Et) presented more difficulty, as, apparently, the rates of the competitive reactions, replacement of halogen and attack on the ester group, did not differ widely. But conditions were found whereby the triaryl-

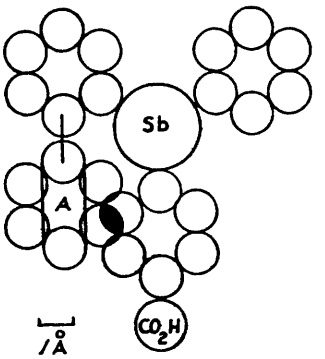


FIG. 1.
C–C *bond, aromatic,* 1·4 Å.
C–C *bond, diphenyl,* 1·48 Å.
C–CO_2H *bond,* 1·56 Å.
C–Sb *bond,* 2·11 Å.
Angle CSbC, 120°.

stibine (II; R = Ph, R′ = CO_2Et) could be obtained in 50—55% yield, and hydrolysis gave *p*-carboxyphenyl-2-diphenylylphenylstibine (II; R = Ph, R′ = CO_2H), m. p. 199—200°.

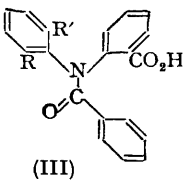
Resolution of the acid was readily accomplished by the use of (+)-1-phenylethylamine. Both diastereoisomers were obtained optically pure, but the yields were low, largely because the salts tended to separate as gels from concentrated solution. The active acids, $[\alpha]_D$ −46·9° and +47·2°, were optically stable at room temperature; the rotations of the pyridine solutions were unchanged when examined after three months. Further, the rotation of a toluene solution of the (−)-acid, $[\alpha]_D^{20}$ −57·4°, was unaffected by one hour's boiling and a solution in *p*-xylene, $[\alpha]_D^{18}$ −52·3°, showed the same value after two hours' boiling, so the compound possesses considerable optical stability. An attempt to racemise the (−)-acid in decalin (b. p. 188—189°) resulted in a fall in rotation from $[\alpha]_D^{22}$ −47·0° to −22·6° in 30 minutes, but oxidation rather than a true racemisation had occurred for the solid, m. p. 290—294°, which separated on cooling the solution was the stibine oxide. No evidence was obtained of the rapid catalytic racemisation observed so frequently with the active stibiafluorenes. The (−)-acid in chloroform was unaffected by dry hydrogen chloride, the most potent catalyst in the stibiafluorene series, until its concentration was sufficient to cause chemical decomposition.

As all attempts to isolate optically active isomers of simple tervalent nitrogen, phosphorus, and arsenic compounds have so far failed, the very considerable optical stability of this stibine suggests that the dissymmetry is caused by restricted rotation within the molecule rather than the stable pyramidal arrangement of the three Sb–C bonds. That restricted rotation of the simple diphenyl type cannot be responsible for the enantiomers is clear, because no group is present in the *meta*-position of the 2-diphenylyl group to give dissymmetry. But scale models and drawings (Fig. 1) indicate considerable hindrance to the free rotation of the groups attached to the antimony atom with a planar arrangement

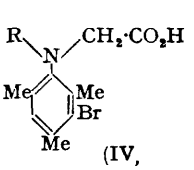
of bonds at 120°, if the two benzene rings of the 2-diphenylyl group remain coplanar, and slight hindrance if these rings are at right angles to each other. On this planar model one can show that synchronised rotation of the groups is possible and can give the molecule symmetrical configuration at least momentarily. Fig. 1 is constructed by using covalent and not van der Waals radii (hydrogen atoms have been omitted for clarity) so that the overlap is underestimated, and A represents an alternative position but not necessarily the " thickness " of the second benzene ring of the diphenylyl group; but the Figure gives a crude picture of the restricted molecule when the antimony bonds are arranged at 120°.

The situation resembles that found in the *N*-benzoyldiphenylamine-2-carboxylic acids (III) studied by Jamison and Turner and their collaborators (*J.*, 1938, **1646**; 1940, **264**; 1955, **145**), and also in the arylamines (IV) examined by Adams and his school (*J. Amer. Chem. Soc.*, 1954, **76**, 5478, and earlier papers listed therein). Unfortunately, in all the optically active compounds obtained, alkyl, acyl, or aroyl in addition to aryl groups are attached to the nitrogen atom so that no completely analogous compound is available for comparison. Meisenheimer and his collaborators investigated substituted triphenylamines (V) (*Ber.*, 1924, **57**, 1744) but failed to obtain evidence of resolution in *N*-phenyl-*N*-*p*-tolylanthranilic acid or *N*-α-naphthyl-*N*-phenylanthranilic acid, although models of these compounds indicate steric interference.

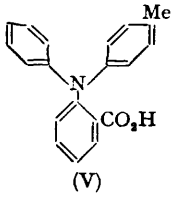
The enantiomers obtained in the nitrogen series are all optically labile with half-lives ranging from little more than a minute at 20° (*J.*, 1955, 145) to 28 hours at 118° (*J. Amer. Chem. Soc.*, 1941, **63**, 2859). Consequently the optical stability of the stibine is rather striking, particularly as, in the substituted *N*-benzoyldiphenylamine-2-carboxylic acids



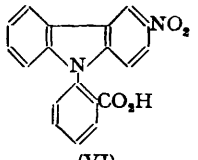
(III)



(IV,



(V)



(VI)

the small diameter of nitrogen results in overcrowding comparable with that occurring in the stibine, as far as can be judged from models and projections. From a purely mechanical viewpoint, therefore, the most hindered nitrogen compounds would not be expected to attain the planar configuration necessary for racemisation at all readily. However, these comparisons are necessarily qualitative and the presence of the benzoyl group in Jamison and Turner's compounds may increase the ease of synchronised rotations of the groups as indicated by models with C–N–C bonds at either 109·5° or 120° (*J.*, 1955, 147). That this synchronised rotation may play a considerable part in racemisation might be inferred by comparison of Meisenheimer's failure to resolve the amine (V) with the successful resolution of 9-*o*-carboxyphenyl-3-nitrocarbazole (VI) (Patterson and Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 1069) in which two of the rings which restrict the rotation of the *o*-carboxyphenyl group are held in a plane. It has been established by Jamison and Turner (*loc. cit.*) and Adams (*J. Amer. Chem. Soc.*, 1940, **62**, 2191) that the dissymmetry of the arylamines is caused by restricted rotation rather than a formally asymmetric tervalent nitrogen atom. But it is improbable that the bonds from nitrogen to the three substituent groups are planar, for triphenylamine has a dipole moment of 0·47 D (Cowley, *J.*, 1952, 3557) and the C–N–C angle has been calculated as 114° (Leonard and Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1564), so that the restriction causing dissymmetry must occur in a rather flat pyramid. The dipole moment of triphenylstibine is 0·57 D (Bergmann and Schütz, *Z. physikal. Chem.*, 1932, **19**, *B*, 401) which leads to a value of 112—113° for the C–Sb–C angle by a simple calculation (the necessary data are not available for the more refined method of Leonard and Sutton), so that the situation is very similar. But the reason for the great difference in optical stability is not obvious, unless one postulates that restriction in the nitrogen series is eased by an inversion of the pyramidal molecule which does not occur readily in the stibine.

The explanation may lie in the difference in atomic structure of the central atom in the two series, for *d*-orbitals are available in antimony and not in nitrogen. The energy required to flatten NH_3 is smaller than that required to flatten PH_3, AsH_3, or SbH_3 (Mulliken, *J. Amer. Chem. Soc.*, 1955, **77**, 887), the stabilisation of the pyramidal form of the last three hydrides being favoured by $p\pi$–$d\pi$ hybridisation. If, in the optically active stibine, the *d*-orbitals of antimony participate in the Sb–C bonding, the increased difficulty of flattening the pyramidal molecule would provide some explanation of the optical stability of the compound.

It seemed of interest to examine the ultraviolet absorption spectrum of 2-diphenylylphenyl-*p*-tolylstibine for comparison with that of triphenylstibine in which the broad absorption band indicates conjugation between the benzene rings and the antimony atom (Campbell and Poller, *Chem. and Ind.*, 1953, 1126). The curves *A* and *B* in Fig. 2 show that the additional benzene ring causes little change in the position of absorption, but increases the intensity as would be expected. The characteristic shift of absorption to

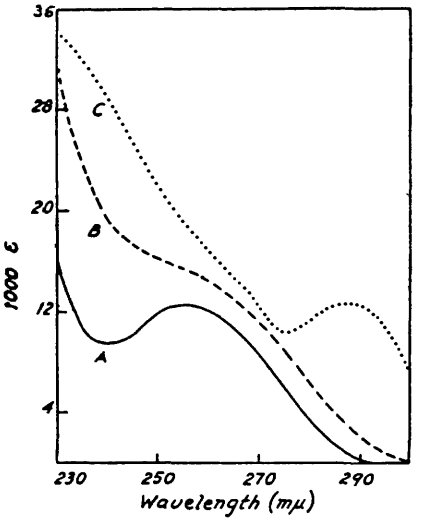


FIG. 2.
A, Triphenylstibine.
*B, 2-Diphenylylphenyl-*p*-tolylstibine.*
*C, 9-*p*-Tolyl-9-stibiafluorene.*

longer wavelength characteristic of the methyl group is absent, or masked by other effects, and the curve is greatly smoothed out. The spectrum of 9-*p*-tolyl-9-stibiafluorene (*J.*, 1950, 3109) is included to show the pronounced shift to longer wavelength which occurs on ring closure.

EXPERIMENTAL

Attempted Preparation of p-*Ethoxycarbonylphenyl-4-diphenylylstibinous Chloride.*—The diazonium antimony chloride double salt, obtained from 4-aminodiphenyl (8·5 g.) in the usual way, was decomposed in ethanol (50 ml.) containing *p*-ethoxycarbonylphenylstibonous chloride (17 g.) and copper powder (0·2 g.) at 50°. As the double salt decomposed, the mixture became dark brown and an insoluble deposit was formed. This solid (5 g.) could not be crystallised satisfactorily and was suspended in acetone (30 ml.) and reduced with stannous chloride (5 g.). Addition of 3·5N-hydrochloric acid (10 ml.) to the filtered solution precipitated a pale grey solid (3 g.) which, after crystallisation from carbon tetrachloride and from benzene, proved to be *di-4-diphenylylstibinous chloride*, m. p. 200° (Found: C, 61·9; H, 4·2. $C_{24}H_{18}ClSb$ requires C, 62·2; H, 3·9%). Acidification of the original dark brown filtrate precipitated diphenyl and ethyl benzoate, but no further organometallic compound was obtained.

*2-Diphenylylphenyl-*p*-tolylstibine.*—2-Diphenylyl-*p*-tolylstibinous chloride (8 g., 0·02 mole) (*J.*, 1950, 3112) in dry benzene (30 ml.) was added to the Grignard reagent prepared from bromobenzene (6·3 g., 0·04 mole) in ether, and the whole boiled for 15 min. After cooling, the mixture was extracted with saturated aqueous ammonium chloride and the benzene–ether layer separated, dried, and evaporated. A pale yellow syrup was obtained but did not crystallise,

consequently bromine in carbon tetrachloride was added to the syrup (0·5 g.) until a faint permanent colour remained, and the dibromide was precipitated by addition of light petroleum (b. p. 60—80°). Recrystallisation from light petroleum gave *2-diphenylylphenyl-*p*-tolylstibine dibromide*, m. p. 169—170° (0·4 g.) (Found: C, 49·7; H, 3·7. $C_{25}H_{21}Br_2Sb$ requires C, 49·8; H, 3·5%). Attempts to reduce this to the stibine by stannous chloride in ethanol containing aqueous hydrochloric acid failed, but produced the corresponding *dichloride*, m. p. 125—126° (Found: C, 57·8; H, 4·1. $C_{25}H_{21}Cl_2Sb$ requires C, 58·4; H, 4·1%). Reduction of this, or of the dibromide, in hot ethanol containing a few drops of ammonia with hydrogen sulphide gave *2-diphenylylphenyl-*p*-tolylstibine*, m. p. 81—83° after recrystallisation from ethanol–ethyl acetate, from which it separated as rosettes of small needles (Found: C, 67·2; H, 5·0. $C_{25}H_{21}Sb$ requires C, 67·7; H, 4·8%). When the main bulk of the syrup obtained in the Grignard reaction was seeded with this material, crystallisation occurred and the pure stibine (5 g.) was obtained.

*2-Diphenylyl-*p*-ethoxycarbonylphenylphenylstibine.*—Initial attempts to prepare this by the same procedure using one or two mols. of Grignard reagent failed but, by reversing the order of addition of the reactants so that the stibinous chloride was initially in excess, the required compound was obtained. The Grignard reagent prepared from bromobenzene (6·3 g., 0·04 mole) was added slowly to 2-diphenylyl-*p*-ethoxycarbonylphenylstibinous chloride (9·2 g., 0·02 mole: *J.*, 1952, 4450) in benzene (40 ml.) at 0°, and the mixture was boiled for 15 min., cooled, and decomposed with saturated aqueous ammonium chloride. The syrup obtained on evaporating the organic layer failed to crystallise, and a small quantity was converted into the *dibromide*, m. p. 148—150° (Found: C, 48·7; H, 3·5. $C_{27}H_{23}O_2Br_2Sb$ requires 49·1; H, 3·5%). Again attempted reduction with stannous chloride in ethanol gave the *dichloride*, m. p. 109—110° (Found: C, 56·5; H, 4·1. $C_{27}H_{23}O_2Cl_2Sb$ requires C, 56·7; H, 4·1%), and hydrogen sulphide in ethanol–ammonia reduced the dibromide to the *stibine*, m. p. 105—107° after recrystallisation from methanol containing a little ether (Found: C, 64·0; H, 4·6. $C_{27}H_{23}O_2Sb$ requires C, 64·7; H, 4·6%). This was used to seed the main reaction product and a semisolid mass resulted, which on trituration with methanol and ether gave the crude stibine (7·3 g.). Two recrystallisations of this from methanol containing a little ether gave the pure stibine (5·5 g.).

p-*Carboxyphenyl-2-diphenylylphenylstibine.*—The ester (4·0 g.) was hydrolysed by boiling 4% alcoholic potassium hydroxide (100 ml.) for ½ hr., then the solution was poured into water and acidified (Congo-red) with dilute hydrochloric acid. The precipitated *acid* (3·5 g.) had m. p. <100° and contained water, despite drying for prolonged periods at room temperature, but separated from absolute ethanol in rosettes of small needles, m. p. 199—200° (Found: C, 63·4; H, 4·1; Sb, 25·5. $C_{25}H_{19}O_2Sb$ requires C, 63·45; H, 4·05; Sb, 25·7%).

Optical Resolution of p-*Carboxyphenylphenyl-*p*-tolylstibine.*—Small-scale experiments indicated that combination of this acid with strychnine, brucine, and ephedrine gave rather soluble salts which separated as gums, but with (+)-1-phenylethylamine a solid was obtained. The first resolution was carried out as follows: the acid (2·8 g.) was suspended in warm acetone (20 ml.) and the addition of (+)-1-phenylethylamine (1 g.) gave a solution which, when kept overnight, deposited a first fraction of salt, $[\alpha]_D$ +2·1° (2·7 g.). This crystallised as rosettes of very small needles covered with a gel-like deposit. Evaporation of the mother-liquor provided a second fraction, $[\alpha]_D$ +16·6° (0·7 g.), which separated initially as a gel, but crystallised overnight. Recrystallisation of the first fraction, twice from acetone and once from ethanol, gave pure (−)-*acid* (+)-*base salt*, m. p. 174—176°, $[\alpha]_D$ −28·6° (0·35 g.) (Found: C, 65·4; H, 5·4. $C_{25}H_{19}O_2Sb,C_8H_{11}N,\frac{1}{2}H_2O$ requires C, 65·7; H, 5·3%). Two recrystallisations of the second fraction from ethanol gave (+)-*acid* (+)-*base salt*, m. p. 168—170°, $[\alpha]_D$ +46·6° (Found: C, 66·9; H, 5·1. $C_{25}H_{19}O_2Sb,C_8H_{11}N$ requires C, 66·7; H, 5·1%). Rotations were measured in "AnalaR" chloroform ($l = 2$, $c \sim 0{\cdot}25$). Ethanol could not be used in place of acetone in the preparation of the salt, because the mixture of diastereoisomerides was too soluble in this solvent but, after a partial separation through acetone, alcohol was an efficient solvent for the final crystallisations.

In a second resolution, the acid (2·3 g.) and (+)-1-phenylethylamine (1·2 g.) were dissolved together in acetone (16 ml.). The first fraction of salt, F1 (2·3 g.), was filtered off after 24 hr., and a second, F2 (0·7 g.), after a further 48 hr. F1 was extracted with hot acetone (10 ml.), and the residue, after one recrystallisation from alcohol, gave pure (−)-acid (+)-base salt, $[\alpha]_D$ −28·8°, unchanged by further crystallisation. The acetone extract of F1 was used as solvent for the recrystallisation of F2, and the resultant salt (1·2 g.) had $[\alpha]_D$ +22·1°. This was recrystallised twice from alcohol and gave 0·3 g. of (+)-acid (+)-base salt, $[\alpha]_D$ +46·9°.

Isolation of (+)- and (−)-Acids.—The salt, $[\alpha]_D$ −28·8° (0·5 g.), was dissolved in ethanol (20 ml.), cooled to −10°, decomposed with 0·1N-sulphuric acid (20 ml.), and treated with water (20 ml.) to complete precipitation. The (−)-*acid*, dried *in vacuo* at room temperature, had m. p. 76—79°, $[\alpha]_D^{20}$ −46·9° (*c* 0·245 in pyridine) (Found: C, 63·2; H, 4·0%).

Similar treatment of the (+)-acid (+)-base salt gave the (+)-*acid*, m. p. 76—80°, $[\alpha]_D^{20}$ +47·2° (*c*, 0·223 in pyridine) (Found: C, 63·1; H, 3·9%). Attempts to crystallise the (−)-acid showed that it was much more soluble than the (±)-form in common organic solvents, from which it separated as a gum. No satisfactory solvent for crystallisation was found. Aqueous ethanol provided a specimen which was not characteristically crystalline (m. p. 135—139°) and this had $[\alpha]_D^{22}$ −40·4° (*c* 0·285 in " AnalaR " chloroform), a value almost identical with that shown by the original specimen, m. p. 76—79°.

Specific rotations in various solvents and the results of attempted racemisations are in Table 1. Freshly distilled thiophen-free toluene, b. p. 110°, *p*-xylene (99·6% pure), b. p. 138°, and decalin, b. p. 188—189°, were used in racemisation attempts. The rotation solutions in toluene and *p*-xylene were boiled under reflux (with precautions against loss of solvent), then cooled rapidly and examined at the temperatures stated. Readings were taken at half-hourly intervals and the maximum change observed was an increase of 0·005° in the rotation of the toluene solution.

A solution of the (−)-acid in decalin, α_D^{23} −0·48°, was boiled for 30 min. and when cooled

TABLE 1.

Wt. (g.) of acid in 20 ml.	Solvent	$[\alpha]_D$	Temp.	Optical stability of solution
0·0490	Pyridine	−46·9°	20°	Stable at 20°
0·0445	Pyridine	+47·2°	20°	Stable at 20°
0·0467	Chloroform	−40·7°	22°	Stable at 22°
0·0453	Toluene	−57·4°	18°	Stable on boiling (1 hr.)
0·1032	*p*-Xylene	−52·3°	18°	Stable on boiling (2 hr.)
0·1020	Decalin	−47·1°	23°	Oxidised on boiling

deposited a solid, m. p. 290—294°. The filtrate had α_D^{23} −0·22°, and this fell to α_D^{23} −0·03° after a total of 105 minutes' boiling. The solid was the *stibine oxide* (Found: C, 61·2; H, 4·1. $C_{25}H_{19}O_3Sb$ requires C, 61·4; H, 3·9%).

The rotation of a solution of the (−)-acid in chloroform was unaffected by a trace of hydrochloric acid, but on introduction of 0·5 ml. of chloroform through which dry hydrogen chloride had been passed for ½ min., the rotation fell from α_D^{20} −0·20° to −0·02° in 26 hr. Removal of

TABLE 2.

Compound	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
Triphenylstibine	2540—2550	12,800	2400	8920
(II; R = Ph, R′ = Me)	2500—2550	16,000	(Inflection)	
9-*p*-Tolyl-9-stibiafluorene	2870	12,400	2770	11,000

the chloroform left a residue which had the characteristic smell of diphenyl and was separated by alkali into an acidic fraction and impure diphenyl, m. p. and mixed m. p. 65—69°. The acidic fraction was not identified.

Absorption Spectra.—These were determined in 95% ethanol (see Table 2 and Fig. 2).

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