234. *The Stereochemistry of Triarylstibines. Part II.* Synthesis of Unsymmetrically Substituted Triarylstibines and Optical Resolution of* p-*Carboxyphenyl*-1-*naphthylphenylstibine.*

By I. G. M. CAMPBELL and A. W. WHITE.

The synthesis of five stibines of the type p-$HO_2C{\cdot}C_6H_4{\cdot}SbPhAr$ is described. Models of these compounds indicate that two are sterically hindered, and one of these (Ar = 1-naphthyl) has been separated into (+)- and (−)-forms, $[\alpha]_D^{18}$ $\pm 35{\cdot}5° \pm 1{\cdot}5°$ (in $CHCl_3$), which are optically stable. No hindrance to the free rotation of the groups around the antimony atom is indicated in the other three, consequently they should be suitable compounds for testing the stability of the pyramidal configuration of tervalent antimony by attempted optical resolution.

IN Part I * the difficulties met in the synthesis of the unsymmetrical diarylstibinous chlorides ArAr'SbCl necessary for the preparation of triarylstibines suitable for stereochemical investigation were outlined. At that time the only known stibinous chlorides of this type contained a 2-diphenylyl group and attempts to obtain others by the route illustrated had failed at the initial step.

$$Ar{\cdot}N_2SbCl_4 + p\text{-}EtO_2C{\cdot}C_6H_4{\cdot}SbCl_2 \xrightarrow[-Cu]{EtOH} p\text{-}EtO_2C{\cdot}C_6H_4{\cdot}SbCl_3{\cdot}Ar + N_2 + SbCl_3$$

(I)

$$(I) \xrightarrow[-EtOH]{SnCl_2} p\text{-}EtO_2C{\cdot}C_6H_4{\cdot}SbClAr \xrightarrow{PhMgBr} p\text{-}EtO_2C{\cdot}C_6H_4{\cdot}SbArPh\ (III)$$

(II)

$$\xrightarrow{Hydrol.} p\text{-}HO_2C{\cdot}C_6H_4{\cdot}SbArPh\ (IV)$$

The striking difference between the ease of isolating the trichloride (I) when Ar was the 2-diphenylyl group and the complete failure when Ar was p-bromophenyl, p-chlorophenyl, or 4-diphenylyl seemed to indicate that an *ortho*-substituent in the diazonium salt was essential for success. This prompted the use of the diazonium double salts from o-chloroaniline and o-toluidine, but in neither case was the required compound obtained. Attempts were then made with 3-aminodiphenyl, *p-cyclo*hexylaniline, and 1- and 2-naphthylamine, as these bases would provide trichlorides having approximately the same molecular weight as the 2-diphenylyl derivatives and possibly also similar melting points. It was then found that the earlier lack of success in obtaining compounds of type (I) can be ascribed, not to the failure of the reaction, but to the difficulty of isolating the product.

In the 2-diphenylyl series the trichlorides crystallise readily, whereas compounds containing other aryl groups remain dissolved in the ethanolic mixture and there undergo decomposition or disproportionation. The latter occurred in attempts to prepare (I;

* Part I, *J.*, 1955, 3116.

Ar = *o*-Me·C_6H_4 or *o*-Cl·C_6H_4), the product, in each case, being di-*p*-ethoxycarbonylphenylstibinic chloride. Similarly, in the initial experiment with *p-cyclo*hexylaniline, disproportionation occurred, but in this case the di-*p-cyclo*hexylphenyl derivative was isolated. Either of the two symmetrical compounds can evidently separate from the reaction mixture, but, so far, it has proved impossible to isolate both. This type of redistribution is not uncommon among compounds of this type and has been observed in similar syntheses of unsymmetrical arsinic [1] and phosphinic acids.[2]

The unsymmetrical trichlorides were isolated in several cases by extraction with benzene and dilute hydrochloric acid. But the compounds which separated from benzene tenaciously retained variable amounts of the solvent; this led to variable melting points and analyses and made it much more difficult to characterise the pure compounds.

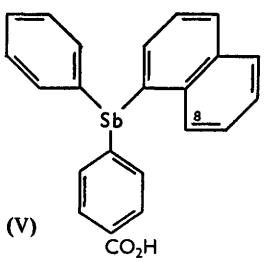
Reduction of the tri- to the mono-chlorides (the second step in the route) also gave trouble until it was realised that the concentration of hydrochloric acid in the ethanol–stannous chloride medium was critical, and that even moderate concentrations encouraged fission of the carbon–antimony bond, thus:

$$p\text{-EtO}_2\text{C·C}_6\text{H}_4\text{·SbClAr} + \text{HCl} \longrightarrow p\text{-EtO}_2\text{C·C}_6\text{H}_4\text{SbCl}_2 + \text{ArH}$$

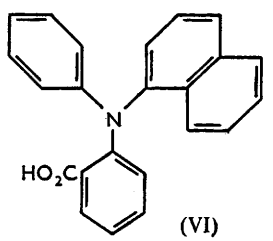
For example, the monochloride (II; Ar = 1-naphthyl), which crystallised well from the ethanol–stannous chloride reaction mixture, when washed with 2N-hydrochloric acid to remove tin salts and then dried *in vacuo* at room temperature, decomposed rapidly into naphthalene and *p*-ethoxycarbonylphenylstibonous chloride.

A further difficulty, which remains unsolved, is the apparent ease with which the chloride (II; Ar = 3-diphenylyl), obtained as a viscous oil, is re-oxidised in air to a quinquevalent antimony derivative.

Conversion of the diarylstibinous chlorides (II), into the triarylstibines (III) by interaction with phenylmagnesium bromide gave the stibine esters as viscous gums from which no crystalline dichlorides or dibromides could be obtained, although bromine was absorbed in approximately the calculated quantity. This is again in contrast to experience in the 2-diphenylyl series (see Part I) where the preparation of pure dibromides permitted the initial isolation of the crystalline stibine esters. However, hydrolysis of the crude products from the Grignard reaction gave the acids (IV), though they were obtained pure only after



(V)



(VI)

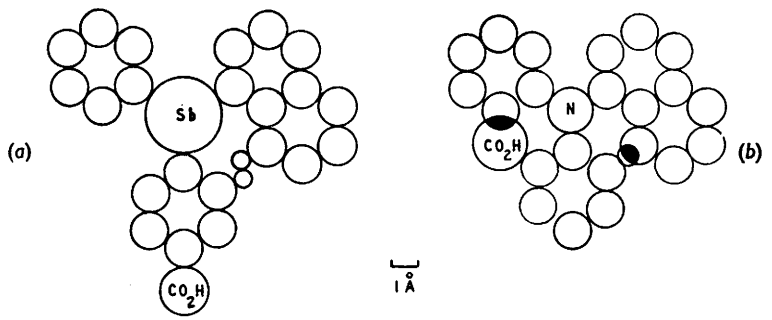
very wasteful crystallisations. The low yield obtained in this reaction was further reduced in the case of the 2-naphthyl isomer because, apparently at some stage in the isolation, oxidation occurred and a portion of the product proved to be the insoluble, high-melting oxide of the triarylstibinecarboxylic acid.

p-Carboxyphenyl-1-naphthylphenylstibine (IV; Ar = 1-naphthyl) was readily resolved into (+)- and (−)-forms by crystallisation of the (−)- and (+)-1-phenylethylamine salts, the (+)-base forming the least soluble salt with the (−)-acid. The more soluble (+)-base-(+)-acid salt was not obtained optically pure. The acids, $[\alpha]_D^{18}$ ±35·5° ± 1·5°, were stable in chloroform and in ethanol at room temperature and in boiling *p*-xylene for two hours. Prolonged boiling in the last solvent produced an opalescent solution

[1] Campbell and Poller, *J.*, 1956, 1200; Poller, Ph.D. Thesis, Southampton, 1955, p. 38.
[2] Doak and Freedman, *J. Amer. Chem. Soc.*, 1952, **74**, 2884.

which made further polarimetric measurements impossible, but the enantiomers obviously possess considerable optical stability. Loss of activity was observed on one occasion only, when a solution in chloroform was left for more than a week in intermittent sunlight. Analysis indicated that some decomposition had occurred: the (±)-acid is light-sensitive and develops a buff to brown colour on prolonged exposure.

A model of this stibine (V), in which the atoms are represented by spheres with normal covalent radii and the antimony atom has a planar arrangement of bonds, indicates that on rotation of the groups, the hydrogen atom at position 8 of the naphthyl group just touches the hydrogens on the *ortho*-positions of the two benzene rings. A Courtauld model,[3] in which the atoms have van der Waals radii and the bonds from antimony are set at the tetrahedral angle, indicates interference, although the restriction to the rotation of the groups is not great—it is, in fact, considerably less than in models of a similar nitrogen compound, *N*-1-naphthyl-*N*-phenylanthranilic acid (VI) whether the bonds from nitrogen are planar, tetrahedral, or pyramidal. In this molecule, the small diameter of nitrogen and the presence of the *ortho*-carboxy-group results in such restriction that the 1-naphthyl group is virtually locked in a plane at right angles to the two phenyl groups. Scale diagrams (Figure, *a* and *b*), in which the nitrogen and antimony bond angles are taken as 120° and restriction is consequently at a minimum, indicate that in the nitrogen compound (VI) the *o*-carboxyphenyl group overlaps both the phenyl group and the 1-naphthyl group, whereas no such overlap occurs in the antimony analogue (V). As covalent radii have been used in the Figures, the restriction is undoubtedly underestimated, but the difference in degree of overcrowding in the two molecules is clear, and, judged on this basis, since stable (+)- and (−)-forms of the antimony compound (V) have been obtained, isolation of enantiomers of the analogue (VI) would be expected. Nevertheless, Meisenheimer and his collaborators were unable to obtain any evidence of resolution, although they examined both the strychnine and the brucine salts of this acid (VI).



C–C, 1·4 Å. C–CO_2H, 1·56 Å. C–Sb, 2·11 Å. C–N, 1·44 Å. ∠CSbC, 120°. ∠CNC, 120°.

The failure to isolate enantiomers of the amine and the successful resolution of the stibine lend support to the suggestion (Part I) that restriction in the nitrogen compound is rendered ineffective by the rapid inversion of the pyramidal configuration, whereas the barrier to inversion in the stibine is sufficiently high to permit the isolation of stable optical antipodes. Further, the results again confirm Weston's prediction, derived from calculations,[5] that optical isomers of tervalent nitrogen compounds should racemise even at very low temperatures, whereas those of antimony should be stable above room temperature.

Experimental

p-cyclo*Hexylaniline*.—Phenyl*cyclo*hexane was nitrated by a modification of Turner and Mayes's method.[6] Nitric acid (145 ml.; *d* 1·5) in glacial acetic acid (60 ml.) was added in 0·5

[3] Hartley and Robinson, *Trans. Faraday Soc.*, 1952, **48**, 847.
[4] Meisenheimer, Angermann, Finn, and Vieweg, *Ber.*, 1924, **57**, 1744.
[5] Weston, *J. Amer. Chem. Soc.*, 1954, **76**, 2645.
[6] Turner and Mayes, *J.*, 1929, 500.

hr. to phenyl*cyclo*hexane (36 ml.) in acetic acid (72 ml.) at 18—20°. The mixture was stirred for a further 0·5 hr., poured on ice, and extracted with benzene. The oil obtained from benzene extraction in three such experiments was distilled through a heated Vigreux column and separated into fractions, b. p. 138—142°/0·3 mm. and 145—150°/0·3 mm. The second fraction solidified and crystallised from ethanol to give *p-cyclo*hexylnitrobenzene, m. p. 58° (64 g.). Refractionation of the lower-boiling oil gave a first cut, b. p. 96°/6 × 10^{-3} mm., which solidified at −10° and crystallised from ethanol to give the *ortho*-isomer, m. p. 45° (Neunhoeffer [7] gives m. p. 45°). From the residue a further 10 g. of the *para*-compound was isolated.

Reduction of this with iron filings and boiling water at 100° gave *p-cyclo*hexylaniline, m. p. 50—55°, in almost quantitative yield, but catalytic reduction gave a purer product. In this method, the nitro-compound (34·2 g.) was reduced in ethanol (200 ml.) at 60° with hydrogen (5 atm.) and Adams platinum catalyst (0·2 g.). The filtered solution was evaporated, leaving the pure amine, m. p. 54—55° (27·2 g., 93%).

3-*Aminodiphenyl*.—3-Nitrodiphenyl was prepared by the Gomberg procedure of Elks, Haworth, and Hey [8] from *m*-nitrobenzenediazonium chloride, benzene, and aqueous sodium acetate. The crude product, b. p. 150°/0·85 mm., crystallised from ethanol and had m. p. 58—60° (47%). This was reduced catalytically under conditions identical with those used in the previous experiment to an amine, m. p. 28—30·5° (acetyl derivative, m. p. 149·5—150°; Fichter and Sulzberger [9] report m. p. 148°).

3-*Amino*-4-*methoxydiphenyl*.—The method recommended by Tarbell, Hirschler, and Hall [10] was used for this preparation. Coupling 4-hydroxydiphenyl with benzenediazonium chloride gave the 3-azo-compound, m. p. 128—130°, which was converted into the methyl ether, m. p. 139°. Reduction of the azo-compound with stannous chloride proved unsatisfactory because an intractable stannichloride was obtained; the use of sodium dithionite gave 4-*methoxy*-3-*phenylhydrazodiphenyl*, m. p. 141° (Found: C, 78·7; H, 6·4. $C_{19}H_{18}ON_2$ requires C, 78·6; H, 6·2%). Catalytic reduction at 60° gave the required amine, m. p. 83°, in almost quantitative yield (ref. 10 gives m. p. 80—81°).

Preparation of the Stibinic Chlorides (I).—The arylamine (0·1 mole) was diazotised in concentrated hydrochloric acid (25 ml.) and water (50 ml.) by solid sodium nitrite (7 g.) at 0—5°. The filtered diazonium salt solution was added to antimony trioxide (16 g.) dissolved in concentrated hydrochloric acid (100 ml.) at −10° to 0°, and the precipitated double salt was filtered off and washed with ice cold ethanol. This was added to a solution of *p*-ethoxycarbonylphenylstibonous chloride (30 g., 0·088 mole) in ethanol (100 ml.). Decomposition of the double salt occurred between 30° and 50°, depending on the nature of the aryl group, and, when evolution of nitrogen ceased, the dark mixture was shaken in a separatory funnel with benzene (100 ml.) and 4N-hydrochloric acid (150 ml.). This usually resulted in the separation of three zones, benzene, acid, and a heavy oil; the last was further extracted with benzene and acid, and the combined extracts dried and evaporated to small bulk. From this concentrated solution the trichloride separated in the cases listed in Table 1(*a*).

Alternatively, when this procedure gave the trichloride in low yield, a solution of pyridine (10 ml.) in concentrated hydrochloric acid (25 ml.) was added to the ethanolic reaction mixture, and the precipitated pyridinium tetrachloroantimonate was filtered off and crystallised from ethanol containing hydrochloric acid. The properties of the salts are recorded in Table 1(*b*). The 3-diphenylyl derivative could not be crystallised satisfactorily except from ethyl acetate and it retained this solvent. Stirring with 2% sodium carbonate for 12 hr. decomposed the tetrachloroantimonate to give the stibinic acid from which the corresponding trichloride was obtained by trituration of the moist acid with cold concentrated hydrochloric acid.

When *o*-toluidine, *o*-chloroaniline, or *p*-bromoaniline was used in this reaction, the required unsymmetrical compound was not obtained. Instead, di-*p*-ethoxycarbonylphenylstibinic chloride, m. p. 183—184° (decomp.), was isolated although not analytically pure (Found: C, 40·0; H, 3·9. Calc. for $C_{18}H_{18}O_4Cl_3Sb$: C, 41·1; H, 3·4%). Alternatively, addition of pyridine hydrochloride in concentrated hydrochloric acid precipitated *pyridinium di-p-ethoxycarbonylphenyl tetrachloroantimonate*, m. p. 244° (decomp.) (Found: C, 42·9; H, 3·6. $C_{23}H_{24}O_4NCl_4Sb$ requires C, 43·0; H, 3·8%). The trichloride was readily reduced by stannous

[7] Neunhoeffer, *J. prakt. Chem.*, 1932, **133**, 95.
[8] Elks, Haworth, and Hey, *J.*, 1940, 1284.
[9] Fichter and Sulzberger, *Ber.*, 1904, **37**, 882.
[10] Tarbell, Hirschler, and Hall, *J. Amer. Chem. Soc.*, 1953, **75**, 1958.

chloride in ethanol (see below) to the *monochloride*, m. p. 134·5—135° (Found: C, 47·3; H, 3·8; Sb, 26·6%. $C_{18}H_{18}O_4ClSb$ requires C, 47·5; H, 4·0; Sb, 26·7%).

Unsymmetrical Diarylstibinous Chlorides (II).—The trichloride was dissolved in the minimum volume of ethanol, and twice the calculated quantity of stannous chloride was added at room temperature. In favourable cases the monochloride crystallised rapidly on cooling of the reaction mixture, and was filtered off and washed with 0·5N-hydrochloric acid. If the monochloride failed to separate, dilute hydrochloric acid was added until a faint turbidity appeared and cooling gave a crystalline deposit. Frequently, attempted recrystallisation of these

TABLE 1. (*a*) *Stibinic chlorides* (I). *p*-$EtO_2C{\cdot}C_6H_4{\cdot}SbCl_3{\cdot}Ar$.

Ar	M. p.	Yield (%)	Formula	Found (%) C	Found (%) H	Required (%) C	Required (%) H
* *p*-Me·C_6H_4	129°	39	$C_{16}H_{16}O_2Cl_3Sb$	44·6	4·1	41·0	3·4
			$C_{16}H_{16}O_2Cl_3Sb,\frac{1}{2}C_6H_6$			45·0	3·8
p-cyclo-$C_6H_{11}{\cdot}C_6H_4$	133—134	36	$C_{21}H_{24}O_2Cl_3Sb$	46·2	4·5	47·0	4·5
1-Naphthyl	135—136	18	$C_{19}H_{16}O_2Cl_3Sb$	44·9	3·4	45·2	3·2
2-Naphthyl	189—190	33	$C_{19}H_{16}O_2Cl_3Sb$	44·7	3·3	45·2	3·2
3-Diphenylyl	140	20	$C_{21}H_{18}O_2Cl_3Sb$	47·3	3·7	47·5	3·4
4-OMe-3-diphenylyl	162—165	15	$C_{22}H_{20}O_3Cl_3Sb$	47·0	3·9	47·1	3·6

(*b*) *Diaryl pyridinium tetrachloroantimonates*, $[p\text{-}EtO_2C{\cdot}C_6H_4{\cdot}SbArCl_4]^-[C_5H_6N]^+$.

p-Me·C_6H_4	230°	—	$C_{21}H_{22}O_2NCl_4Sb$	43·2	3·9	43·2	3·8
† *p-cyclo*-$C_6H_{11}{\cdot}C_6H_4$	240° (decomp.)	36	$C_{26}H_{30}O_2NCl_4Sb$	48·4	4·5	47·9	4·6
1-Naphthyl	216—218	30	$C_{24}H_{22}O_2NCl_4Sb$	46·3	3·5	46·5	3·6
3-Diphenylyl	117—122 (decomp.)	—	$C_{26}H_{24}O_2NCl_4Sb,C_4H_8O_2$	49·3	4·2	49·1	4·4

* After 8 hr. at 100°/15 mm., m. p. 115—120° (Found: C, 41·1; H, 3·8%).
† Found: Sb, 18·8. Required: Sb, 18·7%.

precipitated monochlorides gave sticky oils. That this was caused by partial decomposition of the monochloride by hydrochloric acid, was proved when *p*-ethoxycarbonylphenyl-1-naphthylstibinous chloride, which readily separated without addition of acid, was washed with 2N-hydrochloric acid and dried *in vacuo*. After 12 hr. the material, originally highly crystalline, had become pasty, and naphthalene, m. p. 75—80°, had sublimed. The residue, after being washed with ether, had m. p. 124—127° alone or mixed with *p*-ethoxycarbonylphenylstibinous chloride. The properties of the monochlorides are recorded in Table 2.

TABLE 2. *Stibinous chlorides* (II), *p*-$EtO_2C{\cdot}C_6H_4{\cdot}SbCl{\cdot}Ar$.

Ar	M. p.	Formula	Found (%) C	Found (%) H	Required (%) C	Required (%) H
p-Me·C_6H_4	63—66°	$C_{16}H_{16}O_2ClSb$	48·0	4·2	48·3	4·1
p-cyclo-$C_6H_{11}{\cdot}C_6H_4$	110—111	$C_{21}H_{24}O_2ClSb$	54·1	4·5	54·2	5·2
1-Naphthyl	90	$C_{19}H_{16}O_2ClSb$	52·8	4·0	52·6	3·7
2-Naphthyl	93·5—95	$C_{19}H_{16}O_2ClSb$	52·3	4·1	52·6	3·7
4-OMe-3-diphenylyl	154—155	$C_{22}H_{20}O_3ClSb$	54·2	4·0	54·0	4·1

In the reduction of (I; Ar = 3-diphenylyl) by this method, an oil was precipitated on addition of acid and this was extracted with ether. Evaporation of the ether left a glass which was soluble in benzene. After 12 hr. in a desiccator this glass was only partly miscible with benzene, and the solid residue remaining, after crystallisation from *cyclo*hexane, had m. p. 144·5—145·5° and proved to be the *hydroxy-dichloride* (Found: C, 49·9; H, 3·5. $C_{21}H_{19}O_3Cl_2Sb$ requires C, 49·3; H, 3·7%). This was treated with 4N-hydrochloric acid and then crystallised from benzene, to give the trichloride, m. p. 130—131° (Found: C, 47·3; H, 3·7%). Similar results were obtained when titanous chloride was used, although decolorisation of the reagent indicated complete reduction. The trichloride was also regained when reduction by sulphur dioxide [11] was attempted.

Triarylstibines (IV).—Phenylmagnesium bromide prepared from bromobenzene (3·14 g., 0·02

[11] Lesslie and Turner, *J.*, 1934, 1170.

mole) and magnesium (0·5 g.) in ether (20 ml.) was added during 10 min. to a cooled solution of the monochloride (0·01 mole) in benzene (30 ml.). The addition produced a thick cream-coloured precipitate which gradually became crystalline as the mixture was boiled for 0·25 hr. It was then cooled in ice and shaken with saturated ammonium chloride. The organic layer frequently emulsified at this stage and occasionally it was necessary to filter it from traces of finely divided solid before separation was possible. Removal of the solvents left a pale yellow viscous syrup in all cases. Attempts to crystallise the stibine esters failed and addition of chlorine or bromine in carbon tetrachloride gave no crystalline compound, except in one case (III; Ar = 4-methoxy-3-diphenylyl). In this case chlorine was passed into a solution of the syrup (2·4 g.) in carbon tetrachloride (15 ml.) at <0°. Addition of light petroleum (b. p. 60—80°) precipitated a gum from which the supernatant liquid was decanted. Crystals formed in this liquid and these initiated crystallisation in the gum when triturated with ethanol. The crude product (2·1 g.) was recrystallised from ethanol–ethyl acetate and gave p-*ethoxycarbonylphenyl*-4-*methoxy*-3-*diphenylylphenylstibine dichloride*, m. p. 168—169° (Found: C, 55·5; H, 4·3. $C_{28}H_{25}O_3Cl_2Sb$ requires C, 55·9; H, 4·2%).

In the other four cases the syrup (4 g.) obtained from the Grignard reaction was hydrolysed by boiling it for 0·5 hr. with 4% ethanolic potassium hydroxide (100 ml.). The mixture was poured into water (400 ml.) and extracted with ether. From the clear aqueous solution, dilute hydrochloric acid precipitated the triarylstibinecarboxylic acids as fine powders. After drying *in vacuo* for 24 hr., crystallisation gave the pure acids (IV) with properties listed in Table 3.

TABLE 3. *Triarylstibinecarboxylic acids* (IV), *p*-$HO_2C{\cdot}C_6H_4{\cdot}SbPhAr$.

			Yield		Found (%)			Required (%)		
Ar	M. p.	Solvent	(%)	Formula	C	H	Sb	C	H	Sb
p-MeC_6H_4	161—163°	EtOH	10	$C_{20}H_{17}O_2Sb$	58·7	4·8	29·6	58·4	4·2	29·6
p-cyclo-$C_6H_{11}{\cdot}C_6H_4$	165—166	$AcOH{\cdot}H_2O$	25	$C_{25}H_{25}O_2Sb$	62·8	4·9	25·2	62·7	5·3	25·4
1-Naphthyl	195—196	$EtOH{\cdot}CHCl_3$	38	$C_{23}H_{17}O_2Sb$	62·0	3·7	26·9	61·8	3·8	27·2
2-Naphthyl	170	$EtOH{\cdot}CHCl_3$	18	$C_{23}H_{17}O_2Sb$	62·2	4·0	27·0	61·8	3·8	27·2
4-OMe-3-diphenylyl	196—197	EtOH	20	$C_{26}H_{21}O_3Sb$	62·2	4·0	—	62·1	4·2	24·2

When the crude acid (IV; Ar = 2-naphthyl) was crystallised, the first fraction to separate had m. p. >270° and proved to be the *oxide* (Found: C, 59·7; H, 4·0. $C_{27}H_{17}O_3Sb$ requires C, 59·6; H, 3·7%). The second fraction was the acid, m. p. 170°.

Optical Resolution of p-*Carboxyphenyl*-1-*naphthylphenylstibine*.—(Rotations of salts were measured in " AnalaR " chloroform at room temp.; $l = 2$; c, 0·25—0·35).

In a preliminary experiment, the acid (0·45 g.) was suspended in hot ethanol (5 ml.), and (+)-1-phenylethylamine (0·25 g.) added. Complete dissolution occurred but no salt separated overnight. Addition of ether precipitated a gel which, in 3 hr. became crystalline and was filtered off. This salt (0·27 g.) had m. p. 162—176°, $[\alpha]_D$ −5·0°, raised by one crystallisation from ethyl acetate to $[\alpha]_D$ −14·8°. A second small fraction of salt (0·06 g.) separated slowly from the original preparation and had m. p. 158—180°, $[\alpha]_D$ +45·5°, but the residues formed a glass from which no further crystals could be isolated.

As this appeared to be definite evidence of resolution, the experiment was repeated on a larger scale. The acid (2·2 g.) was added to (+)-1-phenylethylamine (1·2 g., 2 equivs.) in hot ethanol (12 ml.). Immediate dissolution occurred but almost immediate separation of gelatinous crystals [2·35 g.; over 80% of the total (2·8 g.)]. This material was extracted with boiling ethyl acetate (30 ml.), leaving *salt* F1, $[\alpha]_D$ 0° (1·7 g.), and from the extract there separated 0·4 g. of salt, $[\alpha]_D$ +4·6°. Salt F1 was recrystallised twice from ethanol–chloroform and then had m. p. 185°, $[\alpha]_D$ −21·0° ± 0·9° (0·35 g.), unchanged on further recrystallisation (Found: C, 65·2; H, 5·3%. $C_{23}H_{17}O_2Sb,C_8H_{11}N$ requires C, 65·5; H, 5·0%). Working up intermediate fractions yielded a further 0·31 g. of the pure (−)-acid–(+)-base salt, but no fraction as strongly dextrorotatory as that obtained in the initial trial was isolated. Decomposition of the residual salts gave acid $[\alpha]_D$ +6·7° (in $CHCl_3$).

To obtain the (+)-acid, the resolution was repeated with (−)-1-phenylethylamine. The acid (0·85 g.) and (−)-base (0·5 g.) were dissolved together in 8 ml. of hot ethanol. Overnight hard rosettes of tiny needles separated, and had $[\alpha]_D$ +12·7° (0·32 g.). These were recrystallised from ethanol and then had m. p. 185—186°, $[\alpha]_D$ +20·8° ± 1° (0·11 g.) (Found: C, 65·1; H, 5·4%).

Isolation of (+)- *and* (−)-*acids.* The (−)-acid–(+)-base salt (0·21 g.) was dissolved in ethanol (25 ml.) and cooled to −10°. Addition of 0·1N-sulphuric acid gave a milky separation and dilution with water precipitated the (−)-acid, which was filtered off, washed, and dried (0·11 g.). It had an indefinite m. p. (91—100°), $[\alpha]_D^{18}$ −35·5° ± 1·5° (*c* 0·324 in " AnalaR " $CHCl_3$), $[\alpha]_D^{22}$ −30·5° (*c* 0·328 in " AnalaR " benzene) (Found: C, 62·2; H, 4·2. $C_{23}H_{17}O_2Sb$ requires C, 61·8; H, 3·8%).

The (+)-acid–(−)-base salt, decomposed similarly, gave the (+)-acid, m. p. 92—100°, $[\alpha]_D^{18}$ +35·1° ± 1·6° (*c* 0·314 in " AnalaR " $CHCl_3$), $[\alpha]_D^{22}$ +27·1° (*c* 0·259 in 99·6% EtOH) (Found: C, 62·0; H, 4·2%).

Attempted Racemisation.—The (−)-acid (0·0433 g.) was dissolved in *p*-xylene (99·6%; b. p. 138°) (20 ml.) and had α_D^{18} −0·13°, $[\alpha]_D^{18}$ −30·0°. The solution was boiled for 0·5 hr. under reflux, then rapidly cooled to 18°; the rotation was unchanged. After a further 1·5 hours' heating there was still no change in rotation. When the solution had been heated for 8 hr. a faint opalescence made further readings impossible. The (+)-acid (0·0620 g.), α_D^{22} +0·19°, showed no change in rotation after 2 hours' boiling, but again a faint precipitate was obtained on further heating.

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