852. *The Configuration of Heterocyclic Antimony Compounds. Part II.* Symmetric and Enantiomorphic 9-Stibiafluorenes.*

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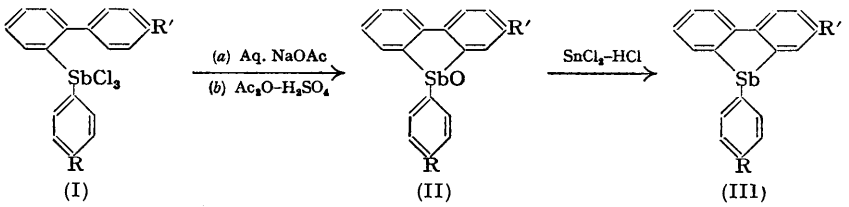
Fractional crystallisation of optically active base salts of 9-*p*-carboxyphenyl-9-stibiafluorene gives no evidence of the existence of diastereoisomerides. On the other hand, 2-amino-9-*p*-tolyl-9-stibiafluorene is resolved into (+)- and (−)-forms by crystallisation of the (+)- and (−)-hydrogen tartrates, and the enantiomers, $[\alpha]_D^{22}$ ±250°, show considerable optical stability. A study of the racemisation of the (+)-base in benzene at 22°, 25·4°, 30°, and 40° indicates that the energy of activation is about 15 kcal./mole, but since the racemisation appears to be subject to adventitious catalysis, this figure is quoted with reservation. The successful optical resolution of the (±)-base, and the failure of all attempts to resolve the stibiafluorene unsubstituted in the diphenyl residue, constitute further evidence that enantiomorphism of this type of heterocyclic compound is dependent on the stable pyramidal disposition of the valency bonds of the tervalent antimony atom and not on the "skew" configuration of the diphenyl residue in the molecule.

In Part I * the preparation and properties of (+)- and (−)-2-carboxy-9-*p*-tolyl-9-stibiafluorene (III; R = Me, R′ = CO_2H) were described, and the reasons for the choice of the 9-stibiafluorenes as a molecular type suitable for investigating the stereochemistry of antimony were discussed. Unfortunately, the discovered asymmetry could not be ascribed with certainty to the stable pyramidal disposition of the bonds of the tervalent antimony atom because the possible twisting of the benzene rings in the tricylic system could deprive the molecule of any symmetry even if the bonds from antimony were planar. However, if the distortion of this part of the molecule to accommodate the antimony atom is the cause of the enantiomorphism, a symmetrically substituted 9-stibiafluorene [*e.g.*, (III; R = CO_2H, R′ = H)] should be a "skew" molecule and consequently should be



resolvable into (+)- and (−)-forms. To test this hypothesis, 9-*p*-carboxyphenyl-9-stibiafluorene was prepared by a method essentially that described in Part I (*loc. cit.*), and optical resolution was attempted. The acid formed unsatisfactory salts with brucine and quinidine but fractional crystallisation of the salts obtained with quinine, ephedrine, and (+)-1-phenylethylamine gave no evidence of separation into diastereoisomerides, and acid regained from the salts was consistently optically inactive. In contrast, 2-amino-9-*p*-tolyl-9-stibiafluorene, which should be dissymmetric if the bonds from antimony are not planar and the tricyclic system remains flat, was found to be readily resolvable through the (+)- and (−)-hydrogen tartrates and gave specimens of the (+)-amine, $[\alpha]_D^{22}$ +250·5° ±1°, and (−)-amine, $[\alpha]_D^{23}$ −248·0° ±2°, in benzene. Despite the fact that non-resolution of the symmetrically substituted acid constitutes negative evidence of an unsatisfactory kind, the striking contrast between the comparatively ready separation of (+)- and (−)-forms of both the unsymmetrically substituted stibiafluorenes so far investigated, and the homogeneity of the three salts of the unsubstituted compound, are an argument in favour of the pyramidal rather than the skew configuration of the molecule.

The resolution of the (±)-amine by use of (+)-tartaric acid was carried out by orthodox

* Part I, *J.*, 1950, 3109. The nomenclature of organic antimony acids in Part I was that recorded in A. D. Mitchell's "British Chemical Nomenclature," Ed. Arnold & Co., London, 1948, p. 64. In the present paper (Part II), however, it is based on that laid down in *J.*, 1951, 3516; *e.g.*, Ph·SbO_3H_2 = phenylstibonic acid; Ph_2SbO_2H = diphenylstibinic acid.

procedures and no difficulty was experienced in the purification of the less soluble diastereoisomeride, (+)-acid (+)-base, m. p. 161—162° (decomp.), $[\alpha]_D$ +216·5°, provided that the ethanol used for crystallisation contained 2% of (+)-tartaric acid, otherwise the salt which separated was contaminated with free base. The more soluble (+)-acid (−)-base salt was never obtained optically pure and invariably separated as a gel, a tiresome characteristic which was mainly responsible for the low yields of optically pure base obtained. Moreover, the usual tendency for aromatic amine salts to develop colour in air was very marked in the case of the more soluble salt. As purification by crystallisation, either of the gelatinous (+)-acid (−)-base salt, or of the optically impure base regained from it, was unsuccessful, (−)-tartaric acid was used to obtain the (−)-acid (−)-base salt, m. p. 160—161° (decomp.), $[\alpha]_D$ −212·8°. [The discrepancy in the specific rotations of the enantiomeric salts arose from racemic acid present in the (−)-tartaric acid used.] As initial experiments indicated that racemisation was appreciable on warming, the (+)- and the (−)-amine were isolated by addition of 0·5N-sodium hydroxide to ethanolic solutions of the salts at −10° and immediate filtration of the crystalline base precipitated. The (+)-amine, $[\alpha]_D^{22}$ 250·5°, could not be recrystallised without some loss of optical activity.

The racemisation, in benzene, of one particular batch of the (+)-base was followed at 22°, 25·4°, 30°, and 40° and the rate constants were found to be 1·15, 1·61, 2·02, and $5{\cdot}16 \times 10^{-2}$ hour^{-1}, respectively. From these constants a linear Arrhenius plot resulted (the value of k_{30} was slightly low), leading to an energy of activation of 15 kcal./mole. However, the racemisation rate of the (−)-base at 22° was not identical with that of the (+)-base at the same temperature and the results obtained with the (+)-base at 30° were not reproducible, although the specimen used for the second experiment was obtained from the same salt and in the same way. Furthermore, on one occasion a portion of base, α_D^{20} +1·58°, $[\alpha]_D^{20}$ +248·4°, remained unchanged in rotation after a day, and after 3 weeks still had α_D +1·14°, $[\alpha]_D$ +179·2°. Obviously the racemisation is very susceptible to traces of adventitious catalyst, a not uncommon phenomenon observed for example in the racemisation of bromosuccinic ester by bromide ion in a concentration not detected analytically (R. Kuhn and T. Wagner-Juaregg, *Naturwiss.*, 1929, **17**, 103). In the present case the nature of the catalyst is obscure, although hydrochloric acid proved to be effective, for a specimen of optically impure (−)-base, α_D^{22} −0·80°, which had remained unchanged in rotation for 3 days, was " touched off " by introducing a trace of the vapour into the polarimeter tube. Racemisation started immediately and the rotation had fallen to zero within 2 days. Also, there occurred a very rapid racemisation, similar to that observed in the original attempts to isolate (+)-2-carboxy-9-*p*-tolyl-9-stibiafluorene (*J.*, 1950, 3111), when a chloroform solution of the (+)-base, α_D^{24} +1·20°, was shaken with 4N-hydrochloric acid. Neither the chloroform solution nor the acid showed any optical activity on polarimetric examination 20 minutes after mixing.

As the racemisation of (+)-2-carboxy-9-*p*-tolyl-9-stibiafluorene in pyridine at 40° was considerably slower than that of the (+)-amine in benzene at the same temperature, the possibility that pyridine was effective in stabilising the asymmetric molecule was investigated, but the (+)-base was found to racemise more rather than less rapidly in the basic solvent.

In view of these results it is clear that a much more detailed study of the racemisation is necessary in order to gain a precise value for the energy of activation, a value of considerable interest if the projected *X*-ray crystallographic examination indicates that the configuration of the stibiafluorenes is, in fact, pyramidal. 2-Amino-9-*p*-tolyl-9-stibiafluorene, a primary aromatic amine, slightly sensitive to light and air, is not an ideal subject for such a study, and the synthesis of further members of the series may disclose a compound more suitable for the purpose.

Experimental

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

p-*Carbethoxyphenyl*-2-*diphenylylstibine Trichloride* (I; R = CO_2Et, R′ = H).—This compound was prepared by the method described previously (*J.*, 1950, 3014) for 2-diphenylyl-*p*-

tolylstibine trichloride. 2-Aminodiphenyl (33·8 g., 0·2 mol.) was diazotised and converted into the antimony chloride double salt, which was isolated, washed with ethanol, and added in portions to *p*-carbethoxyphenylstibonous chloride (68·0 g., 0·2 mol.) in 125 c.c. of ethanol, 75 c.c. of which had been saturated with dry hydrogen chloride. Before all the double salt had been added, the trichloride began to crystallise out. The reaction was completed by warming to 40°, and the product was separated after cooling to 0°. Recrystallisation from ethyl acetate necessitated filtration from insoluble material (2 g.) and yielded the required *trichloride* (21 g., 20%), m. p. 144—146° (Found: C, 47·7; H, 3·7; Sb, 23·0. $C_{21}H_{18}O_2Cl_3Sb$ requires C, 47·5; H, 3·4; Sb, 22·95%). Reduction of the trichloride (1·3 g.) in ethanol (20 c.c.) with stannous chloride (1·5 g.) in 3N-hydrochloric acid (20 c.c.) gave, almost immediately, a crystalline precipitate of p-*carbethoxyphenyl-2-diphenylylstibinous chloride*, m. p. 84—85° (0·8 g.) (Found: C, 55·1; H, 4·4; Sb, 26·6. $C_{21}H_{18}O_2ClSb$ requires C, 54·9; H, 3·95; Sb, 26·5%).

9-p-*Carbethoxyphenyl-9-stibiafluorene* (III; R = CO_2Et, R′ = H).—The stibinic acid obtained by adding a solution of (I; R = CO_2Et, R′ = H) (11 g.) in acetone (150 c.c.) to aqueous sodium acetate was thoroughly dried and dissolved in acetic anhydride (100 c.c.) containing concentrated sulphuric acid (1 c.c.) and kept at 90° for 3 hours, then poured on ice and set aside overnight. The solid obtained was only partly soluble in acetone (50 c.c.), and the residue (5·2 g.) on recrystallisation from ethyl acetate proved to be 9-p-*carbethoxyphenyl-9-stibiafluorene oxide* (II; R = CO_2Et, R′ = H), m. p. 172—173° (decomp.) (Found: C, 57·4; H, 4·0. $C_{21}H_{17}O_3Sb$ requires C, 57·2; H, 3·9%). This oxide dissolved in acetone (40 c.c.) containing 3N-hydrochloric acid (10 c.c.) and was reduced with stannous chloride (5 g.), yielding 9-p-*carbethoxyphenyl-9-stibiafluorene*, m. p. 144—145° (4 g.) (Found: C, 59·9; H, 4·05; Sb, 28·9. $C_{21}H_{17}O_2Sb$ requires C, 59·6; H, 4·05; Sb, 28·8%). On reduction of the filtrate from the separation of the oxide, a further small quantity (0·7 g.) of the cyclic ester was obtained, but the main product was the stibinous chloride, m. p. 84—85° (3·3 g.).

The ester (7·5 g.) was hydrolysed by boiling for ½ hour in ethanol (150 c.c.) and 10% aqueous potassium hydroxide (70 c.c.). The reaction mixture was poured into water (300 c.c.) and acidified (Congo-red) with concentrated hydrochloric acid. Recrystallisation of the dry precipitate from ethanol–chloroform (1 : 1) gave 9-p-*carboxyphenyl-9-stibiafluorene* as small needles, m. p. 231—233° (Found: C, 57·7; H, 3·2; Sb, 30·9. $C_{19}H_{13}O_2Sb$ requires C, 57·75; H, 3·3; Sb, 30·8%).

Salts of 9-p-*Carboxyphenyl-9-stibiafluorene with Optically Active Bases.*—(+)-α-*Phenylethylamine salt.* This was prepared from the acid (1·6 g.) and twice the calculated quantity of (+)-base (1·0 g.) in ethanol–chloroform (1 : 1) (350 c.c.). The salt was collected in three fractions by progressive evaporation of the solvent under reduced pressure: F1, 0·7 g.; F2, 0·8 g.; F3, 0·35 g. All had m. p. 208—209° with shrinkage at 205°. The salt was very insoluble, and specific rotations, measured in dioxan, showed no significant difference, $[\alpha]_D$ +29·0° to +29·5° (*c*, 0·25, room temp.). Three crystallisations of F1 from absolute ethanol gave a salt (0·25 g.), m. p. 208—209°, $[\alpha]_D$ +29·1°, and four recrystallisations of the combined F2 and F3 gave identical material, $[\alpha]_D$ +29·0°. In all, ten different fractions of *salt* were examined, and $[\alpha]_D$ fell between +29·0° and +30·1° (Found: C, 62·6; H, 4·76. $C_{19}H_{13}O_2Sb,C_8H_{11}N$ requires C, 62·8; H, 4·69%).

Ephedrine salt. The acid (2·0 g.) was dissolved by warming it in a solution of ephedrine (0·9 g.) in ethanol (20 c.c.). After 2 hours a first fraction of salt (0·2 g.), m. p. 184—185°, $[\alpha]_D$ +5·67°, had separated, and after a further 10 hours a second fraction (1·5 g.), m. p. 184—185°, $[\alpha]_D$ +5·40°, was collected. Reduction of the volume of ethanol to 5 c.c. then yielded (after 8 hours) a third fraction (0·8 g.), m. p. 183—184°, $[\alpha]_D$ +5·0°. Four recrystallisations of the combined first and second fractions from absolute ethanol gave 0·5 g., m. p. 184—185°, $[\alpha]_D$ +5·47°. Acid regained from this, and also from the salt obtained after three recrystallisations of the third fraction from the original preparation, was inactive in solution in pyridine. The rotations of the *salts* (Found: C, 60·27; H, 5·4. $C_{19}H_{13}O_2Sb,C_{10}H_{15}ON,H_2O$ requires C, 60·25; H, 5·2%) were measured in dioxan at room temperature (*c*, 0·25) and the ephedrine used had $[\alpha]_D$ −14·85° (*c*, 0·505 in dioxan).

Quinine salt. The acid (2·0 g.) and anhydrous quinine (1·6 g.) were dissolved together in a warm mixture of ethanol (20 c.c.) and chloroform (20 c.c.). After 2 hours the salt, in the form of rosettes of small needles (1·1 g.), was filtered off, and the filtrate when kept overnight deposited a second fraction (2·2 g.). The first fraction, m. p. 203—205° (shrinking at 201°), had $[\alpha]_D$ −94·4° (*c*, 0·5 in " AnalaR " chloroform) and was unaltered by two recrystallisations from ethanol containing a little chloroform. The second fraction from the original preparation had m. p. 199—200°, $[\alpha]_D$ −93·6°, and three recrystallisations effected purification but no

separation of stereoisomers, as the final salt had m. p. 203—205°, $[\alpha]_D$ −94·7°. In all, ten different fractions of *salt* (Found: C, 65·0; H, 5·2. $C_{19}H_{13}O_2Sb,C_{20}H_{24}O_2N_2$ requires C, 65·1; H, 5·2%) were examined; they showed no significant difference in $[\alpha]_D$, and acid regained from three of these fractions was inactive in pyridine.

9-p-*Carbethoxyphenyl*-2-*nitro*-9-*stibiafluorene* (III; R = CO_2Et, R′ = NO_2).—The reaction of the antimony chloride double salt of diazotised 2-amino-4′-nitrodiphenyl (10·7 g., 0·05 mol.) in ethanol with *p*-carbethoxyphenylstibonous chloride gave *p*-carbethoxyphenyl-2-4′-nitrodiphenylylstibine trichloride (18 g.), m. p. 88—94° after crystallisation from ethanol containing a little hydrochloric acid. The compound contains solvent of crystallisation and was not analysed, but on reduction with stannous chloride gave p-*carbethoxyphenyl*-2-4′-*nitrodiphenylylstibinous chloride*, m. p. 156—157° (Found: C, 49·5; H, 3·9; Sb, 24·25. $C_{21}H_{17}O_4NClSb$ requires C, 49·9; H, 3·4; Sb, 24·1%). The stibinic acid (8 g.) obtained from the crude trichloride was subjected to the usual cyclisation procedure but even after prolonged heating on a water-bath only a small yield (0·8 g.) of 9-p-*carbethoxyphenyl*-2-*nitro*-9-*stibiafluorene*, m. p. 193·5—195° was obtained (Found: C, 53·7; H, 3·5; Sb, 26·2. $C_{21}H_{16}O_4NSb$ requires C, 53·9; H, 3·45; Sb, 26·0%). The bulk of the material was regained as the stibinous chloride, m. p. 156—157°. Hydrolysis of the cyclic ester gave 9-p-*carboxyphenyl*-2-*nitro*-9-*stibiafluorene* (III; R = CO_2H, R′ = NO_2) as a yellow powder, m. p. 212·5—213·5° (blackening) (Found: C, 52·3; H, 3·1. $C_{19}H_{12}O_4NSb$ requires C, 51·9; H, 2·8%).

2-*Nitro- and* 2-*Amino*-9-p-*tolyl*-9-*stibiafluorene*.—2-Amino-4′-nitrodiphenyl (32·1 g., 0·15 mol.) was converted by the usual series of reactions into 2-4′-*nitrodiphenylyl*-p-*tolylstibine trichloride* (I; R = Me, R′ = NO_2), m. p. 160—162° (22·2 g., 29%) (Found: C, 43·9; H, 2·9. $C_{19}H_{15}O_2NCl_3Sb$ requires C, 44·1; H, 2·9%). The corresponding stibinic acid was cyclised to the stibiafluorene very slowly, and good yields were obtained only when the reaction was allowed to proceed for a period considerably longer than the 3 hours found sufficient in previous cyclisations. When the stibinic acid (21 g.) was dissolved in freshly distilled acetic anhydride (450 c.c.) containing sulphuric acid (1 c.c.) and heated on a boiling-water bath for 4 hours, then poured into water (2 l.), the filtered precipitate was only partly soluble in acetone (50 c.c.). The insoluble portion was shown to be unchanged stibinic acid and not the stibiafluorene oxide, the solubilities being the reverse of those found in the cyclisation of the stibinic acid from (I; R = CO_2Et, R′ = H). Reduction of the insoluble portion (7·1 g.) in a mixture of acetone and 3N-hydrochloric acid with stannous chloride (7 g.) readily gave 2-4′-nitrodiphenylyl-*p*-tolylstibinous chloride, m. p. 147—148°. Addition of stannous chloride to the acetone solution of the soluble fraction gave immediately a pale yellow crystalline deposit of 2-*nitro*-9-p-*tolyl*-9-*stibiafluorene*, m. p. 157—159° (8 g., 50%) after recrystallisation from ethyl acetate, from which it separates as yellow needles (Found: C, 55·75; H, 3·49; Sb, 29·8. $C_{19}H_{14}O_2NSb$ requires C, 55·65; H, 3·44; Sb, 29·7%). When the period of heating was increased to 8 hours the yield was increased to 62%.

Reduction of the nitro- to the amino-group with stannous chloride in ethanol and hydrochloric acid was unsatisfactory, and an attempt to reduce with zinc and alkali gave a very insoluble orange substance, presumably an azo-compound. Satisfactory reduction occurred under the neutral conditions recommended for the preparation of 2-aminofluorene (*Org. Synth.*, Vol. II, p. 448). A solution of the nitro-compound (3·5 g.) in aqueous ethanol (120 c.c.; EtOH : H_2O = 5 : 1) was heated on a boiling-water bath for 4 hours with zinc dust (20 g.) and calcium chloride (2 g.). The filtered solution was evaporated to 40 c.c. and, on cooling, 2-*amino*-9-p-*tolyl*-9-*stibiafluorene* (III; R = Me, R′ = NH_2) (2·9 g.) crystallised as rosettes of pale cream needles, m. p. 132—133° (Found: C, 59·9; H, 4·8; Sb, 32·25. $C_{19}H_{16}NSb$ requires C, 60·0; H, 4·24; Sb, 32·0%).

Resolution of (±)-2-*Amino*-9-p-*tolyl*-9-*stibiafluorene*.—Small-scale tests indicated that the (±)-base formed salts with (+)-camphorsulphonic, (+)-tartaric, dibenzoyltartaric, and (−)-malic acids. The salts obtained from the last two acids were inhomogeneous, containing crystals of the free amine. The (+)-camphorsulphonate on crystallisation gave fractions ranging from $[\alpha]_D$ +18·6° to $[\alpha]_D$ +14·7° (*c*, 1·0 in absolute ethanol), all of which mutarotated to a constant value of $[\alpha]_D$ +12·5° overnight, and optically inactive base was obtained from the two extreme fractions of salt. The hydrogen (+)-tartrate appeared to be the most suitable, and in a first attempt the (±)-amine (3·8 g., 0·01 mol.) in ethanol (50 c.c.) was added to (+)-tartaric acid (1·65 g., 0·011 mol.) in boiling ethanol (20 c.c.), and the solution was filtered from a small gelatinous separation and kept overnight. The properties of the fractions obtained are given in Table 1(*a*); vacuum distillation below 30° was used for evaporation of the mother-liquors, and $[\alpha]_D$ were measured in " AnalaR " acetone between 20° and 23° (*c*, *ca.* 0·5).

The mother-liquors from F3 formed a gel, which was dissolved in ethanol and decomposed with 0·5N-sodium hydroxide, giving a specimen of base, $[\alpha]_D$ −146·5° (*c*, 0·505 in " AnalaR " benzene). Recrystallisation of F1 from ethanol (20 c.c.) gave a fraction of salt A, 0·7 g., $[\alpha]_D$ +206·0°, and similarly F2 gave B, 0·4 g., $[\alpha]_D$ +151·2°. Recrystallisation of A gave 0·4 g. of material, $[\alpha]_D$ +227·5°, but this was obviously a mixture containing pale buff-coloured crystals of the free amine. Recrystallisation of B gave 0·2 g. of salt, m. p. 160—161° (decomp.), $[\alpha]_D$ +216·5°, which later proved to be the optically pure (+)-acid (+)-base salt. The mother-liquors from the crystallisation of B and from the later fractions of A formed gels.

TABLE 1.

(*a*)	Vol. of solution (c.c.)	Time of standing (hrs.)	Wt. (g.)	$[\alpha]_D$	M. p.
F1	70	18	1·85	+26·6°	154° (decomp.)
F2	20	2·5	1·50	−12·0	145—148 (decomp.)
F3	15	0·5	0·32	−83·3	125—142 ,,
(*b*)					
X1	110	22	7·0	+43·4	156° (decomp.)
X2	30	7	2·4	−20·85	128—144
X3	0	—	0·9	−95·0	101—132

In a second resolution the (±)-base (7·6 g.) in ethanol (90 c.c.) was added to a solution of 3·3 g. of (+)-tartaric acid in 20 c.c. of boiling ethanol, and the fractions obtained are listed in Table 1(*b*). Two recrystallisations of X1 gave a fraction of salt Y (2·25 g.), $[\alpha]_D$ +192·0°, and two further recrystallisations of Y from ethanol (20 c.c.) containing (+)-tartaric acid (0·5 g.) gave the (+)-acid (+)-base *salt* as opaque needles, 1·2 g., m. p. 161—162° (decomp.), $[\alpha]_D$ +217·0°, unchanged by further crystallisation (Found : C, 52·4; H, 4·0. $C_{19}H_{16}NSb,C_4H_6O_6$ requires C, 52·1; H, 4·2%). On progressive evaporation of the mother-liquor from Y, a fraction of salt, $[\alpha]_D$ +52·5°, was obtained, followed by a separation of the free *amine*, $[\alpha]_D$ −66·9°, m. p. 131—134° (Found : C, 60·2; H, 4·6. $C_{19}H_{16}NSb$ requires C, 60·0; H, 4·2%).

Recovered base (2 g., $[\alpha]_D$ −30°, approx.) in ethanol (20 c.c.) was added to a hot solution of (−)-tartaric acid (1 g.) in ethanol (10 c.c.) and set aside for 18 hours. The first fraction of salt, 1·12 g., m. p. 145—149°, $[\alpha]_D$ −94·2°, was twice recrystallised from ethanol containing a little (−)-tartaric acid and gave (−)-acid (−)-base *salt*, 0·25 g., m. p. 160—161° (decomp.), $[\alpha]_D$ −212·8°, unchanged in $[\alpha]_D$ on recrystallisation (Found : C, 52·7; H, 4·4%). The rotation of this salt is lower than that of its enantiomer because the (−)-tartaric acid was not quite optically pure, but also the recovered base from which the salt was prepared was brown and a faint colour persisted in the salt in contrast to the colourless enantiomer.

Isolation of (+)- *and* (−)-2-*Amino*-9-p-*tolyl*-9-*stibiafluorene*.—Treatment of a solution of the (+)-acid (+)-base salt (0·5 g.) in ethanol (25 c.c.) with 0·5N-sodium hydroxide at −10° gave a crystalline precipitate of (+)-2-*amino*-9-p-*tolyl*-9-*stibiafluorene* as fine cream needles (0·32 g.), m. p. 136—138°, $[\alpha]_D^{22}$ +250·5°±1° (*c*, 0·530 in " AnalaR " benzene), +213·5°±2° (*c*, 0·281 in " AnalaR " chloroform) (Found: C, 60·35; H, 4·5. $C_{19}H_{16}NSb$ requires C, 60·0; H, 4·2%). Decomposition of the salt without cooling, or in acetone solution, gave specimens of the base which were less optically pure and had $[\alpha]_D$ ranging from +230° to 245°. Decomposition of the (−)-acid (−)-base salt by the same method gave (−)-base, m. p. 136—138°, $[\alpha]_D^{23}$ −248·0°±2° (*c*, 0·248 in " AnalaR " benzene). The m. p.s of the enantiomeric amines when observed in a capillary tube ranged from 125° to 140° when the bath was warmed from room temperature, and from 135° to 142° when the capillary was inserted at 130°. The m. p. quoted above, *viz.*, 136—138°, was observed by microscope when crystals were dropped on to a Kofler hot-stage at 130° and the temperature was raised 3° per minute.

Racemisation of the (+)-*Amine*.—The (+)-amine (*ca.* 0·1 g.) was dissolved in " AnalaR " benzene at the required temperature and made up to 20 c.c., and the racemisation was observed in a water-jacketed polarimeter tube ($l = 2$). The rate constants were evaluated graphically and the results are summarised in Table 2. In Expt. 3, 0·0991 g. of (+)-amine was used, and the initial α_D 2·46° fell to 2·10° in 8 hours. The water-circulating pump ceased overnight and the temperature in the polarimeter tube fell to 22°. The value α_D 1·495° was observed when the solution had regained 30·1° and was used as the initial rotation. The solution, α_D +0·36°, was optically inactive when observed 10 weeks later. The specimens of (+)-amine used in Expts. 3 and 4 were obtained from the same (+)-acid (+)-base salt by decomposition in the same way but at different times. The only observed difference in treatment was in the time of drying *in vacuo*. The solution from Expt. 5 was boiled under reflux for 8 hours and was then optically inactive. The base recovered from the solution as a yellow scale had m. p. 127—

TABLE 2.

Expt.	Temp.	Wt. (g.)	Initial α_D	Final α_D	Time (hr.)	$100k$ *	Half-life (hr.)
(+)-Amine.							
1	22·0°	0·1028	2·58°	0·65°	119·5	1·15	60·3
2	25·4°	0·1019	2·55	0·50	102	1·61	42·9
3	30·1°	—	1·495	0·36	68	2·02	34·3
4	30·8°	0·0511	1·28	0·52	28·75	3·15	22·0
5	40·0°	0·0912	2·20	0·23	45	5·16	13·4
(−)-Amine.							
	23°	0·0496	−1·23	−0·46	100	0·98	70·5
(+)-Amine in pyridine.							
	23°	0·0507	1·26	0·255	58	2·73	25·4

* $k = (1/t) \ln a_0/a_t$ (in hr.$^{-1}$).

131° (Found: C, 60·45; H, 4·6%), and recrystallisation from aqueous ethanol raised the m.p. to 131—132°.

(+)-Amine (0·0562 g.) was dissolved in " AnalaR " chloroform and the solution, α_D +1·20°, was shaken with 4N-hydrochloric acid (2 × 20 c.c.). The chloroform solution was rapidly dried (Na_2SO_4), examined 20—25 minutes after acid treatment, and found to have α_D +0·03°. Removal of the chloroform on a water-bath left a brown glass, which with alkali gave a powder, m. p. 70—91°, and m. p. 120—127° after recrystallisation, indicating considerable decomposition.

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