

### 245. *Organic Antimonial Compounds. Part III.*

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THIS paper describes the preparation and properties of certain stibines and their derivatives and of antimonyl tartrates containing stibonium, arsonium, and phosphonium radicals.

The only mixed stibines hitherto prepared are phenyldimethyl-, phenyldiethyl-, diphenylmethyl-, diphenylethyl-, phenylcyclopentamethylene-, and phenylcyclohexamethylene-stibine (Grüttner, Wiernik, and Krause, *Ber.*, 1915, **48**, 1484, 1759; 1916, **49**, 442; Ingold, Shaw, and Wilson, *J.*, 1928, 1283). With the exception of tetramethylstibonium antimonyl *d*-tartrate (Westphal, *Dissert.*, Berlin, 1895, 28), no antimonyl tartrates of phosphonium, arsonium or stibonium bases have been made, although several ammonium and alkaloidal salts of the tartar emetic type are known.

*Ethyl-di-n-butylstibine* was prepared by adding 50 g. of ethyldiiodostibine (Auger and Billy, *Compt. rend.*, 1904, **139**, 597) in 200 c.c. of ether to the Grignard reagent (12 g. of magnesium, 69 g. of *n*-butyl bromide, 300 c.c. of ether) in an atmosphere of hydrogen. The mixture was treated with ammonium chloride solution, the ethereal layer dried, the ether expelled in a stream of carbon dioxide, and the residual liquid fractionally distilled under reduced pressure. Redistillation gave 4 g. of the stibine (Found: C, 45.1; H, 8.6; Sb, 45.6.  $C_{10}H_{23}Sb$  requires C, 45.3; H, 8.7; Sb, 46.0%), b. p.  $147^{\circ}/43$  mm.,  $d_4^{17}$  1.155. *Ethyl-di-n-amylstibine* (Found: C, 49.0; H, 9.0; Sb, 41.9.  $C_{12}H_{27}Sb$  requires C, 49.1; H, 9.3; Sb, 41.6%), similarly prepared from 75 g. of *n*-amyl bromide, had b. p.  $167^{\circ}/51$  mm. and  $d_4^{23}$  1.094. *Ethyldicyclohexylstibine* (Found: Sb, 38.4.  $C_{14}H_{27}Sb$  requires Sb, 38.4%) has b. p. 122—126°/15 mm. and

$d_4^{25}$  0.914. These three compounds, in similar yields, are obtained as clear liquids, which immediately become cloudy in the air, and char filter-paper. They reduce mercuric salts in the cold, and silver salts on warming, to the metal.

*Di-o-tolyethylstibine*, needles, m. p.  $102^\circ$ , from alcohol (Found : C, 57.6; H, 5.4; Sb, 36.6.  $C_{16}H_{19}Sb$  requires C, 57.7; H, 5.8; Sb, 36.6%), *di-m-tolyethylstibine*, liquid,  $d_4^{25}$  1.321 (Found : C, 58.0; H, 5.7; Sb, 36.8%), and *di-p-tolyethylstibine*, needles, m. p.  $114^\circ$ , from alcohol (Found : C, 57.5; H, 5.8%), have the respective b. p.'s  $196\text{--}201^\circ/10$  mm.,  $211\text{--}216^\circ/15$  mm., and  $226^\circ/5$  mm. They were prepared from 85 g. of the tolyl bromide, 12 g. of magnesium, and 50 g. of ethyldi-iodostibine in 500 c.c. of ether in an inert atmosphere. The product in each case was distilled under reduced pressure, the ditolyl coming over first, followed by the stibine at a much higher temperature.

The difficulty of preparing crystalline derivatives of stibines (J., 1930, 463, 1921) is particularly great when the stibine contains different hydrocarbon radicals. Where all three groups are alike, additive compounds are formed with greater facility, e.g., in the case of triisobutylstibine, of which the following derivatives have been obtained. The double oxide,  $(C_4H_9)_3SbO, Sb_2O_3$  (Found : C, 23.7; H, 4.5; Sb, 60.1.  $C_{12}H_{27}O_4Sb_3$  requires C, 24.0; H, 4.5; Sb, 60.8%), an insoluble powder infusible up to  $240^\circ$ , is precipitated during the aerial oxidation of the stibine. *Triisobutylstibine oxide* [Found : C, 45.2; H, 8.4; Sb, 39.0.  $(C_4H_9)_3SbO$  requires C, 46.6; H, 8.8; Sb, 39.4%] is obtained by shaking an alcoholic solution of the stibine with red mercuric oxide, decanting, and expelling the solvent. The gelatinous mass gradually solidifies. *Triisobutylstibine dichloride* (Found : C, 39.1; H, 7.6; Cl, 20.1.  $C_{12}H_{27}Cl_2Sb$  requires C, 39.6; H, 7.5; Cl, 19.5%) has m. p.  $91^\circ$ , rhombs from ether or carbon tetrachloride; *dibromide* (Found : Br, 35.4.  $C_{12}H_{27}Br_2Sb$  requires Br, 35.3%), m. p.  $88^\circ$ , white rhombic plates from acetone; *di-iodide* (Found : I, 46.0.  $C_{12}H_{27}I_2Sb$  requires I, 46.4%) forms pale yellow crystals, m. p.  $70^\circ$ . *Methyltriisobutylstibonium iodide* [Found : I, 29.4.  $CH_3 \cdot Sb(C_4H_9)_3I$  requires I, 29.2%] is slowly formed in a concentrated ethereal solution of the stibine and methyl iodide; m. p. indefinite above  $155^\circ$ . *Methyltriisobutylstibonium mercuri-iodide* [Found : I, 42.8; Hg, 22.7.  $CH_3 \cdot Sb(C_4H_9)_3I, HgI_2$  requires I, 42.8; Hg, 22.6%], prepared from the methiodide and mercuric iodide in hot alcohol, forms yellow needles, m. p.  $119^\circ$ , after recrystallisation from alcohol. The *mercurichloride*,  $CH_3 \cdot Sb(C_4H_9)_3Cl, HgCl_2$  (Found : Cl, 17.4; Hg, 32.5.  $C_{13}H_{30}Cl_3SbHg$  requires Cl, 17.3; Hg, 32.6%), has m. p.  $117^\circ$ . *Methyltriisobutylstibonium chloroplatinate* (Found : Cl, 20.9.

$C_{26}H_{60}Cl_6Sb_2Pt$  requires Cl, 20.8%), after recrystallisation from alcohol, forms orange needles, m. p. 158°.

With a view to the preparation of mixed tertiary stibines containing the  $\beta$ -naphthyl radical, experiments on the stibonation of naphthalene have been carried out, but owing to poor yields of intermediate substances the original intention has had to be abandoned.  $\beta$ -Naphthylstibonic acid [Found: C, 39.6; H, 2.6; Sb, 40.9.  $C_{10}H_7SbO(OH)_2$  requires C, 40.2; H, 3.0; Sb, 40.8%] is obtained as follows (compare May, J., 1912, 101, 1037; Schmidt, *Annalen*, 1920, 421, 189; Riddell and Basterfield, *Trans. Roy. Soc. Canada*, 1929, 23, III, 45): 96 g. of  $\beta$ -naphthylamine in 3 l. of 2% hydrochloric acid are diazotised, and 300 c.c. of 30% hydrochloric acid added, followed, with continued cooling and stirring, by a solution of 96 g. of antimony trioxide in 300 c.c. of 30% hydrochloric acid. The precipitate is washed with water and added to 6 l. of *N*-sodium hydroxide; when the evolution of nitrogen subsides (4 days), the brown by-product is removed, and the filtrate acidified with hydrochloric acid. The precipitated  $\beta$ -naphthylstibonic acid is washed, dissolved in concentrated hydrochloric acid, and excess of solid ammonium chloride added; ammonium  $\beta$ -naphthylchloroantimonate,  $NH_4Sb(C_{10}H_7)Cl_5$  (Found: Cl, 38.2.  $C_{10}H_{11}NCl_5Sb$  requires Cl, 39.9%), precipitated as a yellow powder, is washed with concentrated hydrochloric acid and added to 1 l. of water, which effects hydrolysis, yielding a pale salmon-coloured precipitate of  $\beta$ -naphthylstibonic acid; this is dried over concentrated sulphuric acid in a desiccator (average yield, 3.5 g.). The acid does not melt below 200°.

$\beta$ -Naphthylstibinous Oxide.—A solution of the stibonic acid in concentrated hydrochloric acid is diluted with aqueous methyl alcohol, cooled with ice, saturated, after addition of sodium iodide, with sulphur dioxide, and poured after several hours on ice and aqueous ammonia; a voluminous precipitate of the oxide is formed. When dry, the oxide (Found: C, 45.7; H, 3.2.  $C_{10}H_7OSb$  requires C, 45.3; H, 2.7%) begins to decompose at 160°.

Several tetra-alkyl-phosphonium, -arsonium, and -stibonium antimonyl tartrates have been prepared by metathesis from silver antimonyl tartrate and the corresponding iodide. Their constitution is proved by the facts that (a) with dilute hydrochloric acid they yield white precipitates which respond to the tests for antimonous oxide, (b) after oxidation to the antimonic state the solutions of the products give with ammoniacal silver nitrate white precipitates which on being warmed yield silver mirrors, (c) in solution they react quantitatively with iodine, (d) on being boiled with alkali solutions they yield a phosphine, an arsine or a stibine,

(e) quantitative elementary analysis yields results in accord with the assumed composition, and (f) their dilute aqueous solutions possess the same molecular rotation as potassium antimonyl *d*-tartrate. These compounds are in general very soluble in water, but difficultly soluble in cold alcohol or in ether. Their aqueous solutions react acid. When strongly heated, the compounds decompose with charring.

Antimony present in the antimonyl state was estimated in these compounds iodometrically; when in the stibonium state the total antimony was converted by treatment with hot concentrated sulphuric acid into the antimonous state and estimated iodometrically. The stibonium antimony in methyltri-*n*-propylstibonium antimonyl tartrate has been obtained by subtracting the result for the former estimation from that for the latter.

*Tetraethylphosphonium antimonyl d-tartrate* (Found: C, 32.2; H, 5.5; Sb, 28.2.  $C_{12}H_{24}O_7PSb$  requires C, 33.3; H, 5.6; Sb, 28.1%) is obtained in aqueous solution when equivalents of tetraethylphosphonium iodide and silver antimonyl *d*-tartrate are mixed in solution, which is filtered, and it is isolated in quantitative yield by evaporating the solvent, the last traces in a vacuum desiccator containing phosphoric oxide. The salt forms a white powder and is very soluble in water but insoluble in ether, acetone, benzene, carbon disulphide, or chloroform. *Tetra-*n*-propylphosphonium antimonyl d-tartrate* (Found: C, 39.1; H, 6.9; Sb, 24.6.  $C_{16}H_{32}O_7PSb$  requires C, 39.3; H, 6.6; Sb, 24.9%) is similar to the preceding compound.

*Dimethyldi-*n*-propylarsonium antimonyl d-tartrate* (Found: C, 30.1; H, 5.0; As, 15.1; Sb, 25.2.  $C_{12}H_{24}O_7AsSb$  requires C, 30.2; H, 5.1; As, 15.7; Sb, 25.5%) is obtained as a white powder from the methiodide of methyl-di-*n*-propylarsine and silver antimonyl *d*-tartrate. *Methyltriethylarsonium antimonyl d-tartrate* (Found: C, 28.5; H, 4.7; As, 16.3; Sb, 25.8.  $C_{11}H_{22}O_7AsSb$  requires C, 28.5; H, 4.8; As, 16.2; Sb, 26.3%) and *tetraethylarsonium antimonyl d-tartrate* (Found: C, 29.9; H, 5.4; As, 15.4; Sb, 25.1.  $C_{12}H_{24}O_7AsSb$  requires C, 30.2; H, 5.1; As, 15.7; Sb, 25.5%) are white deliquescent solids, very soluble in water. *Methyltri-*n*-propylarsonium antimonyl d-tartrate* (Found: C, 33.0; H, 5.9; As, 14.5; Sb, 23.7.  $C_{14}H_{28}O_7AsSb$  requires C, 33.3; H, 5.6; As, 14.8; Sb, 24.1%) and *methyltri-*n*-amylarsonium antimonyl d-tartrate* (Found: C, 40.7; H, 6.4; As, 12.9; Sb, 20.8.  $C_{20}H_{40}O_7AsSb$  requires C, 40.7; H, 6.8; As, 12.7; Sb, 20.7%) are not deliquescent, and the last is distinctly less soluble in water than the others.

*Methyltri-*n*-propylstibonium antimonyl d-tartrate* [Found: C,

29.8; H, 5.1; Sb(-onium), 22.2; Sb(-yl), 22.0.  $C_{14}H_{28}O_7Sb_2$  requires, C, 30.4; H, 5.1; Sb(-onium) 22.1; Sb(-yl), 22.1%], prepared from tri-*n*-propylstibine methiodide, is very soluble in water.

The specific rotations of these antimonyl tartrates were measured in 2% aqueous solutions. The molecular rotations are in the following table; that the property is ionic is indicated by their constancy. In the third column are the  $p_H$  values of *N*/100-aqueous solutions of these salts of antimonyl tartaric acid.

Antimonyl <i>d</i> -tartrate.	$[M]_D$ .	$p_H$ .
Tetraethylphosphonium .....	456.7°	4.0
Tetra- <i>n</i> -propylphosphonium .....	449.3	3.8
Tetraethylarsonium .....	467.7	—
Methyltriethylarsonium .....	453.9	4.0
Dimethyl-di- <i>n</i> -propylarsonium .....	459.0	4.0
Methyltri- <i>n</i> -propylarsonium .....	466.7	3.6
Methyltri- <i>n</i> -amylarsonium .....	457.5	3.6
Methyltri- <i>n</i> -propylstibonium .....	468.2	3.2
Potassium .....	458.0	4.0

Growths of a fungoid nature appear in aqueous solutions of these antimonyl salts after some weeks.

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