CCLI.—*Organic Antimonial Compounds. Part II.*

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The present communication contains an account of the preparation and properties of certain derivatives of the higher tri-*n*-alkylstibines, which were recently prepared by Dyke, Davies, and Jones (this vol., p. 465). Such derivatives have hitherto been but little studied. Berlé (*J. pr. Chem.*, 1855, **65**, 385; *Annalen*, 1856, **97**, 316) prepared the oxide, dichloride, dibromide, di-iodide, sulphate, and dinitrate of a triamylstibine, but only the last was obtained crystalline. Partheil and Mannheim (*Arch. Pharm.*, 1900, **238**, 166) described the preparation of tetra-*n*-propylstibonium mercuri-iodide by heating together *n*-propyl iodide and mercuric antimonide at 180°. They also prepared tetra-*n*-propylstibonium hydroxide, iodide, picrate, mercurichloride, chloroaurate, and chloroplatinate. The action of tri-*n*-butylstibine on chloroplatinic acid has been investigated by Morgan and Yarsley (J., 1925, **127**, 189).

Several difficulties were encountered owing to (1) the extraordinary ease with which the stibines combine with the oxygen of the air, (2) the weak affinity of antimony for higher alkyl groups, in consequence of which the compounds decompose giving antimony on being heated, (3) the very- weakly basic character of the stibinic oxides, which permits of hydrolysis of the salts even by atmospheric moisture, and (4) the low crystallisability of the higher stibinic and stibonium salts.

Oxidation of a higher alkylstibine by atmospheric oxygen results in the precipitation of a double compound, of the general formula R_3SbO,Sb_2O_3, which is difficultly soluble in the stibine, in ether, benzene, alcohol, or water. Simultaneously there is formed a stibinic oxide, R_3SbO, which remains in solution in the stibine. The insoluble double oxide and the trialkylstibinic oxide are the homologues of the ethyl oxides described by Löwig (*Annalen*, 1853, **88**, 323). The double oxide may be regarded as the trialkylstibinic metantimonite, $R_3Sb(SbO_2)_2$. The trialkylstibinic oxide is best prepared by shaking an absolute-alcoholic solution of the stibine with red mercuric oxide. The higher trialkylstibinic oxides are gelatinous substances, which soften when warmed, and ignite on being heated in the air. When concentrated nitric acid is added to a stibine, there ensues a violent reaction, flames appearing, and a residue of antimony oxides remaining.

Combination does not occur when solutions of higher trialkylstibines and of rhombic sulphur in carbon disulphide are mixed. When a mixture of tri-*n*-propylstibine, water, and rhombic sulphur is refluxed, there is formed a double sulphide, $(C_3H_7)_3SbS,Sb_2S_3$, which may be regarded as *tri*-n-*propylstibinic metathioantimonite*. The ethyl homologue has been described by Löwig (*loc. cit.*). The simple *sulphide*, $(C_3H_7)_3SbS$, can be prepared by passing hydrogen sulphide through an alcoholic solution of the stibinic oxide.

The higher trialkylstibines readily combine with chlorine, giving stibinic chlorides, which are also produced by the action of hydrochloric acid on the oxides. Stibinic bromides may be prepared by adding the equivalent of bromine to an ethereal solution of the stibine, or by heating finely powdered antimony with the alkyl bromide in a sealed tube; in contact with water, they are immediately hydrolysed. Stibine di-iodides are formed quantitatively on mixing solutions of the stibine and iodine.

Although Morgan and Yarsley (*loc. cit.*) prepared additive compounds of trimethylstibine with platinous and palladous chlorides, they failed to produce stable derivatives from the ethyl- and *n*-butylstibines. In the present investigation also, an unsuccessful attempt was made with the *n*-amylstibine. Moreover, instantaneous reduction ensued on addition of the higher stibines to cold solutions of mercuric chloride. Chloroauric acid and silver nitrate were also reduced to the metal on warming, and attempts to obtain crystalline addition compounds by mixing alcoholic solutions of zinc chloride and stibines, and preserving the mixtures for several months, led only to the formation of gelatinous precipitates of indefinite composition.

The methiodides of the higher trialkylstibines are formed slowly when their components are mixed. Combination of stibines with ethyl iodide is still more lethargic. When solutions of the stibonium iodides are boiled, there is a slight evolution of stibine; on this account these salts cannot be purified by recrystallisation from water or alcohol, and when they are required pure, attention must be paid to the purity of the stibine and of the alkyl iodide used in their preparation. The corresponding hydroxides are fairly strong bases and bear considerable resemblance to potassium hydroxide in their properties, *e.g.*, the low solubility of their chloroplatinates. On the other hand, the fact that stibine is slowly evolved when aqueous solutions of their salts are boiled indicates hydrolysis.

EXPERIMENTAL.

In preparations involving manipulations of stibines, atmospheric moisture and oxygen were excluded by mixing the reactants in an atmosphere of dry carbon dioxide. For this purpose, the stibine was distilled in a vacuum (Dyke, Davies, and Jones, *loc. cit.*), and dry carbon dioxide was admitted into the receiver, which was then sealed and removed into a wooden chamber, into which the other reactant had already been introduced. A vigorous stream of carbon dioxide was continuously maintained through the chamber, which was provided with glass windows for observation and with arm-holes, which permitted the operator freedom of manipulation from the outside. The reactants, diluted suitably with solvents where necessary, having been thus mixed in absence of air in flasks, the latter were sealed with stoppers and removed for further treatment. It was necessary to exclude moisture rigorously at all stages in the preparations both of stibinic compounds and of stibonium salts. In preparations where water is required, the fact is expressly stated in the sequel.

Estimations of antimony in the stibinic compounds were effected either by the method of Little, Cahen, and Morgan (J., 1909, **95**, 1478; *Analyst*, 1909, **34**, 3) or by that of Schmidt (*Annalen*, 1920, **421**, 244). In stibinic halides the halogen was determined by refluxing with an excess of an alcoholic solution of potassium hydroxide; the resulting solution was diluted with water, the alcohol expelled, and dilute nitric acid and excess of silver nitrate solution were added. Stibonium halides, being ionised in aqueous and alcoholic solution, were analysed by precipitation of silver halides from such solutions. In the chloroplatinates the chlorine was estimated by heating in a tube with anhydrous sodium carbonate, followed by solution in dilute nitric acid and precipitation of silver chloride.

Tri-*n*-propylstibine reacts energetically with atmospheric oxygen, *tri*-n-*propylstibinic metantimonite* [Found: C, 19·3, 19·1; H, 4·2, 3·7; Sb, 66·7. $(C_3H_7)_3SbO,Sb_2O_3$ requires C, 19·3; H, 3·8; Sb, 65·4%] being immediately precipitated as a finely divided, white solid, which, after being washed with ether and dried, remains unchanged even on being heated to 220°.

Tri-n-*propylstibinic oxide* is obtained by shaking an absolute-alcoholic solution of the stibine with red mercuric oxide. Immediate reduction to mercury occurs. The solution is decanted, and the alcohol is then evaporated in a vacuum. The stibinic oxide which remains forms a gelatinous mass [Found: C, 40·2; H, 7·7; Sb, 45·1. $(C_3H_7)_3SbO$ requires C, 40·5; H, 7·9; Sb, 45·6%], soluble in alcohol and possessing a very bitter taste.

When a mixture of tri-*n*-propylstibine, powdered rhombic sulphur, and water is refluxed for two hours, impure *tri*-n-*propylstibinic metathioantimonite* [Found : Sb, 62·3. $(C_3H_7)_3Sb(SbS_2)_2$ requires Sb, 58·7%] is produced as a brown solid, which is insoluble in water, alcohol, or ether. Before analysis it was washed with carbon disulphide. It blackens at about 180°, but it does not melt even at 200°.

Tri-n-*propylstibinic sulphide* is produced when dry hydrogen sulphide is passed into an absolute-alcoholic solution of tri-*n*-propylstibinic oxide. The solution, after filtration, is concentrated by slow evaporation in a desiccator, whereupon small yellowish needles of the sulphide are deposited. This compound [Found : Sb, 44·1. $(C_3H_7)_3SbS$ requires Sb, 43·1%] melts at 88°, and darkens on exposure to the air. When it is boiled with acids, hydrogen sulphide and the stibine are evolved. Tri-*n*-propylstibinic sulphide is decomposed when its alcoholic solution is warmed.

Tri-n-*propylstibinic chloride* [Found : Sb, 37·7. $(C_3H_7)_3SbCl_2$ requires Sb, 37·8%] was made by mixing solutions of chlorine and the stibine in carbon tetrachloride, and evaporating off the solvent in a vacuum. It is a mobile liquid with a pleasant odour, and decomposes on being distilled.

Addition of a solution of bromine in carbon tetrachloride to a similar solution of the stibine yields a solution of *tri*-n-*propylstibinic bromide*, which remains as an oil on evaporation of the solvent in a vacuum. When crystallised from ether, the compound forms colourless crystals, m. p. 45° [Found : C, 26·1; H, 5·3; Br, 38·6, 39·0. $(C_3H_7)_3SbBr_2$ requires C, 26·3; H, 5·2; Br, 38·9%]. Decomposition with deposition of antimony occurs on distillation. The bromide is easily soluble in ether, but when added to water it is immediately hydrolysed.

When ethereal solutions of iodine and the stibine are mixed, *tri*-n-*propylstibinic iodide* [Found : I, 49·4. $(C_3H_7)_3SbI_2$ requires I, 50·3%] is quantitatively produced. It forms a yellow, semi-solid mass.

Methyltri-n-*propylstibonium iodide* was obtained on keeping a mixture of 3 c.c. of tri-*n*-propylstibine and 4 c.c. of methyl iodide for a week; the excess of methyl iodide was evaporated in a vacuum, and the yellowish crystals (yield, 5·8 g.) were well washed with dry ether [Found : I, 32·3. $CH_3(C_3H_7)_3SbI$ requires I, 32·3%]. The salt melts at 140°, and is soluble in water and in alcohol, but insoluble in ether. It possesses a very bitter, salty taste. When the aqueous solution is boiled, stibine is slowly evolved.

On dissolving the methiodide in cold water, shaking the solution with fresh silver oxide, and then removing the solvent under reduced pressure, *methyltri*-n-*propylstibonium hydroxide* remains as an oil. It is soluble in water, absorbs carbon dioxide, and reacts alkaline to litmus. It precipitates cupric, stannous, ferric, aluminium, and zinc hydroxides from solutions of their salts. The *stibonium sulphate* forms an oil, which is easily soluble in water. The *chloroplatinate*, $[CH_3(C_3H_7)_3Sb]_2PtCl_6$ (Found : C, 25·5; H, 5·0; Cl, 22·4. $C_{20}H_{48}Cl_6Sb_2Pt$ requires C, 25·5; H, 5·1; Cl, 22·6%), m. p. 142° (decomp.), is prepared by dissolving the hydroxide in boiling dilute hydrochloric acid, filtering the solution if necessary, and adding excess of chloroplatinic acid to the hot solution; on cooling, glistening reddish-golden plates of the chloroplatinate are deposited.

Ethyltri-n-*propylstibonium iodide* [Found : I, 31·5. $C_2H_5(C_3H_7)_3SbI$ requires I, 31·2%], m. p. 185° (decomp.), is produced when its components are mixed together and kept for a month. At the ordinary temperature its formation is slow, but at 100° a quantitative yield is obtained in 4 hours. It forms large white crystals, soluble in water and in alcohol. The hydroxide forms an oil which attacks filter paper; its aqueous solution is alkaline and precipitates the difficultly soluble metallic hydroxides from solutions of their salts. *Ethyltri*-n-*propylstibonium chloroplatinate* crystallises from dilute solutions in aqueous alcohol as stellate clusters of fine, orange-red needles, m. p. 141° (decomp.) (Found : C, 26·8; H, 5·7; Cl, 21·9. $C_{22}H_{52}Cl_6Sb_2Pt$ requires C, 27·3; H, 5·4; Cl, 22·0%).

Aerial oxidation of tri-*n*-butylstibine yields a precipitate of the *double oxide*, $(C_4H_9)_3SbO,Sb_2O_3$ (Found : C, 23·8; H, 4·8; Sb, 59·3. $C_{12}H_{27}O_4Sb_3$ requires C, 24·0; H, 4·5; Sb, 60·8%). This compound was boiled with alcohol before analysis, to remove adherent stibinic oxide.

Tri-n-*butylstibinic oxide* [Found : C, 46·1; H, 8·8; Sb, 39·2. $(C_4H_9)_3SbO$ requires C, 46·6; H, 8·8; Sb, 39·4%] is produced in good yield on shaking an alcoholic solution of the butylstibine with mercuric oxide. On evaporation of the solvent, the oxide remains as a thick, viscous syrup, possessing a bitter taste and an odour reminiscent of linseed.

Tri-n-*butylstibinic chloride*, prepared similarly to the propyl compound, is a spirituous-smelling, heavy liquid [Found : Cl, 20·0. $(C_4H_9)_3SbCl_2$ requires Cl, 19·5%] which decomposes on being distilled.

Tri-n-*butylstibinic bromide* was prepared by heating together in a sealed tube 4 g. of finely powdered antimony and 10 c.c. of *n*-butyl bromide for 30 hours at 250°. A solid cake of crystals mixed with antimony and liquid resulted, and when the tube was opened, gaseous hydrocarbons escaped. On extraction of the cake with ether, filtration, and evaporation of the solvent in an evacuated desiccator, the bromide remained as an oil [Found : C, 31·3; H, 5·9; Br, 35·5, 34·6. $(C_4H_9)_3SbBr_2$ requires C, 31·8; H, 6·0; Br, 35·3%]. It was also prepared by mixing ethereal solutions of tri-*n*-butylstibine and bromine.

When equivalent solutions of its components in chloroform are mixed, and the solvent is removed in a vacuum, *tri*-n-*butylstibinic iodide* remains as a soft, oily solid [Found: I, 45·8. $(C_4H_9)_3SbI_2$ requires I, 46·4%], slowly decomposed by boiling water.

A mixture of tri-*n*-butylstibine and methyl iodide, when kept in a sealed flask for 2 weeks, yielded, on removal of excess of methyl iodide, *methyltri*-n-*butylstibonium iodide* as a thick oil admixed with crystals [Found: I, 28·5. $CH_3(C_4H_9)_3SbI$ requires I, 29·2%]. When the alcoholic solution is boiled in the air, a precipitate of tri-*n*-butylstibinic metantimonite is slowly produced.

Methyltri-*n*-butylstibonium hydroxide is an oil which, when dissolved in water, precipitates the hydroxides or oxides of the heavy metals from solutions of their salts. On dissolving the hydroxide in alcohol, acidifying with hydrochloric acid, boiling, adding chloroplatinic acid, and cooling, golden plates of the *chloroplatinate*, $[CH_3(C_4H_9)_3Sb]_2PtCl_6$ (Found: C, 30·1; H, 6·1; Cl, 20·8. $C_{26}H_{60}Cl_6Sb_2Pt$ requires C, 30·5; H, 5·9; Cl, 20·8%), m. p. 134° (decomp.), are formed.

Tri-n-*amylstibinic metantimonite*, $(C_5H_{11})_3Sb(SbO_2)_2$ (Found: Sb, 57·7. $C_{15}H_{33}O_4Sb_3$ requires Sb, 56·9%), forms an insoluble, infusible white powder. *Tri*-n-*amylstibinic oxide*, $(C_5H_{11})_3SbO$ (Found: C, 51·4; H, 9·7; Sb, 34·2. $C_{15}H_{33}OSb$ requires C, 51·3; H, 9·5; Sb, 34·7%), forms a thick syrup.

Prepared from its components, *tri*-n-*amylstibinic chloride* is an unstable, sweet-smelling liquid [Found: Cl, 18·2. $(C_5H_{11})_3SbCl_2$ requires Cl, 17·5%], readily decomposed by water.

Tri-n-*amylstibinic bromide*, prepared similarly to the propyl bromide, forms a white pasty mass [Found: Br, 32·4. $(C_5H_{11})_3SbBr_2$ requires Br, 32·3%], slowly decomposed by water.

When a mixture of methyl iodide in excess and tri-*n*-amylstibine was preserved for 3 months out of contact with air, *methyltri*-n-*amylstibonium iodide* was gradually formed. The excess of methyl iodide was removed by evaporation in an evacuated desiccator, and the stibonium iodide, which was a mixture of crystals and oil, was washed with ether (Found: I, 26·8. $C_{16}H_{36}ISb$ requires I, 26·6%). The salt is soluble in water and in alcohol, but insoluble in ether.

Methyltri-*n*-amylstibonium hydroxide was obtained as an oil on treating the iodide in aqueous alcohol with silver oxide, and evaporating the solvent in a vacuum. The hydroxide reacts alkaline to litmus, absorbs carbon dioxide from the air, and is readily soluble in dilute acids. The sulphate is an oil, easily soluble in water.

Prepared as in the case of the butyl compound, the *chloroplatinate* $[CH_3(C_5H_{11})_3Sb]_2PtCl_6$ (Found: C, 34·8; H, 6·6; Cl, 19·0. $C_{32}H_{72}Cl_6Sb_2Pt$ requires C, 34·7; H, 6·6; Cl, 19·2%) forms glistening, brown plates, m. p. 127° (decomp.).

The investigation of derivatives of tri*iso*alkylstibines and of mixed alkylstibines is being pursued.

Summary.

The preparation and properties of the oxides, sulphides, halides, and methiodides of the higher tri-*n*-alkylstibines are described. Attention is drawn to the decreased affinity of antimony for the higher alkyl radicals and to the difficulty of purifying derivatives of the higher stibines either by distillation or by recrystallisation. The action of water in causing hydrolysis and decomposition of stibinic compounds is described, and the necessity of excluding moisture and air during the preparation of these substances is indicated.

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