IV.—*Organic Derivatives of Antimony. Part I. Tricamphorylstibine Chloride and Triphenylstibine Hydroxynitrate and Hydroxysulphate.*

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A comparative study of the interactions taking place between sodium camphor and the trichlorides of phosphorus, arsenic, and antimony has shown that in the case of the arsenic compound the principal products are dicamphorylarsinic and tricamphorylarsinic acids (Trans., 1908, **23**, 2144; 1909, **95**, 1473). The experiments with phosphorus trichloride are still in progress; the present communication deals with the case of antimony trichloride.

The interaction of sodium camphor and antimony trichloride in dry toluene does not lead to the production of any substances soluble in aqueous alkali hydroxides or carbonates. The only product definitely isolated and identified is *tricamphorylstibine chloride*, $(C_{10}H_{15}O)_3SbCl_2$. This substance undergoes destructive hydrolysis so readily that the resulting tricamphorylstibine oxide, $(C_{10}H_{15}O)_3SbO$, is always more or less contaminated with hydrated antimonic oxide arising from the decomposition of the chloride into hydrochloric and antimonic acids and camphor.

As one object of this research was to obtain an organic derivative of antimony sufficiently stable and soluble for employment as a therapeutic agent, attention was now directed to triphenylstibine chloride, $(C_6H_3)_3SbCl_2$, obtained by Michaelis and Reese by the interaction of chlorobenzene, antimony trichloride, and sodium (*Annalen*, 1886, **233**, 43).

As these investigators have stated that this aromatic antimony derivative is possessed of considerable stability, attempts were made to convert this substance into compounds dissolving more readily in aqueous solutions.

When treated with alcoholic silver nitrate, triphenylstibine chloride loses its chlorine quantitatively in accordance with the following equation:

$$(C_6H_5)_3SbCl_2 + 2AgNO_3 = 2AgCl + (C_6H_5)_3Sb(NO_3)_2.$$

The triphenylstibine nitrate is not stable under these conditions, and undergoes partial hydrolysis into a definitely crystalline substance, *triphenylstibine hydroxynitrate*, $(C_6H_5)_3Sb(OH)\cdot NO_3$, which may be recrystallised from hot water without further hydrolysis. In connexion with the formation of this substance, it is of interest to note that Michaelis and Reese describe a triphenylstibine nitrate, prepared by dissolving triphenylstibine in hot fuming nitric acid (*loc. cit.*, p. 52), which is stated to be insoluble in water, but crystallisable from alcohol.

The substitution of silver sulphate for silver nitrate in the foregoing reaction leads to the production of the corresponding *triphenylstibine hydroxysulphate*, $(C_6H_5)_3Sb(OH)\cdot SO_4\cdot Sb(OH)(C_6H_5)_3$, which is less soluble in water than the hydroxynitrate.

EXPERIMENTAL.

Tricamphorylstibine Chloride.—On adding a toluene solution of antimony trichloride to sodium camphor suspended in the same medium, considerable heat was generated, and a bulky precipitate was produced. The mixture was warmed on the water-bath and left for a few days, after which it was treated with water, when a white precipitate of antimony oxides separated. The toluene solution which drained from this precipitate was distilled in steam, and the residue extracted with benzene. From the concentrated benzene extract, a substance separated in colourless, ice-like crystals, this separation being promoted by the addition of light petroleum. After repeated crystallisation from benzene, the product melted and decomposed at 244°, although when rapidly heated it sometimes remained unchanged at 247—248°:

0·1314 gave 0·2660 CO_2 and 0·0840 H_2O. C = 55·21 : H = 7·10.
0·1830 „ 0·3706 CO_2 „ 0·1116 H_2O. C = 55·22; H = 6·77.
0·2235 „ 0·0591 Sb_2S_3. Sb = 18·88.
0·2483 „ 0·1106 AgCl. Cl = 11·02.
$C_{30}H_{45}O_3ClSb$ requires C = 55·90; H = 7·0; Sb = 18·63; Cl = 11·02 per cent.

0·3120, in 25 c.c. chloroform, at 20°, gave $\alpha_D + 9·17°$, whence $[\alpha]_D = 367·3°$.

Tricamphorylstibine chloride dissolves only sparingly in alcohol, and is insoluble in water. In acid solutions it is fairly stable, and may be boiled with 2*N*-hydrochloric acid without decomposition. On warming with 2*N*-sodium hydroxide, the chloride was readily hydrolysed into antimonic and hydrochloric acids and camphor. Destructive hydrolysis occurred on warming the chloride with aqueous sodium hydrogen carbonate at 55°, and continued heating with dilute ammonia led to the liberation of camphor. A similar decomposition took place when the chloride was digested with alcoholic silver nitrate.

Triphenylstibine Hydroxynitrate.—0·621 Gram of triphenylstibine chloride gave 0·419 gram of silver chloride (the calculated amount being 0·421 gram) on warming with two molecular proportions of silver nitrate in alcoholic solution. The filtrate, on concentration, furnished white crystals, which, on analysis, gave numbers corresponding with the partial hydrolysis of the initially formed dinitrate. This hydrolysis was brought to a definite end-point by dissolving the white crystals in boiling water, for, on cooling, the hydroxynitrate separated in lustrous, colourless leaflets, softening at 220°, and melting to a yellow liquid at 224—225°.

When carrying out the process on a larger scale, any slight excess of silver retained in the solution was precipitated by the addition of sodium chloride. The presence of excess of this salt in the filtrate promoted the crystallisation of the hydroxynitrate, the precipitation, under these conditions, being almost complete:

0·2691 gave 0·4932 CO_2 and 0·0942 H_2O. C = 50·00; H = 3·80.
0·3765 „ 0·1461 Sb_2S_3. Sb = 27·72.

0·3300 gave 9·6 c.c. N_2 at 24° and 759 mm. N = 3·19.

$C_{18}H_{16}O_4NSb$ requires C = 50·23; H = 3·72; Sb = 27·9; N = 3·26 per cent.

Triphenylstibine hydroxynitrate is almost insoluble in cold water, but dissolves very readily in alcohol, giving rise to a solution which can be diluted with water very considerably without any deposition of the hydroxynitrate taking place. When reduced with Devarda's alloy (Al-Cu couple) in the presence of alkali, triphenylstibine is produced, and the whole of the nitrogen is eliminated as ammonia. An estimation of nitrogen by this method gave 3·62, the calculated value being 3·19 per cent.

Triphenylstibine hydroxysulphate was prepared by adding an alcoholic solution of triphenylstibine chloride (1 mol.) to a boiling aqueous solution of silver sulphate (2 mols.). The filtrate from the silver chloride was concentrated to remove the alcohol, when the hydroxysulphate separated in colourless nodular crystals, the solution being then distinctly acid, owing to the liberation of sulphuric acid:

0·2602 gave 0·0761 $BaSO_4$. S = 4·01.

$C_{36}H_{32}O_6SSb_2$ requires S = 3·84 per cent.

The hydroxysulphate is almost insoluble in cold water; it dissolves in cold concentrated sulphuric acid, and remains in solution after considerable dilution with water, this increase in solubility indicating its conversion into the normal sulphate.

Triphenylstibine hydroxysulphate melts and decomposes at 252°.

Triphenylstibine hydroxychloride was produced by adding an alcoholic solution of triphenylstibine chloride to a large volume of boiling water and evaporating until crystallisation began. The crystalline deposit, when dried and dissolved in benzene, separated from this solvent in transparent, lustrous, colourless spicules, melting at 218°:

0·2982 gave 0·1240 Sb_2S_3. Sb = 29·70.

$C_{18}H_{16}OClSb$ requires Sb = 29·73 per cent.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant, which has partly defrayed the expenses of this investigation.

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