# CVII.—Aromatic Antimony Compounds. Part III. Some Primary Aryl Derivatives.

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MANY of the most important primary aryl arsenic compounds are readily obtained by heating arsenic acid with aromatic compounds, such as primary amines and phenols. The corresponding antimony compounds cannot be obtained in this way, and an attempt was therefore made to obtain some of them by other methods. The results obtained up to the present, although incomplete, are now published owing to a lengthy unavoidable interruption of this work, and to the publication of similar researches by Morgan and Micklethwait (Trans., 1911, **99**, 2288).

Phenylstibinic acid,  $C_6H_5SbO(OH)_2$ , was prepared according to Hasenbäumer's method (*Ber.*, 1898, **31**, 2910; compare Morgan and Micklethwait, *loc. cit.*; Michaelis and Günther, *Ber.*, 1911, **44**, 2316), but owing to a side reaction it was found necessary to devise a method for the further purification of the product. Phenylstibinic acid on nitration gives rise to a mononitro-derivative, from which, by reduction, a small yield of antimonylaniline,

NH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·SbO,

was obtained:  $C_6H_5 \cdot SbO(OH_2) \longrightarrow NO_2 \cdot C_6H_4 \cdot SbO(OH)_2 \longrightarrow$   $NH_2 \cdot C_6H_4 \cdot SbO(OH_2) \longrightarrow NH_8Cl \cdot C_6H_4 \cdot SbOCl_2$  $NH_2 \cdot C_6H_4 \cdot SbO(OH) \cdot ONa$ 

This compound by gentle oxidation yields aminophenylstibinic acid, which was isolated in the form of its hydrochloride, the yield being very small on account of experimental difficulties. This hydrochloride does not appear to be that of the free acid,  $HCl, NH_2 \cdot C_6H_4 \cdot SbO(OH)_2$ , but that of the acid chloride,

HCl, H<sub>2</sub>N·C<sub>6</sub>H<sub>4</sub>·SbOCl<sub>2</sub>.

This formation of the acid chloride in aqueous solution is a somewhat remarkable and surprising fact, but the author's work on triphenylstibine derivatives (Trans., 1910, **97**, 1958) shows that the hydroxyl groups in compounds of the type  $R_3Sb(OH)_2$  are readily displaced by chlorine, and so this result in the case of aminophenylstibinic acid,  $NH_2C_6H_4$ ·SbO(OH)<sub>2</sub>, is not so extraordinary as it first appeared to be. A small quantity of the sodium salt, probably  $NH_2^{\bullet}C_6H_4$ ·SbO(OH)·ONa, was also isolated, but not in a pure condition.

An attempt was made to reduce nitrophenylstibinic acid directly VOL. CI. 3 Z

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to aminophenylstibinic acid (that is, to reduce the nitro-group to the amino-group without reducing quinquevalent antimony to the tervalent condition) by means of sodium amalgam and methyl alcohol, and also by using ammonium sulphide. In neither case was the attempt successful.

Attempts were also made to obtain the antimony analogue of azobenzene and arsenobenzene,  $C_6H_5$ ·Sb:Sb·C<sub>6</sub>H<sub>5</sub>, by the reduction of phenylstibinic acid, and by the action of sodium on a benzene solution of phenylstibine dichloride,  $C_6H_5$ ·SbCl<sub>2</sub>, but without success.

#### EXPERIMENTAL.

Preparation of Phenylstibinic Acid.—Fifty-seven grams of triphenylstibine were heated with 74 grams of antimony trichloride and a small quantity of xylene in five sealed tubes for forty-eight hours at 240°. The black product was filtered from solid matter, extracted several times with hydrochloric acid, and dried over calcium chloride.\* It was then distilled under diminished pressure in a current of carbon dioxide, and the chief fraction collected at  $150-190^{\circ}/25-30$  mm. This fraction consisted of a viscid oil, which did not crystallise at all readily, but in some cases deposited a few crystals, and still appeared to contain small quantities of antimony trichloride which could not be extracted from the xylene solution with hydrochloric acid. Some more antimony trichloride had been contained in the first runnings, and the fraction of higher boiling point contained diphenylstibine chloride and unchanged triphenylstibine.

The main fraction, consisting of phenylstibine dichloride,  $C_6H_5$ ·SbCl<sub>2</sub>, with smaller quantities of diphenylstibine chloride, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SbCl, and antimony trichloride, was dissolved in ice-cold ether and treated with chlorine. After evaporation of the ether, an oily residue consisting of phenylstibine tetrachloride, C<sub>6</sub>H<sub>5</sub>·SbCl<sub>4</sub>, contaminated with diphenylstibine trichloride, (C6H5)2SbCl3, and traces of antimony pentachloride, was obtained. This was hydrolysed with aqueous ammonia, and the liquid filtered. The residue consisted of triphenylstibine dichloride, diphenylstibinic acid. (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SbO<sub>2</sub>H, and antimonic acid, and the filtrate contained the ammonium salt of phenylstibinic acid. The latter was acidified with dilute sulphuric acid, whereby the acid was precipitated. Twenty-six grams of the crude acid were obtained. In order further to purify the substance, it was dissolved in aqueous sodium

<sup>\*</sup> Great care is necessary in working with these substances. The vapours, when hot, are excessively irritant, and a drop of a dilute xylene solution of the reaction product, allowed to come into contact with the skin, produced a painful sore, the effect lasting for some days.

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carbonate solution, and filtered from a slight insoluble residue consisting probably of antimonic acid and diphenylstibinic acid. The pure acid was then precipitated by acidifying with dilute sulphuric acid. In this way phenylstibinic acid was obtained as a white, microcrystalline powder, which in the moist state possesses a faint characteristic and not unpleasant odour.

Nitration of Phenylstibinic Acid.—This was carried out in a similar fashion to that described by Morgan and Micklethwait (Trans., 1911, **99**, 2296), and the product obtained resembled the *m*-nitrophenylstibinic acid described by these investigators. Some of the crude acid containing both the phenylstibinic and diphenylstibinic acids was nitrated in the same manner, and the product found to contain 5.9 per cent. of nitrogen. It was therefore probably a mixture of nitrophenylstibinic and dinitrodiphenyl-stibinic acids. After dissolving in glacial acetic acid, the first crop of crystals consisted of needles melting at  $210-213^{\circ}$ , and contained 7.2 per cent. of nitrogen, and therefore was the di-*m*-nitrodiphenyl-stibinic acid described by Morgan and Micklethwait (*loc. cit.*).

Reduction of m-Nitrophenylstibinic Acid.—Five grams of nitrophenylstibinic acid were gently warmed on the water-bath for two hours with 18 grams of tin and an excess of 4N-hydrochloric acid, to which a few grams of glacial acetic acid had been added. The solution containing the hydrochloride of the base was filtered, excess of sodium hydroxide added, and the precipitated base washed several times by decantation with sodium hydroxide solution, and finally with water. The precipitate, which in the moist state has an odour somewhat resembling that of dimethylaniline and of *a*-naphthylamine, was collected and dried, the final product consisting of 2.6 grams of a pale yellow powder. It is soluble in hydrochloric acid, forming solutions which give the diazo-reaction, but give no precipitate with hydrogen sulphide. The substance is therefore an aromatic primary amine, and is free from tin and inorganic antimony.

Found: N = 5.9; Sb(as Sb<sub>2</sub>O<sub>4</sub>) = 52.94.

 $C_6H_6ONSb$  requires N = 6.14; Sb = 52.63 per cent.

m-Antimonylaniline,  $NH_2 \cdot C_6H_4 \cdot SbO$ , is a yellow powder, insoluble in water or alkali, soluble in acids, and sparingly so in alcohol. It could not be obtained in well-defined crystals, and it has no definite melting point, but begins to soften and decompose below 200°. The vapour (or fine dust) has an extraordinarily strong irritant action on the nose, throat, and eyes, causing prolonged and violent fits of sneezing.

Oxidation of m-Antimonylaniline.—Dilute alkaline hydrogen peroxide was gradually added to 2 grams of antimonylaniline until

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the latter was almost completely dissolved, and the mixture then warmed on the water-bath until evolution of oxygen ceased. The liquid was filtered, and a small portion of the filtrate acidified with dilute sulphuric acid. No precipitate was produced, but the liquid gave the diazo-reaction, showing that the amino-group had not been destroyed. On acidifying another portion with hydrochloric acid, a crystalline precipitate was produced, and the main bulk of the liquid was therefore acidified with hydrochloric acid and maintained at 70° for two hours. After being set aside for fifteen hours, the precipitate was separated and washed with After drying in a vacuum, 0.34 gram of a hydrochloric acid. silky, crystalline substance was obtained. A small additional quantity of the substance was isolated by evaporation of the mother liquors and extraction of the product with alcohol.

A further quantity (0.14 gram) was prepared by the reduction of another 1.7 grams of *m*-nitrophenylstibinic acid and oxidation of the product by means of sodium peroxide in aqueous suspension.

The substance is soluble in water, forming an acid solution, which can be diazotised. This solution gives a precipitate of silver chloride on treatment with nitric acid and silver nitrate, and is reprecipitated by excess of hydrochloric acid. On heating, it decomposes and blackens, evolving pungent fumes; it does not give the reactions of antimony salts, but does so after fusion with sodium peroxide.

The first preparation gave Cl=31.8, and the second preparation gave Cl=32.0. Mean=31.9.

 $HC!, H_2N \cdot C_6H_4 \cdot SbO(Cl)_2$  requires Cl = 31.7 per cent.,

and therefore the substance appears to be probably the hydrochloride of aminophenylstibinyl chloride, instead of that of the free acid, which requires Cl=11.9 per cent.

### Attempt to Prepare the Sodium Salt of Aminophenylstibinic Acid.

2.26 Grams of nitrophenylstibinic acid were reduced and oxidised as before, but the alkaline filtrate, instead of being acidified with hydrochloric acid, was evaporated to dryness. The product was then extracted with absolute alcohol in a Soxhlet apparatus, and a small quantity of a pale brown, crystalline solid was obtained. This substance chars on heating, and is readily soluble in water. The aqueous solutions have a slightly alkaline reaction, and give a faint diazo-reaction after acidifying with dilute sulphuric acid. Hydrochloric acid produces a slight crystalline precipitate.

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The substance is therefore probably the slightly impure sodium salt of aminophenylstibinic acid.

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