CCVII.—*Aromatic Antimony Compounds. Part I.*
The Oxidation and Nitration of Triphenylstibine.

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VARIOUS aromatic derivatives of antimony of the type R_3Sb and R_3SbX_2 , in which R represents phenyl, tolyl, anisyl, etc., and X represents Cl, Br, NO_3 , or OH, have been prepared by Michaelis and his pupils (Michaelis and Reese, *Annalen*, 1886, **233**, 52; Michaelis and Genzken, *Annalen*, 1887, **242**, 176; Löloff, *Ber.*, 1897, **30**, 2834), but nevertheless far less work has been carried out with these compounds than with the corresponding derivatives of arsenic. Michaelis and Reese showed that the compound $(C_6H_5)_3Sb(OH)_2$ is amphoteric in character, and it therefore appeared to be of interest to observe the effect of the introduction of a nitro-group on the relative stability of the various compounds, such as R_3SbCl_2 , $R_3Sb(OH)_2$, $R_3Sb(NO_3)_2$. Michaelis and Reese prepared the compound $(C_6H_5)_3Sb(NO_3)_2$ by the action of nitric acid on triphenylstibine, but if, at the same time, a nitro-group could be introduced into the benzene nuclei, the basicity of the compound $R_3Sb(OH)_2$ might be so depressed that a nitrate such as $R_3Sb(NO_3)_2$ could no longer be formed, and the resulting compound might be of the type $R_3Sb(NO_3)(OH)$.

On nitration, triphenylstibine yields *trinitrotriphenylstibine dihydroxide*, $(C_6H_4NO_2)_3Sb(OH)_2$. It does not appear to be capable of forming a stable sulphate or nitrate, but a *chloride* has been prepared, and it therefore appeared to be desirable to obtain some further information as to the relative stability of the parent substance, $(C_6H_5)_3Sb(OH)_2$, and its salts, and, if possible, to prepare the hitherto unknown normal sulphate, $(C_6H_5)_3SbSO_4$. Triphenylstibine readily reduces concentrated sulphuric acid, with the formation of the desired sulphate, thus:

and this compound could also be obtained by dissolving the corre-

sponding hydroxide in concentrated sulphuric acid. Dilute sulphuric acid does not attack triphenylstibine, but permanganate and dilute sulphuric acid oxidise it to the hydroxide, $(C_6H_5)_3Sb(OH)_2$. This reaction is of interest from a twofold point of view. On the one hand, it indicates that the sulphate is far less stable than the chloride,* and, on the other hand, it affords fresh evidence of the great stability of the molecule of triphenylstibine as a whole. If alkaline permanganate be used as the oxidising agent, a better yield of the dihydroxide is obtained. Michaelis and Reese state that solutions of this substance in alkali are reprecipitated by mineral acids, but on repeating these experiments it was found that dilute nitric or sulphuric acids produced no precipitate, whilst hydrochloric acid caused precipitation even in very dilute solutions. Probably the experiments of Michaelis and Reese were confined to halogen acids. Similarly, solutions of triphenylstibine sulphate and nitrate in the corresponding concentrated acids can be diluted indefinitely, although these substances themselves are insoluble in dilute acids, but, on addition of dilute hydrochloric acid to their dilute solutions, an immediate precipitate of the chloride is obtained.

The introduction of a nitro-group into the benzene nuclei of the complex $R_3Sb(OH)_2$ not only reduces the salt-forming power of the molecule, but also lowers its stability as a whole. This is shown by the fact that the trinitro-derivative is partly decomposed when boiled with aqueous alkali, yielding a small quantity of nitrobenzene.

EXPERIMENTAL.

The triphenylstibine used in this investigation was prepared by Michaelis and Reese's method, shortened and simplified in some of its details.† The long method of purification after extraction with alcoholic hydrochloric acid, described by these authors, was omitted, the product being instead directly recrystallised from light petroleum. Pure triphenylstibine was thus obtained, the yield being 70 per cent. of the theoretical. The material contained in the petroleum mother liquor was converted into the dichloride, which, after recrystallisation, was still contaminated with traces of an impurity having an extremely irritant action on the mucous membrane. This was finally removed by dissolving the product in concentrated sulphuric acid, pouring the product into aqueous alcohol, and setting aside to crystallise.

* Triphenylstibine hydroxide combines readily with dilute hydrochloric acid, forming the dichloride.

† A stock solution of dry antimony chloride in dry benzene, made up for these preparations, gradually acquired a deep magenta colour even in the dark.

Nitration of Triphenylstibine and Preparation of Trinitrophenylstibine Dihydroxide, $(C_6H_4 \cdot NO_2)_3Sb(OH)_2$.

Triphenylstibine was added, in small quantities at a time, to an excess of a mixture of three parts of sulphuric acid and one part of nitric acid, at about 40°. When cold, the mixture was poured into ice-water, the temperature being kept below 25°. The yellow precipitate thus obtained was recrystallised from glacial acetic acid, in which it is very soluble, and separates in flat, transparent, pale yellow crystals, melting at 190—191°. It is also soluble to some extent in alcohol or ether, but does not crystallise well from these solvents. It is insoluble in water, and almost insoluble in benzene, light petroleum, etc.:

Found, C=41·74; H=2·91; N=7·79, 7·91; Sb=22·06.

$C_{18}H_{14}O_8N_3Sb$ requires C=41·5; H=2·72; N=8·07;
Sb=23·11 per cent.

On treatment with Devarda's alloy no ammonia is evolved. When boiled with glacial acetic acid and zinc dust, or with alcohol, hydrochloric acid, and tin, it yields an easily diazotisable amine, which was not further investigated, as work on this compound is being carried out by Morgan, Mickelthwait, and Whitby (Proc., 1910, **26**, 151).

Trinitrophenylstibine Dichloride, $(C_6H_4 \cdot NO_2)_3SbCl_2$.

This compound is formed, together with the hydroxy-chloride, by boiling trinitrophenylstibine dihydroxide with alcoholic hydrochloric acid. After recrystallising, the product still appeared to be impure, and analysis indicated that it was a mixture of the dichloride and the hydroxy-chloride. The pure dichloride was obtained by the direct nitration of triphenylstibine dichloride, which was dissolved in concentrated sulphuric acid, and then nitrated in the same manner as triphenylstibine. It separates from glacial acetic acid in clusters of small crystals, melting at 157°, which are readily soluble in concentrated nitric acid or glacial acetic acid. As this substance was only obtained in small amount, its properties were not further investigated.

Found, Cl=12·37.

$C_{18}H_{12}O_6N_3Cl_2Sb$ requires Cl=12·73 per cent.

Triphenylstibine Sulphate, $(C_6H_5)_3SbSO_4$.

Five grams of triphenylstibine were warmed with an excess of concentrated sulphuric acid on the water-bath. A vigorous reaction suddenly set in, sulphur dioxide being evolved, and a white pre-

precipitate formed, which was filtered on asbestos, and washed with cold alcohol, a portion being afterwards extracted with this solvent, in which it is only very sparingly soluble. Small crystals were thus obtained, and similar crystals separated on evaporation of the mother liquor after dilution with water. These crystals melt above 300° , and are soluble in concentrated sulphuric acid, very sparingly so in alcohol, and insoluble in water, dilute sulphuric acid, and most other solvents. The substance is decomposed by warming with aqueous sodium hydroxide, forming sodium sulphate and triphenylstibine hydroxide, the latter dissolving in the excess of alkali:

Found, $S=7.30$.

$C_{18}H_{15}O_4SSb$ requires $S=7.17$ per cent.

A solution of the sulphate in sulphuric acid may also be obtained by dissolving triphenylstibine hydroxide in the concentrated acid, and this solution, as also the sulphuric acid mother liquor mentioned above, can be largely diluted without any precipitation occurring, but on adding a drop of hydrochloric acid to solutions of any concentration, a precipitate is formed, which, after recrystallisation from alcohol, was found to have the characteristic crystalline form and melting point of triphenylstibine dichloride.

Oxidation of Triphenylstibine with Permanganate.

(1) *In Alkaline Solution.*—Triphenylstibine was boiled for three hours with alkaline permanganate, the manganese dioxide removed, and a portion of the filtrate acidified with hydrochloric acid. A white precipitate was produced, which was recrystallised from alcohol and found to be triphenylstibine dichloride. Another portion of the filtrate was acidified with dilute sulphuric acid, and in this case no precipitate was formed. Evidently the first product of the oxidation is triphenylstibine hydroxide, which dissolves in the alkali, giving solutions from which hydrochloric acid precipitates the chloride, but which are not precipitated by sulphuric or nitric acids.

(2) *In Acid Solution.*—Five grams of triphenylstibine were warmed on the water-bath with an excess of 1 per cent. permanganate and dilute sulphuric acid. The permanganate was gradually decolorised with a slight evolution of carbon dioxide; more permanganate was added from time to time, and finally the precipitate was collected and extracted with alcohol. In this way, a small quantity of a substance was obtained which melted at 210° , contained no sulphur, and appeared to be identical with triphenylstibine hydroxide, as prepared by Michaelis and Reese. This substance was obtained by them in the form of an amorphous powder, but a modification of their method of preparation led to

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its being obtained in a well-crystallised state. An alcoholic solution of triphenylstibine dichloride was added to an equal volume of 2*N*-aqueous sodium hydroxide, and the mixture set aside. After some days, triphenylstibine hydroxide crystallised out in beautiful leaflets, which were washed with water and dried. The product was then found to melt at 210°, and resembled the product obtained by Michaelis and Reese in its behaviour towards reagents.

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