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DECOMPOSITION OF TETRAPHENYLSTIBONIUM HYDROXIDE

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Although the decomposition of a quaternary phosphonium hydroxide to give a hydrocarbon and a tertiary phosphine oxide is a well known reaction (1), no analogous reaction has been reported for a quaternary stibonium hydroxide. We have now found that tetraphenylstibonium hydroxide undergoes decomposition in xylene solution at 70-80° to produce benzene and triphenylstibine oxide in 90% yield.

Tetraphenylstibonium hydroxide precipitates in quantitative yield when an aqueous solution of tetraphenylstibonium bromide is made slightly alkaline by addition of ammonia water (2). When heated at 110° for several hours, it decomposes. The suggestion has been made (3) that the reaction is simply a dehydration process and that bis-(tetraphenylantimony) oxide is formed. However, no evidence was offered in support of this suggestion.

When a solution of tetraphenylstibonium hydroxide in p-xylene was heated at 70-80° for four days in a nitrogen atmosphere and with rigid exclusion of light, there was obtained benzene and a solid of m.p. 221.5-222.0° which gave the correct elemental analyses for triphenylstibine oxide. An NMR spectrum of the material taken in carbon tetrachloride solution showed two absorption regions with centers at $\delta = 7.28$ ppm and $\delta = 7.58$ ppm. An IR spectrum of a carbon tetrachloride solution showed an absorption peak at 3.3μ, and there were no other peaks in this region. These results are also consistent with the contention that the product is triphenylantimony oxide.

Unfortunately, several conflicting reports have appeared in the literature concerning the preparation and properties of triphenylstibine oxide. Two groups of workers (4,5) have reported that the compound can be prepared by heating triphenylantimony dihydroxide to drive off water and that the oxide has an m.p. of about 300°. However, Bernstein, Halmann, Pinchas and Samuel (6) have provided spectral evidence that the compound produced in this manner is not the simple triphenylstibine oxide. Also, Jensen (4) has indicated that both benzene and water are produced when triphenylantimony dihydroxide is heated above 200° in an evacuated system. Monagle (7) reported that he obtained "triphenylstibine oxide," m.p. 249-251°, by dehydration of the product obtained by treatment of triphenylstibine with hydrogen peroxide. We repeated this preparation and found that the product contained a peroxide group, as evidenced by the fact that it liberated iodine when treated with a solution of potassium iodide in glacial acetic acid. Furthermore, other groups of workers (8,9,10) have reported that material similarly prepared contains peroxides. Finally, Mel'nikov and Rokilskaya (11) have claimed that they obtained triphenylstibine oxide, m.p. 209°, by oxidation of triphenylstibine with selenium oxide. Since triphenylstibine selenide was also produced in this reaction, it is possible that the presumed oxide was actually a mixture of the oxide and selenide.

In view of the confusion surrounding triphenylstibine oxide, we deemed it necessary to provide additional evidence regarding the structure of the compound of m.p. 221.5-222.0° obtained by the decomposition of tetraphenylstibonium hydroxide. Accordingly, the compound was treated with concentrated hydrochloric acid in acetone solution, and triphenylantimony dichloride, identical in all regards with authentic (12) material, was obtained. Also, the compound of m.p. 221.5-222.0° was treated with triphenylantimony dichloride in anhydrous benzene solution, and the known (13) bis(chlorotriphenylantimony) oxide was obtained in quantitative yield.

$$(C_6H_5)_3SbO + (C_6H_5)_3SbCl_2 \longrightarrow (\phi_3SbCl)_2O$$

As a last item in the proof of structure, dimethoxytriphenylantimony, when treated with water in acetone solution, gave methanol and the compound of m.p. 221.5-222.0° (14). Thus, the combination of chemical and spectral evidence cited above offers convincing proof that this compound is the authentic triphenylstibine oxide.

The mechanism of decomposition of quaternary phosphonium hydroxides has been established in a reasonably convincing manner (15,16), but there is presently no evidence whatsoever regarding the mechanism of decomposition of tetraphenylstibonium hydroxide. Studies designed to eludicate this mechanism are presently in progress.

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