

THERMAL DECOMPOSITION OF ALKOXY AND AROXY DERIVATIVES OF PENTAVALENT PHOSPHORUS AND ANTIMONY COMPOUNDS

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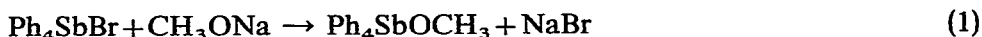
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SUMMARY

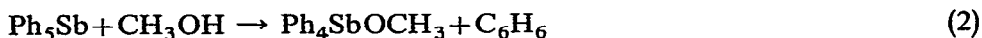
The thermal decomposition of Ph_4POPh and Ph_4SbOR [$\text{R} = \text{CH}_3$; $(\text{CH}_3)_2\text{CH}$; Ph] has been investigated.

The decomposition of tetraphenylphenoxyphosphorane gives triphenylphosphine, phenol and other products resulting from the condensation of the intermediate dehydrobenzene. Alkoxy derivatives of tetraphenylantimony decompose to give triphenylstibine, aldehyde or ketone and benzene. The reaction is accompanied by the formation of simple ethers which is a basic characteristic of the behaviour of tetraphenylphenoxyantimony.

Briles and McEwen¹ have recently described the preparation of tetraphenylmethoxyantimony through the use of the reaction:

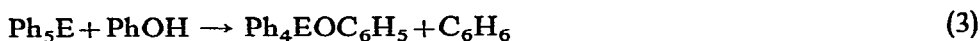


as well as by the reaction of pentaphenylantimony (PPA) with alcohol:



Descriptions of the syntheses of a series of higher alkoxy derivatives have also been given², but these materials have been characterized only by elemental analysis.

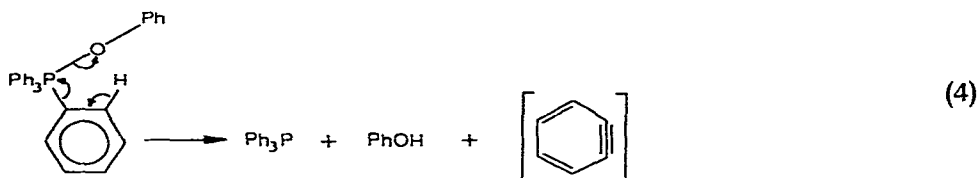
In this study we have prepared tetraphenylphenoxyphosphorane and tetraphenylphenoxyantimony by the reaction:



where $\text{E} = \text{P}$, Sb , although the preparation of tetraphenylphenoxyphosphorane has been described by us previously³. These compounds are derivatives of pentavalent phosphorus and antimony and for this reason it would be interesting to study their thermal decomposition and to compare their behaviour with that of pentaphenylphosphorane⁴ and of pentaphenylantimony⁵ under the same conditions.

Thermal degradation of tetraphenylphenoxyphosphorane was studied at 200° over a time interval of 3 h. The reaction products were found to be triphenylphosphine (82%), phenol (84%), diphenyl ether (15%) and a resinous deposit.

These products may be explained on the basis of an *ortho*-proton attack on one of the phenyl groups forming phenol and dehydrobenzene:



Since triphenylphosphine and phenol are the main products of the decomposition, such an attack must be the major mode of decomposition.

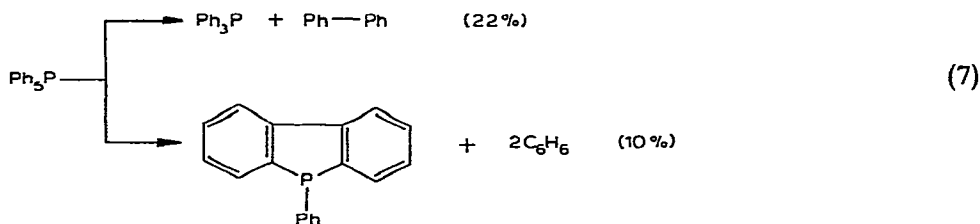
To explain the formation of diphenyl ether a secondary mode of decomposition must occur, namely



It was not possible to isolate any products resulting from the subsequent conversion of dehydrobenzene, although from other work^{6,7} it is known that at slightly lower temperatures a smooth reaction occurs between this compound and triphenylphosphine. The very small amount of resinous material formed during these thermal decompositions corresponds very well however with the possible interaction between dehydrobenzene, (whose theoretical concentration is calculated as 0.6 g) and triphenylphosphine in this system.

It has also been shown that *ortho*-proton attack also occurs during the reaction of tetraphenylphosphonium bromide with various organolithium⁸ compounds. Thus, in the system $\text{Ph}_4\text{PBr} + \text{CH}_3\text{Li} + \text{THF}$ two⁶ competing reactions were observed: (1) the attack of the lithium components on the phosphorus atom, leading to the formation of triphenylmethylenephosphorane in benzene, and (2) the attack of alkyl-lithium on the *ortho*-proton of the phenyl group in tetraphenylphosphine, leading to the formation of phenyl-2,2'-biphenylylenephosphine. By a careful choice of reaction conditions, it was found that the reaction could be made to proceed preferentially by one or other of these two routes.

During the thermal decomposition² of pentaphenylphosphorane (PPP) the dissociation of *ortho*-hydrogen atoms from two of the phenyl groups was also observed with the resulting formation of phenyl-2,2'-biphenylylenephosphine and benzene:



The thermal decomposition of tetraphenylphenoxyantimony under similar conditions (200°, 3 h) was not complete and triphenylantimony and diphenyl ether (each in 64% yield) were formed as well as a small amount of benzene (8%). From the final reaction products it was possible to extract 33% of the original tetraphenylphenoxyantimony.

To explain the formation of these antimony derivatives it is necessary to

assume that an intramolecular process occurs in the system:

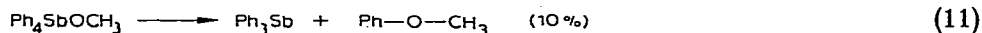
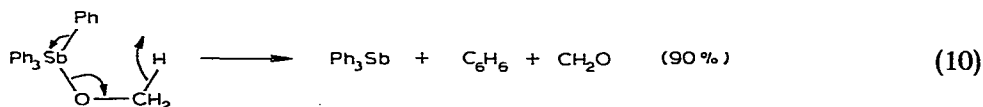


a suggestion in full agreement with that put forward by Wittig⁵ for the thermal decomposition of pentaphenylantimony:



This mechanism has also been confirmed recently by Kei-Wei Shen and co-workers⁹ who studied the decomposition of pentaphenylantimony (PPA) labelled with ¹⁴C in commercial benzene which yielded triphenylantimony and biphenyl having the same activity as the initial substance. After the reaction benzene-¹⁴C was not found in the solution.

Previous studies of the thermal decomposition of PPP¹⁰ and PPA¹¹ in benzene indicated that the reaction products obtained were the same as those in the absence of the solvent. The thermal decomposition of PPA has also been studied in benzene-¹⁴C as a solvent. The results again show that the solvent does not participate in the reaction confirming that PPA decomposes only by an intramolecular route. Tetraphenylmethoxyantimony decomposes smoothly at 180–190° in an hour forming triphenylstibine in quantitative yield and only a small amount (10%) of anisole. In addition, the reaction products contained benzene (approx. 90%) and formaldehyde (only determined qualitatively). Again it may be considered that the process proceeds intramolecularly:



Tetraphenylisopropoxyantimony decomposed rapidly within half an hour at 150–160° giving a 98 % yield of triphenylantimony and an 80 % yield of benzene and acetone respectively.

From these results it follows that in the decomposition of antimony derivatives *ortho*-hydrogen cleavage involving the phenyl groups does not occur. Such behaviour appears to be typical of phosphorus derivatives only.

An additional feature of these decompositions is the reduction in the valency of the central metal atom. In contrast tetraphenylphosphonium hydroxide and tetraphenylantimony hydroxide retain the higher valency of the central metal atoms during thermal decomposition when the corresponding phosphorus and antimony oxides are formed together with benzene:



Tetraphenylphosphonium hydroxide and tetraphenylantimony hydroxide¹² are unstable even at room temperature. The decomposition of the latter has been studied by Briles and McEwen¹³ who have suggested a radical mechanism for the process.

From the studies reported here and elsewhere it follows that compounds of the type Ph_4EX , where $\text{E} = \text{P}, \text{Sb}$ and $\text{X} = \text{Ph}, \text{Hal}, \text{OH}, \text{OAc}$ and OPh decompose by three possible types of mechanism: (1) that exhibited in the decomposition of PPP, (2) that for the decomposition of PPA and (3) that for the decomposition of Ph_4EOH .

The first type of decomposition always occurs with the formation of at least a small quantity of resinous products, whereas decompositions of the second and third type proceed smoothly.

EXPERIMENTAL

Synthesis of tetraphenylphenoxyantimony

A mixture of pentaphenylantimony (5 g, 0.009 mole), phenol (0.85 g, 0.009 mole) and dioxane (25 ml) was shaken at room temperature for 50 h in a tube from which the air had been removed. After this time interval evaporation of the solvent resulted in the isolation of tetraphenylphenoxyantimony which was recrystallized from cyclohexane. Yield 3 g (58%); m.p. 152° . (Found: C, 69.27; H, 5.14. $\text{C}_{24}\text{H}_{20}\text{OSb}$ calcd.: C, 68.86; H, 4.78%.) The compound is readily soluble in chloroform, carbon tetrachloride and benzene and moderately soluble in cyclohexane.

Thermal decomposition of tetraphenylphenoxyphosphorane

All the thermal decompositions described in this study were undertaken in a special tube provided with a side-arm bent parallel to the axis of the tube and with a bulb at its end. Tetraphenylphenoxyphosphorane (4 g, 0.0092 mole) was placed in such a tube which was evacuated and sealed. The contents of the tube were heated to 200° for 3 h. Low-boiling products of the reaction collected in the bulb in the side arm and were shown chromatographically to consist solely of diphenyl ether (0.24 g, 15%) and phenol (0.74 g, 84%). In addition to its chromatographic identification, phenol was also identified as phenyl benzoate (1.70 g); m.p. 69° (as shown by mixed melting point determinations). Triphenylphosphine (2.00 g, 82%, m.p. 77° , was removed from the resulting reaction product by reduced pressure (150° , 5 mm), and the remaining resinous precipitate, 0.70 g, processed with hydroiodic acid (1/1) and also with alcoholic hydrochloric acid in an attempt to obtain trivalent and pentavalent phosphorus compounds respectively. In both cases pure individual phosphorus derivatives were not obtained. Nevertheless, the IR spectrum exhibited qualitatively the presence of a P-C bond with absorption maxima at 704, 748 cm^{-1} .

Thermal decomposition of tetraphenylphenoxyantimony

A. Tetraphenylphenoxyantimony (5 g, 0.0095 mole) was placed in the special tube described above and the latter was evacuated and sealed. The contents of the tube were heated to 200° for 3 h. Diphenyl ether (1.04 g, 64%) and benzene (0.06 g, 8%) condensed in the bulb and were analysed chromatographically. The reaction precipitate was removed at reduced pressure (3 mm), and shown to consist of triphenylantimony (2.15 g, 66.5%, m.p. $140\text{--}160^\circ$, and tetraphenylphenoxyantimony (1.1 g), which existed as a viscous product melting at $166\text{--}175^\circ$. With bromine in carbon tetrachloride, triphenylantimony quantitatively formed the dibromide (3.15 g, m.p. 217° . Tetraphenylphenoxyantimony was recrystallized from cyclohexane,

m.p. 152° (as shown by mixed melting point determinations). The final residue (0.55 g) after distillation *in vacuo* was treated with alcohol saturated with hydrogen chloride and gave tetraphenylantimony chloride (0.46 g), m.p. 202°. When this material is taken into account it follows that only 68% of the initial reagent underwent reaction. After separating the chloride, phenol (0.02 g) was steam-distilled off and identified as the 2,4,6-tribromophenol (0.07 g).

B. Using exactly the same conditions as above, tetraphenylphenoxyantimony (5.0 g, 0.0095 mole) was again decomposed thermally. Diphenyl ether (1.04 g) and benzene (0.08 g) were again analysed chromatographically, and removal of the contents of the reaction tube at reduced pressure (140–160°, 3 mm) again resulted in triphenylantimony (2.17 g, 64%) being isolated. The residue was again distilled *in vacuo* and treated with alcohol saturated with hydrogen chloride forming 1.50 g of tetraphenylantimony chloride corresponding to 1.69 g, (34%) of unreacted starting material.

Thermal decomposition of tetraphenylmethoxyantimony

Treatment of pentaphenylantimony¹ with alcohol gave tetraphenylmethoxyantimony (petr. ether), m.p. 132°. This latter material (3.18 g, 0.0069 mole) was heated at 200° *in vacuo* for 1 h in the special ampoule described above. The liquid products of the reaction consisting of benzene (0.47 g, 87%) and anisole (0.09 g, 12%), condensed in the bulb of the side-arm and were analyzed chromatographically. The remaining products were removed at reduced pressure (140°, 3 mm) giving triphenylstibene (2.39 g), 95%, m.p. 53°, as shown by mixed melting point.

The IR spectrum of the resinous residue (0.25 g) exhibited absorption maxima at 1802, 1738 cm⁻¹, characteristic of the carbonyl group.

Formaldehyde was analyzed both qualitatively and quantitatively (0.02 g, 7%) by the hydroxylamine method.

Thermal decomposition of tetraphenylisopropoxyantimony

Tetraphenylisopropoxyantimony (1.7 g, 0.0036 mole) was heated to 150–160° for 1 h in an evacuated tube similar to that previously described. The liquid products of the reaction, benzene (0.24 g, 85%) and acetone (0.16 g, 78%), condensed in the side-arm bulb and were analysed chromatographically. The solid products of the reaction were removed at reduced pressure (140°, 3 mm) yielding triphenylantimony (1.23 g), 98%, m.p. 53° (as determined by mixed melting point). The IR spectrum of the resinous residue (0.06 g) exhibited absorption maxima at 1672, 1738 cm⁻¹, characteristic of the carbonyl group.

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