

Preparation of Diphenylantimony(v) Tribromide and the Mixed Halides, Diphenylantimony(v) Dibromide Chloride and Bromide Dichloride

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The title compounds have been prepared by reaction between SbBrPh_2 and bromine, SbPh_2Cl and bromine, and SbBrPh_2 and chlorine respectively, and characterized by mass and vibrational spectroscopy.

ALTHOUGH antimony(v) chloride and a number of alkyl- and aryl-substituted compounds are well known,¹ the corresponding pentabromide has not been reported.² The synthesis of this compound probably merits re-investigation following the recent successful preparation of arsenic(v) chloride,³ a compound also previously regarded as unobtainable. Of the possible organo-substituted antimony(v) bromides, compounds such as SbBrR_4 and SbBr_2R_3 are well known.¹ This paper deals with the preparation and spectroscopic characterization of diphenylantimony(v) tribromide and the two mixed bromide chlorides, $\text{SbBr}_2\text{Ph}_2\text{Cl}$ and $\text{SbBrPh}_2\text{Cl}_2$, none of which has been previously described.

Earlier reports^{4,5} have mentioned the preparation of SbBr_3Me_2 , which readily lost methyl bromide at room temperature, and impure samples of $\text{SbBr}_2\text{Me}_2\text{Cl}$.

EXPERIMENTAL

All the solvents were dried over conventional desiccants and redistilled before use. Reactions were carried out in an atmosphere of dry nitrogen.

Diphenylantimony(III) Chloride.—Antimony trichloride (7.6 g, 20 mmol), previously dried over P_4O_{10} and freshly sublimed, and triphenylantimony (14.1 g, 40 mmol) were heated under reflux in dry dichloromethane (200 cm^3) for 60 h.⁶ A small quantity of white solid which had formed was separated by decantation and the volume of the clear solution was reduced to ca. 50 cm^3 . Cooling yielded white crystals, which on recrystallization from dichloromethane had m.p. 70 °C (lit.,⁷ 68 °C) (yield 13.2 g, 71%) (Found: C, 46.0; H, 3.1; Cl, 10.6. Calc. for $\text{C}_{12}\text{H}_{10}\text{ClSb}$: C, 46.2; H, 3.2; Cl, 11.4%). Major peaks in the i.r. spectra at <500 cm^{-1} (Raman data in parentheses) were found at 454s, 305s, 290s, 260ms (255), (172), (106), and (70) cm^{-1} .

In some experiments it was difficult to obtain a crystalline product from the reorganization mixture. In these circumstances the dichloromethane solvent was removed completely and the resulting oil was taken up in the minimum volume of warm glacial acetic acid. Slow cooling to room temperature gave a solid which could be crystallized from either dichloromethane or chloroform.

Diphenylantimony(III) Bromide.—The method was similar to that above but used resublimed antimony(III) bromide; m.p. 77 °C (lit.,⁸ 86 °C) (Found: C, 40.9; H, 2.9. Calc. for $\text{C}_{12}\text{H}_{10}\text{BrSb}$: C, 40.5; H, 2.8%). Major i.r. peaks at <500 cm^{-1} (Raman data in parentheses) were 452s, 292s, 245ms, 225ms (225), (172), (104), and (62) cm^{-1} .

Diphenylantimony(v) Tribromide.—Diphenylantimony(III) bromide (3.6 g, 10 mmol) in dichloromethane (100 cm^3) was cooled to -97 °C and redistilled bromine (1.6 g, 10 mmol) was added. The temperature was allowed to rise slowly, and after concentration of the solution to ca.

30 cm^3 white crystals separated which were recrystallized from chloroform-diethyl ether, yield 3.4 g (83%), m.p. 171 °C (Found: C, 27.6; H, 2.1; Br, 45.7. Calc. for $\text{C}_{12}\text{H}_{10}\text{Br}_3\text{Sb}$: C, 27.9; H, 2.0; Br, 46.5%). Major i.r. peaks (Raman data in parentheses) were at 450s, 284ms, 260s (256), 235s (230), (215), (150), (122), (98), and (80) cm^{-1} .

Diphenylantimony(v) Dibromide Chloride.—Anhydrous bromine (1.6 g, 10 mmol) was condensed at -196 °C into a solution of diphenylantimony(III) chloride (3.1 g, 10 mmol) in dichloromethane (100 cm^3). After allowing the temperature to rise slowly and concentrating the solution, the compound separated on cooling. Recrystallization from dichloromethane or chloroform gave the pure product (yield 4.0 g, 85%), m.p. 181 °C (Found: C, 30.3; H, 2.1. Br, 33.0. Calc. for $\text{C}_{12}\text{H}_{10}\text{Br}_2\text{ClSb}$: C, 30.6; H, 2.1; Br, 33.9%). Major i.r. peaks at <500 cm^{-1} (Raman data in parentheses) were found at 455s, 353w (354), 310(sh), 295s, 260ms (264), 240s, (216), (150), (120), (98), and (76) cm^{-1} .

Diphenylantimony(v) Bromide Dichloride.—Diphenylantimony(III) bromide (3.6 g, 10 mmol) was dissolved in dichloromethane (100 cm^3) and cooled to -90 °C. Dry chlorine (0.7 g, 10 mmol) was then added from a weighed trap and the temperature was allowed to rise slowly to room temperature. On concentration of the solution white crystals were obtained which on recrystallization from dichloromethane gave the pure compound (yield 3.0 g, 70%), m.p. 178–180 °C (Found: C, 34.0; H, 2.3; Br, 19.3. Calc. for $\text{C}_{12}\text{H}_{10}\text{BrCl}_2\text{Sb}$: C, 33.8; H, 2.4; Br, 18.7%). When chlorine was added to SbBrPh_2 at 0 °C in dichloromethane solution oxidation took place but the bulk of the bromine was also displaced. The product was essentially SbPh_2Cl_3 , m.p. 172 °C (lit.,⁹ 175 °C) (Found: C, 36.6; H, 2.6, Br, 1.6. Calc. for $\text{C}_{12}\text{H}_{10}\text{Cl}_3\text{Sb}$: C, 37.7; H, 2.6; Br, 0.0%). Major i.r. peaks at <500 cm^{-1} for $\text{SbBrPh}_2\text{Cl}_2$ were found at 460s, 362m, 310(sh), 298s, 265m, and 247m cm^{-1} .

Spectra.—Infrared spectra on Nujol and halogenocarbon oil mulls were recorded with a Perkin-Elmer 577 spectrometer; Raman data were obtained using a modified Cary 81 spectrometer with an argon-ion laser. Mass spectra were recorded with an MS 902 spectrometer.

DISCUSSION

The three diphenylantimony(v) trihalides can be prepared as white, room-temperature stable, crystalline solids by oxidation of a diphenylantimony(III) halide with the appropriate free halogen. Reaction at low temperature (ca. -80 °C) is desirable when chlorine is used, since at higher temperatures there is a tendency to displace bromine. For example, in the $\text{SbBrPh}_2\text{Cl}_2$ reaction, even with a 1 : 1 ratio of reactants, the yield of

SbBrPh₂Cl₂ is poor at -30 °C and at room temperature the only product is SbPh₂Cl₃. In a similar way, the three bromides SbBr₃Ph₂, SbBr₂Ph₂Cl, and SbBrPh₂Cl₂ are quantitatively converted into the trichloride on treatment with chlorine at room temperature.

Mass-spectrometric and vibrational data supplement the elemental analyses in confirming the nature of the new compounds, and in addition single-crystal X-ray data have been obtained for all three compounds.¹⁰ The compounds show structures based on trigonal-bipyramidal co-ordination about antimony with two phenyl groups and a bromine atom occupying the equatorial positions. Weak intermolecular interactions between an axial halogen atom and antimony link these units into infinite chains.

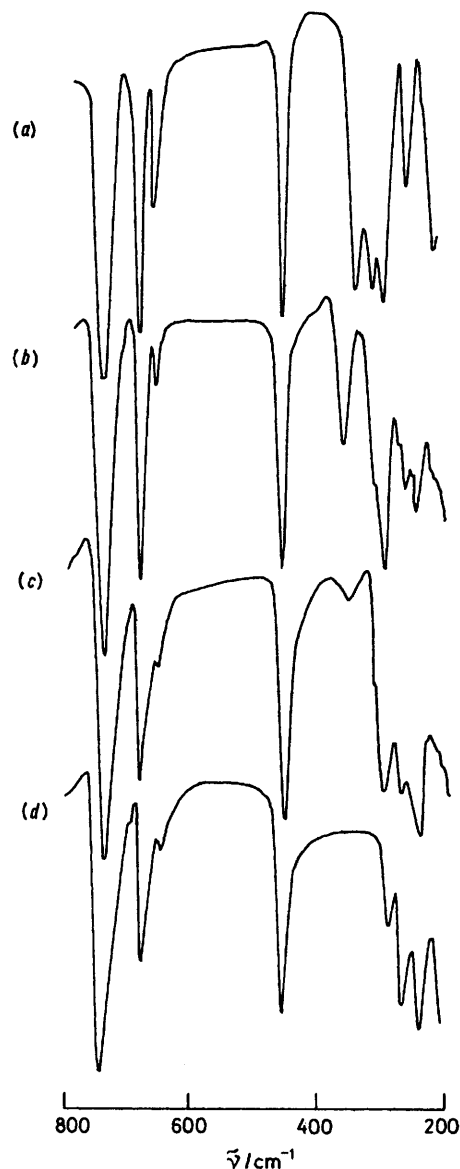
Important peaks in the mass spectra of the compounds are summarized in the Table, and for comparison, data

Fragment ion	Selected peaks from the mass spectra of SbBr _{3-n} Ph ₂ Cl _n			
	Ion intensity (% total ion current)			
	SbBr ₃ Ph ₂	SbBr ₂ Ph ₂ Cl	SbBrPh ₂ Cl ₂	SbPh ₂ Cl ₃
[SbBrPh ₃] ⁺	0.2	1.2	0.7	
[SbPh ₃ Cl] ⁺			1.5	1.0
[SbBr ₂ Ph ₂] ⁺	7.5	7.2		
[SbBrPh ₂ Cl] ⁺		4.3	6.7	
[SbPh ₂ Cl ₂] ⁺		0.7	5.1	10.3
[SbBrPh ₂] ⁺	6.1	3.9	1.9	
[SbPh ₂ Cl] ⁺		1.0	1.1	6.9
[SbBr ₂ Ph] ⁺	0.6	1.9		
[SbBr(Ph)Cl] ⁺		4.3	6.7	
[SbPhCl ₂] ⁺		0.6	0.7	5.4
[SbBr(Ph)] ⁺	8.0	5.8	3.2	
[SbPh(Cl)] ⁺		5.3	7.0	9.6

for SbPh₂Cl₃ are also included. In common with a number of other organo-halides of main-group elements, the parent ion was not observed¹¹ and there was also no evidence for any fragments containing three halogen atoms. Loss of halogen is thus the first fragmentation and, for the trichloride, the [SbPh₂Cl₂]⁺ ion is of high intensity. Somewhat lower intensity is found for the [SbBr₂Ph₂]⁺ ion from SbBr₃Ph₂, but it is surprising to find for the two mixed halides, where loss of bromine might be thought to be more probable, that the intensity of bromine-containing fragments is higher than for the chlorine-containing analogues. This enhancement of intensities also occurs for the [SbPh₂X]⁺ fragments but is less apparent in the [SbPhX₂]⁺ and [SbPh(X)]⁺ species. A possible rationalization of the preferential loss of chlorine during fragmentation of the mixed halides is that the more electronegative chlorine atoms occupy axial positions in the trigonal-bipyramidal structures. Here the bonds are weaker and fragmentation appears to lead to loss of an axial chlorine atom, rather than a bromine atom from its equatorial position.

Although fragmentation of [SbPh₂X₂]⁺ ions can lead to [SbPh₂X]⁺ species, the alternative process, whereby a phenyl group is lost giving [SbPhX₂]⁺ ions, can be observed in all the spectra and appears to be the more probable for the two mixed halides. In the lower *m/e* regions, the fragment-ion intensities for all four compounds are very similar.

Rearrangement ions of the type [SbPh₃X]⁺ appear in all the spectra, while low-intensity fragments containing two chlorine atoms, *i.e.* [SbPh₂Cl₂]⁺ and [SbPhCl₂]⁺, can be identified in the spectrum of SbBr₂Ph₂Cl. The last ion is probably associated with the disorder in the occupancy of the axial positions.¹⁰



Infrared spectra between 800 and 200 cm⁻¹ for (a) SbPh₂Cl₃, (b) SbBrPh₂Cl₂, (c) SbBr₂Ph₂Cl, and (d) SbBr₃Ph₂

The compounds give i.r. spectra which are substantially different in the region below 400 cm⁻¹ (see Figure) but detailed analysis is difficult. General features of the spectra are bands close to the following positions (suggested assignments using Whiffen's¹² notation are given in parentheses): 450(y), 295(t), 260(t), and 210(u) cm⁻¹. The spectra of all the chlorides show a band between 360 and 310 cm⁻¹, decreasing in intensity with decreasing chlorine content, which can be attributed to one of the

antimony–chlorine stretching modes. For SbPh_2Cl_3 there is an additional strong band at 316 cm^{-1} which is also attributed to Sb–Cl stretching. It should be noted here that the solid-state structure of SbPh_2Cl_3 ¹³ differs radically from that of the tribromide and the two mixed halides in being based on a double chloride-bridged dimer with distorted octahedral co-ordination about antimony. Antimony–chlorine stretching vibrations have been assigned in SbPh_3Cl_2 to the 270 cm^{-1} region,¹⁴ but to 305 cm^{-1} in SbPh_2Cl and 356 and 377 cm^{-1} in SbCl_3 .¹⁵

A structural feature common to all three bromides is a bond to antimony in an equatorial position, and a strong band at *ca.* 240 cm^{-1} which decreases slightly in energy with increased bromine content is assigned to this vibration. The band is stronger for $\text{SbBr}_2\text{Ph}_2\text{Cl}$ and SbBr_3Ph_2 and perhaps includes also one of the stretching components of the SbBr_2 (axial) group. The symmetric SbBr_2 component could then be assigned to the Raman band at *ca.* 150 cm^{-1} . For comparison, the SbBr_2 stretching modes in SbBr_2Ph_3 have been assigned at 194 and 160 cm^{-1} .¹⁴

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