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, $SbBr_2Ph_2Cl$ and $SbBrPh_2Cl_2$, 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 $SbBr_2Me_2Cl$.

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 $C_{12}H_{10}ClSb$: 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 $C_{12}H_{10}BrSb$: 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 $C_{12}H_{10}Br_3Sb$: 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 $C_{12}H_{10}Br_2ClSb$: 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 $C_{12}H_{10}BrCl_2Sb$: 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 $C_{12}H_{10}Cl_3Sb$: C, 37.7; H, 2.6; Br, 0.0%). Major i.r. peaks at <500 cm^{-1} for $SbBrPh_2Cl_2$ 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 $SbBrPh_2$–Cl_2 reaction, even with a 1 : 1 ratio of reactants, the yield of

$SbBrPh_2Cl_2$ is poor at −30 °C and at room temperature the only product is $SbPh_2Cl_3$. In a similar way, the three bromides $SbBr_3Ph_2$, $SbBr_2Ph_2Cl$, and $SbBrPh_2Cl_2$ 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.

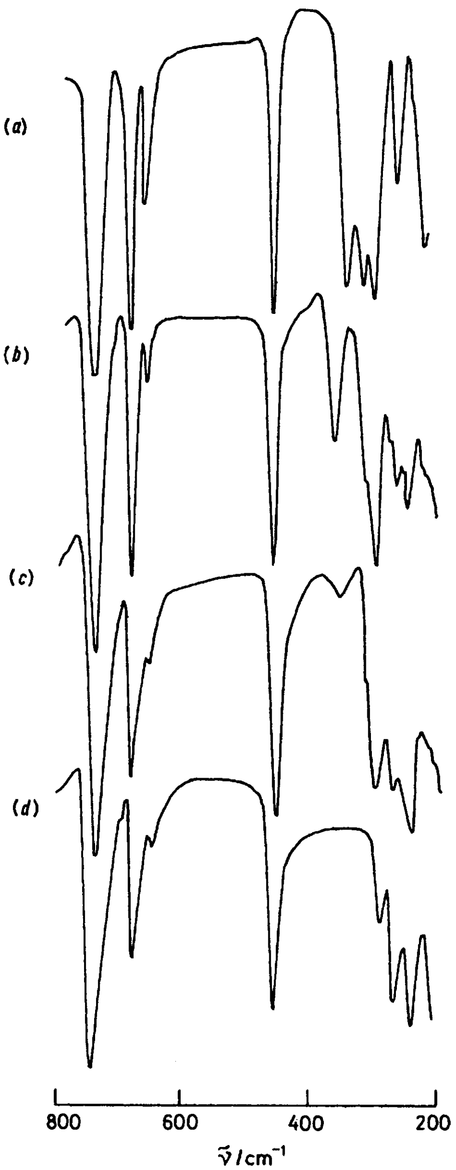
Important peaks in the mass spectra of the compounds are summarized in the Table, and for comparison, data for $SbPh_2Cl_3$ are also included. In common with a number of other organo-halides of main-group elements, the parent ion was not observed [11] and there was also no evidence for any fragments containing three halogen atoms. Loss of halogen is thus the first fragmentation and, for the trichloride, the $[SbPh_2Cl_2]^+$ ion is of high intensity. Somewhat lower intensity is found for the $[SbBr_2Ph_2]^+$ ion from $SbBr_3Ph_2$, 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 $[SbPh_2X]^+$ fragments but is less apparent in the $[SbPhX_2]^+$ 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.

Selected peaks from the mass spectra of $SbBr_{3-n}Ph_2Cl_n$

	Ion intensity (% total ion current)			
Fragment ion	$SbBr_3Ph_2$	$SbBr_2Ph_2Cl$	$SbBrPh_2Cl_2$	$SbPh_2Cl_3$
$[SbBrPh_3]^+$	0.2	1.2	0.7	
$[SbPh_3Cl]^+$			1.5	1.0
$[SbBr_2Ph_2]^+$	7.5	7.2		
$[SbBrPh_2Cl]^+$		4.3	6.7	
$[SbPh_2Cl_2]^+$		0.7	5.1	10.3
$[SbBrPh_2]^+$	6.1	3.9	1.9	
$[SbPh_2Cl]^+$		1.0	1.1	6.9
$[SbBr_2Ph]^+$	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

Although fragmentation of $[SbPh_2X_2]^+$ ions can lead to $[SbPh_2X]^+$ species, the alternative process, whereby a phenyl group is lost giving $[SbPhX_2]^+$ 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 $[SbPh_3X]^+$ appear in all the spectra, while low-intensity fragments containing two chlorine atoms, *i.e.* $[SbPh_2Cl_2]^+$ and $[SbPhCl_2]^+$, can be identified in the spectrum of $SbBr_2Ph_2Cl$. 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*) $SbPh_2Cl_3$, (*b*) $SbBrPh_2Cl_2$, (*c*) $SbBr_2Ph_2Cl$, and (*d*) $SbBr_3Ph_2$

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's [12] 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 $SbBr_2Ph_2Cl$ 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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REFERENCES

[1] M. Dub, ' Organometallic Compounds,' vol. 3, ' Compounds of Arsenic, Antimony and Bismuth,' 2nd edn., 1968; *ibid.*, First Supplement, 1972.

[2] R. R. Holmes, *J. Inorg. Nuclear Chem.*, 1961, **19**, 363.

[3] K. Seppelt, *Z. anorg. Chem.*, 1977, **434**, 5.

[4] G. T. Morgan and G. R. Davies, *Proc. Roy. Soc.*, 1926, **A110**, 523.

[5] G. O. Doak and G. G. Long, *Trans. New York Acad. Sci.*, 1966, **28**, 402.

[6] Netherlands P. Appl., 6,505,216 (*Chem. Abs.*, 1966, **64**, 9766).

[7] K. Issleib and B. Hamann, *Z. anorg. Chem.*, 1966, **343**, 196.

[8] F. F. Blicke, U. O. Oakdale, and F. D. Smith, *J. Amer. Chem. Soc.*, 1931, **53**, 1025.

[9] E. Wiberg and K. Modritzer, *Z. Naturforsch.*, 1957, **B12**, 131.

[10] S. P. Bone and D. B. Sowerby, following paper.

[11] H. Preiss, *Z. anorg. Chem.*, 1972, **389**, 280; K. Henrick, M. Michiewicz, N. Roberts, E. Shewchuk, and S. B. Wild, *Austral. J. Chem.*, 1975, **28**, 1473.

[12] D. H. Whiffen, *J. Chem. Soc.*, 1956, 1350.

[13] J. Bordner, G. O. Doak, and J. R. Peters, jun., *J. Amer. Chem. Soc.*, 1974, **96**, 6763.

[14] B. A. Nevett and A. Perry, *Spectrochim. Acta*, 1977, **A33**, 755.

[15] J. K. Wilmshurst, *J. Mol. Spectroscopy*, 1960, **5**, 343.