THE INFRARED SPECTRA OF SOME PHENYL-SUBSTITUTED PENTAVALENT ANTIMONY COMPOUNDS

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Organometallic compounds of pentavalent antimony are known which have formulas of the type R_3SbY_2 and $(R_3Sb–O–SbR_3)Y_2$ where R may be either alkyl or aryl and where Y is a halogen or other electron attracting group. X-ray diffraction studies of the trimethylantimony dihalides (where the halogen is Cl, Br or I)[1] and of triphenylantimony dichloride[2] have shown that these substances are trigonal bipyramidal molecules. An infrared study of the pentavalent trimethylantimony derivatives concurred as to the structure of the trimethylantimony dihalides but indicated that when Y becomes highly electron-attracting such as perchlorate or nitrate [*e.g.*, $(CH_3)_3Sb(NO_3)_2$ and $[(CH_3)_3Sb–O–Sb(CH_3)_3](ClO_4)_2$] the antimony is no longer pentacovalent, but ions are present instead[3].

Even less is known about the structure and bonding of the phenyl derivatives than is the case with the methyl series of compounds. It was hoped that some elucidation of the structures of the phenyl derivatives might be possible by examination of their infrared spectra. In addition, we were interested in clarifying the conflicting results in the literature regarding the syntheses of the oxybis derivatives.

Most of the phenyl compounds studied here have been prepared by earlier workers. The synthetic results described in the present paper are for new compounds or for cases in which the syntheses differ significantly from previous work. The compounds studied, together with the analytical results and melting points, are listed in Table 1.

RESULTS AND DISCUSSION

Phenyl frequencies

Each of the compounds studied shows the frequencies associated with monosubstituted benzene. Occasionally regions are masked by absorption due to a structure in the Y group which prevents observation of one or more of the expected ring frequencies. As would be expected, the range of each of these phenyl ring frequencies, including those for the trivalent triphenylantimony, is small. These ranges are enumerated in Table 2.

Phenyl–antimony stretching frequencies

The asymmetric C–Sb stretching frequency occurs at 547 cm^{-1} in $(CH_3)_3SbBr_2$[3]. In the phenyl analogue and in other similar pentacovalent antimony compounds, this

BLE 1

E ANTIMONY COMPOUNDS PREPARED TOGETHER WITH THE ANALYTICAL RESULTS

$_3SbY_2$	*Melting point, °C*		*Sb analyses %*	
	Found[a]	*Literature*	*Calcd.*	*Found*
	115–116	115 (ref. 25)	—	—
	212–214	216 (ref. 23)	23.7	23.7
	163–164	153 (ref. 23)	20.1	20.0
$)_3$	143–145	156 (ref. 23)	25.5	25.2
O_2	157–162 (dec.)	—	27.5	27.4
$_3CO_2$	214–215	215 (ref. 24)	25.8	26.4
SO_4	> 300	300–310 (ref. 12)	27.1	26.5
$_3Sb–O–SbPh_3)Y_2$				
	216–218	218 (ref. 4)	30.7	30.2
	252–253	246–249 (ref. 5)	27.6	27.6
$)_3$	237–240	224–225 (ref. 4)	28.8	28.9
$)_4$	> 300	—	26.4	26.7
SO_4	255–259	252 (ref. 4)	29.8	29.7

[a] Melting points were determined on a Thomas-Hoover melting point apparatus calibrated inst U.S.P. melting-point standards. [b] Found: C, 55.56; H, 4.00; F, 9.85. $C_{18}H_{15}F_2Sb$ calcd.: 55.28; H, 3.87; F, 9.72%.

BLE 2

ENYL FREQUENCIES OF Ph_3Sb AND Ph_3SbY_2 BELOW 1600 CM^{-1}

quency	*Intensity range*
8–1578	w–m
1–1479	m–s
8–1438	m–s
7–1336	w–m[a]
4–1311	w–m[a,b,c]
0–1183	w–m[c]
3–1162	w[d]
1–1071	w–m[d]
8–1072	w–m[d,g,h,i]
3–1022	w–m[d]
3–998	m–s
2–738	m–vs[e]
9–694	m–vs
0–617	vw–w[d,j,k,l]
5–471	m–s[f]

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[a] Masked in $Ph_3Sb(C_2H_3O_2)_2$. [b] Masked in $(Ph_3Sb–O–SbPh_3)\ (NO_3)_2$. [c] Masked in Ph_3SbSO_4 lasked in $(Ph_3Sb–O–SbPh_3)(ClO_4)_2$. [e] Frequently two peaks. [f] Almost always two bands erved in this range, only one of which is due to the phenyl ring. [g] Not observed in $(Ph_3Sb–O–$ $Ph_3)(NO_3)_2$. [h] Not observed in Ph_3SbSO_4. [i] Not observed in Ph_3SbBr_2. [j] Not observed in $_3Sb–O–SbPh_3)Cl_2$. [k] Not observed in $Ph_3Sb(NO_3)_2$. [l] Masked by sulfate in $(Ph_3Sb–O–$ $Ph_3)SO_4$.

C(Ph)–Sb frequency should be observed at lower values. Indeed, it has been suggested that the phenyl band occurring near 454 cm^{-1} masks the asymmetric stretching frequency in Ph_3Sb and in Ph_3SbO, but a band observed at 446 cm^{-1} in Ph_3SbS has been assigned to the C(Ph)–Sb stretch[8]. In the present study two bands of medium intensity were usually observed in the vicinity of 450 cm^{-1} which appears to confirm the above assignment. The frequencies of these observed bands are recorded in Table 3.

TABLE 3

FREQUENCIES OF BANDS IN THE 500–400 CM^{-1} REGION

br = broad. Intensity: w = weak, m = medium, s = strong.

Compound	*Frequencies* (cm^{-1})		
Ph_3Sb	454 m	449 m	
Ph_3SbF_2	478 w	452 m, br	437 w
Ph_3SbCl_2	458 m	454 m	
Ph_3SbBr_2	456 m	448 m	
Ph_3SbI_2	450 m	445 m	
$Ph_3Sb(NO_3)_2$	458 s	449 s	
Ph_3SbSO_4	471 m, br	465 m, br	
$Ph_3Sb(HCO_2)_2$	462 m	452 m	
$Ph_3Sb(CH_3CO_2)_2$	462 m	456 m	
$(Ph_3Sb–O–SbPh_3)Cl_2$	456 m	445 m	
$(Ph_3Sb–O–SbPh_3)Br_2$	453 m	446 m	
$(Ph_3Sb–O–SbPh_3)(ClO_4)_2$	453 m	411 m	
$(Ph_3Sb–O–SbPh_3)(NO_3)_2$	454 m, br		
$(Ph_3Sb–O–SbPh_3)SO_4$	460 m	453 m	

In each case a band was noted very near 454 cm^{-1} although in the case of triphenylantimony sulfate there is a broad unresolved band between 470 and 430 cm^{-1}. The wave number of the phenyl frequency is probably reasonably constant and may well be the absorption band occurring near 454 cm^{-1}. The asymmetric antimony–carbon stretching frequency then is either slightly above, slightly below or superimposed on the phenyl frequency. In the case of oxybis(triphenylantimony) diperchlorate an absorption band is observed at 411 cm^{-1} which is definitely lower than bands shown by any of the other compounds in this region; this band may well have a different origin.

If the C–Sb–C bond angles are 120°, the symmetric C(Ph)–Sb stretching frequency is forbidden. Triphenylantimony dichloride is known to have this geometry[2]; the phenyl groups are in the planar positions and the chlorines are in apical positions of a trigonal bipyramid. There is no band above 300 cm^{-1} in the compounds studied that may be assigned to symmetric C(Ph)–Sb stretching. This result is most surprising in the case of triphenylantimony, which by analogy with compounds of its congeners should be a pyramidal molecule. The absence of a band in this region of the spectrum of triphenylantimony suggests three possibilities: (*a*) the dipole moment change is very small so that the absorption shows very little intensity, (*b*) the molecule is somewhat flattened so that the transition is forbidden in the infrared, or (*c*) the symmetric stretching frequency is considerably removed from the asymmetric frequency and occurs well below 300 cm^{-1}.

Absorption near 300 cm^{-1}

Absorption is observed between 300 and 250 cm^{-1} in the spectrum of each of the antimony compounds studied. In a number of cases this absorption is not resolved into discrete bands, but occurs over most of the 300–250 cm^{-1} region. The frequencies of these bands are cited in Table 4.

TABLE 4

FREQUENCIES OF BANDS IN THE 350–250 CM^{-1} REGION

s = strong, m = medium, w = weak, br = broad peak, sh = shoulder.

Compound	*Frequencies*
Ph_3Sb	269 m, 256 m, 250 m sh
Ph_3SbF_2	290 s, 285 s sh
Ph_3SbCl_2	290 s, 285–250 m
Ph_3SbBr_2	290 s, 278 m sh
Ph_3SbI_2	283 s, 275 m sh
$Ph_3Sb(NO_3)_2$	298 s, 290 s, 270 s
Ph_3SbSO_4	299 s
$Ph_3Sb(HCO_2)_2$	360 s, 315 s, 289 m, 270 w br
$Ph_3Sb(C_2H_3O_2)_2$	297 s, 282 s
$(Ph_3Sb–O–SbPh_3)Cl_2$	290 s
$(Ph_3Sb–O–SbPh_3)Br_2$	290 s, 289 w sh
$(Ph_3Sb–O–SbPh_3)(ClO_4)_2$	300 s, 290 sh
$(Ph_3Sb–O–SbPh_3)(NO_3)_2$	300 m sh, 299 m, 290 m sh
$(Ph_3Sb–O–SbPh_3)SO_4$	301 m sh, 299 m sh, 292 m

The one structure that all of the compounds have in common that might contribute to absorption in this region is Ph–Sb–Ph which should show infrared active bending modes. Other structures also undoubtedly produce bands in this region. With the exception of fluorine, antimony–halogen stretching must occur below 300 cm^{-1}, and it is particularly likely that in the spectra of Ph_3SbCl_2 and $(Ph_3Sb–O–SbPh_3)Cl_2$ the antimony–chlorine mode appears between 300 and 250 cm^{-1} (ref. 3).

Sb–O–Sb frequency

In a previous paper we had observed a strong, broad absorption band at 775 cm^{-1} in the spectra of the methyl derivatives $[(CH_3)_3Sb–O–Sb(CH_3)_3](ClO_4)_2$ and $[(CH_3)_3Sb–O–Sb(CH_3)_3]Cl_2$ which we suggested was due to the Sb–O–Sb group[3]. In

TABLE 5

Sb–O–Sb FREQUENCIES

br = broad

Compound	*Frequency*
$(Ph_3Sb–O–SbPh_3)SO_4$	740, br
$(Ph_3Sb–O–SbPh_3)(NO_3)_2$	736, br
$(Ph_3Sb–O–SbPh_3)(ClO_4)_2$	751, 738
$(Ph_3Sb–O–SbPh_3)Cl_2$	762, 769
$(Ph_3Sb–O–SbPh_3)Br_2$	772, 764

the phenyl series, a strong, broad band is observed near 750 cm^{-1} in the spectrum of each compound that contains the Sb–O–Sb structure. These frequencies are reported in Table 5.

Frequencies associated with the Y group

A number of bands found above 300 cm^{-1} in the various spectra are not associated with any of the previously discussed structures, *i.e.* Ph, Sb–O–Sb or C(Ph)–Sb. Such bands below 1600 cm^{-1} which have at least an intensity of "weak" are listed under the heading of the individual compound below. The "medium" and "strong" frequencies must be associated with the particular Y group. Examination of the symmetry of these polyatomic Y groups may lead to a better understanding of the nature of the bond between antimony and the particular polyatomic group (*vide infra*).

Triphenylantimony difluoride. A strong absorption frequency is observed at 505 cm^{-1} in the spectrum of this compound. The band must be due to the asymmetric antimony–fluorine stretching.

Triphenylantimony dinitrate and oxybis(triphenylantimony) dinitrate. In the spectra of both compounds, frequencies are observed which are characteristic of a nitrate group with essentially C_{2v} symmetry. These frequencies are listed below in cm^{-1}.

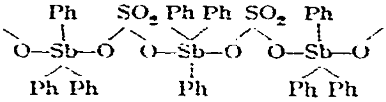
	ν_4	ν_1	ν_2	ν_6
$Ph_3Sb(NO_3)_2$	1535 s	1280 s	950 s	807 w
$(Ph_3Sb{-}O{-}SbPh_3)(NO_3)_2$	1492 s	1280 s	980 s	804 w

The values for ν_1 and ν_4 were taken from spectra of Fluorolube mulls, the remainder from Nujol mulls. Also the spectra of both compounds show an unassigned weak band, 832 cm^{-1}. Ferraro[9,10] has defined $\Delta = \nu_4 - \nu_1$ and has found that the magnitude of Δ is a measure of the covalent character of the nitrate group. A completely symmetrical nitrate ion would have $\Delta = 0$, while the covalent compound CH_3ONO_2 has $\Delta = 385$ cm^{-1}. For $Ph_3Sb(NO_3)_2$, $\Delta = 1535$ cm^{-1} $-$ 1280 cm^{-1} = 255 cm^{-1}, and $(Ph_3Sb{-}O{-}SbPh_3)(NO_3)_2$ has $\Delta = 1492$ cm^{-1} $-$ 1280 cm^{-1} = 212 cm^{-1}. These values correspond to the most covalent character found by Ferraro in inorganic compounds, *e.g.* $(NH_4)_2Ce(NO_3)_6$, $\Delta = 245$; $Hf(NO_3)_4 \cdot 4H_2O$, $\Delta = 245$ and $Zr(NO_3)_4 \cdot 4H_2O$, $\Delta = 260$. The values for the phenyl derivatives are in contrast to the value for trimethylantimony dinitrate which is essentially an ionic substance in the solid state with a Δ value of 59 cm^{-1} (ref. 3).

Triphenylantimony sulfate and oxybis(triphenylantimony) sulfate. A sulfate ion (T_d) is highly symmetrical and hence is characterized by a simple infrared spectrum with bands at 1104 and 613 cm^{-1} (ref. 11). Lowering of the symmetry by distortion of the ion or by covalent bond formation increases the number of infrared active modes and thus produces a considerably more complex spectrum.

A number of absorption bands in the spectra of mulls of these two compounds are probably associated with the sulfate group. These frequencies are as follows: Ph_3SbSO_4: 1282 s, 1140 s, 950–850 s, 623 m br; $(Ph_3Sb{-}O{-}SbPh_3)SO_4$: 1245 m, 1237 m, 1124 s, 971 m, 931 s, 850 w, 610 m, 580 m, 370 w. In each case the number of absorption frequencies observed is too high for T_d symmetry. Becke-Goering and Thielemann[12] have studied Ph_3SbSO_4 and, solely as part of a suggested reaction mechanism, they have suggested the possible existence of a zwitterion, Ph_3Sb^{+}–O–

SO_3^-. The infrared spectrum of the compound also was reported and is essentially in agreement with our spectrum. Although spectra have been studied in which the sulfate group is covalently bound by one (C_{3v}) or by two (C_{2v}) bonds[11], our spectra do not unambiguously fit either of these cases. Considering the spectra, the relatively high melting point and the slight solubility of Ph_3SbSO_4 even in polar solvents, a polymeric structure would be possible, for example



Oxybis(triphenylantimony) sulfate is more soluble in organic solvents and melts lower than triphenylantimony sulfate. Unfortunately it is not sufficiently soluble in organic solvents to permit molecular weight determinations.

Oxybis(triphenylantimony) diperchlorate. The bands listed in Table 6 are assigned to the perchlorate group. In addition weak unassigned bands at 973 and 658 cm^{-1} are observed.

As indicated in Table 6 the perchlorate group in this compound is assigned in terms of T_d symmetry[13]. This is the case even though ν_3 and ν_4 are split and the theoretically infrared inactive ν_1 has medium intensity. Evidence from the theoretically infrared inactive ν_2 is unavailable since this frequency occurs at 460 cm^{-1} in the Raman spectrum of the perchlorate ion[14]. In the spectrum of this compound 460 cm^{-1} is masked by a phenyl ring frequency at 450 cm^{-1}. Splitting (such as is observed in this compound) and the activity of ν_1 are also observed in the infrared spectra of alkali and alkaline earth metal perchlorates. This behavior cannot be accounted for by ligand field splitting and has been ascribed to the effects of a distortion of the perchlorate in the crystal lattice[15]. In any event the observed spectrum is similar to that reported for these metallic, ionic perchlorates.

TABLE 6

PERCHLORATE FREQUENCIES

I = infrared; R = Raman; s = strong; m = medium; sh = shoulder.

$(Ph_3Sb$-O-$SbPh_3)(ClO_4)_2$	*ClO_4^- ion*[13]	*Assignment T_d symmetry*
1111 s 1064 s sh 1050 s sh 1030 s sh	1110 (I, R)	ν_3
923 m	932 (R)	ν_1
625 m sh 619 m	626 (I, R)	ν_4
	460 (R)	ν_2

Since the perchlorate group in oxybis(triphenylantimony) diperchlorate is ionic, each of the antimony atoms is bonded by four covalent bonds. Thus the antimony atoms should be exhibiting tetrahedral instead of trigonal bipyramidal geometry. This would mean that both a symmetric and asymmetric C(Ph)–Sb stretching frequency would be infrared active. As noted earlier this is the only compound which has a spectrum showing a band at 411 cm^{-1}. This band may well be the symmetric C(Ph)–Sb stretching frequency.

Triphenylantimony diformate and triphenylantimony diacetate. A number of frequencies are observed in the spectra of these compounds which so far have not been discussed. These are as follows: $Ph_3Sb(HCO_2)_2$: 1650 vs, 1610 w, 1367 m, 1339 w, 1333 w, 1230 vs, 844 w, 832 w, 777 m, 772 m, 360 m, 314 m; $Ph_3Sb(CH_3COO)_2$: 1628 s, 1376 m, 1318 s, 1008 w, 930 m, 915 w, 686 m, 672 m, 609 w, 486 w. The medium and strong frequencies (with the exception of the frequencies at 360 and 314 cm^{-1} in the spectrum of triphenylantimony diformate) and many of the weak frequencies may be assigned to the formate[16] or acetate[17] moieties.

The $-CO_2-$ group of both the acetate and the formate ion has C_{2v} symmetry and gives rise to an asymmetric and a symmetric stretching frequency. These are listed for the sodium carboxylates in Table 7. If carboxylates act as bidentate groups, their symmetry is not greatly altered, and the number of infrared active frequencies might not be expected to change from that of the free ion[18,19,20]; the frequencies could shift appreciably, however, if the metal–oxygen bonds are strong. Formation of a single covalent bond shifts the frequencies associated with carbon–oxygen stretching. In the case of the covalent methylacetoxysilanes, C–O(Si), stretching is observed between 1267 and 1200 cm^{-1} while C=O stretching is found between 1765 and 1725 cm^{-1} (ref. 21). Both the $Ph_3Sb(HCO_2)_2$ (1650 and 1230 cm^{-1}) and the $Ph_3Sb(CH_3COO)_2$ (1628 and 1318 cm^{-1}) spectra show definite shifts of the carbon–oxygen stretching frequencies from that observed in free ions (see Table 7); this fact would seem to indicate considerable covalent character between the carboxylate groups and the antimony. If an antimony–oxygen stretching frequency occurs in the spectrum of $Ph_3Sb(C_2H_3O_2)_2$, it must be below 300 cm^{-1}. In the case of the formate, however, two well defined bands are observed in the spectrum at 360 and at 315 cm^{-1} which cannot be ascribed to the $Ph_3Sb{<}$ group and which are not observed in the spectrum of the formate ion. The only structure left which can give rise to these bands is Sb–O.

TABLE 7

C–O STRETCHING FREQUENCIES (CM^{-1})

$NaC_2H_3O_2$[17]	$NaCHO_2$[16]	
1582	1620	asym. str.
1425	1377	sym. str.

Hydrolysis of Ph_3SbY_2

Compounds of the type $Ar_3Sb(OH)Y$ have been reported by several investigators. Thus, Morgan, Micklethwait and Whitby[4] reported the preparation of $Ph_3Sb(OH)Cl$ by the hydrolysis of Ph_3SbCl_2 in aqueous alcohol, and Wittig and Clauss[5] have reported the preparation of $Ph_3Sb(OH)Br$ by a similar procedure. It has also been reported[4] that, when triphenylantimony dichloride is treated with two equivalents of silver nitrate or silver sulfate in aqueous alcohol, the corresponding hydroxy nitrate, $Ph_3Sb(OH)NO_3$, or hydroxy sulfate, $(Ph_3SbOH)_2SO_4$ is obtained. Other workers, however, have been unable to obtain these hydroxy compounds, but have obtained instead compounds of the type $(Ph_3SbY)_2O$[6,7]. We have repeated both the work of Morgan, Micklethwait and Whitby and of Wittig and Clauss. None of the resulting compounds give hydroxyl bands in the infrared, and the analytical results are in good agreement with the oxide structure, $(Ph_3SbY)_2O$.

It was pointed out in an earlier paper[3] that the trialkylantimony dihalides are extensively hydrolyzed in aqueous solution, but that these hydrolyses are reversible and that the product obtained on recrystallizing trialkylantimony dihalides (or other trialkylantimony compounds of the type R_3SbY_2) from aqueous solution depends on the relative solubilities of the various species present. Thus, the fact that oxybis(triphenylantimony) dichloride is obtained when triphenylantimony dichloride is recrystallized from aqueous alcohol is a reflection of the relative solubilities of the two compounds under these conditions. Kolditz, Gitter and Rösel[7] have implied that triphenylantimony dichloride is stable in the presence of hydrolytic solvents, although they obtained evidence of solvolysis in methanol. Since triphenylantimony dihalides are almost insoluble in water, it is not easy to determine their degree of hydrolysis. We have found, however, that a 0.005 *M* solution of triphenylantimony dichloride in 50 % aqueous alcohol gives a pH reading of 1.3 with a glass electrode at 25°. The concentration of HCl required to give the same pH reading in 50 % aqueous alcohol was found experimentally to be 0.004 *N*. Thus 0.005 *M* triphenylantimony dichloride in 50 % aqueous alcohol is hydrolyzed approximately 80 % if the hydrolysis proceeds according to the equation:

$$Ph_3SbCl_2 + 2H_2O \rightleftharpoons Ph_3Sb(OH)Cl + H_3O^+ + Cl^-$$

EXPERIMENTAL

Preparation of compounds

Triphenylantimony dichloride was a commercial product (Eastman Organic Chemical No. 4430) and was used without further purification since antimony analysis agreed well with the theoretical values and the melting point agreed with a recent literature value[22]. Triphenylantimony dibromide and triphenylantimony diiodide were prepared by halogenation of triphenylantimony (Eastman Organic Chemical No. 1553) essentially by the procedure of Michaelis and Reese[23]. Purification of the diiodide was effected by dissolving the reaction product in benzene and adding petroleum ether to incipient crystallization. By repeating this procedure several times, an almost white product was obtained. The diiodide cannot be recrystallized from a warm solvent. When a solution of the purified diiodide is warmed, even in a non-polar solvent such as benzene, the solution rapidly becomes yellow or brown. The product that crystallizes from the colored solution is yellow, and of course, cannot be purified by further similar recrystallizations. Triphenylantimony dinitrate was prepared from triphenylantimony and fuming nitric acid[23]. The crude product was recrystallized from hot nitric acid. Triphenylantimony diacetate was prepared from triphenylantimony dihydroxide and glacial acetic acid[24], and the product was recrystallized from hot glacial acetic acid. Oxybis(triphenylantimony) dibromide was prepared by the procedure of Wittig and Clauss[5]. The corresponding chloride was prepared by this same procedure and also by the procedure of Kolditz, Gitter and

Rösel[7]. Oxybis(triphenylantimony) dinitrate and oxybis(triphenylantimony) sulfate were prepared by the procedure of Morgan, Micklethwait and Whitby, and both products were recrystallized from alcohol[4].

Triphenylantimony difluoride has been previously prepared from triphenylantimony dichloride and hot aqueous potassium fluoride solution[25]. We obtained the same compound upon addition of an aqueous solution of silver fluoride (Aceto Chemical Co., 50 % solution) to triphenylantimony dichloride in aqueous ethanol. The difluoride was also obtained as the sole product in an attempt to prepare the fluoroborate. This was accomplished as follows: triphenylantimony dichloride (2.17 g, 0.005 mole) was dissolved in 200 ml of boiling alcohol and 0.1 mole of silver fluoroborate (Baker and Adamson, 47 % solution) was added. After removal of the precipitated silver chloride, the solvent was evaporated to 15 ml. On cooling 1.55 g of triphenylantimony difluoride (79 %) separated from the solution. The m.p., mixed m.p. and infrared spectrum indicated that the product was identical with that obtained from silver fluoride.

Triphenylantimony diformate was prepared by dissolving triphenylantimony dihydroxide (2.69 g) in 10 ml of hot formic acid. On standing overnight in the refrigerator crystals of the diformate separated from solution. The yield was 1.01 g, 33 %. The crystals were recrystallized from hot formic acid.

Triphenylantimony sulfate could not be prepared by the procedure of May[26]; all attempts to prepare the compound by warming triphenylantimony with conc. sulfuric acid resulted in splitting of the carbon–antimony bond. The desired sulfate was obtained by adding triphenylantimony dichloride (3.0 g) in small portions to 10 ml of conc. sulfuric acid in a flask surrounded by an ice bath. There was a vigorous evolution of hydrogen chloride after each addition. When all of the solid had been added, dissolved hydrogen chloride was removed by connecting the flask to a water aspirator and evacuating for a short time. The clear solution was added to 20 g of ice to produce a sticky solid. The liquid was removed by decantation and the solid triturated repeatedly with separate portions of ether until a white solid resulted and the ether was free from sulfuric acid. No suitable solvent for recrystallizing the product was found.

Oxybis(triphenylantimony) diperchlorate was obtained by treatment of a hot solution of triphenylantimony dichloride (2.17 g, 0.005 mole) in 200 ml of alcohol with an alcoholic solution of silver perchlorate (2.07 g, 0.01 mole). After standing overnight the silver chloride was removed, and the filtrate was diluted with alcohol to a volume of 250 ml. Due to several explosions encountered during the preparation of oxybis(trimethylantimony) diperchlorate, small aliquots (10–50 ml) of this alcoholic solution were evaporated *in vacuo* over calcium chloride. No explosions were encountered, however, and the preparation appears to be less hazardous than in the case of the trimethyl compound. The white crystals obtained were recrystallized from an alcohol–ether mixture.

Determination of spectra

Each compound was mulled in Nujol and the spectrum recorded between 4000 and 250 cm^{-1} with a Perkin–Elmer 521 infrared spectrophotometer. All measurements below 500 cm^{-1} were made with the instrument purged with dry nitrogen and with mulls between cesium bromide plates. In cases where bands of interest might be masked by the Nujol, the spectra were also observed with the compounds mulled in Fluorolube.

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SUMMARY

In compounds of the type Ph_3SbY_2 and $(Ph_3Sb–O–SbPh_3)Y_2$ the C(Ph)–Sb asymmetric stretching frequency occurs between 471 and 445 cm^{-1}. Absorption due to Sb–O–Sb occurs near 750 cm^{-1}. In triphenylantimony dinitrate the nitrate group is considerably more covalent than in trimethylantimony dinitrate. The spectral results with compounds of the type Ph_3SbY_2 are consistent with a trigonal bipyramidal molecule. X-ray diffraction studies by previous workers have clearly demonstrated such a structure for only Ph_3SbCl_2.

Oxybis(triphenylantimony) diperchlorate appears to contain a perchlorate ion. The other compounds of the type $(Ph_3Sb–O–SbPh_3)Y_2$ which we have studied appear to be covalent and probably consist of two trigonal bipyramidal Ph_3SbY groups sharing an apical oxygen atom.

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