

## ANTIMONY

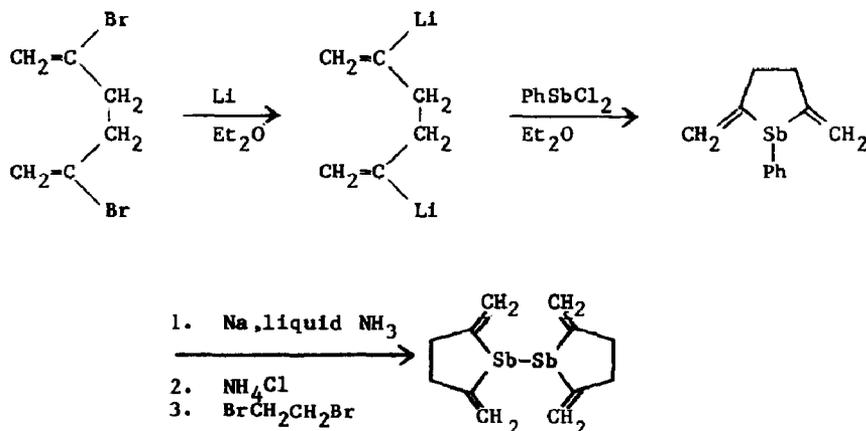
## ANNUAL SURVEY COVERING THE YEAR 1987

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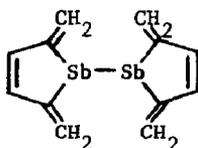
Except for our Annual Survey covering the year 1985, no book or review devoted exclusively to organoantimony compounds was published in 1987. The chemistry of organoarsenic, -antimony, and -bismuth compounds [1] and their use as ligands [2] have been reviewed, however, in a new seven volume compendium on coordination chemistry. In addition, information about organoantimony compounds has been included in surveys of recent publications on the organometallic chemistry of the main-group elements [3], on the main-group elements of Groups IV and V [4], and on the organic derivatives of arsenic, antimony, and bismuth [5]. Organoantimony compounds have been briefly mentioned in review articles on the following subjects: ylides and imines of arsenic, antimony, and bismuth [6], RE-bridged metal carbonyl clusters (where E was N, P, As, Sb, or Bi) [7], the silicon group [8], reactions of metal carbonyls with Group V and Group VI ligands [9], and diffraction studies of organometallic compounds [10]. A few organoantimony compounds have been discussed in a new two volume work on inorganic homo- and heterocycles [11].

2,2',5,5'-Tetrakis(methylene)bistibolane has been prepared by the following sequence of reactions [12]:



The compound crystallized from pentane at  $-78^\circ\text{C}$  as an orange, thermochromic solid that decomposed at  $45^\circ\text{C}$ . In common with most distibines, solutions

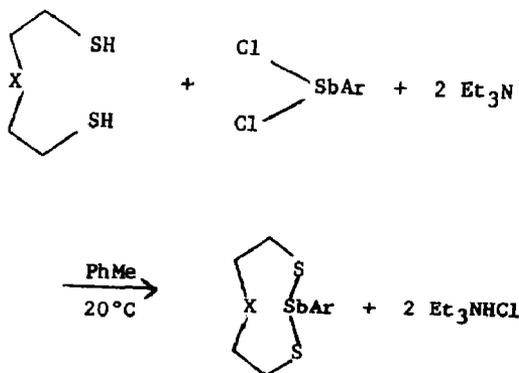
of the substance were light yellow. Its UV spectrum in pentane exhibited a structureless maximum at 300 nm ( $\epsilon 43,000$ ). The diffuse reflectance spectrum of the solid had a broad absorption band centered at 475 nm. Thus, there was a red shift of 175 nm on crystallization. Although it was not possible to obtain crystals of suitable quality for a single-crystal X-ray diffraction study, it was concluded that the compound (like other thermochromic distibines and dibismuthines studied) probably had a structure in which the metal atoms were arranged in chains with alternating long and short separations:  $\cdots\text{Sb}-\text{Sb}\cdots\text{Sb}-\text{Sb}\cdots$ . The band structures of this distibine and the related (but still unknown) 2,2',5,5'-tetrakis(methylene)bistibolene(I) were calculated by using the tight-binding model based on extended Hückel calculations.



I

The valence band was found to be independent of the ring since it was localized on the antimony atoms. The conduction band, however, was almost entirely localized on the carbon  $\pi$ -orbitals, and its energy was lowered by a greater degree of conjugation of the carbon skeleton. It was suggested that the distibine I might be a particularly attractive synthetic goal.

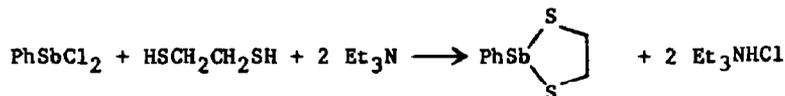
Oxadithia- and trithiastibocanes have been synthesized by the interaction of a dithiol and an aryldichlorostibine [13]:



(where X was O or S and Ar was 4-Tol or 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)

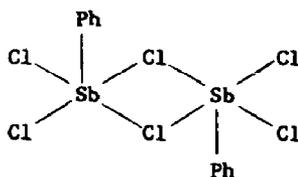
The four stibocanes were crystalline solids, which were stable in dry air at room temperature. The 4-tolyl derivatives were colorless, while the 4-nitrophenyl derivatives were yellow. All of the stibocanes were investigated by thermogravimetric analysis and by  $^{13}\text{C}$  NMR, IR, and Raman spectroscopy. The X-ray crystal structure of the 4-nitrophenyltrithiastibocane was also determined. The eight-membered ring was found to exhibit a boat-chair conformation. There were significant 1,5-transannular  $\text{Sb}^{\text{III}}\text{S}$  interactions (319 pm) and  $\text{Sb}^{\text{III}}\text{S}$  and  $\text{Sb}^{\text{III}}\text{O}$  intermolecular contacts (339 and 353 pm, respectively). Each antimony atom was, therefore, six-coordinated. The two  $\text{Sb}^{\text{III}}\text{S}$  distances observed by X-ray diffraction were correlated with vibrational bands at 236 and 218  $\text{cm}^{-1}$ . A logarithmic relationship between transannular  $\text{Sb}^{\text{III}}\text{S}$  distances and the corresponding vibrational frequencies was observed for a series of related trithiastibocanes.

2-Phenyl-1,3-dithia-2-stibolane has been prepared in a 40% yield by a previously described method [14]:



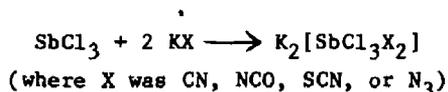
Its  $d_5$ -phenyl analog was obtained in a similar manner. The mass spectra of both substances were in agreement with the assigned structures. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the phenyl compound suggested that it existed in  $\text{CD}_2\text{Cl}_2$  solution as isolated molecules in which the five-membered ring had a half-chair conformation. An X-ray diffraction study showed that in the solid state the ring was midway between an envelope and a half-chair conformation. It also showed that the molecules formed helical chains by the intermolecular connection between the antimony atom of one molecule and a sulfur atom of another. The intramolecular Sb-S distances were 243 and 246 pm, while the intermolecular  $\text{Sb}^{\text{III}}\text{S}$  distance was 334 pm. Both types of antimony-sulfur distances were found to correlate with IR and Raman bands:  $\nu(\text{Sb-S})$  307-342,  $\nu(\text{Sb}^{\text{III}}\text{S})$  222-224  $\text{cm}^{-1}$ .

The reduction of ammonium phenylpentachloroantimonate,  $[\text{NH}_4][\text{PhSbCl}_5]$ , in 1 M hydrochloric acid with an excess of solid sodium sulfite and subsequent addition of 2,2'-bipyridine (bipy) to the reaction mixture resulted in the precipitation of a salt of composition  $[\text{bipyH}_2][\text{Ph}_2\text{Sb}_2\text{Cl}_6]$  [15]. An X-ray diffraction study showed that the anionic moiety contained two  $\text{PhSbCl}_2$  units linked by two slightly unsymmetrically bridging chlorine atoms:

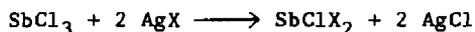


Each antimony atom had a distorted square-pyramidal coordination, in which the phenyl groups were in apical positions. The Sb-Cl distances in the bridge were about 0.6 Å longer than the terminal Sb-Cl bonds. It was concluded that there was ample space *trans* to each phenyl group for a lone pair of electrons on the antimony atom.

The treatment of antimony trichloride with potassium pseudohalides in THF solution has been found to yield anionic complexes of antimony [16]:

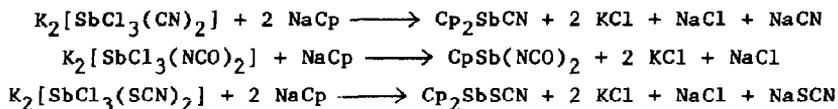


The IR spectra of the salts thus obtained indicated that the pseudohalide groups were attached to the antimony through the terminal atom with the lower electronegativity, *i.e.*, C in CN, N in NCO, and S in SCN. On the other hand, the reaction of antimony trichloride with silver pseudohalides in THF produced antimony pseudohalides in which the pseudohalide group was attached to the antimony through the terminal atom with the higher electronegativity:

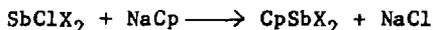


(where X was NC, OCN, or NCS)

When the potassium trichlorodipseudohaloantimonates were allowed to react with sodium cyclopentadienide in THF, cyclopentadienyl derivatives of antimony were obtained:



The antimony chlorodipseudohalides gave only monocyclopentadienyl derivatives:

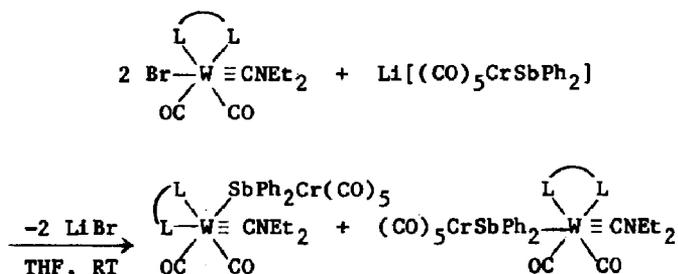


(where X was NC, OCN, or NCS)

Cyclopentadienyldiazidostibine, CpSb(N<sub>3</sub>)<sub>2</sub>, was also described, but its method of synthesis was not explicitly given. The IR spectra of the dicyclopentadienyl compounds suggested the presence of both centrally σ-bonded and π-bonded rings. In the monocyclopentadienyl derivatives, the

ring appeared to be centrally  $\sigma$ -bonded. The electrical conductivities of the antimony chloropseudohalides (about  $1.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) and of the cyclopentadienyl derivatives (about  $0.32 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) in nitrobenzene were very low and indicated that they were essentially non-ionic. Their molecular weights in nitrobenzene and in acetone showed that they were monomeric in these solvents. The electrical conductivities of the potassium trichlorodipseudohaloantimonates in nitrobenzene were high (about  $52.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) and indicated that these substances were dissociated into three ions. This conclusion was supported by molecular weight determinations.

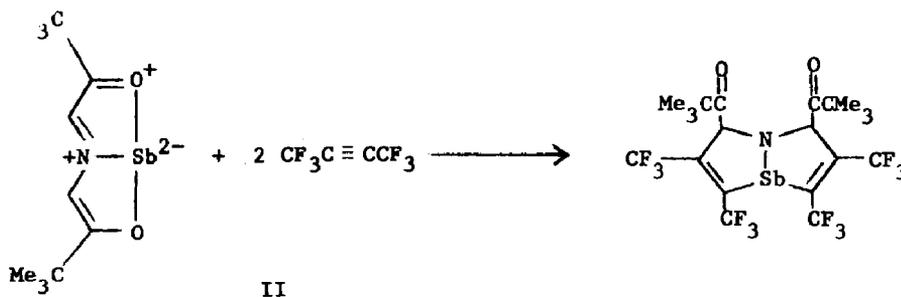
New neutral diethylaminocarbyne complexes of tungsten have been obtained by the following type of reaction [17]:



(where  $L_2$  was 2,2'-bipyridine or 1,10-phenanthroline)

In these complexes, the antimony atom occupied a bridging position between two transition metal atoms. PMR investigations at low temperatures showed that these bridged complexes existed as a mixture of *cis* and *trans* isomers and that the thermodynamic equilibria favored the *cis* complexes. Temperature dependent PMR spectra suggested a dynamic process in which the chelating ligand  $L_2$  switched between two *cis* and two *cis/trans* positions, relative to the carbyne ligand, and caused a rapid interconversion of the two isomers at room temperature.

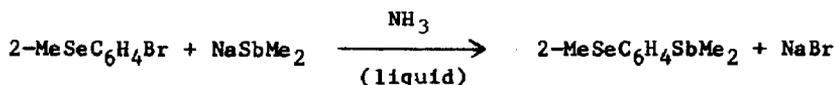
Two mol of hexafluoro-2-butyne have been found to add to one mol of the tricoordinate hypervalent antimony compound II [18-20]:



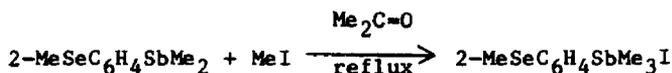
The yield of the adduct was 71% after recrystallization from pentane. Its structure was determined by multinuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$ ) NMR and by X-ray

diffraction. Attempts to prepare a 1:1 adduct of hexafluoro-2-butyne and II were unsuccessful.

A hybrid bidentate ligand has been obtained by means of the following reaction [21]:



The colorless, air-sensitive liquid thus obtained was easily quaternized to a solid, mp 160°C:



The PMR spectrum of the tertiary stibine exhibited a singlet at  $\delta 0.95$  for the methyl groups bonded to the antimony. On quaternization, the singlet shifted downfield to  $\delta 1.9$ . The position of the MeSe PMR signal was almost the same in both compounds ( $\delta 2.3$  for the stibine;  $\delta 2.4$  for the methiodide). The  $^{77}\text{Se}$  NMR spectrum of the methiodide was also recorded, while the stibine was further characterized by  $^{13}\text{C}$  and  $^{77}\text{Se}$  NMR spectroscopy and by mass spectrometry. The base peak in the mass spectrum corresponded to the  $(\text{M-Me})^+$  ion; the intensity of the molecular ion was 12%.

Although tris(trifluoromethyl)stibine has been known since 1957, the method that was employed for its synthesis required heating a mixture of trifluoroiodomethane and metallic antimony at high pressure (>50 atm) in a rotating steel cyclinder at 165-170°C. This stibine has now been conveniently prepared in yields of 75-83% by means of the following type of reaction [22]:

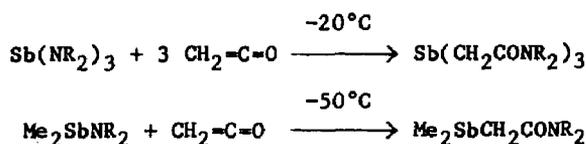


(where X was Cl, Br, or I)

The interaction of bis(trifluoromethyl)cadmium and the antimony trihalides was investigated in a number of solvents. The reactions were very slow in diglyme and DMSO, but fast in pyridine, glyme, acetonitrile, and DMF. Acetonitrile proved to be the solvent of choice, because there appeared to be no side reactions between this liquid and the organocadmium compound. The rate of reaction of the antimony trihalides decreased in the order  $\text{SbCl}_3 > \text{SbBr}_3 > \text{SbI}_3$ . This order corresponded to the order of the extent of dissociation of the trihalides as indicated by conductivity and molecular weight measurements. The reactions were conveniently monitored by  $^{19}\text{F}$  NMR spectroscopy. As the reaction proceeded,  $^{19}\text{F}$  NMR signals appeared at -60.4, -52.3, and -41.2 ppm, corresponding to mono-, bis-, and tris(trifluoro-

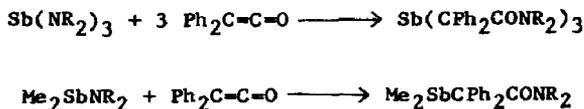
methyl)antimony species. The chemical shifts and the  $^{19}\text{F}$ - $^{13}\text{C}$  coupling constants did not depend on which halogen was present in the antimony trihalide employed. It was inferred that intermediates formed in these reactions included the cations  $\text{CF}_3\text{Sb}^{2+}$  and  $(\text{CF}_3)_2\text{Sb}^+$ . The antimony-containing fragments observed in the mass spectrum of tris(trifluoromethyl)stibine were identified as  $(\text{CF}_3)_3\text{Sb}^+$ ,  $(\text{CF}_3)_2\text{SbCF}_2^+$ ,  $(\text{CF}_3)_2\text{Sb}^+$ ,  $\text{CF}_3\text{SbF}^+$ ,  $\text{CF}_3\text{Sb}^+$ ,  $\text{SbF}_2^+$ ,  $\text{SbF}^+$ , and  $\text{Sb}^+$ . The mp of the stibine was  $-58^\circ\text{C}$ , the bp  $71.7^\circ\text{C}$ .

The formation of carbon-antimony bonds has been accomplished by the insertion of ketene or diphenylketene into the antimony-heteroatom linkage of *N,N*-dialkylamino-, alkoxy-, and ethylthiostibines [23]. Thus, ketene reacted with tris(dialkylamino)stibines or dialkylaminodimethylstibines in ether to give good yields of  $\alpha$ -metallated acetamides:



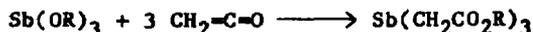
(where R was Me or Et)

The structure of the insertion products were determined by elemental analyses and by IR, NMR and mass spectroscopy. The IR spectra showed a strong C=O stretching vibration in the  $1610\text{--}1620 \text{ cm}^{-1}$  region. The PMR spectra contained a singlet,  $\delta 2.5\text{--}2.8$ , for the methylene groups attached directly to antimony. There were also characteristic peaks due to the magnetically nonequivalent alkyl groups bonded to nitrogen. Possibly because of steric hindrance, diphenylketene reacted more slowly with the aminostibines:



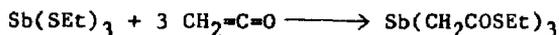
(where R was Me or Et)

Tris(alkoxycarbonylmethyl)stibines were easily obtained in high yield at room temperature:



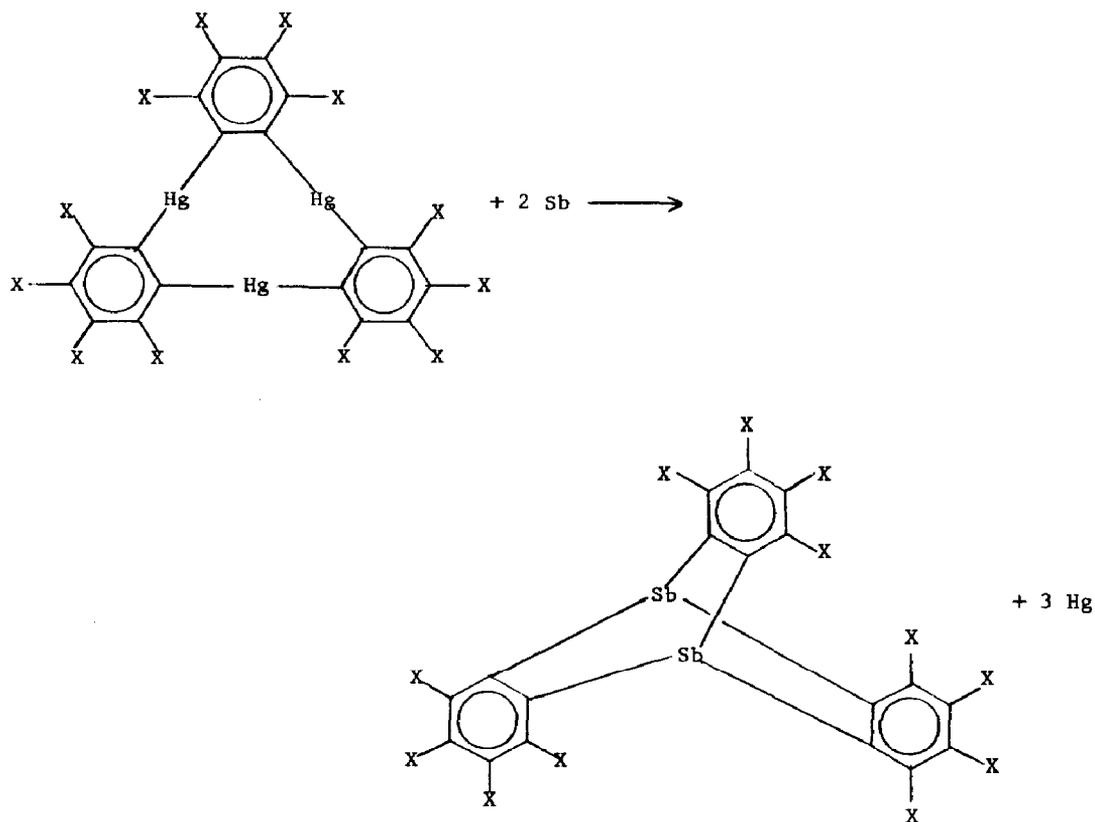
(where R was Et, Pr,  $\text{Me}_2\text{CH}$ , or Bu)

Tris(ethylthio)stibine reacted slowly with ketene in refluxing benzene to give a 50% yield of adduct:



The IR spectrum exhibited the carbonyl stretching frequency at  $1662 \text{ cm}^{-1}$ .

Two distibatriptycenes have been prepared by the following type of reaction [24]:

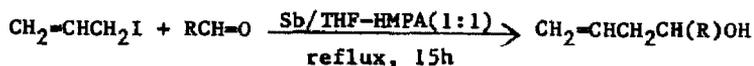


(where X was H or Cl)

The unsubstituted compound (*i.e.*, where X was H) was obtained in about 1% yield by the interaction of *o*-phenylenemercury trimer and antimony in a sealed, evacuated tube at  $260^\circ\text{C}$  for 6 h. The composition  $\text{C}_{18}\text{H}_{12}\text{Sb}_2$  was unambiguously established by accurate mass measurements of the peaks present in the molecular ion cluster. The product separated from hexane with 0.5 mol of solvent per mol of 1,6-distibatriptycene; the solvent of crystallization could be driven off by heating the product overnight at  $85^\circ\text{C}$ . An attempt to prepare the compound from 1,2-diiodobenzene and antimony yielded

small amounts of triphenylene as the only isolable substance. Similarly, attempts to obtain a "mixed" triptyrene by the interaction of tris(2-chlorophenyl)arsine and excess antimony at 260°C were also unsuccessful. The reaction between tetrachloro-*o*-phenylenemercury and antimony required a temperature of at least 300°C; the yield of the perchloro-1,6-distibatriptycene was 60-70%. The compound gave hemi-solvates on recrystallization from DMF, diethylformamide, pyridine, or nitrobenzene; the hemi-solvates were stable on vacuum drying at room temperature. The solubility of the compound in organic solvents was so low that solutions could be obtained only by slow extraction of the solid with boiling solvent.

The use of metallic antimony for inducing the alkylation of aldehydes by allyl iodide has been found to give good yields (55-100%) of the corresponding homoallylic alcohols [25]:



(where R was Ph, 4-MeOC<sub>6</sub>H<sub>4</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, Me(CH<sub>2</sub>)<sub>6</sub>, *trans*-PhCH=CH, or Me<sub>2</sub>C=CHCH<sub>2</sub>CH<sub>2</sub>C(Me)=CH)

The ratio of allyl iodide to aldehyde to antimony was 1.2:1:1.2. Allylic bromides and phosphates were less reactive than allylic iodides and gave poor yields of the coupling products. However, these disadvantages were overcome by the addition of one equivalent of lithium iodide to the reaction mixture. In all cases, the use of  $\alpha,\beta$ -unsaturated aldehydes gave only 1,2-addition products. Ketones reacted very sluggishly. Thus, the interaction of 2-octanone and allyl iodide in the presence of antimony gave only 17% of the adduct after 90 h's reflux. Ester and cyano groups were unaffected under these conditions. Although no mechanism has been proposed for this new synthetic procedure, the intermediacy of some type of organo-antimony compound appears likely.

The treatment of toluene solutions of antimony trichloride or tribromide with varying quantities of hexaethylbenzene has been shown to give only 1:1 complexes in almost quantitative yield [26]:



(where X was Cl or Br)

The substances thus obtained were colorless, crystalline, and thermally stable; the melting points of the trichloride and tribromide complexes were 109.5 and 108°C, respectively. Their <sup>1</sup>H and <sup>13</sup>C NMR spectra in arene solution (toluene, xylenes, mesitylene, *etc.*) indicated a rapid exchange of

bound and excess (*i.e.*, free) hexaethylbenzene and hence relatively weak bonding between the trihalide molecules and the ligand. Solutions of the complexes were found to be electrically nonconducting. Determination of the crystal structure of the trichloride complex by X-ray diffraction showed the presence of molecular units in which the antimony atom was located almost exactly above the ring center at a distance of 2.96 Å. This relatively long distance confirmed the NMR evidence for weak forces between the components of the complex. The Sb-Cl distances and the Cl-Sb-Cl angles in the complex were similar to the corresponding distances and angles in crystalline antimony trichloride. The arrangement of molecules in the unit cell of the complex clearly showed that there were no specific contacts between the individual monomers.

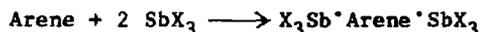
The interaction of mesitylene (1,3,5-trimethylbenzene) and antimony trichloride or tribromide has also been found to give good yields of colorless 1:1 complexes [27]. The melting points of the two complexes were 40-41°C and 56-58°C, respectively. X-ray structural analysis of the latter compound showed that one arene molecule was coordinated to each antimony atom and that these complexes (like the corresponding hexaethylbenzene complexes) could be characterized as "open-face sandwich" species. To a good approximation, the mesitylene molecules were centered over the metal atoms, but deviations from strict  $\eta^6$ -hapticity were greater than for the corresponding bismuth trichloride complex (see Bismuth. Annual Survey Covering the Year 1987). The  $C_6H_3Me_3 \cdot SbBr_3$  units were linked through a complicated network of loosely bound, bridging bromine atoms to form a two-dimensional coordination polymer. In spite of bridging by the bromine atoms and the bonding between the antimony atoms and the arene rings, the antimony maintained the pyramidal relationship with three bromine atoms that is characteristic of the free  $SbBr_3$  molecule. Similarly, the non-bridging Sb-Br distances and the Br-Sb-Br angles in the complex were not unusual. The distance between the antimony atom and the center of the aromatic ring varied from 3.22 to 3.33 Å.

Crystals of the Menshutkin complex  $PhH \cdot 2SbCl_3$  have been grown from the melt and have been studied by X-ray diffraction [28]. The metal atoms were acentrically  $\eta^2$ -bonded on opposite sides of the benzene ring plane; the distances between these atoms and the ring were 322 and 330 pm. When intermolecular  $Sb \cdots Cl$  contacts were taken into account, each antimony atom could be described as having a deformed pentagonal-bipyramidal coordination with the benzene molecule of each  $PhH \cdot 2SbCl_3$  unit being in an axial position for both antimony atoms.

The temperature dependence of the  $^{121}Sb$  NQR frequencies for the complex  $2SbCl_3 \cdot o$ -xylene has been studied from 77 K to about 280 K [29]. The results showed the occurrence of a phase transition at about 139 K.

(Differential thermal analysis performed between 98 and 210 K, however, exhibited no thermal anomaly around the transition temperature.) Although X-ray diffraction data were not available, it was concluded that the  $2\text{SbCl}_3$ -*o*-xylene unit was basically asymmetric and that the two antimony atoms in this unit had a different coordination environment.

Pentamethylbenzene (in toluene) and hexamethylbenzene (in benzene) have been shown to react with antimony trichloride or tribromide to give good yields of colorless 1:2 complexes [30]:



(where Arene was  $\text{C}_6\text{HMe}_5$  or  $\text{C}_6\text{Me}_6$  and X was Cl or Br)

The melting points of the four complexes ranged from 105 to 185°C. X-ray analysis of the hexamethylbenzene complexes showed that their structures were built up of tetrameric  $\text{Sb}_4\text{X}_{12}$  units which were crosslinked through double-sided arene coordination at each metal atom with four other tetramers so as to give a three-dimensional organometallic polymer. In both complexes, significant deviations from ideal  $\eta^6$ -coordination were observed. Thus, the two antimony atoms linked to each aromatic molecule were shifted in opposite directions from the center of the ring. The Sb-C distances varied from 3.28 to 3.61 Å in the trichloride and from 3.36 to 3.70 Å in the tribromide. The positions of the antimony atoms and the associated bridging halogen atoms in the lattice were accounted for by assuming a 50:50 disorder relative to the crystallographic symmetry elements.

The synthesis, reactions, and physical properties of a considerable number of new triarylantimony(V) compounds have been described [31]. One synthetic method involved the oxidative addition of a halogen, interhalogen, pseudohalogen, or sulfur to a triarylstibine:



(where Ar was 2- $\text{FC}_6\text{H}_4$ , 2- $\text{ClC}_6\text{H}_4$ , or 2- $\text{MeC}_6\text{H}_4$  and  
XY was  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{ICl}$ ,  $\text{IBr}$ ,  $\text{N}\equiv\text{CSSC}\equiv\text{N}$ , or S)

The solvents used for these reactions included petroleum ether, acetonitrile, and carbon tetrachloride. The stibine sulfides could also be obtained by passing hydrogen sulfide into an alcoholic ammonia solution of a triarylantimony dihalide. The molecular weights of the stibine sulfides (determined cryoscopically in benzene) indicated that they existed as monomers. Diazides and diisocyanates were prepared by the metathetical reaction of a triarylantimony dihalide with the appropriate metallic salt. The

diisothiocyanates could also be obtained by this method. The molar conductance of 0.001 M acetonitrile solutions of the newly synthesized halide and pseudohalide derivatives ranged from 15 to 40  $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$ , values that indicated that the substances were non-electrolytes. The pseudohalides were shown to be monomeric by cryoscopic measurements in benzene. Their IR spectra exhibited absorptions characteristic of covalently bonded pseudohalide groups. The PMR spectrum of tri-4-tolylantimony diisothiocyanate exhibited two doublets centered at  $\delta 7.92$  and  $7.21$  (due to twelve aromatic protons) and a nine proton singlet at  $\delta 2.36$  (due to three methyl groups). It was concluded that all of the dihalides and dipseudohalides had trigonal-bipyramidal structures in which the aryl groups occupied the equatorial positions and the anionic groups occupied the axial positions.

A conductometric titration study of the reaction of tris(pentafluorophenyl)stibine in acetonitrile with bromine, iodine, iodine chloride, or iodine bromide has been reported [32]. Ionic species were not observed in any case. When a solution of bromine was added dropwise to a solution of the stibine, the bromine was instantly decolorized until the molar ratio of halogen to stibine exceeded 1:1. At this point the solution acquired a yellow color and showed a very low molar conductivity. It was concluded that a covalent 1:1 adduct had been formed:



There was no conductometric evidence for adduct formation of any kind when iodine was added to a solution of the stibine, and all attempts to prepare tris(pentafluorophenyl)antimony diiodide were unsuccessful. When either interhalogen was used, a strong dark-brown color developed in the solution immediately after the titration was started. The interaction of the stibine and the interhalogens appeared to obey the following stoichiometry:

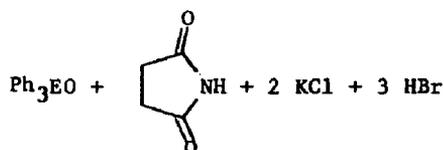
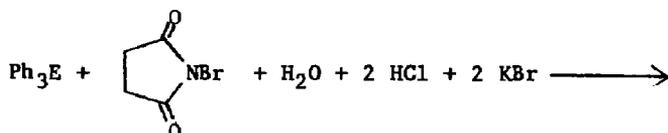


(where X was Cl or Br)

Attempts to isolate interhalogen adducts of the type  $(\text{C}_6\text{F}_5)_3\text{SbIX}$  were uniformly unsuccessful. Instead, the dichloride or dibromide was always obtained when the stibine was allowed to react with iodine chloride or iodine bromide. A report from another laboratory in 1985 claimed that the interhalogen adducts  $(\text{C}_6\text{F}_5)_3\text{SbIX}$  were readily prepared by interaction of the stibine and the interhalogen in acetonitrile at  $-10^\circ\text{C}$  [33].

A simple, direct oxidimetric method has been described for the analysis of milligram and microgram amounts of triphenylphosphine, -arsine, -stibine,

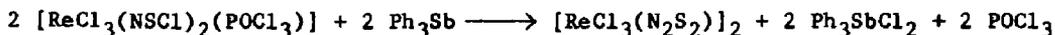
or bismuthine [34]. The method involved dissolution of the sample in methanol, addition of potassium bromide and hydrochloric acid, and titration of the resulting solution with aqueous *N*-bromosuccinimide to a methyl red end-point (*i.e.*, decolorization of the indicator). The oxidations proceeded rapidly at room temperature and appeared to obey the following stoichiometry:



(where E was P, As, Sb, or Bi)

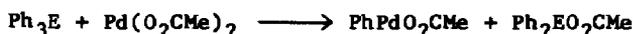
The oxides of type  $\text{Ph}_3\text{EO}$  formed in these reactions were isolated by extraction and crystallization from benzene. The white solids thus obtained were identified by their melting points and mixed melting points with authentic samples. No sign of any bromination of the phenyl groups was observed.

Triphenylstibine has been used as a reducing agent in the following reaction [35]:



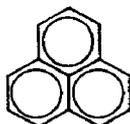
The formulation of the rhenium-containing product as a dimer was based on its IR spectrum. It contained traces of triphenylstibine or triphenylantimony dichloride but was suitable for further synthetic applications.

Stereospecific phenylation of alkenylsilanes of the type (*E*)- or (*Z*)- $\text{RCH}=\text{CHSiMe}_3$ , where R was Ph, Hex, or  $\text{MeOCH}_2$ , has been carried out with phenylpalladium acetate generated *in situ* from various sources [36]. The reactions were accompanied by inversion of the starting geometry with respect to the R and  $\text{Me}_3\text{Si}$  groups. Palladium(II) acetate was used as a starting material in one method of obtaining the organopalladium compound:



(where E was P or Sb)

An interest in potentially conducting organometallic systems has prompted a theoretical investigation of the still unknown substances in which one or more CH groups of the odd alternant hydrocarbon phenalenyl radical(III) have been replaced by antimony atoms [37]. Extended Hückel calculations were performed, and the results obtained suggested that the "stibaphenalenylys" might indeed be good conductors. Two main features



III

appeared to be characteristic of all of these antimony compounds: (a) the molecules should show an inherent propensity to form infinite stacks dependent on strong intermolecular Sb<sup>•••</sup>Sb bonding, and (b) the band structure of the stacks should exhibit a few bands that are less than half-filled. It was concluded that these features might allow the stibaphenalenylys to behave as highly conducting organic "metals".

The Fourier-transform IR and the Raman spectra of triphenylphosphine, -arsine, and -stibine in the solid state at *ca* 80 K have been recorded over the ranges 3500-40 cm<sup>-1</sup> (IR, 1 cm<sup>-1</sup> resolution) and 1650-30 cm<sup>-1</sup> (Raman, 2 cm<sup>-1</sup> resolution) [38]. Detailed band assignments were also given. The data was said to be more extensive, more complete, and of higher quality than those obtained in previous studies. The greatest improvement appeared to be in the low wavenumber region of both the IR and Raman spectra.

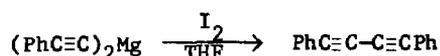
The enthalpies of solvation for compounds of the type Ph<sub>3</sub>E (where E was N, P, As, Sb, or Bi) have been determined at 25°C for the polar solvents methanol, dimethyl sulfoxide, acetonitrile, pyridine, and tetrahydrothiophene as well as for the nonpolar solvents benzene and tetrachloromethane [39]. The values were calculated from the known heats of crystallization and the heats of solution that were measured calorimetrically in the present investigation. In both the polar and the nonpolar solvents, low values of much the same magnitude were found. It was concluded that these results indicated that the solvation was essentially due to London forces.

The relationship between the adsorption behavior of polar organic compounds on anodically polarized nickel electrodes and Pearson's hard-soft acid-base principle has been studied by AC impedance and DC polarization measurements [40]. The polar organic compounds (which were of interest as corrosion inhibitors) included compounds of the type Pr<sub>2</sub>Y, where Y was O, S, Se, or Te, and of the type Pr<sub>3</sub>E, where E was N, P, or Sb. The results obtained indicated that a compound classified as a soft base was more

readily chemisorbed on the nickel surface (considered a soft acid) than was a compound classified as a hard base. It was also concluded that the inhibition efficiency of a soft base corrosion inhibitor was greater than that of a hard base inhibitor.

A process known as vacuum chemical epitaxy has been employed for the preparation of thin films of gallium antimonide, GaSb [41]. Triethylgallium and triethylstibine were used as the sources of the two metals. The utilization efficiency of the stibine was enhanced by the use of a thermal cracker located at the point of injection of the gaseous compound and by employing a hot-wall reaction chamber.

Triphenylstibine has been shown to "activate" the PdCl<sub>2</sub>-CuI catalyzed reaction of iodine with the magnesium salt of phenylacetylene [42]:



The yield of 1,4-diphenyl-1,3-butadiyne was 26%. Triphenylphosphine was more effective as an activator and led to a yield of 82%.

Certain organometallic compounds have been found to be useful as cocatalysts for the molybdenum(V) chloride polymerization of 1-chloro-1-alkynes of the type R-C≡C-Cl, where R was Bu, Hex, Oct, or  $\pi\text{-C}_{14}\text{H}_{29}$  [43]. Thus, when triphenylstibine was added in a 1:1 ratio to the molybdenum compounds, the yields of poly(1-chloro-1-alkynes) were excellent, and their weight-average molecular weights approached  $1 \times 10^6$ . The structure of the polymers was studied by UV, IR, and <sup>13</sup>C NMR spectroscopy.

A study has been reported of hyperconjugation in phenyl derivatives of the main-group elements of Groups II, III, IV, and V [44]. It was shown that hyperconjugation increased with an increase in chemical bond polarizability (which was assumed to be proportional to the bond refraction,  $R_D$ ). For thirty-five of the compounds studied (including triphenylstibine), the following linear relationship was observed between the  $\sigma_p^+ - \sigma_p$  value of the substituent on the phenyl ring and the sum of the refractions of the bonds involved in hyperconjugation:

$$\sigma_p^+ - \sigma_p = -(0.0213 \pm 0.0009)\Sigma R_D + (0.15 \pm 0.02)$$

Triphenylamine, -phosphine, -arsine, -stibine, and -bismuthine have been separated by means of a reversed-phase bonded octadecylsilane column [45]. The mobile phase was methanol-water (70:30, v/v). The results obtained were used to calculate the holistic total surface areas (TSA's) for the flat, propeller, and twisted conformations of each compound. Correlations were calculated between the TSA's and the natural logarithms of the capacity factors.

Triphenylstibine has been said to contribute to the green strength of rubber compositions used for tires [46]. It has also been employed as a component of fire-resistant epoxy potting compositions for semi-conductors [47]. Phenyl esters have been prepared by the oxidation of benzene with molecular oxygen in the presence of a carboxylic acid and a catalyst consisting of a mixture of palladium acetate and triphenylstibine [48]. The preparation of polyoxazolidones has been catalyzed by organoantimony compounds of the type  $R_xSbI_y$ , where R was an organic group such as phenyl,  $x$  and  $y$  were 1,2,3, or 4, and  $x + y$  was equal to or less than 7 [49].

There have been numerous recent articles on the use of tertiary stibines as ligands in a variety of metal complexes. The metals coordinated to the antimony in these complexes included cobalt [50,51], iridium [52,53], iron [54,55], mercury [56], molybdenum [57-61], nickel [62], osmium [63], palladium [64-68], platinum [69-71], rhodium [72], ruthenium [73-78], silver [79-83], and tungsten [59-61].

In 1986 Bordner and coworkers [84] determined the structure of crystalline triphenylstibine oxide, obtained by the thermal decomposition of  $Ph_4SbOH$ . The oxide proved to consist of dimeric  $(Ph_3SbO)_2$  molecules containing the 1,3,2,4-dioxadistibetane ring. This structure has now been confirmed by Ferguson and coworkers [85]. The triphenylstibine oxide was obtained by the hydrolysis of the ylide  $Ph_3SbC(SO_2C_6H_4Me-4)_2$  and characterized by elemental analysis and spectra. The X-ray analysis was of somewhat higher precision than that reported in the previous study, although the molecular geometry reported in both papers was essentially the same.

In 1972 the thermal decomposition of  $Ph_4SbOH$  was shown to occur at 50-70°C in *p*-xylene solution (in a nitrogen atmosphere, in the dark) to yield triphenylstibine oxide and benzene [86]. McEwen and Chupka [87] reported considerable evidence that this decomposition occurred, at least in large part, by a free radical mechanism. In a paper largely devoted to disproving the theory that the *C*-, *O*-, and *N*-phenylation of various substrates by organobismuth(V) reagents occurred by a free radical mechanism, Barton and coworkers [88] have reinvestigated the decomposition of  $Ph_4SbOH$ . Rather than *p*-xylene at 50-70°C, they used anhydrous  $PhCl$  at 110°C. Nor did these authors state that the rather rigid conditions (nitrogen atmosphere, in the dark) specified by McEwen were used. The yields of triphenylstibine oxide and benzene reported were essentially 100%, either in the presence of various amounts of the radical-trapping agent  $Ph_2C=CH_2$  or in the absence of this compound. From these results Barton and coworkers concluded that, contrary to McEwen and Chupka, this reaction did not occur by a free radical mechanism. It should be noted, however, that the "triphenylstibine oxide" obtained by Barton's group melted at 305°C, whereas McEwen and coworkers reported a mp of 221.5-222.0°C for the authentic compound; they also

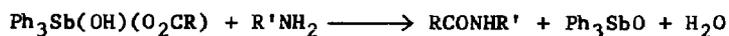
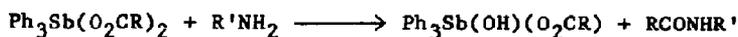
reported [86] that a compound, mp 302-303°C, was formed when triphenylstibine oxide was refluxed in *p*-xylene solution in the air. They believed that this compound was diphenylstibinic anhydride,  $\text{Ph}_2\text{Sb}(\text{O})\text{OSb}(\text{O})\text{Ph}_2$ , but X-ray diffraction studies [84] later showed it to be a complex tricyclic compound, hexa- $\mu$ -oxooctaphenyltetraantimony. The closeness of the two mp's (305° and 302-303°C) and the reaction conditions employed by Barton's group suggest that they may have actually been dealing with this compound rather than triphenylstibine oxide.

Nomura and coworkers [89] have used triphenylantimony dicarboxylates for the preparation of amides according to the equation:



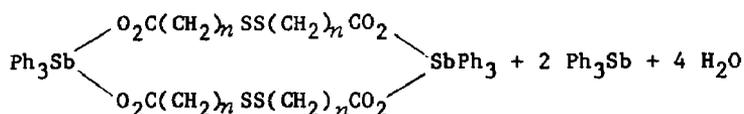
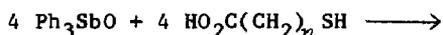
The reaction was first tried with  $\text{Me}(\text{CH}_2)_5\text{NH}_2$  and  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CMe})_2$  to yield 87%  $\text{Me}(\text{CH}_2)_5\text{NHCOMe}$  after heating at 50°C for 10 h. Triphenylstibine oxide was recovered quantitatively from the reaction. This aminolysis was then extended to several other amines ( $\text{PhCH}_2\text{NH}_2$ ,  $\text{MeCH}(\text{NH}_2)\text{Et}$ , cyclohexylamine,  $\text{PhNH}_2$ , and  $\text{Me}_3\text{CNH}_2$ ). Except for  $\text{Me}_3\text{CNH}_2$  (where the yield was only 10% after heating for 15 h), the yields of amides were excellent. Aniline required heating for 40 h to give an 84% yield of  $\text{PhNHCOMe}$ . The other amides were obtained in yields of 79-97%. In addition to  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CMe})_2$ , several other antimony carboxylates were used in the aminolysis reaction with  $\text{Me}(\text{CH}_2)_5\text{NH}_2$ . Thus,  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CCF}_3)_2$  and  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CPh})_2$  gave the corresponding amides in 40 and 20% yields, respectively, after heating for 24 h;  $\text{Ph}_4\text{SbO}_2\text{CMe}$  and  $\text{Sb}(\text{O}_2\text{CMe})_3$  gave  $\text{MeCONH}(\text{CH}_2)_5\text{Me}$  in only 16 and 15% yields, respectively, after 24 h. The interesting antimony compound  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CCH}_2\text{NHCOCH}_2\text{Ph})_2$  reacted with  $\text{Me}(\text{CH}_2)_5\text{NH}_2$  to give the corresponding amide in 82% yield after 5 h at 50°C. This result suggested that the reaction could be used in peptide syntheses.

Since it is well known that triphenylstibine oxide reacts with carboxylic acids to yield the corresponding dicarboxylates  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CR})_2$ , the authors then tried the oxide or  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CMe})_2$  as catalysts for the aminolysis of carboxylic acids. The acids used were  $\text{MeCO}_2\text{H}$ ,  $\text{PrCO}_2\text{H}$ , and  $\text{PhCO}_2\text{H}$ , and the amines were  $\text{Me}(\text{CH}_2)_5\text{NH}_2$ ,  $\text{PhCH}_2\text{NH}_2$ , cyclohexylamine, and  $\text{PhNH}_2$ . An excess of the amine was heated with the acid in the presence of small amounts of the antimony compound. The yields of amides obtained by this procedure were usually excellent. Thus,  $\text{MeCO}_2\text{H}$  and  $\text{Me}(\text{CH}_2)_5\text{NH}_2$  when heated at 100°C for 10 h in the presence of  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CMe})_2$  gave a 100% yield of  $\text{MeCONH}(\text{CH}_2)_5\text{Me}$ ; in the absence of  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CMe})_2$  under the same reaction conditions, the yield of amide was 15%. It was believed by the authors that the reaction between  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CR})_2$  and  $\text{R}'\text{NH}_2$  occurred in two steps:



The first step was very rapid, and the second step was slow. This conclusion was based on a study of the kinetics of the reaction between  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CMe})_2$  and  $\text{Me}(\text{CH}_2)_5\text{NH}_2$  at several different temperatures.

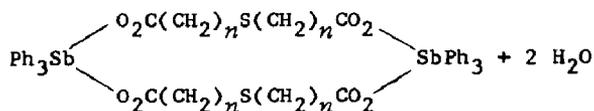
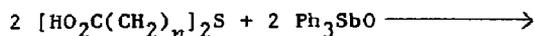
Nomura and coworkers [90] have found that when either thioglycollic or  $\beta$ -thiopropionic acid was heated with triphenylstibine oxide in benzene at  $80^\circ\text{C}$  for 6 h, macrocyclic 18- or 22-membered rings containing disulfide bonds were formed:



(where  $n$  was 1 or 2)

The same two compounds were formed when either of the two disulfides  $(\text{HO}_2\text{C}(\text{CH}_2)_n\text{S})_2$  (1 equivalent) was treated with 1 equivalent of the oxide at room temperature. Since Nomura and coworkers had shown in previous papers that the oxide would oxidize mercaptans to disulfides, and that small amounts would catalyze the oxidative coupling of mercaptans, it was presumed that the oxide first reacted with mercaptans to form antimony dimercaptides which then underwent reductive elimination to give  $(\text{HO}_2\text{C}(\text{CH}_2)_n\text{S})_2$ . It was also shown that  $\text{HO}_2\text{CCH}_2\text{CH}_2\text{SH}$  (10 mmol) in the presence of 1 mmol of the oxide gave  $(\text{HO}_2\text{CCH}_2\text{CH}_2\text{S})_2$  in 95% yield when heated for 2 h in benzene.

In addition to the above cyclic disulfides, the authors found that the sulfides  $[\text{HO}_2\text{C}(\text{CH}_2)_n]_2\text{S}$  would react with the oxide to give macrocyclic rings:



(where  $n$  was 1 or 2)

The two macrocyclic disulfides were characterized by IR and NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectrometry, elemental analyses, and molecular weight determinations.

However, no data were given for the corresponding sulfides.

The hydrolysis of triorganoantimony(V) compounds of the type  $R_3SbY_2$ , where Y is usually but not always halogen, may lead to the formation of compounds of the type  $(R_3SbY)_2O$ . Further hydrolysis usually leads to polymeric compounds of the type  $(R_3SbO)_n$ . No intermediate compounds between the two types of hydrolysis products have hitherto been described. Rüter and coworkers [91] have now described two compounds of the type  $Ph_3Sb(Y)OSbPh_3OSb(Y)Ph_3$ , where Y was 2,4-( $O_2N$ ) $_2C_6H_3SO_3$  or 2,4,6-( $O_2N$ ) $_3C_6H_2SO_3$ . The two compounds were prepared from  $(Ph_3SbO)_2$  and either 2,4-( $O_2N$ ) $_2C_6H_3SO_3H$  or 2,4,6-( $O_2N$ ) $_3C_6H_2SO_3H$  in acetone solution. 2,2-Dimethoxypropane was added as a water-trapping agent. They were obtained as yellow microcrystalline powders with mp's of 204-206°C and 202-206°C, respectively. The crystal structure of the compound  $Ph_3Sb(Y)OSbPh_3OSb(Y)Ph_3$  (Y = 2,4-( $O_2N$ ) $_2C_6H_3SO_3$ ) was determined by X-ray diffraction. The Sb-O-Sb angle was 140.8°, similar to that found in the  $(Ph_3SbY)_2O$  type of compound. Of particular interest were the terminal Sb-O distances in the Sb-O-Sb-O-Sb chain. Thus, the Sb-O distances of the middle Sb atom were 203.5 pm, which corresponded to a normal covalent bond distance in organoantimony(V) compounds. In the terminal Sb atoms, however, the Sb-O bond distance was 192.1 pm. The IR data suggested that the Sb-OSO $_2$ Ar bonds possessed considerable ionic character.

In a paper devoted largely to inorganic compounds of the type  $Sb(S_2CNR_2)_3$ , prepared from  $Sb_2O_3$  and dithiocarbamic acids, Nomura and coworkers [92] have included the reaction of  $PhSbO_3H_2$ ,  $(Ph_3SbO)_n$ , and  $Ph_4SbOH$  with the carbamic acid  $HS_2CNEt_2$ . The latter compound was prepared *in situ* from  $CS_2$  and  $HNEt_2$ . In the reaction of  $PhSbO_3H_2$ , the Sb was reduced to give  $PhSb(S_2CNEt_2)_2$ , a known compound. The Sb was also reduced in the reaction of  $(Ph_3SbO)_n$  with  $HS_2CNEt_2$  to give  $Ph_3Sb$  and the disulfide  $[Et_2NC(S)S]_2$ . By contrast  $Ph_4SbOH$  and  $HS_2CNEt_2$  gave the organoantimony(V) compound  $Ph_4SbS_2CNEt_2$ , but only in a small yield (30%). The two organoantimony compounds were characterized by elemental analyses, IR,  $^1H$ , and  $^{13}C$  NMR spectrometry.

Huber and coworkers [93] have oxidized  $Mes_3Sb$  (where Mes was 2,4,6-trimethylphenyl) in acetone solution with  $H_2O_2$  and obtained, not the corresponding oxide, but the dihydroxide  $Mes_3Sb(OH)_2$ . It was a microcrystalline powder, mp 202°C, and was characterized by elemental analyses, IR, and PMR spectrometry. The molecular weight, determined in  $CHCl_3$  solution, was 509 (calcd., 513). The band at 520  $cm^{-1}$  in the IR spectrum was assigned to  $\nu_{as}(Sb-O)$ , and the sharp band at 3650  $cm^{-1}$  to  $\nu(O-H)$ . Attempts to dehydrate this dihydroxide to obtain the oxide were unsuccessful.

The reaction of the dihydroxide with sulfonic acids  $R'SO_3H$  was quite different from the previously reported [94] reactions of antimony

dihydroxides, *e.g.*  $\text{Me}_3\text{Sb}(\text{OH})_2$ , or oxides, *e.g.*  $(\text{Ph}_3\text{SbO})_2$ , which reacted to give sulfonates of the types  $\text{R}_3\text{Sb}(\text{O}_3\text{SR}')_2$ ,  $\text{R}_3\text{Sb}(\text{OH})\text{O}_3\text{SR}'$ , or  $(\text{R}_3\text{SbO}_3\text{SR}')_2\text{O}$ . All attempts to convert trimesitylantimony dihydroxide into similar types of sulfonates were unsuccessful. When 1:1 molar ratios of this dihydroxide to  $\text{R}'\text{SO}_3\text{H}$  ( $\text{R}'$  was Ph or  $\text{CF}_3$ ) or a 1:2 molar ratio where  $\text{R}'$  was Ph was employed, complexes of the type  $\text{Mes}_3\text{SbO}^+\text{HO}_3\text{SR}'$  were obtained. The new compounds were characterized by IR and PMR spectrometry. They were soluble in MeOH and  $\text{CHCl}_3$ . Molecular weight determinations of the  $\text{PhSO}_3\text{H}$  complex in these two solvents indicated that the complex was monomolecular and undissociated in  $\text{CHCl}_3$  (mol. wt. found, 677; calcd., 653), but was largely dissociated in methanol (mol. wt. found, 346). Conductivity values in the same solvents were consistent with the molecular weight determinations. In the IR spectrum of the  $\text{PhSO}_3\text{H}$  complex, bands at 1235 and 1135  $\text{cm}^{-1}$  were assigned to  $\nu_{\text{as}} \text{SO}_3$  and a band at 1035  $\text{cm}^{-1}$  to  $\nu_{\text{s}} \text{SO}_3$ . Splitting of the asymmetric band was attributed to the ionic character of the bond between the O of the stibine oxide and the sulfonic acid; this was related to a partial transfer of a H from the sulfonic acid to the Sb-bonded O by formation of a strong hydrogen bond. The strong band at 2970  $\text{cm}^{-1}$  was within the range associated with short hydrogen bridges. The band at 690  $\text{cm}^{-1}$  was assigned to  $\nu \text{SbO}$ ; it was shifted by 5  $\text{cm}^{-1}$  to a lower wave number by deuteration. Similar assignments were made for the IR spectrum of  $\text{Mes}_3\text{SbO}^+\text{HO}_3\text{SCF}_3$ . An X-ray diffraction study of the complex  $\text{Mes}_3\text{SbO}^+\text{HO}_3\text{SPh}$  was also carried out. The geometry of the Sb atom was that of a distorted tetrahedron, with all of the C-Sb-C angles larger than and the O-Sb-C angles smaller than, the tetrahedral angle of 109.47°. The Sb-O distance of 189.4 pm was the shortest Sb-O distance recorded to date and suggested appreciable double bond character in the Sb-O bond. The O...O distance for the hydrogen bonded  $\text{PhSO}_2\text{O}-\text{H}^+\text{OSbMes}_3$  was also in the range associated with short O-H...O hydrogen bonds.

Although arsenic hydroxyhalides such as  $\text{Ph}_3\text{As}(\text{OH})\text{Cl}$  are known and the crystal structure of this compound has been determined, no structural data on similar Sb compounds have been published and the existence of such compounds has been questioned. Ferguson and coworkers [95] have now prepared and determined the crystal structure of an antimony hydroxyhalide,  $(2,6\text{-Me}_2\text{C}_6\text{H}_3)_3\text{Sb}(\text{OH})\text{I}$ . The compound was prepared by the hydrolysis of  $(2,6\text{-Me}_2\text{C}_6\text{H}_3)_3\text{SbI}_2$  in 10% aqueous methanol. It was obtained as orange plates, mp 214-216°C, and was characterized by elemental analyses and IR spectrometry. The geometry of the Sb atom was that of a distorted tetrahedron. The C-Sb-C angles were greater than tetrahedral (mean 115°) and the O-Sb-C angles were less than tetrahedral (97.4-106.9°). The O(H)...I distance was shorter than the sum of the van der Waals radii, and the Sb-O distance (1.907 Å) was significantly shorter than the Sb-O distance in  $\text{Ph}_4\text{SbOH}$  and was only 0.013 Å longer than the Sb-O distance reported for

$\text{Mes}_3\text{SbO}^+\text{HO}_3\text{SPh}$ , where considerable double bond character was ascribed to the Sb-O bond. All of the crystal structure data were in accord with a stibonium salt structure for the compound which also contained a hydrogen-bonded iodide ion,  $(2,6\text{-Me}_2\text{C}_6\text{H}_3)_3\text{Sb}^+\text{O-H}^-\text{I}^-$ . Further, the unequivocal location of the hydroxyl H at 0.91 Å from the O atom was in agreement with the salt-like character of the compound as opposed to a hydrogen-bonded adduct,  $(2,6\text{-Me}_2\text{C}_6\text{H}_3)_3\text{SbO}^+\text{HI}$ . The IR spectrum of the compound was also in agreement with the assigned structure. It contained a broad peak with a maximum at  $2940\text{ cm}^{-1}$ , and closely resembled the spectrum of the compound  $[\text{Ph}_3\text{AsOH}]\text{ClO}_4$ .

Nomura, Matsuda, and their coworkers have recently published a number of papers on the use of organoantimony compounds in organic synthesis. In particular, they have utilized organoantimony(V) compounds as catalysts for condensation reactions. In continuation of this work, Nomura and coworkers [96] have found that triphenylstibine oxide was a valuable catalyst for the condensation of diamines with  $\text{CO}_2$  to form cyclic urea compounds. For example, *N*-methylethylenediamine and  $\text{CO}_2$  in a steel autoclave at a pressure of  $50\text{ kg/cm}^2$  and a temperature of  $150^\circ\text{C}$  in the presence of  $\text{Ph}_3\text{SbO}$  and the molecular sieve MS-3A gave 1-methylimidazolidin-2-one in 85% yield. Similarly, *N*-methyl-1,3-propylenediamine gave the corresponding tetrahydropyrimidin-2-one. The triphenylstibine oxide used in this investigation was prepared by the method of Venezky and coworkers [97].

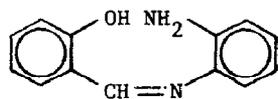
Several patents describing the industrial use of organoantimony(V) compounds have been recently issued. Triphenylstibine oxide has been used as a toner for the development of electrostatic images [98]. Compounds of the type  $\text{Ph}_2\text{Sb}(\text{O})(\text{CH}_2)_n\text{Sb}(\text{O})\text{Ph}_2$  (where  $n$  was 1, 3, 4, 5, or 6) and  $\text{Ph}_2\text{Sb}(\text{O})\text{C}_6\text{H}_4\text{Sb}(\text{O})\text{Ph}_2$  have been used as catalysts for the condensation of glycol esters of dicarboxylic acids [99]. Thus, terephthalic acid and  $\text{HOCH}_2\text{CH}_2\text{OH}$  with  $\text{Ph}_2\text{Sb}(\text{O})\text{CH}_2\text{Sb}(\text{O})\text{Ph}_2$  gave a colorless transparent polymer. Another patent [100] described the use of halogenated tetraarylstibonium compounds as toners for electrostatic image development.

Crystal structure studies on a number of molecules of the type  $(\text{Ph}_3\text{SbY})_2\text{O}$ , where Y was a negative group such as  $\text{PhSO}_3$ ,  $\text{CF}_3\text{SO}_3$ , Cl,  $\text{N}_3$ ,  $\text{HOCH}_2\text{CH}_2\text{SO}_3$ , and  $\text{Me}_3\text{COO}$ , have revealed that the Sb-O-Sb angle could be straight ( $180^\circ$ ) or bent. Tiekink [101] has now reported an X-ray diffraction study on the compound  $(\text{Ph}_3\text{SbCl})_2\text{O}$ , which was obtained as a benzene solvate. The crystal structure revealed that the molecule contained two unequal  $\text{Ph}_3\text{SbCl}$  groups connected by an oxygen, with the Sb-O-Sb angle equal to  $139.0^\circ$ . The geometry of the Sb atom was that of a trigonal bipyramid with axial O and Cl atoms. The Sb-Cl distances were not equal, 2.553 and 2.582 Å. This result suggested that the Sb-Cl bond was only partially covalent. The Sb-O distances, however, were nearly equal, 1.980 and 1.986 Å. The two Cl-Sb-O angles were  $177.0^\circ$  and  $174.0^\circ$ .

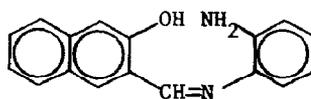
The crystal structure of the heterocyclic organoantimony(V) compound, 1,1-dichloro-1-methyl-1 $\lambda^5$ -stibacyclohexane, has been determined by Spek and coworkers [102]. The six-membered ring was in the chair conformation. The endocyclic C-Sb-C angle was 106.0°, the exocyclic C-Sb-C angle was 127.0°. The configuration of the Sb atom was a slightly distorted trigonal bipyramid. The distortion of the coordination polyhedron was of the non-Berry type. The two Cl atoms were in axial positions with a Cl-Sb-Cl angle of 176.65°. The Sb atom was exactly in the equatorial plane.

Although the crystal structures of two triphenylantimony dicarboxylates  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CR})_2$  (R = Me or Ph) have been determined, no molecular structure of a trialkylantimony dicarboxylate has hitherto been reported. Preut and coworkers [103] have now prepared trimethylbis(2-thenoato)antimony (by the reaction between  $\text{Me}_3\text{Sb}(\text{OH})_2$  and 2-thenoic acid in  $\text{CHCl}_3$  solution) and determined its crystal structure by X-ray diffraction. The molecule was a distorted trigonal bipyramid with the two carboxylate groups in axial positions. There were weak interactions between the carbonyl O atoms of the carboxyl groups and the Sb atom, but these interactions were less pronounced than were similar interactions in the two  $\text{Ph}_3\text{Sb}(\text{O}_2\text{CR})_2$  compounds. Thus, the Sb-O distances between the Sb atom and the carbonyl O atoms were somewhat longer, and one of the equatorial C-Sb-C angles deviated less from 120° in the trimethyl compound than in the two triphenyl compounds. There was no interaction between the Sb atom and the S atoms in the rings.

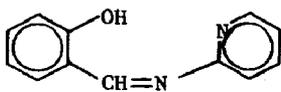
Schiff base complexes of the type  $\text{R}_3\text{Sb}(\text{Br})\text{L}$ , where R was Ph or Me and HL was a Schiff base, have been reported by Jha and Joshi [104]. The following Schiff bases were employed:



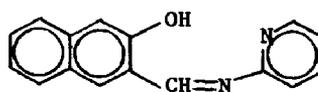
IV



V



VI

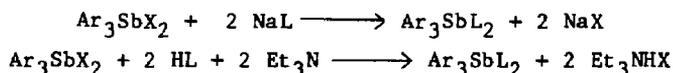


VII

The complexes were prepared by the reaction between  $\text{R}_3\text{SbBr}_2$  and the sodium salt of the Schiff base in refluxing benzene. They were characterized by elemental analyses and by IR and PMR spectra. The  $^{13}\text{C}$  NMR spectrum of the

complex formed from the Schiff base V and  $\text{Ph}_3\text{SbBr}_2$  was also obtained. Molecular weights of the complexes were determined cryoscopically in benzene; they were found to be non-dissociating monomers in this solvent. The structures assigned to the new compounds were based on the IR and NMR spectral results. The absence of an OH band in the IR spectra and the disappearance of the OH peak in the PMR spectra of the complexes (as compared with the free ligands) established that all of the complexes contained an Sb-O bond. In all four of the complexes obtained from the Schiff bases IV and V, it was believed that the Sb atom was heptacoordinate, *i.e.*, the ligands were tridentate with the O atom and both the amino and azomethine N atoms coordinated to the Sb atom. It was found that the methyl groups gave two signals with an intensity ratio of 1:2. A pentagonal bipyramid was suggested as the structure of the molecule with either one or two methyl groups in apical positions. By contrast, the spectral results of the complexes formed from the Schiff bases VI and VII were better accounted for by a structure in which the Sb atom was hexacoordinate, *i.e.*, the ligands were bidentate. IR results but no PMR results were given for the complexes formed from  $\text{Me}_3\text{SbBr}_2$  and VI or VII. It was proposed that the pyridine N did not coordinate with the Sb atom for steric reasons. Octahedral geometry was suggested for the configuration of the Sb atom.

Singhal and coworkers [105] have described the preparation of a number of organoantimony(V) compounds of the type  $\text{Ar}_3\text{SbL}_2$ , where Ar was 4- $\text{FC}_6\text{H}_4$  or 4- $\text{ClC}_6\text{H}_4$  and HL was a variety of compounds such as imides, oximes, and carboxylic acids. They were prepared from the corresponding dichloride or dibromide and either the sodium salt or the free ligand in the presence of  $\text{Et}_3\text{N}$ :

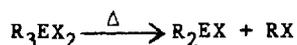


The resulting products possessed either Sb-N or Sb-O bonds. Those containing Sb-N bonds were derived from such compounds as phthalimide, benzimidazole, isatin, rhodanin, succinimide, imidazole, 2-methylimidazole, benzoxazolin-2-one, or benzthiazolin-2-thione. Those containing Sb-O bonds were derived from such compounds as the oximes of acetone, cyclohexanone, or acetophenone, and from 3-nitro-, 2-chloro-, or 4-aminobenzoic acids. The reactions were carried out at room temperature in benzene solution. The resulting compounds were stable crystalline solids, which were characterized by elementary analyses and IR spectroscopy. They were tested for antiviral, antibacterial, antifungal, and insecticidal activity.

The relative gas-phase ionization potentials of two organoarsenic(V) compounds ( $\text{Me}_3\text{AsCl}_2$  and  $\text{Me}_3\text{AsF}_2$ ) and three organoantimony(V) compounds

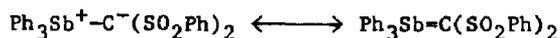
(Me<sub>3</sub>SbCl<sub>2</sub>, Me<sub>3</sub>SbF<sub>2</sub>, and Me<sub>4</sub>SbF) have been reported by Ebel and coworkers [106] from the He I and in part the He II photoelectron spectra of the gaseous molecules. Two different photoelectron spectrometers were used. The resolution was better than 25 meV for Me<sub>3</sub>AsCl<sub>2</sub>, Me<sub>3</sub>AsF<sub>2</sub>, and Me<sub>3</sub>SbCl<sub>2</sub> but only 40–50 meV for Me<sub>3</sub>SbF<sub>2</sub> and Me<sub>4</sub>SbF. The ionization potentials have an estimated accuracy of  $\pm 0.10$  eV for the first three compounds and  $\pm 0.15$  eV for the last two compounds. Assignments of the peaks of the photoelectron spectra were based on D<sub>3h</sub> symmetry for the compounds of type Me<sub>3</sub>EX<sub>2</sub> (where E was As or Sb) and C<sub>4v</sub> symmetry for Me<sub>4</sub>SbF and the use of the known ionization potentials of Me<sub>3</sub>E and Me<sub>5</sub>Sb as well as simple molecular orbital models.

In addition to the photoelectron spectra of these compounds, the gas-phase pyrolysis of Me<sub>3</sub>AsCl<sub>2</sub> and Me<sub>3</sub>SbCl<sub>2</sub> was studied by means of the photoelectron spectra of the pyrolysis products at several different temperatures. The pyrolysis of all five compounds (Me<sub>3</sub>EX<sub>2</sub>, where X was Cl or F, and Me<sub>4</sub>SbF) was studied by use of high temperature field ionization mass spectrometry. This latter investigation was undertaken in order to investigate the reductive elimination reaction:



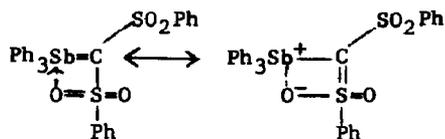
This reaction, at least for R<sub>3</sub>SbX<sub>2</sub>, is known to proceed with high yield where X is iodine but is less satisfactory as the halogen becomes more electronegative. It was concluded, based on both the photoelectron and mass spectrometry results, that the arsenic compounds were significantly more labile than the corresponding antimony compounds and that the chlorine compounds were more labile than the fluorine compounds. Loss of HX was observed for Me<sub>3</sub>AsCl<sub>2</sub>, Me<sub>3</sub>AsF<sub>2</sub>, and Me<sub>3</sub>SbCl<sub>2</sub> but not for Me<sub>3</sub>SbF<sub>2</sub>. This loss of HX occurred with formation of Me<sub>2</sub>ECH<sub>2</sub>X as detected in both the photoelectron and the mass spectra. For all four compounds, Me<sub>3</sub>E and Me<sub>2</sub>EX were formed in the pyrolysis. Finally, Me<sub>4</sub>SbF was pyrolyzed in the temperature range 1043–1404 K, and the only product observed was Me<sub>3</sub>Sb.

The first X-ray diffraction study of a stibonium ylide has been reported by Ferguson and coworkers [107]. The compound was triphenylstibonium bis(phenylsulfonyl)methylide hemi(chlorobenzene)solvate:



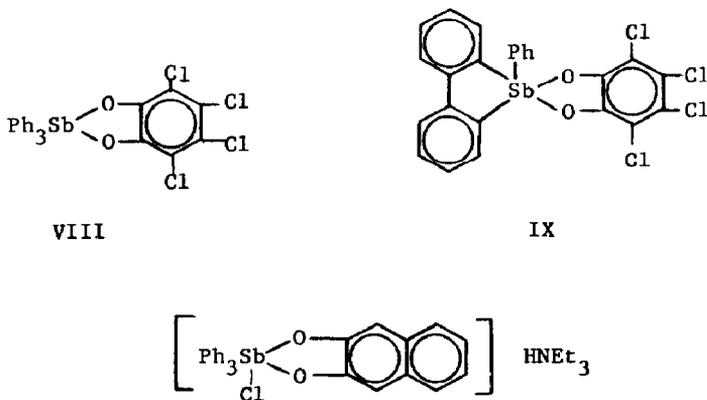
The configuration of the Sb atom lay between tetrahedral and trigonal-bipyramidal with one Sb...O distance shorter than the sum of the van der Waals radii, and one long S...O distance. The Sb-C distance was also short, and lay between the sums of the covalent radii for an Sb-C single

bond and an Sb-C double bond. The short Sb<sup>δ+</sup>O bond suggested that the compound was a resonance hybrid of the following two canonical forms, with the second form contributing considerably to the structure:



There were no close contacts between the solvate molecule and the stibonium compound.

The fact that the Sb atom in  $\text{Ph}_5\text{Sb}$  possesses square-pyramidal geometry rather than trigonal-bipyramidal geometry has been the subject of considerable speculation. It has been suggested that lattice stabilization is the cause of the unexpected geometry. Another Sb compound with square-pyramidal geometry is the partially hydrated compound  $[\text{Ph}_3\text{Sb}(\text{OEt})_2]_2\text{H}_2\text{O}$ , which contains both 5- and 6-coordinate Sb atoms in the crystal. In this case hydrogen bonding may act to stabilize the square-pyramidal 5-coordinate form. Compared to P and As, the geometry of 5-coordinate Sb compounds has not been studied extensively. Two new papers from Holmes's laboratory have added considerably to our knowledge of the geometry of organoantimony(V) compounds. In the first paper [108] the crystal structures of the following three compounds were reported:

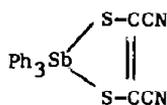


X

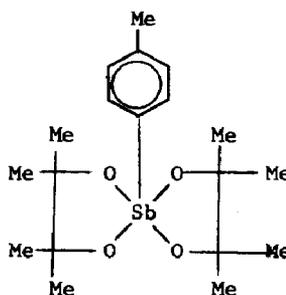
Compound VIII, a known compound, was prepared by the oxidative addition of 3,4,5,6-tetrachloro-1,2-benzoquinone to  $\text{Ph}_3\text{Sb}$ . X-ray diffraction studies revealed that the Sb atom was essentially trigonal-bipyramidal with one oxygen atom and one phenyl group in axial positions. The O-Sb-C angle involving the two axial substituents was  $163.0^\circ$ . Compound IX, prepared from 5-phenyldibenzostibole and the tetrachlorobenzoquinone, was

obtained as yellow crystals, mp 250–251°C. It was characterized by elemental analyses and PMR spectroscopy. The X-ray diffraction study, however, was not performed on this crystalline compound but on a solvated form,  $(C_6Cl_4O_2)(C_{12}H_8)SbPh \cdot 0.25PhH \cdot 0.25CH_2Cl_2$ . The unit cell contained one PhH molecule with  $C_2$  symmetry, and one  $CH_2Cl_2$  molecule, which was disordered about an inversion center in such a way that the Cl atoms were inversion related. There were two independent spirocyclic molecules. Both molecules were rectangular-pyramidal with the phenyl group in apical position. In one molecule the displacement from the bipyramidal toward the rectangular-pyramidal form was 88%; in the other molecule the displacement was 71.8%. The reaction between  $Ph_3SbCl_2$  and naphthalene-1,2-diol in the presence of  $Et_3N$  led unexpectedly to the formation of compound X containing 6-coordinate Sb. The Sb-Cl distance, however, was unusually long, and it was suggested that this was due in part to hydrogen bonding of the Cl to the hydrogen of the  $Et_3NH$  cation. The geometry of the Sb atom was essentially square-pyramidal with one Ph group in apical position, and with a sixth weak Sb-Cl bond.

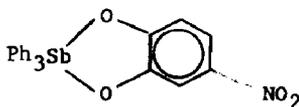
In the second paper from Holmes's laboratory [109] the preparation and crystal structures of three more heterocyclic organoantimony(V) compounds were reported:



XI

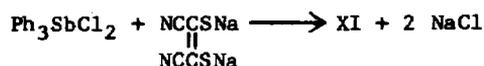


XII



XIII

Compound XI was prepared from  $Ph_3SbCl_2$  by the following procedure:



The compound, after recrystallization from  $CH_2Cl_2$ , was characterized by its PMR spectrum and by elemental analyses. An X-ray diffraction study revealed that the geometry of the Sb atom deviated to only a small degree from

trigonal-bipyramidal with one Ph group and one S atom in axial positions. The small deviations from trigonal-bipyramidal geometry were in the anti-Berry direction. The Sb-S (axial) bond was considerably longer than the Sb-S (equatorial) bond, but the differences between the Sb-C (axial) and Sb-C (equatorial) bond lengths were less pronounced. The spirocyclic compound XII was prepared by the reaction between 4-tolylstibonic acid and pinacol in 2,2-dimethoxypropane solution, and was recrystallized from  $\text{CH}_2\text{Cl}_2$  and Skelly B. It was characterized by its PMR spectrum and elemental analyses. The X-ray diffraction study of this compound revealed that the Sb atom was essentially bipyramidal with two O atoms in axial positions. The Sb-O (axial) bond lengths were considerably longer than the Sb-O (equatorial) bond lengths and the O-Sb-O angle for the two axial O atoms was  $169.4^\circ$ . The O-Sb-O angle for the two equatorial O atoms, however, was  $117^\circ$ , instead of  $120^\circ$  for the idealized trigonal-bipyramidal angle. This distortion was the opposite to that expected if the distortion was following the Berry coordinate, *i.e.*, trigonal bipyramid  $\rightarrow$  rectangular pyramid. The 4-tolyl group had essentially no effect on the geometry of this molecule, since the corresponding compound in which a phenyl group (rather than a 4-tolyl group) was in equatorial position had essentially the same geometry. This was in marked contrast to the two compounds  $(4\text{-MeC}_6\text{H}_4)_5\text{Sb}$ , which is a trigonal bipyramid, and  $\text{Ph}_5\text{Sb}$ , which is a square pyramid. Compound XIII was prepared by the addition of 4-nitrocatechol to  $\text{Ph}_3\text{SbCl}_2$  in benzene solution, followed by the addition of  $\text{Et}_3\text{N}$ . After recrystallization, it was characterized by its PMR spectrum. An X-ray diffraction study of this compound revealed that the geometry of the Sb atom was displaced 67.8% from trigonal-bipyramidal toward rectangular-pyramidal. This displacement, which was unusual for a monocyclic compound of this type, was attributed to the fact that the molecule existed in the solid state as weakly connected dimers. This dimerization acted to promote opening of one of the O-Sb-C angles from the normal angle of  $120^\circ$  to  $143.4^\circ$ .

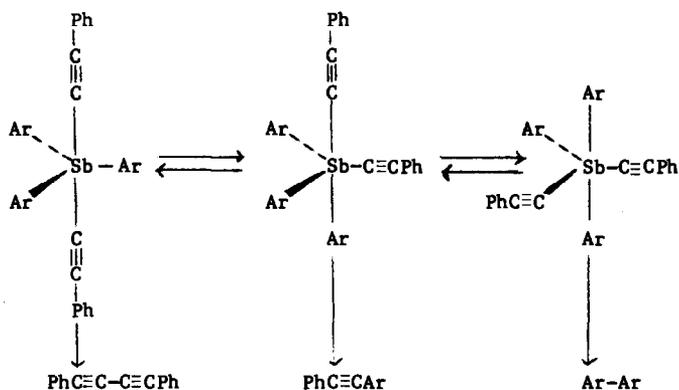
Having determined in these two papers the crystal structures of six heterocyclic organoantimony(V) compounds and having the crystal structures of three other cyclic and six acyclic organoantimony(V) compounds from results reported in the chemical literature, the authors were able to compare the effect of chemical structure on the distortion of the energetically more stable trigonal-bipyramidal geometry toward rectangular-pyramidal geometry and to compare these effects with those previously reported for pentacoordinate compounds of P, As, Si, Ge, and Sn. In general, it was concluded that the structural principles found for the 5-coordinate compounds of these elements applied to the organoantimony(V) compounds. Thus, the presence of two unsaturated ring systems produced compounds in which the Sb atom was essentially square-pyramidal, and distortions of bipyramidal geometry towards rectangular geometry followed the Berry coordi-

nate. With the limited number of organoantimony(V) compounds available, however, there was not a wide distribution of compounds intermediate between the two geometries, *i.e.* the compounds were either close to trigonal-bipyramidal or to square-pyramidal. With organoantimony(V) compounds, lattice effects seemed to be of much greater importance than with the other elements with 5-coordinate geometry. This fact may be attributed to the higher degree of stereochemical nonrigidity of the antimony compounds.

Akiba and coworkers [110] have prepared three organoantimony(V) compounds of the type  $\text{Ar}_3\text{Sb}(\text{C}\equiv\text{CPh})_2$ , where Ar was Ph, 4-MeC<sub>6</sub>H<sub>4</sub>, or 4-ClC<sub>6</sub>H<sub>4</sub>. They were synthesized in the following manner:



The resulting compounds were both thermally unstable and susceptible to atmospheric moisture. The compound where Ar was 4-ClC<sub>6</sub>H<sub>4</sub> was especially unstable and probably contained some LiBr as an impurity, but repeated recrystallization resulted in decomposition. All three compounds were characterized by PMR spectrometry. When heated to 110°C, they underwent reductive elimination with the production of organoantimony(III) compounds and ligand coupling products. Three types of coupling products were possible, PhC≡C-C≡CPh, PhC≡C-Ar, and Ar<sub>2</sub>. With all three compounds, two of these coupling products, PhC≡C-C≡CPh and PhC≡C-Ar, were always found, but no biaryls were produced. Where Ar was Ph or 4-MeC<sub>6</sub>H<sub>4</sub>, the total yield of coupling products approached 100% (99 and 93%, respectively). The ratio of PhC≡C-C≡CPh:PhC≡C-Ar was 76:24 where Ar was 4-MeC<sub>6</sub>H<sub>4</sub>, and 66:34 where Ar was Ph. With the compound (4-ClC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sb(C≡CPh)<sub>2</sub>, the total yield of coupling products was only 64% and the ratio of PhC≡C-C≡CPh:4-ClC<sub>6</sub>H<sub>4</sub>C≡CPh was 1:1. Since it was known from crystal structure studies that in the compound Me<sub>3</sub>Sb(C≡CMe)<sub>2</sub>, the two PhC≡C groups occupy axial positions, the authors assumed that the three new compounds had similar structures (at least in the solid state). They postulated also that elimination occurred only from the axial positions. To account for the two different elimination products they postulated the following equilibria:



These equilibria were shifted to the right in the order 4-MeC<sub>6</sub>H<sub>4</sub>, Ph, 4-ClC<sub>6</sub>H<sub>4</sub>, but no products from the structure where both C≡CPh groups were in equatorial positions were found.

Other work from Akiba's laboratory has found that dipropynyltrimethylantimony reacted with acid chlorides in the presence of catalytic amounts of the palladium compounds Pd(PPh<sub>3</sub>)<sub>4</sub> or PhCH<sub>2</sub>PdCl(PPh<sub>3</sub>)<sub>2</sub> to yield propynyl ketones, but not methyl ketones [111]. It was suggested that the first step of the reaction involved oxidative addition of the antimony compound to Pd(0) at the propynyl-antimony bond.

The conductivities of the pentaphenyl compounds Ph<sub>5</sub>E, where E was P, As, or Sb, have been determined in the solvents MeNO<sub>2</sub>, PrBr, Me<sub>2</sub>CO, DMF, and THF [112]. A plot of conductivity vs. the square root of concentration revealed that these compounds were weakly dissociated electrolytes. However, the conductivity of Ph<sub>5</sub>P was greater than the conductivities of Ph<sub>5</sub>As and Ph<sub>5</sub>Sb. The highest values of the conductivities were obtained in MeNO<sub>2</sub>, the lowest values in THF.

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