# ANTIMONY

## ANNUAL SURVEY COVERING THE YEAR 1971

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Although no review devoted solely to organoantimony compounds appeared in 1971, these substances have been included in a general survey of sigma-bonded organometallic compounds [1]. There have also been a number of articles and books in which certain aspects of organoantimony chemistry have been briefly examined. The subjects discussed in these publications included: thermochemistry [2], spectroscopic properties [3], preparative utility of redistribution reactions [4], preparation and properties of substances of the type $R_2SbM$ (where R was alkyl, cycloalkyl, or phenyl and M was Li or Na) [5], and the utilization of organoantimony compounds for the preparation of compounds containing Ge–Sb [6] and C–Te [7] bonds.

Matsumura and Okawara [8] have reported that the Ph–Sb bonds of bis(diphenylstibino)methane were readily cleaved by hydrogen chloride in chloroform:

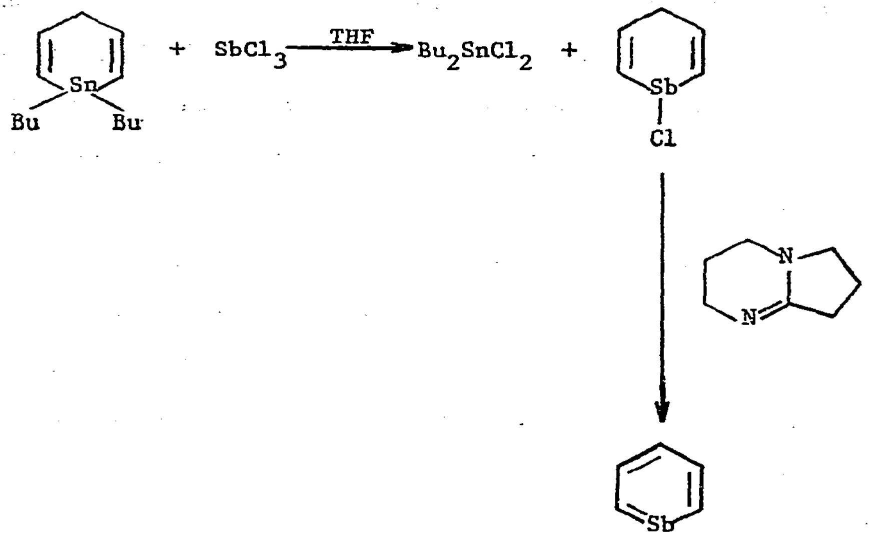
$$Ph_2SbCH_2SbPh_2 + 4HCl \longrightarrow Cl_2SbCH_2SbCl_2 + 4PhH$$

Bis(dichlorostibino)methane was found to be a colorless, crystalline compound, which was hydrolyzed easily to give the di-stiboso compound, $OSbCH_2SbO$. Treatment of bis(dichlorostibino)methane with Grignard reagents in the presence of *N,N,N',N'*-tetramethylethylenediamine yielded di-tertiary stibines:

$$Cl_2SbCH_2SbCl_2 + 4RMgX \longrightarrow R_2SbCH_2SbR_2 + 4MgClX$$

(where R was Me or Ph, and X was I or Br)

The preparation of stibabenzene (antimonin) has been achieved by Ashe [9], who earlier in 1971 described phospha- and arsabenzene. The following reaction scheme was employed:



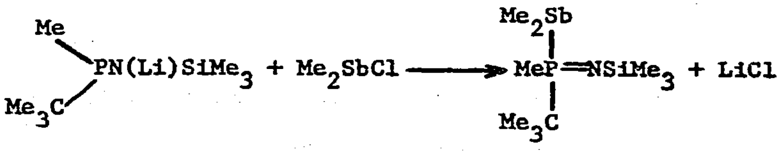
The chlorostibine obtained in the first step was apparently relatively stable. Thus, it could be obtained in pure form by recrystallization from heptane, and it melted with decomposition at 115-117°. In contrast, stibabenzene was extremely labile and rapidly polymerized at -80° to an intractable brown tar. Stibabenzene was most conveniently handled in dilute solution under an inert atmosphere, although even these solutions slowly precipitated the brown polymer. The PMR spectrum of stibabenzene exhibited a doublet at very low field ($\tau$ -0.7) and a multiplet in the normal aromatic region. The doublet ($J = 11$ Hz) was attributed to the $\alpha$ protons, and the multiplet to the $\beta$ and $\gamma$ protons. Ashe concluded that the chemical shift values were consistent with an appreciable ring current for stibabenzene. Like the mass spectra of its nitrogen, phosphorus, and arsenic analogs, the mass spectrum of stibabenzene showed the molecular ion as the base peak. In all four mass spectra (as well as that of benzene), the molecular ion exhibited significant fragmentation by loss of acetylene. The mass spectrum of stibabenzene was distinctive, however, in showing large peaks for $Sb^+$ and for the $C_5H_5^+$ fragment formed by loss of the metal atom. The UV spectrum of stibabenzene had intense peaks at 236 and 312 nm. The molar absorptivities for these bands were approximately $10^4$, but the facile polymerization of this compound made an exact determination difficult. Similar intense bands at lower wavelengths had previously been noted for phospha- and arsabenzene.

Leebrick and Remes [10] have patented alkoxides and mercaptides of the types $RSb(OR)_2$, $R_2SbOR$, $RSb(SR)_2$, and $R_2SbSR$. The alkoxides were prepared by the reaction of a halo- or dihalostibine with an alcohol in the presence of a base (usually ammonia). For example, *n*-butoxydiphenylstibine was obtained by the following reaction:

$$Ph_2SbCl + BuOH + NH_3 \longrightarrow Ph_2SbOBu + NH_4Cl$$

The mercaptides were prepared by the reaction of a halo- or dihalostibine with an alkali metal salt of a mercaptan or by the interaction of a bis-(diarylantimony) or bis(dialkylantimony) oxide and a mercaptan. It was claimed that the patented compounds were useful as fungicides and bactericides.

Scherer and Gick [11] have described a number of organometallic derivatives of phosphine imides. An organoantimony compound included in this study was prepared by means of the following reaction:



$$(Me)(Me_3C)PN(Li)SiMe_3 + Me_2SbCl \longrightarrow MeP(SbMe_2)(CMe_3){=}NSiMe_3 + LiCl$$

The product was studied by means of PMR and IR spectroscopy.

Koketsu and co-workers [12] have found that dimethylaminodimethylstibine readily added to organic isocyanates or isothiocyanates:

$$Me_2SbNMe_2 + RNCO \longrightarrow RN(SbMe_2)CONMe_2$$

(where R was Me, Et, $Me_3C$, or Ph)

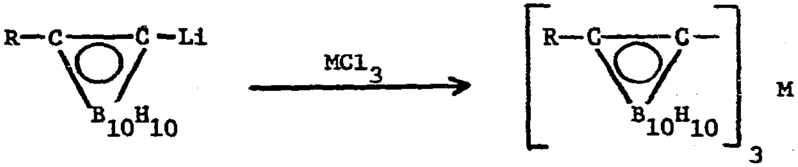
$$Me_2SbNMe_2 + RNCS \longrightarrow RN(SbMe_2)CSNMe_2$$

(where R was Me or Ph)

The reactions took place exothermally in ether at room temperature. The structure of the addition products was established by IR and PMR data as well as elemental analysis. Most of the compounds were very hygroscopic liquids, which decomposed on exposure to air to give white solids. Hydrolysis of the addition products with dilute hydrochloric acid yielded the corresponding trisubstituted urea or thiourea. The dimethylaminodimethylstibine used in this study was prepared by the interaction of equimolar amounts of dimethylchlorostibine and the lithium salt of dimethylamine:

$$Me_2SbCl + LiNMe_2 \longrightarrow Me_2SbNMe_2 + LiCl$$

Bregadze and co-workers [13] have reported that the reaction of methyl- or phenylcarboranyllithium with antimony or bismuth trichloride gave tris(methylcarboranyl)stibine, tris(phenylcarboranyl)stibine, or tris-(phenylcarboranyl)bismuthine:



(where R was Me or Ph and M was Sb or Bi)

The stibines and bismuthine were resistant to oxygen, sulfur, hydrogen peroxide, hydrogen chloride, and sulfuric acid; and they did not form stable complexes with pyridine or α,α'-dipyridyl. Attempted bromination of tris(phenylcarboranyl)stibine with bromine in chloroform led largely to recovery of the unchanged stibine; when bromine and aluminum chloride in carbon tetrachloride were used, there was considerable C-Sb bond cleavage.

Azerbaev and co-workers [14] have prepared several tertiary stibines of the type $MeCR(OR')C{\equiv}CSbPh_2$ (where R was Me or Et and R' was Me, Et, or Ac) by the reaction of the corresponding terminal alkynes $MeCR(OR')C{\equiv}CH$ with ethylmagnesium bromide, treatment of the resulting reaction mixture with diphenylchlorostibine, and subsequent hydrolysis. The same method was used in a second paper [15] to obtain other acetylenic stibines of the type $RC{\equiv}CSbPh_2$, where R was Ph, $CH_2OH$, PrMeC(OH), 1-hydroxycyclopentyl, or 1-hydroxycyclohexyl. The stibines described in both papers were air-sensitive and thermally unstable but could be converted to the corresponding antimony(V) dichlorides, dibromides, and diiodides.

Davies and Hook [16] have studied the reactions of tertiary stibines and bismuthines with *tert*-butyl hydroperoxide and with molecular oxygen. The hydroperoxide reacted vigorously with the stibines and gave good yields of the corresponding stibine oxides:

$$R_3Sb + Me_3COOH \longrightarrow R_3SbO + Me_3COH$$

(where R was Me or Et)

This reaction was not accompanied by C-Sb bond cleavage. The stibine oxides were converted by excess hydroperoxide into pentacoordinate derivatives of antimony:

$$R_3SbO + 2Me_3COOH \longrightarrow R_3Sb(OOCMe_3)_2 + H_2O$$

The reaction of tertiary stibines with molecular oxygen appeared to be rather complex. Thus, trimethylstibine and dimethylphenylstibine reacted with oxygen to yield methanol and white, water-soluble peroxidic solids. The autoxidation of triethylstibine and diethylphenylstibine yielded similar solids; triethylstibine also gave ethanol and acetaldehyde, while ethanol was the only volatile product isolated from the oxidation of diethylphenylstibine. Since free radical traps such as phenothiazine and galvinoxyl inhibited the autoxidations, it was concluded that these reactions proceeded by a radical chain mechanism. The autoxidation of dimethylbromostibine and diethylbromostibine was also included in this study. The dimethyl compound absorbed 0.48 mole of oxygen per mole of substrate, while the diethyl compound absorbed 0.65 mole of oxygen; in the latter case some cleavage of the C-Sb bond was noted, and ethanol and acetaldehyde were obtained. These oxidations also appeared to follow a homolytic chain process, in which the bromostibines were converted to compounds of type $R_2Sb(O)Br$ (where R was Me or Et).

Davies and co-workers [17] have also investigated the reaction of triethylstibine with the *tert*-butoxy radical formed either by the photolysis of di-*tert*-butyl peroxide or the thermolysis of di-*tert*-butyl hyponitrite at 80°. These radicals, which were generated in the cavity of an ESR generator, induced an $S_H2$ reaction at the antimony and yielded ethyl radicals:

$$Me_3CO\cdot + Et_3Sb \longrightarrow Me_3COSbEt_2 + Et\cdot$$

Analogous reactions with triethylarsine and triethylbismuthine are mentioned under Arsenic and Bismuth, respectively.

The flash photolysis of trimethylstibine in argon has been found to produce excited antimony atoms, $Sb_2$, Me, and several unidentified species [18]. No additional species were detected when the photolysis was carried out in the presence of hydrogen, methane, ethylene, carbon monoxide, or carbon dioxide. The failure to observe SbH in the presence of hydrogen or the hydrocarbons was considered surprising. The UV absorption spectrum of trimethylstibine consisted of a continuum between 210 and 240 nm with a maximum at 225 nm ($\varepsilon$, $1 \times 10^4$).

Cullen and co-workers [19] have reported that the UV absorption spectrum of tri-1-propynylstibine, $(MeC{\equiv}C)_3Sb$, in heptane exhibited maxima at 229.0 nm ($\varepsilon$, 9100) and 243.2 nm ($\varepsilon$, 9100), which were attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively.

Jacobus [20] has studied the barrier to pyramidal inversion in diisopropyl-*p*-tolylstibine by means of PMR spectroscopy. The tertiary stibine was prepared by the interaction of isopropylmagnesium bromide and *p*-tolyldichlorostibine:

$$p\text{-}MeC_6H_4SbCl_2 + 2Me_2CHMgBr \longrightarrow p\text{-}MeC_6H_4Sb(CHMe_2)_2 + 2MgClBr$$

The expected diastereotopicity of the isopropyl methyl groups was observed in the PMR spectrum of the stibine dissolved in deuterated chloroform or in 1-methylnaphthalene. In the latter solvent, the resonances of these groups consisted of two doublets ($J = 6$ Hz) with a chemical shift difference of 0.06 ppm. These resonances did not coalesce at temperatures up to 200°; in fact, no evidence of even the beginning of collapse was noted. It was concluded from this result that the barrier to inversion was greater that 26 kcal/mole.

The *meta* and *para* isomers of tris(fluorophenyl)- and tris(chlorophenyl)-stibine have been prepared via the Grignard reaction, and their magnetic resonance spectra have been recorded [21]. The PMR spectrum of tris(*p*-fluorophenyl)stibine was in agreement with the theoretical pattern required for an AA'XX' system and permitted the determination of the chemical shifts and coupling constants of the aromatic protons. The $^{19}F$ NMR spectrum consisted of the expected triplet of triplets and also yielded chemical shift and coupling constant data. The PMR spectrum of tris(*p*-chlorophenyl)-stibine consisted of a single peak at $\delta$ 7.26; the lack of fine structure was attributed to the decoupling effect of the $^{123}Sb$ NQR resonance at 92.20 MHz. The PMR spectra of the *meta* -substituted compounds were very complex; chemical shifts and coupling constants of the individual protons were not determined. A tentative analysis of the $^{19}F$ NMR spectrum of tris(*m*-fluorophenyl)stibine could, however, be made.

Smit and Dijkstra [22] have calculated the fundamental stretching and bending frequencies of triethynylstibine from an estimate of the force constants and apex angle of the $SbC_3$ pyramid. They concluded that the frequencies of the $A_1$- and $E$-type carbon-antimony stretching modes coincided at 474 $cm^{-1}$, a value near to the 477 $cm^{-1}$ band assigned as the $A_1$-type by Miller and Lemmon [23]. The $A_1$- and $E$-type $SbC_3$ bending modes were calculated to be 88 $cm^{-1}$ and 81 $cm^{-1}$, respectively.

IR spectroscopy has been used to investigate the hydrogen bonds formed in carbon tetrachloride solutions of phenol and triphenylamine, -phosphine, -arsine, or -stibine [24]. As the heteroatom was varied, the energy of the hydrogen-bonded complexes decreased in the order: $P > Sb \sim As > N$.

Brodersen and co-workers [25] have prepared methyldiphenylstibine by the following sequence of reactions:

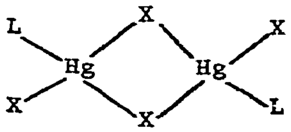
$$3MeMgI + SbCl_3 \longrightarrow Me_3Sb + 3MgClI$$

$$Me_3Sb + I_2 \longrightarrow Me_3SbI_2 \xrightarrow[50\ Torr]{100^\circ} Me_2SbI + MeI$$

$$Me_2SbI + I_2 \longrightarrow Me_2SbI_3 \xrightarrow{20^\circ} MeSbI_2 + MeI$$

$$MeSbI_2 + 2PhMgBr \longrightarrow MePh_2Sb + 2MgBrI$$

The tertiary stibine thus obtained was a colorless solid which melted at about 30°. Treatment of acetone or methanol solutions of the stibine with mercuric halides yielded dimeric, halogen-bridged complexes of the following type:



(where L was $MePh_2Sb$ and X was Cl, Br, or I)

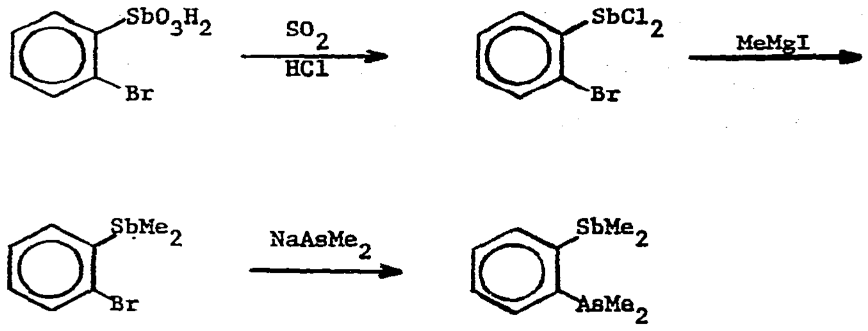
Although it has been found possible to prepare a variety of adducts of tin(IV) chloride and bromide with nitriles, amines, phosphines, and arsines, attempts to obtain adducts with triphenylstibine resulted in reduction to divalent tin [26]. The following reaction was suggested:

$$Ph_3Sb + SnX_4 \longrightarrow Ph_3SbX_2 + SnX_2$$

(where X was Cl or Br)

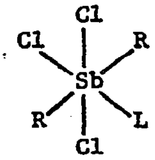
There were numerous papers published that described the use of tertiary stibines as ligands in transition metal complexes. The metals coordinated to the antimony in these complexes included chromium [27-29], cobalt [30, 31], copper [32, 33], gold [34], iridium [35, 36], iron [37-39], molybdenum [27-29], nickel [40-45], osmium [46], palladium [47, 48], platinum [47-51], rhodium [35, 52], ruthenium [53-57], tungsten [27-29, 58], and vanadium [59].

Little work on stibonic acids was published in 1971. *o*-Bromobenzenestibonic acid was used for the preparation of a chelating arsenic-antimony ligand [44]. The following reaction sequence was employed:



Gill [60] has reported that captostibone (*o*-carboxymethylthiobenzenestibonic acid) was effective in the treatment of experimental *Trypanosoma evansi* infections of rodents. The chemotherapeutic index of the drug in mice was 3.4, which was higher than that of two other antimonials used in the treatment of surra (a disease caused by *T. evansi* and occurring in horses, cattle, and other domestic animals).

Nishii, Matsumura, and Okawara [61] have described the preparation and spectral properties of adducts of the type $R_2SbCl_3L$, where R was Me, Et, or Ph and L was one of the following oxygen donors: dimethyl sulfoxide (DMSO), hexamethylphosphoric triamide (HMPA), triphenylphosphine oxide (TPPO), and pyridine N-oxide (PyO). Similar adducts of antimony pentachloride and these oxygen donors were prepared for comparison. With the exception of $Ph_2SbCl_3 \cdot HMPA$, which was not sufficiently soluble in nitrobenzene, all of the adducts gave normal cryoscopic molecular weights in this solvent. This result immediately suggested the presence of hexacoordinated antimony. In all the adducts, the frequency of the S-O, P-O, or N-O stretching vibration was appreciably lower than the corresponding frequency in the free ligand. A strong band due to the Sb-O mode was observed in the DMSO and PyO complexes; in the other adducts the Sb-O frequency was obscured by the presence of strong ligand bands. The frequency shift of the S-O, P-O, or N-O vibration was found to increase with the acid strength of the acceptor, *i.e.*, in the order $SbCl_5 > Ph_2SbCl_3 > Et_2SbCl_3 \simeq Me_2SbCl_3$. The PMR and far IR spectra of the adducts were consistent with the following octahedral arrangement:



It was assumed that the barriers to intramolecular rearrangement in these complexes was relatively high and that, therefore, rapid pseudorotation of the groups attached to the antimony was not occurring.

Goel and Ridley [62] have prepared trimethyl- and triphenylantimony diazides, diisocyanates, and diisothiocyanates by the metathetical reaction between the corresponding organoantimony dichloride or dibromide and the appropriate silver or sodium pseudohalide. The compounds were white crystalline solids, which were shown by conductivity measurements to behave as molecular species in acetonitrile or nitromethane. Molecular weight measurements in benzene solution showed that the compounds were monomeric. The diazides and diisocyanates were extremely sensitive towards hydrolysis, and stringent precautions to exclude moisture were required during the preparation of these compounds. Hydrolysis of the organoantimony pseudohalides yielded compounds containing Sb-O-Sb bonds:

$$2R_3SbX_2 + H_2O \longrightarrow (R_3SbX)_2O + 2HX$$

(where R was Me or Ph and X was $N_3$, NCO, or NCS)

The IR spectra of all twelve compounds indicated that they possessed trigonal-bipyramidal coordination around the antimony. The presence of Sb-N linkages in the diisocyanates and diisothiocyanates was also deduced from the IR spectra.

The structure of oxybis(triphenylantimony) diazide, prepared as described in the above paragraph, was elucidated by means of X-ray crystallography [63]. The Sb-O-Sb angle (139.8°) was much larger than tetrahedral as a consequence of phenyl----phenyl interaction between the two halves of the molecule. Each antimony atom was in a slightly distorted trigonal-bipyramidal environment with the bridging oxygen at one apex and the azide group at the other. The O-Sb-N and N-N-N bond angles were, as expected, nearly linear. The structure of oxybis(triphenylantimony) diperchlorate, which could not be obtained in satisfactory form for X-ray analysis, was investigated by means of IR. It was concluded that this compound had a structure analogous to that of the diazide. A dihydrate of oxybis(triphenylantimony) diperchlorate was also studied by IR and appeared to contain ionic perchlorate groups and (presumably) tetrahedrally coordinated antimony.

Goel and co-workers [64] have reported a detailed study of the far IR and laser-Raman spectra of fourteen compounds of the type $R_3SbX_2$ (where R was Me or Ph and X was F, Cl, Br, NCS, $ONO_2$, $O_2CMe$, or $O_2CCD_3$). Particular emphasis was placed on making assignments for the Sb-C and Sb-X stretching vibrations. The asymmetric Sb-Me stretching frequency appeared in both the IR and Raman spectra at *ca.* 570-590 $cm^{-1}$. As expected for $D_{3h}$ skeletal symmetry, the symmetric Sb-Me mode was only Raman active; it was observed as a very strong band between 550 $cm^{-1}$ and 525 $cm^{-1}$. It was concluded from these results that the three methyl carbon atoms and the antimony atom were coplanar. The Sb-O asymmetric stretching mode of trimethylantimony diacetate appeared as a very strong IR band at 279 $cm^{-1}$ and was shifted to 268 $cm^{-1}$ upon deuteration of the acetate groups. The corresponding Sb-O band of triphenylantimony diacetate was observed in the IR at 288 $cm^{-1}$ and was shifted to 277 $cm^{-1}$ in the deuterated compound. The other Sb-X frequencies in this series of compounds ranged from 161 $cm^{-1}$ (for the Sb-Br symmetric stretch in triphenylantimony dibromide) to 509 $cm^{-1}$ (for the Sb-F asymmetric stretch in triphenylantimony difluoride).

Woods and Long [65] have carefully examined the vibrational spectra of trimethylantimony dichloride, trimethylantimony dibromide, and their fully deuterated analogs. IR and laser-Raman spectra were determined between 600 and 33 $cm^{-1}$, and assignments of the skeletal modes were made on the basis of a $D_{3h}$ model. The asymmetric Sb-Me stretching frequency appeared in the Raman at 571 $cm^{-1}$ for trimethylantimony dichloride and at 565 $cm^{-1}$ for the dibromide; similar values for these vibrations had earlier been noted in the IR. The symmetric Sb-Me stretching vibration, which was active only in the Raman, was observed at 522 $cm^{-1}$ for the dichloride and at 514 $cm^{-1}$ for the dibromide. The vibrational spectra of the deuterated compounds gave corresponding bands at 526 and 479 $cm^{-1}$ for the dichloride and at 521 and 473 $cm^{-1}$ for the dibromide. The results obtained with the deuterated compounds helped to confirm the indicated assignments, since the ratios of the frequencies of the methyl compounds to those of the deuterated compounds were in good agreement with the theoretical ratio calculated on the basis of an increase in mass of the methyl group from 15 to 18. Using Wilson's *FG* matrix method and considering the methyl groups as point masses, Woods and Long [65] carried out normal coordinate analyses on trimethylantimony dichloride and dibromide. Sets of valence force constants were obtained which gave almost perfect agreement between observed and calculated frequencies. In addition, sets of valence force constants for antimony pentachloride and pentamethylantimony were calculated from data in the literature. Comparison of the force constants for antimony pentachloride and trimethylantimony dichloride showed that the methyl groups weakened the axial Sb-Cl bonds. The equatorial Sb-C stretching force constants decreased in the order $Me_3SbCl_2 > Me_2SbBr_2 > Me_5Sb$. Similar conclusions have also been reached by Goel and co-workers [64].

Brill and Hugus [66] have obtained NQR data for trimethylantimony dichloride, trimethylantimony dibromide, and their fully deuterated analogs in order to analyze hydrogen-deuterium isotope effects in NQR spectroscopy. They found that the $^{123}$Sb nuclear quadrupole coupling constant increased about 0.5% upon deuteration. In contrast, the $^{35}$Cl and $^{79}$Br coupling constants were slightly lower in the deuterated compounds. It was suggested that these results could be explained by consideration of the difference in the vibrational amplitude of the H and D atoms.

Although earlier work had specified the use of mercuric chloride, Nesmeyanov and Borisov [67] have reported the addition of antimony pentachloride to acetylene in the absence of any catalyst:

$$3CH\equiv CH + SbCl_5 \longrightarrow (CHCl{=}CH)_3SbCl_2$$

The reaction product was purified by vacuum distillation and was found by PMR analysis to be a mixture of geometrical isomers. The pure *trans-trans-trans* isomer was obtained by recrystallization of the mixture from alcohol.

Borisov and co-workers [68] have examined the IR spectra of tris-(2-chlorovinyl)stibine, tris(2-chlorovinyl)antimony dichloride, tris(2-chlorovinyl)antimony dibromide, and a number of related organometallic compounds. Although provisional olefinic band assignments could be made, it was found that the *cis* and *trans* isomers did not differ enough in their olefinic frequencies to allow a differentiation between the geometrical isomers.

Several organoantimony glycolates and thioglycolates have been prepared by the interaction of organoantimony dialkoxides and glycolic or thioglycolic acid [69]:

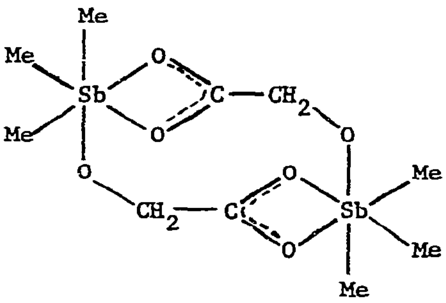
$$R_3Sb(OR')_2 + HXCH_2CO_2H \longrightarrow R_3Sb(XCH_2CO_2) + 2R'OH$$

(where R was Me, cyclohexyl, or Ph, R' was Me or Et, and X was O or S)

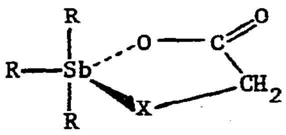
The dialkoxides required for these synthesis were obtained by the reaction of the corresponding dibromides with sodium alkoxides:

$$R_3SbBr_2 + 2NaOR' \longrightarrow R_3Sb(OR')_2 + 2NaBr$$

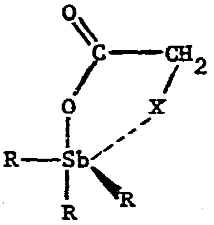
With the exception of trimethylantimony thioglycolate, which appeared to decompose readily, the structure of the glycolates and thioglycolates were deduced from their molecular weights (in chloroform) and their IR and PMR spectra. The results obtained with trimethylantimony glycolate indicated that a monomer-dimer equilibrium existed in chloroform solution at room temperature; at concentrations above 1.5%, the dimer predominated. Below about -15°, only the dimer was observed over a wide concentration range. The following structure was proposed for the dimeric species:



The tricyclohexylantimony and triphenylantimony glycolates and thioglycolates were clearly monomeric in chloroform, and their IR spectra in chloroform suggested that the carboxylate groups were attached to the antimony atom by an ester-like linkage:



or



In the solid state, the IR spectrum (and presumably the structure) of triphenylantimony thioglycolate was similar to that in solution. In contrast, the solid state spectra of the other triphenylantimony and tricyclohexylantimony compounds indicated that the carbonyl groups were coordinated to the antimony atoms. It was suggested that these compounds in the solid state were derivatives of hexa-coordinated antimony comparable to the dimeric form of trimethylantimony glycolate.

Okawara and co-workers [70] have prepared 4:1 complexes of trimethylstibine sulfide with cobalt(II), zinc(II), and cadmium(II) nitrate. With trimethylstibine sulfide and cobalt(II) nitrate, the authors also obtained a 2:1 complex. The IR spectra of all of the complexes indicated that the ligand coordinated to the metal through the sulfur atom. In the solid state, the IR spectrum of $(Me_3SbS)_2Co(NO_3)_2$ suggested that the compound was a molecular species containing bidentate nitrato groups and six-coordinate cobalt. The 4:1 complexes, in contrast, appeared to have uncoordinated nitrate anions in the solid state and thus to contain cations of the type $[M(SSbMe_3)_4]^{2+}$, where M was Co, Zn, or Cd. The electronic spectrum of the 4:1 complex of cobalt indicated a tetrahedral arrangement of the four ligands around the transition metal ion. In methylene chloride solution, the IR and electronic spectra of the 2:1 complex were similar to the corresponding solid state spectra; hence the structure of this compound was probably essentially the same in both phases. This conclusion was consistent with the low electrical conductivity of the 2:1 complex in methylene chloride and in nitromethane. On the other hand, spectral and conductivity data suggested that the 4:1 complexes dissociated in solution to yield 2:1 complexes and free ligand:

$$(Me_3SbS)_4M(NO_3)_2 \rightleftharpoons (Me_3SbS)_2M(NO_3)_2 + 2Me_3SbS$$

The above reaction appeared to go completely in methylene chloride and to a moderate extent in nitromethane.

Gavrilenko and co-workers [71] have prepared several complex stibonium salts by the following metathetical reactions carried out in toluene:

$$Me_4SbI + NaAlEt_4 \longrightarrow [Me_4Sb][AlEt_4] + NaI$$

$$Et_4SbI + NaAlEt_4 \longrightarrow [Et_4Sb][AlEt_4] + NaI$$

$$Et_4SbI + NaAlEt_2H_2 \longrightarrow [Et_4Sb][AlEt_2H_2] + NaI$$

These reactions were accelerated by the addition of small amounts (3-5 mole %) of triethylaluminum. This catalytic effect was apparently due to the conversion of the slightly soluble tetraalkylantimony iodide into a soluble complex of the type $[R_4Sb][AlEt_3I]$. The following sequence of reactions was proposed:

$$R_4SbI + Et_3Al \longrightarrow [R_4Sb][AlEt_3I]$$

$$[R_4Sb][AlEt_3I] + NaAlEt_4 \longrightarrow [R_4Sb][AlEt_4] + NaAlEt_3I$$

$$NaAlEt_3I \longrightarrow NaI + Et_3Al$$

In the absence of solvent, a complex stibonium salt was actually obtained via the interaction of a tetraalkylantimony iodide and triethylaluminum:

$$Me_4SbI + Et_3Al \longrightarrow [Me_4Sb][Et_3AlI]$$

Attempts to prepare complexes of the type $[R_4Sb][AlH_4]$ were unsuccessful. It was suggested that they were either too soluble or they readily underwent decomposition to tertiary stibines.

The laser-Raman spectra of tetraphenylantimony hydroxide, fluoride, chloride, bromide, sulfate, and perchlorate have been studied with a view to differentiating tetracoordinated species from those that are pentacoordinated [72]. Structural conclusions were based largely on the low-frequency ("X-sensitive") region of the spectrum. It was concluded that the perchlorate was a four-coordinate derivative of antimony, but the other compounds appeared to be five-coordinate and probably trigonal-bipyramidal in the solid state. In methanol solution, the fluoride continued to behave as the molecular species $Ph_4SbF$, but the other compounds were four-coordinate. The Raman spectrum of an aqueous solution of tetraphenylantimony chloride suggested the presence of the five-coordinate $Ph_4SbOH_2^+$ cation.

Williams and McKinney [73] have examined the electrochemical behavior of buffered solutions of tetraphenylantimony bromide at uncoated and mercury-coated carbon electrodes. Product analysis studies with the uncoated electrodes suggested a one-step reduction process:

$$Ph_4Sb^+ + H^+ + 2e^- \longrightarrow Ph_3Sb + PhH$$

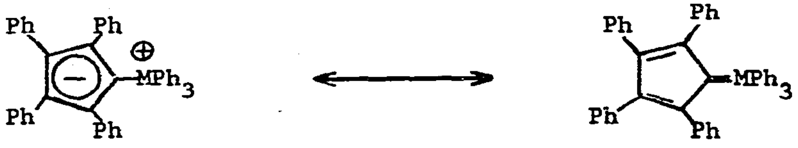
Two one-electron reduction steps were noted with the mercury-coated electrodes, and it was shown that mercury was intimately involved in the reactions. Triphenylstibine and diphenylmercury were isolated from large scale, controlled-potential reductions with the mercury-coated electrodes.

There have been several papers on the use of organoantimony compounds as analytical reagents for the determination of microgram quantities of fluoride. Carmichael and Whitley [74] developed a rapid method for separating fluoride from aqueous solution by the addition of tetraphenylantimony sulfate and extraction of the resulting tetraphenylantimony fluoride into chloroform. The fluorine present in the organic layer was determined by isotope dilution with $^{18}F$. Other halides interfered with the extraction, but sulfate and phosphate did not. Jean [75] described a similar analytical method in which the tetraphenylantimony fluoride was extracted with hexane-chloroform (40:25) and the quantity extracted was measured by UV spectrometry. The maximum was near 264 nm (ε, about $3.2 \times 10^3$). Three or four successive extractions were necessary for a quantitative separation. A detailed study of the extraction of tetraphenylstibonium fluoride by organic solvents has been made with the aid of $^{18}F$ and $^{124}Sb$ labelling [76]. The tagged antimony compounds were prepared via the following reaction:

$$PhBr + Ph_3\,{}^{124}Sb \xrightarrow{AlCl_3} Ph_4\,{}^{124}SbBr$$

Treatment of the bromide with aqueous base yielded tetraphenylantimony hydroxide, which could be easily converted to other tetraphenylantimony compounds by reaction with acids. The stability constant of tetraphenylantimony fluoride in water was found to be $3.6 \times 10^3$. It was also shown that many ions interfered with the extraction process. The use of triphenylantimony dichloride for the extraction of fluoride from aqueous solution has been proposed in a preliminary communication [77]. This compound appeared to convert the fluoride into triphenylantimony hydroxyfluoride, which could be extracted with benzene or carbon tetrachloride. At pH's between 2 and 7, the separation was said to be complete and was unaffected by the presence of aluminum ion, which was complexed by 1,2-diaminocyclohexanetetraacetic acid.

Although ylids of type I have been prepared by the interaction of diazotetraphenylcyclopentadiene and molten triphenylphosphine, -arsine, -stibine, or -bismuthine, Lloyd and Singer [78] were unable to extend this method to the synthesis of the 2,3,4-triphenylcyclopentadienylides of triphenylarsine or -stibine.



I

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

Tricarbonylmolybdenum complexes of I (where M was P or As) were easily obtained by the reaction of the ylid with tris(acetonitrile)molybdenum tricarbonyl [79]. However, all attempts to synthesize the corresponding antimony complex yielded only intractable carbonyl-containing products. Further information about these ylids and their complexes has been given under Arsenic. The preparation and PMR spectrum of the 7-norbornadienyltriphenylstibonium ion [80] have also been discussed under Arsenic.

Schmidbaur and co-workers have investigated the cleavage of pentamethylantimony by a number of organic and inorganic acids. The carefully controlled reaction of pentamethylantimony with mercaptans at temperatures ranging from -30° to +20° was found to yield methane and a new class of compounds of the type $Me_4SbSR$ [81]:

$$Me_5Sb + RSH \longrightarrow Me_4SbSR + MeH$$

(where R was Me, Et, $PhCH_2$, or Ph)

The thiophenoxide and thioalkoxides thus prepared were stable only if kept below room temperature. On warming they decomposed to thioethers and trimethylstibine:

$$Me_4SbSR \longrightarrow Me_3Sb + MeSR$$

They were very soluble in non-polar solvents and gave normal molecular weights in benzene. Their PMR spectra in this solvent indicated that the four methyl groups were equivalent, presumably because of ligand reorganization (pseudorotation).

Attempts to prepare compounds of the type $Me_3Sb(SR)_2$ by the interaction of pentamethylantimony and two moles of a mercaptan at 40-60° yielded decomposition products [82]:

$$Me_5Sb + 2RSH \longrightarrow 2MeH + Me_3Sb + RSSR$$

(where R was Me, Et, $PhCH_2$, or Ph)

The desired compounds could be prepared, however, via the low temperature reaction of trimethylantimony dichloride with mercaptans in the presence of triethylamine:

$$Me_3SbCl_2 + 2RSH + 2Et_3N \longrightarrow Me_3Sb(SR)_2 + 2Et_3NHCl$$

The pure substances were obtained as colorless crystals, which decomposed at room temperature to give disulfides and trimethylstibine. They were monomeric in benzene, and their PMR spectra suggested that they possessed trigonal-bipyramidal structures in which the methyl groups (bonded to the antimony) were in equatorial positions. The kinetics of the decomposition reactions were studied by means of PMR and indicated that an intramolecular redox process was involved.

Tetramethylantimony azide, cyanide, and thiocyanate have been prepared by the cleavage of pentamethylantimony with hydrazoic acid, hydrocyanic acid, and thiocyanic acid, respectively [83]:

$$Me_5Sb + HX \longrightarrow Me_4SbX + MeH$$

(where X was $N_3$, CN, or SCN)

Tetraphenylantimony azide and thiocyanate were obtained in a similar manner:

$$Ph_5Sb + HX \longrightarrow Ph_4SbX + PhH$$

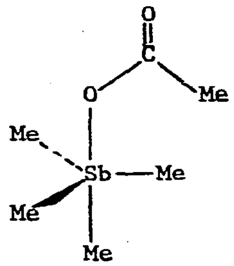
The azides and thiocyanates were crystalline compounds, which melted at about 200° with decomposition. They were quite soluble in dimethyl sulfoxide and acetonitrile but were insoluble or only slightly soluble in less polar solvents such as petroleum ether, benzene, and diethyl ether. All of the compounds were very sensitive to hydrolysis. Tetramethylantimony cyanide was especially hygroscopic. It decomposed on standing at room temperature, and its melting point (108° with decomposition) was much lower than that of the other pseudohalides. A detailed IR and Raman study of the tetramethylantimony compounds indicated that they consisted of slightly distorted tetrahedral stibonium cations and pseudohalide anions. It was concluded from this study and from the general properties of both the methyl and phenyl compounds that they probably possessed salt-like structures.

The reaction of pentamethylantimony with carboxylic acids has also been found to cause cleavage of the C-Sb bond [84]:

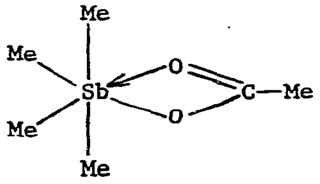
$$Me_5Sb + RCO_2H \longrightarrow Me_4SbO_2CR + MeH$$

(where R was H, Me, $CF_3$, $CCl_3$, Et, $CMe_3$, or Ph)

Pentaphenylantimony was converted in an analogous manner to tetraphenylantimony formate and acetate. The physical properties of tetramethylantimony acetate were investigated in great detail. The compound was observed to be low melting (76° with decomposition), soluble in non-polar solvents, and volatile enough to be sublimed at room temperature. It gave a normal molecular weight in benzene, and its mass spectrum suggested that the compound was also monomeric in the vapor phase. The molecular ion was not detected in the mass spectrum, but there were relatively strong peaks corresponding to $Me_3SbO_2CMe^+$, $Me_4Sb^+$, $Me_3Sb^+$, $Me_2Sb^+$, $MeSb^+$, and $Sb^+$. The PMR spectrum showed that the four methyl groups bonded to the antimony atom were magnetically equivalent, both at room temperature and -45°. The vibrational spectra of the acetate in solution and in the melt suggested the following trigonal-bipyramidal structure:

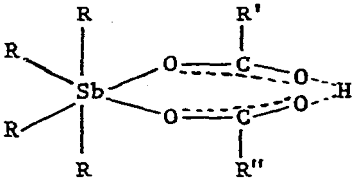


In the solid state, however, the compound appeared to contain a chelating acetate group and, therefore, hexacoordinated antimony:



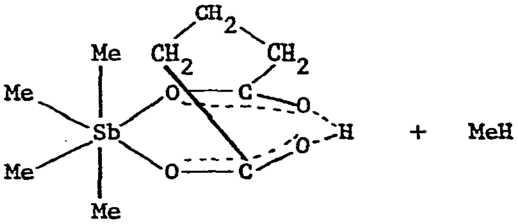
Although the other tetramethylantimony and tetraphenylantimony compounds were investigated less completely, it was concluded that they also possessed non-ionic, molecular structures.

The tetramethylantimony and tetraphenylantimony carboxylates described in the above paragraph were able to react with a second mole of a carboxylic acid to form stable 1:1 adducts, $R_4SbO_2CR'\cdot R''CO_2H$ [85]. Cryoscopic and ebullioscopic molecular weight determinations in benzene showed that these adducts existed as monomeric molecules. Their IR spectra demonstrated the presence of strong O-H----O hydrogen bonds. The PMR spectra of the tetramethylantimony compounds exhibited a $Me_4Sb$ singlet, signals due to the R' and R" groups (these groups were magnetically equivalent when R' and R" were the same), and a sharp singlet at extremely low fields for the proton participating in hydrogen bonding. The equivalence of the four methyl groups bonded to the antimony was attributed to ligand reorganization processes. It was concluded that the properties of the adducts were consistent only with a structure in which the antimony atom was chelated with a hydrogen dicarboxylate group:



The importance of the hydrogen bond in these molecules was shown by the fact that carboxylic esters were unable to form adducts with the tetramethylantimony carboxylates. A compound in which the R' and R'' groups were linked was obtained by the interaction of pentamethylantimony and glutaric acid:

$$Me_5Sb + HO_2C(CH_2)_3CO_2H \longrightarrow$$



In contrast to this result, the reaction of pentamethylantimony with oxalic, malonic, or succinic acid did not lead to analogous bicyclic chelates.

Doleshall, Nesmeyanov, and Reutov [86] have investigated the synthesis and chemical properties of two alkyltetraphenylantimony compounds (the alkyl group was methyl or ethyl). The methyl compound was obtained by two methods:

$$Ph_2MeSbF_2 + 2PhMgBr \longrightarrow Ph_4SbMe + 2MgFBr$$

$$Ph_4SbF + MeMgBr \longrightarrow Ph_4SbMe + 2MgFBr$$

Ethyltetraphenylantimony was prepared only by the interaction of tetraphenylantimony fluoride and the ethyl Grignard reagent. The use of antimony fluorides was essential in these syntheses since the use of chlorides or bromides resulted in "symmetrization" of the alkyltetraphenylantimony compounds, *i.e.*, the formation of appreciable amounts of pentaphenylantimony. The symmetrization reactions were apparently caused by interaction of the alkyltetraphenylantimony compound and the Grignard reagent. The antimony fluorides reacted with the Grignard reagents much faster than did the chlorides or bromides, and hence the formation of the alkyltetraphenylantimony compound was able to outpace its symmetrization. Organolithium compounds were even more effective in causing symmetrization. Thus, the interaction of methyltetraphenylantimony and *n*-butyllithium followed by treatment of the reaction mixture with benzophenone yielded significant amounts of pentaphenylantimony and triphenylcarbinol. The following mechanism was suggested:

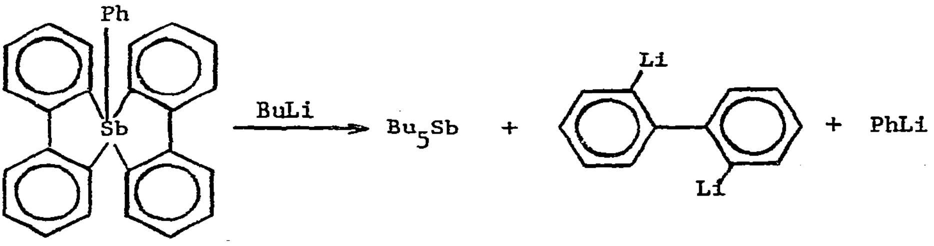
$$Ph_4SbMe + BuLi \rightleftharpoons [Ph_4BuSbMe]Li \rightleftharpoons Ph_3BuSbMe + PhLi$$

$$Ph_4SbMe + PhLi \rightleftharpoons [Ph_5SbMe]Li \rightleftharpoons Ph_5Sb + MeLi$$

$$Ph_2CO + PhLi \longrightarrow Ph_3COLi \xrightarrow{H_2O} Ph_3COH$$

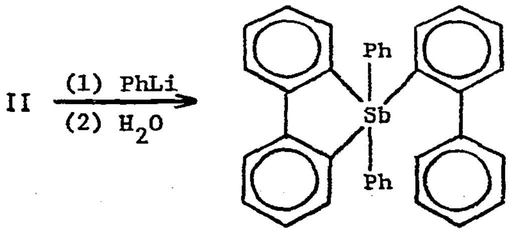
The alkyltetraphenylantimony compounds were crystalline and fairly soluble in organic solvents. Treatment of methyltetraphenylantimony with hydrogen bromide, boron trifluoride (in ether), or mercuric acetate resulted in cleavage of a Ph-Sb bond and formation of triphenylmethylantimony bromide, tetrafluoroborate, and acetate, respectively. The bromide and tetrafluoroborate were characterized by conversion to the known triphenylmethylantimony iodide; the acetate was not actually isolated but was directly converted to the tetrafluoroborate. In contrast to an earlier report by Henry and Wittig [87], the present workers [86] were unable to prepare an ylid from either triphenylmethylantimony iodide or tetrafluoroborate. Treatment of either the iodide or tetrafluoroborate with phenyllithium yielded a mixture containing tetraphenylmethylantimony and pentaphenylantimony; the latter compound was undoubtedly formed via the symmetrization reaction discussed earlier in this paragraph.

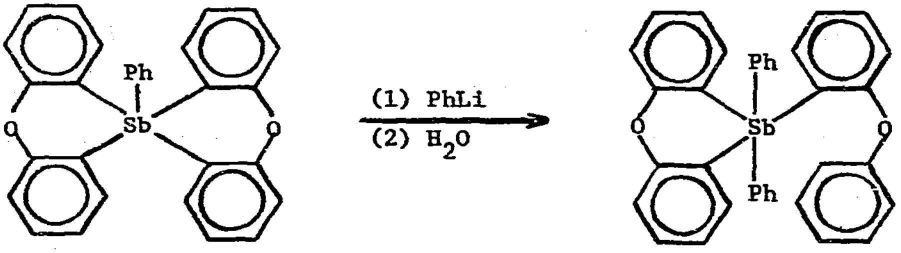
Hellwinkel and Bach [88] have reported that the reaction of the spiran II with an excess of *n*-butyllithium resulted in cleavage of all Ar–Sb bonds:



II

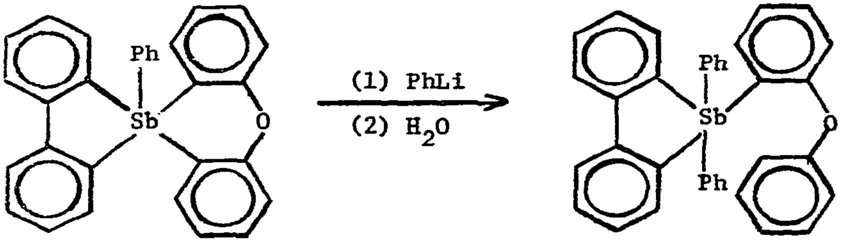
The pentabutylantimony formed in this reaction was not actually isolated but was identified by treatment of the reaction mixture with dilute hydrochloric acid and precipitation of the resulting tetrabutylstibonium ion as the tetraphenylborate $[Bu_4Sb][Ph_4B]$. The presence of organolithium compounds in the original reaction mixture was shown by the formation of biphenyl and benzene on hydrolysis. The reaction of phenyllithium with the spirans II and III cleaved one heterocyclic ring and gave products containing an additional phenyl group:





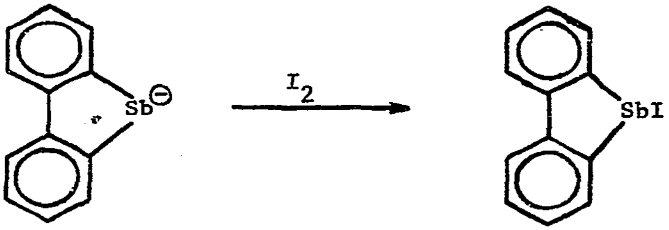
III

When the mixed spiran IV reacted with phenyllithium, the six-membered heterocyclic ring was cleaved:



IV

Treatment of the spiran II with lithium aluminum hydride or with alkali metals yielded the anionic species V, which was identified by conversion to the iodostibine VI.



V VI

Schlosser and co-workers [89] have found that pentaphenylantimony slowly underwent nucleophilic exchange reactions with methyllithium or *n*-butyllithium. Thus, when an excess of *n*-butyllithium was used, the following reaction took place to a large extent:

$$Ph_5Sb + 5BuLi \longrightarrow Bu_5Sb + 5PhLi$$

Treatment of the reaction mixture with 1,2-dibromoethane gave an 83% yield of bromobenzene (presumably via reaction with the phenyllithium). The pentabutylantimony could not be distilled even in a high vacuum but was characterized by reaction with hydrobromic acid, which gave a 48% yield of tetrabutylantimony bromide. The latter compound was identified by converting it to the known tetraphenylborate. The reaction of pentaphenylantimony with an excess of methyllithium appeared to go only to a minor extent. A small amount of pentamethylantimony distilled from the reaction mixture and was carefully treated with bromine. The resulting tetramethylantimony bromide was converted to the tetraphenylborate; only a 5% yield (based on the pentaphenylantimony used) of pure tetramethylantimony tetraphenylborate was obtained.

The square-pyramidal structure of pentaphenylantimony has in the past been attributed to crystal packing forces. During 1971, it was found that pentacyclopropylantimony in the liquid phase also existed as a square-pyramidal molecule [90]. This conclusion was based on a detailed IR and laser-Raman study, which showed that the low frequency spectrum of the cyclopropyl compound was in better agreement for $C_{4v}$ than for $D_{3h}$ skeletal symmetry. The synthesis of pentacyclopropylantimony was accomplished by the following sequence of reactions:

$$3c\text{-}C_3H_5Li + SbCl_3 \longrightarrow (c\text{-}C_3H_5)_3Sb + 3LiCl$$

$$(c\text{-}C_3H_5)_3Sb + Br_2 \longrightarrow (c\text{-}C_3H_5)_3SbBr_2$$

$$(c\text{-}C_3H_5)_3SbBr_2 + 2c\text{-}C_3H_5Li \longrightarrow (c\text{-}C_3H_5)_5Sb + 2LiBr$$

Pentacyclopropylantimony was a yellowish liquid, which boiled at 100° at 0.15 torr. Its PMR spectrum recorded with a 60 MHz spectrometer consisted of a complex multiplet centered at $\tau$ 8.7.

## REFERENCES

1 W. T. Reichle, in M. Tsutsui, ed., *Characterization of Organometallic Compounds*, Part II, Wiley-Interscience, New York, 1971, pp. 798-807.

2 J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London, 1970, pp. 486-487.

3 N. N. Greenwood, ed., *Spectroscopic Properties of Inorganic and Organometallic Compounds*, Vol. 4, The Chemical Society, London, 1971, pp. 153, 174, 197-198, 288, 304-305, 558.

4 K. Moedritzer, in E. I. Becker and M. Tsutsui, eds., *Organometallic Reactions*, Vol. 2, Wiley-Interscience, New York, 1971, pp. 5, 26-27, 31-32, 66, 78, 100.

5 D. D. Davis and C. E. Gray, *Organometal. Chem. Rev., Sect. A*, 6 (1970) 283.

6 M. Lesbre, P. Mazerolles, and J. Satgé, *The Organic Compounds of Germanium*, Wiley-Interscience, New York, 1971, pp. 278, 279, 671, 672.

7 K. J. Irgolic and R. A. Zingaro, in E. I. Becker and M. Tsutsui, eds., *Organometallic Reactions*, Vol. 2, Wiley-Interscience, New York, 1971, pp. 186, 272.

8 Y. Matsumura and R. Okawara, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 113.

9 A. J. Ashe, III, *J. Amer. Chem. Soc.*, 93 (1971) 6690.

10 J. R. Leebrick and N. L. Remes (M & T Chemicals, Inc.), U.S. Pat. 3,530,158; *Chem. Abstr.*, 75 (1971) 6106j.

11 O. J. Scherer and W. Gick, *Chem. Ber.*, 104 (1971) 1490.

12 J. Koketsu, M. Okamura, and Y. Ishii, *Bull. Chem. Soc. Jap.*, 44 (1971) 1155.

13 V. I. Bregadze, D. N. Sadzhaya, and O. Yu. Okhlobystin, *Soobshch. Akad. Nauk Gruz. SSR,* 63 (1971) 77; *Chem. Abstr.,* 75 (1971) 98644j.

14 I. N. Azerbaev, A. Yusupov, I. A. Poplavskaya, and V. S. Bazalitskaya, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.,* 21 (1971) 45; *Chem. Abstr.,* 76 (1972) 34367j.

15 I. N. Azerbaev, A. Yusupov, and I. A. Poplavskaya, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.,* 21 (1971) 84; *Chem. Abstr.,* 75 (1971) 36268f.

16 A. G. Davies and S. C. W. Hook, *J. Chem. Soc., C,* (1971) 1660.

17 A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., B,* (1971) 1823.

18 J. Connor, P. J. Young, and O. P. Strausz, *J. Amer. Chem. Soc.,* 93 (1971) 822.

19 W. R. Cullen, D. C. Frost, and W. R. Leeder, *J. Fluorine Chem.,* 1 (1971/72) 227.

20 J. Jacobus, *J. Chem. Soc., D,* (1971) 1058.

21 R. F. de Ketelaere, F. T. Delbeke, and G. P. van der Kelen, *J. Organometal. Chem.,* 30 (1971) 365.

22 W. M. A. Smith and G. Dijkstra, *J. Mol. Struct.,* 8 (1971) 263.

23 F. A. Miller and D. H. Lemmon, *Spectrochim. Acta, Part A,* 23 (1967) 1099.

24 L. M. Epshtein, Z. S. Novikova, L. D. Ashkinadze, S. O. Rabicheva, and L. A. Kazitsyna, *Izv. Akad. Nauk SSSR, Ser. Khim.,* (1970) 2379.

25 K. Brodersen, R. Palmer, and D. Breitinger, *Chem. Ber.,* 104 (1971) 360.

26 D. Cunningham, M. J. Frazer, and J. D. Donaldson, *J. Chem. Soc., A,* (1971) 2049.

27 E. O. Fischer, W. Bathelt, and J. Müller, *Chem. Ber.,* 104 (1971) 986.

28 J. Chatt, G. J. Leigh, and N. Thankarajan, *J. Organometal. Chem.,* 29 (1971) 105.

29 D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem.*, 9 (1970) 1691.

30 J. F. White and M. F. Farona, *Inorg. Chem.*, 10 (1971) 1080.

31 A. V. Ablov, A. M. Gol'dman, and O. A. Bologa, *Zh. Neorg. Khim.*, 16 (1971) 1763.

32 F. H. Jardine, A. G. Vohra, and F. J. Young, *J. Inorg. Nucl. Chem.*, 33 (1971) 2941.

33 F. H. Jardine and F. J. Young, *J. Chem. Soc., A*, (1971) 2444.

34 G. C. Stocco and R. S. Tobias, *J. Amer. Chem. Soc.*, 93 (1971) 5057.

35 L. Vaska and J. Peone, Jr., *Suom. Kemistilehti, B*, 44 (1971) 317.

36 H. van Gaal, H. G. A. M. Cuppers, and A. van der Ent, *J. Chem. Soc., D*, (1970) 1694.

37 W. R. Cullen, J. R. Sams, and J. A. J. Thompson, *Inorg. Chem.*, 10 (1971) 843.

38 J. A. de Beer, R. J. Haines, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc., A*, (1971) 3271.

39 J.-J. Legendre, C. Girard, and M. Huber, *Bull. Soc. Chim. Fr.*, (1971) 1998.

40 J. R. Ferraro, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 823.

41 N. Almasi, St. Farkas, and E. Cimpianu, *Stud. Univ. Babes-Bolyai, Ser. Chem.*, 16 (1971) 101; *Chem. Abstr.*, 76 (1972) 13436r.

42 C. A. McAuliffe and D. W. Meek, *Inorg. Chim. Acta*, 5 (1971) 270.

43 L. Baracco, M. T. Halfpenny, and C. A. McAuliffe, *J. Chem. Soc., D*, (1971) 1502.

44 B. R. Cook, C. A. McAuliffe, and D. W. Meek, *Inorg. Chem.*, 10 (1971) 2676.

45 B. R. Higginson, C. A. McAuliffe, and L. M. Venanzi, *Inorg. Chim. Acta*, 5 (1971) 37.

46 A. Araneo, V. Valenti, F. Cariati, and A. Sgamellotti, *Ann. Chim.* (Rome), 60 (1970) 768; *Chem. Abstr.*, 74 (1971) 134271a.

47 J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Inorg. Chem.*, 10 (1971) 2032.

48 P. L. Goggin, R. J. Knight, L. Sindellari, and L. M. Venanzi, *Inorg. Chim. Acta*, 5 (1971) 62.

49 H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 10 (1971) 18.

50 H. Masai, K. Sonogashira, and N. Hagihara, *J. Organometal. Chem.*, 26 (1971) 271.

51 D. I. Hall and R. S. Nyholm, *J. Chem. Soc., A*, (1971) 1491.

52 J. N. Crosby and R. D. W. Kemmitt, *J. Organometal. Chem.*, 26 (1971) 277.

53 B. E. Prater, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 1071.

54 B. E. Prater, *J. Organometal. Chem.*, 27 (1971) C17.

55 M. T. Halfpenny and L. M. Venanzi, *Inorg. Chim. Acta*, 5 (1971) 91.

56 Y. Masada and T. Yasui, *Kogyo Kagaku Zasshi*, 74 (1971) 2405; *Chem. Abstr.*, 76 (1972) 33919d.

57 J. Miller and A. L. Balch, *Inorg. Chem.*, 10 (1971) 1410.

58 R. A. Brown and G. R. Dobson, *J. Inorg. Nucl. Chem.*, 33 (1971) 892.

59 A. Davison and J. E. Ellis, *J. Organometal. Chem.*, 31 (1971) 239.

60 B. S. Gill, *Trans. Roy. Soc. Trop. Med. Hyg.*, 65 (1971) 347.

61 N. Nishii, Y. Matsumura, and R. Okawara, *J. Organometal. Chem.*, 30 (1971) 59.

62 R. G. Goel and D. R. Ridley, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 21.

63 G. Ferguson, R. G. Goel, F. C. March, D. R. Ridley, and H. S. Prasad, *J. Chem. Soc., D*, (1971) 1547.

64 R. G. Goel, E. Maslowsky, Jr., and C. V. Senoff, *Inorg. Chem.*, 10 (1971) 2572.

65 C. Woods and G. G. Long, *J. Mol. Spectrosc.*, 38 (1971) 387.

66 T. B. Brill and Z Z. Hugus, Jr., *J. Chem. Phys.*, 53 (1970) 1291.

67 A. N. Nesmeyanov and A. E. Borisov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1971) 2103.

68 A. E. Borisov, V. V. Klinkova, and N. A. Chumaevskii, *Dokl. Akad. Nauk SSSR,* 200 (1971) 64; *Chem. Abstr.,* 76 (1972) 45342y.

69 Y. Matsumura, M. Shindo, and R. Okawara, *J. Organometal. Chem.,* 27 (1971) 357.

70 J. Otera, T. Osaki, and R. Okawara, *Inorg. Chem.,* 10 (1971) 402.

71 V. V. Gavrilenko, Yu. N. Karaksin, and L. I. Zakharkin, *Zh. Obshch. Khim.,* 41 (1971) 1511.

72 J. B. Orenberg, M. D. Morris, and T. V. Long, II, *Inorg. Chem.,* 10 (1971) 933.

73 T. R. Williams and P. S. McKinney, *J. Electroanal. Chem. Interfacial Electrochem.,* 30 (1971) 131.

74 I. A. Carmichael and J. E. Whitley, *Analyst,* 95 (1970) 393.

75 M. Jean, *Anal. Chim. Acta,* 57 (1971) 438.

76 D. Aulagnier, H. Chermette, C. Martelet, J.-P. Schlienger, and J. Tousset, *Bull. Soc. Chim. Fr.,* (1971) 1135.

77 H. Chermette, C. Martelet, D. Sandino, and J. Tousset, *C. R. Acad. Sci., Paris, Ser. C,* 273 (1971) 543.

78 D. Lloyd and M. I. C. Singer, *J. Chem. Soc., C,* (1971) 2941.

79 D. Cashman and F. J. Lalor, *J. Organometal. Chem.,* 32 (1971) 351.

80 P. Schipper and H. M. Buck, *Phosphorus,* 1 (1971) 93.

81 H. Schmidbaur and K.-H. Mitschke, *Chem. Ber.,* 104 (1971) 1837.

82 H. Schmidbaur and K.-H. Mitschke, *Chem. Ber.,* 104 (1971) 1842.

83 H. Schmidbaur, K.-H. Mitschke, J. Weidlein and St. Cradock, *Z. Anorg. Allg. Chem.,* 386 (1971) 139.

84 H. Schmidbaur, K.-H. Mitschke, and J. Weidlein, *Z. Anorg. Allg. Chem.,* 386 (1971) 147.

85 H. Schmidbaur and K.-H. Mitschke, *Angew. Chem., Int. Ed. Engl.,* 10 (1971) 136.

86 G. Doleshall, N. A. Nesmeyanov, and O. A. Reutov, *J. Organometal. Chem.,* 30 (1971) 369.

87 M. C. Henry and G. Wittig, *J. Amer. Chem. Soc.*, 82 (1960) 563.

88 D. Hellwinkel and M. Bach, *J. Organometal. Chem.*, 28 (1971) 349.

89 M. Schlosser, T. Kadibelban, and G. Steinhoff, *Justus Liebigs Ann. Chem.*, 743 (1971) 25.

90 A. H. Cowley, J. L. Mills, T. M. Loehr, and T. V. Long, II, *J. Amer. Chem. Soc.*, 93 (1971) 2150.