ANTIMONY

ANNUAL SURVEY COVERING THE YEAR 1979 *

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Except for the Annual Survey covering the year 1978, no review devoted exclusively to organoantimony chemistry appeared in 1979. A section on organic compounds of antimony and bismuth was included, however, in a new six volume compendium on organic chemistry [1]. Organoantimony compounds were also mentioned in a review of recent work on compounds of nitrogen, phosphorus, arsenic, antimony, and bismuth [2] and in an article on cyclic pentacoordinate derivatives of the main group elements [3]. A twenty-three page review on organic compounds of arsenic, antimony, and bismuth was published in 1978 [4].

A study has been reported of the reactions of the primary alkylstibines $RSbH_2$ (where R was Me, Et, or Bu) with a number of halogen-containing species [5]. The alkylstibines were found to react rapidly with iodine, iodine monochloride, or carbon tetraiodide to yield the corresponding alkyldiiodostibines together with purple-black solids, the analysis of which corresponded to $(RSbI_{0.4})_x$. The interaction of methylstibine and dimethyliodoarsine also gave one of these solids in addition to dimethylarsine and tetramethyldiarsine; no methyldiiodostibine or methyliodostibine, MeSbHI, was detected in the reaction mixture. In contrast to these results with the iodine-containing reagents, the reaction of the alkylstibines with hydrogen chloride or organosilicon chlorides (Me_2SiCl_2, Me_3SiCl, or Ph_3SiCl) produced lustrous, pale-green, polymeric solids analyzing for $(RSb)_x$. When the reaction between methylstibine and dimethyldichlorosilane was monitored by PMR, it was discovered that a small amount of hydrogen chloride was initially formed but eventually disappeared. The concentration of the silicon compound remained nearly constant at its initial level, and only the concentration of methylstibine decreased

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* Antimony, Annual Survey covering the year 1978 see J. Organometal. Chem., 180 (1979) p. 111 - 141.

until it was completely consumed. It was also found that hydrogen was a product of the reaction. Thus, the overall reaction could be represented by the following equation:

$$x\,\mathrm{MeSbH_2} \longrightarrow (\mathrm{MeSb})_x + x\,\mathrm{H_2}$$

It was suggested that the initial formation of hydrogen chloride occurred via a halogen-hydrogen exchange:

$$\mathrm{MeSbH_2} + \mathrm{Me_2SiCl_2} \longrightarrow \mathrm{MeSbHCl} + \mathrm{Me_2SiHCl}$$

$$x\,\mathrm{MeSbHCl} \longrightarrow (\mathrm{MeSb})_x + x\,\mathrm{HCl}$$

The hydrogen chloride thus produced then catalyzed the decomposition of the methylstibine:

$$\mathrm{MeSbH_2} + \mathrm{HCl} \longrightarrow \mathrm{MeSbHCl} + \mathrm{H_2}$$

$$x\,\mathrm{MeSbHCl} \longrightarrow (\mathrm{MeSb})_x + x\,\mathrm{HCl}$$

The reactions of the alkylstibines with carbon tetrachloride and methyldichloroarsine were also investigated. It was found that carbon tetrachloride converted the stibines to dichlorostibines but produced no polymeric products:

$$\mathrm{RSbH_2} + 2\,\mathrm{CCl_4} \longrightarrow \mathrm{RSbCl_2} + 2\,\mathrm{CHCl_3}$$

Ethylstibine and methyldichloroarsine underwent rapid hydrogen-chlorine exchange followed by the slow elimination of hydrogen chloride to form the ladder-structure polymeric solid $(\mathrm{MeAs})_x$:

$$\mathrm{EtSbH_2} + 2\,\mathrm{MeAsCl_2} \longrightarrow \mathrm{EtSbCl_2} + 2\,\mathrm{MeAsHCl}$$

$$x\,\mathrm{MeAsHCl} \longrightarrow (\mathrm{MeAs})_x + x\,\mathrm{HCl}$$

No solid product containing antimony or ethyl groups could be detected.

Tetraethyldistibine has been found to react with an equimolar quantity of pentacarbonyl(tetrahydrofuran)chromium (photochemically generated in THF solution) to yield a mononuclear complex [6]:

$$\mathrm{Cr(CO)_5(THF)} + \mathrm{Et_2SbSbEt_2} \xrightarrow{\mathrm{THF}} \mathrm{(OC)_5CrSbEt_2SbEt_2} + \mathrm{THF}$$

The tungsten complexes $(OC)_5WSbR_2SbR_2$ (where R was Me, Et, or Ph) were prepared in a similar manner. When two moles of pentacarbonyl-(tetrahydrofuran)chrominum or -tungsten were allowed to react with one mole of tetra-*tert*-butyldistibine or tetraphenyldistibine, binuclear complexes were obtained:

$$2\ M(CO)_5(THF) + R_2SbSbR_2 \xrightarrow{THF} (OC)_5MSbR_2SbR_2M(CO)_5 + 2\ THF$$

(where M was Cr or W and R was Me_3C or Ph)

The mono- and binuclear complexes were characterized by IR, Raman, PMR, and mass spectra.

A mono- and a binuclear complex of vanadium have been prepared by the following photoinduced reactions [7]:

$$[Et_4N][V(CO)_6] + Ph_2SbSbPh_2 \xrightarrow{THF} [Et_4N][(OC)_5VSbPh_2SbPh_2] + CO$$

$$2\ CpV(CO)_4 + Ph_2SbSbPh_2 \xrightarrow{THF} Cp(OC)_3VSbPh_2SbPh_2V(CO)_3Cp + 2\ CO$$

(where Cp was cyclopentadienyl)

The two antimony-containing complexes were characterized by IR and ^{51}V NMR spectra. They were also compared with a number of analogous complexes in which tetraphenyldiarsine or a diphosphine was the ligand.

Attempts to prepare diphenylfluorostibine by fluorination of diphenylchlorostibine (with potassium fluoride, silver fluoride, or arsenic trifluoride) or by partial phenylation of antimony trifluoride (with phenylmagnesium bromide, phenyllithium, or triphenylstibine) have been unsuccessful [8]. Thus, there was no reaction upon refluxing diphenylchlorostibine with potassium fluoride in methanol for long periods of time, while treatment with silver fluoride or arsenic trifluoride led to oxidative fluorination and phenyl group migration:

$$3\ Ph_2SbCl + 4\ AgF \longrightarrow 2\ Ph_3SbF_2 + 4\ Ag + SbCl_3$$

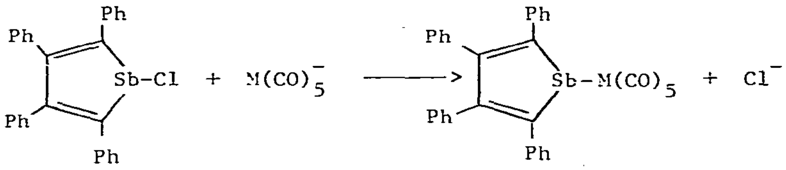
$$9\ Ph_2SbCl + 4\ AsF_3 \longrightarrow 6\ Ph_3SbF_2 + 4\ As + 3\ SbCl_3$$

Similar results were observed when the substrate was diphenylbromostibine. No reaction occurred on refluxing antimony trifluoride with triphenylstibine in dichloromethane or methanol, nor was any change observed when a mixture of the two antimony compounds was melted and held at 150°C for 40 h. With phenylmagnesium bromide or phenyllithium, it was not possible to achieve partial phenylation even when the stoichiometric quantity of the reagent was used at temperatures as low as $-90^{\circ}C$; in all cases, the product isolated was pure triphenylstibine. The desired fluorostibine was finally obtained by a method that had been described in 1966 [9]:

$$2[NH_4]_2[PhSiF_5] + SbF_3 \xrightarrow{H_2O} Ph_2SbF + 2[NH_4]_2[SiF_6]$$

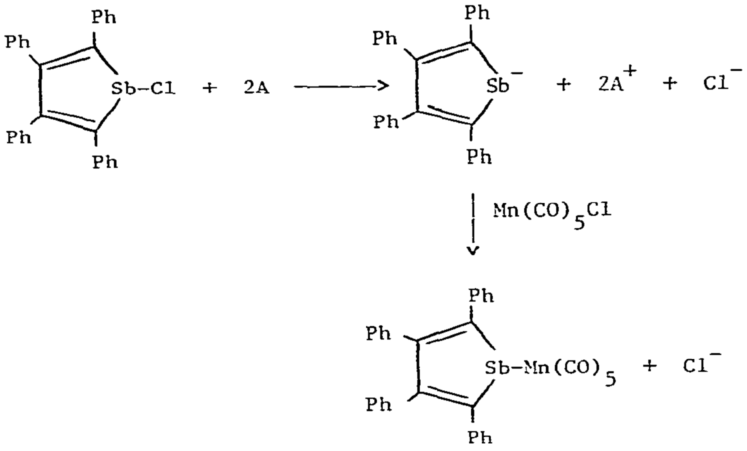
The substance proved to be a white, air-stable, crystalline solid that melted at $154^{\circ}C$ and was insoluble in non-polar organic solvents. The relatively high melting point and low solubility of the fluorostibine suggested that it was a fluorine-bridged polymer analogous to antimony trifluoride. The presence of fluorine bridge was supported by mass spectrometric data that showed $Ph_2SbF_2^+$ as the highest *m/e* ion (22.4% of the total ion current). An X-ray analysis clearly showed the presence of strong intermolecular fluorine bridges leading to infinite chains of Ph_2SbF units. The geometry about the antimony atom was distorted trigonal-bipyramidal, with the phenyl groups and the lone pair of electrons occuping the three equatorial positions and the fluorines in the two axial positions. An unusual feature of the structure was the small difference between the intra- and intermolecular Sb-F distances (2.166(5) and 2.221(5) Å, respectively). The angle at the bridging fluorine was $140.2(3)^{\circ}$. The mean C-Sb distance was 2.13 Å and the C-Sb-C angle was $99.9\ (4)^{\circ}$.

1-Chloro-2,3,4,5-tetraphenylstibole has been found to react virtually quantitatively with the pentacarbonyl anions of manganese and rhenium according to the following equation [10]:



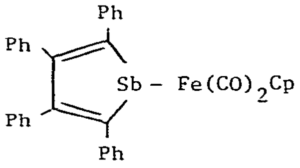
(where M was Mn or Re)

Treatment of the chlorostibole with either sodium amalgam or lithium wire in THF yielded an air-sensitive red stibole anion that reacted with pentacarbonylchloromanganese to yield the same type of antimony-manganese complex illustrated above:



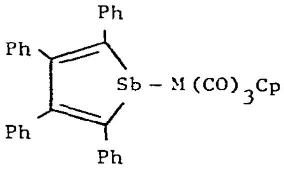
(where A was Li or Na)

The considerably lower yield (20-40%) obtained by the second approach was attributed to incomplete formation of the stibole anion. The IR spectra of the two antimony-metal complexes exhibited four strong, well-resolved metal-carbonyl stretching modes. The mass spectra showed molecular ions (M^+) and stepwise loss of carbon monoxide down to $[M-5CO]^+$. Both of the synthetic methods described above were used for the preparation of the following iron compound:



(where Cp was cyclopentadienyl)

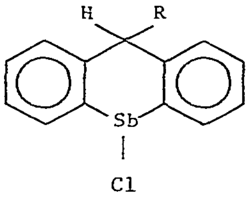
The IR spectrum of this substance showed the expected two peaks in the carbonyl-stretching region, and the PMR spectrum consisted of a singlet corresponding to the cyclopentadienyl group and a multiplet for the phenyl groups. The compound was not stable enough to allow a useful mass spectrum to be obtained. Molybdenum and tungsten complexes of the following type were obtained by reactions between the chlorostibole and the appropriate anions:



(where M was Mo or W)

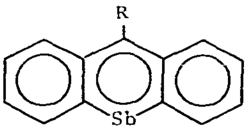
These compounds were also characterized by elemental analysis and by IR and PMR spectra. In all of the antimony complexes, the antimony to transition-metal bond underwent rapid fission with chlorine or bromine to form the corresponding halostibine and the transition-metal complex halide.

Attempts have been made to dehydrohalogenate 5-chloro-5,10-dihydro-dibenz[*b*,*e*]antimonin (I) and its 10-phenyl derivative (II) to the fully aromatic antimonins (III and IV) by treatment with 1,5-diazabicyclo[5.4.0]-undec-5-ene (DBU) [11].



I R = H

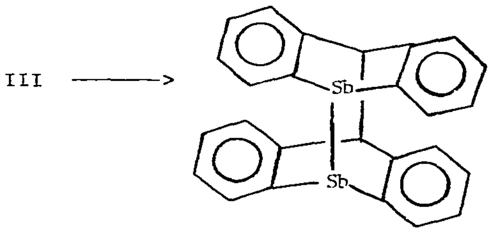
II R = Ph



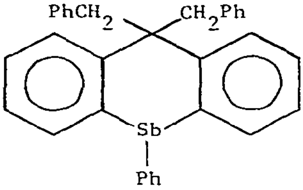
III R = H

IV R = Ph

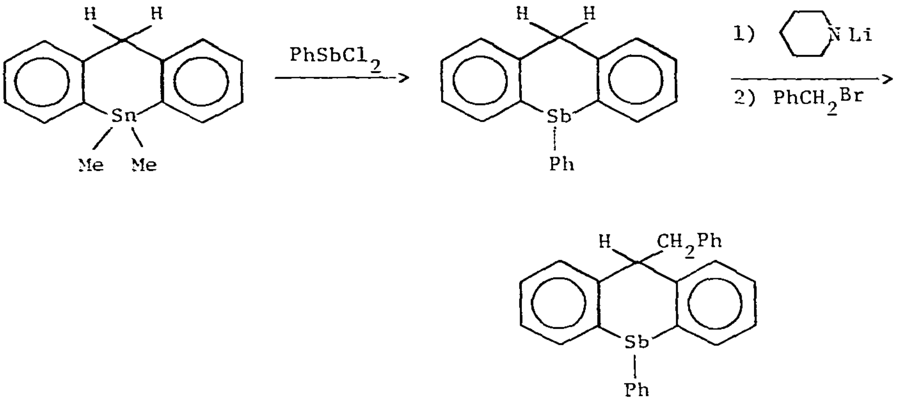
The reaction of I with DBU in dimethylformamide gave 92% of the expected amount of DBU·HCl plus a yellow solid that appeared to be a dimer formed from the desired antimonin:



The dimeric structure was assigned on the basis of a satisfactory elemental analysis, a mass spectrum, and an IR spectrum that indicated a rather symmetrical structure. Treatment of the 10-phenyl derivative II with DBU also resulted in the formation of DBU·HCl. The reaction mixture, however, yielded neither the desired antimonin IV nor a well defined dimer but mainly polymeric material of unknown structure. A second approach to the synthesis of IV was also investigated, namely, the pyrolysis of the dibenzyl compound V (pyrolysis of the arsenic analog of V had been found [12] to yield the arsenic analog of IV). Unfortunately, attempts to benzylate the monobenzyl derivative VI were unsuccessful. The latter compound was prepared in the following manner:



V

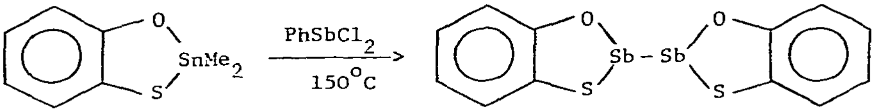


VI

Pyrolysis of VI yielded a mixture in which the desired antimonin IV could not be detected. The products of the pyrolysis included 1,2-diphenylethane and a mixture of dimeric and polymeric substances.

It has been reported that the interaction of 2,2-dimethyl-1,3,2-

benzoxathiastannole and phenyldichlorostibine gave an 82% yield of a compound containing an Sb-Sb bond [13,14]:



The stoichiometry of this curious reaction was not elucidated, but the spectral properties of the product were said to coincide with those of an authentic sample obtained by a procedure described in the literature.

Four tertiary stibines of the type *o*-$Me_2SbC_6H_4EMe_2$ (where E was N, P, As, or Sb) have been included in a study of the synthesis and properties of various chelating ligands analogous to *o*-phenylenebis-(dimethylarsine) [15]. The amine-stibine was obtained by two methods:

$$Me_2SbNa + o\text{-}BrC_6H_4NMe_2 \longrightarrow o\text{-}Me_2SbC_6H_4NMe_2 + NaBr$$

$$o\text{-}Me_2NC_6H_4MgBr + Me_2SbBr \longrightarrow o\text{-}Me_2SbC_6H_4NMe_2 + MgBr_2$$

The phosphine-stibine was prepared by the following reaction:

$$Me_2PLi + o\text{-}BrC_6H_4SbMe_2 \longrightarrow o\text{-}Me_2SbC_6H_4PMe_2 + LiBr$$

The arsine-stibine was prepared by a method previously described [16] and also by the following reaction:

$$Me_2SbNa + o\text{-}BrC_6H_4AsMe_2 \longrightarrow o\text{-}Me_2SbC_6H_4AsMe_2 + NaBr$$

The di-tertiary stibine was obtained in an analogous manner:

$$Me_2SbNa + o\text{-}BrC_6H_4SbMe_2 \longrightarrow o\text{-}Me_2SbC_6H_4SbMe_2 + NaBr$$

All of the compounds prepared in this study were foul-smelling air-sensitive liquids. The PMR spectra of the stibines exhibited singlets at about τ 9.1 for the methyl groups bonded to the antimony. Quaternization of all the ligands occurred easily on treatment with methyl iodide; in all cases mono-methiodides were formed. The methyl resonance of each Me_3E^+ group was downfield from that of the corresponding Me_2E group. In the case of the ligands with two different Me_2E groups, the PMR spectral data indicated that quarternization occurred preferentially in the order P > As > Sb > N. Mass spectra of all the ligands were also recorded. The base peak for the four antimony-containing ligands was the $(M-Me)^+$ ion. One curious result was that the mass spectrum of the phosphine-stibine showed ions corresponding to the di-tertiary phosphine and the di-tertiary stibine; and, similarly, the mass spectrum of the arsine-stibine showed ions corresponding to the di-tertiary arsine and the di-tertiary stibine. It was suggested that these unexpected ions were formed by rearrangements occurring in the mass spectrometer.

Tris(pentachlorophenyl)stibine has been prepared by the following reaction carried out at -78°C [17]:

$$3\ C_6Cl_5Li + SbCl_3 \longrightarrow (C_6Cl_5)_3Sb + 3\ LiCl$$

The stibine was unaffected by hydrochloric acid but readily underwent oxidative halogenation:

$$(C_6Cl_5)_3Sb + X_2 \longrightarrow (C_6Cl_5)_3SbX_2$$

(where X was Cl or Br)

All three organoantimony compounds were air-stable solids that melted without decomposition. Their molar conductivities in nitromethane showed that they were non-conductors in this solvent. Absorptions due to the pentachlorophenyl group were identified in the IR spectra of the three substances. The Sb-Cl stretching frequency of tris-(pentachlorophenyl)antimony dichloride appeared as a strong band at 300 cm^{-1}.

The reaction of one mole of tris(trimethylsilyl)stibine with three or more moles of *tert*-butyl iodide has been found to result in cleavage of all three Si-Sb bonds [18]:

$$(Me_3Si)_3Sb + 3\ Me_3CI \xrightarrow{25^oC} (Me_3C)_3Sb + 3\ Me_3SiI$$

When less than three moles of *tert*-butyl iodide were used, however, the products included bis(trimethylsilyl)-*tert*-butylstibine, trimethylsilyl-di-*tert*-butylstibine, and tetrakis(trimethylsilyl)distibine, $(Me_3Si)_2SbSb(SiMe_3)_2$. In contrast to the results obtained with *tert*-butyl iodide, however, the interaction of tris(trimethylsilyl)stibine and methyl iodide (regardless of the relative amounts of reactants employed) yielded only trimethylstibine and trimethyliodosilane:

$$(Me_3Si)_3Sb + 3\ MeI \xrightarrow{25^oC} Me_3Sb + 3\ Me_3SiI$$

The preparation of triphenylstibine by the interaction of antimony trichloride and PhMgBr·*n*THF (where *n* was 1 or 3) has been described in a Soviet patent [19]. The solvents used for this reaction included THF-benzene mixture containing 10-70 wt.% of THF. The formation of trialkylstibines by the uncatalyzed addition of stibine to olefins has been claimed in a Canadian patent [20].

Cyclopentadienyl-di-*tert*-butylstibine has been prepared by the following reaction [21]:

$$\mathrm{CpLi} + (\mathrm{Me_3C})_2\mathrm{SbCl} \longrightarrow \mathrm{CpSb(CMe_3)_2} + \mathrm{LiCl}$$

(where Cp was cyclopentadienyl)

The interaction of cyclopentadienyldimethylstibine and pentamethylstannanamine led to the formation of a doubly-substituted cyclopentadiene containing both antimony and tin:

$$\mathrm{CpSbMe_2} + \mathrm{Me_3SnNMe_2} \longrightarrow \mathrm{C_5H_4(SbMe_2)(SnMe_3)} + \mathrm{Me_2NH}$$

Small amounts of symmetrically substituted derivatives of the type $C_5H_4Y_2$ (where Y was $SbMe_2$ or $SnMe_3$) were also detected in the reaction mixture. The structure and dynamic behavior of the antimony-containing cyclopentadienes discussed in this study were investigated by PMR and ^{13}C NMR spectroscopy.

Cyclopentadienyldimethylstibine and cyclopentadienyl-di-*tert*-butylstibine have been included in a comparative study of the reactivity of cyclopentadienyl derivatives of Group IV (Si,Ge, and Sn) and Group V (As and Sb) elements with various compounds containing the arsenic-halogen or antimony-halogen bond [22]. The two tertiary stibines were found to react rapidly at room temperature according to the following equations (where Cp was cyclopentadienyl and R was Me or Me_3C):

$$\mathrm{CpSbR_2} + \mathrm{Me_2AsCl} \longrightarrow \mathrm{CpAsMe_2} + \mathrm{R_2SbCl}$$

$$\mathrm{CpSbR_2} + \mathrm{MeAsCl_2} \longrightarrow \mathrm{Cp(Me)AsCl} + \mathrm{R_2SbCl}$$

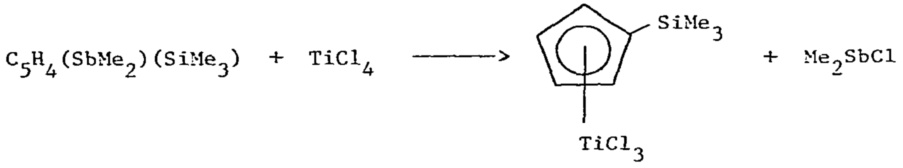
$$\mathrm{CpSbR_2} + \mathrm{AsX_3} \longrightarrow \mathrm{CpAsX_2} + \mathrm{R_2SbX}$$

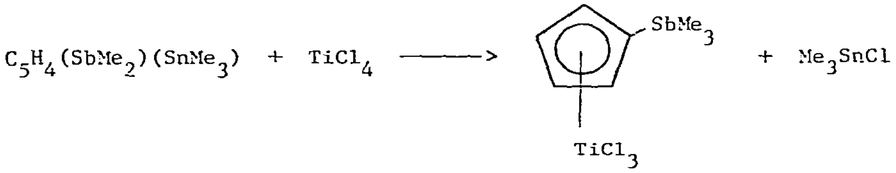
(where X was F, Cl, Br, or I)

$$\mathrm{CpSbR_2} + \mathrm{SbX_3} \longrightarrow \mathrm{CpSbX_2} + \mathrm{R_2SbX}$$

(where X was Cl or I)

A number of substituted cyclopentadienyltitanium trichlorides were prepared by the interaction of doubly-substituted cyclopentadienes with titanium tetrachloride. Included in this study were two organoantimony compounds, which reacted in the following manner:





The cyclopentadienyldialkylstibines mentioned in the above two paragraphs have been quaternized by treatment with methyl iodide [23]:

$$CpSbR_2 + MeI \longrightarrow [CpSb(Me)R_2]I$$

(where R was Me or Me_3C)

The influence of quaternization of the antimony on the structure and dynamic behavior of the cyclopentadienyl group was investigated by means of PMR spectroscopy. The mass spectra of the methiodides were also determined.

Methylenebis(diphenylstibine) has been included in a study of the effect of organometallic groups on the acidity of carbon-hydrogen bonds [24]. Treatment of this compound in ether at 20°C with one mole of lithium dicyclohexylamide and hexamethylphosphoric triamide (HMPT) resulted in 68% deprotonation in 2 h:

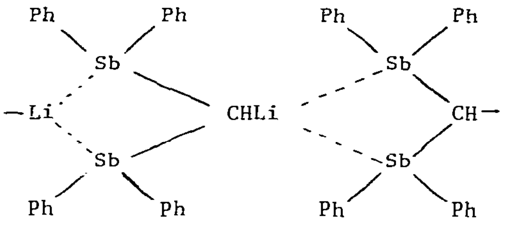
$$(Ph_2Sb)_2CH_2 + LiNR_2 \longrightarrow (Ph_2Sb)_2CHLi + R_2NH$$

(where R was cyclohexyl)

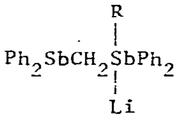
The extent of deprotonation was established by adding deuterium oxide to the reaction mixture and using NMR to determine the amount of deuterated product formed:

$$(Ph_2Sb)_2CHLi + D_2O \longrightarrow (Ph_2Sb)_2CHD + LiOD$$

It was suggested that the intermediate organolithium compound may be stabilized by intermolecular interactions of the following type:



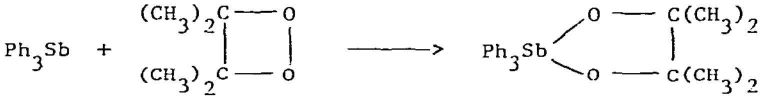
The reaction of methylenebis(diphenylstibine) with bases less bulky than lithium dicyclohexylamide yielded adducts of the following postulated structure:



$\mathrm{Ph_2SbCH_2}\overset{\mathrm{R}}{\underset{\mathrm{Li}}{\mathrm{Sb}}}\mathrm{Ph_2}$

(where R was Bu, Ph, $(Me_2CH)_2N$, or piperidino)

The interaction of equal molar amounts of triphenylstibine and tetramethyl-1,2-dioxetane in deuterated chloroform at room temperature has been found to give a 77% yield of a stable insertion product [25]:



The remaining 23% of the dioxetane was catalytically decomposed by the stibine to acetone. In deuterated benzene the yield of insertion product was only 30% while 70% of the dioxetane underwent decomposition. A quantitative yield of the insertion product was obtained when the solvent was deuterated chloroform and a large excess of dioxetane was used. An investigation of the kinetics of the reaction in xylene or chloroform showed that the reaction was first order with respect to each reagent. Triphenylstibine was found to react slightly less rapidly than triphenylphosphine but significantly more rapidly than triphenylarsine. The results obtained in this study were believed to be consistent with a concerted (biphilic) insertion of the group V atom into the peroxy bond of the dioxetane.

The photochemical reduction of uranyl ions with triphenylstibine in a dioxane-water medium has been reported to yield uranium(IV) and triphenylstibine oxide [26]. The products of the photolysis were separated and analyzed by means of TLC. The authentic sample of stibine oxide required in this study was prepared by hydrogen peroxide oxidation, but no information about the properties of this substance was mentioned. The rate of the reduction was first order with respect to uranyl ion and triphenylstibine. It was affected by the anion employed and followed the decreasing order: uranyl sulfate > uranyl acetate > uranyl nitrate. The absorption spectrum of uranyl ion in the presence of triphenylstibine did not indicate any ground state interaction between the two reactants. A comparison of the results obtained in this investigation with previously published studies showed that the rate of reduction of uranyl ion followed the order: triphenylphosphine > triphenylarsine > triphenylstibine. This order was explained by the relative electron-donating capacity of the three substrates.

Triphenylstibine has been included in a study of nitration vs. oxidation on treatment of heteroorganic compounds with nitronium hexafluorophosphate or tetrafluoroborate [27]. It was found that the stibine gave a 98% yield of triphenylstibine oxide, mp 282.5°C. The following mechanism was suggested:

$$Ph_3Sb \ + \ NO_2^+ \ \rightleftarrows \ [Ph_3SbNO_2]^+ \ \longrightarrow \ [Ph_3SbONO]^+ \ \rightleftarrows \ Ph_3SbO \ + \ NO^+$$

Difluorodiphenylsulfur has been used for the oxidative fluorination of triphenylphosphine, -arsine, and -stibine [28]:

$$Ph_3E \ + \ Ph_2SF_2 \ \longrightarrow \ Ph_3EF_2 \ + \ Ph_2S$$

(where E was P, As, or Sb)

The reactions were carried out in deuterated chloroform at about 30°C, and the yields were said to be quantitative. The fluorinated products were characterized by ^{19}F NMR spectroscopy. Difluorodiphenylsulfur was obtained by the direct fluorination of diphenylsulfide with fluorine in trichlorofluoromethane at -78°C.

The oxidation of triarylstibine by mercury(II) or copper(II) compounds has been found to proceed in the following manner [29]:

$$Ar_3Sb \ + \ 2\ MY_2 \ \longrightarrow \ Ar_3SbY_2 \ + \ 2\ MY$$

(where Ar was Ph or p-MeC_6H_4, M was Hg or Cu, and Y was Cl, Br, I, O_2CMe, or NCS)

The pentavalent antimony compounds thus formed were isolated in good yields (70-85%) and were easily purified. The triarylstibines were prepared by the reaction of an anhydrous antimony trihalide, an aryl halide, and sodium in refluxing benzene.

Conductometric titrations have been employed to study the interaction of iodine and triphenylamine, -phosphine, -arsine, or -stibine in dioxane-THF [30]. The results obtained indicated that 1:1 complexes were formed, which existed as equilibrium mixtures of intimate and solvent-separated ion pairs. A model was suggested for using refractometric measurements to determine the equilibrium constants for the formation of the 1:1 complexes.

A compound containing an Sb-N bond has been obtained by the following reaction [31] :

$$Ph_3Sb + (Cl_3Si)(Me_3Si)NCl \longrightarrow [Ph_3SbN(SiCl_3)(SiMe_3)]Cl$$

The addition product, which was formulated as a stibonium salt, decomposed on heating to yield triphenylantimony dichloride and substances of undetermined structure.

The reaction between the twelve Lewis bases of the type $Me_nE(CF_3)_{3-n}$ (where E was P, As, or Sb and n was 0, 1, 2, or 3) and six Lewis acids (diborane, boron trifluoride, boron trichloride, boron tribromide, dimethylbromoborane, and trimethylborane) in benzene solution has been studied by means of PMR and ^{19}F NMR spectroscopy [32]. The base strengths decreased in the order $Me_3E > Me_2ECF_3 > MeE(CF_3)_2 > (CF_3)_3E$ with the phosphines > arsines > stibines. The acid strengths decreased in the order $"BH_3" > BBr_3 > BCl_3 > BF_3 > Me_2BBr > Me_3B$.

A study has been reported of the gas-phase IR and the liquid-phase Raman spectra of bis(trifluoromethyl)stibine and the halostibines $(CF_3)_2SbX$, where X was Cl, Br, or I [33]. The assignment of the observed absorption bands was based on C_s local symmetry and was aided by a normal coordinate analysis. The structural data needed for this analysis were obtained by extrapolation from known bond length and bond angle values of related compounds.

PMR spectroscopy has been used to study the molecular structure of 4-methylarsabenzene and 4-methylstibabenzene partially oriented in the nematic liquid crystal phase of *N*-(*p*-ethoxybenzylidene)-*p*-butylaniline [34]. For 4-methylstibabenzene, the results ruled out structures with C-C bond alternation and favored a model in which the $C_\alpha-C_\beta$ distance was only slightly longer than the $C_\beta-C_\gamma$ distance (1.400 ± 0.012 Å *vs.* 1.392 ± 0.012 Å). Other structural parameters for this model included a C-Sb distance of 2.050 ± 0.003 Å and a C-Sb-C angle of $92.8 \pm 0.2°$.

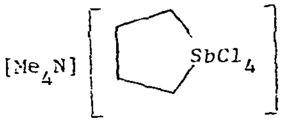
X-ray diffraction has been employed to determine the crystal and molecular structure of tri-*p*-tolylstibine [35]. As expected, the molecule was pyramidal with the antimony atom at the apex. The C-Sb bond distance (2.141 Å) was in close agreement with values previously reported for the C-Sb single bond in other organoantimony compounds. The C-Sb-C angle was 97.3°, a value intermediate between the C-Bi-C angle (94°) in triphenylbismuthine and the C-As-C angle (102°) in tri-*p*-tolylarsine. The angle between the planes of the aromatic rings in tri-*p*-tolylstibine was 90.08°. Each of these planes formed an angle of 54.8° with the plane defined by the three carbon atoms bonded to the antimony. Intermolecular distances were consistent with normal van der Waals interactions.

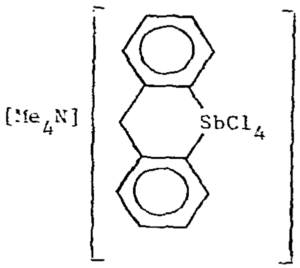
A gas-liquid chromatographic study of the primary alcohols ROH (where R was Et, Pr, Bu, or $CHF_2(CF_2)_3CH_2$) over squalene containing Ph_3E (where E was P, As, Sb, or Bi) showed that hydrogen-bond strengths for all the alcohols decreased in the order $Ph_3P > Ph_3As > Ph_3Sb > Ph_3Bi$ [36]. Triphenylamine was found to form a relatively weak hydrogen bond. The order of hydrogen-bond strengths deduced from the GLC study was interpreted in terms of *p*-π conjugation in the triphenyl compounds and was supported by NMR data for complexes formed by interaction of these compoud[s] with 2,6-di-*tert*-butylphenol.

There have been numerous recent articles on the use of tertiary stibines as ligands in transition metal complexes. The metals coordinated to the antimony in these complexes included chromium [23, 37], copper [38], gold [39], iron [40], manganese [41, 42], palladium [43, 44], platinum [45], rhodium [46,47], ruthenium [48, 49], and tungsten [23, 50].

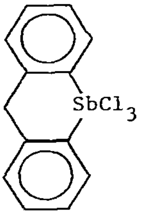
Two organometallic compounds, 4-(chloromercurio)benzenesulfonyl fluoride and pyridinium *p*-(fluorosulfonyl)phenylpentachloroantimonate, have been prepared by Wyrich and coworkers [51] as irreversible protease inhibitors. The antimony compound $[C_5H_6N]$ $[p\text{-}Cl_5SbC_6H_4SO_2F]$ was obtained from *p*-aminobenzenesulfonyl fluoride *via* the Scheller reaction and conversion of the resulting stibonic acid to the pentachloroantimonate.

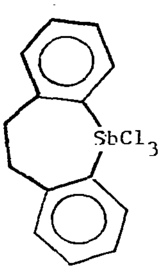
Barbieri and coworkers [52] have reported on the ^{121}Sb Mössbauer spectra of a series of five heterocyclic organoantimonate(V) compounds in which the antimony atom is a member of a heterocyclic ring and in which the C-Sb-C linkage is of necessity *cis*. Two of these five compounds are listed below:





In all of these heterocyclic antimony compounds the heterocyclic rings were either 5- or 6- membered. Two non-anionic heterocyclic antimony(V) compounds were also investigated:





Ground state quadrupole coupling constants (e^2qQ_g), asymmetry parameters (η), and the chemical isomer shifts (δ) relative to $Ca^{121}SnO_3$ were listed in tabular form. The preparation and chemical properties of all of the compounds under investigation in the present paper have been reported in a previous paper [53].

Since Mössbauer studies on *trans*-$[R_2SbCl_4]^-$ ions had been reported previously, a comparison between *cis*- and *trans*-organoantimony compounds with octahedral geometry was made possible by the present study. In accordance with prediction, the quadrupole coupling constants for *cis*- and *trans* — compounds were in the approximate ratio −1:2. The large value of the asymmetry parameter η for all five heterocyclic organoantimony anions suggested that the ideal octahedral geometry had been distorted by formation of the heterocyclic ring. A point-charge model, developed in terms of the C-Sb-C angle and the partial field gradient contributions of the ligands, provided a satisfactory correlation between the electric field gradient parameters and the expected stereochemistry. Similar studies were carried out with the two heterocyclic antimony trichlorides. However, with these compounds the value of η was much more sensitive to bond angles and electric field gradient parameters, and in consequence it was more difficult to deduce structural information for these compounds.

The chemical isomer shift was found to be more positive for the *cis*-$[R_2SbCl_4]^-$ ions than for the corresponding *trans* compounds. These results were in strict analogy to the corresponding *cis*- and *trans*-tin compounds. This result has been taken to indicate a greater *s*-electron density at the Mössbauer nucleus of the *trans*— R_2SbL_4 octahedral species.

Bone and Sowerby [54] have reported on several new organoantimony compounds including the mixed halo compounds diphenylantimony dibromide chloride and diphenylantimony bromide dichloride. Both diphenylchlorostibine and diphenylbromostibine were obtained from the reaction between triphenylstibine and antimony trichloride or antimony tribromide, respectively. The reaction between diphenylbromostibine and bromine at -97°C gave diphenylantimony tribromide, a compound which had not been previously reported. From diphenylchlorostibine and a stoichiometric amount of bromine at -196°C, diphenylantimony dibromide chloride was obtained as a crystalline compound, m.p. 181°C. Similarly, from diphenylbromostibine and the stoichiometric amount of chlorine at -90°C, diphenylantimony bromide dichloride was obtained. It was found that chlorine displaced bromine from the bromo compounds when chlorination was carried out at higher temperatures. Thus, diphenylbromostibine and chlorine gave only diphenylantimony trichloride at room temperature. Mass spectral peaks as well as major peaks in the IR and Raman spectra of the new organoantimony(V) compounds were reported.

Having prepared these three new organoantimony(V) compounds, Bone and Sowerby [55] then determined their crystal structure. This was of interest since it had previously been shown that diphenylantimony trichloride was dimeric and that each antimony atom possessed octahedral geometry with Sb-Cl-Sb bridges [56]. By contrast, all three of the bromine-containing compounds (diphenylantimony tribromide, diphenylantimony dibromide chloride, and diphenylantimony bromide dichloride) were monomeric with the antimony atom possessing distorted trigonal-bipyramidal geometry. In the case of diphenylantimony bromide dichloride, the two chlorine atoms were in axial position, and the Cl-Sb-Cl angle was 178.3°. It might be expected that in diphenylantimony dibromide chloride one bromine and one chlorine atom would be in axial positions. The Sb-Br distance, however, was 2.48 Å and the bromine had a high (0.077) thermal parameter. These results were taken as an indication of disorder in the occupancy of the axial positions, and calculations were performed to determine the site-occupancy factors of the axial atoms as variables.

The two bonds from antimony to the axial halogens had different lengths in all three compounds with the halogen at the greater distance being involved in weak intermolecular bonding to a neighboring antimony atom. In the case of diphenylantimony dibromide chloride, where there was disorder in the site-occupancy of the axial atoms, the bridging halogen (Sb-X-Sb) had greater bromine occupancy than chlorine occupancy.

The Sb-Br equatorial positions decreased from 2.478 Å in Ph_2SbBr_3 to 2.462 Å in Ph_2SbBr_2Cl to 2.446 Å in $Ph_2SbBrCl_2$. There was a similar but less pronounced shortening of the Sb-C bond in all three compounds. This result was attributed to increased electronegativity of atoms in axial positions in going from Ph_2SbBr_3 to $Ph_2SbBrCl_2$. The major distortion from trigonal-bipyramidal geometry was in a C-Sb-C angle of ∿ 154°, with a decrease in the other two equatorial angles to ∿ 102°.

This large distortion in the equatorial angles was attributed to the intermolecular interaction between the central Sb atom and an axial halogen atom.

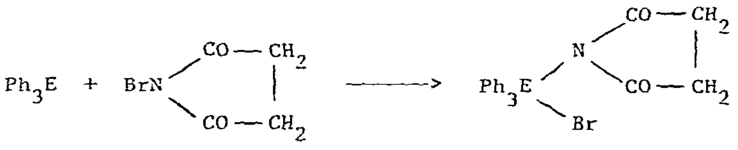
In an attempt to prepare the compound Ph_2SbBr_2F, diphenylfluorostibine was brominated in dichloromethane solution at -90°C [57]. The crystalline material obtained had the formula $Ph_2SbBr_{2.5}F_{0.5}$. An X-ray crystal structure determination showed that the compound was dimeric and should be formulated as $Ph_2SbBr_2F \cdot Ph_2SbBr_3$. The two antimony atoms were linked by a strong fluorine bridge. One antimony atom was approximately octahedral (two phenyl groups, three bromine atoms and a fluorine atom), while the second antimony possessed essentially trigonal-bipyramidal coordination. This paper was a preliminary report on a new compound, and only a few intramolecular distances and angles were reported.

Triphenyl- and tri-*p*-tolylantimony dibromide have been found to react with imides, amides, and related compounds in the presence of triethylamine to give antimony(V) compounds of the type $Ar_3Sb(NR_2)_2$ [58]:

$$Ar_3SbBr_2 + 2\ HNR_2 + 2\ Et_3N \longrightarrow Ar_3Sb(NR_2)_2 + 2\ Et_3N \cdot HBr$$

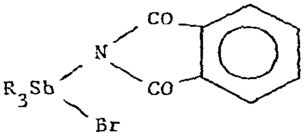
Among the nitrogen-containing compounds used in the above reaction were succinimide, phthalimide, benzimidazole, benzoxazol-2-one, benzotriazole, and others. A total of nine compounds derived from triphenylantimony dibromide and nine from tri-*p*-tolylantimony dibromide were reported. Molar conductances of the compounds in acetonitrile solution showed that all of the compounds were non-electrolytes in that solvent. IR (carbonyl stretching bands) and PMR data were given. The Sb-N bond was cleaved in these compounds by either bromine or $TeCl_4$ to yield Ar_3SbX_2, where X = Br or Cl, respectively. However, refluxing in methanol solution did not result in cleavage of the Sb-N bond. An attempt to prepare a monobromide from one mole of succinimide and one mole of triphenylantimony dibromide gave only the diamide.

Dahlmann and Winsel [59] have reported on a series of organoarsenic, organoantimony, and organobismuth compounds formed by the reaction between triphenylarsines, -stibines or -bismuthines and various *N*-haloamides. Thus *N*-bromosuccinimide reacted with triphenylarsine, -stibine, or -bismuthine in the following manner:



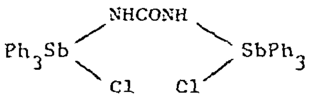
(E = As, Sb, or Bi)

Triphenylstibine also was found to react with *N*-chlorosuccinimide to give the corresponding chloro compound. Both triphenyl- and trimethylstibine reacted with *N*-bromophthalimide to give compounds of the following type:

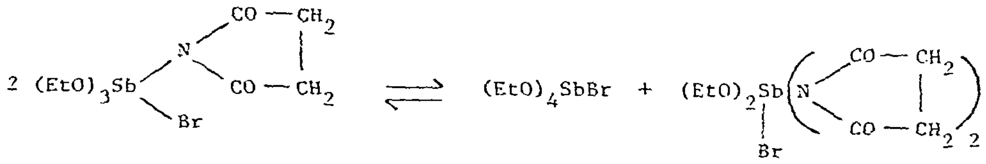


(R = Ph or Me)

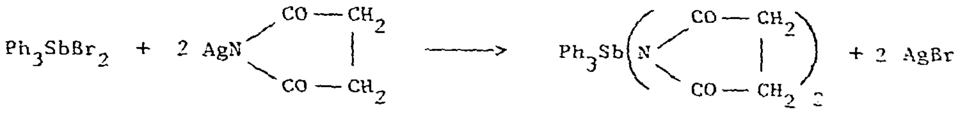
Triphenylstibine and *N*,*N*'-dichlorourea gave the following compound:



It was expected that triethoxystibine would react with *N*-bromosuccinimide or *N*-bromophthalimide in a similar manner to triphenylstibine. However, the only compound isolated was tetraethoxystibonium bromide. It was suggested that the expected compounds were formed and then rearranged:



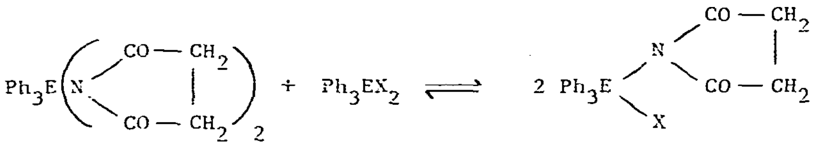
From triphenylantimony dibromide and silver succinimide, compound III was obtained as follows:



III

Triphenylbismuth dibromide reacted with silver succinimide in a similar fashion.

PMR data and IR data on the carbonyl frequencies were reported. From the PMR data it was concluded that in solution the following equilibrium occurred:



(E = Sb or Bi, X = Br or Cl)

A large series of triarylantimony dicarboxylates $Ar_3Sb(O_2CR)_2$ (where Ar = Ph or p-MeC_6H_4 and R = H, $ClCH_2$, $BrCH_2$, CCl_3, Et, Me_2CH, $PhCH_2$, PhCH=CH, MeCH=CH, $Me(CH_2)_2CH_2$, $Me(CH_2)_{15}CH_2$, $MeCOCH_2CH_2$, o-$MeC_6H_4OCH_2$, m-$MeC_6H_4OCH_2$, and p-$ClC_6H_4OCH_2$) have been prepared by the reaction between the triarylantimony dibromide and the carboxylic acid in the presence of triethylamine [60]. Excellent yields of the carboxylates were obtained. The compounds were crystalline solids which were non-electrolytes in acetonitrile solution. The IR spectra of the compounds gave carbonyl bands which were not in agreement with carboxylate ions. Their PMR spectra suggested that the two carboxylate groups were equivalent. On the basis of these results the authors suggested that the compounds were trigonal bipyramids with a planar Ar_3Sb moiety. The toxicities of the compounds against male and female cockroaches were slight, and the activity appeared to be independent of the R group.

The crystal structure of the interesting peroxy compound $Ph_3Sb(OOCMe_3)_2$ has been determined using X-ray crystallography [61]. The antimony atom possessed trigonal-bipyramidal geometry with the two peroxy groups in axial positions.

Goel and Ridley [62] have reported that the Sb-O-Sb bond in the compound $(Ph_3SbCl)_2O$ was cleaved by methanol and by acetylacetone according to the following equations:

$$(Ph_3SbCl)_2O + 2\ MeOH \rightleftharpoons 2\ Ph_3Sb(OMe)Cl + H_2O$$

$$(Ph_3SbCl)_2O + 2\ acacH \rightleftharpoons 2\ Ph_3Sb(acac)Cl + H_2O$$

(where acacH = acetylacetone)

The cleavage by methanol was carried out in the hot, but acetylacetone reacted with $(Ph_3SbCl)_2O$ at room temperature. The yields in these two reactions were 90% and 25%, respectively.

It was also reported that methanol and acetylacetone reacted with triphenylstibine oxide according to the following equations:

$$Ph_3SbO + 2\ MeOH \rightleftharpoons Ph_3Sb(OMe)_2 + H_2O$$

$$Ph_3SbO + acacH \rightleftharpoons Ph_3Sb(acac)OH + H_2O$$

The triphenylstibine oxide used was a polymeric material, m.p. 290°, and was obtained from a commercial source. Both reactions were carried out by allowing the reactants to stand together overnight. The reaction with acetylacetone was carried out in benzene. If Ph_3SbO or $Ph_3Sb(acac)OH$ were refluxed with acacH, the product obtained was $Ph_3Sb(O_2CMe)_2$. Raman, IR, and PMR spectra for the new compounds were reported and assignments for some of the bands were made. It was concluded that $Ph_3Sb(acac)Cl$ and $Ph_3Sb(acac)OH$ had octahedral geometry and that for both compounds two isomers were present. In one isomer a Cl or an OH and one phenyl group were in *trans* positions, while in the other isomer two phenyl groups were *trans*. These results are in contrast to those reported by Meinema and coworkers [63] who have stated that $Ph_3Sb(acac)Cl$ exists as only one isomer.

In a study of the basicity of tertiary arsine oxides in non-aqueous media, Yakshin and coworkers [64] have compared the basicity of tri-*n*-octyl- and triphenylarsine oxides with the corresponding tri-*n*-octyl- and triphenylstibine oxides. Potentiometric titrations were carried out in nitromethane solutions using perchloric acid as the titrant. A saturated solution of LiCl in nitromethane served as a salt bridge, and the reference electrode was an AgCl electrode. It was found that there was very little change in the base properties of tri-*n*-octylstibine oxide or triphenylstibine oxide as compared with the corresponding arsine oxides. The pK_a values for the conjugate acids of tri-*n*-octylstibine oxide and triphenylstibine oxide were 16.58 and 12.76, respectively, whereas the corresponding arsine oxides gave values of 16.36 and 12.58, respectively.

Bhattacharya and Saxena [65] have studied the reaction between hexaphenyl- or hexa-*p*-tolyldilead and a number of organoantimony(V) compounds. Hexaphenyldilead reacted with triphenyl- or tri-*p*-tolylstibine sulphide with reduction of the antimony(V) compound to triphenyl- or tri-*p*-tolylstibine and the formation of bis(triphenyllead) sulfide. In a similar manner, hexa-*p*-tolyldilead underwent reaction with triphenyl or tri-*p*-tolylstibine sulfide to give bis(tri-*p*-tolyllead) sulfide and the corresponding triarylstibines. The authors suggested that the mechanism involved an insertion of a sulfur atom from the antimony(V) sulfides into the Pb-Pb bond. Triphenylstibine oxide, triphenylantimony dithiocyanate, triphenylantimony dichloride, triphenylantimony dibromide, and tri-p-tolyantimony dibromide also reacted with hexaphenyldilead, but with these organoantimony(V) compounds the lead compounds formed were tetraphenyllead and a diphenyllead derivative:

$$Ph_6Pb_2 \ + \ Ph_3SbX_2 \longrightarrow Ph_4Pb \ + \ Ph_2PbX_2 \ + \ Ph_3Sb$$

(where X = Cl, Br, NCS, or 1/2 O)

The authors suggested that the mechanism involved disproportionation of the lead compound followed by reduction of the antimony(V) species by the unstable Pb(II) compound:

$$Ph_6Pb_2 \rightleftharpoons Ph_4Pb \ + \ Ph_2Pb$$

$$Ph_2Pb \ + \ Ph_3SbX_2 \rightleftharpoons Ph_2PbX_2 \ + \ Ph_3Sb$$

No proof for either of the suggested reaction mechanisms was offered. Triorganoantimony dihalides or pseudohalides did not react with hexaphenylditin even on prolonged heating.

The compound $RSO_2N{=}SbPh_3$, where R was Ph or p-MeC_6H_4, has been found to react with several acid chlorides R'COCl, when R' was Ph, p-ClC_6H_4, or CCl_3, to give compounds of the type $[RSO_2N(COR')SbPh_3]Cl$ [66]. The reaction of $PhSO_2N{=}SbPh_3$ with Me_3SiCl or $PhCH_2Cl$ resulted in cleavage of the Sb-N bond and the formation of Ph_3SbCl_2 and $PhSO_2N(SiMe_3)_2$ or $PhSO_2N(CH_2Ph)_2$, respectively. The Sb-N bond was also cleaved when $SnCl_4$ or $GeCl_4$ (or the corresponding tetrabromides) reacted with $RSO_2N{=}SbPh_3$ to form $RSO_2N{=}SnCl_2$ or $RSO_2N{=}GeCl_2$ (or the corresponding dibromides).

Douglas [67] had previously reported a 2:2 adduct of tetracyanoethylene and triphenylphosphine and tentatively assigned a structure. Suitable crystals for X-ray crystallography, however, could not be obtained. Accordingly, an attempt was made to prepare the tetracyanoethylene adduct of triphenylstibine. The crystal structure of the resulting compound has now been reported by Breneman [68]. The compound, however, was quite different from the phosphorus compound in that it possessed the molecular formula $[Sb(C_{23}H_{15}N_3O)]_2O.1/2\ C_6H_6$ and was named μ-oxo-bis[1,1,2-tricyano-ethenoxo(triphenyl)antimony(III)] benzene (2/1). A personal communication from the author, however, indicates that the substance is an Sb(V) derivative. The crystal structure of the compound revealed that each antimony atom possessed approximately trigonal-bipyramidal geometry with an Sb-O-Sb bridge. The three phenyl groups on each Sb atom were in equatorial positions, with the bridging oxygens in axial positions. The other axial position on each antimony atom was a occupied by a $(CN)_2C{=}C(CN)O$ group. The locations of the solvent benzene molecules were also given.

The crystal structure of triphenylantimony diacetate has been determined by Sowerby [69] by means of X-ray crystallography. The molecule was a distorted trigonal bipyramid with the two acetate groups in axial positions. The O-Sb-O angle was 176.1°. There was a marked distortion of the equatorial angles. One C-Sb-C angle was 148.2°, while the planarity of the C_3Sb unit was maintained by a decrease in the other two angles to 105.9°.

In the structure of the acetate moiety the Sb-O distance between the Sb and the carbonyl oxygen was 2.779 Å, compared with a value of 3.6 Å for the sum of the appropriate van der Waals radii. The Sb-O-C(O)Me angle was 108.1° rather than the 120° expected by the author. Both of these findings were taken as evidence that intramolecular interactions between the Sb and the carbonyl oxygen were of importance.

In view of these results indicating some degree of intramolecular bonding in triphenylantimony diacetate, Sowerby investigated the crystal structure of tetraphenylantimony formate, where there is just one ligand capable of intramolecular bonding [70]. The compound was prepared by the action of formic acid on pentaphenylantimony. The IR spectrum in the solid state gave bands at 1630 and 1280 cm^{-1} which suggested that the compound might be a trigonal bipyramid with a unidentate formate group. There was very little change in this spectrum in going from a mull to a chloroform solution, suggesting but little tendency towards bidentate behavior. The trigonal-bipyramidal structure was confirmed by the X-ray crystallographic study. The formate group and one phenyl group were in axial positions. The mean (equatorial) phenyl-Sb-phenyl (axial) angle was 95.9°; the (equatorial) phenyl-Sb-O angle was 84.0°. That there was but little intramolecular interaction between the carbonyl oxygen and the Sb atom was shown by the Sb...O=C distance of 3.291 Å, a value only slightly less than the sum of the van der Waals radii.

A series of fifteen antimony dithiocarbamates and five related compounds are the subject of an ^{121}Sb Mössbauer study by Stevens and Trooster [71]. Both organoantimony(III) and organoantimony(V) compounds as well as inorganic antimony compounds were studied. The compounds included the following: $Sb(S_2CNEt_2)_{3-n}X_n$, where X = Cl, Br, or I and n = 0-3; $R_nSb(S_2CNEt_2)_{3-n}$, where R = Me or Ph and n = 1 or 2; $Sb(S_2CNBu_2)_3$; $Sb(S_2CNBu_2)_2L$, where L = 0.5 Cd_2I_6 or I_3: $Me_4Sb(S_2CNEt_2)$; and $Me_3Sb(S_2CNMe_2)_2$. Isomer shifts (δ) were expressed relative to InSb: positive shifts implied an Sb(V) compound, negative shifts an Sb(III) compound. Isomer shifts, quadrupole coupling constants, and asymmetry parameters (η) were listed in tabular form for all of the compounds studied. Five of the compounds contained Sb(V) while the other compounds were all Sb(III) compounds. On the basis of their Mössbauer spectra as well as previously determined IR spectra, structures for the various compounds were assigned. Thus, for the compounds $RSb(S_2CNEt_2)_2$ (R = Me or Ph), which have similar Mössbauer parameters, it was concluded that the antimony possessed octahedral symmetry with the inclusion of a sterically active lone pair in one of the six positions. The compound $Me_4Sb(S_2CNEt_2)$ was found to be ionic with a diethyldithiocarbamate anion. The Mössbauer spectra of the three compounds $Me_3Sb(S_2CNMe_2)_2$, $Me_3Sb(S_2PEt_2)_2$, and $Me_3Sb[S_2C_2(CN)_2]$, where $S_2C_2(CN)_2$ was maleonitriledithiolate, were similar and were assigned trigonal-bipyramidal structures.

A number of compounds of the type *p*-$FC_6H_4CO_2X$, where X = HgPh, $SnPh_3$, $PbPh_3$, $SbPh_2$, $SbPh_4$, or CPh_3, have been prepared by Nesmeyanov and coworkers [72], and their ^{19}F NMR spectra in a number of solvents have been studied. A comparison of the chemical shifts of the fluorine when measured in a solvent such as $CHCl_3$ indicated that the electron acceptor capacity of the various groups decreased in the order $Ph_3C > Ph_2Sb > Ph_3Sn > PhHg > Ph_3Pb >> Ph_4Sb$. This was taken to mean an increase in the polarity of the M-O bond in the order $Sb^{III}-O < Sn-O < Hg-O < Pb-O << Sb^{V}-O$. However, it was found that the shielding of the fluorine atom in these compounds depended not only on the various groups but also varied with the solvent. Changing from a non-polar solvent such as $CHCl_3$ or toluene to a coordinating solvent such as THF, pyridine, or DMSO had very little effect on the ^{19}F chemical shift in *p*-$FC_6H_4CO_2H$, *p*-$FC_6H_4CO_2Me$, or *p*-$FC_6H_4CO_2SbPh_4$, but did have considerable effect on the ^{19}F chemical shift of the other compounds studied. Thus, the relative shielding of the fluorine was increased from 1.1 to 3.1 ppm in all compounds of the type *p*-$FC_6H_4CO_2X$, except where X = $SbPh_4$.

In 1978 Epshtein and coworkers [73] reported on the reaction between dimethyl sulfoxide (DMSO) and *o*- and *p*-nitrophenols or certain organometallic derivatives of these nitrophenols. They demonstrated that DMSO and the phenols (or their derivatives) formed complexes which dissociated into ions without the formation of ion pairs. These authors [74] have now reported a study of *o*- and *p*-nitrothiophenol and a number of organometallic derivatives of *p*-nitrothiophenol of the type *p*-$O_2NC_6H_4SX$, where X was HgPh, $SnPh_3$, $PbPh_3$, $SbPh_2$, or $SbPh_4$. The UV spectra of the compounds in benzene solution were reported in tabular form. The bathochromic shift in the long-wave absorption bands of the UV spectra for *p*-nitrothiophenol and its organometallic derivatives was found to increase in the order H < Ph_3Sn < Ph_2Sb < Ph_3Pb < PhHg <

Ph_4Sb. The authors suggested that there was a certain parallelism between this sequence and the ^{19}F shielding in some p-fluorothiophenol derivatives also studied in this investigation or reported in previous papers [75]. The integral intensities of the absorption bands showed an even closer relationship to the ^{19}F shielding data. The ^{19}F data reflect the effect of the substituent group on the electron density distribution in the ground state of the molecule, but the electronic spectral data reflect the electron density distribution in both the ground and the excited state.

The addition of small quantities of DMSO to benzene solutions of the various compounds led to spectral changes quite similar to those produced in p-nitrophenol and its similarly substituted organometallic compounds. However, the p-nitrophenol — DMSO complexes were generally much more stable than the corresponding p-nitrothiophenol complexes. Exceptions to this generalization were the DMSO complexes with p-$O_2NC_6H_4SSbPh_4$ and p-$O_2NC_6H_4SHgPh$, which were 2 and 2.5 times stronger than the corresponding nitrophenol complexes. Conductometric data of the complexes in DMSO were reported, and conclusions as to the ionization of the various complexes were drawn. There was a marked difference between the properties of p-$O_2NC_6H_4SSbPh_2$ and p-$O_2NC_6H_4SSbPh_4$. The $SbPh_4$ group was a more active electron donor than the $SbPh_2$ group, and the Sb(V) complex was also found to dissociate into ions more readily.

In a paper devoted to organotin compounds [77], one tetraphenylstibonium salt, $[Ph_4Sb][Ph_2C_6H_{11}Sn(N_3)NCS]$ (where C_6H_{11} = cyclohexyl), has been mentioned. Analytical data, molar conductances, and some IR data on this and other tetraarylonium salts ($[Ar_4M]^+$ where M = N, As, or P) were listed in tabular form.

Tatzel and coworkers [78] have reported on the vibrational spectra of a series of anions of the type $[AlMe_4]^-$, $[GaMe_4]^-$, and $[InMe_4]^-$, in which the cation was Na^+, K^+, $[Me_4P]^+$, $[Me_4As]^+$, and $[Me_4Sb]^+$. The only antimony compound reported was $[Me_4Sb][Me_4In]$. A new procedure for the determination of force constants was reported, and a set of force constants for the tetramethyl anions of the Group III elements were obtained.

A series of tetramethylarsonium and tetramethylstibonium salts containing gallium or indium in the anion has been prepared by Widler and Weidlein [79]. The antimony compounds prepared were $[Me_4Sb]$ $[MeGaBr_3]$, $[Me_4Sb][Me_2GaBr_2]$, and $[Me_4Sb][MeInI_3]$. The IR and Raman spectra of all of the compounds were reported, and assignments of the various bands were made.

In a study of the influence of electrode material on the reduction of onium salts, Butin and coworkers [80] have reported on the use of several tetraphenylstibonium salts $[Ph_4Sb]X$, where X was BF_4, Cl, Br, or I.

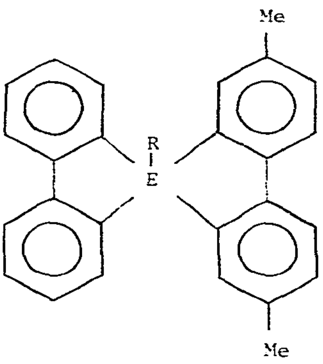
In a paper devoted to copper(II) compounds, the compound $[Ph_4Sb][CuCl_3]$ was described, together with some similar phosphonium and arsonium cuprates [81].

The interesting tin complex $[Me_4Sb]_2[Cp_4Sn]$ was obtained by the reaction between pentamethylantimony and dicyclopentadienyltin(II) [82]:

$$2\ Me_5Sb + 2\ Cp_2Sn \longrightarrow [Me_4Sb]_2[Cp_4Sn] + 1/n\ [Me_2Sn]_n$$

The elemental analysis on the product was consistent with the presence of 5% of a dimethyltin polymer. In an attempt to prepare other complexes of Sn(II) the reaction between pentamethylantimony and $SnCl_2$ was carried out in the hope of obtaining either $[Me_4Sb][MeSnCl_2]$ or $[Me_4Sb]_2[Me_2SnCl_2]$. Instead the compound obtained was $[Me_4Sb][SnCl_3]$. The compound $[Me_4Sb]_2[Cp_4Sn]$ was spontaneously inflammable in the air. Its PMR spectra revealed a ratio of approximately 1:2 for Cp:Me.

In continuation of previous work on pseudorotation in spirocyclic compounds of phosphorus, arsenic, and antimony, Hellwinkel and co-workers [83] have prepared new spirocyclic compounds of the following type:



(E = P, Sb, R = Ph; E = As, R = Ph or 2-biphenylyl)

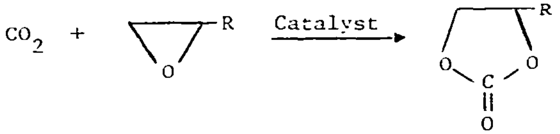
The synthesis of the four compounds was described in detail. At low temperatures in bromobenzene solution two distinct methyl signals in the PMR spectra were obtained for each compound. These signals coalesced reversibly as the temperature was raised. The temperatures for coalescence for the three compounds were P, 89°C; As, 72.5°C; Sb, 40°C. From these results the authors calculated free enthalpies of activation of 18.2, 17.2 and 15.4 kcal mol^{-1}, respectively. The ligand exchange process was interpreted as a Berry pseudorotation in which the phenyl or biphenylyl group must occupy an axial position in the transition state.

Commandeur and coworkers [84] have recently reported on the chlorination of aromatic compounds by the use of various metal chlorides. One of the most satisfactory chlorides for this purpose was $SbCl_5$. Both chlorobenzene and toluene were chlorinated by this reagent with the chlorination proceeding largely in p-position, especially in the case of chlorobenzene. In order to explain this specificity several mechanism were proposed in which p-orientation was preferred because of crowding in the o-positions. Thus, in all of the mechanisms proposed, key intermediates were compounds (or complexes) which contained C-Sb bonds. The complexes were either π-complexes or σ-complexes, the compounds were substituted arylantimony tetrachlorides. It was suggested that these complexes or compounds decomposed with rupture of a C-Sb bond and replacement of the antimony by chlorine. The authors were unable to isolate or identify by NMR or IR spectroscopy any compounds or intermediates containing C-Sb bonds in the reaction mixtures.

In a second paper [85] these same authors reported on the reaction of a number of organoantimony(V) compounds with either $SbCl_5$ or $SbCl_3 + Cl_2$. In each case the C-Sb bond was cleaved and replaced by chlorine under the reaction conditions employed.

The synthesis, by conventional reactions, of a number of organoantimony(V) compounds was reported. Many of these compounds have not been previously reported. They were characterized by elemental analysis and by PMR spectra. Among the compounds reported were $(p\text{-}ClC_6H_4)_5Sb$, $(p\text{-}MeC_6H_4)_5Sb$, $(p\text{-}ClC_6H_4)_3Sb(p\text{-}MeC_6H_4)_2$, $(p\text{-}MeC_6H_4)_3Sb(p\text{-}ClC_6H_4)_2$, and $(p\text{-}ClC_6H_4)_3SbF_2$. It was found in the halogenation reactions that the $p\text{-}ClC_6H_4\text{-}Sb$ bond was cleaved in preference to the $p\text{-}MeC_6H_4\text{-}Sb$ bond.

Organoantimony(V) compounds have been found to be effective catalysts for the reaction between epoxides and CO_2 to form ethylene carbonate derivatives [86]:



(R = H, Me, CH_2Cl, or Ph; catalyst = Ph_5Sb, Ph_4SbBr, Ph_3SbBr_2, Ph_3SbCl_2, or Me_3SbBr_2)

Catalytic activity of the organoantimony(V) compounds was superior to that of organotin compounds described in a previous paper. The reactivity of the epoxides substituted by various R groups was in the order Me > Ph > H > CH_2Cl. The yields of ethylene carbonate compounds were usually > 90%.

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