

ANTIMONY

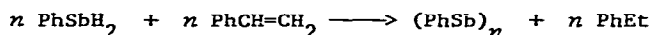
ANNUAL SURVEY COVERING THE YEAR 1976 *

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No book or critical review devoted exclusively to organoantimony chemistry was published in 1976. A review on organoarsenic, -antimony, and -bismuth compounds was included, however, in Volume 5 of The Chemical Society's *Specialist Periodical Reports* on organometallic chemistry [1], and Okawara and Matsumura [2] have published an interesting review of their work on stibines, stibine sulfides, and hexacoordinate organoantimony compounds. Information about organoantimony compounds has also been given in review articles devoted to recent work on organometallic and organometalloidal compounds [3], pentaalkyl and trialkylidene derivatives of the Group V elements [4], a comparison of selenium and tellurium ylids with those of nitrogen, phosphorus, arsenic, antimony, and bismuth [5], phosphorus, arsenic, and antimony complexes of the main group elements [6], per- and polyfluorinated derivatives of the main group elements [7], the stoichiometry, structure, stability, and thermal decomposition of organometallic compounds [8], and the chemistry of the representative elements of Group V [9]. A review on nitrogen, phosphorus, arsenic, antimony, and bismuth compounds has been included in a serial publication concerned with molecular structures by diffraction methods [10], and several organoantimony compounds that were subjected to X-ray analysis in 1974 or 1975 have been listed in Volume 7 of *Molecular Structures and Dimensions* [11]. The Czech nomenclature of organic compounds of phosphorus, arsenic, antimony, and bismuth has been described as being based on the IUPAC rules issued in 1973 [12].

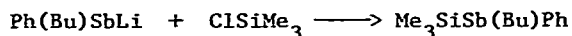
Phenylantimony, $(\text{PhSb})_n$, has been prepared by the interaction of phenylstibine and styrene in benzene [13]:



The substance crystallized from the reaction mixture as yellow-orange crystals, the analysis of which corresponded to the formula $(\text{PhSb})_6 \cdot \text{PhH}$. The same substance could also be obtained by the reaction of phenylstibine with phenylacetylene, 1,4-diphenylbutadiene, ethyl acrylate, acrylonitrile, or allylamine. Cryoscopic determination of the molecular weight of phenylantimony was prevented

* Antimony, Annual Survey covering the year 1975 see J. Organometal. Chem., 130(1977)365-403.

by its slight solubility in nonpolar solvents. Treatment of a suspension of 1 mole of phenylantimony in liquid ammonia with 2 moles of sodium resulted in a red-violet solution of disodium phenylstibide. Addition of ethyl bromide to the reaction mixture gave a colorless solution from which diethylphenylstibine and a small amount of triethylstibine could be isolated. The interaction of equivalent quantities of phenylantimony and sodium in liquid ammonia resulted in a deep-red solution of $\text{Ph}(\text{Na})\text{Sb}-\text{Sb}(\text{Na})\text{Ph}$. The latter substance reacted with ethyl bromide to give 1,2-diethyl-1,2-diphenyldistibine, $\text{Ph}(\text{Et})\text{Sb}-\text{Sb}(\text{Et})\text{Ph}$, and a small amount of diethylphenylstibine. In a similar manner, the deep-red solution reacted with 1,3-dichloropropane and 1,4-dichlorobutane to give the expected heterocyclic distibines. The cleavage of phenylantimony with butyllithium proved to be a complicated reaction that gives several stibides including lithium butylphenylstibide. The latter substance was characterized by its reaction with trimethylchlorosilane:



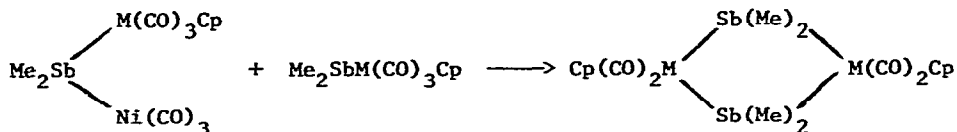
A study has been made of the high-resolution proton and ^{13}C NMR spectra of phosphabenzene, arsabenzene, and stibabenzene [14]:



(where M was P, As, or Sb)

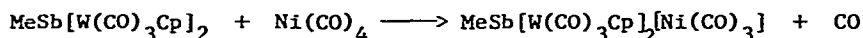
The proton spectrum of each of the three compounds consisted of an AB_2X_2 pattern in which the signal attributed to the α -protons (X_2) was downfield of the γ - $\beta(\text{AB}_2)$ multiplet. The downfield shift of the α -protons increased (relative to the protons of benzene) from 1.24 ppm for phosphabenzene to 2.31 ppm for arsabenzene and 3.57 ppm for stibabenzene. The shifts of the β - and γ -protons followed the same qualitative downfield trend, but the magnitudes of these shifts were much smaller. The observed downfield shifts were explained in terms of the diamagnetic anisotropies of the Group V elements. The ^{13}C chemical shifts of the α -carbon atoms of the three heteroaromatic compounds also occurred at very low fields, while the β -carbon atoms were only slightly deshielded (relative to benzene) and the γ -carbons had almost the same chemical shifts as benzene. The deshielding of the α -carbons increased in going from phosphabenzene to arsabenzene to stibabenzene. For stibabenzene this deshielding amounted to nearly 50 ppm relative to benzene. The diamagnetic effect of the heteroatoms was also invoked as a possible explanation of the extreme α -carbon deshielding. All of the one-bond $^{13}\text{C}-^1\text{H}$ coupling constants were close to the value of 159 Hz observed with benzene.

In another paper [17] it was reported that certain dinuclear species containing the Me_2Sb group could be converted to four-membered ring systems by the following type of reaction:



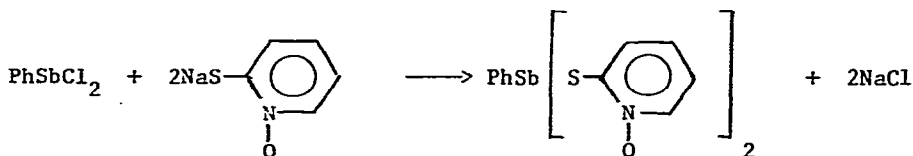
(where M was Mo or W)

The cyclic tungsten compound could also be prepared by simply warming the pure dinuclear species in methylcyclohexane. A trinuclear species in which the MeSb group was present as a bridging unit was prepared in the following manner from a tungsten compound described in an earlier paper:



Attempts to cyclize this substance were unsuccessful.

It has been claimed in a patent [18] that bis(1-oxopyridine-2-thiolato)-phenylstibine possessed excellent broad spectrum bactericidal and fungicidal activity and that it was a desirable component of soaps, shampoos, surgical scrub products, *etc.* The compound was prepared by the following reaction:



Ferricenium salts have been obtained by the reaction of a trivalent phosphorus, arsenic, antimony, or bismuth halide with ferrocene in an inert organic solvent [19]. Methylchlorostibine was one of the halides employed. Reaction times could be significantly shortened by irradiation with Pyrex-filtered sunlight. Since these reactions did not occur when oxygen was rigorously excluded, it was concluded that molecular oxygen was the electron acceptor. The composition of the anion varied with the particular halide employed and with the initial molar ratio of halide to ferrocene. In every case the anion contained a Group V element bonded to halogen, *e.g.*, BiCl_4^- . The actual composition of the ferrocenium salt obtained with methylchlorostibine was not reported.

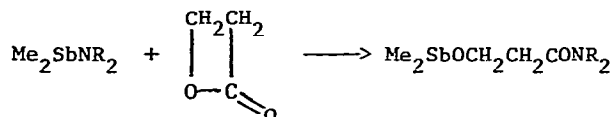
Methyldiiodostibine, dimethylbromostibine, and dimethyliodostibine have

been included in a study of the photoelectron spectra of compounds of the types MeMX_2 and Me_2MX , where M was N, P, As, or Sb and X was F, Cl, Br, or I [20]. The spectra were interpreted in terms of a "composite molecule" approach derived for C_{3v}/C_8 systems. Substituent group orbitals were classified with respect to their orientations in space, and ionization energies were then assigned. The assignments were confirmed by considering photoelectron data of the isoelectronic Me_3M and MX_3 compounds and by EHMO calculations with partial inclusion of spin orbit coupling. The authors critically discussed correlations between the photoelectron ionization energies and various molecular and atomic properties.

An improved pulsed NQR spectrometer suitable for the meter and decimeter ranges has been described and used to determine the spectra of a variety of inorganic, organic, and organometallic compounds [21]. The ^{121}Sb and ^{123}Sb NQR transition frequencies observed with diphenylchlorostibine were among the results reported. Quadrupole coupling constants and asymmetry parameters were also given.

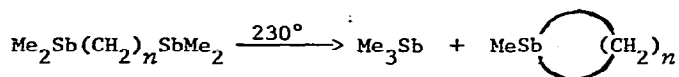
^{13}C NMR spectroscopy has been used to study the transmission of electronic effects in compounds of the type Ph_2SbX , where X was Cl, Br, O_2CMe , $\text{SC}_6\text{H}_4\text{F-p}$, or Ph [22]. The shielding of the ^{13}C nuclei *para* to X was found to increase in the order $\text{Cl} < \text{Br} < \text{O}_2\text{CMe} < \text{SC}_6\text{H}_4\text{F-p} < \text{Ph}$. It was concluded that electronic interactions through the C-Sb and Sb-X bonds were mainly of an inductive character.

A kinetic study has been made of the following type of reaction between an N,N-disubstituted aminodimethylstibine and β -propiolactone [23]:



The kinetics were found to be second order, and the reaction rate increased with increasing polarity of the solvent. The effect of the substituents on the reaction rate was explained in terms of the Taft equation, and a dipolar transition state was suggested.

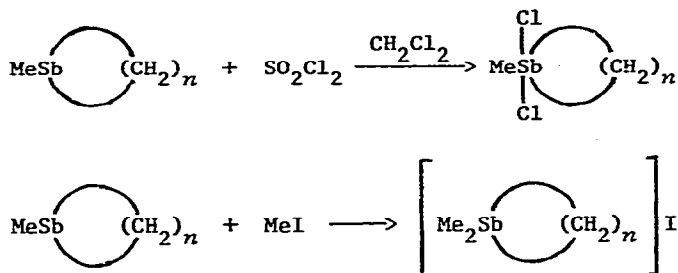
1-Methylstibolane and 1-methylantimonane have been prepared in good yields by the thermolysis of tetramethylene(dimethylstibine) and pentamethylene(dimethylstibine), respectively [24]:



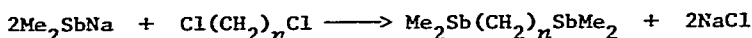
(where n was 4 or 5)

Attempts to extend this method to the synthesis of four- or seven-membered rings resulted in intermolecular disproportionation and the formation of trimethylstibine and polymeric material. The heterocyclic stibines obtained in

this study were not analyzed as such but were converted into the corresponding antimony(V) dichlorides or were quaternized with methyl iodide:

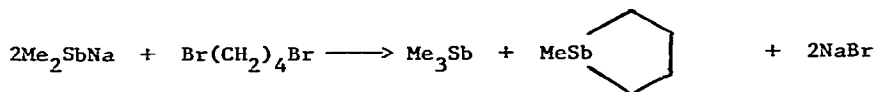


The quaternary antimony compounds were quite soluble in water and were described as being "salt-like in nature". All the di-tertiary stibines that were subjected to thermolysis could be prepared by the reaction of sodium dimethylstibide with α,ω -dichloroalkanes in liquid ammonia:



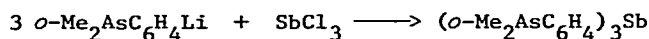
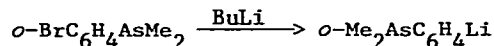
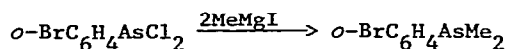
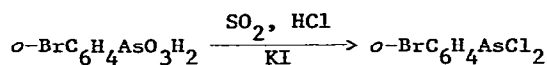
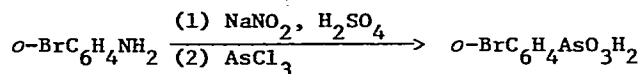
(where n was 3, 4, 5, or 6)

Replacement of the dichloroalkanes by the corresponding dibromoalkanes gave nearly quantitative yields of di-tertiary stibines when n was 3 or 6. For $n = 4$, however, the reaction took a different course and gave mainly 1-methylstibolane and trimethylstibine:



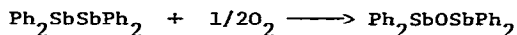
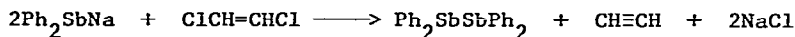
The interaction of sodium dimethylstibide and 1,5-dibromopentane in liquid ammonia gave about 30-40% of cyclic reaction product, *i.e.*, 1-methylantimonane. The main product was the expected di-tertiary stibine. The IR spectra of the heterocyclic stibines exhibited a characteristic absorption in the 460-470 cm^{-1} region. This band was assigned to ring skeletal vibrations. The antimonane derivatives showed two bands in the 900-920 and 980-1010 cm^{-1} region that were not observed in the spectra of the stibolane derivatives. All of the antimony compounds showed bands in the 500-600 cm^{-1} region that were assigned to asymmetric and symmetric Sb-C stretching vibrations. The antimony(V) dichlorides exhibited a broad absorption band at 270-280 cm^{-1} that was assigned to ν_{asym} (Sb-Cl) and suggested a *trans* arrangement of the two chlorine atoms.

A detailed description of the preparation of the quadridentate ligand tris(*o*-dimethylarsinophenyl)stibine has been published [25]. The following sequence of reactions was employed:

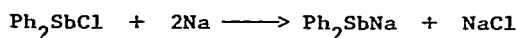


The tertiary stibine thus prepared was a white solid, mp 135°, that showed a single methyl resonance at τ 8.80 in the PMR spectrum

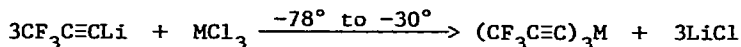
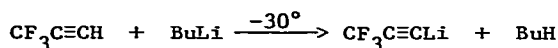
The reaction of sodium diphenylstibide with either *cis*- or *trans*-1,2-dichloroethene has been found to yield oxybis(diphenylantimony), evidently formed by oxidation of tetraphenyldistibine [26]. The following reaction sequence was suggested:



Varying the mode of addition (*i.e.*, adding the stibide to the dichloroethene or *vice versa*) or the solvent (*i.e.*, neat liquid ammonia or a mixture of ammonia and THF) did not change the product, and in no case was evidence for the formation of either *cis*- or *trans*-vinylenebis(diphenylstibine) obtained. The sodium diphenylstibide used in this study was prepared by the interaction of diphenylchlorostibine and sodium in liquid ammonia at -33°:



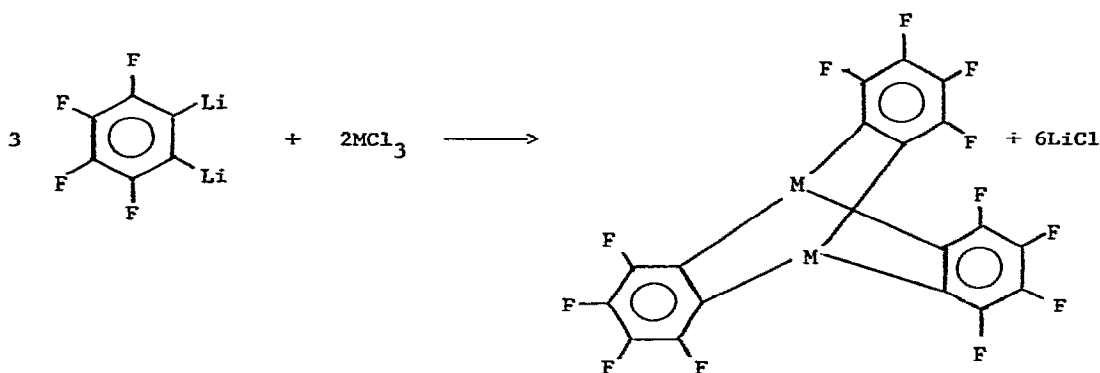
Trifluoropropynyl derivatives of phosphorus, arsenic, and antimony have been prepared by the following procedure [27]:



(where M was P, As, or Sb)

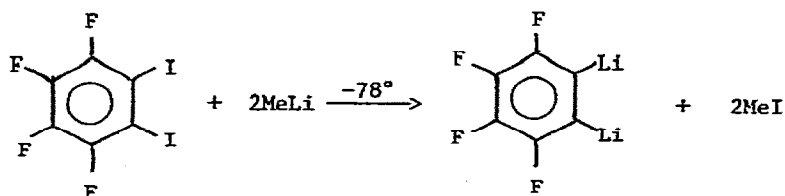
The tertiary stibine was a colorless compound that melted at 55–56° with decomposition or polymerization. It was stable at liquid nitrogen temperature for many months. The mass spectra of the phosphine, arsine, and stibine were determined, and fragmentation pathways were proposed. The strongest peak in all three spectra was attributed to the $[\text{CF}_3\text{C}\equiv\text{CC}\equiv\text{CCF}_2]^+$ rearrangement ion. The $[\text{CF}_3]^+$ ion was also observed in the three spectra and was undoubtedly formed by numerous pathways. All three compounds apparently lost a trifluoropropynyl radical from the molecular ion to yield the $[(\text{CF}_3\text{C}\equiv\text{C})_2\text{M}]^+$ ion and lost another such radical to give the $[\text{CF}_3\text{C}\equiv\text{CM}]^+$ ion. Loss of the remaining trifluoropropynyl radical to give As^+ or Sb^+ was observed for the arsine and stibine. One of the peaks exhibited by the three spectra was attributed to the $[\text{C}_9\text{F}_7]^+$ rearrangement ion, formed by loss of P, As, or Sb and 2F from the molecular ion. Strong fragmentation peaks of $[\text{C}_9\text{F}_7]^+$ were also observed in the spectra of the three compounds.

Perfluorinated arsenic, antimony, and bismuth analogs of triptycene have been prepared in good yields by the following reaction [28]:



(where M was As, Sb, or Bi)

The dilithio derivative used in the above reactions was obtained by the interaction of 1,2-diiodotetrafluorobenzene and methyllithium:

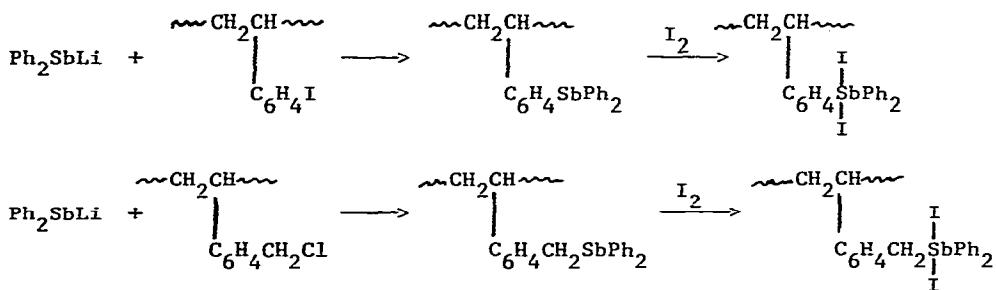


The ^{19}F NMR spectra of the triptycene analogs exhibited two signals of equal area.

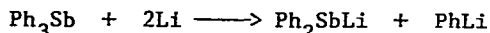
The arsa- and stibatriptycenes discussed in the above paragraph have been obtained in 13% and 12% yields, respectively, by the direct reaction of 1,2-diodotetrafluorobenzene with elemental arsenic or antimony at 300° [29]. The molecular weights of the products were determined by mass spectrometry. The presence of two antimony isotopes helped to establish the identity of the parent ion of the stibatriptycene as $\text{C}_{18}\text{F}_{12}\text{Sb}_2^+$; other prominent peaks in the mass spectrum were attributed to the $(\text{C}_6\text{F}_4)_2\text{Sb}^+$, $\text{C}_6\text{F}_4\text{Sb}^+$, SbF_2^+ , SbF^+ , and Sb^+ ions. X-ray powder diffraction studies showed that the arsa- and stibatriptycenes were isostructural. The two compounds were also characterized by IR and ^{19}F NMR spectroscopy. An attempt to synthesize a mixed arsa-stibatriptycene by heating a mixture of arsenic and antimony with 1,2-diodotetrafluorobenzene at 300° for three days gave only the arsatriptycene.

The preparation of triphenylstibine has been described in a Czechoslovakian patent [30]. Phenylmagnesium chloride was first obtained by heating chlorobenzene with magnesium shavings at $140\text{--}160^\circ$ in the presence of bromobenzene, iodine, and anisole or phenetole. The resulting solution was then refluxed with antimony trichloride and finally treated with aqueous acetic acid or ammonium chloride. The anisole or phenetole was then removed from the organic layer by distillation, and the triphenylstibine recovered in 61-68% yield.

Antimony-containing ion exchange resins have been used for the selective uptake of fluoride ion from acidic solutions [31]. The resins were prepared by the reaction of iodopolystyrene or chloromethylated polystyrene with lithium diphenylstibide and subsequent oxidation to antimony(V) diiodide derivatives:



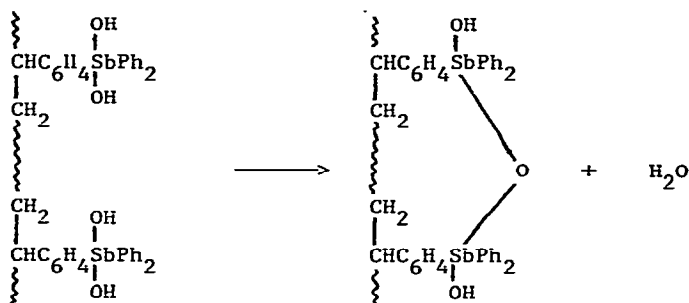
The lithium diphenylstibide was obtained by the lithium cleavage of triphenylstibine in THF:



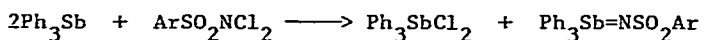
The phenyllithium was removed from the THF solution by precipitating it as pentaphenylantimony with triphenylantimony dibromide:



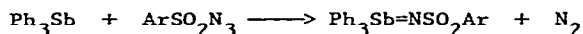
Unfortunately, only the antimony-containing resins of low exchange capacity were found to be stable on regeneration. The resins with moderate capacity underwent a rapid decrease in their capacity after a number of regenerations. This loss of exchange capacity was attributed to the formation of oxygen bridges between antimony atoms:



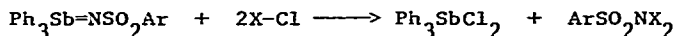
The oxidation of triphenylstibine with *N,N*-dichloroarenesulfonamides has been found to yield triphenylantimony dichloride and a triphenylstibine imide [32]:



The imides were also obtained by the interaction of triphenylstibine and an arenesulfonyl azide:

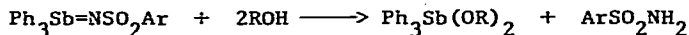


The antimony-nitrogen bonds of the imides were readily split by hydrogen chloride or chlorine:



(where X was H or Cl)

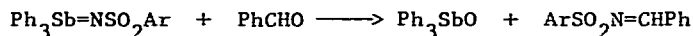
The imides did not react with unsubstituted alcohols but were readily cleaved by fluorinated alcohols or phenols:



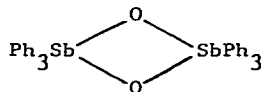
(where R was $\text{CHF}_2(\text{CF}_2)_5\text{CH}_2$ or Ar)

Although the imides in which Ar was *p*-ClC₆H₄, *p*-BrC₆H₄, or *p*-O₂NC₆H₄ were

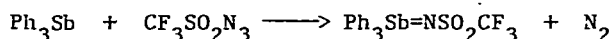
unaffected by benzaldehyde, the imides in which Ar was Ph or *p*-MeC₆H₄ reacted readily:



The triphenylstibine oxide formed in this reaction melted at 220–221° and crystallized readily from benzene. Its molecular weight determined ebullioscopically in benzene or dichloroethane proved to be twice the formula weight. The following structure was suggested:



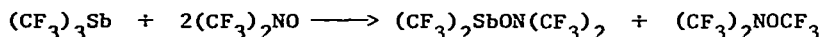
In a paper largely devoted to the oxidative imination of phosphorus(III) compounds, the reaction of triphenylstibine with trifluoromethanesulfonyl azide has been briefly described [33]:



The reaction occurred rapidly at 20° in petroleum ether and gave a quantitative yield of the stibine imide. In contrast to these results, neither triphenylarsine nor the trihalides of arsenic and antimony reacted with the sulfonyl azide.

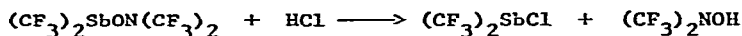
In a paper devoted to oxidative-addition reactions of the compounds Ph₃M, where M = N, P, As, Sb or Bi, Glidewell [34] has described the reaction of Ph₃Sb with S₂Cl₂, SCl₂, SeO₂, and Pb(OAc)₄. Both S₂Cl₂ and SCl₂ reacted with Ph₃Sb to give Ph₃SbCl₂. This was in contrast to Ph₃As and Ph₃P where the corresponding sulfides Ph₃AsS and Ph₃PS were formed. Ph₃Sb(OAc)₂, prepared from Ph₃Sb and Pb(OAc)₄, was hydrolysed to Ph₃Sb(OH)₂. The reaction of Ph₃Sb with SeO₂ also gave Ph₃Sb(OH)₂. This latter result was in contrast to the work of some earlier investigators who reported the formation of Ph₃SbSe. The mass spectrum of Ph₃Sb (as well as Ph₃N, Ph₃P, Ph₃As, and Ph₃Bi) and the mass spectra of Ph₃SbS, Ph₃Sb(OH)₂, and Ph₃Sb(OAc)₂ were reported.

The interaction of one mole of tris(trifluoromethyl)stibine and two moles of bis(trifluoromethyl)nitroxyl has been found to proceed smoothly at -74° according to the following equation [35]:

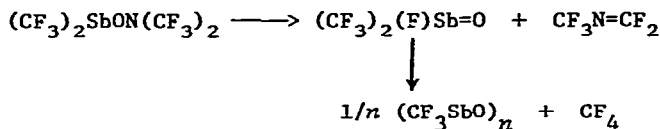


The nitroxystibine thus obtained reacted with anhydrous hydrogen chloride to

give a quantitative yield of bis(trifluoromethyl)hydroxylamine:

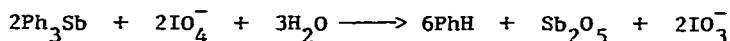


On standing at room temperature, the nitroxystibine decomposed to yield volatile products and an intractable, non-sublimable solid that probably contained CF_3 -Sb bonds. The following mode of decomposition was suggested:



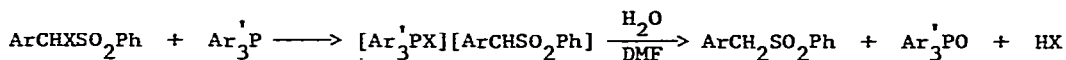
The gas-phase infrared spectrum of the nitroxystibine was studied and compared with the spectra of the corresponding phosphorus and arsenic compounds.

A new iodimetric procedure for the micro- or submicro-determination of antimony(III) in antibilharzial compounds has been shown to be applicable to triphenylstibine [36]. The method was based on oxidation of the sample with an excess of periodate in an acetate buffer, masking of the unreacted periodate with molybdate, and finally titration of the iodate that was released. The reaction between triphenylstibine and periodate was found to obey the following stoichiometry:



The method was simple, highly sensitive, and rapid (about 10 minutes per determination).

Triphenylarsine and triphenylstibine have been included in a study of the reaction of triarylphosphines with α -halo sulfones [37]:

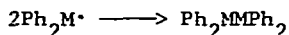
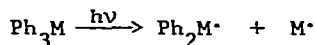


(where X was Cl, Br, or I)

Triphenylphosphine was found to react more than a thousand times as fast as the arsine or stibine. In fact, the rates of the arsine and stibine reactions were too slow to measure, and no evidence that they actually occurred was obtained.

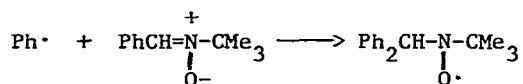
The irradiation of isopentane solutions of triphenylarsine, -stibine, and -bismuthine with UV light ($\lambda = 250$ nm) at 300 K has been found to lead to the appearance of a new band in the electronic spectra of these compounds: at 295 nm for the arsine, 320 nm for the stibine, and 360 nm for the bismuthine [38].

It was suggested that the new absorption band should be assigned to dimers of $\text{Ph}_2\text{M}^\cdot$ radicals formed by photolysis:



(where M was As, Sb, or Bi)

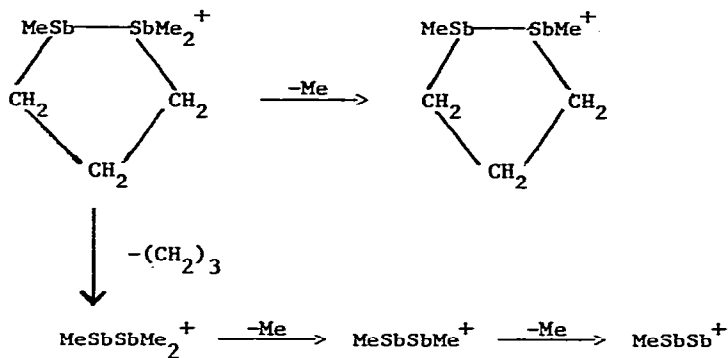
Direct observation of the radicals initially formed was difficult because of their short lifetimes. Accordingly, *N*-(*tert*-butyl)- α -phenylnitrone was used to trap the phenyl radicals produced during the irradiation:



The nitroxide thus formed was relatively stable, and its structure was unambiguously determined by ESR measurements. By means of the trapping technique it was shown that the quantum yield of radicals formed in the photolysis was 0.05 for the arsine, 0.1 for the stibine, and 0.15 for the bismuthine.

An experimental and theoretical investigation of the electronic spectra of a number of triarylamines, -phosphines, -arsines, -stibines, and -bismuthines has shown that an increase in the atomic number of the heteroatom was accompanied by an increase in the energy of the lowest singlet and triplet excited levels of the compound [39]. This result appeared to be consistent with a quantum-mechanical model that included the mixing of the electronic states of the aromatic system with states involving the *s* and *p* orbitals of the heteroatom. As the temperature was varied in the 77–300 K range, it was found that there were changes in the positions and intensities of the absorption bands. These changes were attributed to changes in the angles of rotation of the aryl rings.

A description of the mass spectrum of trimethylenebis(dimethylstibine) has been included in a paper devoted to the mass spectra of seven bidentate and two tridentate ligands containing phosphorus, arsenic, or antimony [40]. The di-tertiary stibine did not exhibit a molecular ion in its mass spectrum; the heaviest fragment observed corresponded to the loss of one methyl group. It was suggested that the loss of this methyl group was followed by the formation of a cyclic species, which fragmented according to the following scheme:



An important fragmentation pathway of the di-tertiary stibine involved the loss of Me_2Sb^+ ; indeed, the base peak of the spectrum corresponded to this fragment. The presence of $\text{C}_3\text{H}_9\text{Sb}^+$ ions in the spectrum suggested that methyl groups could migrate from one antimony atom to the other.

The dipole moments of triphenylstibine, tri-*p*-tolylstibine, tetraphenylantimony chloride, tri-*p*-tolylantimony dichloride, and compounds of the type Ph_3SbX_2 (where X was F, Cl, Br, or I) have been determined and correlated with structure [41].

By using the rigid-rotor harmonic oscillator approximation and by assuming ideal gas behavior, a group of Russian investigators [42] has calculated the thermodynamic functions S_T° , C_{pT} , $(H_T - H_{298})/T$, and $(G_T - H_{298})/T$ for trimethylstibine in the temperature range 298.15–1000 K.

New laser transitions at 24 wavelengths between 1.152 and 12.02 μ have been observed with nine metal atoms including antimony [43]. Pulsed discharges were employed to produce the metal atoms by dissociation of metal halides, hydrides, or alkyls. The antimony compound used in this investigation was trimethylstibine.

The ^{60}Co -radiolysis of benzene in the presence of 1×10^{-2} M triphenylstibine has been found to yield cyclohexane and a much smaller quantity of hexane [44]. Radiolysis of cyclohexane containing the same amount of the stibine gave methylcyclopentane plus negligible quantities of pentanes, hexanes, 1-hexene, benzene, and cyclohexene. In mixtures of benzene and cyclohexane containing the stibine, the main product was again methylcyclopentane. When no stibine was added, the main product of the irradiation of mixtures of benzene and cyclohexane was 1-hexene, although some methylcyclopentane was also formed. The results obtained in this investigation were used to deduce possible mechanisms for the formation of the observed products of the radiolysis experiments.

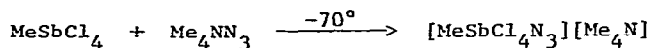
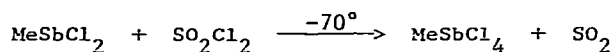
In the presence of a suitable catalyst, the condensation of isoprene and methyl acrylate has been found to give a 70% yield of a mixture of the *cis* and *trans* isomers of methyl 6-methyl-2,5-heptadienoate [45]. The catalyst system employed contained cobalt(II) acetylacetonate, an organoaluminum reducing agent, and an electron-donating modifier such as triphenylphosphine, triphenylstibine,

or triphenoxystibine. When triphenylstibine was used as the modifier, about a 20% yield of the conjugated ester, methyl *trans*-6-methyl-3,5-heptadienoate, was also obtained.

A Japanese patent [46] has claimed that the addition of tertiary phosphines, arsines, or stibines stabilized the rhodium catalysts used in the manufacture of aldehydes and alcohols from olefins. A photographic UV-sensitive recording material that contained triphenylstibine has been described in a German patent [47].

Tertiary stibines have continued to be popular as ligands in transition metal complexes. The metals coordinated to the antimony in these complexes included chromium [48-50], cobalt [51, 52], copper [53], iron [54, 55], manganese [56, 57], mercury [58], molybdenum [59, 60], nickel [61-63], osmium [64], palladium [62, 65-68], platinum [62, 66, 67, 69, 70], rhodium [67, 71], ruthenium [72], and vanadium [73]. Like other compounds of relatively weak donor capacity, triphenylstibine has been found not to react with bis(acetylacetonatotricarbonylrhenium) [74].

Dehnicke and Nadler [75] have prepared the inorganic antimony compounds $[\text{Cl}_5\text{SbXSbCl}_5][\text{NH}_4]$, where X is F or CN, by the reaction between SbCl_5 and NH_4F or NH_4CN , respectively. They also prepared the organoantimony compound $[\text{MeSbCl}_4\text{N}_3][\text{NMe}_4]$ by the following series of reactions:



The intermediate MeSbCl_4 was not isolated, and the reaction was carried out in CH_2Cl_2 solution. The IR and Raman spectra of the compound were reported, and the possible structure of the anion (C_{2v} or C_s symmetry) was discussed.

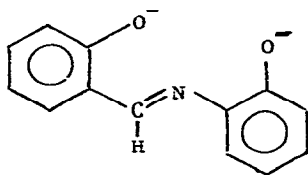
Dehnicke and Nadler [76] have examined the IR and Raman spectra of Me_2SbCl_3 both in solution (CH_2Cl_2 , CHCl_3 and C_6H_6) and in the solid state. On the basis of their results they have concluded that the compound possessed trigonal-bipyramidal geometry (C_{2v}) in solution with two equatorial methyl groups, but was dimeric in the solid state with bridging chlorine atoms and with the methyl groups *trans* to each other.

The results obtained from the IR and Raman spectra were then extended in another paper [77] to the ^{121}Sb -Mössbauer spectra of Me_2SbCl_3 and a series of related organo- and inorganic antimony compounds. The conclusion based on the IR and Raman spectra that Me_2SbCl_3 was dimeric with bridging chlorine atoms was confirmed by the Mössbauer spectrum. All but one of the remaining compounds were also found to be dimeric with F, CN, NCO, and N_3 groups bridging the antimony atoms. Only the compound $[\text{Me}_4\text{N}][\text{MeSbCl}_4\text{N}_3]$ was found to be monomeric.

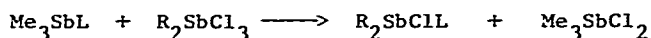
Yagupol'skii and coworkers [78] have prepared a series of aromatic organo-

antimony(V) fluorides from the corresponding oxy compounds and sulfur tetrafluoride. The reactions were carried out under extremely mild conditions, and large yields of the fluoro compounds were obtained. Thus, a 98% yield of Ph_2SbF_3 was obtained by passing SF_4 through a suspension of diphenylstibinic acid in methylene chloride at -10° . Tetrafluorophenylantimony was obtained as a complex $\text{PhSbF}_4 \cdot \text{SF}_4$, but the SF_4 was readily removed by heating *in vacuo*. Either triphenylstibine oxide or triphenylbis(trifluoroacetoxy)antimony underwent reaction with SF_4 to give difluorotriphenylantimony. Both trifluorodiphenylantimony and tetrafluorophenylantimony underwent reaction with phenylmagnesium bromide to yield pentaphenylantimony. The reaction between either diphenyltrifluoroantimony or triphenyldifluoroantimony and boron trichloride replaced the fluorines on antimony with chlorines.

In continuation of previous work on octahedral six-covalent complexes of antimony Meinema, Noltes, and coworkers [79] have now reported on the preparation and spectral properties of a series of organoantimony compounds of the type R_2SbClL , where R was Ph or Me and L was a tridentate ligand containing two donor oxygen atoms and a donor nitrogen atom of the Schiff-base type. For example, in the compound Me_2SbClL , L^{2-} possessed the following structure:



These compounds were prepared by the metathetical reaction:



IR and PMR spectral data for the compounds were given and correlated with the assigned structures. The compounds were postulated to contain octahedral geometry with linear Me-Sb-Me or Ph-Sb-Ph bonds. Several tin complexes of similar structure were also prepared.

A series of compounds of the type $[\text{Ph}_2\text{SbX}_4][\text{Ph}_4\text{As}]$ and $[\text{Ph}_2\text{SbCl}_3\text{Y}][\text{Ph}_4\text{As}]$, where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{N}_3$ and NCS and where $\text{Y} = \text{Br}$ or N_3 , have been prepared by Bertazzi [80]. The syntheses were relatively straight-forward. For example, the $[\text{Ph}_2\text{SbF}_4]^-$ and $[\text{Ph}_2\text{SbBr}_4]^-$ salts were obtained from $\text{Ph}_2\text{SbCl}_3 \cdot \text{H}_2\text{O}$ and the stoichiometric amount of Ph_4AsCl in a solution of HF or HBr in MeOH . In a somewhat similar manner $\text{Ph}_2\text{SbCl}_3 \cdot \text{H}_2\text{O}$, Ph_4AsCl , and NaN_3 or KNCS in MeOH gave the $[\text{Ph}_2\text{Sb}(\text{N}_3)_4]^-$ and $[\text{Ph}_2\text{Sb}(\text{NCS})_4]^-$ salts. Both IR and Raman spectra of the salts were given and assignments of the various bands were made.

Bertazzi and coworkers [80a] have reported the ^{121}Sb Mössbauer spectra of a large series of six-coordinate antimonate(V) anions of the type $[\text{PhSbX}_5]^-$, where X = F, Cl, or Br, and $[\text{Ph}_2\text{SbX}_4]^-$, where X = F, Cl, Br, N_3 , or NCS. Mixed anions such as $[\text{Ph}_2\text{SbCl}_3(\text{N}_3)]^-$ and $[\text{Ph}_2\text{SbCl}_3(\text{NCS})]^-$ were also studied. In each case the cation was NH_4^+ , NMe_4^+ or Ph_4As^+ . Several methyl-containing anions $[\text{Me}_2\text{SbCl}_4]^-$ and $[\text{Me}_2\text{SbF}_4]^-$ were also included as well as the compound Me_2SbCl_3 .

From the Mössbauer data obtained conclusions were drawn concerning the structure and chemical bonding in the compounds under discussion. From the spectrum of Me_2SbCl_3 it was concluded that this compound probably was hexacoordinate in the solid state with bridging chlorine bonds and *trans* organic groups.

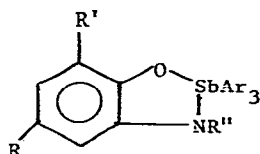
Bowen and Long [81] have reported on antimony(V) orbital populations as determined by antimony-121 Mössbauer data. Both inorganic antimony halides and such organic halides as R_2SbX_3 , R_3SbX_2 and R_4SbX , where R was an alkyl or aryl group and X was either bromine or chlorine, were included in this study. The electron population along the Sb-R bond, σ_{R} , tended to increase as the number of electronegative groups attached to antimony increased. The 5s character of the apical bonds in the trigonal bipyramidal molecules R_3SbX_2 and R_4SbX was appreciable but varied only slightly among the different compounds studied. Since X-ray studies on the molecule Ph_2SbCl_3 have shown that this compound is a dimer with bridging Cl atoms and possesses octahedral geometry, the Mössbauer isomer shifts (δ) and quadrupole coupling constants (e^2qQ) were interpreted in the light of this geometry. Two other compounds, $(p\text{-CH}_3\text{C}_6\text{H}_4)\text{PhSbCl}_3$ and $(p\text{-FC}_6\text{H}_4)\text{-PhSbCl}_3$ have similar isomer shifts and coupling constants and accordingly probably also possess similar octahedral geometry. The major advantage of the analysis described in this paper is that it enables a combination of both isomer shifts and quadrupole coupling constant data to be used to obtain parameters of chemical interest for comparison among the different geometries.

In a paper devoted to Mössbauer quadrupole splitting in five-coordinate organotin compounds, Bancroft and coworkers [82] have noted that partial quadrupole splitting constants for five-coordinate antimony compounds were 6.76 times the quadrupole splitting of the corresponding isoelectronic tin compounds. They then calculated the partial quadrupole splitting for a series of ligands attached to antimony and compared them with values found in the chemical literature. From these results they have calculated the quadrupole coupling constants for a number of known organoantimony compounds whose quadrupole coupling constants are known. For compounds of the type R_3SbL_2 (where L is an atom or group such as halogen, NO_3 , alkyl, aryl, or other such group) the agreement is excellent, but with compounds of the type Ph_4SbL the calculated values consistently were greater than the magnitude of the observed coupling constants. The reason for this discrepancy was the subject of some speculation.

Ebina and coworkers [83] have reported on a series of triarylantimony complexes formed from dibromotriarylantimony(V) compounds and certain diketones.

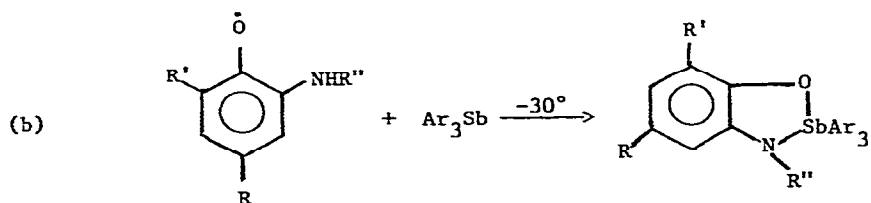
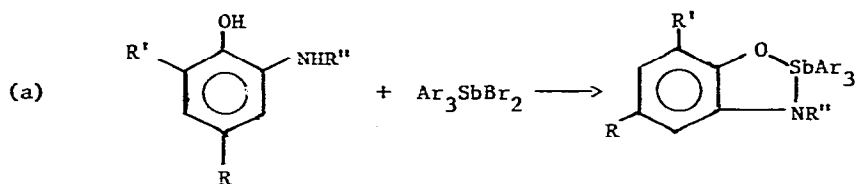
The two diketones used were 1,1,1-trifluoropentane-2,4-dione and 4,4,4-trifluoro-1-phenylbutane-1,3-dione. They reacted with the triarylantimony compounds Ar_3SbBr_2 ($\text{Ar} = \text{Ph}$ or $p\text{-ClC}_6\text{H}_4$) to form oxygen-bridged enol-type β -diketone complexes of the type $(\text{Ar}_3\text{SbL})_2\text{O}$, where $\text{HL} = \beta$ -diketone. However, when these complexes were boiled for several hours in a moist organic solvent, or allowed to stand for several days in the same solvent, complexes of a β -diketone hydrate were obtained. These were formulated as $\text{Ar}_3\text{Sb}[\text{CF}_3\text{C}(\text{O})_2\text{CH}_2\text{COR}]$ and contained three oxygen links to the antimony atom, two from the *gem*-diol and one from the carbonyl oxygen. An X-ray crystal structure of one of the compounds showed it to possess a deformed octahedral geometry.

A series of 2,3-dihydro-1,3,2 λ^5 -benzoxazastiboles have been prepared and their reactions studied [84]:

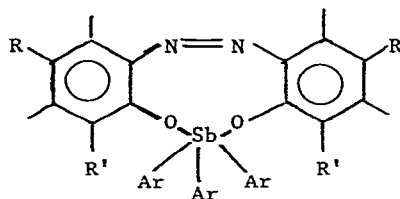


(where R and R' were alkyl groups, and Ar was phenyl, a substituted phenyl, or C_6D_5)

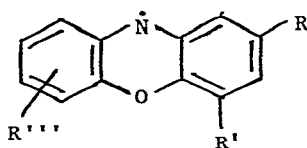
In all but one case (where R'' was ethyl) R'' was hydrogen. The compounds were prepared either from the aminophenol and a triaryldibromoantimony or from an aminoaroxyl and a tertiary stibine. These two reactions are illustrated in the following equations:



In the above reaction (b), the temperature must be kept at -30° or below, or the product obtained is the following azo compound:



This product was also synthesized by reaction (a). It was cleaved by mineral acids to give an antimony-free azo compound through cleavage of the two Sb-O bonds to yield hydroxyl groups. Under oxidative conditions the stiboles were cleaved to form phenoxazinyl radicals which were studied by means of their ESR spectra. Thus when lead dioxide was added to a solution of the oxastiboles and warmed to 100° in an ESR tube, the ESR spectrum of the resulting solution was believed to contain the following type of radical:

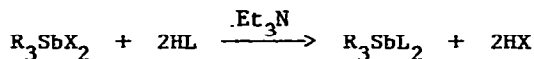


(where an Ar group originally linked to Sb became the aromatic ring containing the R''' group)

Dahlmann and Winsel [85] have reported on the kinetics of the decomposition of the two peroxides $\text{Ph}_3\text{Sb}(\text{X})\text{O} - \text{OSb}(\text{X})\text{Ph}_3$, where X was bromine or chlorine. The rate of decomposition was followed by means of UV spectral methods. The organic product of the decomposition was $\text{Ph}_3\text{Sb}(\text{X})\text{OSb}(\text{X})\text{Ph}_3$ and the bromine compound was shown to yield singlet oxygen during the decomposition. A mechanism for the decomposition reaction was suggested.

The crystal structure of bis(isocyanato)triphenylantimony has been reported by Ferguson and coworkers [86]. The molecule is a trigonal bipyramid with three equatorial phenyl groups and two axial isocyanato groups, and the isocyanato groups are bonded to the antimony through nitrogen atoms.

A series of pentavalent antimony (and bismuth) compounds have been prepared by the metathetical reaction between trialkyl- or triarylantimony (or bismuth) dihalides and carboxylic acids or phenols [87]:



(where X = Cl or Br and HL = carboxylic acid or a phenol)

Properties of the resulting complexes were studied by IR and NMR spectra. Where phenols or aryl carboxylic acids were used, the chemical shifts of the aryl protons were influenced not only by the inductive effect of the anion but also by the magnetic anisotropic effect of the benzene ring.

It has previously been concluded by several groups of workers that penta-covalent antimony compounds of the type $R_3SbX(OH)$ do not exist as such but rather form oxides of the type $(R_3SbX)_2O$. In the present paper Kawasaki [88] has prepared a series of compounds of the type $R_3Sb(L)OH$, where R = Me, Ph, or *p*-MeC₆H₄, and L = the oxinato, 3-methyloxinato, or 5-chlorooxinato group. In these compounds it seems certain that the antimony atom was hexacoordinate as judged by UV, IR, and PMR data.

Laskorin and coworkers [89] have calculated overlap integrals for a series of compounds RR'R'MX, where M was N, As, or Sb and X was O or S. The dependence of the sum of the overlap integrals along the bonds of the heteroatoms with the immediate environment was shown graphically.

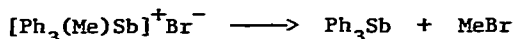
The reproducibility, sensitivity, and speed of response of ion-selective solid-membrane electrodes prepared from a mixture of Ph_3SbCl_2 , graphite, and paraffin have been studied [90]. The optimum pH range of the electrode response and a list of interfering anions were given.

The effect of halogen on the kinetics of isotopic exchange in the system $Ph_3Sb-Ph_3SbCl_2$ in 1-propanol has been studied by means of ¹²⁵Sb labelling [91].

The interfacial copolymerization of 1,1'-cobalticiniumdicarboxylic acid hexafluorophosphate and Ph_3SbCl_2 in 0.5 N NaOH gave a 50-90% yield of a copolymer [92]. Some properties of the copolymer were described.

Bordner and coworkers [93] have reported on the crystal structure of fluoro(methyl)triphenylantimony, $Ph_3(Me)SbF$, as determined by X-ray diffraction. The molecule is a trigonal bipyramid with one axial and two equatorial phenyl groups. The methyl group is equatorial and the fluorine axial.

Parris, Long, and coworkers [94] have observed that the electrical conductance of $Ph_3(Me)SbBr$ in acetonitrile decreased slowly with time and that in aged solutions in acetonitrile there were not only ¹H NMR signals for the starting compound, but also signals for MeBr and Ph_3Sb . The compound in solution was obviously decomposing according to the equation:



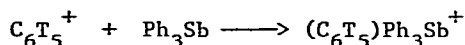
The authors were able to follow the decomposition kinetically and found that it obeyed a second-order rate law:

$$\text{rate} = k^{\circ} \alpha^2 C^2 \frac{\gamma_A \gamma_B}{\gamma_{\ddagger}}$$

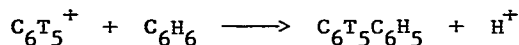
where k° was the rate constant, α the degree of dissociation of the salt at concentration C and γ_A , γ_B and γ_{\ddagger} were the activity coefficients of the ions (A, B) and the transition state (\ddagger). Preparation of the new compound $\text{Ph}_3(\text{Me})\text{SbBr}$ was described, and elemental analyses were given.

The crystal structure, as determined by X-ray diffraction, of the two compounds $[\text{Me}_4\text{M}][\text{MeInCl}_3]$, where $\text{M} = \text{As}$ or Sb , has been determined [95]. Both the cations and the anion were tetrahedral, although the latter was distorted. Both Sb-C distances and C-Sb-C angles were given. The anions and cations were found to form double layers in the crystal.

In continuation of previous work in the field of tritiated phenyl derivatives, Nefedov and coworkers [96] have studied the reaction of tritiated phenyl cations, formed by the β -decay of tritium in C_6T_6 , with aryl derivatives of Sb, Te, and I. In the case of Ph_3Sb a 73% yield of $(\text{C}_6\text{T}_5)\text{Ph}_3\text{Sb}^+$ was formed by the reaction:



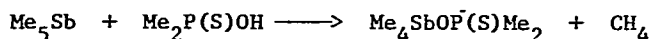
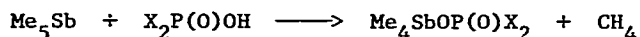
In a second reaction tritium labelled biphenyl was formed:



In a paper devoted to the conductivity of onium compounds in organic solvents Tsentovskii and coworkers [97] reported that, in contrast to tributylarsine, tributylstibine did not react with butyl halides to form quaternary halides.

Shah [98] has reported on the preparation of several arsine and stibine imides of the type $\text{Ph}_3\text{M}=\text{NSO}_2\text{C}_6\text{H}_4\text{R}-p$ and their activity against several pathogenic microorganisms including *Plasmodium berghei*. Their toxicity in mice was also determined. The three antimony compounds prepared and tested were $\text{Ph}_3\text{Sb}=\text{NC}_6\text{H}_4\text{R}-p$, where $\text{R} = \text{H}, \text{Me}, \text{or Et}$.

Compounds of the type $\text{Me}_4\text{SbOP}(\text{O})\text{X}_2$ (where $\text{X} = \text{Cl}, \text{F}, \text{H}, \text{or Me}$) as well as the compound $\text{Me}_4\text{SbOP}(\text{S})\text{Me}_2$ have been prepared by the reaction between pentamethylantimony and the appropriate phosphorus compounds [99]:

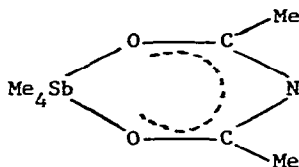


IR, Raman, ^1H , ^{31}P and, in the case of $\text{Me}_4\text{SbOP}(\text{O})\text{F}_2$, ^{19}F NMR spectra were ob-

tained. It was concluded that in the cases where $X = \text{Cl}, \text{F},$ or H the compounds were ionic with a slightly distorted tetrahedral structure. With $\text{Me}_4\text{SbOP}(\text{O})\text{Me}_2$ and $\text{Me}_4\text{SbOP}(\text{S})\text{Me}_2$, however, in the solid state, in the melt, and in solution in non-polar solvents, the compounds possessed five-covalent antimony, presumably with trigonal-bipyramidal geometry.

Nesmeyanov and coworkers [100] have noted that the reaction between the compounds Ph_5M ($\text{M} = \text{P}, \text{As},$ or Sb) and $[\text{PhN}_2]\text{BF}_4$ led to the formation of the corresponding $[\text{Ph}_4\text{M}]\text{BF}_4$ derivatives.

The reaction between diacetamide $\text{CH}_3\text{CONHCOCH}_3$ and either Me_3Ga or Me_5Sb was the subject of a paper by Eberwein and coworkers [101]. In the reaction of diacetamide with Me_5Sb a hexacovalent antimony compound was formed:



The PMR, IR, and Raman spectra of the compounds were listed and assignments of the IR and Raman bands were made.

It is well known that pentaphenyl- and pentacyclopropylantimony possess tetragonal-pyramidal geometry (C_{4v} symmetry) in both the solid state and in solution whereas penta-*p*-tolylantimony is a trigonal bipyramid, at least in the solid state. The reason for these differences has remained a puzzling question for some time. Kuykendall and Mills [102] have now reported on an ^1H and ^{13}C NMR investigation of penta-*p*-tolylantimony in solution over a wide temperature range.

The ^1H NMR was reported between 30 and -129° and the single methyl signal was found to increase in width as the temperature was lowered, but even at -129° it remained a singlet. From the data obtained an activation energy of 1.60 kcal/mol for the exchange process was calculated. Similarly a line shape study of the *ortho* and the *meta* ^{13}C spectral peaks yielded an activation energy of 1.46 kcal/mol. It is apparent that penta-*p*-tolylantimony is still fluxional as low as -130° . Methyl ^1H and ^{13}C NMR data for a number of other *p*-tolylantimony compounds, as well as tri- and penta-*p*-tolylarsenic and toluene were reported, but no obvious trends were noted and the conclusion was reached that the solution stereochemistry of Group V pentacoordinate compounds is still puzzling.

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