ANTIMONY *

ANNUAL SURVEY COVERING THE YEAR 1977

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Although no book or critical review devoted exclusively to organoantimony compounds appeared in 1977, an extensive (483 page) monograph on the organometallic chemistry of antimony and bismuth was published in the Soviet Union in 1976 [1]. There have also been several recent reviews in which organoantimony compounds were briefly mentioned. Thus, these substances were included in a short article devoted to new work on arsenic, antimony, and bismuth chemistry [2], a survey of the heterocyclic chemistry of phosphorus, arsenic, antimony, and bismuth that was described in the literature from mid-1971 to the end of 1973 [3], a review devoted mainly to the stereochemistry of phosphorus [4], a comprehensive summary of the structural chemistry of organic compounds of phosphorus, arsenic, antimony, and bismuth [5], an article on the biological effects of organometallic compounds [6], and a review of organotin phosphines, arsines, stibines, and bismuthines as possible starting materials for homogeneous catalysts [7]. Organoantimony compounds that were subjected to X-ray analysis in 1975 or 1976 were listed in Volume 8 of *Molecular Structures and Dimensions* [8]. Organoantimony compounds have also been discussed in books on the vibrational spectra of organometallic compounds [9] and on homoatomic rings, chains, and macromolecules of the main group elements [10].

The reaction of dibenzylmercury with methylstibine has been shown to give a quantitative yield of a purple-black solid, the analysis of which corresponded to $(MeSb)_x$ [11,12]:

$$x\ MeSbH_2 + x\ (PhCH_2)_2Hg \longrightarrow (MeSb)_x + 2x\ PhMe + x\ Hg$$

It was suggested that the solid was possibly an anolog of the ladder-structure polymer $(MeAs)_x$. The methylstibine used in this study was

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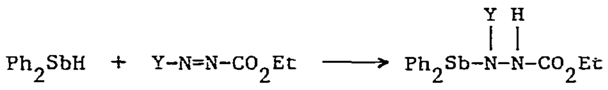
* Antimony, Annual Survey covering the year 1976 see J. Organometal. Chem., Vol. 147 (1978) 205-231.

prepared by the lithium aluminum hydride reduction of methyldichlorostibine in dibutyl ether. The interaction of methyldichlorostibine and dibenzylmercury resulted in replacing one chlorine with a benzyl group:

$$2\ MeSbCl_2 + (PhCH_2)_2Hg \longrightarrow 2\ MeSb(Cl)CH_2Ph + HgCl_2$$

The chlorostibine thus obtained was identified by PMR spectroscopy. Even when a substantial excess of dibenzylmercury was used, substitution of both chlorines was not observed.

A study has been made of the addition of P-H, As-H, and Sb-H groups to the nitrogen-nitrogen double bond [13]. The reaction of diphenylstibine with ethyl phenyldiazenecarboxylate or diethyl diazenedicarboxylate was found to yield a substituted hydrazine:



$$Ph_2SbH + Y\text{-}N{=}N\text{-}CO_2Et \longrightarrow Ph_2Sb\text{-}\overset{\overset{Y}{|}}{N}\text{-}\overset{\overset{H}{|}}{N}\text{-}CO_2Et$$

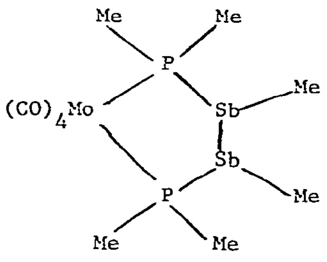
(where Y was Ph or CO_2Et)

Concurrently, the starting materials underwent an oxidation-reduction reaction, which produced another type of hydrazine derivative:

$$2\ Ph_2SbH + Y\text{-}N{=}N\text{-}CO_2Et \longrightarrow Ph_2SbSbPh_2 + Y\text{-}NH\text{-}NH\text{-}CO_2Et$$

The extreme sensitivity of the antimony-containing hydrazines to oxygen, light, and moisture made it impossible to obtain these compounds in pure form. They were identified only by their mass spect

The interaction of methyldibromostibine and the dilithium salt *cis*-$Mo(CO)_4(Me_2PLi)_2$ has been found to yield the following unusual type of coordination compound [14]:



The structure of this substance was established by elemental analysis and by IR, PMR, ^{31}P NMR, and mass spectroscopy. The dilithium salt required for the synthesis was obtained by deprotonation of *cis*-tetracarbonylbis(dimethylphosphine)molybdenum(0) with either butyl- or methyllithium.

The previously reported formation of boryldimethylstibine, Me_2SbBH_2, by the interaction of dimethylbromostibine and sodium borohydride has been shown to be in error [15]. The products of the reaction have now been reported to be separable by a high-vacuum microcolumn (at -78°) into trimethylstibine and a fraction said to be a mixture of trimethylstibine and dimethylstibine. Heating a mixture of tetramethyldistibine and diborane for two hours at 100° also failed to yield boryldimethylstibine. Instead, a substance was obtained that appeared to contain trimethylstibine, pentaborane, and possibly dimethylstibine. It was concluded that a monomeric boryldimethylstibine would probably be very unstable and difficult to prepare.

The interaction of dialkylbromostibines and magnesium in tetrahydrofuran has been found to give good yields of tetraalkyldistibines [16]:

$$2\ R_2SbBr + Mg \longrightarrow R_2SbSbR_2 + MgBr_2$$

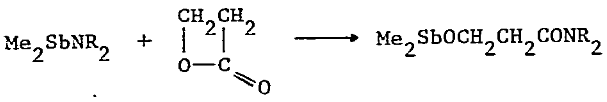
(where R was Me or Et)

Tetramethyldistibine was also obtained when trimethylstibine was allowed to react with sodium in liquid ammonia and ammonium bromide was then added to the reaction mixture. The following overall equation was suggested:

$$2\ Me_3Sb + 2\ Na + 2\ NH_4Br \longrightarrow Me_2SbSbMe_2 + 2\ MeH + 2\ NH_3 + 2\ NaBr$$

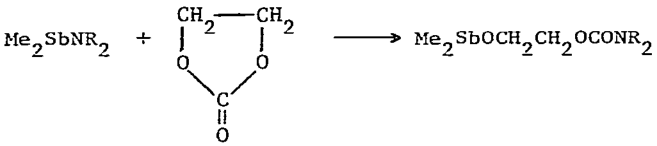
The recombination kinetics of iodine atoms in the presence of gaseous bis(trifluoromethyl)iodophosphine and bis(trifluoromethyl)-iodoarsine has been investigated over a range of pressures and temperatures [17]. The process was found to follow a third order rate law. The rate constant of the recombination reaction in the presence of bis(trifluoromethyl)iodostibine was determined by extrapolation.

IR spectroscopy has been used to make a kinetic study of the reaction between N,N-dialkylaminodimethylstibines and β-propiolactone [18]:



The kinetics were found to be second order. Although there was not a linear relationship between the rate constant and the basicity of the nitrogen atom in the dialkylamino compound, the reaction rate did increase with the electron density on the nitrogen atom and could be rationalized with the aid of the Taft equation. Hyperconjugation effects appeared to play an important role in the reaction.

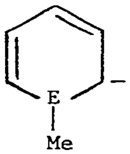
The reaction between N,N-dialkylaminodimethylstibines and ethylene carbonate has also been found to follow second order kinetics [19]:



(where R was Me, Et, Bu, cyclohexyl, $PhCH_2$, *etc.*)

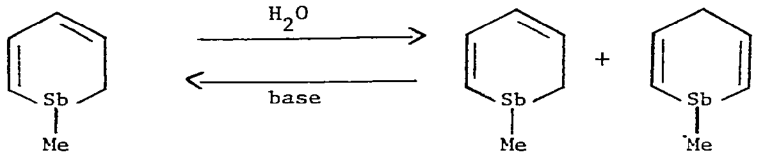
As in the reactions discussed in the above paragraph, the reaction rate increased with an increase in the electron donating ability of alkyl groups attached to the nitrogen atom. Correlations with the Taft equation were good, but additional contributions from hyperconjugation effects were significant in some cases. It was concluded that the rate determining step was a nucleophilic attack of the nitrogen atom on the carbonyl group of ethylene carbonate.

The reaction of phosphabenzene (phosphorin), arsabenzene (arsenin), or stibabenzene (antimonin) with methyllithium has been shown to yield anions of the following type [20]:

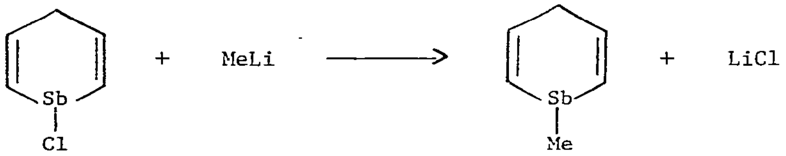


(where E was P, As, or Sb)

The structure of these ions was established by PMR and ^{13}C NMR spectroscopy. Treatment of the antimony-containing species with water gave a mixture of two tertiary stibines, each of which could be converted to the original anion by treatment with strong base:



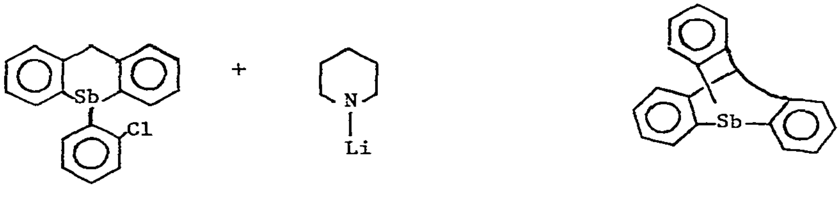
The second of the two stibines was independently prepared by the interaction of equimolar quantities of methyllithium and 1-chloro-1,4-dihydroantimonin:



The preparation of molybdenum-carbonyl complexes of the Group V heterobenzenes discussed above has also been reported [21]. Thus, the boron trifluoride etherate catalyzed interaction of stibabenzene and tris(pyridine)molybdenum tricarbonyl was found to yield air-stable red-brown crystals, the analysis of which corresponded to stababenzene-molybdenum tricarbonyl, $C_5H_5SbMo(CO)_3$. This substance exhibited a molecular ion in the mass spectrum and was also characterized by PMR and ^{13}C NMR spectroscopy. It was concluded that the substance was a π complex and was stabilized by donation of the high energy π electrons of the stibabenzene to the molybdenum. Attempts to prepare the bismuth analog of stibabenzenemolybdenum tricarbonyl were frustrated by the extreme lability of bismabenzene.

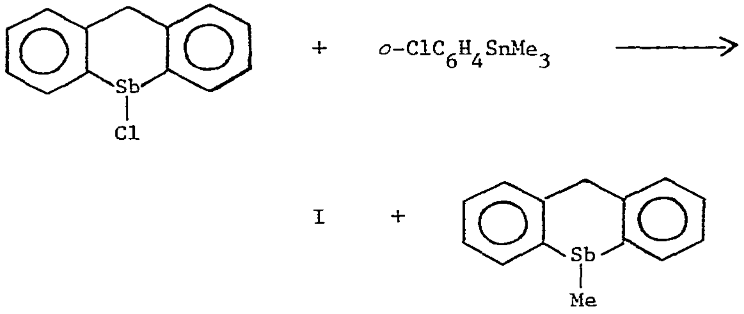
Stibatriptycene has been prepared in 20% yield by cyclization of 5-(*o*-chlorophenyl)-5,10-dihydrodibenz[*b,e*]antimonin(I) with an excess of lithium piperidide [22].

The reaction probably proceeded by the generation of a carbanionic center at the 10-position of I and a subsquent nucleophilic attack of this center on the benzyne formed from the *o*-chlorophenyl substituent. The dihydroantimonin I required for this synthesis was obtained by the



I

reaction of 5-chloro-5,10-dihydrodibenz[*b*,*e*]antimonin with either *o*-chlorophenylmagnesium bromide or (*o*-chlorophenyl)trimethylstannane. The yield of I was only 15% when the Grignard reagent was employed. The stannane gave I in a 28% yield, but the main product was 5-methyl-5,10-dihydrodibenz[*b*,*e*]antimonin, which was obtained in a 51% yield:



The two products were readily separated by sublimation. The structure of stibatriptycene was confirmed by IR, PMR, ^{13}C NMR, and mass spectroscopy. The IR spectrum had relatively few absorption peaks because of the rather high symmetry of the molecule. The PMR spectrum was of the $(ABCD)_3X$ type, where X was the bridgehead proton. The ^{13}C NMR spectrum showed only seven lines, which could be assigned to the seven types of carbon atoms. The mass spectrum exhibited a molecular ion at *m/e* 362 as well as doubly and triply charged molecular ions of appreciable intensity. The base peak of the mass spectrum was *m/e* 241 and arose by expulsion of antimony from the molecular ion.

The chelating ligand *o*-phenylenebis(dimethylstibine) was first described in 1974. Full details of the synthesis of this compound and of some of its complexes have now been reported [23]. The following series of reactions was employed:

$$3\ \mathrm{MeMgI} \quad + \quad \mathrm{SbCl_3} \quad \longrightarrow \quad \mathrm{Me_3Sb} \quad + \quad 3\ \mathrm{MgICl}$$

$$\mathrm{Me_3Sb} \quad + \quad \mathrm{Br_2} \quad \longrightarrow \quad \mathrm{Me_3SbBr_2}$$

$$\mathrm{Me_3SbBr_2} \quad \xrightarrow{\Delta} \quad \mathrm{Me_2SbBr} \quad + \quad \mathrm{MeBr}$$

$$\mathrm{Me_2SbBr} \quad + \quad 2\ \mathrm{Na} \quad \longrightarrow \quad \mathrm{Me_2SbNa} \quad + \quad \mathrm{NaBr}$$

$$2\ \mathrm{Me_2SbNa} \quad + \quad o\text{-}\mathrm{BrC_6H_4I} \quad \longrightarrow$$

$$o\text{-}\mathrm{Me_2SbC_6H_4SbMe_2} \quad + \quad \mathrm{NaBr} \quad + \quad \mathrm{NaI}$$

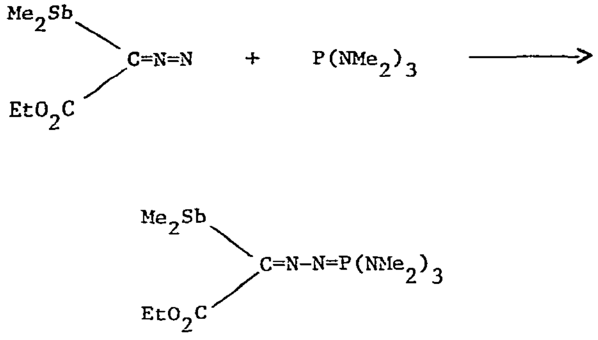
The di-tertiary stibine was difficult to obtain, since the yield in the last step was only 9%. The major product of the reaction was tetramethyldistibine, which was apparently formed by an oxidative coupling of the dimethylstibide ion. When *o*-dibromobenzene was used as the aromatic substrate, the yield of the di-tertiary stibine was further reduced (to 2-5%); none of the desired compound was obtained when *o*-dichlorobenzene was used. The di-tertiary stibine readily formed square-planar complexes of the type $[\mathrm{MX_2(distib)}]$, where M was Pd or Pt, X was Cl, Br, I, or SCN, and distib was *o*-phenylenebis(dimethylstibine). Nickel chloride gave a five-coordinate diamagnetic complex $[\mathrm{NiCl(distib)_2}]\mathrm{Cl}$. Ultraviolet irradiation of THF solutions of chromium, molybdenum, or tungsten hexacarbonyl and the ligand gave the octahedral complexes $[\mathrm{M(CO)_4(distib)}]$, where M was Cr, Mo, or W. A comparison of the electronic spectra of the palladium and nickel complexes with the spectra of the analogous complexes of these metals with *o*-phenylenebis-(dimethylarsine) suggested that the di-tertiary stibine had a weaker ligand field strength.

An antimony derivative of cyclopentadienylmanganesetricarbonyl has been prepared from the corresponding lithium compound [24]:

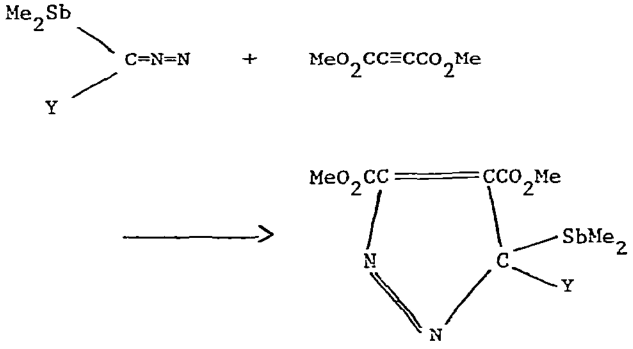
$$3\ \mathrm{(CO)_3MnC_5H_4Li} \quad + \quad \mathrm{SbCl_3} \quad \longrightarrow \quad [\mathrm{(CO)_3MnC_5H_4}]_3\mathrm{Sb} \quad + \quad 3\ \mathrm{LiCl}$$

Thermal decomposition of this substance at 330° gave manganese, antimony, carbon monoxide, and a polymeric hydrocarbon.

Lorberth and his co-workers have continued their investigations of organometallic derivatives of diazoalkanes. In one of these studies they described the preparation of an antimony-containing phosphazine by means of the following addition reaction [25]:

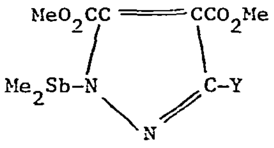


A second paper [26] included ^{13}C NMR data on (diazomethylene)bis-(dimethylstibine) and ethyl diazo(dimethylstibino)acetate. It was concluded that electron release by the organometallic substituent led to strong shielding of the carbon atom linked to the diazo group. A third paper [27] reported a systematic study of 1,3-dipolar cycloaddition reactions of organometallic diazoalkanes with dimethyl acetylenedicarboxylate. For example, the antimony-containing diazo compounds reacted in the following manner:

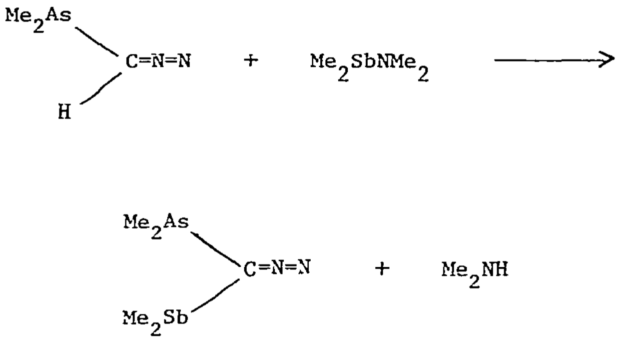


(where Y was Me_2Sb or CO_2Et)

Migration of a dimethylstibino group from carbon to nitrogen yielded the following type of pyrazole:



The preparation of diazoalkanes containing both arsenic and germanium, tin, lead, antimony, or bismuth was described in a fourth paper [28]. These substances were obtained by the interaction of (diazomethyl)dimethylarsine and an organometallic derivative of an amine. Thus, an organoarsenic-organoantimony compound was prepared by the following reaction:



The IR, PMR, and ^{13}C NMR spectra of this diazoalkane derivative revealed additive contributions of both the dimethylarsino and dimethylstibino groups.

The interaction of one mole of tris(pentafluorophenyl)stibine and two moles of bis(trifluoromethyl)nitroxyl has been found to proceed smoothly at room temperature according to the following equation [29]:

$$(C_6F_5)_3Sb \quad + \quad 2\ (CF_3)_2NO \quad \longrightarrow \quad (C_6F_5)_3Sb[ON(CF_3)_2]_2$$

The pentavalent antimonial thus obtained (in 87% yield)was a stable, white solid that was not hydrolyzed by moist air. The identity of the product was established by its elemental analysis and IR spectrum. On being heated at 100° for six days with anhydrous hydrogen chloride, the antimony-oxygen bonds were cleaved and high yields of tris(pentafluorophenyl)antimony dichloride and bis(trifluoromethyl)hydroxylamine were obtained:

$$(C_6F_5)_3Sb[ON(CF_3)_2]_2 \ + \ 2\ HCl \ \longrightarrow \ (C_6F_5)_3SbCl_2 \ + \ 2\ (CF_3)_2NOH$$

The interaction of tellurium tetrachloride and the triphenyl derivatives of nitrogen, phosphorus, arsenic, or antimony has been investigated [30]. Triphenylamine was found to undergo a Friedel-Crafts type of reaction:

$$2\ Ph_3N + TeCl_4 \longrightarrow (4\text{-}Ph_2NC_6H_4)_2TeCl_2 + 2\ HCl$$

In contrast, triphenylphosphine, -arsine, and -stibine gave the corresponding dichlorides and elemental tellurium:

$$2\ Ph_3E + TeCl_4 \longrightarrow 2\ Ph_3ECl_2 + Te$$

(where E was P, As, or Sb)

An *in situ* polarographic technique has been used to study the rate of reduction of *tert*-butyl hydroperoxide by triphenylphosphine, -arsine, or -stibine in 1:1 methanol-benzene containing 0.3 M lithium chloride [31]. Second-order kinetics were observed in each case. The stibine reacted about 44 times as fast as the arsine and almost as fast as the phosphine. The reactivity of the stibine was considered anomalous, since it had been expected that the rates would decrease in the order $Ph_3P > Ph_3As > Ph_3Sb$.

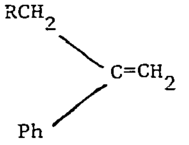
A reinvestigation of the interaction of triphenylstibine and selenium dioxide has been included in a paper on the reactions of the latter compound with various triaryl derivatives of nitrogen, phosphorus, arsenic, antimony, and bismuth [32]. It was found that the antimony and selenium compounds reacted in boiling benzene or ethanol in the following manner:

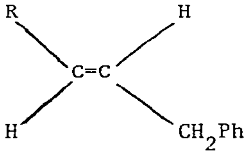
$$2\ Ph_3Sb + 3\ SeO_2 \longrightarrow 2\ Ph_3SbO\cdot SeO_2 + Se$$

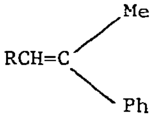
The addition compound thus formed reacted very slowly with triphenylstibine in boiling solvents to give trace amounts of elemental selenium, but pure triphenylstibine oxide was not obtained. In no case was there evidence for the formation of triphenylstibine selenide. This result is in agreement with the work of Glidewell [33] in 1976 but is in contrast to the earlier work of Mel'nikov and Rokitskaya [34] who reported that triphenylstibine reacts with selenium dioxide to give a mixture of triphenylstibine oxide and triphenylstibine selenide.

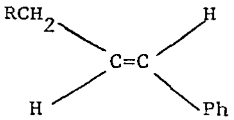
In contrast to triphenylphosphine and triphenylarsine, triphenylstibine has been found not to react with selenium sulfide (SeS_2) in boiling benzene [35]. This lack of reactivity was ascribed to the inability of triphenylstibine to form a Lewis acid-base complex.

The interaction of triphenylphosphine, -arsine, -stibine, or -bismuthine and a palladium(II) salt in the presence of an excess of 1-octene or ethyl acrylate has been shown to give biphenyl as well as phenylated derivatives of the olefinic compound [36]. For example, when equimolar amounts of triphenylstibine and palladium(II) acetate were allowed to react with a ten fold excess of 1-octene in acetonitrile at 25°, a 70% yield of biphenyl and a 113% yield of phenylated octenes were obtained (yield data were based on moles of product formed per mole of palladium salt used). The following phenylated octenes were identified in the reaction mixture:









When ethyl acrylate was used, biphenyl and ethyl cinnamate were formed. All reactions were allowed to proceed until precipitation of palladium black was complete (usually 24 hours). Triphenylantimony dichloride was also found to cause phenylation of olefins in the presence of palladium(II) salts, but details of these reactions were not given. It was concluded that the mechanism of the phenylation reactions involved the intermediate formation of phenylpalladium species.

π-Allylpalladium complexes of the type $LPdX{\cdot}SbPh_3$ (where L was π-allyl and X was Cl, Br, or I) have been prepared by the interaction of triphenylstibine and the bis(π-allylpalladium halides), $(LPdX)_2$ [37]. When the antimony-containing complexes were heated in toluene at 100° for six hours, they decomposed into a variety of products. Where X was Cl or Br, almost all of the palladium was reduced to the free metal, a substantial amount of triphenylantimony dihalide was isolated, and some antimony trihalide was formed. Where X was I, however, only 67% of the palladium was converted to the free metal, an 18% yield of $(Ph_3Sb)_2PdI_2$ was obtained, and no triphenylantimony diiodide or antimony triiodide was detected. In all three decompositions, the following products were formed: metallic antimony, benzene, triphenylstibine, allylbenzene, halobenzene, and traces of biphenyl.

The chlorine-containing complex also yielded 6% allyltoluenes, while the iodine-containing complex gave 20% 1,5-hexadiene (biallyl). Triphenylstibine itself was found not to decompose at 100°. Between 350 and 400°, it gave metallic antimony, benzene, biphenyl, and polyphenyls.

The behavior of triphenylamine, -phosphine, -arsine, -stibine, and -bismuthine in anhydrous liquid hydrogen bromide has been investigated [38]. Triphenylstibine was found to undergo partial solvolysis:

$$Ph_3Sb \quad + \quad (3-x)HBr \longrightarrow (3-x)PhH \quad + \quad Ph_xSbBr_{3-x}$$

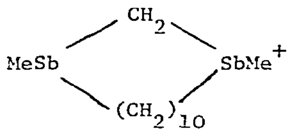
Not surprisingly, the semi-solid substance formed in this reaction gave, after hydrolysis, a positive test for halide.

A radical formed by x-irradiation of a single crystal of triphenylstibine has been examined by ESR and identified as $Ph_2Sb\cdot$ [39]. Analysis of the ESR spectral parameters indicated that the unpaired electron was localized on the $5p\pi$ valence orbital of the antimony atom and that the C-Sb-C angle was about 98°. It was concluded that the $Ph_2Sb\cdot$ radical was very similar in structure to the $Ph_2P\cdot$ and $Ph_2As\cdot$ radicals, which had been investigated earlier.

In another study, ultraviolet irradiation of a single crystal of triphenylstibine produced ESR signals that were also assigned to the diphenylantimony radical [40]. Phenyl radicals were presumably formed by homolytic cleavage of one of the C-Sb bonds of the triphenylstibine but were not observed. The ESR data suggested that the $Ph_2Sb\cdot$ radical was planar and that the unpaired electron was in a nearly pure $5p$ orbital, which was perpendicular to the C-Sb bonds and the nonbonding electron pair of the antimony atom. In agreement with the work discussed in the above paragraph, it was concluded that C-Sb-C angle of the radical was between 95° and 100°.

Triphenylstibine and the *ortho*, *meta*, and *para* isomers of tritolylstibine have been included in an investigation of the mass spectra of some triaryl derivatives of phosphorus, arsenic, antimony, and bismuth [41]. In agreement with earlier work, the most intense peak in the mass spectrum of triphenylstibine was the $PhSb^+$ ion, while the molecular ion was the second most intense peak. Over 98% of the total ion current was accounted for by the $PhSb^+$ (77.4%), Ph_3Sb^+ (14.9), and Ph_2Sb^+ (6.0%) ions. The *m*- and *p*-tolyl compounds showed very similar fragmentation patterns. In both cases, over 70% of the ion current was carried by $C_7H_7Sb^+$ ions; the next two most abundant peaks were $C_{21}H_{21}Sb^+$ and $C_{14}H_{14}Sb^+$ ions. Tri-*o*-tolylstibine had a significantly different spectrum. The base peak was the molecular ion, which carried 40.7% of the ion current; the $C_{14}H_{14}Sb^+$ and $C_7H_7Sb^+$ ions carried 18.3% and 14.6%, respectively. An important peak in the spectrum of the *ortho* compound was $C_7H_6Sb^+$ (16.3% of the ion current). The differences observed with the *ortho* isomer were attributed to steric effects. In all four spectra, the Sb^+ ion carried only 0.3% of the ion current.

A study has been reported of the mass spectra of two di-tertiary stibines $Me_2Sb(CH_2)_nSbMe_2$ (where *n* was 6 or 10) and of a number of related di-tertiary phosphines and di-tertiary arsines [42]. The spectra of the stibines illustrated the relative weakness of the C-Sb bond. For example, the base peaks in both cases were hydrocarbon fragments. No molecular ion was observed in one case (where *n* was 6), and the relative intensity of the molecular ion in the other case was only 0.9%. The major fragments containing one antimony atom were Me_2Sb^+, $C_2H_4Sb^+$, and $MeSb^+$. Both spectra also exhibited prominent peaks ascribed to Sb^+. A moderately intense peak corresponding to a fragment containing two antimony atoms was noted in the spectrum of each stibine. Thus, the spectrum of 1,6-hexanediylbis(dimethylstibine) exhibited the $Me_2Sb(CH_2)_6SbMe^+$ ion, while the spectrum of 1,10-decanediylbis(dimethylstibine) had a peak that was assigned the following cyclic structure:



It was concluded that the effect on the mass spectrum of varying the number of CH_2 groups in the phosphine, arsine, or stibine was considerably less than that produced by changes in the Group V element or in the terminal substituents.

^{19}F NMR spectroscopy has been used to investigate the transmission of electronic effects in compounds of the type $4\text{-}FC_6H_4EAr_2$, where E was CH, N, Sb, or Bi and Ar was Ph or a substituted-phenyl group [43]. Correlations of the observed fluorine chemical shifts with the polar constants (σ^o or σ) of the substituents suggested that electronic effects of the substituents were transmitted through the Ar-CH, Ar-Sb, and Ar-Bi linkages predominantly by an inductive mechanism. In contrast, transmission of electronic effects through the Ar-N linkage involved conjugation of the nitrogen lone pair with the aromatic rings and the substituents bonded to them. A dual parameter correlation of the ^{19}F chemical shifts with the inductive (σ_I) and resonance (σ_R^o or σ_R) constants of the substituents on the Ar rings led to similar conclusions. The largely inductive character of electronic transmission through the antimony and bismuth atoms was ascribed to the absence of conjugation of the lone pairs and vacant *d*-orbitals of the metals with the π-electronic systems of the aromatic rings.

A Fourier transform spectrometer has been used to record the ^{13}C NMR spectra of triphenylphosphine, -arsine, -stibine, and -bismuthine and of a number of related metal carbonyl complexes, chalcogenides, and quaternary onium iodides [44]. The data obtained were used to calculate a parameter σ_R^o for each compound by means of the following equation:

$$\delta_p(^{13}C) - \delta_m(^{13}C) = -22.06\ \sigma_R^o$$

(where $\delta_p(^{13}C)$ and $\delta_m(^{13}C)$ were, respectively, the chemical shifts of the carbons *para* and *meta* to the Group V atom)

This parameter appeared to be a measure of the resonance interaction between the benzene ring and a substituent attached to it. The σ_R^o value for triphenylstibine was small and negative (-0.014) and suggested slight conjugative interaction between the lone pair on the antimony atom and the π system of the benzene rings.

Triphenylstibine has been included in a study of the effect of the substituent on the ^{13}C chemical shifts of a large number of monosubstituted benzenes [45]. For central atoms belonging to the same period of the periodic table, there was a linear relationship between the group electronegativity of the substituent and both the ^{13}C chemical shift of the ring carbon atom directly bonded to the substituent and the ^{13}C chemical shift of the carbon atom *meta* to the substituent. Only three compounds containing fifth period elements were studied, *viz.* trimethylphenylstannane, triphenylstibine, and iodobenzene.

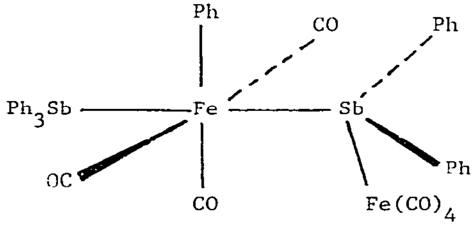
The dipole moments of triphenylstibine, tri-*p*-tolylstibine, and tris(*p*-chlorophenyl)stibine have been determined by means of dielectric constant and refractive index measurements on benzene solutions of these substances to be 0.85D, 1.37D, and 1.73D, respectively [46]. These values led to an estimate for the C-Sb-C valence angle of 94°. Earlier workers had concluded from dipole moment studies that the C-Sb-C angle in triphenylstibine was considerably larger, *viz.* 113°.

In a study in another laboratory, a similar experimental method was used to determine the dipole moments of compounds of type Ph_3E

and $(XC_6H_4)_3E$, where E was P, As, Sb, or Bi and X was 4-F, 4-Cl, 4-Me, 3-F, or 3-Cl [47]. The results obtained with triphenylstibine (0.86D) and tri-*p*-tolylstibine (1.36D) were in excellent agreement with the data given in the above paragraph. A considerably lower value (1.54D) was found, however, for tris(*p*-chlorophenyl)stibine. The experimental dipole moments obtained in this investigation were used to calculate group moments, bond moments, and conformational parameters. It was concluded among other things that the C-Sb-C valence angle in this set of compounds varied from about 95° in the *meta* and *para* isomers of tris(fluorophenyl)stibine to 101° in tri-*p*-tolystibine.

The ^{121}Sb Mössbauer spectra of triphenylstibine, tris(*o*-methoxyphenyl)stibine, and tris(*p*-methoxyphenyl)stibine have been determined and compared with the spectra of a large number of coordination compounds of these and other tertiary stibines [48]. Spectra were obtained for square-planar complexes of the type $[MX_2L_2]$ (where M was Pd or Pt, X was Cl, I, or NO_2, and L was a tertiary stibine), for the five-coordinate complexes $[PtI_2L_3]$, and for $[RhCl_3(SbPh_3)]$. In every case, coordination resulted in a large increase in isomer shift and a decrease in quadrupole coupling constant. These changes were in the directions expected for delocalization of the antimony lone pair on to the transition metal.

A study has been made of the ^{57}Fe and ^{121}Sb Mössbauer spectra of $Ph_3SbFe(CO)_4$ and of an interesting compound containing both a penta- and a hexacoordinated iron atom [49]:



There was a large change (-1.29 to +1.68 at 4 K) in the ^{121}Sb chemical shift upon complexing triphenylstibine to $Fe(CO)_4$. This change corresponded to a change in valency from antimony(III) to antimony(V) and apparently resulted from a σ-donation of the antimony lone pair to the iron. The spectra of the other compound studied indicated that both antimony atoms in this substance had similar electronic environments, that they were σ-bonded to the iron atoms, and that they should be regarded as antimony(V).

A method of orbital population analysis that utilizes both

^{121}Sb Mössbauer isomer shifts and quadrupole coupling constants has been developed for a number of Sb(III) compounds [50]. A linear relationship between the isomer shift and the number of *s* electrons was inadequate for these compounds, but an empirical quadratic equation proved satisfactory. The electron propulation along the bonds between the antimony and the atoms linked to it was calculated for stibosobenzene, bis(diphenylantimony) oxide, trimethylstibine, triphenylstibine, and a number of unsymmetrical stibines of types Ph_2RSb and PhR_2Sb, where R was methyl, vinyl, propyl, or allyl.

The UV spectra of tetraphenylsilane and of the triaryl compounds of the type Ar_3E (where Ar was Ph or mesityl and E was B, Ga, N, P, As, Sb, or Bi) have been determined at 77 K and 295 K [51]. The effects of temperature on the position and intensity of the absorption bands were discussed in terms of the electronic structure of the valence shell of the heteroatom, its ability to participate in $p\pi$ conjugation, and the steric effects associated with this conjugation.

Negative values have been obtained at 298 K for the enthalpies of mixing equimolar amounts of triethylaluminum, triethylgallium, dimethylzinc, or dimethylcadmium with trimethylarsine, trimethylstibine, dimethyl sulfide, dimethyl selenide, or dimethyl telluride [52]. The results obtained were discussed in terms of the donor-acceptor complexes formed by the two mixed compounds. In every case, the enthalpy of mixing trimethylarsine with one of the Lewis acids was greater in absolute value than the corresponding quantity for trimethylstibine.

The fluorescence quenching of aromatic compounds (for example, acenaphthene, azulene, or fluoranthene) by triethylamine or by triphenylamine, -phosphine, -arsine, or -stibine has been examined in both polar and non-polar solvents [53]. The quenching did not involve simply electron or charge transfer, but a heavy atom effect involving the Group V element also occurred. It was concluded that if an intermediate charge-transfer or ion pair state was formed in polar solvents, it was possibly of higher energy than the lowest singlet or triplet state and might decay to one of these levels.

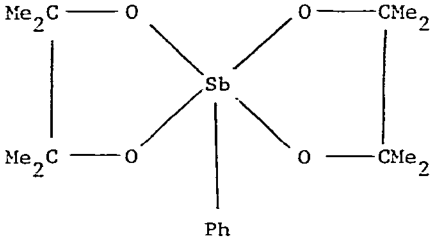
A kinetic study has been made of the behavior of ground state antimony atoms in the presence of various gases [54]. The atoms were generated by the low energy pulsed irradiation of trimethylstibine and were monitored photoelectrically by means of atomic absorption spectroscopy. The rate data obtained were compared with analogous data previously obtained for ground state bismuth atoms.

Previously published electron-diffraction and spectroscopic information about trimethylamine, -phosphine, -arsine, -stibine, and -bismuthine has been used to derive force fields, r.m.s. amplitudes of vibration along the internuclear vectors, and perpendicular amplitude correction coefficients for these molecules [55]. The carbon-heteroatom r.m.s amplitude increased only slightly (from 0.049 to 0.058 Å) in going from nitrogen to bismuth. The carbon-heteroatom force constants decreased, however, by over 60% (from 5.3 to 1.8 mdyn $Å^{-1}$). There was also evidence for an increased tendency for torsional motion of the methyl groups in going from the amine to the bismuthine. For each of the compounds, the amplitude data were used to derive zero-point average structures and to make estimates of partial equilibrium structures. The calculated zero-point average lengths of the C-N, C-P, C-As, C-Sb, and C-Bi bonds in the five molecules were 1.458, 1.844, 1.979, 2.169, and 2.263 Å, respectively.

A large number of complexes have been described in which tertiary stibines were coordinated to transition metals. The metals bonded to the antimony in these complexes included chromium [23,56], copper [57], iron [49,58-61], manganese [62], mercury [63], molybdenum [23,64,65], nickel [23,66,67], osmium [68], palladium [23,37,48,69-71], platinum [23,48,70], rhodium [48], silver [72], and tungsten [23,56,73].

The reactions of phenylstibonic acid, $PhSbO(OH)_2$, with the diacetates of Co(II), Ni(II), and Cu(II) have been reported by Larionov and co-workers [74]. Two different types of compounds were obtained by displacement of either one or two acetate groups by phenylstibonic acid. The compounds obtained had the compositions $M(OAc)(HL)(H_2L)$ and $M(HL)_2(H_2L)$, where M = Co, Ni, or Cu and H_2L = phenylstibonic acid. Pyrolysis of these compounds led to the formation of Co, Ni, or Cu antimonates.

The crystal structure of the cyclic antimony compound II has been determined by Wieber and co-workers [75] by use of single crystal X-ray diffraction.



II

The geometry was found to be that of a slightly distorted trigonal bipyramid with an equatorial phenyl group. The O-Sb-O angle for the two axial oxygen atoms was 167.4° and for the two equatorial oxygen atoms was 118.3°. The equatorial - axial O-Sb-O angles varied between 82.6° and 94.4°. The ^1H and ^{13}C NMR spectra of the compound were determined in CCl_4 and $CDCl_3$, respectively. The ^1H spectrum was invariant between room temperature and -50° and showed two methyl singlets. These singlets showed reversible coalesence in naphthalene solution at 103°. The ^{13}C carbon atoms of the methyl groups gave two signals of relative intensity 1:1 at δ 25.11 and 25.566 ppm. The ^{13}C signal of the carbon attached to oxygen was a singlet at 877.025 ppm. From these results the authors were unable to determine the geometry of the molecule in solution, but they suggested that the NMR results might be explained by a low temperature pseudorotation.

Bowen and Long [76] in an earlier paper had shown that ^{121}Sb Mössbauer shifts and quadrupole coupling constants could be combined to calculate orbital election populations at Sb(V) along the Sb-L bonds. In that paper relatively few six-coordinate Sb compounds with octahedral geometry were considered. However, Mössbauer data on a large number of six-coordinate Sb compounds have become available, and Bowen and Hedges [77] have now made use of the new data and applied their model to this group of octahedral compounds.

They have divided these new compounds into three separate groups namely compounds of the type $(SbPhX_5)^-$, $(SbR_2X_4)^-$, and compounds with two R groups but with one or two X groups bridging two Sb atoms (where R in both sets of compounds was either Ph or Me). A table of orbital populations and bond hybridizations for all of the compounds under consideration was given. It was readily seen that the results varied with the X substituent. Comparing the species $(PhSbX_5)^-$ and $(R_2SbX_4)^-$, the relative *s* character of the Sb-R bond was higher when only one organic group was present. In agreement with electronegativities the orbital populations decreased in the order $\sigma_{Me} > \sigma_{Ph} >> \sigma_{Br} > \sigma_{Cl} > \sigma_{NCS}$. By contrast, where X = F or N_3, the Sb-F or Sb-N_3 bonds had considerably more *s* character than Sb-R bonds. The authors thus concluded that Mössbauer data provided strong evidence of variable hybridization in octahedral complexes of Sb(V).

Although SbF_3 has been widely used as a fluorinating agent for aromatic compounds containing trichloromethyl groups, it has been found that not all chlorines are replaced by fluorine when the trichloromethyl groups are deactivated by adjacent electron withdrawing groups. Antimony pentafluoride is a more powerful fluorinating agent, but it is unsuitable for fluorinating benzene derivatives since it substitutes fluorine atoms in the benzene rings. Yagupol'skii and co-workers [78] have now investigated $PhSbF_4$ and Ph_2SbF_3 as fluorinating agents. The first of these was found to be a powerful fluorinating agent for $PhCCl_3$. Thus, at a reaction temperature of 50-55° and a reaction time of 2 hours, it gave a yield of 91% $PhCF_3$ with no $PhCF_2Cl$. The trifluoride Ph_2SbF_3 was much less efficient and yielded a mixture of $PhCF_3$ and $PhCF_2Cl$. Both Ph_3SbF_2 and SbF_3 were far inferior to $PhSbF_4$.

In continuation of their earlier work on Sb(V) halides, Popov and Kondratenko [79] have reported on the synthesis of a number of organoantimony(V) compounds. Some of these had been prepared earlier by other methods. Diphenylstibinic acid was prepared by the chlorination of fluorodiphenylstibine with chlorine followed by hydrolysis of the dichloride:

$$Ph_2SbF + Cl_2 \longrightarrow Ph_2SbFCl_2$$

$$Ph_2SbFCl_2 + H_2O \longrightarrow Ph_2SbO_2H$$

Iodobenzene difluoride was found to be a useful fluorinating agent. Thus, the following reaction was carried out:

$$Ph_2SbF + PhIF_2 \longrightarrow Ph_2SbF_3 + PhI$$

The compounds Ph_3SbF_2 and $(p\text{-}MeC_6H_4)_3SbF_2$ were prepared in a similar manner from Ph_3Sb or $(p\text{-}MeC_6H_4)_3Sb$ and $PhIF_2$. The two compounds $Ph_3Sb(O_2CCF_3)_2$ and $(p\text{-}MeC_6H_4)_3Sb(O_2CCF_3)_2$ were prepared from the corresponding stibines and mercury bis(trifluoroacetate). The latter antimony compound was also prepared from $(p\text{-}MeC_6H_4)_3SbO$ and CF_3CO_2H in methanol solution.

Difluorotri-*p*-tolylantimony, which, as mentioned above, was prepared from $(p\text{-}MeC_6H_4)_3Sb$ and $PhIF_2$, was also prepared from $(p\text{-}MeC_6H_4)_3Sb$ and XeF_2. In yet another reaction $(p\text{-}MeC_6H_4)_3SbO$ or $(p\text{-}MeC_6H_4)_3Sb(O_2CCF_3)_2$ were found to react with SF_4 in CH_2Cl_2 solution at -10° to yield $(p\text{-}MeC_6H_4)_3SbF_2$. The three bromo compounds Ph_2SbBr_3, Ph_3SbBr_2, and $(p\text{-}MeC_6H_4)_3SbBr_2$ were prepared from the corresponding chlorides or fluorides by the reaction:

$$Ar_{5-n}SbX_n \xrightarrow{BBr3} Ar_{5-n}SbBr_n$$

(where Ar = Ph or p-MeC_6H_4, X = F or Cl, and n = 2 or 3)

It had been earlier reported that $PhSbO_3H_2$ reacted initally with SF_4 to form the complex $PhSbF_4 \cdot SF_4$, which lost SF_4 when heated in vacuo. The authors have similarily prepared the complexes p-$ClC_6H_4SbF_4 \cdot SF_4$ and p-$MeC_6H_4SbF_4 \cdot SF_4$. The compound Ph_2SbF_3, however, did not form a complex with SF_4 but did form complexes with stronger Lewis bases such as DMSO, Ph_3PO, and hexamethylphosphoric triamide. By contrast Ph_3SbF_2 failed to form complexes with SF_4, DMSO, and Ph_3PO. Similar results were obtained with Ph_3SbCl_2 and Ph_3SbBr_2. The ease of complex formation thus appeared to be in the order $PhSbX_4 > Ph_2SbX_3 > Ph_3SbX_2$.

An interesting reaction between trialkyl- or triarylphosphines and trimethylantimony dibromide has been reported by Graves and Van Wazer [80]. The reaction involves transfer of a methyl group from Sb to P as follows:

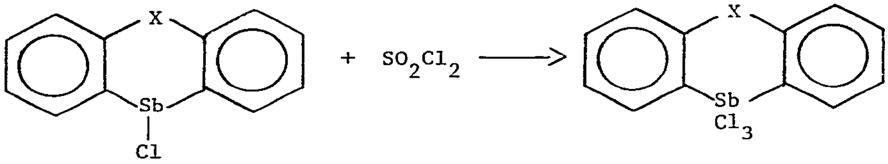
$$Me_3SbBr_2 + R_3P \longrightarrow [MePR_3]^+[Me_2SbBr_2]^-$$

(where R = Ph or Bu)

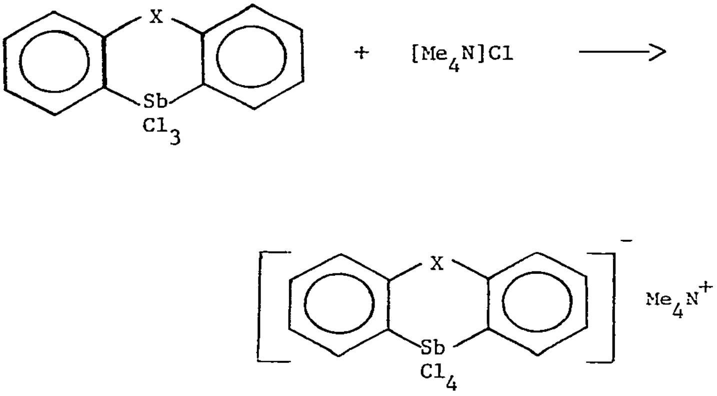
Molar conductivities of the reaction products were found to compare well with values reported for similar 1:1 electrolytes. The products were characterized by elementary analyses and both ^1H and ^{31}P NMR spectra.

Graves and Van Wazer [81] have reported that Me_3SbBr_2 and Ph_3SbBr_2 reacted with phosphinic acids of the type RP(H)(O)OH, where R = Ph or PhCH=CH, to form compounds of the type $Me_3Sb[OP(O)(H)R]_2$ and $Ph_3Sb[OP(O)(H)R]_2$. The compounds were shown to possess P-O-Sb bonds rather that P-Sb bonds from the ^1H NMR spectral data which showed the absence of an OH signal (present in the starting phosphinic acids) and the presence of a P-H signal in the products. The ^1H NMR spectra also demonstrated that $R'_3Sb(Br)OP(O)(H)R$ was formed when the reactants were combined in a 1:1 ratio, but the intermediate bromo compounds were not isolated.

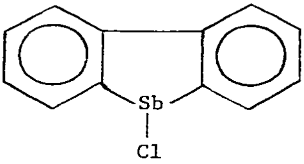
It had been previously shown by a nember of research groups that antimony(V) compounds of the type R_2SbX_3, where X = halogen, reacted with mono-, bi- and tridentate ligands to form thermally stable hexacoordinate Sb(V) complexes in which the two R groups were generally *trans*. Similarly, it had been shown that both Ph_2SbCl_3 and Me_2SbCl_3 in the solid state possess hexacoordinate antimony geometry with bridging chlorine atoms and with the two organic groups in *trans* position. Meinema and co-workers [82] have now prepared a number of hexacoordinate Sb(V) compounds containing two organic groups which must be in *cis*- positions, and examined their IR spectra. One group of compounds was prepared by the following series of reactions:



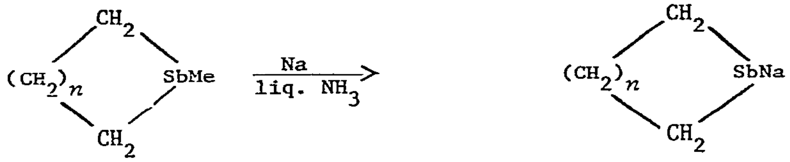
(where X = O, CH_2, or CH_2CH_2)



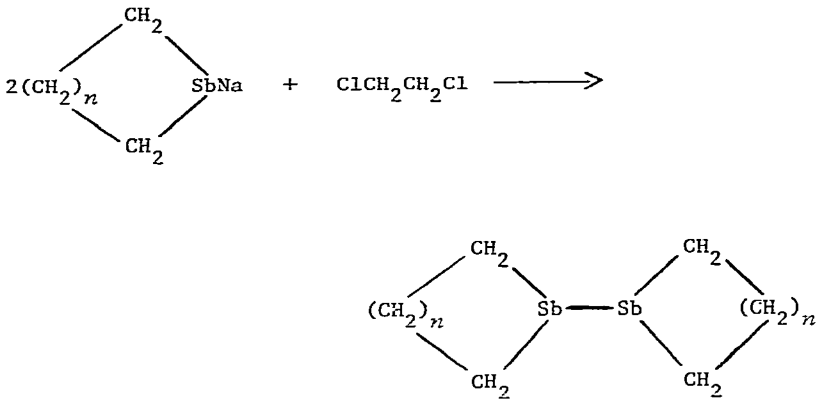
A similar series of reactions was carried out with the five-membered ring compound:

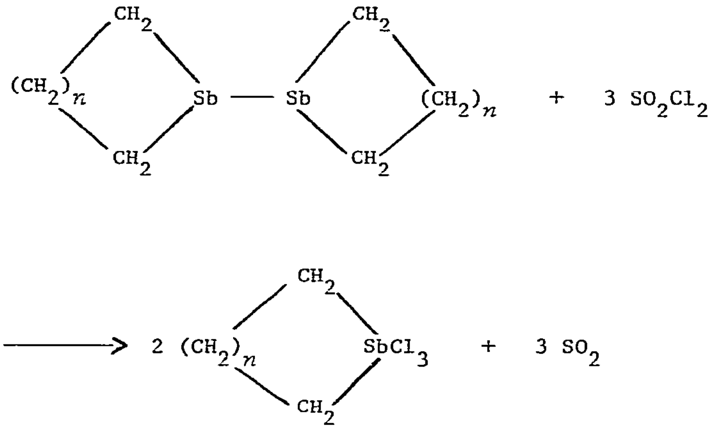


Formation of the hexacoordinate antimony compound by reaction with $[Me_4N]Cl$ was unsuccessful in the case where X = CH_2CH_2, presumably for steric reasons. The new compounds prepared were crystalline solids which decomposed upon heating and which were characterized by elementary analysis. Another group of compounds prepared contained aliphatic organic groups rather than aromatic groups. They were prepared by the following series of reactions:



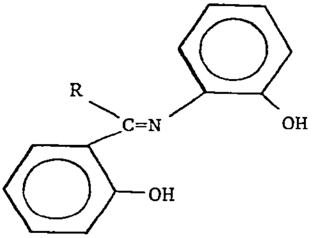
(where n = 2 or 3)





The five-membered ring compound was unstable and slowly decomposed on storage; the six-membered ring compound was stable at room temperature but decomposed when heated in petroleum ether solution The two hexacovalent compounds formed from the two trichlorides by reaction with $[Me_4N]Cl$ both decomposed to inorganic antimony compounds on storage. A comparison of the IR data of the heterocyclic trichloro-*cis*-diarylantimony(V) compounds with the corresponding tetrachloro-*cis*-diarylantimonate complexes did not reveal the frequency decrease of ν(Sb-Cl) modes which was expected to occur when the coordination number of antimony was expanded from five to six. This effect was observed, however, in the *cis*-dialkylantimony compound involving the six-membered heterocylic ring system. In the case of the trichloro-*cis*-dialkylantimony(V) compound involving a six-membered ring, two strong absorptions at 370 cm^{-1} and 295 cm^{-1} were observed which were assigned to ν(Sb-Cl) equatorial and ν(Sb-Cl) apical, respectively. The authors were unable, however, to conclude whether this compound possessed trigonal-bipyramidal geometry with a five-coordinate Sb atom or a hexacoordinate Sb atom with bridging chlorine atoms.

Three hexacoordinate antimony complexes of the type Ph_3SbLCl and Ph_3SbL' (where L = the anion of oxine and L' was the dianion of III) have been prepared by Ruddick and Sams [83].



III

(where R was H or Me)

The three complexes gave similar Sb Mössbauer spectra with quadrupole coupling constants e^2qQ in the range −16 to −18 mm/s and with the asymmetry parameter η of the electric field gradient close to unity. These results ruled out the trigonal-bipyramidal structure (usually found for triorganoantimony complexes) since η would not differ sensibly from zero, and also ruled out the *fac*-octahedral structure, which would allow little or no quadrupole interaction. Three other structures were considered, a *mer*-octahedral structure if the Schiff bases were tridentate and the oxine bidentate, and either *cis*- or *mer*- TBP structures if these ligands were bi- or monodentate, respectively. While the Mössbauer data were not compatible with the *cis*- TBP structure, they were compatible with the other two structures. However, on the basis of previous work with the ligands used in the present paper, the authors concluded that the *mer*-octahedral structure was the most probable.

Kawasaki and co-workers [84] have reported on the rate constants and the activation parameters E_a, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta C^{\neq}$, as determined by ^{1}H NMR line broadening techniques for the halogen exchange reactions:

$$\mathrm{Me}_n\mathrm{Ph}_{3-n}\mathrm{Sb(L)Cl} + \mathrm{Me}_n\mathrm{Ph}_{3-n}\mathrm{Sb^{*}(L)Br} \rightleftharpoons \mathrm{Me}_n\mathrm{Ph}_{3-n}\mathrm{Sb(L)Br} + \mathrm{Me}_n\mathrm{Ph}_{3-n}\mathrm{Sb^{*}(L)Cl}$$

(where n = 1 to 3, and where L = 8-quinolato or a number of substituted 8-quinolato ligands)

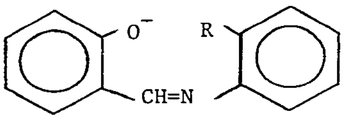
The preparation of these compounds was described, and spectral data (^{1}H NMR, IR, and UV) were reported for all of the compounds. From UV λ_{max} values it was concluded that the Sb in all of these compounds was hexacoordinated. In the exchange reaction the rate constant and activation energy were found to decrease as the number of phenyl groups increased, and the activation entropy became increasingly negative in the above order. The rate constant decreased and the activation energy became larger when an electron-withdrawing substituent was introduced into the 5-position of the 8-quinolato ligand.

From the results it was concluded that the exchange reaction did not go through a dissociative process but rather through a bridging intermediate. A good linear correlation between the Taft σ^o value and log (k/k_o) for the MePhSb(L)X exchange system was found. The compound $\mathrm{(Me)(Ph)(PhCH_2)Sb(L)O_2CMe}$ was prepared (where L = 2-methyloxinato) but the authors were unable to prepare the bromide $\mathrm{(Me)(Ph)(PhCH_2)Sb(L)Br}$ (where L = oxinato). From spectral data the authors concluded that the acetate contained pentacoordinate and not hexacoordinate antimony. From ^{1}H NMR they further concluded that the compound possessed a chiral center and that the rate of conversion between enantiomers was relatively slow.

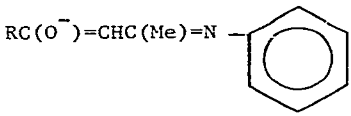
Ebina and co-workers, in a preliminary communication [85], had reported that two fluorinated β-diketones reacted with triaryldibromoantimony compounds to form complexes of the type $\mathrm{(Ar_3SbL)_2O}$, where HL = a β-diketone, and that these complexes, when boiled in a moist solvent, gave novel β-diketone hydrate complexes in which the β-diketone hydrate acted as a tridentate ligand to the Sb atom. In a second paper Ebina and co-workers [86] now have reported X-ray crystal data for one of these complexes, namely tris(p-chlorophenyl)-5,5,5-trifluoro-4,4-dihydroxy-2-pentanonatoantimony(V).

The coordination around the Sb was shown to be a distorted octahedron with the β-diketone hydrate bonding to the Sb through two hydroxyl O atoms and one carbonyl O atom in facial positions.

The ^{121}Sb Mössbauer spectra of a series of hexacoordinate organoantimony compounds containing anions of tridentate Schiff base ligands have been reported by Bertazzi and co-workers [87]. The compounds were of the types R_2SbClL and R_3SbL, where R was Me or Ph and L was a dianion of the following types:



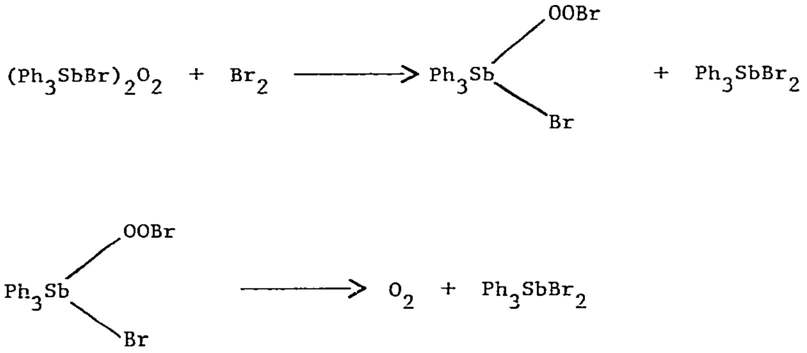
(where R = O^- or S^-)



(where R = Me or Ph)

The compounds possessed essentially octahedral geometry with a meridionally disposed tridentate ligand and a T-shaped R_3Sb or *trans*- R_2Sb moiety. These conclusions on the geometry of the molecule were deduced from the Mössbauer data. Conclusions as to the amount of *s*-character associated with the Sb atom in the various complexes under investigation were deduced from the chemical isomer shift values.

Dahlmann and Winsel [88] have studied the decomposition of both bis(bromotriphenylantimony) peroxide and bis(chlorotiphenylantimony) peroxide. The bromo compound reacted with bromine or iodine according to the following reaction scheme to yield singlet oxygen:



$$(Ph_3SbBr)_2O_2 + Br_2 \longrightarrow Ph_3Sb(OOBr)(Br) + Ph_3SbBr_2$$

$$Ph_3Sb(OOBr)(Br) \longrightarrow O_2 + Ph_3SbBr_2$$

The decomposition was catalysed by Ph_3SbI_2. All reactions were carried out in chlorobenzene as the solvent. Graphs showed the rate of oxygen development as a function of time in the presence of bromine, iodine, or Ph_3SbI_2. The reaction was much faster with Ph_3SbI_2 than with Br_2 or I_2. The product in the case of Ph_3SbI_2 and $(Ph_3SbCl)_2O_2$ was $(Ph_3SbCl)_2O$.

The reaction of the peroxide $Ph_3Sb(OOH)_2$ with Et_3Tl led to the formation of $Ph_3Sb(OOTlEt_2)_2$ [89]. This compound readily underwent rearrangement to yield the compound $Ph_2(PhO)Sb(OOTlEt_2)(OTlEt_2)$. Reaction of $Ph_3Sb(OOH)_2$ with Ph_2SnCl_2 led to the formation of a pol $[Ph_2SnOOSbPh_3(OO)]_x$.

Pinchuk and co-workers [90] have reported on the preparation of N-sulfonylborazines. The reactions used were as follows:

$$ArSO_2NX_2 \;+\; BX_3 \longrightarrow 2\,X_2 \;+\; (ArSO_2NBX)_x$$

$$ArSO_2N{=}SbPh_3 \;+\; BX_3 \longrightarrow Ph_3SbX_2 \;+\; (ArSO_2NBX)_x$$

(where X was Br or Cl)

Nevett and Perry [91] have reported on the IR and Raman spectra of the dihalides R_3SbX_2, where R = Me or Ph and X = F, Cl, Br, or I. Assignments for all of the bands were made. A comparison of the observed fundamental frequencies and those calculated by normal coordinate analyses was made.

The normal coordinate analyses on the trimethylantimony dihalides Me_3SbX_2, where X = F, Cl, Br, or I, were reported in a separate paper by these same authors [92]. Sets of seven force constants were evaluated for each molecule by the use of each of the following force fields: general valence, modified Urey-Bradley, and orbital valence. Fundamental vibrational frequencies were then evaluated from these force constants and compared with the observed values published in the preceeding paper. The orbital valence force constants led to better agreement between calculated and observed frequencies. The force constant data showed that Sb-C equatorial stretching force constants were consistently larger than Sb-X axial stretching constants.

A comparison was also made between the force constants for the Me_3SbX_2 molecules and Me_5Sb. Force constants for the latter were taken from literature values. The values for the equatorial stretching force constants (termed fr) were considerably greater for the Me_3SbX_2 molecules than for Me_5Sb. This fact could be correlated with an increase in the Sb-C bond strength which accompanies an increase in the electronegativity of the Sb atom when two methyls are replaced by two electronegative halogen atoms. By similar reasoning the decrease in fr in going from Me_3SbF_2 to Me_3SbI_2 was readily explained. The large decrease in the axial stretching force constants (termed fd) in going from Me_3SbF_2 to Me_3SbI_2 was explained by the large differences in the masses of the halogen atoms.

McEwen and co-workers have previously reported on the decompositon of hydroxytetraphenylantimony in *p*-xylene to yield triphenylstibine oxide and benzene, and have shown that th reaction proceeded by a radical chain mechanism. The pres [illegible] aper [93] deals with the decomposition of hydroxytetraarylantimony compounds of the type $XC_6H_4(C_6H_5)_3SbOH$. The reactions were carried out at 30-50° since temperatures above 50° caused decomposition of triarylstibine oxides. At these temperatures the reactions were incomplete, but the product ratio of PhH and PhX could be determined by means of a material balance of the products of the reaction.

It was believed that the thermolytic reaction followed the following pathways:

$$XC_6H_4Ph_3SbO^{\bullet} \longrightarrow XC_6H_4Ph_2SbO + Ph^{\bullet}$$

$$XC_6H_4Ph_3SbOH + Ph^{\bullet} \longrightarrow XC_6H_4Ph_3SbO^{\bullet} + PhH$$

$$XC_6H_4Ph_3SbO^{\bullet} \longrightarrow Ph_3SbO + XC_6H_4^{\bullet}$$

$$XC_6H_4Ph_3SbOH + XC_6H_4^{\bullet} \longrightarrow XC_6H_4Ph_3SbO^{\bullet} + PhX$$

The ratios 3 PhX/PhH could then be used as a measure of the relative departure aptitudes of the groups from the radical $XC_6H_4Ph_3Sb\text{-}O^{\bullet}$. These ratios for various X substituents were: X = *p*-NO_2, 5.6; *m*-NO_2, 9.4; *p*-Cl, 2.5; *m*-Cl, 4.6; *p*-CH_3, 1.3; *m*-CH_3, 0.78; *p*-OCH_3, 2.6; *m*-OCH_3, 2.5. The authors concluded that these results, when compared with cleavage reactions that are known to go by an ionic mechanism, offered strong support for the radical cleavage mechanism they have suggested.

The authors also reported that the hydrolytic cleavage of pentaphenylantimony in an aprotic organic solvent with 1 mole of water led to the formation of hydroxytetraphenylantimony and benzene in essentially quantitative yields. This reaction obeyed second-order kinetics with a specific rate constant of 1.3×10^{-4} L $mol^{-1}s^{-1}$. They suggested that this reaction might be used for the determination of water or other hydroxylic compounds in inert organic solvents.

A series of organoarsenic and organoantimony compounds of the type Me_4AsX and Me_4SbX, where X = OMe, OEt, OCD_3, ONH_2, $ONMe_2$, ON=CHMe, or $ON=CMe_2$, have been prepared by means of the following reaction [94]:

$$Me_5E + HX \longrightarrow Me_4EX + CH_4$$

(where E = As or Sb and X was one of the groups mentioned above)

The compounds were characterized by elementary analyses. The ^1H NMR spectra of these compounds were given. At room temperature only a single methyl signal for the methyl groups attached to the As or Sb was seen but at low temperatures a number of the compounds studied gave two signals in a ratio of 3:1, corresponding to equatorial and axial methyl groups. Thus, the compound Me_4AsOMe at -100^o gave signals at $\delta = 1.45$ and $\delta = 0.00$ ppm, whereas the corresponding antimony compound gave only a single signal at -110^o. By contrast the antimony compounds Me_4SbONH_2, $Me_4SbONMe_2$, and $Me_4SbON=CHCH_3$ showed axial and equatorial methyl groups at -85^o. The IR and Raman spectra of the compounds were reported, and assignments of the bands were made for several of the arsenic and antimony compounds.

A study has been made of the electrical conductivities in aqueous solution of the nitrates, acetates, and lactobionates of the cationic species Ph_4E^+, where E = P, As, or Sb [95]. The conductivities were extrapolated to infinite dilution in order to obtain the limiting equivalent conductivities (Λo). The value for Ph_4Sb^+ was 19.8 Ω^{-1} cm^2 mol^{-1}.

A patent has been issued on the use of onium salts of the type [RR'R''R'''E] X, where the various R groups were aryl or aralkyl and E was N, P, As, or Sb, as antifogging agents in silver halide photographic films which are polyester supports and are subject to treatment under severe conditions [96].

Improved methods for the preparation of $Ph_3Sb(OAc)_2$ and Ph_5Sb have been described by Thepe, Garascia, and co-workers [97]. The diacetate was prepared from Ph_3Sb and 30% hydrogen peroxide in a solution of glacial acetic acid and acetic anhydride. An 85% yield of the product was obtained. Pentaphenylantimony was obtained in a crude yield of 94% from Ph_3SbBr_2 and PhMgBr. The product was recrystallized from acetonitrile.

Pinchuk and co-workers [98] have found that *N,N*-dichloroarenesulfonamides reacted with various tetra- or pentaarylmetal compounds with the elimination of one mole of aryl chloride at

40-80°. At higher temperatures a second mole of aryl chloride was eliminated to give an imidometal compound:

$$ArSO_2NCl_2 + MPh_n \xrightarrow{40-80^\circ} ArSO_2N(Cl)MPh_{n-1} \xrightarrow{130-140^\circ} ArSO_2N{=}MPh_{n-2}$$

(where M = Sn, Pb, or Sb and n = 4 for Sn or Pb and n = 5 for Sb)

In the case of Sb, the compound $PhSO_2N(Cl)SbPh_4$, m.p. 123-125°, was isolated in 80% yield. The authors, however, were unable to obtain pure $PhSO_2N{=}SbPh_3$, but its presence was confirmed by reaction of the impure compound with phenols:

$$ArSO_2N{=}SbPh_3 + 2\ PhOH \longrightarrow ArSO_2NH_2 + Ph_3Sb(OPh)_2$$

The reason why Ph_5Sb occurs in the solid state with square-pyramidal geometry whereas both Ph_5P and Ph_5As appear to possess trigonal-bipyramidal geometry, again in the solid state, has been the subject of considerable speculation. Although these results have been rationalized as crystal packing effects, no experimental evidence for this explanation has been forthcoming. Indeed, Brock and Ibers [99] had previously attempted to assess the magnitude of lattice effects for Ph_5Sb and concluded that any lattice effects favoring the square-pyramidal geometry for this compound were not offset by more dominant intramolecular interactions which favored the trigonal-bipyramidal form. These authors further suggested that their inability to theoretically predict the correct geometry for Ph_5Sb might be attributed to their having neglected Coulombic interactions. More recently a new set of nonbonded potential functions for C and H atoms which included Coulombic terms has become available. Brock [100] has made use of this new data and calculated that when Coulombic terms were included the results were more in harmony with experimental results. Thus, the degree of relative stabilization of the square-pyramidal geometry rises in going from Ph_5P to Ph_5Sb and this stabilization was increased when Coulombic potentials were used. The difference in molecular energies between the two Ph_5E geometries was greatly dependent on the exact molecular model used and changes as small as 0.01Å in the E-C bond length could affect the intramolecular energy difference by as much as 5kJ mol^{-1} or more. The resulting uncertainty was most important in the case of Ph_5As where a difference of a few kJ mol^{-1} could affect the prediction of the more favorable crystal structure when the

Coulombic potentials were used. For Ph_5P the signs and magnitudes of the energies clearly favored trigonal-bipyramidal geometry. For Ph_5Sb the Sb-C bond lengths for both geometries have been known with considerable accuracy from previous experiments and the square-pyramidal geometry was clearly favored.

The calculation also showed that only a small percentage of Ph_5Sb molecules should possess square-pyramidal geometry in solution. The crystallization process thus was responsible for isolating a molecular conformation in the solid state which may not be readily observable in solution.

An error in our annual surveys of organoantimony [101] and organobismuth [102] chemistry for 1975 has been kindly called to our attention by Professor M. Wieber of the University of Würzburg.
In discussing a paper by Ouchi, Honda, and Kitazima [103], we erroneously stated that they had described compounds of the type $Ph_3Sb(SSCR)_2$ and $Ph_3Bi(SSCR)_2$. Actually these authors had prepared triphenylantimony dicarboxylates and triphenylbismuth dicarboxylates by the following type of reaction:

$$Ph_3EBr_2 + 2\ RSCH_2CO_2H + 2\ Et_3N \longrightarrow Ph_3E(O_2CCH_2SR)_2 + 2\ Et_3NH^+\ Br^-$$

(where E was Sb or Bi and R was Me, Et, Pr, Me_2CH, Bu, Ph, or $PhCH_2$)

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