ANTIMONY

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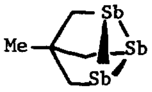
The preparation, reactions, and properties of most of the important classes of organoantimony compounds have been thoroughly reviewed in three new volumes of the *Gmelin Handbook of Inorganic Chemistry*. The first [1] of these volumes described tertiary stibines, the second [2] compounds of trivalent antimony with one or two C-Sb bonds, and the third [3] compounds of antimony(V) with four, five, or six C-Sb bonds. An extensive review of structure and bonding in organic derivatives of antimony(V) has also been recently published [4]. In addition, information about organoantimony compounds has been included in surveys of recent work on the main-group elements of Group V [5] and on organic derivatives of arsenic, antimony, and bismuth [6]. Ashe [7] has published an interesting account of work, mainly from his laboratory, on arsabenzene (arsenin), stibabenzene (antimonin), and bismabenzene (bismin). Organoantimony compounds have been very briefly mentioned in review articles on the following subjects: Mössbauer spectroscopy [8], the use of new organometallic reagents in organic synthesis [9], the biological methylation of metals and metalloids [10], substitution reactions of metal carbonyls with Group V and Group VI ligands [11], and diffraction studies of organometallic compounds [12].

4-Methyl-1,2,6-tristibatricyclo[2.2.1.0^{2,6}]heptane has been prepared by the following sequence of reactions [13]:

$$MeC(CH_2Br)_3 \; + \; 3\ NaSbPh_2 \xrightarrow[NH_3]{liquid} MeC(CH_2SbPh_2)_3 \; + \; 3\ NaBr$$

$$MeC(CH_2SbPh_2)_3 \; + \; 6\ HCl \xrightarrow{CH_2Cl_2} MeC(CH_2SbCl_2)_3 \; + \; 6\ PhH$$

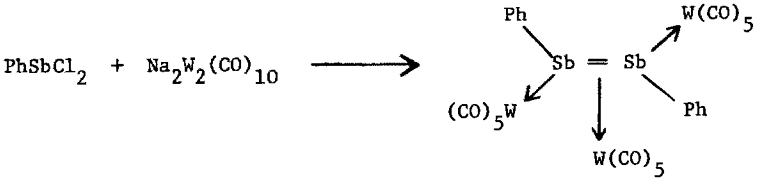
$$MeC(CH_2SbCl_2)_3 \; + \; 6\ Na \xrightarrow{THF}$$



$+ \; 6\ NaCl$

The composition and structure of the yellow all-*cis* cyclic tristibine was established by elemental analysis, osmometric molecular weight measurements, and both FD and EI mass spectroscopy. The compound was sublimable, very senitive to oxidation, and readily soluble in THF. Treatment of the tristibine with $Cr(CO)_5 \cdot THF$ (generated by the irradiation of a THF solution of hexacarbonylchromium with UV light) gave a dark-red 1:1 pentacarbonylchromium complex. The Raman spectrum of the complex exhibited a band at 227 cm^{-1}, which was assigned to the Cr-Sb stretching vibration.

Although diphenyldistibene (the antimony analog of azobenzene) has never been isolated as a free, monomeric molecule, a tungsten complex of this species has now been reported [14]. The complex was prepared by the reductive dehalogenation of phenyldichlorostibine in THF at 20°C:



It was obtained as red crystals, mp 110°C (dec.), and was stable in air at 20°C. The structure of this substance was established by elemental analysis, spectroscopic data (IR, UV, and PMR), and X-ray diffraction. The Sb-Sb bond distance was only 270.6(4) pm, a value significantly less than the Sb-Sb single bond distance. It was concluded that the diphenyldistibene was coordinated as a σ-ligand via both free electron pairs and as a π-ligand via the double bond.

Low-temperature X-ray diffraction has been employed to study the structure of tetra-*tert*-butyltetrastibetane, $(Me_3CSb)_4$ [15]. The compound exhibited an all-*trans* configuration in which the four-membered ring was folded and the bulky alkyl groups occupied pseudo-equatorial positions. The average C-Sb and Sb-Sb bond distances were 221 pm and 282 pm, respectively; the latter value was similar to that reported in other compounds containing the Sb-Sb single bond. The average Sb-Sb-Sb and Sb-Sb-C bond angles were 85° and 99°, respectively. The tetra-*tert*-butyltetrastibetane used in this investigation was obtained by the reduction of *tert*-butyldichlorostibine with magnesium.

Even in the presence of trimethylchlorosilane, the interaction of dibutylbromostibine or butyldibromostibine with magnesium in THF has been shown to result exclusively in antimony-antimony coupling [16]:

$$2\ Bu_2SbBr + Mg \longrightarrow Bu_2SbSbBu_2 + MgBr_2$$

$$BuSbBr_2 + Mg \longrightarrow 1/x\ (BuSb)_x + MgBr_2$$

On the other hand, antimony-silicon coupling predominated in the reactions of diphenylbromostibine or di-*tert*-butylchlorostibine with trimethylchlorosilane and magnesium in THF:

$$R_2SbX + Me_3SiCl + Mg \longrightarrow R_2SbSiMe_3 + MgClX$$

(where R was Ph or Me_3C and X was Br or Cl)

Both antimony-antimony and antimony-silicon coupling were observed in the reactions of phenyldibromostibine or *tert*-butyldichlorostibine with trimethylchlorosilane and magnesium in THF. When the phenyl compound was allowed to react with the magnesium and the silane was then added dropwise, the following reactions occurred:

$$PhSbBr_2 + Mg \longrightarrow 1/x\ (PhSb)_x + MgBr_2$$

$$PhSbBr_2 + 2\ Me_3SiCl + 2\ Mg \longrightarrow PhSb(SiMe_3)_2 + 2\ MgClBr$$

In contrast, when a THF solution containing both phenyldibromostibine and trimethylchlorosilane was added to the magnesium with vigorous stirring, distibines were obtained:

$$2\ PhSbBr_2 + 2\ Me_3SiCl + 3\ Mg \longrightarrow$$

$$Ph(Me_3Si)SbSb(SiMe_3)Ph + 2\ MgClBr + MgBr_2$$

$$PhSbBr_2 + 3\ Me_3SiCl + 5/2\ Mg \longrightarrow$$

$$Ph(Me_3Si)SbSb(SiMe_3)_2 + 2\ MgClBr + 1/2\ MgCl_2$$

The reaction of *tert*-butyldichlorostibine with trimethylchlorosilane and magnesium in THF yielded both tetra-*tert*-butyltetrastibetane and *tert*-butylbis(trimethylsilyl)stibine:

$$4\ Me_3CSbCl_2 + 4\ Mg \longrightarrow (Me_3CSb)_4 + 4\ MgCl_2$$

$$Me_3CSbCl_2 + 2\ Me_3SiCl + 2\ Mg \longrightarrow Me_3CSb(SiMe_3)_2 + 2\ MgCl_2$$

In addition, tris(trimethylsilyl)stibine, di-*tert*-butyl(trimethylsilyl)stibine, and tri-*tert*-butylstibine were also isolated from this reaction. In the reactions of phenyldibromostibine or *tert*-butyldichlorostibine with trimethylchlorosilane and magnesium, the ratio of antimony-antimony to antimony-silicon coupling was strongly influenced by the reaction conditions.

Tetrapropyldistibine and tetraphenyldistibine have been prepared by dehalogenation of the corresponding bromostibines with magnesium [17]:

$$2\ R_2SbBr\ +\ Mg\ \xrightarrow{THF}\ R_2SbSbR_2\ +\ MgBr_2$$

(where R was Pr or Ph)

Several tetraalkyldistibines were found to react with air to yield bis(dialkylantimony) oxides:

$$R_2SbSbR_2\ +\ 1/2\ O_2\ \longrightarrow\ R_2SbOSbR_2$$

(where R was Me, Et, Pr, Me_2CH, or Bu)

Bis(dimethylantimony) oxide was also prepared by the hydrolysis of dimethylbromostibine with aqueous sodium hydroxide:

$$2\ Me_2SbBr\ +\ 2\ OH^-\ \longrightarrow\ Me_2SbOSbMe_2\ +\ 2\ Br^-\ +\ H_2O$$

Treatment of distibines with sulfur gave analogous sulfides:

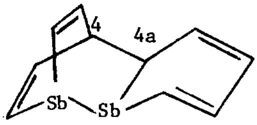
$$R_2SbSbR_2\ +\ 1/8\ S_8\ \longrightarrow\ R_2SbSSbR_2$$

(where R was Me, Et, Pr, or Ph)

The structures of these sulfides were deduced from elemental analysis and IR, PMR, and mass spectral data. Mass spectral data of the five distibines R_2SbSbR_2, where R was Me, Et, Me_2CH, Bu, or Ph, were also reported, and fragmentation patterns were discussed.

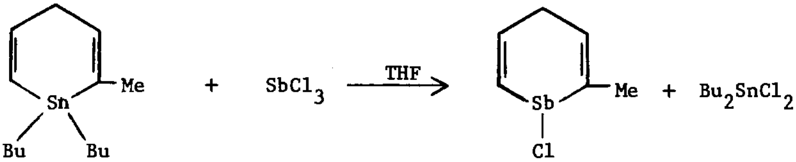
The IR spectra of liquid tetramethyldistibine, liquid tetraethyldistibine, and solid tetraphenyldistibine as well as the Raman spectra of liquid tetramethyldistibine at 25 to 100°C (including the depolarization values of the bands), solid tetramethyldistibine at 0°C, liquid tetraethyldistibine, and solid tetraphenyldistibine have been reported and discussed [18]. Assignments of the bands were made based on their positions, relative intensities, and polarization values. The Raman spectrum of the tetramethyl compound exhibited peaks at 175 and 145 cm^{-1}, which were assigned to the Sb-Sb stretching vibration. In contrast, both tetraethyldistibine and tetraphenyldistibine showed only a single Sb-Sb band (at 163 and 141 cm^{-1}, respectively). It was concluded that these results were consistent with the presence of both *gauche* and *trans* conformers in the tetramethyl compound and only a single conformer in the other two distibines.

The dimerization of stibabenzene (antimonin) has been investigated with the aid of PMR spectroscopy [19]. When this compound was cooled to -40°C in a tetrahydrofuran-d_8 solution, it reversibly formed the following Diels-Alder dimer:

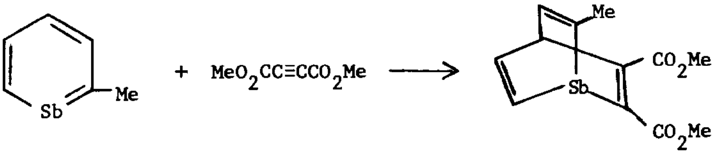


The dimer exhibited a closely spaced PMR spectrum in which absorption of the eight non-equivalent vinyl protons occurred between δ 5.8 and δ 6.5. All of the signals were assigned by analysis of the partially decoupled 360 MHz spectrum and by comparison with the PMR spectrum of the dimer obtained from stibabenzene-3,5-d_2. A high-field triplet at δ 2.82 was assigned to H_{4a}, while a multiplet at δ 4.57 was assigned to the diallylic bridgehead proton H_4.

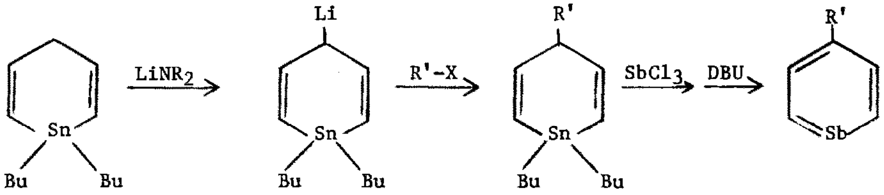
The pronounced lability of pure stibabenzene promoted an investigation of alkyl-substituted analogs in the hope that these compounds would be more stable. The first step in the attempted synthesis of 2-methylstibabenzene involved the formation of a heterocyclic chlorostibine:



Addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to the reaction mixture and subsequent codistillation with THF gave a yellow solution that showed a PMR spectrum with only very broad ill-defined peaks in the aromatic region (δ 11-7). A 1:1 Diels-Alder adduct of 2-methylstibabenzene and dimethyl acetylenedicarboxylate could be obtained, however, by addition of the latter compound to the yellow solution:



It was concluded that 2-methylstibabenzene was even more labile than stibabenzene. Two 4-alkylstibabenzenes were then prepared by the following route:



(where R was Me_2CH and R' was Me or Me_3C)

Both 4-alkylstibabenzenes were easily distillable liquids and were markedly more stable toward polymerization than the unsubstituted compound. Neither of the 4-alkyl derivatives formed detectable quantities of Diels-Alder dimer, although 4-methylstibabenzene was easily converted to the expected Diels-Alder adduct with dimethyl acetylenedicarboxylate. The PMR spectra of the stibabenzenes showed very low field signals for the α-protons because of the very large diamagnetic anisotropy of the antimony atom.

Electron transmission spectroscopy has been employed to study temporary negative ion formation in phosphabenzene, arsabenzene, and stibabenzene in the gas phase [20]. The observations made by this technique allowed the determination of the electron affinities (EA's) of the unstable anionic states of these molecules. The trends in the π* EA's (including the values previously obtained for benzene and pyridine) were compared with the trends in the ionization potentials (IP's) of the five substances. The results of this comparison were interpreted in light of the variation in carbon-heteroatom bond lengths and heteroatom electronegativities. The ground anionic states of phosphabenzene, arsabenzene, and stibabenzene were found to be stable and hence inaccessible by electron scattering methods. The measured trends in the EA's and IP's, however, allowed estimates for the energies of these states to be made. Anionic states other than those associated with occupation of the π* orbitals were also observed in this study, and possible assignments were discussed.

The extended Hückel method has been employed to examine the origin of the thermochromic effect in 2,2',5,5'-tetramethyl-1,1'-distibole by calculating the electronic structures of this molecule and of its solid-state structure, which has been found to contain a colinear chain of antimony atoms [21]. For simplicity of computation, the methyl groups were replaced by hydrogen atoms. The observed red shift on crystallization of the distibine was well accounted for by the calculations.

The molecular and crystal structure of tetrakis(trimethylsilyl)distibine, $(Me_3Si)_2SbSb(SiMe_3)_2$, and tetraphenyldistibine have been compared by X-ray diffraction [22]. The former compound was intensely red in the solid state, but only slightly yellow in solution or in the melt. As in 2,2',5,5'-tetramethyl-1,1'-distibole, the crystal structure was characterized by a nearly linear sequence of antimony atoms. The Sb-Sb bond length was 286.7(1) pm, while the intermolecular Sb-Sb contact was 399 pm. This latter value was significantly shorter than the sum of the van der Waals radii (440 pm). This shortening probably allowed the type of electronic interactions responsible for the red color of the crystals. In contrast, tetraphenyldistibine was yellow in the solid state. There was no colinear arrangement of antimony atoms, and the shortest intermolecular Sb-Sb contact was 429 pm, a value not considered significantly different from the sum of the van der Waals radii. The Sb-Sb bond length of 284.4(1) pm was very close to the sum of the covalent radii (286 pm).

Chiral derivatives of iron have been prepared by the following type of exchange reaction [23]:

$$Cp(CO)_2FeSbMe_2 \; + \; R_3P \longrightarrow Cp(CO)(R_3P)FeSbMe_2 \; + \; CO$$

[where Cp was η^5-cyclopentadienyl and R_3P was Me_3P, $PhPMe_2$, or $(MeO)_3P$]

The compound in which R_3P was $(MeO)_3P$ rearranged at room temperature in the following manner:

$$Cp(CO)[(MeO)_3P]FeSbMe_2 \longrightarrow Cp(CO)[(MeO)_2P(O)]FeSbMe_3$$

Treatment of the rearranged product with trimethyl phosphite led to cleavage of the iron-antimony bond:

$$Cp(CO)[(MeO)_2P(O)]FeSbMe_3 \; + \; (MeO)_3P \longrightarrow$$

$$Cp(CO)[(MeO)_2P(O)]FeP(OMe)_3 \; + \; Me_3Sb$$

The chiral compound in which R_3P was Me_3P proved to be a Lewis base of high nucleophilicity. Thus, it readily reacted with methyl iodide to form a chiral cationic complex:

$$Cp(CO)(Me_3P)FeSbMe_2 \; + \; MeI \longrightarrow [Cp(CO)(Me_3P)FeSbMe_3]I$$

It also underwent addition reactions with the iron complexes $Cp(CO)_2FeCl$ and $Cp(CO)(Me_3P)FeBr$:

$$Cp(CO)(Me_3P)FeSbMe_2 \; + \; Cp(CO)(L)FeX \longrightarrow$$

$$[Cp(CO)(Me_3P)FeSb(Me)_2Fe(CO)(L)Cp]X$$

(where L was CO and X was Cl, or where L was Me_3P and X was Br)

The new compounds prepared in this investigation were characterized by spectroscopy (IR, NMR, and mass) and by elemental analysis.

The reaction of chlorophosphines with one of the chiral iron compounds mentioned in the above paragraph has been found to involve oxidation of the antimony and reduction of the phosphorus [24]:

$$\mathrm{Cp(CO)(Me_3P)FeSbMe_2} + 2\ \mathrm{Ph(R)PCl} \longrightarrow$$

$$\mathrm{Cp(CO)(Me_3P)FeSb(Cl)_2Me_2} + \mathrm{Ph(R)PP(R)Ph}$$

(where Cp was η^5-cyclopentadienyl and R was Me or Ph)

The resulting Sb(V) compound was barely air-sensitive and dissolved without decomposition in benzene, nitromethane, and acetonitrile. Its covalent structure was reflected by its low conductivity in the last solvent. X-ray structural analysis showed a trigonal-bipyramidal configuration around the antimony atom. The two methyl groups and the chiral iron substituent occupied the equatorial positions while the more electronegative chlorine atoms occupied the axial positions. The C-Sb bond lengths (215 pm) agreed quite well with those in other Sb(V) compounds; the Sb-Cl bond lengths (260 pm) were, however, distinctly longer. The bulkiness of the $\mathrm{Cp(CO)(Me_3P)Fe}$ group caused the Fe-Sb-Cl angle to be significantly greater than the ideal value of 90° and the Me-Sb-Me angle to be considerably less than 120°. It was concluded that this substance was the first transition metal derivative of pentavalent antimony in which the antimony atom was bonded to three different substituents.

Dialkylhalostibines have been prepared by the thermal decomposition of trialkylantimony dihalides [25]:

$$\mathrm{R_3SbX_2} \longrightarrow \mathrm{R_2SbX} + \mathrm{RX}$$

(where R was Me or $\mathrm{Me_2CH}$ and X was Cl, Br, or I)

This procedure proved reasonably satisfactory except for the case in which R was $\mathrm{Me_2CH}$ and X was Cl. In fact, no really good method for obtaining pure diisopropylchlorostibine was developed. When triisopropylantimony dichloride was heated at 220°C for two hours at 90 torr, the resulting reaction mixture after distillation contained 60% of the chlorostibine, 25% of the starting material, and 10% of triisopropylstibine. The pure chlorostibine could not be isolated from this mixture by further distillation. When triisopropylantimony dichloride was heated at 220°C for four hours at normal pressure, a good yield of pure isopropyldichlorostibine could be obtained:

$$2\ (Me_2CH)_3SbCl_2 \longrightarrow Me_2CHSbCl_2 + (Me_2CH)_3Sb + 2\ Me_2CHCl$$

Halogenation of the diisopropylhalostibines produced unstable trihalides, which eliminated isopropyl halide to give an isopropyldihalostibine:

$$(Me_2CH)_2SbX + X_2 \longrightarrow (Me_2CH)_2SbX_3 \longrightarrow Me_2CHSbX_2 + Me_2CHX$$

Only the dibromo- and diiodostibines could be obtained in useful yields and purities by this procedure. Methyldiiodostibine was prepared by the disproportionation of dimethyliodostibine in dimethoxyethane at room temperature:

$$2\ Me_2SbI \longrightarrow MeSbI_2 + Me_3Sb$$

The triisopropylantimony dibromide and diiodide used in this study were obtained in the usual way, *i.e.*, by the halogenation of the tertiary stibine:

$$(Me_2CH)_3Sb + X_2 \longrightarrow (Me_2CH)_3SbX_2$$

(where X was Br or I)

The dichloride was prepared by two procedures. In one procedure, isopropylmagnesium chloride was allowed to react with antimony trichloride in ether, and the reaction mixture was then refluxed for 30 minutes. Presumably the following sequence of reactions was involved:

$$3\ Me_2CHMgCl + SbCl_3 \longrightarrow (Me_2CH)_3Sb + 3\ MgCl_2$$

$$(Me_2CH)_3Sb + 2/3\ SbCl_3 \longrightarrow (Me_2CH)_3SbCl_2 + 2/3\ Sb$$

The other procedure consisted of the interaction of preformed triisopropylstibine and antimony trichloride in ether at 0°C. The IR, PMR, and mass spectra of the various organoantimony compounds obtained in this investigation were reported and discussed.

(*o*-Diphenylstibinophenyl)diphenylbismuthine has been prepared by the following sequence of reactions [26]:

$$o\text{-}ClC_6H_4Br + Mg \xrightarrow{\text{ether}} o\text{-}ClC_6H_4MgBr$$

$$o\text{-}ClC_6H_4MgBr + Ph_2BiCl \xrightarrow[\text{THF}]{\text{ether}} o\text{-}ClC_6H_4BiPh_2 + MgBrCl$$

$$o\text{-}ClC_6H_4BiPh_2 + LiSbPh_2 \xrightarrow{\text{THF}} o\text{-}Ph_2SbC_6H_4BiPh_2 + LiCl$$

The compound was isolated as white needles in 57% yield. Its PMR and mass spectra were reported and compared with those of other triarylbismuthines. The base peak in the mass spectrum was the Bi^+ ion, while the relative intensities of $PhBi^+$ and $PhSb^+$ ions were 87% and 52%, respectively. Further information about this work is given under Bismuth.

The photostimulated reaction of potassium diphenylstibide with 4-bromoanisole or 4-chlorobenzophenone in liquid ammonia has been found to yield four tertiary stibines [27]:

$$ArX + KSbPh_2 \xrightarrow{h\nu} Ph_3Sb + ArPh_2Sb + Ar_2PhSb + Ar_3Sb$$

(where X was Br or Cl and Ar was 4-methoxyphenyl or 4-benzoylphenyl)

A similar reaction was observed with 4-chlorobenzophenone even in the dark. The results obtained in these reactions were explained by an $S_{RN}1$ mechanism involving tertiary stibine radical anion intermediates that reacted in part by electron transfer and in part by aryl-Sb bond breaking. The various tertiary stibines formed in this investigation were identified by GC/MS analysis.

In a paper on redox reactions of antimony(III) *O,O*-disubstituted phosphorodithioates with ferric chloride, the interaction of dibromoantimony(V) tris(*O,O*-diethylphosphorodithioate), $[(EtO)_2PS_2]_3SbBr_2$, and phenyllithium in ether was incidentally mentioned [28]. Attempts to isolate the diphenylantimony(V) derivative $Ph_2Sb[S_2P(OEt)_2]_3$ from the reaction mixture were unsuccessful; triphenylstibine and lithium *O,O*-diethyl phosphorodithioate were obtained instead. The dibromoantimony(V) derivative used in this study was obtained via the interaction of antimony(III) tris(*O,O*-diethyl phosphorodithioate) and bromine water at -65°C; it was apparently not analyzed or otherwise characterized.

In another paper from the same laboratory, a study of the interaction of *O,O*-disubstituted phosphorodithioates and various nucleophiles was reported [29]. The reaction of an excess of phenyllithium with antimony tris(*O,O*-diisobutyl phosphorodithioate) in benzene-ether solution led to the isolation of triphenylstibine in 60% yield:

$$3\ PhLi + [(Me_2CHCH_2O)_2PS_2]_3Sb \longrightarrow Ph_3Sb + 3\ LiS_2P(OCH_2CHMe_2)_2$$

No triphenylphosphine could be found in the reaction mixture. It was concluded that some variation of the S_N2 (Sb) mechanism was operative in this reaction.

The molybdenum(IV) complex $MoO(S_2CNEt_2)_2$ has been found to extract an oxygen atom from organic compounds such as pyridine *N*-oxide or dimethyl sulfoxide to form pyridine or dimethyl sulfide, respectively, and the molybdenum-

(VI) complex *cis*-$MoO_2(S_2CNEt_2)_2$. Because of the ease of oxidation and difficulty in handling the molybdenum(IV) compound, the reaction has hitherto not been used in organic synthesis. Lu and coworkers [30] have now reported that triphenylphosphine reduced the molybdenum(VI) compound to the molybdenum(IV) compound. This finding enabled the latter compound to be used as an excellent deoxygenating reagent in catalytic amounts. Thus, triphenylstibine oxide was reduced to triphenylstibine in 86% yield:

$$Ph_3SbO + Ph_3P \xrightarrow{MoO(S_2CNEt_2)_2} Ph_3Sb + Ph_3PO$$

In this reaction triphenylstibine oxide, triphenylphosphine, and the molybdenum(IV) complex were employed in a ratio of 1:1:0.02. The solvent was benzene, and the reaction was carried out at 40°C for 20 hours. Other compounds that were deoxygenated in excellent yields by this procedure were pyridine *N*-oxide, dimethylsulfoxide, azoxybenzene, and triphenylarsine oxide.

In a second study [31] from the same laboratory, the ability of tertiary derivatives of nitrogen, phosphorus, arsenic, antimony, and bismuth to abstract oxygen from *cis*-$MoO_2(S_2CNEt_2)_2$ was found to decrease in the order $Ph_3P >> Et_3N \sim Ph_3As > Ph_3Sb > Ph_3Bi > Ph_3N$. In general, the molybdenum compound was converted to $Mo_2O_3(S_2CNEt_2)_4$. Triphenylstibine yielded a substantial amount of this substance, but only a trace of triphenylstibine oxide could be isolated from the reaction mixture.

The oxidation of triphenylphosphine, triphenylarsine, and triphenylstibine by potassium peroxydisulfate in 60% aqueous acetonitrile has been found to obey the following stoichiometry [32]:

$$Ph_3E + S_2O_8{}^{2-} + H_2O \longrightarrow Ph_3EO + 2\ SO_4{}^{2-} + 2\ H^+$$

(where E was P, As, or Sb)

The reactions followed second-order kinetics - first order in Ph_3E and in $S_2O_8^{2-}$. The results obtained indicated a rate-determining nucleophilic displacement of the Ph_3E molecule on the peroxide linkage of the latter species. The relative order of the rates was $Ph_3P > Ph_3Sb > Ph_3As$. This order was attributed to two conflicting trends: the increased availability of *d* orbitals on descending the periodic table and the decrease in E-O bond strength in going from P to As to Sb. The oxidation of triphenylstibine gave a crystalline triphenylstibine oxide, which did not melt even above 280°C and which liberated iodine from potassium iodide in glacial acetic acid. These properties were believed to be consistent with the characteristics of a polymeric material previously prepared by the oxidation of triphenylstibine with hydrogen peroxide.

A number of carbonyl sulfide complexes of palladium have been prepared and allowed to react with triphenylphosphine, triphenylarsine, or triphenylstibine [33]. For example, when the complex PdS(COS)·3MeOH and triphenylstibine were refluxed in a DMSO–MeOH solution for about five minutes, the complex $Pd(SbPh_3)_2COS$ separated out in about 70% yield. An unspecified amount of triphenylstibine oxide could be isolated from the filtrate. The reactions of the palladium-triphenylstibine complex with a number of small molecules (O_2, I_2, MeI, $HgCl_2$, or HCl) were also investigated. In most cases there was little or no reaction except for decomposition to products which could not be characterized. The complex was said *not* to react when oxygen was bubbled for 15 minutes through a solution of the compound in benzene; some triphenylstibine oxide, however, was recovered from the reaction mixture.

The interaction of triphenylphosphine, -arsine, and -stibine with molecular oxygen at 77 K has been attributed to the formation of charge-transfer complexes in which oxygen acted as the acceptor [34]. Equilibrium constants of complex formation were obtained by studying the quenching effect of oxygen on the luminescence spectra of the triphenyl compounds. Charge-transfer complexes of these compounds with tetracyanoethylene were studied by means of electronic absorption spectroscopy. A linear correlation was found between the equilibrium constants of the oxygen complexes and the charge-transfer frequencies observed in the electronic spectra of the tetracyanoethylene complexes.

Excellent yields of trialkyl- and triarylantimony difluoride have been obtained by the oxidative fluorination of tertiary stibines in acetonitrile at a platinum anode [35]:

$$R_3Sb \xrightarrow{Et_4NBF_4} R_3SbF_2 + 2\,e^-$$

(where R was Bu, $Me(CH_2)_4$, Ph, or 2,4,6-$Me_3C_6H_2$)

The electrolyses were conducted at 20°C in an atmosphere of argon. The difluorides were characterized by elemental analysis and by IR and ^{19}F NMR spectroscopy.

A study has been made of the role of the dielectric constant of the solvent on the stoichiometry of charge-transfer complexes of the type $Ph_3E \cdot nI_2$ (where E was N, P, As, or Sb) and on their transformation into ion pairs [36]. Conductometric, refractometric, and differential refractometric methods were used in this investigation. The stoichiometry of the complexes varied with the dielectric constant, and their conversion into ion pairs was facilitated by solvents of high dielectric constant. The refractometric method gave good results in solvents of low dielectric constant, while the conductometric technique worked best with solvents of high dielectric constant.

Trialkylstibines have been used as antimony sources in several investigations [37-41] of the growth of thin alloy films by a process known as organometallic vapor phase epitaxy. This procedure was said to produce alloys with good surface morphology and other desirable characteristics. Antimony-doped tin oxide films have been prepared by the simultaneous oxidation of tetramethyltin and trimethylstibine at relatively low temperatures, *i.e.* 450-585°C [42]. This deposition technique allowed the growth of films that had excellent electrical conductivity and that retained the high transparency of undoped tin oxide. Tertiary stibines have also been mentioned in the patent literature as procatalysts [43] or accelerators [44,45].

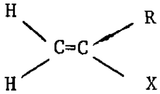
In addition to the papers already discussed [23,33], there have been numerous other recent articles that mentioned the use of tertiary stibines as ligands in transition metal complexes. The metals coordinated to the antimony in these complexes included cobalt [46-49], gold [50,51], iridium [52], iron [53-58], manganese [47,55], molybdenum [59-65], nickel [66,67], osmium [68,69], palladium [70-74], platinum [75-79], rhenium [80,81], rhodium [52, 82-84], ruthenium [85,86], and tungsten [62,65,87,88].

Triphenylamine, -phosphine, -arsine, and -stibine have been included in a study of the photodissociation of molecules containing heteroatoms [89]. CNDO/S-CI calculations of the changes in carbon-heteroatom bond order in excited triplet states were performed for the Group V derivatives. The results obtained suggested that the most probable primary intramolecular photochemical process for these molecules was predissociation from the T level and that the efficiency of the predissociation depended significantly on the atomic number of the heteroatom.

The gas-phase He I photoelectron (p.e.) spectra of tris(trifluoromethyl)-amine, -phosphine, -arsine, and -stibine have been described and compared to the p.e. spectra of the corresponding trimethyl compounds [90]. The trifluoromethyl group was found to cause a nearly parallel stabilization of all molecular orbital energies. This property was used in this study as a valuable aid to the more precise interpretation of the p.e. spectra of the methyl derivatives. Thus, overlapping bands associated with the ionization of σ- and π-type skeletal molecular orbitals were readily resolved on replacing methyl with trifluoromethyl groups.

Trimethylstibine has been included in a determination of the general inertia defect values of a variety of pyramidal and tetrahedral molecules [91]. The calculations were based on a simple normal coordinate analysis approach. It was found that the inertia defect values were small and positive and increased with the mass of the molecule. These values were used for the estimation of the rotational constant about the unique axis of the pyramidal molecules.

The inductive substituent constant of the divinylstibino group has been calculated from an investigation of olefinic geminal proton-proton PMR coupling constants [92}. A total of 161 substituents (X) was included in the study. It was concluded that this type of coupling constant may be one of the very few observables that measure inductive substituent constants correctly. The use of this method was restricted to terminal olefin derivatives of the following type:



A number of papers have been published in the past few years from the laboratory of R. R. Holmes on the geometry of pentacoordinate phosphorus compounds. In particular Holmes and coworkers have elucidated the structural principles that influence the pentacoordinate phosphorus atom to be displaced from trigonal bipyramidal geometry towards square or rectangular pyramidal geometry. These structural principles have now been extended to pentacoordinate arsenic and antimony compounds [93]. The crystal structures of two phenyl spiroarsoranes were determined. While no new pentacoordinate organoantimony compounds were prepared, the known geometry of several antimony(V) compounds were compared with similar pentacoordinate compounds of phosphorus and arsenic. It was concluded that the order of nonrigidity for Group V pentacoordinate compounds was in the order Sb > As > P and that the same principles that influence the geometry of pentacoordinate phosphorus compounds applied to arsenic and antimony compounds.

Bajpai and Srivastava [94] have prepared a series of phosphinimines of the type $Ph_3EN{=}PPh_3$, where E was Ge, Sn, or Pb, and of the type $R_3E(N{=}PPh_3)_2$, where E was Sb or Bi. The antimony compounds were prepared by the reaction between the pentacovalent compounds R_3SbX_2 and $Ph_3P{=}NH$:

$$R_3SbX_2 \ + \ 2\ Ph_3P{=}NH \ \longrightarrow \ R_3Sb(N{=}PPh_3)_2 \ + \ 2\ HX$$

(where R = Ph, X = Cl, Br, or OMe; R = cyclohexyl, X = Cl; R = p-MeC_6H_4, X = Br)

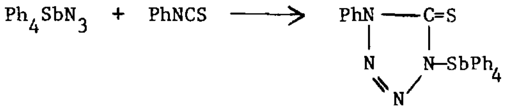
Thus, Ph_3SbCl_2 and $Ph_3P{=}NH$ in toluene solution were refluxed for five hours. After removal of the solvent and volatile material, the oily residue was triturated with hexane to give a crystalline material which was recrystallized from benzene/hexane. The reactions of Ph_3SbBr_2 and of $(p\text{-}MeC_6H_4)_3SbBr_2$ were carried out in methanol solution in the presence of Et_3N. All of the antimony-containing products were crystalline, air-stable solids. They were monomeric in benzene solution and non-electrolytes in acetonitrile. All the compounds gave strong bands in their IR spectra at $\sim$ 1170 cm^{-1} which were assigned to

P-N stretching. The compounds were unaffected by water or methanol but the Sb-N bond was cleaved by $PhTeCl_3$ or $TeCl_4$. Thus $Ph_3Sb(N{=}PPh_3)_2$ and $PhTeCl_3$ gave Ph_3SbCl_2 and $PhTe(N{=}PPh_3)Cl_2$.

Four patents have described the preparation of ylids containing both a Group VA element (P, As, or Sb) and the sodium salt of a sulfonic acid [95-98]. The ylids were subsequently treated with bis(cyclooctatriene)nickel to produce sulfonated nickel ylid catalysts which were useful for the oligomerization of ethylene.

The crystal structure of triphenylantimony dibenzoate has been determined by Lebedev and coworkers [99]. The atomic parameters, bonds lengths, and bond angles were given. The geometry of the molecule was found to be a distorted trigonal bipyramid with oxygen atoms in axial positions.

Bhattacharya and coworkers [100] have studied the reactions of azides of the type Ph_3EN_3 (E = Sn or Pb) and of the type Ph_4EN_3 (E = P, As, or Sb) with arylisothiocyanates. While triphenyllead azide did not react with phenylisothiocyanate, the other azides reacted to give tetrazoles. Thus, tetraphenylantimony azide and phenylisothiocyanate, when heated on a water bath for four hours in the absence of a solvent, reacted in the following manner:

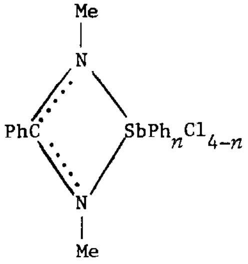


In addition to phenylisothiocyanate, *p*-bromophenyl-, *p*-tolyl-, and *o*-tolylisothiocyanates were used. *p*-Bromophenylisothiocyanate was found to be the most reactive, and the two tolylisothiocyanates the least reactive of the isothiocyanates employed. The phosphorus and arsenic azides reacted exothermally with the isothiocyanates, whereas the antimony compound required heating and a longer reaction time in order to complete the reaction. From these observations the authors suggested a mechanism which involved an attack of the azido nitrogen adjacent to the Group IV or Group V element on the electron-deficient carbon of the isothiocyanate, followed by a nucleophilic attack of the isothiocyanate nitrogen on the terminal nitrogen of the azide group. The compounds were characterized by elemental analyses; with one antimony and one arsenic compound a limited amount of IR and UV data was also given. Molar conductance measurements in acetonitrile indicated that all of the products were non-electrolytes in this solvent. Hydrolysis of the antimony-containing tetrazole by refluxing in dilute HCl for 6-7 hours yielded tetraphenylantimony chloride and 1,4-dihydro-1-phenyl-5*H*-tetrazole-5-thione.

In addition to the reaction of the azides (Ph_3EN_3 and Ph_4EN_3) with arylisothiocyanates, the reaction of these compounds with carbon disulfide was investigated. In each case the isothiocyanates, Ph_3ENCS (E = Sn or Pb) and Ph_4ENCS (E = P, As, or Sb), were formed. The authors suggested that, as in the case of the isothiocyanates, ring compounds were first formed, but that these decomposed with loss of nitrogen and sulfur to give the isothiocyanates; and indeed sulfur was isolated from the reaction mixture.

Organoantimony, organotin, and organotellurium compounds have been used as catalysts for the reaction of carbon dioxide with epoxides to form cyclic carbonates [101]. The catalytic activity of the organometallic compounds decreased in the order Sb > Te > Sn; pentavalent antimony compounds were more effective than trivalent antimony compounds. The kinetics of the reaction using Ph_3SbBr_2 as the catalyst was studied.

Hartke and Wolff [102] have previously described the synthesis of the four *N,N'*-dimethylbenzamidine-antimony(V) complexes of the following type:



Both IR and NMR (^{13}C and ^{1}H) spectra were reported. In order to further elucidate the structures of these four compounds, ^{121}Sb Mössbauer studies have now been reported for all four compounds at 4 K [103]. Both Raman and IR spectra were also reported in the region below 600 cm^{-1}, and the crystal structure of the compound $Ph_2Cl_2Sb(N_2Me_2CPh)$ was determined by X-ray diffraction. Values for the asymmetry parameter (η), the quadrupole splitting (ΔE^Q), the isomer shift relative to InSb (δ), and the line width (Γ) were given for all of the compounds. Configurations for all four compounds were assigned on the basis of the quadrupole splitting values. In each compound the antimony atom possessed octahedral geometry and the two nitrogen atoms were of necessity *cis*. In the compound where $n = 1$, the phenyl group and one chlorine were in *trans*-position. In the compound where $n = 2$, two chlorine atoms were in *trans* position. The X-ray diffraction study of this compound showed that the structure consisted of discrete $Ph_2Cl_2Sb(N_2Me_2CPh)$ molecules with a greatly distorted octahedral geometry for the Sb atom. The Cl-Sb-Cl angle was 172.4°, and the N-Sb-N angle was 60.6°. Finally, the complex in which $n = 3$ possessed a phenyl group and a chlorine atom in *trans* position. The Raman and IR spectra of these compounds were in accord with the assigned structures based on the Mössbauer spectra.

Nomura and coworkers have previously reported on the use of organoantimony compounds as catalysts for the cycloaddition reaction of carbon dioxide to oxiranes to form cyclic carbonates. The most effective catalysts were Ph_4SbBr, and to a lesser extent, Ph_3SbBr_2. The present paper extended the study to include organometallic compounds of Sn, Te, Ge, Si, and Bi [104]. These were less effective catalysts than organoantimony(V) compounds. However, in the presence of a Lewis base such as triethylamine, pyridine, or triphenylphosphine, the catalytic activities of Ph_3SnBr and Ph_3SnI were greatly enhanced, surpassing Ph_4SbBr. Addition of a Lewis base to the organoantimony(V) compound had little or no effect on its catalytic activity.

Nomura and coworkers [105] have studied the polymerization of ethylene oxide catalysed by triphenylantimony dibromide. Although the antimony compound alone induced polymerization, the rate of polymerization was greatly increased by the simultaneous addition of triphenylphosphine. The rate curve for the polymerization reaction, in the presence of both substances, showed an inflection point, which suggested that the reaction occurred in two steps which the authors termed a cationic polymerization process (first step) and a coordinated polymerization process (second step). In the suggested mechanism, the second step involved a nucleophile attack of Ph_3P on antimony to form a six-coordinate antimony atom. In addition to triphenylantimony dibromide, tri-*p*-tolylantimony dibromide and tris(*p*-chlorophenyl)antimony dibromide were used as catalysts. A Hammett plot, obtained from these three antimony compounds, gave ρ values of + 1.7 and + 1.0 for the two steps of the reaction. These results were believed to be accord with the suggested polymerization mechanism.

Sille, Weidlein, and Haaland [106] have reported the preparation of a number of trivinylarsenic and trivinylantimony compounds, and have determined the IR, Raman, and the ^1H and ^{13}C NMR spectra of the compounds they reported. Trivinylarsine and trivinylstibine were obtained from vinylmagnesium chloride in THF solution. These were readily converted to trivinylarsenic and trivinylantimony dichlorides by treatment with SO_2Cl_2. The reaction of either dichloride with two molar equivalents of MeLi or MeC≡CNa gave mixtures of products of the type $R_xE(CH{=}CH_2)_{5-x}$ (where R = Me or MeC≡C and E = As or Sb), which could not be separated. Similarly, inseparable mixtures of products were obtained from either of the dichlorides and sodium ethoxide. However, the difluorides $(CH_2{=}CH)_3AsF_2$ or $(CH_2{=}CH)_3SbF_2$ were obtained by the reaction between the dichloride and either KF or CsF. The pure difluorides $(CH_2{=}CH)_3AsF_2$ or $(CH_2{=}CH)_3SbF_2$ were separated from the reaction mixtures by fractional distillation. There was evidence from the ^{13}C spectra of the reaction mixtures that the mixed halides $(CH_2{=}CH)_3AsFCl$ or $(CH_2{=}CH)_3SbFCl$ were formed, but they were not isolated. All of the trivinyl compounds were oily liquids which could be purified by vacuum distillation, but with some decomposition. The reaction between $(CH_2{=}CH)_3SbCl_2$ and $SbCl_5$ gave the solid "ate" compound $[(CH_2{=}CH)_3SbCl]\ [SbCl_6]$ which melted with decomposition at ∿ 105°C.

The IR and Raman spectra of all of the compounds were determined, and (except for the "ate" compound) assignments of all of the bands were made. It was concluded, on the basis of these spectra, that $(CH_2{=}CH)_3As$ and $(CH_2{=}CH)_3Sb$ were trigonal-pyramidal and that the As(V) and Sb(V) compounds were trigonal-bipyramidal molecules with slightly twisted vinyl groups. In the spectra of the "ate" compound there was a marked decrease in the intensity of the C=C valence band at 1585 cm^{-1} (this decrease was not seen in the other trivinyl compounds). The authors could offer no explanation for this effect. The ^1H and ^{13}C NMR spectra of the compounds $(CH_2{=}CH)_3E$ and $(CH_2{=}CH)_3EX_2$ (E = As or Sb and X = Cl or F) were determined in several solvents and at various temperatures. Since the three protons of the vinyl groups were magnetically non-equivalent, complex NMR spectra were obtained. Quantum mechanical calculations (based on a modified BASIC version of the known FORTRAN program LAOCOON III) of the chemical shifts and coupling constants were carried out, and the observed chemical shifts compared with the calculated values.

An ^{121}Sb-Mössbauer study at 4.2 K of the three antimony(V) compounds $Me_3Sb(OH)_2$, Me_3SbO, and Ph_3SbS has been reported by Pebler and coworkers [107]. Values of the isomer shift (δ, relative to $Ba^{121}SnO_3$), the quadrupole coupling constant (e^2qQ), the halfline width (Γ), and the asymmetry parameter (η) were given and compared with literature values for Me_3SbCl_2, Me_3SbBr_2, and Ph_3SbO. The results for $Me_3Sb(OH)_2$ and Me_3SbO were in agreement with trigonal-bipyramidal structures for these two compounds with the three methyl groups in equatorial positions. It was suggested that $Me_3Sb(OH)_2$ was polymeric with the axial oxygens connected by hydrogen bonds. The structure suggested for the oxide contained two bridging axial oxygen atoms. By contrast the very small quadrupole splitting indicated that the Sb atom in Ph_3SbS was tetrahedral. This observation was confirmed by an X-ray diffraction single crystal study of the molecule. Bond distances and bond angles were reported. The very short Sb-S bond distance of 224 pm indicated that there was considerable Sb-S π bonding. A preliminary report on the crystal structure of triphenylantimony sulfide appeared in 1981 [108].

Manhas and Trikha [109] have studied the IR spectra of a large number of inorganic and organometallic compounds which contained either acetato or trifluoroacetato groups. The crystal structures of all of these compounds were known from the work of other investigators. They compared the directions of shifts of the IR frequencies of γ_{asym} OCO and γ_{sym} OCO with respect to the frequencies for the corresponding carboxylate ions and were able to classify the type of carboxylate binding in the various compounds they investigated. Thus the two acetato groups in the compound $Ph_3Sb(O_2CMe)_2$ were classified as unidentate.

The use of triphenylantimony dichloride as a fire retardent for brominated epoxy resins has been described [110]. The use of triphenylstibine oxide as a cracking catalyst to increase the yield of gasoline has been claimed in a patent application [111].

The reactions between tetraphenylantimony chloride and $ZrCl_4$, $NbCl_5$, or WCl_6, and between triphenylantimony dichloride and these same transition metal chlorides have been reported by Sharma and coworkers [112]. With tetraphenylantimony chloride, the ionic compounds $[Ph_4Sb]_2[ZrCl_6]$, $[Ph_4Sb][NbCl_6]$, and $[Ph_4Sb][WCl_6]$ were formed. The reactions were carried out in benzene solution in a nitrogen atmosphere and it was concluded that in benzene solution the reactive tungsten compound was WCl_5 (i.e. WCl_6 was reduced to WCl_5 in benzene solution). Conductance measurements in nitrobenzene solution demonstrated that the Nb and W compounds were 1:1 electrolytes and the Zr compound a 2:1 electrolyte in nitrobenzene. The IR spectra of the compounds were reported.

Triphenylantimony dichloride and the three transition metal chlorides formed 1:1 adducts. These were insoluble in organic solvents and gave high m.p.'s. It was also found that triphenylstibine reduced WCl_6 to WCl_3 in benzene solution, but $NbCl_5$ and $ZrCl_4$ did not react with the stibine.

In a later paper Sharma and coworkers reported on the reactions between tetraphenylantimony chloride, triphenylantimony dichloride, or triphenylstibine and the anhydrous halides BCl_3, VCl_3, or $SnCl_4$ [113]. The reactions were carried out in an organic solvent in a nitrogen atmosphere. With Ph_4SbCl ionic complexes $[Ph_4Sb]BCl_4$, $[Ph_4Sb]VCl_4$, and $[Ph_4Sb]_2SnCl_6$ were obtained. The molar conductivities of these compounds in dimethylformamide (and of the tin compound in nitrobenzene) were reported. The boron and vanadium compounds were 1:1 electrolytes and the tin compound a 2:1 electrolyte. Triphenylantimony dichloride formed the complexes $Ph_3SbCl_2 \cdot 2BCl_3$ and $Ph_3SbCl_2 \cdot VCl_3$ with BCl_3 and VCl_3, respectively. An attempt to form a complex between Ph_3SbCl_2 and $SnCl_4$ was unsuccessful. Triphenylstibine underwent reaction with VCl_3 or $SnCl_4$ with cleavage of the C-Sb bond. IR spectral data on all of the compounds were reported. Magnetic susceptibility data for the vanadium compounds were also reported.

In a third paper from the Indian group the reactions of Ph_4SbCl, Ph_3SbCl_2, and Ph_3Sb with $FeCl_3$ were reported [114]. The reactions were carried out in benzene solution in a nitrogen atmosphere. When one molar equivalent of Ph_4SbCl was added to one molar equivalent of ferric chloride, the compound $[Ph_4Sb][FeCl_4]$ was obtained. However, addition of three molar equivalents of Ph_4SbCl to two molar equivalents of $FeCl_3$ gave the compound $[(Ph_4Sb)(FeCl_4)]_2 \cdot Ph_4SbCl$. Both of these compounds were ionic with molar conductance values of 29.2 and 63.7 mhos $cm^2\ mol^{-1}$, respectively. The Mössbauer, IR, and PMR spectra of the two compounds were reported. On the basis of the IR and Mössbauer results it was concluded that the second compound should be formulated as $[(Ph_4Sb)(FeCl_4)]_2\cdot Ph_4SbCl$ rather than as $[Ph_4Sb]_3[Fe_2Cl_9]$. Magnetic susceptibility data for both compounds were also reported. Only one complex, $(FeCl_3)_2\cdot Ph_3SbCl_2$, was obtained from $FeCl_3$ and Ph_3SbCl_2. From IR data it was concluded that the complex involved chlorine bridges. Triphenylstibine and $FeCl_3$ gave Ph_3SbCl_2 and $FeCl_2$.

In continuation of earlier work on the application of vibrational spectroscopy to the estimation of electron-donating properties of the organometallic groups $OEPh_n$ and $SEPh_n$ (where E is a metal such as Hg, Sn, Pb, or Sb and n is 1, 3, 3, or 4, respectively), Epstein and coworkers [115] have measured the integral intensities of two bands in the IR spectra of *p*-nitrophenol, *p*-nitrothiophenol, and *p*-nitroaniline, as well as derivatives of these compounds. The two bands studied were phenyl vibrations in the 1600 cm^{-1} region (νAr) and symmetrical vibrations of the nitro groups ($\nu_s NO_2$). The organometallic compounds were of the type $p\text{-}O_2NC_6H_4OEPh_n$, $p\text{-}O_2NC_6H_4SEPh_n$, and $p\text{-}O_2NC_6H_4NHHgPh$, where again E was Hg, Sn, Pb, or Sb. From the integral intensity data the author have derived equations for predicting values for several different substituent constants, namely σp^+, $\sigma_R{}^+(P)$ and $\sigma_R{}^+(T)$. The substituent constants were listed for measurements made in two different solvents, CH_2Cl_2 and DMSO, and they were found to be solvent dependent. All of the organometallic groups including Ph_4SbO and Ph_4SbS were found to be electron-donating. The electron donating ability of the Ph_nEO and Ph_nES groups were in the order Sb > Pb > Hg > Sn in DMSO. In CH_2Cl_2, however, the order was Sb > Pb > Sn > Hg for Ph_nEO compounds, but Sb > Hg > Pb > Sn for Ph_nES compounds.

The thermal decomposition of tetraphenylantimony mercaptides, Ph_4SbSR, in the solid state has been reported in earlier papers. The present paper by Bedi and coworkers [116] extended this study to the thermal decomposition of these mercaptides in solution, and to the decomposition, both in solution and in the solid state, of unsymmetrical mercaptides of the type $Ar_3Ar'SbSAr''$ The preparation of a number of new organoantimony compounds was reported. Tetraphenylantimony mercaptides Ph_4SbSAr (Ar = $p\text{-}MeC_6H_4$, $o\text{-}MeOC_6H_4$, and $p\text{-}MeOC_6H_4$) were obtained from Ph_4SbCl and the appropriate thiol in the presence of Et_3N. (Tri-*p*-tolyl)phenylantimony phenylmercaptide was obtained by means of the following reaction sequence:

$$(p\text{-}MeC_6H_4)_3Sb + PhN_2BF_4 \longrightarrow (p\text{-}MeC_6H_4)_3PhSbBF_4 + N_2$$

$$(p\text{-}MeC_6H_4)_3PhSbBF_4 + NaI \longrightarrow (p\text{-}MeC_6H_4)_3PhSbI + NaBF_4$$

$$(p\text{-}MeC_6H_4)_3PhSbI + PhSH + Et_3N \longrightarrow (p\text{-}MeC_6H_4)_3PhSbSPh + Et_3NHI$$

In a similar manner the compounds $(p\text{-}MeC_6H_4)_3PhSbSC_6H_4OMe\text{-}p$, $Ph_3(p\text{-}MeC_6H_4)SbBF_4$,

$Ph_3(p\text{-}MeC_6H_4)SbI$, and $Ph_3(p\text{-}MeC_6H_4)SbSC_6H_4OMe\text{-}p$ were prepared. An attempt was also made to prepare $Ph_3MeSbSC_6H_4OMe\text{-}p$ from Ph_3MeSbI, $p\text{-}MeOC_6H_4SH$, and Et_3N. Although the desired mercaptide could not be isolated, the products of the reaction indicated that it had been formed and immediately decomposed.

The thermal decomposition of $Ph_4SbSC_6H_4OMe\text{-}p$ (m.p. 106-107°C) was studied under a variety of conditions, namely, in refluxing C_6H_6, C_6D_6, cyclohexene, cyclohexane, $CHCl_3$, and CCl_4; at 34°C in $CDCl_3$ or CCl_4, and neat at 130°C. The products of decomposition were identified by GLC, GC-MS, and by PMR. The principal decomposition products were Ph_3Sb and $p\text{-}MeOC_6H_4SPh$, with small amounts of $(p\text{-}MeOC_6H_4S)_2$ and Ph_2. Thus, in refluxing benzene the yields of these four products were 95%, 86%, 8%, and 4%, respectively. In $CDCl_3$ and CCl_4 at 34°C the amount of $p\text{-}MeOC_6H_4SPh$ was markedly decreased and the amount of $(p\text{-}MeOC_6H_4S)_2$ markedly increased. In cyclohexane and in CCl_4, the solvent-derived products $p\text{-}C_6H_{11}SC_6H_4OMe$, PhCl, and $p\text{-}Cl_3CSC_6H_4OMe$ were obtained. These latter results indicated that free radicals played a major role in these reactions. No evidence for a radical attack on the solvent was found when C_6H_6, $CHCl_3$, or cyclohexene was used, nor was any deuterium incorporated into Ph_2 or $p\text{-}MeOC_6H_4SPh$ when the reaction was carried out in refluxing C_6D_6.

The decompositions of $Ph_4SbSC_6H_4OMe\text{-}o$ and $Ph_4SbSC_6H_4Me\text{-}p$ in $CDCl_3$ or in CCl_4 at 34°C were also studied. The relative rates of decomposition in $CDCl_3$ were $Ph_4SbSC_6H_4OMe\text{-}o > Ph_4SbSC_6H_4OMe\text{-}p > Ph_4SbSC_6H_4Me\text{-}p$. The rate of decomposition of $Ph_4SbSC_6H_4OMe\text{-}o$ in $CDCl_3$ or CCl_4 was zero order in the substrate. Some Ph_4SbCl was also formed in the decomposition of $Ph_4SbSC_6H_4OMe\text{-}o$ in these solvents.

The thermal decomposition of three mercaptides, Ar$_3$Ar'SbSAr", (Ar = Ph, Ar' = $p\text{-}MeC_6H_4$, Ar" = $p\text{-}MeOC_6H_4$; Ar = $p\text{-}MeC_6H_4$, Ar' = Ph, Ar" = $p\text{-}MeOC_6H_4$; Ar = $p\text{-}MeC_6H_4$, Ar' = Ar" = Ph) was studied under reaction conditions similar to those used for the tetraphenylantimony mercaptides. In addition the three compounds were injected directly into the port of the mass spectrometer (port temperature 250°C); the same products were found as under the other reaction conditions, but the relative amounts of products were not the same. Under all reaction conditions a wide variety of reaction products was always found. These included the compounds Ar$_3$Sb, Ar$_2$Ar'Sb, ArAr$_2$'Sb, Ar$_3$'Sb, Ar"SSAr", ArSAr", Ar'SAr", ArH, and Ar'H. When the reactions were carried out in CCl_4, the compounds ArCl, Ar'Cl, and Cl$_3$CSAr" were also found. A radical mechanism, similar to that proposed in earlier papers, was suggested to explain the formation of the mixed sulfides and the arenes. The finding of all possible mixed triarylstibines was unanticipated. The authors suggested that these were formed by a series of radical reactions such as:

$$\mathrm{Ar'\cdot + Ar_3Sb \longrightarrow Ar'Ar_2Sb + Ar\cdot}$$

They found that refluxing Ph_3Sb and $(p\text{-}MeC_6H_4)_3Sb$ in $CHCl_3$ or peroxide-free THF brought about no exchange, but when the two stibines were refluxed in a old sample of THF containing peroxides, considerable exchange occurred. Some exchange also occurred when the two stibines in peroxide-free THF and in the presence of a radical initiator were injected directly into the chromatograph.

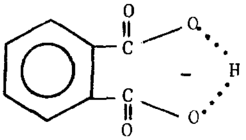
The reaction of pentamethylantimony with acids, alcohols, mercaptans, or water to form methane and a tetramethylantimony compound is well known:

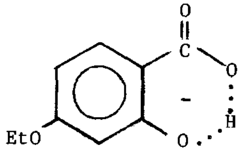
$$Me_5Sb + HX \longrightarrow Me_4SbX + MeH$$

However, with two molar equivalents of acid the reaction does not produce two moles of methane but rather a crystalline ionic product of the type $[Me_4Sb]RCOO \cdot RCO_2H$ as follows:

$$Me_5Sb + 2\ RCO_2H \longrightarrow MeH + [Me_4Sb]RCO_2 \cdot RCO_2H$$

Milewski-Mahrla and Schmidbaur [117] have now investigated the structure of the crystalline products derived from the following six acids: benzoic, phthalic, 4-ethoxysalicylic, oxalic, salicylic, and malic. By means of X-ray diffraction the crystal structures of the compounds derived from benzoic, phthalic, and 4-ethoxysalicylic acids were determined. The anions were hydrogen-bonded dimers of the type $[RCO_2....H....O_2CR]^-$. With phthalic and 4-ethoxysalicylic acids intramolecular hydrogen bonds were formed as follows:





The structure of the Me_4Sb cation varied with the acid. With phthalic acid it was largely undistorted but with benzoic acid the antimony tetrahedron was distorted by the close proximity of the two carboxylate groups. With 4-ethoxysalicylic acid the O-Sb distance was as short as that found in other compounds containing an Sb-O bond, so that the antimony in this compound was pentacoordinate. NMR data (^1H and ^{13}C) and elemental analyses were given for all of the compounds prepared.

The IR and Raman spectra of solid $Me_4N[Me_2SbF_4]$ and $Me_4N[Me_2SbCl_4]$, and the Raman spectra of the two compounds in acetonitrile solution, have been reported by Bertazzi and coworkers [118]. The antimony atoms in the two anions possessed octahedral geometry (D_{4h} symmetry) with the methyl groups in *trans*-position. Assignments for the various skeletal vibrations in the spectra below 1000 cm^{-1} were made.

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