ANTIMONY

ANNUAL SURVEY COVERING THE YEAR 1980*

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Except for the Annual Survey covering the year 1979, no review devoted exclusively to organoantimony chemistry appeared in 1980. Information about organoantimony compounds was included, however, in a new edition of a monograph on organometallic compounds [1] and in a short survey of recent work on organic derivatives of arsenic, antimony, and bismuth [2]. Organoantimony compounds were also briefly mentioned in a review of the use of new organometallic reagents in organic synthesis [3].

An investigation of the reduction of propyl- and butyldiiodostibine at a mercury electrode has been reported [4]. The reduction involved a two-electron step and produced an insoluble, easily oxidized, presumably polymeric substance:

$$RSbI_2 + 2e^- \longrightarrow 1/x\ (RSb)_x + 2I^-$$

(where R was Pr or Bu)

In basic media, electrochemical oxidation of the diiodostibines was also observed. The diiodostibines were prepared by prolonged heating (in an inert atmosphere at 100–150°C) of a solution of trimethylstibine in the appropriate alkyl iodide with a metallic iodide. The stoichiometry of this curious reaction was not elucidated. The diiodostibines were slightly soluble in alcohol and a little more soluble in acetic acid or dimethylformamide. They were only very slightly sensitive to air oxidation.

The interaction of diisopropyl- or dibutylbromostibine and magnesium in tetrahydrofuran (THF) has been found to give a modest yield of the corresponding tetraalkyldistibine [5]:

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*Previous review see J. Organometal. Chem., 203 (1980) 327 – 357.

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

(where R was Me_2CH or Bu)

A smaller amount of the trialkylstibine was also formed in each case. Both distibines were yellow, air-sensitive liquids, which could be distilled without decomposition only at reduced pressure. The PMR spectrum of the tetraisopropyldistibine clearly showed the diastereotopic environment of the isopropyl groups. The reduction of isopropyl- or butyldibromostibine with magnesium in THF yielded black, insoluble, air-sensitive, presumably polymeric solids of empirical formula RSb:

$$RSbBr_2 + Mg \longrightarrow 1/x\ (RSb)_x + MgBr_2$$

When these solids were heated strongly *in vacuo*, they decomposed to give both the corresponding distibine and the tertiary stibine. The isopropyldibromostibine used in this investigation was prepared by the following sequence of reactions:

$$(Me_2CH)_2SbBr + Br_2 \xrightarrow{-40^\circ C} (Me_2CH)_2SbBr_3$$

$$(Me_2CH)_2SbBr_3 \xrightarrow{100^\circ C} Me_2CHSbBr_2 + Me_2CHBr$$

Unlike the corresponding bromo compound, dimethyliodostibine has been found *not* to react with magnesium in THF to form tetramethyldistibine [6]. In the presence of trimethylchlorosilane *and* magnesium, however, dimethyl- or diethyliodostibine caused cleavage of the THF ring and formation of a trimethylsiloxy-substituted tertiary stibine:

$$R_2SbI + Me_3SiCl + C_4H_8O + Mg \longrightarrow Me_3SiO(CH_2)_4SbR_2 + MgICl$$

(where R was Me or Et)

The following sequence of reactions was suggested:

$$R_2SbI + Me_3SiCl \longrightarrow R_2SbCl + Me_3SiI$$

$$Me_3SiI + C_4H_8O \longrightarrow Me_3SiO(CH_2)_4I$$

$$Me_3SiO(CH_2)_4I + Mg \longrightarrow Me_3SiO(CH_2)_4MgI$$

$$Me_3SiO(CH_2)_4MgI + R_2SbCl \longrightarrow Me_3SiO(CH_2)_4SbR_2 + MgICl$$

The tertiary stibines thus prepared were colorless, spontaneously inflammable, water-sensitive liquids. Their structures were established by elemental analysis and by IR, PMR, and mass spectroscopy. It was also noted that the interaction of dimethyl- or diethylbromostibine and magnesium in THF was not affected by the presence of trimethylchlorosilane; *i.e.*, a good yield of tetraalkylstibine was obtained under these conditions.

Polymeric nickel carbonyl complexes containing bridging bidentate ligands have been prepared by the following type of reaction in pentane at room temperature [7]:

$$(Ph_2Sb)_2MMe_2 + Ni(CO)_4 \longrightarrow 1/x\ [Ph_2SbMMe_2SbPh_2Ni(CO)_2]_x + 2\,CO$$

(where M was C, Ge, or Sn)

The polymers were yellow solids that were not appreciably soluble in organic solvents. No information about the value of x was obtained. A polymeric chromium carbonyl complex containing tetramethyldistibine was obtained in a similar manner:

$$Me_2SbSbMe_2 + Cr(CO)_4(nor) \longrightarrow 1/x\ [Me_2SbSbMe_2Cr(CO)_4]_x + nor$$

(where nor was bicyclo[2.2.1]hepta-2,5-diene)

This complex was also a solid and was described as being completely insoluble in organic solvents. The reaction of one mole of the bidentate tin ligand with two moles of pentacarbonyl(tetrahydrofuran)chromium (photochemically generated in THF solution) yielded a binuclear complex:

$$(Ph_2Sb)_2SnMe_2 + 2\,Cr(CO)_5(THF) \longrightarrow Me_2Sn[SbPh_2Cr(CO)_5]_2 + 2\ THF$$

In contrast to this result, the reaction of the analogous carbon or germanium bidentate ligand with pentacarbonyl(tetrahydrofuran)chromium yielded pentacarbonyl(triphenylstibine)chromium, which was identified by its mass spectrum. Apparently, these bidentate ligands decomposed to triphenylstibine under the conditions of these reactions.

The interaction of equimolar quantities of diethylbromostibine and vanadocene in hexane at 40°C has been shown to result in oxidation of the vanadium [8]:

$$Cp_2V + Et_2SbBr \longrightarrow Cp_2VBr + \tfrac{1}{2}\ Et_2SbSbEt_2$$

(where Cp was cyclopentadienyl)

The vanadocene monobromide precipitated from the solution as a bright blue solid, and the tetraethyldistibine was isolated from the mother liquor by vacuum distillation. Under other reaction conditions, it was found possible for diethylbromostibine to convert vanadocene to vanadocene dibromide.

An X-ray crystal structure of tetraphenyldistibine has shown that in the solid state this molecule existed in the staggered *trans* conformation [9]. The Sb-Sb bond length was 283.7 pm, a value that agreed well with other estimates for the Sb(III)-Sb(III) single bond distance. The Sb-Sb-C and C-Sb-C bond angles were only a few degrees larger than 90^{o}, and hence it was concluded that the antimony atom was primarily using *p*-orbitals for bonding and that the lone pair had essentially *s*-character. The C-Sb distances were in the range of comparable compounds and were about equal to the sum of the covalent radii of Sb(III) and sp^2-carbon atoms.

X-ray diffraction has also been employed to determine the crystal and molecular structure of a binuclear complex of tetraphenyldistibine, *viz.* $(OC)_5CrSbPh_2SbPh_2Cr(CO)_5$ [10]. This compound was found to have a centrosymmetric structure with the center of inversion in the middle of the Sb-Sb bond. The tetraphenyldistibine moiety acted as a bifunctional ligand that bridged the two $Cr(CO)_5$ fragments in a *trans* arrangement. The Cr-Sb distance (2.626Å) was significantly longer than the corresponding bond length of 2.497Å previously observed in the pentacarbonylchromium complex of triphenylstibine, $Ph_3SbCr(CO)_5$. The Sb-Sb distance (2.866Å) was only slightly longer than that observed in tetraphenyldistibine itself.

Pyrolysis of triphenylantimony dibromide at 220°C has been shown to cause the elimination of bromobenzene, and vacuum distillation of the residue yielded diphenylbromostibine admixed with about 25% phenyldibromostibine [11]. The formation of the latter compound was attributed to the following disproportionation reaction:

$$2\ Ph_2SbBr \longrightarrow PhSbBr_2 + Ph_3Sb$$

Treatment of the mixture of bromo- and dibromostibine with bromine in carbon tetrachloride and cooling of the resulting solution resulted in the precipitation of diphenylantimony tribromide. Thermal decomposition of this compound at 180°C gave a good yield of pure phenyldibromostibine:

$$Ph_2SbBr_3 \longrightarrow PhSbBr_2 + PhBr$$

The PMR spectra of both the tribromide and the dibromostibine consisted of two well separated multiplets, the intensities of which were in the ratio of 3:2. The IR spectrum of the dibromostibine exhibited a strong absorption at 240 cm^{-1} which had previously been noted in the spectrum of the tribromide and had been attributed to Sb-Br stretching. The mass spectrum of the dibromstibine showed an intense peak for the molecular ion; the base peak corresponded to $PhSbBr^{+}$.

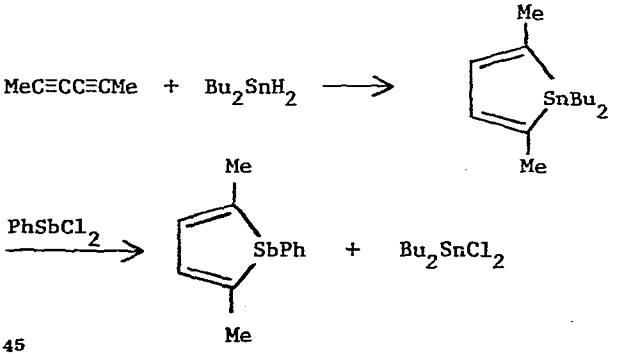
In connection with a study of dicoordinate radicals of the main Group V elements, a chlorostibine was prepared in the following manner [12]:

$$2\ (Me_3Si)_2CHLi\ +\ SbCl_3 \longrightarrow [(Me_3Si)_2CH]_2SbCl\ +\ 2\ LiCl$$

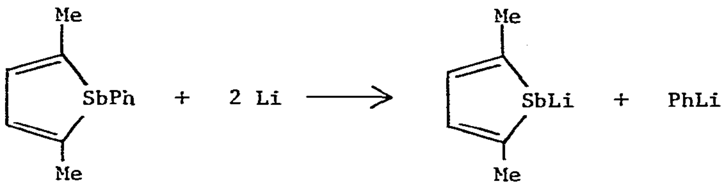
Attempts to convert this compound into a radical by photolysis in the presence of an electron-rich olefin resulted in the formation of metallic antimony.

The structure of diphenylacetatostibine, Ph_2SbO_2CMe, has been studied by IR spectroscopy and X-ray crystallography [13]. The IR data suggested that this compound had a polymeric structure with bridging acetato groups and that this structure was partially broken down in carbon tetrachloride and was completely destroyed in chloroform. No ion with an *m/e* value greater than that of the molecular ion was observed in the mass spectrum, and hence it was concluded that any intermolecular Sb····O bonds present in the solid did not persist under mass spectrometric conditions. The crystal structure determination confirmed the polymeric structure indicated by the IR evidence. The antimony atoms were found to be linked by the acetato groups into infinite chains. Coordination about each antimony was pseudo trigonal-bipyramidal. Two phenyl groups and the antimony lone pair occupied the equatorial positions, while one axial position was occupied by an oxygen of the bonded acetato group and the other axial position was occupied by an oxygen atom of the bridging acetato group. The effect of the lone pair was to reduce the O-Sb····O angle to around 168° and the C-Sb-C angle to around 95°. The intermolecular Sb····O bond distance had a mean value of 2.55Å, corresponding to a bond order of 0.19.

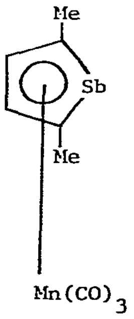
1-Phenyl-2,5-dimethylstibole has been prepared by the following sequence of reactions [14]:



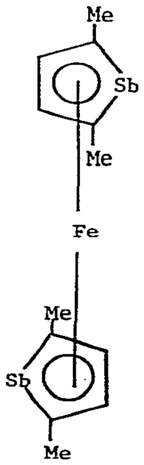
Treatment of the stibole with lithium in THF resulted in cleavage of the Ph-Sb bond:



Reaction of the lithium stibide with methyl iodide gave the expected 1,2,5-trimethylstibole as a light yellow oil, while treatment with bromomanganese pentacarbonyl yielded a complex in which the antimony-containing anion served as a 6 π-electron aromatic ligand:

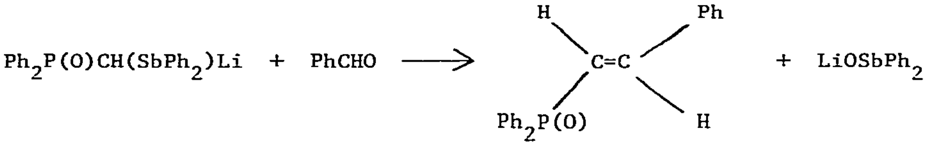


The reaction of the stibide with ferrous chloride gave a 1:2 mixture of 2,2',5,5'-tetramethyl-1,1'-distibole and the following ferrocene-like compound:



The latter compound was deep red and air-stable; it was separated from the deep blue distibine by fractional sublimation. Metal π-coordination of the rings in the manganese and iron complexes was clearly indicated by the upfield shifts of the ^{1}H and ^{13}C NMR signals relative to the uncomplexed stiboles. The iron complex was destroyed by the acidic conditions that would be required for Friedel-Crafts acylation or deuterium exchange.

The preparation of diphenylphosphoryl-substituted olefins has been accomplished by the interaction of an aldehyde or ketone and a compound of the type $Ph_2P(O)CH(G)Li$, where G was $SnPh_3$, $PbPh_3$, $SbPh_2$, or TePh [15]. For example, the following reaction gave a 25% yield of olefin in THF at -70°C:



The lithiated tertiary stibine required for this synthesis was obtained by the following sequence of reactions:

$$\begin{tikzcd}
Ph_2P(O)CH_2Li + Ph_2SbBr \arrow[r] & Ph_2P(O)CH_2SbPh_2 + LiBr \arrow[d, "{LiN(CHMe_2)_2}", "{THF,\ -70^{\circ}C}"'] \\
& Ph_2P(O)CH(SbPh_2)Li + (Me_2CH)_2NH
\end{tikzcd}$$

One organoantimony compound has been included in a study of trimethylsilyldiazomethanes of the type $Me_3SiC(Y)N_2$, where Y was Me_3Si, Me_3Ge, Me_3Sn, Me_3Pb, Me_2As, Me_2Sb, or Me_2Bi [16]. The compound was prepared by deprotonation of trimethylsilyldiazomethane:

$$Me_3SiCHN_2 + Me_2SbNMe_2 \longrightarrow Me_3SiC(SbMe_2)N_2 + Me_2NH$$

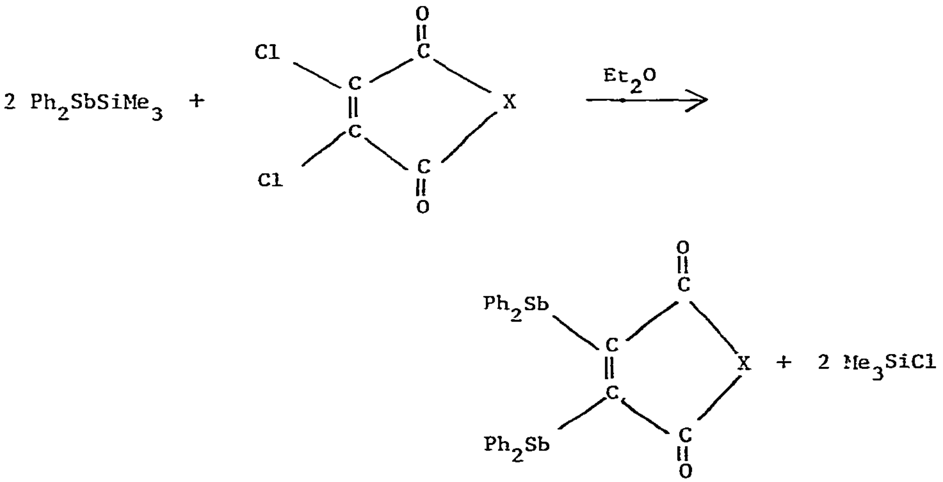
It was an orange liquid that was distilled *in vacuo* and solidified between -15° and -20°C. Its structure was established by elemental analysis and by IR, PMR, and ^{13}C NMR spectroscopy.

The ^{121}Sb Mössbauer spectra of the four compounds of the type Me_nSbCl_{3-n} (where n was 0,1,2,or 3) have been determined at 4.2 K [17]. The data were interpreted by treating the lone pair electron orbital as a ligand and determining its effect on the overall antimony bonding. In addition, it was possible to assign partial quadrupole splitting and partial chemical shift values for the lone pair. A group of thirteen antimony(III) dithiocarbamate complexes were also studied by ^{121}Sb Mössbauer spectroscopy at liquid helium temperature. For most of these complexes, a good interpretation of the data would have been impossible without assuming the presence of stereochemically active lone pair electrons.

Bis(diphenylstibino) derivatives of 2,5-furandione (maleic anhydride) and 2,5-thiophenedione have been prepared by the following series of reactions [18].

$$Ph_3Sb + 2\ Li \xrightarrow{THF} Ph_2SbLi + PhLi$$

$$Ph_2SbLi + Me_3SiCl \xrightarrow{THF} Ph_2SbSiMe_3 + LiCl$$



(where X was O or S)

Characteristic UV and IR bands of these compounds were determined and compared with those of the corresponding phosphines and arsines. A strong shift of the C=C stretching vibration to lower wavenumbers was observed in the IR spectra of all of these compounds (relative to the 3,4-dichloro derivatives used as starting materials). This finding prompted the X-ray diffraction study of the crystal and molecular structure of 3,4-bis(diphenylstibino)-2,5-furandione. As anticipated, the maleic anhydride moiety was almost planar. The surroundings of the two antimony atoms were not exactly equivalent. One antimony atom was in the same plane as the maleic anhydride ring, but the other was 25 pm out of this plane. Each antimony atom was pyramidally bonded to three carbon atoms. The bond distances of the antimony bonded to the C=C linkage were in the 216-217 pm range, while the Sb-Ph distances were between 213 pm and 216 pm. The C=C and C=O bond distances were 134 pm and 118-119 pm, respectively. All of the bond distances discussed appeared to be normal. The expected lengthening of the C=C bond was not, therefore, observed.

X-ray diffraction has been used to determine the structures of tri-*p*-tolylstibine and a number of other tertiary derivatives of Group V elements [19]. The stibine was found to have C_3 symmetry with C-Sb-C angles of 96.7°. The C-Sb bond distance of 2.133Å was in good agreement with values previously reported for other organoantimony compounds.

The oxidative addition of bis(trifluoromethyl)nitroxyl to trimethyl- or dimethyl(trifluoromethyl)stibine has been found to occur rapidly at room temperature [20]:

$$Me_2RSb + 2\ (CF_3)_2NO \longrightarrow Me_2RSb[ON(CF_3)_2]_2$$

(where R was Me or CF_3)

The pentavalent antimony compounds thus prepared were volatile white solids that yielded bis(trifluoromethyl)hydroxylamine on hydrolysis in moist air. Treatment with anhydrous hydrogen chloride also resulted in cleavage of the Sb-O bonds:

$$Me_2RSb[ON(CF_3)_2]_2 + 2\ HCl \longrightarrow Me_2RSbCl_2 + 2\ (CF_3)_2NOH$$

The oxidative addition reactions presumably involved stepwise addition and the intermediacy of tetracovalent antimony radicals.

Second order rate constants have been recorded for the following type of oxidation [21]:

$$Ph_3Sb + 4\text{-}RC_6H_4SO_2N_3 \longrightarrow 4\text{-}RC_6H_4SO_2N{=}SbPh_3 + N_2$$

(where R was NO_2; MeCO, CO_2Et, Cl, H, NHCOMe, MeO, Me, or Me_2N)

The constants decreased in the order given above for R. A Hammett plot gave a ρ value of 1.53. Activation parameters were also determined for these reactions, and two possible mechanisms were suggested. It was concluded *inter alia* that the nucleophilicity of triphenylstibine was less than that of triphenylphosphine.

The oxidation of triphenylphosphine, -arsine, and -stibine by *tert*-butyl hydroperoxide in benzene at 298.15K has been studied calorimetrically [22]. The following type of reaction was involved:

$$Ph_3E + Me_3COOH \longrightarrow Ph_3EO + Me_3COH$$

(where E was P, As, or Sb)

The enthalpies of these reactions were -359.4, -246.0, and -240.6 kJ mol^{-1}, respectively, for the phosphine, arsine, and stibine. By using data from the literature it was also possible to calculate that the enthalpies of formation of the crystalline phosphine oxide, arsine oxide, and stibine oxide were -82.4, +98.7, and +135.4 kJ mol^{-1}, respectively. Finally, the energies of dissociation of the P=O, As=O, and Sb=O bonds in these oxides were calculated to be 556, 443, and 440 kJ mol^{-1}, respectively. In this work it was assumed that the compounds obtained by oxidation of the phosphine, arsine, and stibine were monomeric, even though there are references in the literature to the existence of dimeric and polymeric modifications of triphenylstibine oxide.

A study of the anodic oxidation of five triarylstibines Ar_3Sb, where Ar was Ph, $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, $2,4,6\text{-}Me_3C_6H_2$, or $(MeO)_3C_6H_2$, has been carried out in acetonitrile by voltammetry with a stationary or a rotating platinum electrode [23]. The first step in the oxidation yielded an intermediate radical cation:

$$Ar_3Sb \longrightarrow Ar_3Sb^{\overset{+}{\cdot}} + e^-$$

The ease of oxidation was appreciably dependent on the structure of the aryl group, and the half-wave potential was found to be correlated with the sum of the σ constants of the substituents on the benzene rings. The radical cations were not stable under the conditions of these experiments and apparently reacted with water that was present in the acetonitrile. The following series of reactions was suggested:

$$Ar_3Sb^{\overset{+}{\cdot}} + H_2O \longrightarrow Ar_3\overset{+\cdot}{Sb}OH_2 \xrightarrow{H_2O} Ar_3\dot{Sb}OH + H_3O^+$$

$$Ar_3\dot{Sb}OH \longrightarrow Ar_3\overset{+}{Sb}OH + e^-$$

The overall two-electron oxidation in the presence of water could, therefore, be represented by the following equation:

$$Ar_3Sb + 2\ H_2O \longrightarrow Ar_3\overset{+}{Sb}OH + H_3O^+ + 2\ e^-$$

In addition to the oxidation, there was evidence of a slower reaction that involved the protonation of the stibine and the consequent lowering of the concentration of the depolarizer at the surface of the electrode:

$$Ar_3Sb + H_3O^+ \rightleftharpoons Ar_3SbH^+ + H_2O$$

Anodic oxidation in the presence of acetate ions resulted in the formation of a triarylstibine oxide:

$$Ar_3Sb + H_2O + 2\ MeCO_2^- \longrightarrow Ar_3SbO + 2\ MeCO_2H + 2\ e^-$$

The interaction of triphenylstibine and oxygen in benzene has been found to be promoted by UV radiation [24]. Immediately after the completion of the photooxidation, the reaction mixture was homogeneous; and IR analysis suggested that the product was phenyl diphenylstibinate. On standing at room temperature, the solution deposited a white solid that was shown to be diphenylstibinic acid. Phenol, biphenyl, and resinous products were also found to be present. The yield of diphenylstibinic acid was close to one mole per mole of oxygen consumed. It was suggested that the primary reaction was the excitation of triphenylstibine and the formation with oxygen of a labile reversible complex, which rearranged to phenyl diphenylstibinate:

$$Ph_3Sb \xrightarrow{h\nu} Ph_3Sb^*$$

$$Ph_3Sb^* + O_2 \longrightarrow [Ph_3Sb \cdot O_2] \longrightarrow Ph_2SbO_2Ph$$

This ester, presumably, then decomposed by one of two reactions:

$$Ph_2SbO_2Ph \longrightarrow Ph_2SbO_2H +$$

$$Ph_2SbO_2Ph + H_2O \longrightarrow Ph_2SbO_2H + PhOH$$

Electronic spectroscopy has been used to study the complexing of molecular oxygen with the compounds Ph_3E, where E was N, P, As, Sb, or Bi [25]. It was found that the coordination was promoted by an increase in the π-electron density associated with the aromatic rings. Data on the π-donor ability of these rings were obtained from absorption spectra of charge-transfer complexes of the Ph_3E compounds with tetracyanoethylene. These complexes were assumed to be of the π,π-type where the tetracyanoethylene behaved as a π-acceptor by making use of its antibonding molecular orbitals. The observed charge-transfer frequencies (ν_{ct}) permitted qualitative evaluation of the π-donor ability of the Ph_3E molecules, since ν_{ct} values decreased as the donor properties increased. It was thus found that triphenylamine had a high π-donor ability ($\nu_{ct} \sim 11{,}400\ cm^{-1}$), triphenylphosphine a much lower π-donor ability ($\nu_{ct} \sim 21{,}400\ cm^{-1}$), and triphenylarsine, -stibine, and -bismuthine approximately equal π-donor properties (ν_{ct} being 18,500, 19,000, and 18,600 cm^{-1}, respectively).

The one-electron oxidation of compounds of the type Ph_3E (where E was N, P, As, Sb, or Bi) by radical cations of the type $(4\text{-}RC_6H_4)_3N^{\overset{+}{\cdot}}$

(where R was Br, MeO, Me, or Ph) has been found to be first order in each reactant [26]. The rate depended strongly on both E and R.

Conductometric titrations of triphenylstibine in acetonitrile with iodine monochloride or iodine trichloride have been reported as part of an investigation of mixed halogen adducts of triphenylphosphine, triphenylarsine, and triphenylstibine [27]. When iodine monochloride was added to a triphenylstibine solution, there was virtually no rise in conductance until the mole ratio of the reactants was 1:1. From that point on, the conductance began to rise and reached a maximum when the ratio of iodine monochloride to stibine was 1.5:1. It then fell to a low value again and leveled off at a ratio of 2:1. The triphenylantimony dihalides Ph_3SbClI and Ph_3SbCl_2 were isolated from the solution at the 1:1 and 2:1 ratios, respectively. Since triphenylantimony dihalides had previously been shown to be virtually non-conducting in acetonitrile, it was assumed that the chloride iodide had been formed at the 1:1 ratio and the dichloride had been formed at the 2:1 ratio:

$$Ph_3Sb + ICl \longrightarrow Ph_3SbClI$$

$$Ph_3SbClI + ICl \longrightarrow Ph_3SbCl_2 + I_2$$

Between mole ratios 1:1 and 2:1, the solution had a UV spectrum that suggested the presence of triiodide ion. It was assumed, therefore, that as the reaction proceeded from the 1:1 to the 2:1 ratio the iodine formed combined with unreacted triphenylantimony chloride iodide to produce an ionic tetrahalide:

$$Ph_3SbClI + \tfrac{1}{2}\, ICl \longrightarrow \tfrac{1}{2}\, Ph_3SbCl_2 + \tfrac{1}{2}\, Ph_3SbCl^+I_3^-$$

The addition of more iodine monochloride then converted the ionic tetrahalide to non-ionic substances:

$$\tfrac{1}{2}\, Ph_3SbCl^+I_3^- + \tfrac{1}{2}\, ICl \longrightarrow \tfrac{1}{2}\, Ph_3SbCl_2 + I_2$$

That the ionic tetrahalide does form in acetonitrile was confirmed by the results obtained from a conductometric titration of triphenylantimony chloride iodide with iodine:

$$Ph_3SbClI + I_2 \longrightarrow Ph_3SbCl^+I_3^-$$

Attempts to prepare the tetrahalide as a crystalline solid, however, were not successful. When iodine trichloride was added to a solution of triphenylstibine, a maximum in conductance was observed between the 0.5:1 and 1:1 (ICl_3: Ph_3Sb) mole ratios. The low conductance values at the 0.5:1 and 1:1 ratios were explained by assuming that dihalides were formed at these ratios:

$$Ph_3Sb + \tfrac{1}{2}\,ICl_3 \longrightarrow \tfrac{1}{2}\,Ph_3SbCl_2 + \tfrac{1}{2}\,Ph_3SbClI$$

$$\tfrac{1}{2}\,Ph_3SbClI + \tfrac{1}{2}\,ICl_3 \longrightarrow \tfrac{1}{2}\,Ph_3SbCl_2 + \tfrac{1}{2}\,I_2 + \tfrac{1}{2}\,Cl_2$$

Between the 0.5:1 and 1:1 ratios, the solution was dark red and the UV spectrum showed that triiodide ion was present. Again, it was assumed that the ionic tetrahalide $Ph_3SbCl^{+}I_3^{-}$ had been formed by the interaction of triphenylantimony chloride iodide and iodine. And once again, it proved impossible to isolate the tetrahalide. No ionic adducts of any type were suggested by conductometric titrations of triphenylantimony dichloride with bromine, iodine, iodine monochloride, iodine monobromide, or iodine trichloride.

A conductometric method has been used to investigate complex formation between a variety of electron donors and acceptors in acetonitrile solution [28]. The stoichiometry of the complex was deduced from the concentrations of donor and acceptor at the peak conductivity observed when the concentration of donor or acceptor was plotted against conductivity. This procedure led to the conclusion that the stoichiometry of the triphenylstibine—iodine complex was 1:3. In another laboratory, however, differential refractometric studies led to the conclusion that triphenylstibine and iodine form a 1:1 complex in chloroform [29]. The equilibrium constant for this interaction was also determined.

The determination of the purity of triphenylstibine by oxidation with chloramine B and iodometry of the excess oxidant was improved by the use of 1:2 chloroform-acetic acid as the solvent instead of acetic anhydride [30]. The time required for an analysis was one hour.

A study has been reported of the response characteristics of a hydrogen-atmosphere flame-ionization detector for gas chromatography when the atmosphere was doped with small amounts of methane, silane, germane, or phosphine [31]. Of particular interest was the finding that a number of metal-containing compounds (including triphenylstibine) gave *negative* responses when phosphine was used as the doping agent.

Trimethylstibine has been used as the antimony source in several studies of the growth of thin alloy films by a process known as organometallic vapor-phase epitaxy [32–35]. The technique was said to produce crystals with good surface morphology and to allow ready control of the alloy composition.

A Japanese patent [36] has described the polymerization of the cyclic trimer of phosphonitrile chloride in the presence of triphenylstibine and iodine to give gel free poly(phosphonitrile chloride). The yield was 91% under these conditions, but in the absence of iodine the yield was only 70%.

In a study of the radiolysis of air-saturated carbon tetrachloride, triphenylstibine has been used as a scavenger for chlorine molecules in order to eliminate the following back reaction [37]:

$$CCl_3\cdot + Cl_2 \longrightarrow CCl_4 + Cl\cdot$$

The *G* values of Cl_2 formation and CCl_4 depletion were determined, kinetic calculations were carried out, and a mechanism was proposed.

5-Phenyl-5*H*-dibenzostibole and its phosphorus and bismuth analogs have been included in a study of the electronic spectra of a number of fluorene-like molecules [38]. The absorption, fluorescence, and phosphorescence spectra of these substances were analyzed in terms of the effect of the heteroatom on the nature and position of the lowest excited state. It was concluded among other things that the heteroatom exerted an appreciable effect on the lifetime of the phosphorescent state.

The deactivation of electronically excited molecules of the type Ph_3E (where E was N, P, As, Sb, or Bi) has been found to depend on the atomic number of E, the state of aggregation (gas, liquid solution, or solid solution), and the experimental conditions [39]. In the gaseous and liquid states, photodissociation became more efficient with increasing atomic number. In solid solutions at 77K, the probability of two-quantum photoprocesses decreased with increasing atomic number.

Four organotin complexes of triphenylstibine have been prepared by allowing the components to react in a mixture of benzene and ethanol [40]:

$$R_3SnCl + Ph_3Sb \longrightarrow R_3SnCl\cdot SbPh_3$$

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

The complexes were white or cream-colored and were soluble in benzene or acetone. Electrical conductance measurements in acetone or nitrobenzene showed that they were non-electrolytes, while ebullioscopic studies showed that they were dissociated in refluxing benzene. The Sn-Cl stretching vibration in the IR spectra of the complexes was about 100 cm^{-1} lower than in the parent organotin chlorides; this effect was attributed to an increase in the ionic character of the Sn-Cl bond upon adduct formation. The ^{119}Sn Mössbauer spectrum of the triethyltin chloride complex gave isomer shift and quadrupole splitting values of 1.502 mm/sec and 3.683 mm/sec, respectively. These values were considered typical of adducts of triethyltin chloride in which the tin was five-coordinate.

The 1:1 complexes of triethylstibine with the trialkylgallium compounds R_3Ga, where R was Me, Et, Pr, or Bu, have been studied by means of IR (250-4000 cm^{-1}) and Raman (50-4000 cm^{-1}) spectroscopy [41]. The observed bands were assigned, and the effects of complexing on the spectra were noted.

There have been a large number of 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 chromium [42-46], cobalt [47-49], copper [50], gold [51], iridium [52], iron [53-55], manganese [56], mercury [50], molybdenum [42, 45, 57], nickel [7, 45], palladium [58, 59], platinum [59-64], rhodium [65-70], ruthenium [71-75], silver [50], and tungsten [42, 43, 76, 77]. The thermal disproportionation of azaferrocene to ferrocene has been found to be accelerated by σ-donor ligands of the type Ph_3E, where E was P, As, or Sb [78].

Stevens and coworkers [79] have investigated the ^{121}Sb Mössbauer spectra of three types of compounds, $R_2Sb(OMe)_3$ (R = Me or Et), $R_2Sb(OAc)_3$ (R = Me or Et), and $R_2Sb(O)OH$ (R = Et, Bu, or Ph). An improved synthetic procedure for preparing $Et_2Sb(OMe)_3$ was given; tetraethyldistibine was chlorinated with sulfuryl chloride to give Et_2SbCl_3 which was then converted to $Et_2Sb(OMe)_3$ with sodium methoxide in anhydrous methanol.

Mössbauer parameters, quadrupole coupling constants (e^2qQ), isomer shifts (δ), and asymmetry parameters (η), for all of the compounds under investigation, were given in tabular form, and the Mössbauer spectrum of $Me_2Sb(OMe)_3$ at 4.2 K was shown. For the two $R_2Sb(OMe)_3$ compounds two structures were considered, a bipyramidal and a dimeric octahedral structure. Although the Mössbauer spectrum could not distinguish between these two structures, other evidence was in accord with the dimeric structure. Two structures were also considered for the two triacetato compounds, an octahedral structure with a bidentate and two monodentate acetato groups, and a trigonal bipyramid with three monodentate acetato groups. Again, Mössbauer spectra could not distinguish between the two structures but other evidence supported the octahedral structure.

The authors pointed out that the most striking result in the Mössbauer spectra of the three stibinic acids was the fact that the asymmetry parameters were all equal to 1.0. These results were in essential agreement with a previous Mössbauer study of di-*p*-tolystibinic acid by Bowen and Long [80], where the asymmetry parameter (η) was 0.9. In that paper Bowen and Long concluded that the antimony possessed trigonal-bipyramidal geometry with the two aryl groups and the hydroxyl group in equatorial positions and two bridging oxygens in axial positions (not equatorial as stated by Stevens and coworkers). Stevens and coworkers questioned the interpretation of Bowen and Long and suggested rather that in all four stibinic acids the antimony possessed tetrahedral geometry of the type SbA_2B_2, where A is an alkyl or aryl group and B is oxygen. They suggested that these structures were supported by crystal structure results with two dialkylarsinic acids which have been shown by X-ray diffraction to be monomeric with tetrahedral arsenic atoms. It should be pointed out, however, that both dialkyl- and diarylstibinic acids are amorphous solids, generally insoluble in organic solvents, and have all the properties of polymeric materials, whereas arsinic acids are crystalline solids, soluble in many organic solvents. From their physical properties, as well as other chemical evidence, it is difficult to see how the stibinic acids can be monomeric with the structure $R_2Sb(O)OH$.

By refluxing Ph_3SbBr_2 and the sodium salt of a 1,3-diketone, Jain and coworkers [81] have obtained compounds of the type $Ph_3SbBr(RCOCHCOR')$ (where R = R' = Me and Me_3C or R = Me, R' = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *p*-ClC_6H_4, *p*-BrC_6H_4, and where R = CF_3 and R' = 2-thienyl). It was also found that $Ph_3Sb(OMe)_2$ reacted with 1,3-diketones to yield compounds of the type $Ph_3SbOMe(RCOCHCOR')$ (where R = R' = Me and R = Me, R' = Ph). Although it was not found possible to replace both bromines in Ph_3SbBr_2 or both methoxy groups in $Ph_3Sb(OMe)_2$ with diketone groups, the bromine atom in $Ph_3SbBr(MeCOCHCOPh)$ was replaced by an OEt or a $MeCO_2$ group. No experimental details of these last two reactions, or analytical data on the resulting compounds were given.

The IR spectra of the monobromo and monomethoxy compounds suggested that they were chelated and thus possessed octahedral geometry around the antimony atom. The PMR spectra showed only one methine signal for all of the monobromo compounds, regardless of whether R = R' or R ≠ R'. In compounds where R = R' = Me, or R = R' = Me_3C, only one methyl signal was observed. This evidence pointed to the existence of only one isomer in solution. It also suggested but did not prove that two phenyl groups were in *cis*-position. In compounds where R ≠ R' (R = Me), only one methine and one methyl signal were observed. In two compunds $Ph_3SbOMe(RCOCHCOR')$, where R = R' = Me and R = Me, R' = Ph, two methine signals were seen suggesting that both *cis* and *trans* isomers were present.

Compounds of the type $Ph_3Sb(ON{=}CRR')_2$ have been prepared by Jain and coworkers [82]. The synthesis was carried out by the reaction between triphenylantimony dichloride and the sodium salt of the ketoxime:

$$Ph_3SbCl_2 + 2\ NaON{=}CRR' \longrightarrow Ph_3Sb(ON{=}CRR')_2 + 2\ NaCl$$

(R = R' = Me, Et; R = Me, R' = Et; R = Me, R' = Pr; R = Me, R' = Ph; R = Et, R' = Pr)

The dimethyl compound was also prepared by two other methods:

$$Ph_3SbCl_2 + 2\ Me_2C{=}NOH + 2\ Et_3N \longrightarrow Ph_3Sb(ON{=}CMe_2)_2 + 2\ Et_3NHCl$$

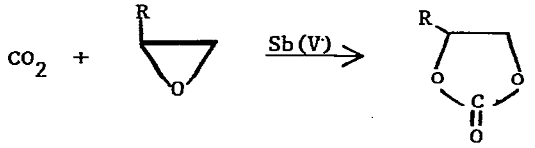
$$Ph_3Sb(OMe)_2 + 2\ Me_2C{=}NOH \longrightarrow Ph_3Sb(ON{=}CMe_2)_2 + 2\ MeOH$$

In addition to the above compounds derived from ketoximes, the compound $Ph_3Sb[ON{=}C(NH_2)Ph]_2$ was prepared from $Ph(NH_2)C{=}NONa$ and triphenylantimony dichloride.

All of the new compounds were white crystalline solids with sharp melting points. They gave normal molecular weights by cryoscopic determinations. They were hydrolytically unstable. Their IR and PMR spectra were reported. In the PMR spectra of the compounds $Ph_3Sb(ON{=}CRR')_2$ there was only one signal for each of the R and R' groups. From this result the authors suggested that there was free rotation around the Sb-O bonds, and that the compounds probably existed as trigonal bipyramids with two axial Sb-O bonds.

The new antimony compounds decomposed when heated at temperatures of 170-230°C *in vacuo* to yield two volatile fractions and a black undistillable residue. In the case of $Ph_3Sb(ON{=}CMe_2)_2$, the lower boiling fraction was identified as the oxime, $Me_2C{=}NOH$, and the higher boiling fraction as triphenylstibine.

The five compounds, Ph_5Sb, Ph_4SbBr, Ph_3SbCl_2, Ph_3SbBr_2, and Me_3SbBr_2, were all effective catalysts for the reaction of carbon dioxide with epoxides to form ethylene carbonate (or substituted ethylene carbonates) [83]:



Triphenylstibine, chlorodiphenylstibine, and antimony trichloride were ineffective as catalysts. A reaction mechanism for the reaction was suggested. In contrast to mono- and dialkyltin halides, the antimony(V) compounds did not effect polymerization of epoxides.

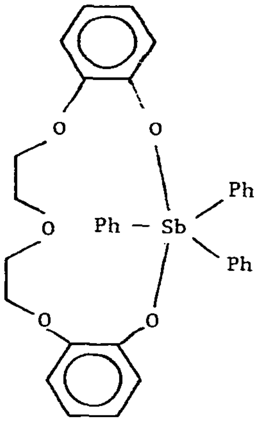
In a second paper [84] from this same laboratory the use of organoantimony compounds for the polymerization of ethylene oxide was investigated. The reaction was carried out in glass ampoules in a stainless steel autoclave under nitrogen at 120°C. Both triphenylstibine and pentaphenylantimony as well as tetraphenylantimony bromide were inactive. Triphenylantimony dichloride, triphenylantimony dibromide, and trimethylantimony dibromide were effective catalysts in that order (as judged by the yields of polymer). The polymers, however, were of low molecular weight. Triphenylstibine oxide was also an effective catalyst and produced a polymer of about twice the molecular weight of the polymers produced by the dihalides.

A third paper [85] from this laboratory described the effect of adding a Lewis base (Et_3N, Bu_3N, pyridine, Bu_3P, or Ph_3P) to Ph_3SbBr_2 in the polymerization of ethylene oxide. In every case the yields of polymer were markedly increased. The yields, however, were independent of the basicity of the Lewis bases, and also of the concentration of the added bases.

The problem of the stereochemistry of five-coordinate compounds of the groups V elements has been extensively studied in recent years, particularly for heterocylic phosphorus compounds and less so for arsenic compounds. Heterocyclic five-covalent compounds of antimony have been largely neglected. Hall and Sowerby [86] have now reported on the compound formed by the reaction between triphenylantimony dichloride and catechol. The reaction was carried out by mixing the two reactants in dry dichloromethane and passing in dry ammonia gas to precipitate ammonium chloride. From the filtrate crystals of the antimony-catechol compound were obtained which were subjected to X-ray diffraction. The compound was found to be a hydrate with the compostion $(Ph_3SbO_2C_6H_4)_2 \cdot H_2O$. It contained antimony with both fivefold and sixfold coordination. The antimony atom with fivefold coordination possessed a distorted square-pyramidal arrangement with one phenyl group in the apical position. The other antimony atom possessed a distorted octahedral arrangement with the water molecule weakly coordinated in the sixth position.

A considerable number of organoantimony compounds have been tested as agents for retarding the combustion of epoxy resins [87]. Three of the compounds were tertiary stibines. The remainder were pentacovalent compounds Ph_3SbY_2, where Y was a halogen, a carboxyl groups, or ½ O. Tri-*p*-tolylantimony dichloride and dibromide were also included. The compounds were effective in concentrations of *ca.* 1% Sb in the epoxy resin (the latter hardened with anhydrides or animes containing aromatic groups) but were not efficient for epoxy resins of cycloaliphatic character.

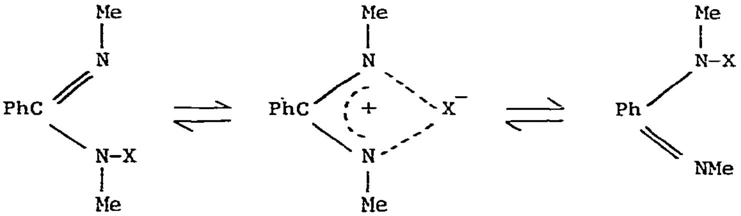
Sokolova and coworkers [88] have reported that the condensation of (o-$NaOC_6H_4OCH_2CH_2)_2O$ with Ph_3SbCl_2 led to the formation of the following cyclic compound:



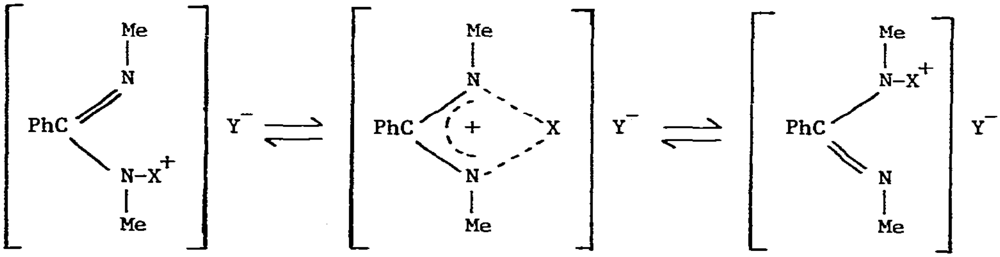
The crystal structure of the compound was determined.

A method has been described for the determination of L groups in compounds of the type R_3SbL_2, where R was an alkyl or aryl group and L was a halogen (Cl or Br) or a carboxylate group [89].

The N → N' migration of substituents in N-heterosubstituted N,N'-dimethylbenzamidines has been studied by Hartke and Wolff [90]. Examples of the reactions involved are as follows:



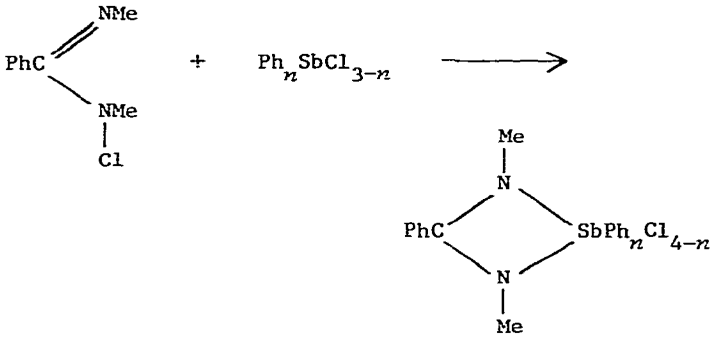
(where X = Cl, SPh, or Ph_2P)



(where X = Ph_3P, Y = Br, Cl, or ClO_4; X = SPh_2, Y = SbF_6; X = Ph_3As, Y = Cl)

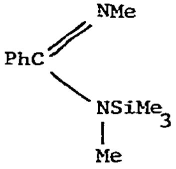
The migratory ability of the substituent was followed by PMR spectra at various temperatures.

Quite different results were obtained with antimony compounds. Four of these were prepared as follows:



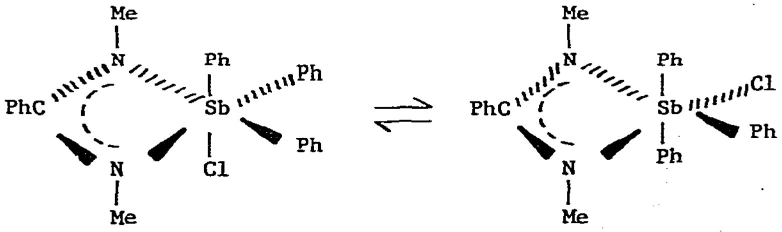
(where n = 0, 1, 2, or 3)

The compound where n = 3 was also prepared from Ph_3SbCl_2 and



This compound was extremely sensitive to light and to moisture; traces of water led to the formation of $(Ph_3SbCl)_2O$. The hydrolytic stability increased as the phenyl groups were replaced by chlorines. The compound where n = 4 was stable to both water and light.

The structure of these antimony compound was studied by means of both ^1H and ^{13}C NMR. Unlike the phosphorus and arsenic compounds, the antimony compounds possessed a chelated structure with hexacoordinated antimony. It was further concluded that three of these existed in two isomeric forms in equilibrium. Thus, for the compound where n = 3 the following equilibrium was believed to occur:



Similar equilibria were postulated for the compounds where $n = 2$ or 1.

In addition to NMR spectroscopy of these antimony compounds, their IR spectra, both in the solid state (Nujol mull or KBr pellets) and in solution in the region 1500 to 250 cm^{-1}, were reported and assignments of the principal bands were made. The ^{13}C NMR spectra of the phenyl carbons of all four antimony compounds were also reported and compared with the ^{13}C spectra of the antimony compounds Ph_3Sb, Ph_3SbCl_2, and $(Ph_3SbCl)_2O$.

Boodts and Bueno [91] have reported on an unstable complex formed between triphenylstibine oxide and iodine in dichloromethane solution. Both UV and IR spectral data were utilized in the study of complex formation. From the UV data it was concluded that triphenylstibine oxide and iodine found a 1:1 complex which was in equilibrium with the free oxide and iodine. The reaction was studied at several temperatures, and an equilibrium constant, as well as various thermodynamic values, were calculated.

The IR spectra of triphenylstibine oxide and its complex with iodine, and also with hydrogen peroxide, were reported in the region 400-950 cm^{-1}. There was relatively little difference in the spectra of all three materials. The authors noted, however, that there was considerable difference between the spectrum of triphenylstibine oxide in this region and the spectra of other compounds of the type Ph_3EO (Ph_3AsO and Ph_3PO). In the spectrum of triphenylstibine oxide, bands in the 660 cm^{-1} region were attributed to ν(SbO) vibrations and in the 480 cm^{-1} region to δ(SbO) vibrations. From a comparison of this spectrum with that of Ph_3SnO (which is known to be polymeric), the authors concluded that triphenylstibine oxide is not polymerized. Furthermore, because the ΔH^o value for the triphenylstibine oxide-iodine complex is somewhat smaller than ΔH^o values for iodine complexes of other oxo bases (*e.g.* Ph_2SO, Ph_3PO, Ph_2SeO), the authors concluded that the bonding between antimony and oxygen in triphenylstibine oxide has more pronounced double bond character.

It should be noted that there have been a considerable number of previous papers in the chemical literature pertaining to the structure of triphenylstibine oxide and that the question as to the exact structure of this compound has not been satisfactorily settled. It seems probable, however, that triphenylstibine oxide exists in at least two distinct forms, a polymeric form of unknown molecular weight, an a monomeric form in equilibrium with a polymeric form in solution [92]. Which type of triphenylstibine oxide is obtained apparently depends on the method employed for its synthesis. The synthetic method employed by Boodts and Bueno (oxidation of triphenylstibine by hydrogen peroxide) has led in other laboratories to the formation of the polymeric form, although the m.p. they report for their compound (220-221°C) corresponded to that of the lower molecular weight form [92]. Since it is not clear which form of triphenylstibine oxide was employed in this work, the conclusions of Boodts and Bueno are open to some question.

Sahai and coworkers have previously demonstrated that the molecular complexes $Ph_3E \cdot I_2$ (where E = N, P, As, or Sb) ionize in polar solvents to $[Ph_3EI]$ I which subsequently adds another iodine molecule to form $[Ph_3EI]\ I_3$. Other studies have indicated the coexistence of both intimate and solvent-separated ion pairs in equilibrium in the following manner:

$$Ph_3MI^+, I_3^- + n\ \text{THF} \rightleftharpoons Ph_3MI^+//I_3^-$$

(intimate ion pair) (solvent-separated ion pair)

The present paper by Sahai and Singh [93] described the use of both refractometric and conductometric methods for determining the values of the equilibrium constants (K), and the values of the solvation number (*n*) for the three compounds $[Ph_3EI]I_3$, where E = P, As, or Sb. The values obtained by the two methods were in reasonably good agreement.

In the first of several papers on anionic tin compounds [94], tetraphenylstibonium salts (as well as tetraphenylammonium, -arsonium, and -phosphonium salts) of the type $[Ph_4Sb]\ [Ar_nSnY_{5-n}]$, where *n* was 3 or 2, Y was Cl or Br, and Ar was phenyl or *p*-tolyl, and of the type $[Ph_4Sb]_2\ [Ph_2SnY_2Y_2']$, where Y = Cl, Y' = Br or Y = Y' = Br, were described. They were white crystalline solids, soluble in polar solvents.

The study was then extended [95] to the chemistry of tin-containing anions in which a pseudo halogen was attached to the tin, and again the cation was R_4E, where E was N, P, As, or Sb, and R was an ethyl or an aryl group. Examples of the compounds prepared were $[Ph_4Sb]$ $[Ph_3SnN_3Cl]$ and $[Ph_4Sb]\ [Ph_3Sn(NCS)Br]$.

In a third paper in the series Bhattacharya and coworkers [96] described a series of anionic tin compounds of the type $[R_4E][(C_6H_{11})_2SnY_2Y_2']$ where C_6H_{11} was cyclohexyl, Y and Y' were halogen or pseudo halogens, R was an alkyl or aryl group, and E was N, P, As, or Sb. Also described were compounds of the type $[R_4E]\ [C_6H_{11}Ph_2SnY_2]$ and $[R_4E]_2$ $[(C_6H_{11})_2SnY_2Y_2']$. The two stibonium compounds described were $[Ph_4Sb]$ $[C_6H_{11}Ph_2Sn(NCS)Br]$ and $[Ph_4Sb]_2\ [(C_6H_{11})_2\ SnCl_2(N_3)_2]$.

The cleavage of Group IV tetraaryl compounds of the type Ar_4Si, Ar_4Ge, Ar_4Sn, or Ar_4Pb by antimony pentachloride has been reported by Bhattacharya and coworkers [97]. With Ph_4Si and Ph_4Ge one aryl group was cleaved:

$$Ph_4M \xrightarrow{SbCl_5} Ph_3MCl + Ph_4SbCl + SbCl_3$$

(where M = Si or Ge)

(Although the authors stated that $SbCl_3$ was one of the products of the above reaction, this product was not mentioned in the experimental section.) Tetraphenyltin and antimony pentachloride gave diphenyltin dichloride and diphenylantimony trichloride, while tetra-*p*-tolyltin and antimony pentachloride gave the analogous *p*-tolyl compounds. Tetra-*p*-tolyllead and antimony pentachloride gave di-*p*-tolyllead dichloride and di-*p*-tolylantimony trichloride. In addition to the tetraaryl compounds, several mixed alkyl-aryl compounds of tin were treated with $SbCl_5$. The tin compounds used were Bu_2SnPh_2, $Bu_2Sn(p\text{-}C_6H_4Me)_2$, Bu_3SnPh, and $Bu_3Sn(p\text{-}C_6H_4Me)$. In all these compounds, the aryl groups were cleaved by $SbCl_5$ to yield Bu_2SnCl_2 or Bu_3SnCl and the corresponding diarylantimony trichlorides.

A number of anionic antimony species derived from the Ar_3SbCl_2 compounds were also prepared and characterized. Thus, Ph_2SbCl_3 and Et_4NCl gave $[Ph_2SbCl_4]$ $[Et_4N]$. A similar reaction with Bu_4NBr gave $[Ph_2SbCl_3Br]$ $[Bu_4N]$. In addition to the tetralkylammonium halides, tetraphenylphosphonium bromide and tetraphenylantimony bromide were used to give salts such as $[Ph_2SbCl_3Br]$ $[Ph_4P]$, $[(p\text{-}MeC_6H_4)_2SbCl_3Br][Ph_4Sb]$, or $[Ph_2SbCl_3Br]$ $[Ph_4Sb]$. When this last compound was refluxed with an excess (> 4 mol) of sodium azide or ammonium thiocyanate, all four halogens of the anion were replaced to yield the compounds $[Ph_2Sb(N_3)_4]$ $[Ph_4Sb]$ and $[Ph_2Sb(NCS)_4]$ $[Ph_4Sb]$, respectively. Two other compounds prepared were $[Ph_2SbCl_3NCS]$ $[Ph_4P]$ and $[Ph_2SbCl_3N_3]$ $[Ph_4Sb]$, but the method used for the preparation of these two compounds was not given.

The authors stated that the anionic antimony complexes behaved as 1:1 electrolytes in acetonitrile with molar conductances in the range 120.4-147.5 ohm^{-1} cm^2 mol^{-1}. The azido and thiocyanato compounds, however, presumably possessed $Sb\text{-}N_3$ and Sb-NCS linkages on the basis of their IR spectra.

Ivanov and coworkers [98] have studied the exchange of the PhHg and the Ph_4Sb groupings between the compounds $PhCO_2HgPh$ and $ArCO_2H$ or the compounds $PhCO_2SbPh_4$ and $ArCO_2H$, where Ar was a substituted phenyl group. In the exchange involving the antimony compound the equilibrium constants K obeyed the equation:

$$\log K = -0.37\ pK_a + 4.02$$

(where pK_a values refer to the acid $ArCO_2H$)

Bond polarities were found to increase in the order H-O < Hg-O < Sb-O.

Tetraphenylphosphonium, -arsonium, and -antimony chlorides, as well as triphenylamine, -phosphine, -arsine, and -stibine have been tested as pesticides against *Tribolium confusum* and *Tribolium castaneum* larvae [99]. Tetraphenylantimony chloride was active and significantly altered pupation and emergence. Only triphenylstibine was active among the trivalent compounds studied. It was more potent than tetraphenylantimony chloride.

A number of tetraphenylantimony mercaptides of the type $Ph_4SbSC_6H_4R$, where R was H, p-MeO, o-MeO, p-Me, and p-Br, have been prepared by the metathetical reaction between tetraphenylantimony chloride and an aryl mercaptan [100]. The resulting mercaptides were recrystallized from chloroform-hexane solutions and always contained small amounts of chloroform which could not be removed without decomposition of the antimony compounds.

The mercaptides decomposed on heating, rapidly above their melting points but more slowly at lower temperatures. The products of the decomposition included the compounds Ph_3Sb, RC_6H_4SPh, $(RC_6H_4S)_2$, Ph_2, and PhH. When several of the mercaptides were heated to 60°C with $Me_3CN{=}O$ (a spin-trapping agent) in the cavity of an ESR spectrometer, the free radical $Me_3C(Ph)N{-}\dot{O}\cdot$ was detected. This led to the belief that the thermal decomposition involved a free radical mechanism.

Wardell and Grant [101] have now investigated the reactions of several tetraphenylantimony mercaptides with acyl halides, allyl halides, sulfenyl halides, halogens, triphenyltin chloride, and chloromethyl methyl sulfide. With all of these compounds complete halide-mercaptide exchange occurred. With bromine and iodine the following reaction occurred:

$$2\ Ph_4SbSC_6H_4R + X_2 \longrightarrow 2\ Ph_4SbX + (RC_6H_4S)_2$$

(where X = Br or I)

With iodine the mercaptide used was $o\text{-}MeOC_6H_4SSbPh_4$ and with bromine $p\text{-}MeOC_6H_4SSbPh_4$. These two mercaptides were used in most of the other reactions studied; in a few cases Ph_4SbSPh and $p\text{-}BrC_6H_4SSbPh_4$ were used. The reaction of the mercaptide with allyl bromides occurred without allylic rearrangement:

$$Ph_4SbSC_6H_4R + trans\text{-}R'CH{=}CHCH_2Br \longrightarrow Ph_4SbBr + R'CH{=}CHCH_2SC_6H_4R$$

Benzoyl chloride and sulfenyl chlorides reacted instantaneously as follows:

$$p\text{-}MeOC_6H_4SSbPh_4 + PhCOCl \longrightarrow p\text{-}MeOC_6H_4SCOPh + Ph_4SbCl$$

$$p\text{-}MeC_6H_4SSbPh_4 + 2,4\text{-}(NO_2)_2C_6H_3SCl \longrightarrow$$
$$2,4\text{-}(NO_2)_2C_6H_3SSC_6H_4OMe\text{-}o + Ph_4SbCl$$

Benzoyl peroxide and p-$MeOC_6H_4SSbPh_4$ gave $Ph_4SbOCOPh$ and $(p$-$MeOC_6H_4S)_2$. The reaction between p-tolylsulfonyl chloride and either o-$MeOC_6H_4SSbPh_4$ or p-$MeOC_6H_4SSbPh_4$ led to the formation of several products as indicated by the PMR or mass spectra of the reaction mixture. p-Chlorophenyl p-chlorobenzenethiosulfonate and o-$MeOC_6H_4SSbPh_4$ gave p-$ClC_6H_4SO_2SbPh_4$, isolated in 61% yield; the mass spectrum of the filtrate obtained after removal of the antimony compound indicated the presence of three different sulfides, namely $(p$-$ClC_6H_4S)_2$, $(o$-$MeOC_6H_4S)_2$, and p-$ClC_6H_4SSC_6H_4OMe$-o. Chloromethyl methyl sulfide and p-$MeOC_6H_4SSbPh_4$ gave Ph_4SbCl in 87% yield and an oil which consisted principally of $MeSCH_2SC_6H_4OMe$-p; p-$BrC_6H_4SbPh_4$ reacted with this same sulfide in a similar manner. Chloromethyl methyl sulfide was also used in a competitive reaction between p-$MeOC_6H_4SSbPh_4$ and $PhSSbPh_4$. The results indicated that $PhSSbPh_4$ was only slightly more reactive than the p-methoxy compound.

In addition to the above antimony compounds, the reaction of $ClCH_2SMe$ and p-$MeOC_6H_4SSnPh_3$ was investigated. The reaction was found to be extremely slow, proceeding to only 10% in five days. The same reaction, but in the presence of Ph_4SbCl, resulted in the much faster formation of p-$MeOC_6H_4SCH_2SMe$. This result suggested an equilibrium between Ph_4SbCl and p-$MeOC_6H_4SSnPh_3$ to form some p-$MeOC_6H_4SSbPh_4$. In addition to the reactions of the compounds $RC_6H_4SSbPh_4$ with various reagents, the PMR, IR, and mass spectra of these compounds were reported.

Photoelectron spectroscopy (XPS) has been used as a means of determining the binding energy of the inner electrons of a series of phosphorus, arsenic, antimony, and bismuth compounds [42]. Two trivalent antimony compounds (Ph_3Sb and $(p$-$MeC_6H_4)_3Sb$) and a number of pentacovalent antimony compounds were used in this study. The paper is described in greater detail in the Bismuth section.

Antimony(V) polyesters have been prepared by condensation of organoantimony(V) compounds and Lewis bases or diacid salts [102].

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