Journal of Organometallic Chemistry, 442 (1992) 1–60
Elsevier Sequoia S.A., Lausanne
JOM 23090AS

ANTIMONY

ANNUAL SURVEY COVERING THE YEAR 1990

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(Received July 30, 1992)

The preparation, reactions, and physical properties of organoantimony(V) compounds containing one, two, or three C-Sb bonds have been thoroughly reviewed in a new volume of the *Gmelin Handbook of Inorganic Chemistry* [1]. Ashe [2] has written an interesting account of work (mainly from his own laboratory) on thermochromic distibines and dibismuthines. Akiba [3] has published a review in Japanese of theoretical and structural studies of hypervalent compounds of silicon, sulfur, tin, and antimony and of the application of these substances to organic synthesis. In addition, information about organoantimony compounds has been given in surveys of recent publications on the main-group elements of Group V [4] and on organic derivatives of arsenic, antimony, and bismuth [5]. Organoantimony compounds have also been briefly mentioned in review articles on the following subjects: multiple bonds involving the main-group elements of Group V [6], organophosphorus, organoarsenic, and organoantimony polytungstates and polymolybdates [7], borepins, arsoles, and stiboles [8], cyclopentadienyl complexes of the main-group elements [9], and the structures of organometallic compounds determined by diffraction methods [10].

A compound containing In-Sb bonds has been prepared by the following sequence of reactions [11]:

$$\begin{tikzcd}
R_2SbSiMe_3 \arrow[r, "EtOH", "THF"'] & R_2SbH \arrow[r, "MeLi"] & R_2SbLi \arrow[d, "Me_2InCl"] \\
 & & {[Me_2In(\mu\text{-}SbR_2)]_3}
\end{tikzcd}$$

(where R was Me_3C)

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[*] Antimony, Annual Survey covering the year 1989, see J. Organomet. Chem., 404 (1991) 49. Reprints for this Survey are not available.

Di-*tert*-butylstibine and its lithio derivative were unstable at ambient temperature and were not isolated. The final product was obtained in 46% yield as pale orange crystals, mp 139-141°C. It was characterized by NMR (^1H and ^{13}C) and by X-ray diffraction. A six-membered ring with alternating antimony and indium atoms was observed; the ring had a distorted twist-boat conformation that was devoid of symmetry. The average In-Sb bond length of 2.855(2) Å was close to the sum of the covalent radii for indium and antimony (2.84 Å). The compound was used for growing films of InSb on silicon wafers in a horizontal hot-wall reactor. X-ray photoelectron spectroscopy showed that the films had an In to Sb stoichiometry of 1:1 and that the carbon impurity level was barely detectable (about 1000 ppm). X-ray diffraction indicated that the films were polycrystalline. A gallium trimer $[Me_2Ga(\mu\text{-}SbR_2)]_3$, where R was CMe_3, was prepared in 74% yield by a procedure virtually identical to that used for the analogous indium compound. It was also characterized by NMR(^1H and ^{13}C) and by X-ray diffraction. Preliminary experiments indicated that it was a useful precursor for the preparation of GaSb.

X-ray diffraction has been employed to determine the crystal and molecular structure of tetramesityldistibine, $(2,4,6\text{-}Me_3C_6H_2)_4Sb_2$ [12]. The substance was found to exist as discrete molecules with no short intramolecular contacts. The Sb-Sb bond length was 2.8481(9) Å, a value that agreed well with other determinations of the Sb(III)-Sb(III) single bond distance. With respect to the Sb-Sb bond, the mesityl groups adopted a staggered conformation in which the non-bonding electron pairs on the antimony atoms were *anti* to one another. The Sb-Sb-C and C-Sb-C bond angles ranged from 92.6° to 109.0°. The C-Sb distances, 2.181-2.201(8) Å, were similar to those found in comparable compounds and were about equal to the sum of the covalent radii of Sb(III) and sp^2-carbon atoms. The closest intermolecular contact between antimony atoms was 6.40 Å. This value far exceeded the sum of the van der Waals radii (4.40 Å) and thus precluded the type of extended bonding between the antimony atoms of neighboring molecules that has been found in thermochromic distibines.

The redox properties of tetraphenyldistibine [13,14], bis(diphenylantimony) oxide, triphenylstibine, and butyldiphenylstibine [14] have been investigated by polarography and cyclic voltammetry. The uptake of two electrons by the distibine yielded the diphenylstibide anion:

$$Ph_2SbSbPh_2 + 2\,e^- \longrightarrow 2\,Ph_2Sb^-$$

Two-electron oxidation of the distibine gave a cationic species:

$$Ph_2SbSbPh_2 \longrightarrow 2\,Ph_2Sb^+ + 2\,e^-$$

Addition of chloride ion to a solution containing this cation yielded a chlorostibine:

$$Ph_2Sb^+ + Cl^- \longrightarrow Ph_2SbCl$$

A perchlorate salt was obtained when the oxidation was performed with tetrabutylammonium perchlorate as the supporting electrolyte:

$$Ph_2Sb^+ + ClO_4^- \longrightarrow Ph_2Sb^+ClO_4^-$$

The cation could be reduced to the diphenylstibide anion *via* a neutral intermediate:

$$Ph_2Sb^+ + e^- \longrightarrow Ph_2Sb$$

$$Ph_2Sb + e^- \longrightarrow Ph_2Sb^-$$

Electroreduction of bis(diphenylantimony) oxide in THF also gave the above anion. The following stoichiometry was suggested, but no oxygen-containing anion was detected:

$$(Ph_2Sb)_2O + 2\,e^- \longrightarrow Ph_2Sb^- + Ph_2SbO^-$$

Oxidation of the diphenylstibide ion yielded the expected distibine:

$$2\,Ph_2Sb^- \longrightarrow Ph_2SbSbPh_2 + 2\,e^-$$

A tertiary stibine was obtained by the reaction of the anion with tetrabutylammonium hexafluorophosphate used as the supporting electrolyte:

$$Ph_2Sb^- + Bu_4N^+ \longrightarrow Ph_2SbBu + Bu_3N$$

The electroreduction of both butyldiphenylstibine and triphenylstibine also yielded the diphenylstibide ion:

$$Ph_2SbBu + 2\,e^- \longrightarrow Ph_2Sb^- + Bu^-$$

$$Ph_3Sb + 2\,e^- \longrightarrow Ph_2Sb^- + Ph^-$$

When triphenylstibine was reduced in DMF, the diphenylstibide ion appeared to react with residual water present in the solvent:

$$Ph_2Sb^- + H_2O \longrightarrow Ph_2SbH + OH^-$$

The secondary stibine, however, was relatively unstable and decomposed:

$$3\,Ph_2SbH \longrightarrow 2\,Ph_3Sb + SbH_3$$

Two compounds containing V-Sb bonds have been prepared in the following manner [15]:

$$Cp_2VCl + Ph_2SbLi \xrightarrow[-78°C]{THF} Cp_2VSbPh_2 \cdot 3\,THF$$

(where Cp was η^5 - cyclopentadienyl)

$$(Me_3CO)_2VCl_2 + Ph_2SbLi \xrightarrow[-78°C]{THF} (Me_3CO)_2VSbPh_2 \cdot 3\,THF$$

The stoichiometry of the second reaction was not elucidated, but it was noted that two mol of lithium diphenylstibide were required for each mol of the vanadium compound. The V-Sb bond in both bimetallic compounds could be cleaved by several reagents and by thermolysis. Thus, the interaction of the cyclopentadienyl vanadium compound and hydrogen chloride gave diphenylchlorostibine:

$$Cp_2VSbPh_2 + 3\,HCl \longrightarrow Cp_2VCl_2 + Ph_2SbCl + 3/2\,H_2$$

The V-Sb bond was also cleaved by acetic acid:

$$\begin{tikzcd} Cp_2VSbPh_2 + MeCO_2H \arrow[r] & CpV(SbPh_2)(O_2CMe) + CpH \arrow[d, "MeCO_2H"] \\ & CpV(O_2CMe)_2 + Ph_2SbO_2CMe \end{tikzcd}$$

The reaction with bromine appeared to proceed by the following course:

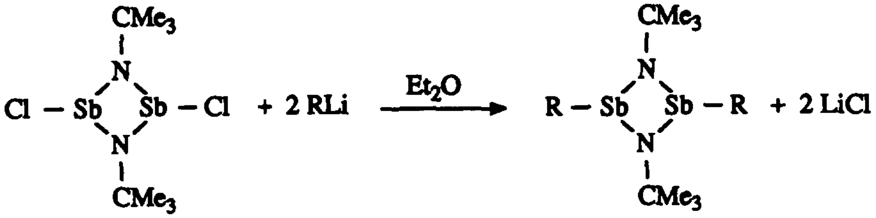
$$Cp_2VSbPh_2 + 5/2\,Br_2 \longrightarrow Cp_2VBr_2 + Ph_2SbBr_3$$

The reaction of the *tert*-butoxy vanadium compound with hydrogen chloride gave diphenylchlorostibine and hydrogen:

$$\begin{tikzcd} (Me_3CO)_2VSbPh_2 + 2\,HCl \arrow[r] & {[(Me_3CO)_2VCl]} + Ph_2SbCl + H_2 \arrow[d] \\ & \tfrac{1}{2}\,(Me_3CO)_4V + \tfrac{1}{2}\,[VCl_2] \end{tikzcd}$$

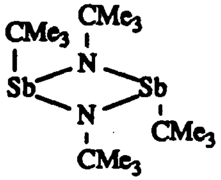
Thermolysis of Cp_2VSbPh_2 at 120°C yielded tetraphenyldistibine, while triphenylstibine was isolated from the thermolysis of $(Me_3CO)_2VSbPh_2$ under similar conditions.

Organolithium reagents have been employed for replacing the chlorine atoms in 1,3-di-*tert*-butyl-2,4-dichloro-1,3,2,4-diazadistibetidine with alkyl groups [16]:



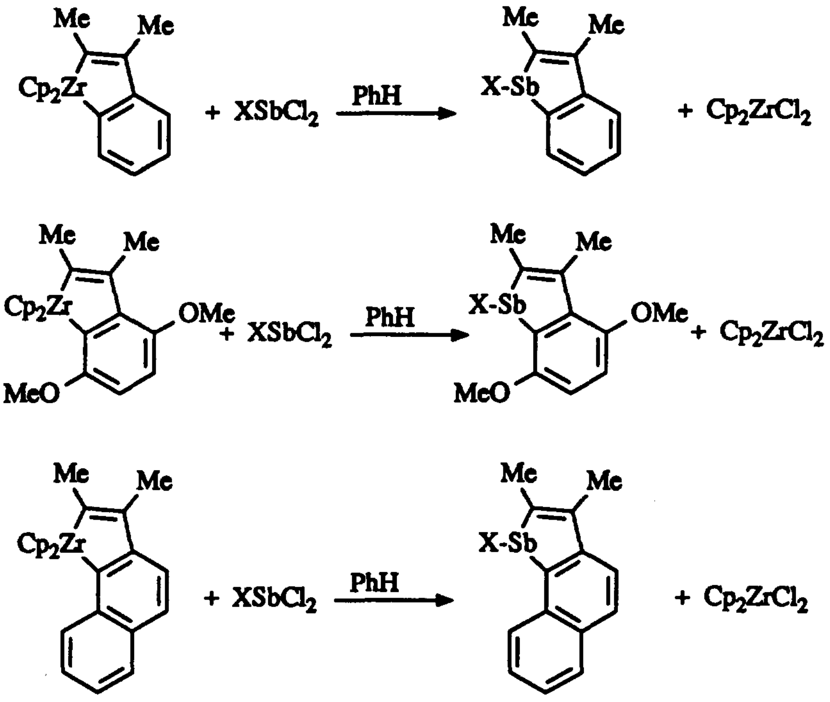
(where R was Me or Me_3C)

The ^1H and ^{13}C NMR spectra of the 2,4-dimethyl compound indicated that it was a single geometrical isomer. Two geometrical isomers (designated *trans* and *cis*) were isolated from the reaction in which R was *tert*-butyl. An X-ray determination of the *trans* isomer showed that it possessed the following structure:



The four-membered Sb_2N_2 ring was planar: the N-Sb-N angle was 78.3(2)°, while the Sb-N-Sb angle was 101.7(2)°. The antimony atom was pyramidally coordinated, but the nitrogen atom was nearly planar. The Sb-N bond length (2.05 Å) appeared to be slightly shorter than the lengths previously reported in other compounds.

Six new benzo[*b*]stiboles have been prepared by the reaction of zirconocene derivatives with either antimony trichloride or phenyldichlorostibine [17]:



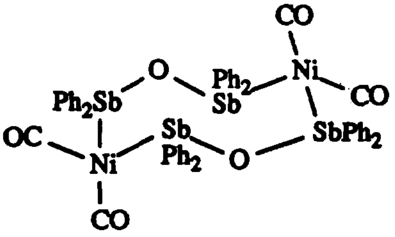
(where X was Ph or Cl)

The antimony compounds obtained by these reactions were crystalline solids and were moderately air stable. The three chlorostibines on being stored for prolonged periods in air, however, decomposed to give unidentified substances. The tertiary stibines were considerably more robust and could be stored in the laboratory atmosphere without apparent decomposition. All six compounds were less stable in solution than in the solid state. They were characterized by spectroscopy (IR, PMR, and ^{13}C NMR) and by combustion analysis or high-resolution mass spectrometry. Molecular weight determinations showed that the compounds were monomeric in benzene solution. An X-ray crystal structure determination was carried out on the dimethoxy stibole in which X was Ph. The antimony-containing ring was planar and orthogonal to the plane of the phenyl ring. The shortest intermolecular Sb-Sb distance was 4.75 Å. The geometry about the antimony atom, the bond distances, and the bond angles were all in good agreement with the data previously obtained with other structurally characterized stibole derivatives.

The interaction of either phenyldichlorostibine or diphenylchlorostibine and the tetramethylammonium salt of the electron-rich $[Ni_6(CO)_{12}]^{2-}$ dianion in THF solution at room temperature has been found to give a nickel stibinidene carbonyl dianion $[Ni_{10}(SbPh)_2(CO)_{18}]^{2-}$ in 50-60% yield [18]. The estimated yield obtained with the dichlorostibine was based on the following equation:

$$2\,[Ni_6(CO)_{12}]^{2-} + 2\,PhSbCl_2 \longrightarrow$$
$$[Ni_{10}(SbPh)_2(CO)_{18}]^{2-} + Ni(CO)_4 + NiCl_2 + 2\,Cl^- + 2\,CO$$

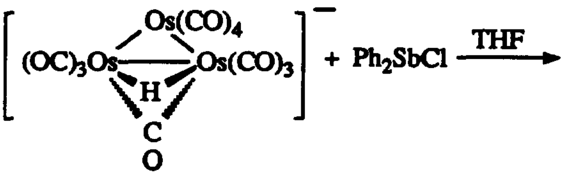
The structure of the new dianion was established by X-ray crystallographic examinations of four different ionic compounds. It was found to possess a closo 1,12-disubstituted icosahedral $Ni_{10}Sb_2$ core encapsulated by two antimony-attached phenyl substituents, ten terminal carbonyl ligands (one per nickel atom), and four doubly bridging and four triply bridging carbonyl ligands. The $Ni_{10}Sb_2$ core could also be viewed as a pentagonal antiprism of ten nickel atoms that are capped on the upper and lower pentagonal faces with antimony atoms. Another nickel-antimony complex, $Ni_2(CO)_4(\mu_2\text{-}Ph_2SbOSbPh_2)_2$, was obtained in about 5% yield from the reaction of the $[Ni_6(CO)_{12}]^{2-}$ dianion with diphenylchlorostibine in THF solution. An X-ray diffraction analysis plus information obtained from laser desorption/Fourier transform mass spectrometry (LD/FTMS) established the structure of this complex. The molecule was shown to contain an eight-membered $(NiSbOSb)_2$ ring with a chair-like conformation:

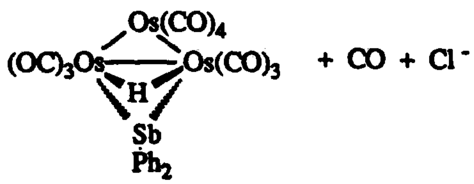


The origin of the bis(diphenylantimony) oxide in this complex was attributed to the partial hydrolysis of the diphenylchlorostibine by water adventitiously introduced with the solvent. The reaction of the $[Ni_6(CO)_{12}]^{2-}$ dianion with diphenylchlorostibine appeared to give a third nickel-antimony compound, $Ni(CO)_3(SbClPh_2)$. This substance was, however, not isolated from solution; its proposed existence was based on the fact that its IR carbonyl frequencies were virtually identical to those previously reported for $Ni(CO)_3(SbClEt_2)$ and $Ni(CO)_3(SbPh_3)$.

The bis(diphenylantimony) oxide complex, $Ni_2(CO)_4(\mu_2\text{-}Ph_2SbOSbPh_2)_2$, described in the above paragraph has been studied not only by laser desorption (LD) but also by electron impact (EI) ionization Fourier transform mass spectrometry (FTMS) [19]. Only low-mass ion peaks were observed in the EI/FT spectra. Thus, the prominent peaks found in the 70 eV positive-ion EI spectrum corresponded to $PhSb^+$, Sb^+, and Ph^+. Positive-ion spectra at 20, 10, and 7 eV showed an additional peak identified as Ph_3Sb^+. Negative-ion EI spectra did not provide any additional information. In contrast to the results obtained with EI, the ion peaks observed in positive- and negative-ion LD/FT spectra clearly showed the existence of monooxygen-antimony-phenyl fragments. Most important was the observation of the Ph_2SbO^- and the $Ph_2Sb(O)Ni(CO)^-$ ions. The results obtained in this investigation were considered entirely consistent with the structure revealed by X-ray diffraction.

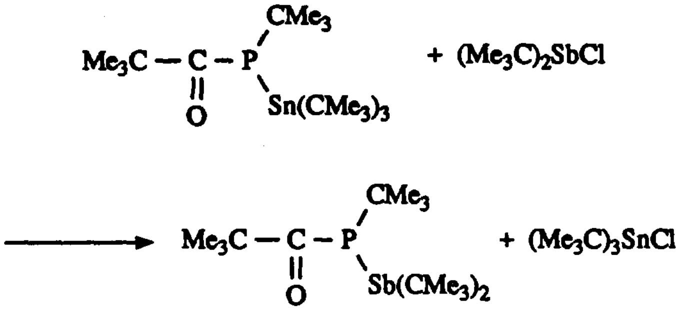
A bridged triosmium cluster compound has been obtained by the reaction of diphenylchlorostibine with the $[(Ph_3P)_2N]^+$ salt of a hydrido-anion [20]:





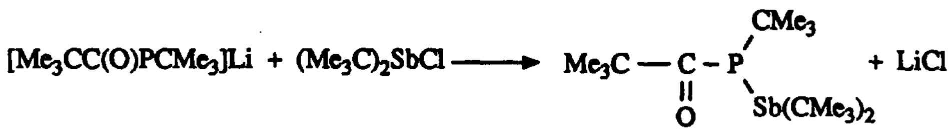
After purification by TLC, the compound was obtained from hexane as yellow-orange crystals and was characterized by microanalysis and spectroscopy (IR, PMR, and mass). An X-ray crystallographic study showed that the triosmium framework defined an isosceles triangle in which the non-bridged edges had Os-Os distances that were 0.09 Å shorter than the Os-Os distance of the bridged edge. The Os-Sb-Os angle was 68.7(2)°. The Sb-Ph distances and the C-Sb-C angle were similar to those found in many other trivalent derivatives of antimony.

A compound containing a P-Sb bond has been prepared by the quantitative interaction of di-*tert*-butylchlorostibine and a tin-substituted acylphosphine [21]:



$$Me_3C-C(=O)-P(CMe_3)Sn(CMe_3)_3 + (Me_3C)_2SbCl \longrightarrow Me_3C-C(=O)-P(CMe_3)Sb(CMe_3)_2 + (Me_3C)_3SnCl$$

The same substance was obtained by the use of the lithium salt of an acylphosphine:



$$[Me_3CC(O)PCMe_3]Li + (Me_3C)_2SbCl \longrightarrow Me_3C-C(=O)-P(CMe_3)Sb(CMe_3)_2 + LiCl$$

The ^{31}P NMR spectrum of the product exhibited a single singlet, $\delta = 0.7$ ppm. All of the operations involved in this investigation were conducted in an atmosphere of dry argon.

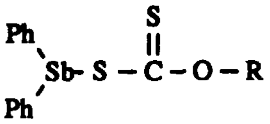
The interaction of diphenylchlorostibine or diphenylacetatostibine and potassium alkyl xanthates in a 1:1 molar ratio has been found to give the expected xanthatostibines [22]:

$$Ph_2SbCl + ROCS_2K \xrightarrow[\text{reflux}]{\text{PhH}} Ph_2SbS_2COR + KCl$$

$$Ph_2SbO_2CMe + ROCS_2K \xrightarrow[\text{reflux}]{\text{PhH}} Ph_2SbS_2COR + KO_2CMe$$

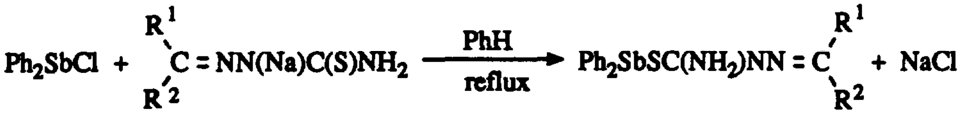
(where R was Me, Et, Pr, Me_2CH, Bu, or Me_2CHCH_2)

All of these compounds were yellow, viscous liquids and were monomeric in chloroform solution at 45°C as well as in benzene at its freezing point. Their IR and ^{13}C NMR spectra suggested that the alkyl xanthate ligands were monodentate; *i.e.*, the compounds had structures of the following type:



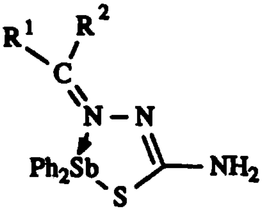
The appearance of only one set of signals for the carbon atoms of the two phenyl groups showed that these groups were equivalent. The PMR spectra of the complexes displayed the expected signals for the protons of the alkyl and aryl groups.

Another series of organoantimony(III) compounds containing Sb-S bonds have been obtained by the reaction of diphenylchlorostibine with the sodium salts of thiosemicarbazones in a 1:1 molar ratio [23]:



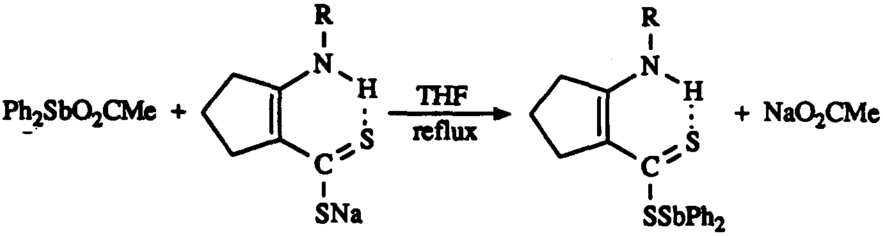
(where R^1 was H and R^2 was Ph, $MeOC_6H_4$, or PhCH=CH;
and where R^1 was Me and R^2 was Ph, MeC_6H_4, or $MeOC_6H_4$)

All of the compounds were light yellow solids with sharp melting points. They were shown to be monomeric by osmometric molecular weight determinations in chloroform. On the basis of IR and NMR (^1H and ^{13}C) studies, it was concluded that the thiosemicarbazone moiety in these compounds was behaving as a bidentate ligand:



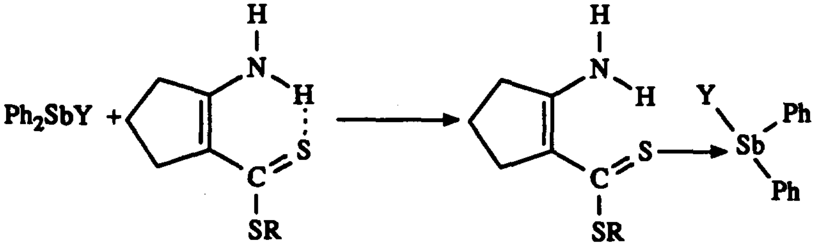
The appearance of only one set of ^{13}C NMR signals for the two phenyl groups attached to the antimony atom indicated the equivalent nature of these groups.

The reaction of diphenylacetatostibine with the sodium salts of 2-amino- or 2-alkylaminocyclopentene-1-carbodithioic acids has also been found yield compounds containing the Sb-S bond [24]:



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

The compounds were yellow sticky solids, which were soluble in common organic solvents. They were monomeric in chloroform at 40°C and underwent slow decomposition after being stored at room temperature for a few weeks. The IR and NMR (^{1}H and ^{13}C) spectra of these substances clearly established the monodentate character of the carbodithioic ligands. When *S*-alkyl derivatives of 2-aminocyclopentene-1-carbodithioic acid were allowed to react with diphenylchlorostibine or diphenylacetatostibine, only simple adducts were obtained:



(where Y was Cl or $MeCO_2$ and R was Me or CH_2NEt_2)

The adducts were moisture-sensitive, sticky solids. They were soluble in common organic solvents and were monomeric in chloroform or benzene solution. Their IR and NMR (^1H and ^{13}C) spectra supported the existence of a coordinate bond between the antimony atom and the double bonded sulfur of the dithiocarboxylate group. The PMR spectrum was consistent with a weakening of the hydrogen bonding between the nitrogen and sulfur atoms.

Other diphenylantimony(III) derivatives containing the Sb-S bond have been obtained by the interaction of diphenylmethoxystibine (prepared *in situ*) and *N*-alkyl-2-mercaptoacetamides [25]:

$$Ph_2SbCl + NaOMe \xrightarrow[\text{reflux}]{\text{PhH}} Ph_2SbOMe + NaCl$$

$$Ph_2SbOMe + HSCH_2CONHR \xrightarrow[\text{reflux}]{\text{PhH}} Ph_2SbSCH_2CONHR + MeOH$$

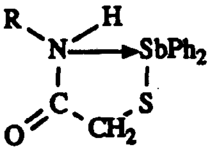
(where R was Et, Pr, Me_2CH, Bu, Me_2CHCH_2, or Et(Me)CH)

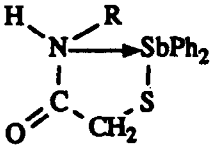
Two of these derivatives were also prepared by the reaction of diphenylacetatostibine and an *N*-alkyl-2-mercaptoacetamide:

$$Ph_2SbO_2CMe + HSCH_2CONHR \xrightarrow[\text{reflux}]{\text{MePh}} Ph_2SbSCH_2CONHR + MeCO_2H$$

(where R was Et or Me_2CH)

The second method appeared to have the advantage that no filtration was required and that the progress of the reaction could be followed by estimating the liberated acid. All of the derivatives were obtained in excellent yields (90 ± 2%) as yellow viscous liquids that were soluble in common organic solvents and monomeric in chloroform at 45°C. Spectral studies (IR, PMR, and ^{13}C NMR) indicated that the substances obtained in this investigation were mixtures of geometrical isomers in which the ligand behaved as a bidentate moiety:





The dithiophosphinate $Ph_2SbS_2PPh_2$ and the dithiophosphate $Ph_2SbS_2P(OCHMe_2)_2$ have been found to exhibit antitumor activity [26]. Thus, both substances produced strong tumor inhibition effects in mice bearing the Ehrlich ascites tumor. Moreover, the dithiophosphate gave a cure rate of 30%. These substances were said to be the first organoantimony(III) compounds that possessed antitumor properties.

Seven compounds containing Sb-Mo bonds have been obtained by the following type of reaction [27]:

$$3\,Ph_2SbER + C_7H_8Mo(CO)_3 \xrightarrow{CH_2Cl_2} [Ph_2SbER]_3Mo(CO)_3 + C_7H_8$$

(where E as S and R was Et, $CHMe_2$, CH_2Ph, Ph, or $4\text{-}MeC_6H_4$; where E was O and R was Et or Ph; and where C_7H_8 was cycloheptatriene)

The substances were obtained in fair yields as yellow or light yellow solids. The sulfur-containing compounds had a disagreeable odor and were only moderately sensitive to hydrolysis or oxidation; the oxygen analogs, however, quickly decomposed in air. An X-ray structure of the compound in which E was S and R was Ph showed octahedral coordination around the molybdenum with each carbonyl group being *trans* to an antimony atom. Chromium analogs of four of the above compounds were prepared in the following manner:

$$3\,Ph_2SbER + (MeCN)_3Cr(CO)_3 \xrightarrow{MeCN} [Ph_2SbER]_3Cr(CO)_3 + 3\,MeCN$$

(where E was S and R was Et, $CHMe_2$, or CH_2Ph; and where E was O and R was Et)

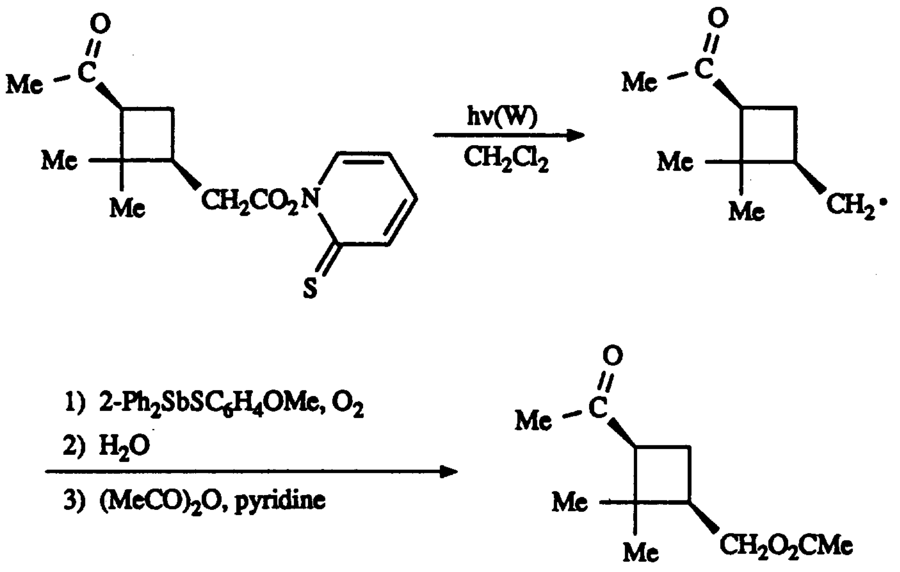
They were yellow or light yellow solids that were easily hydrolyzed or oxidized, and they quickly decomposed on being slightly warmed in acetonitrile solution. Tetracarbonyl-1,5-cyclooctadienemolybdenum also underwent substitution reactions with phenylthio- and alkylthiodiphenylstibines:

$$2\,Ph_2SbSR + (1{,}5\text{-}C_8H_{12})Mo(CO)_4 \xrightarrow{CH_2Cl_2} [Ph_2SbSR]_2Mo(CO)_4 + 1{,}5\text{-}C_8H_{12}$$

(where R was Et, $CHMe_2$, or Ph)

The phenylthio product was resin-like in consistency, but the other two substances were crystalline. All three compounds were stable under nitrogen for some time, and they exhibited an unpleasant odor. IR and NMR spectroscopy were used to characterize the fourteen antimony-containing substances prepared in this investigation.

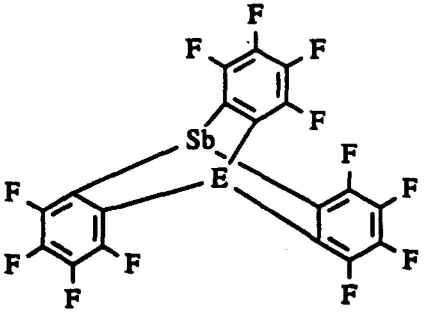
The mixed anhydride of (+)-*cis*-pinonic acid and *N*-hydroxy-2-thiopyridone has been decarboxylated and the resulting radical converted into an acetate [28]:



The organoantimony compound required for this synthesis was prepared by the following reaction sequence:

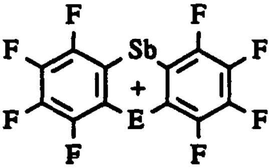
$$\begin{tikzcd} Ph_3Sb + 4\text{-}MeC_6H_4SO_3H \cdot H_2O \arrow[r, "\Delta", "PhH"'] & 4\text{-}Ph_2SbO_3SC_6H_4Me \arrow[d, "\begin{array}{l} 2\text{-}MeOC_6H_4SH \\ \text{(two-fold excess)} \end{array}"] \\ & 2\text{-}Ph_2SbSC_6H_4OMe \end{tikzcd}$$

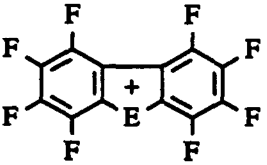
Mass and ^{19}F NMR spectral data have been reported for a number of dodecafluoro-1,6-disubstituted triptycenes [29]. Included in this study were three antimony compounds of the following type:



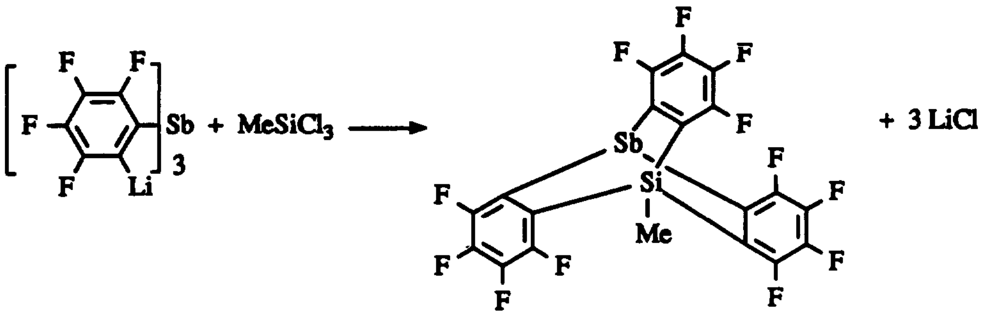
(where E was P, As, or Sb)

A comparison was made of the mass spectra recorded under both electron impact (EI) and fast atom bombardment (FAB) conditions. The fragmentation processes were relatively simple in both types of spectra. Molecular ions and $C_6F_4E^+$ fragments were rather abundant in the spectra of all three compounds. Other ions observed included heterocyclic species of the following types:





The ^{19}F NMR spectrum of the $(C_6F_4)_3Sb_2$ triptycene was typical of an AA'XX' system, and the various coupling constants were calculated under the assumption that there was no inter-ring fluorine-fluorine coupling. The "mixed" triptycenes exhibited the expected four resonances in their ^{19}F NMR spectra. When phosphorus was one of the heteroatoms, phosphorus-fluorine coupling split the resonance due to the fluorine *ortho* to phosphorus into a doublet. An attempt was also made to prepare a silicon-containing triptycene by the following reaction:



A mixture was obtained, however, that was shown by high-resolution mass spectrometry to consist of the desired "mixed" triptycene plus the $(C_6F_4)_3Sb_2$ and $(C_6F_4)_3(SiMe)_2$ triptycenes. The presence of the three compounds in the reaction mixture was ascribed to exchange reactions occurring during the attempted synthesis.

An examination has been made of the reactivity of bis(trifluoromethyl)tellurium with several Group 5A and 6A elements and their halides [30]. The interaction of the tellurium compound and elemental antimony at 170°C was found to yield very small amounts (about 3%) of tris(trifluoromethyl)stibine:

$$3\,(CF_3)_2Te + 2\,Sb \rightarrow 2\,(CF_3)_3Sb + 3\,Te$$

The yields of the stibine were estimated by ^{19}F NMR spectroscopy. When the tellurium compound and antimony triiodide were heated together at 170°C, only trace amounts (about 0.2%) of the tertiary stibine were detected. Mass spectrometry was employed to confirm the formation of the tris(trifluoromethyl)stibine in the above reactions.

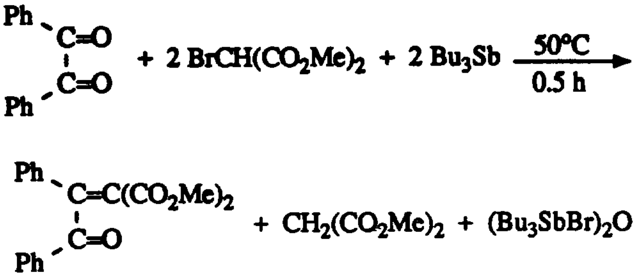
Professor Yao-Zeng Huang and his coworkers have continued in 1990 to publish interesting papers on the uses of antimony compounds in organic synthesis. One of these papers described the use of tributylstibine to mediate the olefination of aldehydes with bromomalonic esters [31]:

$$RCH{=}O + 2\,BrCH(CO_2R')_2 + 2\,Bu_3Sb \xrightarrow[0.5\ h]{50^\circ C}$$

$$RCH{=}C(CO_2R')_2 + CH_2(CO_2R')_2 + (Bu_3SbBr)_2O$$

(where R was Me_2CHCH_2, Ph, $4\text{-}O_2NC_6H_4$, geranyl, 2-furyl, or pyridyl and where R′ was Me or Et)

A similar olefination reaction occurred with one of the carbonyl groups of benzil:

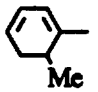


$$\begin{array}{l}\mathrm{Ph}\diagdown\\ \quad \mathrm{C{=}O}\\ \quad \mathrm{C{=}O}\\ \mathrm{Ph}\diagup\end{array} + 2\,\mathrm{BrCH(CO_2Me)_2} + 2\,\mathrm{Bu_3Sb} \xrightarrow[0.5\ \mathrm{h}]{50^\circ\mathrm{C}} \begin{array}{l}\mathrm{Ph}\diagdown\\ \quad \mathrm{C{=}C(CO_2Me)_2}\\ \quad \mathrm{C{=}O}\\ \mathrm{Ph}\diagup\end{array} + \mathrm{CH_2(CO_2Me)_2} + \mathrm{(Bu_3SbBr)_2O}$$

The olefination of aldehydes by dibromomalonic esters was also mediated by tributylstibine:

$$\mathrm{RCH{=}O} + \mathrm{Br_2C(CO_2R')_2} + 2\,\mathrm{Bu_3Sb} \xrightarrow[0.5\ \mathrm{h}]{\mathrm{RT}} \mathrm{RCH{=}C(CO_2R')_2} + \mathrm{(Bu_3SbBr)_2O}$$

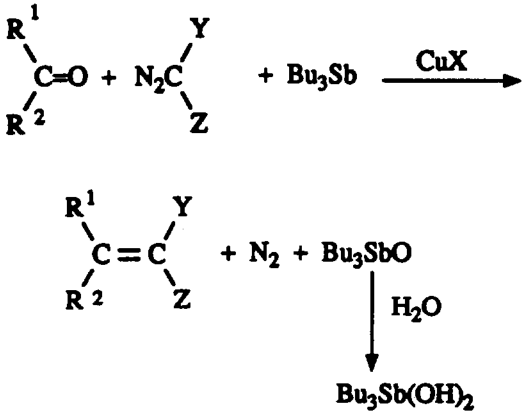
(where R was Pr, Ph, 4-$O_2NC_6H_4$, 2-thienyl, 2-pyrrolyl, or



and R′ was Me or Et)

Cyclobutanone, cyclopentanone, and benzil were olefinated in a similar manner by dibromomalonic esters in the presence of tributylstibine. The yields of olefins obtained by the reactions discussed in this paragraph ranged from 86-100%. Two plausible mechanisms were proposed for these tributylstibine-mediated olefinations.

A second paper from Huang's laboratory was concerned with the use of tributylstibine and a catalytic amount of a copper(I) salt to mediate the olefination of diazo compounds with a variety of aldehydes and ketones [32]:



$$\mathrm{R^1R^2C{=}O + N_2CYZ + Bu_3Sb \xrightarrow{CuX} R^1R^2C{=}CYZ + N_2 + Bu_3SbO}$$

$$\mathrm{Bu_3SbO \xrightarrow{H_2O} Bu_3Sb(OH)_2}$$

(where both Y and Z were CO_2Me or C(O)Me; where Y was H and Z was CO_2Et; and where X was Cl, Br, or I)

The aldehydes used in this procedure were 2-methylpropanal, hexanal, citral, cinnamaldehyde, furfural, thiofurfural, benzaldehyde, 4-methylbenzaldehyde, 4-methoxybenzaldehyde, and 4-chlorobenzaldehyde. The ketones were 3-pentanone, cyclopentanone, cyclohexanone, and benzophenone. The yields obtained with the aldehydes ranged from 81 to 98%; with the ketones, from 30-88%. When aldehydes were used, the olefins obtained had the *E* configuration. The mechanism suggested for these reactions involved the intermediacy of a tributylstibonium ylide. For example, when the substrates were benzaldehyde and dimethyl diazomalonate, the following sequence of reactions was proposed:

$$\mathrm{Bu_3Sb + N_2C(CO_2Me)_2 \xrightarrow[80^\circ C]{CuI} Bu_3Sb{=}C(CO_2Me)_2 + N_2}$$

$$\mathrm{Bu_3Sb{=}C(CO_2Me)_2 + PhCHO \longrightarrow PhCH{=}C(CO_2Me)_2 + Bu_3SbO}$$

When attempts were made to isolate the intermediate ylide, dimethyl malonate was obtained. This failure was attributed to the hydrolysis of the ylide by moist air:

$$\mathrm{Bu_3Sb{=}C(CO_2Me)_2 + 2\,H_2O \longrightarrow Bu_3Sb(OH)_2 + CH_2(CO_2Me)_2}$$

The use of trialkoxystibines in the presence of allyl bromide to convert aldehydes to acetals was reported in a third paper by Huang's group [33]:

$$R^1CHO + Sb(OR^2)_3 + CH_2{=}CHCH_2Br \xrightarrow{80°C}$$

$$R^1CH(OR^2)_2 + CH_2{=}CHCH_2Sb(O)(Br)OR^2$$

(where R^1 was an alkyl or aryl group and R^2 was Et or Me_2CH)

The yields of acetals thus obtained ranged from 85 to 99%. Ketones were much less reactive to acetalization. Thus, even at 100°C for 16 h, only a 25% conversion to acetal was achieved with 4-nitroacetophenone. When an equimolar mixture of benzaldehyde and acetophenone was heated with triethoxystibine and allyl bromide at 80°C for 16 hr, a 96% yield of acetal was obtained from the aldehyde, but the ketone gave no acetal. The reactions discussed in this paragraph could be carried either without solvent or in such solvents as THF or petroleum ether. The authors noted that this method of preparing acetals was especially suitable for acid-sensitive aldehydes. They also suggested a reasonable mechanism for these reactions.

A patent describing the value of tertiary stibines as catalysts for the alkenylation of aldehydes has been issued to Huang and coworkers [34]:

$$R^1CHO + XCH_2Y \xrightarrow{R^2_3Sb} R^1CH{=}CHY$$

(where R^1 was alkyl, cycloalkyl, aryl, heteroaryl, etc., R^2 was alkyl, cycloalkyl, or aryl, Y was CHO, acyl, aroyl, carboxy, cyano, sulfinyl, sulfonyl, etc., and X was halo)

Huang and his coworkers have also reported that the combination of antimony trichloride and a suitable reducing agent was useful for the allylation of aldehydes [35,36]. Thus, the reaction of an aldehyde with allyl iodide for several hours in the presence of antimony trichloride and metallic iron or aluminum was found to give a good yield (79-99%) of the corresponding homoallylic alcohol:

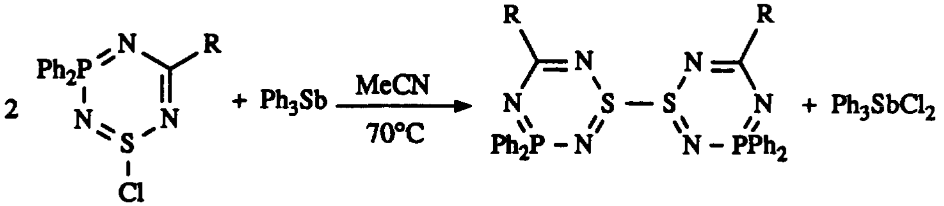
$$\mathrm{RCHO} + \mathrm{CH_2{=}CHCH_2I} \xrightarrow[\mathrm{DMF,\ RT}]{\mathrm{SbCl_3/Fe\ or\ Al}} \mathrm{RCH(OH)CH_2CH{=}CH_2}$$

(where R was Ph, 4-ClC_6H_4, 2-HOC_6H_4, 4-HOC_6H_4, 4-$MeOC_6H_4$, or $Me(CH_2)_5$)

The less reactive allyl bromide reacted with aldehydes to give the homoallylic alcohols at 60°C for 4.5-7 h. Addition of sodium iodide to the reaction mixture, however, allowed the temperature to be reduced to ambient. When a mixture of benzaldehyde and acetophenone was subjected to the allylation reaction, the ketone was recovered unchanged. Although no precise reaction mechanism was proposed, it was suggested that an allylantimony reagent was formed as an intermediate by the oxidative addition of an allyl halide to zerovalent antimony generated *in situ* by the reduction of the antimony trichloride with metallic iron or aluminum.

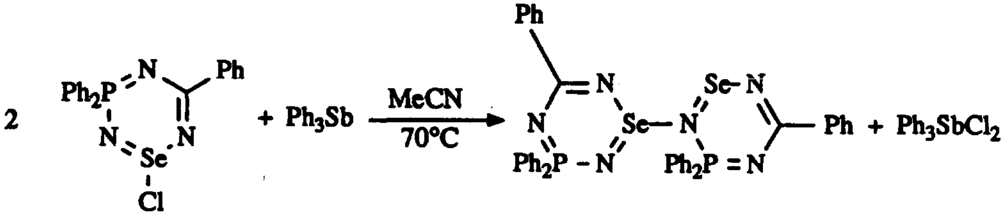
Several publications from Huang's laboratory have described synthetic applications of organic derivatives of antimony(V). These papers are discussed later in this review.

Two compounds containing unusually long S-S bonds have been prepared by the following type of reaction [37]:

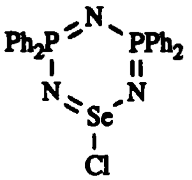


(where R was Ph or 4-MeC_6H_4)

When a 1-chloro-1,3,2,4,6-selenaphosphatriazine was allowed to react with triphenylstibine, however, a compound containing an inter-ring Se-N bond was obtained:

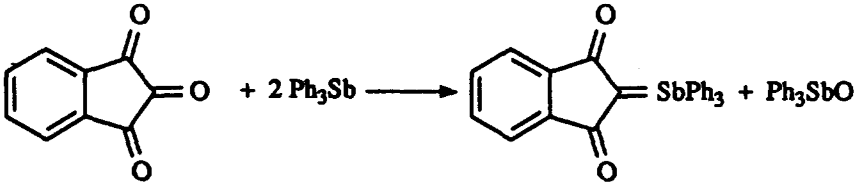


Radical dimers could not be prepared by the reaction of triphenylstibine with the following compound (1-chloro-1,3,5,2,4,6-selenadiphosphatriazine):



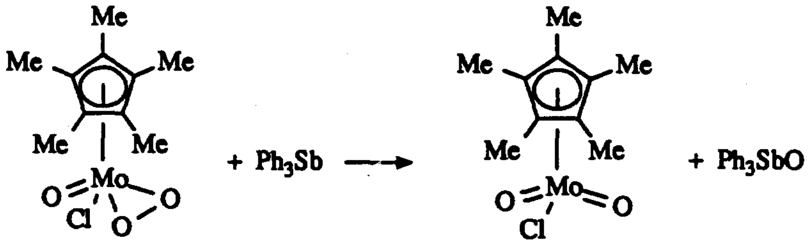
Such reactions gave pale yellow solutions that slowly deposited red precipitates of amorphous selenium.

The reaction of 1,2,3-indantrione with triphenylstibine in ether or benzene has been found to give good yields of an antimony ylide and triphenylstibine oxide [38]:



The elemental analysis, IR, and mass spectra of the ylide were consistent with its assumed structure. When the ylide was fused with sulfur, the C=Sb bond was cleaved and triphenylstibine sulfide was obtained. Oxidation of the ylide with 30% H_2O_2 in glacial acetic acid at 100°C yielded phthalic acid and triphenylstibine oxide (as a hydrate).

The oxidation of triphenylstibine has been accomplished by a peroxo derivative of (η^5-pentamethylcyclopentadienyl)molybdenum [39]:



No information was given about the properties of the triphenylstibine oxide prepared by this reaction.

A Soviet patent has described the oxidation of triphenylstibine by means of an excess of *tert*-butyl hydroperoxide in an inert organic solvent at room temperature [40]:

$$Ph_3Sb + 3\,Me_3COOH \longrightarrow Ph_3Sb(OOCMe_3)_2 + Me_3COH + H_2O$$

The tritiated compounds $Ph_2SbC_6T_5$ and $[Ph_3SbC_6T_5]BF_4$ have been obtained in 17.7% and 30.8% yields, respectively, by a procedure described as a "nuclear-chemical" method [41,42]. The synthesis was carried out by allowing triphenylstibine to react with multiply tritiated benzene (C_6T_6) and potassium tetrafluoroborate. It was proposed that the two tritiated antimony compounds were formed by the following sequence of reactions:

$$C_6T_6 \xrightarrow{-\beta^-} [C_6T_5He]^+ \longrightarrow C_6T_5^+ + He$$

$$C_6T_5^+ + Ph_3Sb \longrightarrow Ph_3\overset{+}{Sb}C_6T_5$$

$$Ph_3\overset{+}{Sb}C_6T_5 + BF_4^- \longrightarrow [Ph_3\overset{+}{Sb}C_6T_5]BF_4^-$$

$$Ph_3\overset{+}{Sb}C_6T_5 \longrightarrow Ph_2SbC_6T_5 + Ph^+$$

Further information about this work is discussed in the Annual Survey of Bismuth.

Iodonium tetrafluoroborates have been used for the polyfluoroalkylation of triphenylstibine [43]:

$$[Ph\overset{+}{I}CH_2(CF_2CF_2)_nH]BF_4^- + Ph_3Sb \longrightarrow [Ph_3\overset{+}{Sb}CH_2(CF_2CF_2)_nH]BF_4^- + PhI$$

(where *n* was 2 or 3)

The reactions occurred when suspensions of the reactants in dichloromethane were boiled for 3 h. The stibonium salts were colorless, stable, crystalline substances; they were readily soluble in polar solvents, less soluble in water, and insoluble in ethers and hydrocarbons. The yields were 54% (where *n* was 2) and 72% (where *n* was 3).

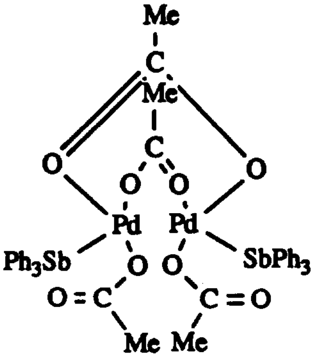
In a study concerned with the catalysis of nucleophilic substitution by nucleophiles, it has been shown that the failure of triphenylstibine to react with methyl iodide was a thermodynamic and not a kinetic problem [44]. Thus, the interaction of the stibine and methyl triflate in acetonitrile readily produced a salt:

$$Ph_3Sb + CF_3SO_3Me \xrightarrow[35°C]{MeCN} MeSbPh_3^+ \; CF_3SO_3$$

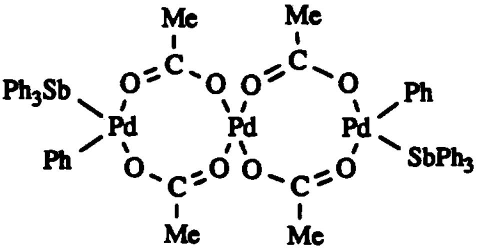
Treatment of this salt with sodium iodide in acetonitrile gave quantitative yields of triphenylstibine and methyl iodide in about two days:

$$MeSbPh_3{}^+ + I^- \xrightarrow[35°C]{MeCN} Ph_3Sb + MeI$$

A paper published in 1988 reported that the interaction of triphenylstibine and palladium(II) acetate resulted in an almost quantitative yield of biphenyl. A search has now been made for possible intermediates in this process [45]. When equimolar quantities of the stibine and the palladium compound were added to $CDCl_3$ in a NMR tube, the formation of a complex could be detected immediately. Addition of pentane yielded a crystalline substance of composition $Pd_2(O_2CMe)_4(SbPh_3)_2$. When the complex was heated in $CDCl_3$ at 60°C, biphenyl (in 96% yield) as well as elemental palladium and antimony were obtained. The complex was shown by X-ray crystallography to have the following structure:

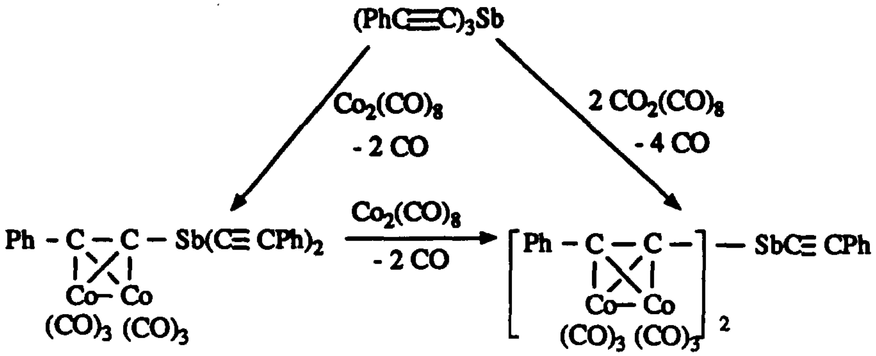


In a second type of experiment conducted in THF-dioxane at 45°C for 1 h, a different complex was obtained on the addition of hexane. Crystallographic examination showed that this complex had the following structure:



It is not certain that this complex was a real intermediate in the reaction. Thus, on heating the substance at 70°C in THF for several hours, only 45% of the phenyl groups present were converted to biphenyl.

Two complexes of tris(phenylethynyl)stibine and octacarbonyldicobalt have been prepared by the following scheme [46]:



The reactions were carried out in a 1:1 mixture of pentane and toluene at 25°C. The phenylethynyl complexes, which were characterized by analytical and spectroscopic (IR, PMR, and ^{13}C NMR) data, were said to exhibit η^2 "side-on" coordination and to contain sterically hindered carbon-cobalt tetrahedrane cluster units. There was no evidence of coordination between the cobalt and antimony atoms. The reaction of one mol of tris(phenylethynyl)stibine with three mol of octacarbonyldicobalt gave a mixture of the previously mentioned $PhC{\equiv}CSb[(\eta^2\text{-}C{\equiv}CPh)Co_2(CO)_6]_2$ and a small amount of a compound said to be $Sb[(\eta^2\text{-}C{\equiv}CPh)Co_2(CO)_6]_3$. Purification of the latter substance has not yet been accomplished.

Cupric acetate has been found to catalyze the protonolysis of the carbon-antimony bonds of triphenylstibine [47]:

$$Ph_3Sb + 3\,MeCO_2H \xrightarrow{Cu(O_2CMe)_2} (MeCO_2)_3Sb + 3\,PhH$$

The reaction required heating the stibine for 8 h at 110°C with an excess of acetic acid (10 mol per mol of antimony compound). Benzoic or propionic acid could be used in place of the acetic acid. A number of cupric salts other than the acetate also catalyzed the dephenylation reaction, but cuprous and cupric halides had no detectable activity. It was suggested that the mechanism of the reaction involved the intermediacy of phenylcopper. Further information about this work is included in the Annual Survey of Bismuth.

Tris(trifluoromethyl)stibine has been included in a study of the possible trifluoromethylation reactions of trifluoromethyl iodide and several organometallic reagents with furan, thiophene, pyrrole, and 1,4-benzoquinone [48]. The stibine did not prove to be very useful. Its photochemical reaction with furan for 72 h did, however, give a 12.1% yield of 2-trifluoromethylfuran. The product was characterized by a variety of spectral methods (MS, ^{19}F and ^{1}H NMR, and IR).

A detailed study has been made of the effects of growth temperature and vapor phase composition on the composition of gallium phosphide antimonide and indium phosphide antimonide obtained by a process termed organometallic vapor phase epitaxy (OMVPE) [49]. Trimethylstibine was used as the source of the antimony in this investigation. The growth temperature was in the 500-600°C range for the gallium compound and in the 460-580°C range for the indium compound.

Trimethyl- and triethylstibine have been discussed in a survey of the pyrolysis and growth reactions occurring during the atmospheric pressure OMVPE growth of several III/V semiconductors [50]. Both stibines were said to be acceptable sources of antimony for the growth of InSb, GaSb, and related alloys, but their use in conjunction with the trimethyl derivatives of Group III metals could presumably result in high levels of carbon contamination. The low pyrolysis temperature of triethylstibine appeared to make this substance especially suitable as a source of antimony for the low temperature growth of small band gap III/V semiconductors. The pyrolysis temperature of trimethylstibine was somewhat higher than optimum for the growth of alloys of this type.

The UV absorption spectrum of trimethylstibine in the gas phase has been determined in a study of the potential application of UV absorption spectroscopy for the measurement of the partial pressures of the reactants in metalorganic chemical vapor deposition (MOCVD) reactors [51]. The spectrum of the stibine exhibited two strong peaks in the 190-270 nm region: one at 225 nm and the other about 201 nm. It was concluded that UV spectroscopy offered great promise as a method of continuously monitoring the composition of the reactants during MOCVD.

An investigation has been reported of the effects of the ratio of trimethylstibine to triethylgallium on epilayer properties of gallium antimonide (GaSb) grown by low-pressure MOCVD [52]. It was found that the surface morphology and the photoluminescence spectrum were strongly dependent on this ratio. A growth temperature of 600°C and a growth pressure of 100 torr were employed in this study.

The recent patent literature has described the preparation of a variety of trivalent organoantimony compounds said to be useful in chemical vapor deposition processes. Thus, a European patent application has claimed the interaction of trialkylstibines and antimony trihalides as a method of synthesizing halo- and dihalostibines of the type R_nSbX_{3-n}, where R was a C_1-C_4 alkyl group, X was a halogen, and n was 1 or 2 [53]. A U.S. patent application has mentioned the preparation of compounds of the type R_nSbX_{3-n}, where R was an alkyl, cycloalkyl, benzyl, or aryl group, X was H, Cl, Br, or I, and *n* was 1,2, or 3 [54]. For example, trineopentylstibine was obtained by sonicating a mixture of magnesium powder and neopentyl chloride in ether for 1 h, refluxing the mixture for 15 h, and then adding the resulting solution to antimony trichloride in ether at 0°C. A German Offenbarung has included compounds of the type $R^1{}_{3-m}M[(CHR^2)_nSbR^3R^4]_m$, where M was Al, Ga, or In, R^1, R^3, and R^4 were H, alkyl, cycloalkyl, alkenyl, cycloalkenyl, or aryl, R^2 was H or alkyl, and *m* was 2 or 3 [55]. The application of certain trivalent organoantimony compounds for a number of electronic purposes (in addition to organometallic vapor phase epitaxy) has been claimed in a European patent application [56]. The compounds included a number of perfluorinated or partially fluorinated primary, secondary, and tertiary stibines.

The structure of pyrolytic films of antimony oxide deposited on gallium arsenide (GaAs) or silicon by the decomposition of triethylstibine has been investigated [57]. The triethylstibine was vaporized and transported to the reaction zone by bubbling argon through toluene or butyl alcohol solutions of the stibine. The etching rate of the films by hydrochloric acid (0.49-2.12 M) was then studied. Among other things, it was found that the solvent used in the deposition process had a pronounced effect on the etching rate. Thus, films prepared from solutions of triethylstibine in toluene etched 5-6 times as fast as films prepared from butyl alcohol solutions.

Colorless crystals of triphenylstibine (mp 326.5 K), obtained by slow evaporation of an acetone/water solution, have been examined by X-ray diffraction [58]. Two independent molecules were found in each asymmetric unit; they differed in the dihedral angles between the planes of the phenyl rings. The average C-Sb distance was 2.155(9) Å, while the C-Sb-C angles ranged from 95.1(3) to 98.0(3)°.

Triphenylstibine has been included in a study of the surface ionization (SI) mass spectrometry of organometallic compounds of elements of main groups III, IV, or V [59]. The SI spectrum of the stibine exhibited neither its molecular ion nor the Sb^+ species. Apparently, phenyl dissociation from triphenylstibine was so rapid on the heated surface employed that the intact molecular species could not survive. The absence of the Sb^+ ion was attributed to the high ionization energy (IE) of antimony.

A study has been made of the nature of the metal-containing impurities in high-purity diethylzinc [60]. The combined methods of mass spectrometry and GC were used to show that the volatile metal-containing impurities consisted predominantly of ethyl derivatives. One of these substances was triethylstibine. Another paper from the same laboratory described the determination of liquid-vapor coefficients at 296-375 K for infinitely dilute solutions of tetraethylsilane, tetraethylgermane, tetraethylstannane, tetraethylplumbane, diethylmercury, triethylaluminum, triethylgallium, triethylindium, triethylarsine, or triethylstibine in diethylzinc [61]. Distillation was shown to be an effective method for purifying diethylzinc.

The mechanism of Cd^{2+} transfer in methanol across surfactant monolayers has been studied by means of *dc*-polarography [62]. The surfactants included triphenylarsine, -stibine, and -bismuthine. The ability of these substances to inhibit the reduction of the Cd^{2+} decreased in the order $Ph_3Bi > Ph_3Sb > Ph_3As$.

The addition of triphenylstibine to molybdenum(V) chloride has been found to increase the catalytic activity of the latter substance for the polymerization of 1-(*n*-alkylthio)-1-propynes [63]. The presence of the stibine increased both the yield and the weight-average molecular weight of the polymer. Triphenylstibine has also been employed as a component of fire-retardant epoxy resin-based optical disk substrates [64].

A study of the HOMO-LUMO separation in the graph spectra of heterocyclobutadienes has included structures of the following type [65]:

(where E was CH, N, P, As, or Bi)

The stability, reactivity, and electronic spectra of the molecules were discussed in relation to the HOMO-LUMO separation. It was noted that the replacement of CH by Sb resulted in raising the LUMO for $n \rightarrow \pi^*$ transitions but lowering it in the case of $\pi \rightarrow \pi^*$ transitions.

In addition to a paper already discussed [45], there have been a considerable number of other recent publications that mentioned the use of tertiary stibines as ligands in transition metal complexes. The metals coordinated to the antimony in these complexes included chromium [66], copper [67,68], europium [69], gold [70,71], iridium [72,73], iron [74-79], molybdenum [66,80,81], nickel [82,83], osmium [78,84-86], palladium [82,86-89], platinum [82,90], rhenium [91-93], rhodium [90,94-96], ruthenium [78,96-104], and tungsten [68,80,81].

Colorless, transparent crystals of a 1:2 complex of 9,10-dihydroanthracene and antimony tribromide have been obtained in 72% yield by heating a toluene solution of the components at reflux temperature for 1 h and then slowly cooling the reaction mixture to -30°C [105]:

The compound, which melted at 95-96°C, was stable at room temperature under nitrogen or *in vacuo*, but was extremely hygroscopic. X-ray crystallography showed that two molecules of antimony tribromide together with one molecule of dihydroanthrance formed the building blocks of a three-dimensional coordination polymer. The two antimony tribromide acceptor molecules were attached on opposite sides of the planar dihydroanthracene donor molecule. Each antimony atom was located almost exactly above the center of a benzene ring (at a distance of 3.27 Å) and hence could be referred to as hexahapto-bonded (η^6). The building blocks of the coordination polymer were associated by intermolecular Sb····Br contacts. The coordination sphere of each antimony atom contained not only three closely bonded bromine atoms at 2.502(1), 2.532(1), and 2.538(1) Å but also two more at 3.500(1) and 3.669(1) Å and a sixth one at 4.035(1) Å. Each antimony atom could be considered to be in a greatly distorted pentagonal-bipyramidal environment (with the arene molecule assigned to one of the vertices). Attempts to prepare complexes of 9,10-dihydroanthracene and antimony *trichloride* yielded solids of ambiguous stoichiometry. Single crystals could not be obtained.

The interaction of 1,2,4,5-tetramethylbenzene(durene) and antimony trichloride in boiling petroleum ether has been found to give a 97% yield of a 1:2 complex [106]:

$$\text{Durene} + 2\,SbCl_3 \longrightarrow Cl_3Sb \cdot \text{Durene} \cdot SbCl_3$$

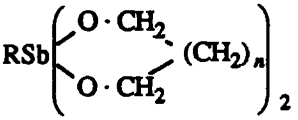
The clear, colorless crystals thus obtained melted at 98°C. X-ray analysis demonstrated that the structure consisted of tetrameric Sb_4Cl_{12} units that were crosslinked through double-sided arene coordination at each antimony atom with four other tetramers so as to give a three-dimensional organometallic polymer. The antimony atoms were in a distorted trigonal-bipyramidal environment and showed a slight deviation from centric (η^6) coordination. The dimensions of the coordinated durene molecules were nearly the same as those of the free arene. Bridging and terminal Sb-Cl distances were also in the usual range. Treatment of pentamethylbenzene with antimony trichloride or tribromide in petroleum ether under reflux conditions also yielded crystalline products of 1:2 stoichiometry:

$$C_6HMe_5 + 2\ SbX_3 \longrightarrow X_3Sb \cdot C_6HMe_5 \cdot SbX_3$$

(where X was Cl or Br)

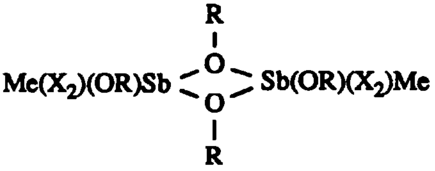
The yield of the trichloride complex was 86%, mp 144°C; the yield of the tribromide complex was 89%, mp 105°C. Both complexes proved to be isostructural with the previously described hexamethylbenzene derivatives of antimony trichloride and tribromide. A sharp melting substance (mp 105°C) containing arsenic and antimony in a ratio of 1:5.2 was obtained by heating stoichiometric amounts (1:1:1) of arsenic trichloride, antimony trichloride, and hexaethylbenzene in petroleum ether. A similar reaction of arsenic and antimony tribromides with hexaethylbenzene in petroleum ether yielded large colorless crystals, mp 124°C, that had an arsenic:antimony ratio of 1:1.86. In both cases recrystallization failed to yield substances in which the ratio of the two elements was 1:1. Single crystal X-ray structure determinations of the 1:5.20 (X = Cl) and 1:1.86 (X = Br) phases were unsuccessful because of severe disorder.

Wieber and coworkers [107] have described attempts to prepare open-chain esters of mono-alkyl stibonic acids, $RSb(OR')_4$, as well as spirocyclic esters of the following type:



Oxidation of organoantimony(III) compounds of the type $MeSb(OR)_2$ (where R was Me or Et) with either thionyl chloride or bromine in methylene dichloride solution at -60°C, with the exclusion of light, gave the following bridged compounds:

$$2\ MeSb(OR)_2 + 2\ SO_2Cl_2\ (\text{or } 2\ Br_2) \xrightarrow[-60°C]{CH_2Cl_2}$$

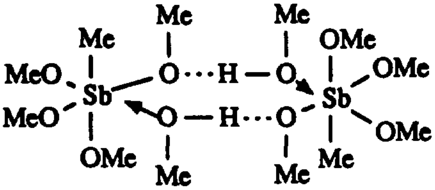


$$Me(X_2)(OR)Sb \overset{\overset{R}{|}}{\underset{\underset{R}{|}}{<_{O}^{O}>}} Sb(OR)(X_2)Me$$

(where R was Me or Et and X was Cl or Br)

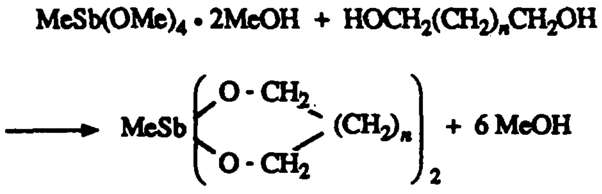
The products were colorless (R = Me) or yellow (R = Et) hygroscopic crystals, unstable in the light. They were characterized by elemental analyses and, for the compound where R was Et and X was Br, by mass spectroscopy. In addition, both ^{1}H and ^{13}C NMR spectra were reported. For both compounds where R was Me or Et, the ^{1}H and ^{13}C NMR spectra clearly distinguished between the bridging alkoxy group and the free alkoxy groups. Finally, an X-ray diffraction study of the compound, where R was Me and X was Br, was reported. The geometry around each antimony atom was octahedral. The Sb-O bond distances of the two bridging groups were 213.4 and 213.7 pm, and the non-bridging Sb-O bond distance was 196.2 pm. The Sb-O-Sb angles for the 4-membered ring were 107.8°, and the O-Sb-O angles were 72.2°.

When either compound $[MeSb(OMe)_2X_2]_2$, where X was Br or Cl, was treated with sodium methoxide in methanol at 0°C in the dark, the compounds $MeSb(OMe)_4{\bullet}(MeOH)_n$, where *n* was 2 or 3, were obtained. All attempts to remove the methanol from these complexes were unsuccessful. The authors speculated that the dimeric compound was stabilized by possessing the following structure:



The compounds $[MeSb(OEt)_2X_2]_2$, when similarly treated with NaOEt, gave the compound $MeSb(OEt)_4{\bullet}\ 2EtOH$. However, the solvent-free compound $MeSb(OEt)_4$ was obtained by crystallizing the solvent-containing product from pentane at -78°C. The solvated compound $MeSb(OEt)_4{\bullet}\ 2EtOH$ could also be prepared by crystallizing the compound $MeSb(OMe)_4{\bullet}\ nMeOH$ from ethanol. The ^{1}H and ^{13}C NMR spectra of the two ethoxy compounds were in accord with dimeric structures with bridging ethoxy groups.

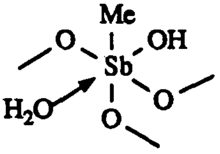
In addition to the open chain compounds, several spirocyclic esters were prepared from the methoxy compound $MeSb(OMe)_4{\bullet}\ 2MeOH$ and the appropriate diol:



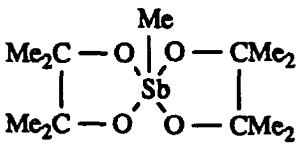
(where n was 0, 1, or 2).

Both *meso*- and racemic 2,3-butanediol were used in the above reaction. The cyclic ester from pinacol was also prepared. The products were characterized by elemental analyses, mass, IR, and ^1H NMR spectra. When solutions of four of the spirocyclic compounds, as well as solutions of the two open chain esters, were allowed to stand for some time, solids precipitated from solution. Molecular weight determinations of the spirocyclic compounds in solution showed them to be monomolecular when freshly prepared, but the molecular weights increased when the solutions were allowed to stand. Apparently, the compounds polymerized. The ^1H NMR spectra of the spirocyclic compounds were of considerable interest. The compound prepared from *meso*-2,3-butanediol gave 2 multiplets for the OCH groups and 2 doublets for the CCH_3 groups, but the compound from the racemic 2,3-butanediol gave a multiplet for the OCH groups and a multiplet for the CCH_3 groups. These results were explained by Berry pseudorotation. The spirocyclic compound obtained from pinacol gave two singlets at $\delta = 1.05$ and 0.97 ppm in a ratio of 1:1 at room temperature. Temperature dependent studies between -70°C and 50°C showed no alteration of the peaks. However, in toluene-d_8, on raising the temperature, the methyl peaks all became equivalent. The coalescence temperature was 70°C, from which an activation energy of $\Delta G^{\#} = 77.15$ KJ/mol^2 for the pseudorotation was calculated.

Although arylstibonic acids have been known for many years, all previous attempts to prepare the analogous alkylstibonic acids have been unsuccessful. Wieber and Walz [108] have now reported the successful synthesis of methylstibonic acid. Two different methods have been employed, the hydrolysis of a tetraalkoxymethylantimony compound or the oxidation of dimethoxymethylstibine with hydrogen peroxide. The hydrolysis method employed either $MeSb(OMe)_4 \cdot 2MeOH$ or $MeSb(OEt)_4$ dissolved in methylene dichloride at 0°C. A methylene dichloride-water-alcohol mixture was added dropwise and the solution stirred for 2 h. Removal of the solvent gave an alcohol adduct which was dissolved in water saturated with dinitrogen. Removal of the water gave the desired product as a white powder. The oxidation of $MeSb(OMe)_2$ was carried out in methylene dichloride solution at 0°C with a hydrogen peroxide-methanol-methylene dichloride mixture, and the product purified in the same manner as that prepared by hydrolysis. Elemental analysis of the white powder gives results corresponding to the empirical formula CH_5O_3Sb. Differential thermal analysis showed an endothermic change at about 140°C and exothermic decomposition at 200°C. Thermogravimetric analysis and gas chromatography showed that the thermal decomposition involved loss of water and methane. ^1H NMR gave a singlet at $\delta = 2.10$ for the methyl group and a broad multiplet, $\delta = 2.00\text{-}1.30$ ppm, for the OH signal. IR and Raman spectral studies indicated the presence of an Sb-O-Sb group. Titration of the compound with 0.1 N sodium hydroxide, with phenolphthalein as the indicator, was of considerable interest. The initial end point was found with a Na:Sb ratio of 1:2, but the end point was time-dependent. At higher temperatures, a final end point at a Na:Sb ratio of 1:1 could be reached. These results were similar to those found for arylstibonic acids and can best be explained by assuming a polymeric structure for stibonic acids and depolymerization when they are treated with alkali. The ratio of Na:Sb of 1:2 would suggest a polymerization number of 2 for methylstibonic acid in aqueous solution. The following structure was suggested for hydrated methylstibonic acid that possessed the general formula $(MeSbO_2)_n \cdot m\, H_2O$ (where *n* and *m* were synthesis dependent):



Methylstibonic acid was found to react with pinacol to give the following spiran:



A monosodium salt of methylstibonic acid was also prepared. An aqueous solution of the acid was treated with one molar equivalent of aqueous sodium hydroxide. The initial solution was strongly alkaline but reached a final pH value of 8.5 after being stirred for 6 hr. The solvent was removed *in vacuo* and the residue dissolved in water.

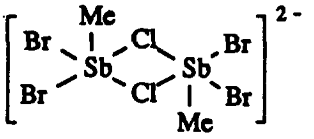
Addition of ethanol gave the sodium salt in crystalline form. It possessed the formula $[MeSb(OH)_3O]_2Na_2 \cdot 6\,H_2O$.

Wieber and Walz [109] have prepared and studied the spectra, structure, and physical properties of a number of pentahalomethyl- and pentahalophenylantimonate(V) compounds, as well as trihalomethylantimonate(III) compounds and phenyltetrahaloantimony compounds. The trihalomethylantimonate(III) compounds were prepared by the following method:

$$MeSbBr_2 + R_4EX \xrightarrow[RT]{CH_2Cl_2} R_4E[MeSbBr_2X]$$

(where X was Cl or Br and R_4E was Bu_4N, Et_4N, Ph_4P, or Ph_4Sb)

The thermal stability of the antimonates in polar solvents increased from those with tetraalkyl cations (mps about 80°C) to those with tetraaryl cations (mps 177-197°C). The IR spectra of the compounds, where the anion was $[MeSbClBr_2]$, showed a strong absorption band, $\upsilon = 245$ cm, which was assigned to chlorine bridges. The anion thus was believed to possess the following structure:



The equivalent conductivities of the compounds $R_4E[MeSbBr_2Cl]$ and $R_4E[MeSbBr_3]$ in acetonitrile solution were in the range $\Lambda = 86 - 110\ cm^2\Omega^{-1}mol^{-1}$, corresponding to 1:1 electrolytes.

Compounds of the type $Ph_4E[MeSbCl_5]$ and $Ph_4E[MeSbCl_4Br]$ were prepared from $MeSbCl_2$, SO_2Cl_2, and Ph_4EX (where E was P or Sb and X was Cl or Br:

$$MeSbCl_2 + SO_2Cl_2 + Ph_4EX \xrightarrow[-78°C]{CH_2Cl_2} Ph_4E[MeSbCl_4X] + SO_2$$

The above reactions (as well as reactions to prepare other compounds containing methyl- or phenylpentahaloantimony anions and phenyltetrahaloantimony compounds) were carried out in the dark. Although nearly all of these compounds were light sensitive, they varied considerably in this respect. The two compounds

$Ph_4E[MeSbCl_4Br]$ (E = P or Sb) decomposed only slowly on standing for a long period in the light. The mps of the four compounds of the type $Ph_4E[MeSbCl_4X]$ (X was Cl or Br) varied between 140-196°C. Compounds of the type $Ph_4E[MeSbBr_3Cl_2]$ and $Ph_4E[MeSbBr_2Cl_3]$, where E was P or Sb, were prepared by chlorination:

$$Ph_4E[MeSbBr_3] + Cl_2 \xrightarrow[-78^\circ C]{CH_2Cl_2} Ph_4E[MeSbBr_3Cl_2]$$

$$Ph_4E[MeSbBr_2Cl] + Cl_2 \xrightarrow[-78^\circ C]{CH_2Cl_2} Ph_4E[MeSbBr_2Cl_3]$$

Similarly, compounds of the type $Ph_4E[MeSbBr_4Cl]$ and $Ph_4E[MeSbBr_5]$ were prepared by bromination of the same two starting materials. (Only the compound where E was Sb was prepared for the last of the above compounds.) These compounds were considerably less stable than compounds where the anions were $[MeSbCl_5]^-$ or $[MeSbCl_4Br]^-$. They decomposed without melting when heated, and decomposed on standing in solution at room temperature:

$$Ph_4E[MeSbCl_{4-n}Br_{n+1}] \longrightarrow MeBr + Ph_4E[SbCl_{4-n}Br_n]$$

An order of stability of these compounds was formulated with the most stable anion being $[MeSbCl_5]^-$ and the least stable being $[MeSbBr_5]^-$.

Two compounds, $PhSbCl_2Br_2$ and $PhSbBr_4$, were prepared by bromination of $PhSbCl_2$ or $PhSbBr_2$, respectively. The first was yellow, the second brown in color, and both were thermally unstable and decomposed at 50° and 47°C, respectively; they decomposed in solution in the light:

$$PhSbBr_2X_2 \longrightarrow PhBr + SbX_2Br$$

$$PhSbBr_2X_2 \longrightarrow PhSbX_2 + Br_2$$

(where X was Cl or Br)

An attempt to prepare $PhSbCl_4$ by chlorination of $PhSbCl_2$ gave only Ph_2SbCl_3 and $SbCl_5$. In addition to the compounds of the type $Ph_4E[MeSbCl_{5-n}Br_n]$, compounds of the type $R_4E[PhSbCl_{5-n}Br_n]$ were prepared by chlorination or bromination of the requisite antimonate(III) compound. For these compounds, R_4E was Et_4N or Ph_4P. The two compounds $Et_4N[PhSbCl_3Br_2]$ and $Et_4N[PhSbBr_5]$ were also prepared by the following reaction:

$$PhSbBr_2X_2 + Et_4NBr \xrightarrow{CH_2Cl_2} Et_4N[PhSbBr_3X_2]$$

(where X was Cl or Br)

The tetraphenylphosphonium salts showed an increase in color (from yellow to deep orange) and a decrease in the mps with increasing number of bromine atoms in the anion. The tetraethylammonium salts were considerably less stable than the tetraphenylphosphonium salts. All of these compounds were sufficiently stable to be handled in solution in the light, but those with the most bromine in the anion did lose bromine on standing:

$$R_4E[PhSbBr_4X] \longrightarrow R_4E[PhSbBr_2X] + Br_2$$

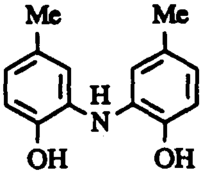
(where X was Cl or Br)

The various compounds described in this paper were characterized by elemental analyses, PMR, and IR spectra. Conductivity data in acetonitrile solution were listed for many of the compounds. For those compounds with chlorine atoms in the anion, the IR bands for the Sb-Cl bonds were listed in tabular form. From this data, suggestions were made for the structures of the anions. For all compounds with anions of the type $[PhSbCl_nBr_{5-n}]^-$, as well as for the cations Ph_4P^+ and Ph_4Sb^+, and for the two compounds $PhSbCl_2Br_2$ and $PhSbBr_4$, the X-sensitive bands of the phenyl groups in the IR spectra were listed in tabular form. A band at about $\surd = 210$ cm^{-1} was assigned to the Sb-Br stretching mode.

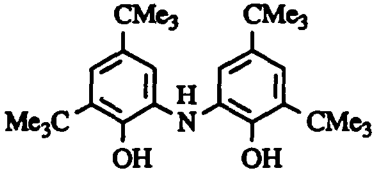
The crystal structures of three phenylantimonate compounds, $NH_4[PhSbCl_5]$, $NH_4[PhSbBr_5]$, and $Me_2NH_2[PhSbCl_5]$, have been determined by X-ray diffraction [110]. All three compounds were orthorhombic. The geometry of the antimony atoms was octahedral in each case.

The compound $2NH_4[PhSbF_5]{\bullet}NH_4[HF_2]$ was prepared by the reaction of $PhSbO_3H_2$ and excess NH_4F in HCl solution [111]. Crystals were obtained by crystallization from an EtOH-HF mixture, and the crystal structure was determined. The geometry around the antimony atom was distorted octahedral. Several anion-cation contacts were less than the sum of the van der Waals radii; this fact suggested the presence of N-H···F-H bonds.

Ohkata and coworkers [112] have studied the reaction of organoantimony(III) and organoantimony(V) compounds with the two tridentate ligands I and II.

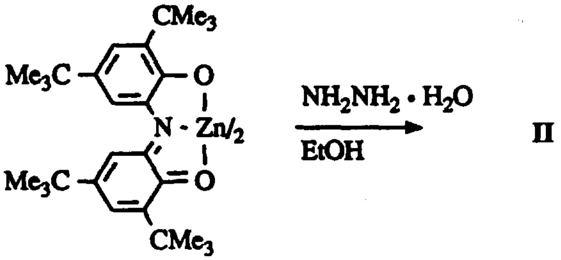


I

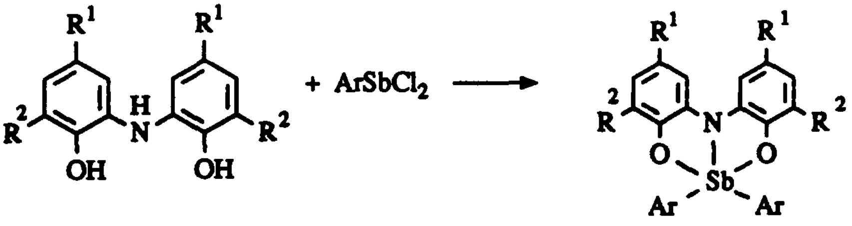


II

Compound I was known while compound II was prepared by demetallation of the corresponding zinc derivative:

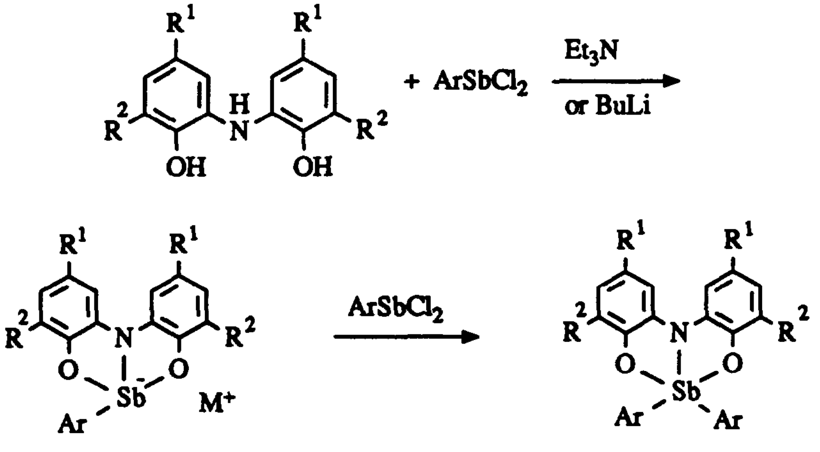


The reaction of I or II with 4-tolyl- or 4-methoxyphenyldichlorostibine (1 equivalent in the presence of Et_3N or BuLi) unexpectedly gave the antimony(V) compounds III, IV, V, and VI:



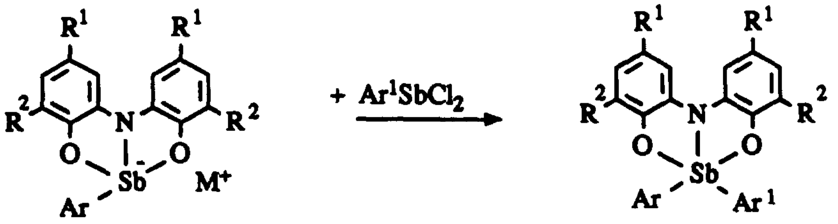
III $R^1 = Me, R^2 = H, Ar = 4\text{-}MeC_6H_4$
V $R^1 = Me, R^2 = H, Ar = 4\text{-}MeOC_6H_4$
V $R^1 = R^2 = Me_3C, Ar = 4\text{-}MeC_6H_4$
VI $R^1 = R^2 = Me_3C, Ar = 4\text{-}MeOC_6H_4$

The yields were comparatively small, 11-20%, but the yield of the dimethyl compound III was increased to 49% when 3 equivalents of the dichlorostibine were used. The same compound III was obtained in 72% yield from $(4\text{-}MeC_6H_4)_2SbCl_3$ and I. A mechanism involving formation of an anionic antimony intermediate, followed by attack of a second molecule of the dichlorostibine, was suggested for the unexpected result:



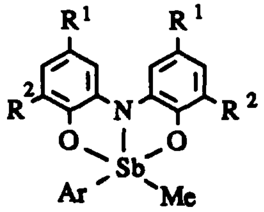
(where M was Et_3NH or Li)

The presumed intermediate anionic Sb species could be trapped by use of $4\text{-}MeOC_6H_4SbCl_2$ or MeI added to the reaction using $4\text{-}MeC_6H_4SbCl_2$. Thus, addition of $4\text{-}MeOC_6H_4SbCl_2$ gave the following results:



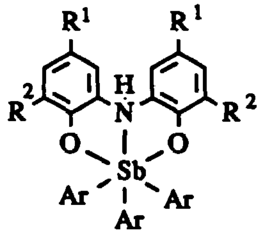
(where R^1 was Me, R^2 was H, Ar was 4-MeC_6H_4, and Ar^1 was 4-$MeOC_6H_4$)

The yield of the mixed diaryl compound was 14%. When methyl iodide was used with either of the tridentate ligands and 4-$MeC_6H_4SbCl_2$, the following compounds were obtained:



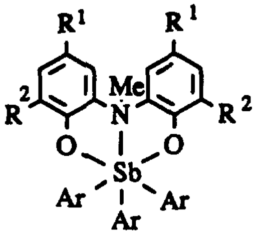
(where R^1 was Me, R^2 was H; or where R^1 and R^2 were Me_3C; and where Ar was 4-MeC_6H_4)

Treatment of III or V with 4-MeC_6H_4Li and an acid gave the following tri-4-tolyl compounds:

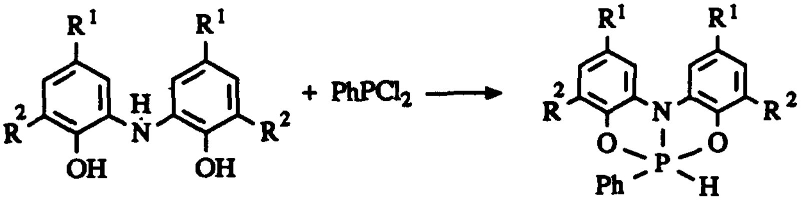


(where R^1 was Me and R^2 was H, or where R^1 and R^2 were Me_3C)

The ^{1}H NMR spectra of these compounds showed the presence of two different 4-tolyl groups in a 2:1 ratio. Deprotonation of either of these two compounds followed by treatment with MeI gave the following compounds:



The authors also found that treating either of the two tridentate ligands I or II with $PhPCl_2$ gave only a monophenyl compound:



The new compounds were characterized by ^{1}H NMR spectra and by elemental analyses (not reported).

The cleavage of aryl-tin bonds in symmetrical and unsymmetrical tetraorganotin compounds by electrophilic reagents has been investigated by Bhattacharya and Pakdaman [113]. The electrophilic reagents used were chlorine, bromine, iodine chloride, iodine bromide, and antimony pentachloride. The following cleavage reactions were carried out with antimony pentachloride:

$$2\ Ph_3SnC_6Cl_5 + SbCl_5 \longrightarrow 2\ Ph_2(C_6Cl_5)SnCl + Ph_2SbCl_3$$

$$Ph_2Sn(C_6Cl_5)_2 + SbCl_5 \longrightarrow Ph(C_6Cl_5)SnCl_2 + Ph(C_6Cl_5)SbCl_3$$

Elemental analyses were reported for $Ph(C_6Cl_5)SbCl_3$.

Coordination polymers of the type $[(Me_3Sn)_2(Me_3Sb)M(CN)_6]_\infty$ where M was Fe or Ru, have been prepared by Eller and coworkers [114]. Two methods were used for their preparation. In one method the polymers precipitated when the reactants were mixed in aqueous solution:

$$2\,Me_3SnCl + Me_3SbBr_2 + K_4[M(CN)_6] \xrightarrow[-2\,KBr,\,-2\,KCl]{H_2O} [(Me_3Sn)_2(Me_3Sb)M(CN)_6]_\infty$$

A second method involved an ion-exchange type reaction:

$$[NH_4(Me_3Sn)_3M(CN)_6]_\infty \xrightarrow[-\,NH_4^+,\,-\,Me_3Sn(H_2O)_2^+]{Me_3SbBr_2,\,H_2O} [(Me_3Sn)_2(Me_3Sb)M(CN)_6]_\infty$$

Elemental analyses as well as IR, Raman, and UV-visible spectra were reported.

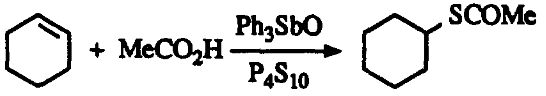
Nomura and coworkers [115] have devised an excellent method for converting carboxylic acids into the corresponding thiolic acids using triphenylstibine oxide and tetraphosphorus decasulfide. In a preliminary experiment they prepared $Ph_3Sb(O_2CMe)_2$ from 1 equivalent of Ph_3SbO and 2 equivalents of $MeCO_2H$ in PhH, and then treated the resulting solution with P_4S_{10}. The mixture was filtered and the filtrate subjected to fractional distillation to give MeCOSH in 74% yield. In subsequent reactions carboxylic acids were added to a mixture of Ph_3SbO and P_4S_{10} in benzene and the pure thiolic acid obtained by fractional distillation:

$$2\,RCO_2H + Ph_3SbO \xrightarrow{PhH} [Ph_3Sb(O_2CR)_2] \xrightarrow{P_4S_{10}} 2\,RCOSH$$

(where R was Me, Ph, Pr, Me_2CH, Me_3C, or BuC(Et)H)

The yields varied from 82-95%. In addition to the monothiolic acids, 1,6-hexanedithiolic acid was prepared in 64% yield. An attempt to convert acrylic acid to the corresponding thiolic acid was unsuccessful. Although the IR and NMR spectra of the crude reaction mixture indicated that the desired acid was formed, the pure acid could not be obtained by distillation.

The reaction was also used to prepare esters of thiolic acids:



$$PhCH=CH_2 + MeCO_2H \xrightarrow[P_4S_{10}]{Ph_3SbO} PhCH_2CH_2SCOMe$$

The above esters were obtained in 46% and 43% yields, respectively. The reaction of acetic acid, allylamine, Ph_3SbO, and P_4S_{10} led to the formation of *N*-(2-propenyl)acetamide in 85% yield:

$$CH_2{=}CHCH_2NH_2 + MeCO_2H \xrightarrow[P_4S_{10}]{Ph_3SbO} MeCONHCH_2CH{=}CH_2$$

The thiolic acids prepared in this study were characterized by elemental analyses, IR, ^1H and ^{13}C NMR, and mass spectroscopy.

Baechler and coworkers [116] have studied the transfer of oxygen, sulfur, or selenium between two Group V elements with P, As, or Sb compounds serving as donors and P or As compounds acting as acceptors. One type of transfer reaction studied was the following:

$$Ph_3E{=}Y + Ph_2MeE' \xrightleftharpoons{PhBr} Ph_3E + Ph_2MeE'{=}Y$$

(where E was P, As, or Sb, E′ was P or As, and Y was O or S)

Three different reactions involving antimony(V) compounds were studied:

$$Ph_3SbO + Ph_2MeP \xrightarrow[160°C]{PhBr} Ph_3Sb + Ph_2MePO$$

$$Ph_3SbS + Ph_2MeP \xrightarrow[30°C]{PhBr} Ph_3Sb + Ph_2MePS$$

$$Ph_3SbS + Ph_2MeAs \xrightarrow[30°C]{PhBr} Ph_3Sb + Ph_2MeAsS$$

These three reactions all went essentially to completion, in contrast to many of the reactions involving transfer from phosphorus or arsenic. It was found, however, that the transfer of oxygen from Ph_3SbO to Ph_2MeP was slower than the transfer of oxygen from Ph_3AsO to Ph_2MeP. The authors suggested that this effect was caused by triphenylstibine oxide existing in solution in oligomeric forms. It was found that the second-order kinetic plot for the Ph_3SbO to Ph_2MePO reaction deviated considerably from linearity, whereas the other reactions studied gave straight line kinetic plots. The triphenylstibine oxide used was a commercial product and was said to be markedly hygroscopic. It was concluded that the transfer reactions were consistent with a decrease in covalent bond energies in going from P to Sb and from O to Se.

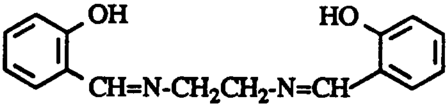
The preparation of antimony(V) complexes of arylamidoximes, $ArC(NH_2)=NOH$, have been reported by Hodali and Hussein [117]. The antimony(V) compounds used were $SbCl_5$ and Ph_3SbBr_2. Six different oximes $RC_6H_4C(NH_2)=NOH$ were employed (where R was H, 2-Br, 4-Br, 3-Me, 4-Me, or 4-O_2N) to form complexes with $SbCl_5$. The reactants, in a 1:1 molar ratio, were mixed in CH_2Cl_2 solution to yield precipitates which were recrystallized from $CHCl_3$-hexane. The resulting 1:1 complexes were characterized by elemental analyses, IR, and ^1H NMR spectroscopy. Molar conductances in dimethylformamide indicated that they were non-electrolytes. It was concluded, on the basis of the spectral results, that coordination between the antimony and the azomethine nitrogen led to complex formation. The complexes of Ph_3SbBr_2 were prepared by adding a THF solution of Ph_3SbBr_2 to a THF suspension of the sodium salt of the oxime. The mixture was refluxed, the sodium bromide removed, and the product isolated by removal of the solvent. The reactants were used in a molar ratio of 1:2 and the complexes were of the type $ArC(NH_2)=N\text{-}O\text{-}Sb\text{-}O\text{-}N=(NH_2)CAr$. It was concluded on the basis of the IR and ^1H NMR spectra that one oxime was linked to antimony by an O-Sb bond only, but that the second oxime was bidentate containing an O-Sb and a H_2N-Sb linkage. Structures involving hexacoordinate antimony were suggested for both types of compounds.

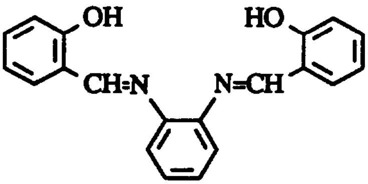
Carraher and coworkers have previously reported on the condensation of various Group IV reactants with such naturally occurring polysaccharides as cellulose, xylan, dextran, and similar hydroxyl-containing natural products. The present paper [118] described the condensation of triphenylantimony dichloride with xylan. Xylans are plant cell-wall components containing xylopyranose units with two adjacent hydroxyl groups. The xylan employed in the present study was a commercial product obtained from larchwood; its molecular weight was in the range 23,000-25,000. The condensation reactions were carried out by adding an aqueous solution of the xylan in the presence of a base (sodium hydroxide or triethylamine) to a chloroform solution of triphenylantimony dichloride in a Waring Blendor. The product was obtained as a water-insoluble precipitate, which was washed with water and organic solvents. Larger yields of products were obtained when the reactions were carried out in the presence of phase-transfer reagents (18-crown-6 or dibenzo-18-crown-6). Mass spectral and IR data on the products were reported. Molecular weights and antimony analyses were also carried out, but the results were not reported.

The Mössbauer spectra of four inorganic antimony compounds ($SbCl_3$, $SbBr_3$,

SbI_3, and $SbCl_5$) and one organic antimony compound (Me_3SbCl_2) have been determined in frozen dichloroethane [119]. The Mössbauer spectra of $SbCl_3$ in frozen cumene and in the crystalline state, and the spectrum of crystalline Me_3SbCl_2 were also obtained. By determining the spectra in frozen solvents, it was expected that complex intermolecular interactions encountered in the crystalline state could be avoided. Indeed, it was found that the isomer shifts of $SbCl_3$ in the crystalline state were more negative than those observed in frozen solutions. By contrast, the value of the isomer shifts of Me_3SbCl_2 in the crystalline state and in frozen solution were almost equivalent. The Mössbauer spectra of all of the compounds were carried out at 20 K. The isomer shifts for all five compounds in frozen organic solvents were compared with the electron density at the antimony nucleus calculated by Hartree-Fock molecular orbital computations. The data obtained were then used to derive a value for $\Delta R/R = -(11 \pm 2) \times 10^{-4}$ for the 37.15 keV M1 transition of ^{121}Sb, where $\Delta R/R$ is the relative change of the effective charge radius between the excited and the ground state of the Mössbauer nucleus.

Saxena and coworkers [120] have prepared a series of triarylantimony(V) compounds of the type Ar_3SbL, where Ar was $4\text{-}FC_6H_4$, $4\text{-}ClC_6H_4$, C_6F_5, or $4\text{-}MeC_6H_4$, and where LH_2 was either of the following two Schiff bases derived from salicylaldehyde:





Three different reaction methods were used to prepare the complexes. In one method the Schiff bases were condensed with the triarylantimony dichloride, Ar_3SbCl_2, in the presence of triethylamine. In a second method the Schiff bases were condensed with the triarylantimony dimethoxide. Finally, the Schiff bases were converted to their disodium salts and condensed with the triarylantimony dichloride. Benzene was the solvent used in all three types of reactions. The yields varied from 56-91%. The products were characterized by elemental analyses, IR, and PMR spectroscopy. The IR spectral results were in accord with a structure containing Sb-O bonds. Thus, the hydrogen-bonded OH groups in the free ligands were absent in the antimony complexes and the C-O bands were shifted to higher frequencies on complexation. The C=N stretching frequencies, except in one case, were not significantly affected by complexation. PMR data were reported on four of the antimony complexes. In the complex obtained from $(4\text{-MeC}_6H_4)_3SbCl_2$ two different methyl groups (ratio 2:1) were reported. This result led the authors to suggest that the Schiff bases were tetradentate, and that the structure of the complexes was pentagonal-bipyramidal with two oxygens, two nitrogens, and one aryl group forming the equatorial plane, and two aryl groups located in axial positions to this plane.

A number of organoantimony and organobismuth papers have appeared from the laboratory of F. Huber in Dortmund, Germany. The latest paper described the preparation and structure of compounds of the type $R^1_3M(O_2CR^2)_2$, where R^1 was Me, Ph, or 4-MeOC_6H_4, M was Sb, and R^2 was 2-pyridyl, or where R^1 was Ph or 4-MeC_6H_4, M was Bi, and R^2 was 2-pyridyl [121]. A sixth compound prepared was $Me_3Sb(O_2CCH_2R^2)_2$, where R^2 was 2-pyridyl. These compounds were obtained by condensing the appropriate antimony compound ($Me_3Sb(OH)_2$, Ph_3SbO, or $(4\text{-MeOC}_6H_4)_3SbO$) or bismuth compound ($Ph_3BiCO_3$ or $(4\text{-MeC}_6H_4)_3BiCO_3$) with 2-pyridinecarboxylic acid or 2-pyridylacetic acid. The reaction of 2-pyridylacetic acid with triphenylstibine oxide gave a brown oil which could not be crystallized or purified. The compounds were characterized by elemental analyses, Raman, and IR spectroscopy. In addition, X-ray diffraction studies were carried out on two of the compounds, bis(2-pyridinecarboxylato)triphenylantimony and bis(2-pyridylacetato)trimethylantimony. The first of these compounds was a distorted trigonal bipyramid with two carboxylate oxygens in axial positions and three phenyl groups in equatorial positions. In addition, there was interaction between the antimony and the carbonyl oxygen of one carboxylate group, and the antimony and other pyridine nitrogen of the other pyridine carboxylate group. In bis(2-pyridylacetato)trimethylantimony there were two different molecules in the asymmetric unit. Both molecules were distorted trigonal bipyramids, but they differed considerably in the O-Sb-O axial angles, the C-Sb-C equatorial angles, and the Sb-O(=C) contacts. In both molecules there was coordination between the carbonyl oxygens and the antimony atoms.

The preparation of two stibonium ylides in solution (and without isolation) was first reported from Wittig's laboratory. One of these was $Ph_3Sb{=}CH_2$, obtained from methyltriphenylantimony iodide and phenyllithium. It was reported to react with benzophenone to yield diphenylacetaldehyde [122]. Another ylide, $Me_2(CH_2C_6H_5)$-

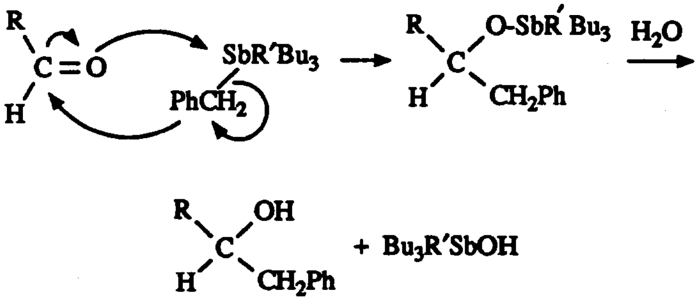
Sb=CHPh, obtained from dimethyldibenzylantimony bromide and phenyllithium, was reported to undergo rearrangement to give dimethyl(1,2-diphenylethyl)stibine [123]. By contrast, Doleshall and coworkers [124] reported that methyltriphenylantimony iodide or tetrafluoroborate, when treated with phenyllithium, gave a mixture of methyltetraphenylantimony and pentaphenylantimony:

$$\mathrm{MePh_3SbX + PhLi \longrightarrow MePh_4Sb + LiX}$$

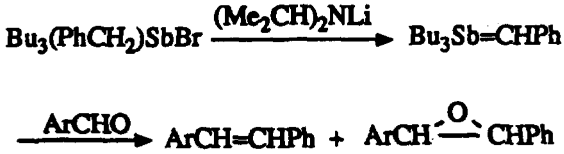
$$\mathrm{5\ MePh_4Sb \rightleftharpoons Me_5Sb + 4\ Ph_5Sb}$$

(where X was I or Ph_4B)

Huang and coworkers [125] have now reported a somewhat different result. When benzyltributylantimony bromide (or in one case, benzyltriethylantimony bromide) was treated in THF solution with an alkyl- or phenyllithium reagent, followed after 0.5 hr by the addition of benzaldehyde and then by water, the product, isolated in 90-92% yields, was 1,2-diphenylethanol. In addition to benzaldehyde, substituted benzaldehydes, $4\text{-}XC_6H_4CHO$ (X = Me, Cl, or MeO), cinnamaldehyde, or pyridinecarbaldehyde (isomer not stated) all gave the corresponding homobenzyl alcohols in excellent yields (74-86%). One ketone, cyclohexanone, gave 1-benzylcyclohexanol in 35% yield. The authors suggested that the mechanism of the reaction did not involve formation of an ylide, but the addition of the alkyl- or phenyllithium reagent to form a pentalkyl- or tetraalkylphenylantimony compound. The antimony compound then underwent nucleophilic addition to the carbonyl compound, followed by hydrolysis:



If benzyltributylantimony bromide was treated with lithium diisopropylamide instead of an alkyl- or phenyllithium compound, and the mixture then treated with an aldehyde, a mixture of alkene and epoxide was formed:



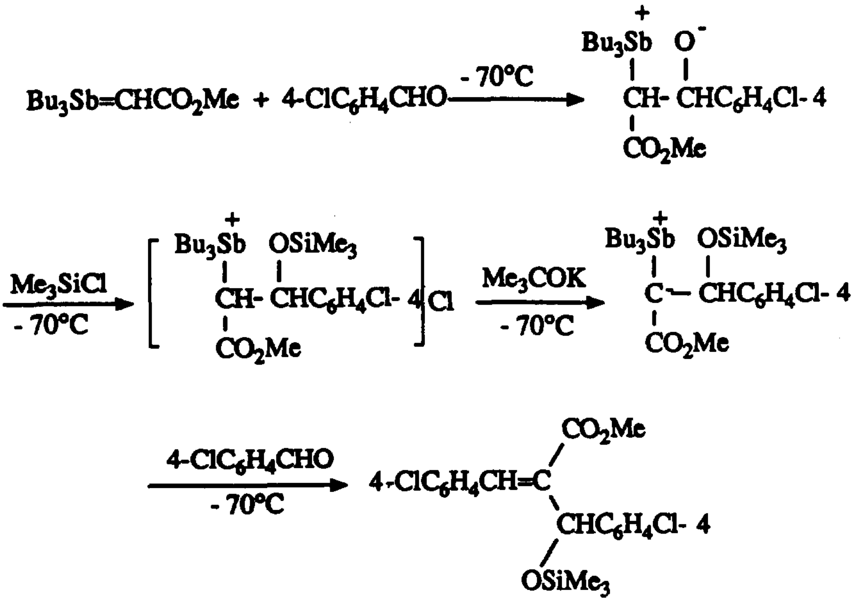
$$Bu_3(PhCH_2)SbBr \xrightarrow{(Me_2CH)_2NLi} Bu_3Sb{=}CHPh$$

$$\xrightarrow{ArCHO} ArCH{=}CHPh + ArCH\overset{O}{—}CHPh$$

The aldehydes used were PhCHO, 4-ClC$_6$H$_4$CHO, and 4-MeC$_6$H$_4$CHO, and the yields of alkene and epoxide were 60 and 35, 56 and 21, and 53 and 23%, respectively.

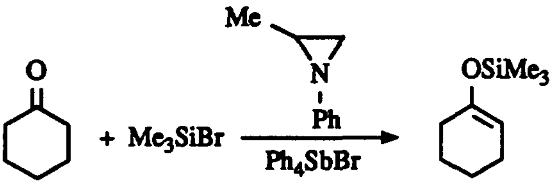
Although a number of triphenylstibonium ylides have been prepared, these have been, with one exception, incapable of undergoing the Wittig reaction. Huang and coworkers [126] have recently described the preparation of several quaternary antimony compounds of the type [R$_3$SbCH$_2$COY]Br, where R was Et or Bu and Y was OEt or NEt$_2$. In continuation of previous reports on the use of organoantimony compounds in organic synthesis, they have now prepared several tributylstibonium ylides and showed that these underwent the normal Wittig reactions with both aldehydes and ketones to form alkenes in high yields [127]. The compounds used to prepare the ylides were all of the type [Bu$_3$SbCH$_2$Y]Br, where Y was CO$_2$Me, CO$_2$Et, CN, CONEt$_2$, or . In a typical procedure, [Bu$_3$SbCH$_2$CO$_2$Me]Br in THF was treated with potassium *tert*-butoxide at -20°C for 10 minutes, after which benzaldehyde was added and the reaction allowed to come to room temperature. The desired methyl cinnamate was obtained in 90% yield by column chromatography. From 4-chlorobenzaldehyde and the same ylide, a 92% yield of 4-ClC$_6$H$_4$CH=CHCO$_2$Me was obtained. Other aldehydes used in the Wittig reaction included 4-nitrobenzaldehyde, cinnamaldehyde, 3,4-dimethoxybenzaldehyde, and heptanal. All of the alkenes were in the E configuration, and the yields varied from 56-92%. In addition to aldehydes, several ketones underwent the Wittig reaction. Thus, cyclohexanone and acetophenone both reacted with Bu$_3$Sb=CHCO$_2$Me to give the alkenes in 77 and 74% yields, respectively. 2-Pentanone and benzophenone reacted with Bu$_3$Sb=CHCO$_2$Et to give the alkenes in 84 and 35% yields, respectively. All of the alkenes were known compounds and were identified by comparing their IR and ^{1}H NMR spectra and their mps or bps with authentic samples.

The stibonium ylides were air sensitive and could not be isolated under atmospheric conditions. That they were indeed formed was proved by trapping the ylide as a trimethylsiloxy intermediate:

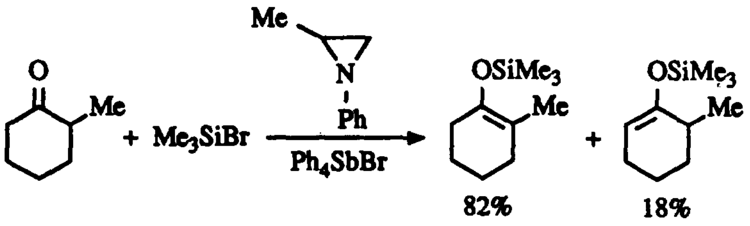


The final product, methyl 2-(4-chlorobenzylidene)-3-(4-chlorophenyl)-3-trimethylsiloxypropionate, was isolated as an oil. It was characterized by elemental analyses, ^1H NMR, IR, and mass spectroscopy.

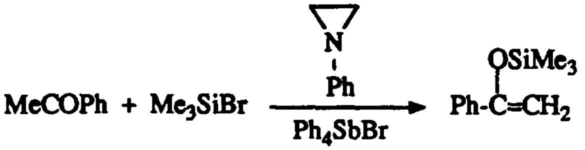
Tetraphenylantimony bromide has been found to be an excellent catalyst for the synthesis of trimethylsilyl enol ethers from ketones, trimethylsilyl bromide, and aziridines [128]. Thus, cyclohexanone, trimethylsilyl bromide, *N*-phenyl-2-methylaziridine, and tetraphenylantimony bromide gave a 100% yield of 1-cyclohexenyl trimethylsilyl ether:

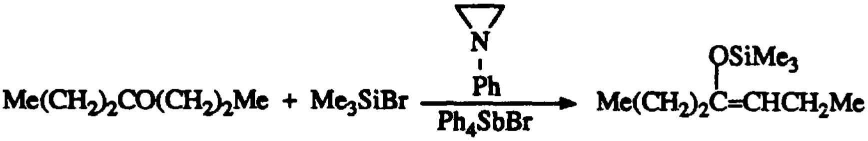


In the absence of the antimony catalyst, the yield of enol ether was 63%. The reaction was quite regioselective as shown by the following result:



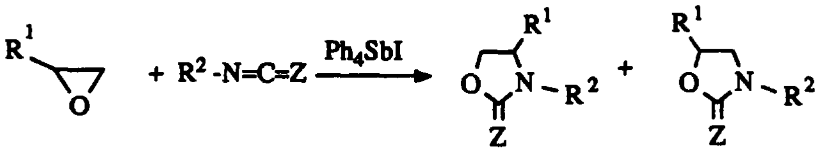
No silyl ether was obtained when tetraphenylantimony chloride and trimethylsilyl chloride were used. Acetophenone and 4-heptanone were also silylated, but the yields were only 18% and 39%,respectively.





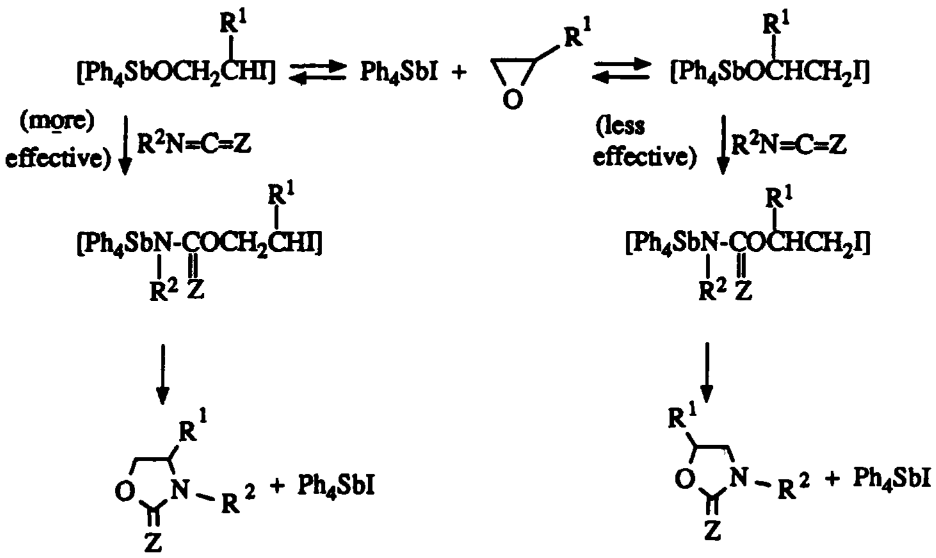
Cyclopentanone gave the silylated enol ether in 76% yield.

Fujiwara and coworkers have previously reported (in several papers) that the condensation of mono-substituted oxiranes with such heterocumulenes as isocyanates or carbodiimides (in which the reactions were catalyzed by tetraphenylantimony iodide) led to the predominant formation of the 3,4-disubstituted oxazoldine-2-ones or oxazolidine-2-imines, respectively. In nearly all reactions studied, small amounts of the 3,5-disubstituted products were formed:



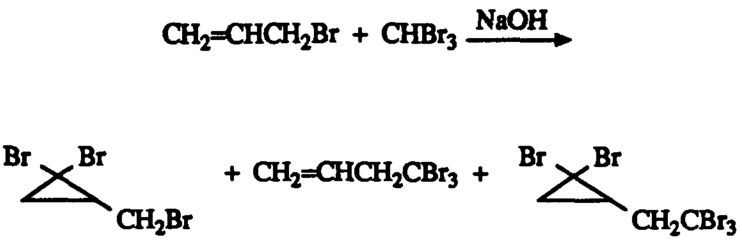
(where Z was O or NH)

By contrast, the cycloaddition reaction with conventional catalysts such as quaternary ammonium salts and lithium salts generally led to selective formation of 3,5-disubstituted products. Tetraphenylantimony bromide was reported to be less selective than the iodide. Thus, the reaction of methyloxirane with phenylcarbodiimide, catalyzed by tetraphenylantimony bromide, gave 3-phenyl-4-methyl- and 3-phenyl-5-methyloxazolidine-2-imine in 41 and 59% yields, respectively, whereas tetraphenylantimony iodide gave 100% of the 3,4-isomer. The authors [129] have now proposed a mechanism for the tetraphenylantimony iodide-catalyzed reaction as follows: (a) ring opening of the oxirane by the catalyst; (b) insertion of the heterocumulene to form an antimony carbamate; and (c) cyclization of the carbamate to the oxazoline with the reformation of the catalyst. The authors believed that both α- and β-cleavage of the oxirane ring would occur, but that the product of α-cleavage would be more likely to react with the heterocumulene:



The authors reported experimental details of several reactions performed to substantiate the mechanism proposed above.

Dehmlow and Wilkenloh [130] have previously reported that the use of tetraphenylarsonium chloride as a phase transfer catalyst markedly affected the course of the reaction of allyl bromide with bromoform:



VII VIII IX

Thus, the use of Me_4NCl as the catalyst in the above reaction gave yields of 15% VII and 2% of VIII, whereas the use of Ph_4AsCl yielded 7% of VII, 82% of VIII, and 9% of IX. The authors have now investigated the use of a number of other phase transfer catalysts including tetraphenylantimony chloride [131]. This was far less successful than the arsenic compound, yielding 7% of VII, 12% of VIII, and 1% of IX.

The positive-ion fast atom bombardment mass spectra of 15 different tetraalkylstibonium salts have been reported in a paper from Huang's laboratory [132]. In five of the salts the anion was Br^-, in the other salts the anion was Ph_4B^-. All of the cations were of the type $[R_3SbR^1]^+$, where R was Bu (except for one salt where R was Et) and R^1 was an alkyl or alkenyl group such as CH_2Ph, CH_2CO_2Me, CH_2CN, $CH_2CH{=}CH_2$, or $CH_2CH{=}CHCH_3$. Typically, the intact cation was the base peak. The principal fragments were $[R_3Sb]^{+\bullet}$, $[R_2Sb]^+$, $[R_2SbH_2]^+$, $[RSbR^1]^+$, $[RSbH]^+$, $[RSb\text{-}H]^+$, and $[R_2SbR^1]^{+\bullet}$. In most cases cluster ions $[M{+}C]^+$ were found (where C^+ was the intact cation). Thus, when the anion was Br^-, such adduct ions as $[M{+}(R\text{-}H)Sb]^+$, $[C{+}R\text{-}H]^+$, and $[C{+}R^1\text{-}H]^+$ were detected. When the anion was $[Ph_4B]^-$, interesting cluster ions such as $[M{+}(BR^1\text{-}H)]^+$ and $[M{+}(BR^1\text{-}3H)]^+$ were found. All of the ionic fragments found in the mass spectra with their relative abundances were given in tabular form.

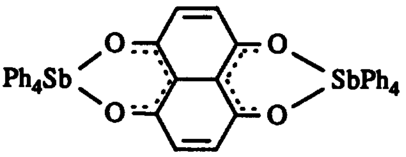
Tetraphenylantimony picrate was one of six different quaternary compounds studied for their ionic association and mobility in propylene carbonate solution [133]. The compound was prepared from tetraphenylantimony bromide and sodium picrate. It was recrystallized from aqueous acetone. All of the compounds studied, including the corresponding tetraphenylarsenic and tetraphenylphosphorus picrates, were found to be associated in propylene carbonate and to form solvent-separated ion pairs.

Molecular motion in the tetramethylstibonium cation in the solid state has been studied in five different stibonium compounds, $[Me_4Sb]X$, where X was Cl, Br, I, PF_6, or BF_4 [134]. PMR was used for the determinations in the temperature range $95 \leq T/K$

≤ 340. The crystal structure of Me_4SbI was determined by single crystal X-ray diffraction. The cation was a distorted tetrahedron; some bond distances and bond angles for this compound were listed. In this study the second moments M_2 and the line widths $\Delta B(^1H)$ for all five compounds were determined as a function of temperature. The values of the second moment were calculated by use of the VanVleck equation. In the three tetramethylstibonium halides, three different states of motion are possible. In the high temperature region, overall tumbling of the cation plus methyl group reorientation would be expected. At low temperatures, only methyl group reorientation about threefold axes would be expected. Analysis of $M_2(^1H)$ as a function of temperature confirmed these expectations. With tetramethylstibonium hexafluorophosphate and tetrafluoroborate, both the cation and anion were found to tumble at higher temperatures.

Single ion free energies of a number of anions and cations have been estimated from experimental solubilities in mixed ethanol-water solutions [135]. Tetraphenylantimony tetraphenylborate was one of the compounds investigated. In a second paper by the same author [136] the transfer free energies of the ions Ph_4As^+, Ph_4Sb^+, and Ph_4B^- were calculated in mixed DMSO/DMF solutions.

Arnold, Mansel, and Klar [137] have studied the reaction of naphthazarine (5,8-dihydroxy-1,4-naphthoquinone) with tetraphenylantimony ethoxide. Tetraphenylantimony bromide (2 mmol) in dioxane was treated with potassium ethoxide, and, after removal of potassium bromide, the solution was treated with naphthazarine (1 mmol). The color of the solution changed from red-violet to dark blue. After the addition of ligroin, a dark blue microcrystalline product was obtained. The structure of this compound was determined by X-ray diffraction. It possesses the following structure:



The naphthazarine dianion acted as a bifunctional chelating ligand in which two 2,2′-connected 1,3-diketonato groups were fixed in a coplanar position by two *cis*-ethenediyl bridges. The chelating rings were folded at the O/O axes, and the two antimony centers were arranged in *trans*-positions relative to the plane of the naphthazarine dianion. In addition to the antimony compound described above, three other compounds were prepared and characterized by elemental analyses. One compound, obtained from naphthazarine and tetraphenylantimony ethoxide in a 1:1 ratio, contained one tetraphenylantimony group in the molecule. The other two compounds were prepared from tetra-4-tolylantimony ethoxide and naphthazarine or from tetraphenylarsenic ethoxide and naphthazarine by using the ethoxide and naphthazarine in a 2:1 ratio in both cases.

In a paper on the synthesis of polyhedral aluminosilsesquioxanes as models for aluminosilicates, Feher and Welle [138] have described the use of tetramethylantimony siloxides as mild sources of siloxide anions. The synthesis of two different anionic clusters containing the Si-O-Al linkage, and in which the cation was Me_4Sb^+, was described. One new Sb(V) compound containing the Ph_4Sb-O-Si group was also prepared and characterized.

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