ANTIMONY

ANNUAL SURVEY COVERING THE YEAR 1975

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No book or critical review concerned exclusively with organoantimony compounds was published in 1975. A short (138 page) monograph on the chemistry of arsenic, antimony, and bismuth did appear [1], however, and there were also several brief surveys devoted in whole or in part to recent work on the organo-derivatives of the three elements [2-5]. In addition, information about organoantimony compounds has been given in review articles on the following subjects: unsaturated organometallic heterocycles [6], bimetallic organometallic compounds [7], transition metal complexes of Group VA and VIA donor ligands [8,9], perfluoroorganophosphorus, -arsenic, -antimony, and -bismuth compounds [10], novel $(p\text{-}p)\pi$ bonds between carbon and elements of Group IIIA, IVA, or VA [11], X-ray diffraction studies of the molecular structures of a number of nitrogen, phosphorus, arsenic, antimony, and bismuth compounds [12], and NMR [13], NQR [14], and vibrational spectroscopy [15,16]. Several organoantimony compounds that were subjected to X-ray analysis in 1973 or 1974 have been listed in Volume 6 of *Molecular Structures and Dimensions* [17], and a tabulation of ^{121}Sb Mössbauer data has been given in *Mössbauer Effect Data Index Covering the 1974 Literature* [18].

The reduction of phenyldichlorostibine with lithium borohydride has been

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found to give phenylstibine [19]:

$$PhSbCl_2 + 2\ LiBH_4 \xrightarrow{-70°} PhSbH_2 + 2\ LiCl + B_2H_6$$

The latter compound was a clear, refractive, air-sensitive liquid that crystallized at -38°. Even at -70° in an argon atmosphere, phenylstibine partially decomposed in 2 or 3 weeks. It was, however, relatively stable in inert solvents such as ether, hexane, and benzene. The addition of a small amount of an organolithium compound to an ether solution of phenylstibine resulted in the liberation of hydrogen and the formation of presumably polymeric phenylantimony:

$$n\ PhSbH_2 \xrightarrow{RLi} (PhSb)_n + n\ H_2$$

When 2 moles of butyl- or phenyllithium were treated with 1 mole of phenylstibine, however, only 0.5 mole of hydrogen was liberated. The following reaction sequence was suggested:

$$PhSbH_2 + RLi \longrightarrow PhSb(H)Li + RH$$

$$2\ PhSb(H)Li \longrightarrow Ph(Li)Sb\text{-}Sb(Li)Ph + H_2$$

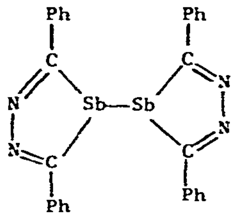
$$Ph(Li)Sb\text{-}Sb(Li)Ph + RLi \longrightarrow PhSbLi_2 + Ph(R)SbLi$$

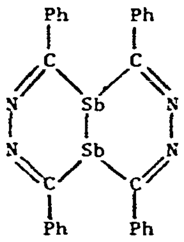
(where R was Bu or Ph)

Treatment of the mixture of stibides thus obtained with an alkyl or aryl halide gave a mixture of tertiary stibines which were characterized as their dibromides. Dropwise addition of phenylstibine to a solution of sodium in liquid ammonia resulted in the formation of disodium phenylstibide:

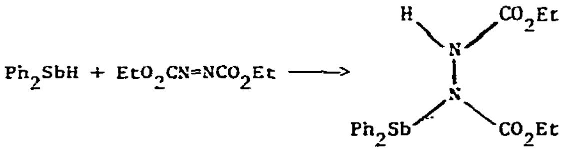
$$PhSbH_2 + 2\ Na \longrightarrow PhSbNa_2 + H_2$$

The latter substance reacted with ethyl bromide to yield diethylphenylstibine and with 1,4-dichlorobutane to give the heterocyclic compound, 1-phenylstibolane. When the reaction mixture obtained from phenylstibine and sodium in liquid ammonia was treated with the azine PhC(Cl)=N-N=C(Cl)Ph, however, a substance was obtained in which there were no Ph-Sb bonds. The following possible structures for this substance were suggested:





A study has been made of the addition of P-H, As-H, and Sb-H groups to the nitrogen-nitrogen double bond [20]. The reaction of diphenylstibine with diethyl azodiformate in the absence of air, moisture, and light was found to produce a substituted hydrazine:



The compound was identified only by its mass spectrum, since it was impossible to obtain it except in admixture with the by-products tetraphenyldistibine and diethyl bicarbamate, $EtO_2CNHNHCO_2Et$.

tert-Butyldibromostibine has been prepared by the interaction of equimolar amounts of *tert*-butylmagnesium chloride and antimony tribromide at -50° [21]:

$$Me_3CMgCl + SbBr_3 \longrightarrow Me_3CSbBr_2 + MgBrCl$$

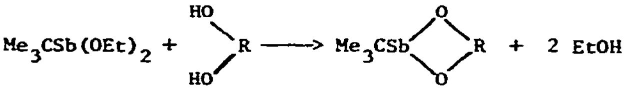
The compound was a yellow, crystalline substance that readily reacted with oxygen and moisture. Although it could be purified by vacuum distillation (bp 73-78° at 0.2 torr), it decomposed gradually on standing even at 0°.

Treatment of the dibromostibine with sodium methoxide or ethoxide yielded the corresponding dialkoxystibines:

$$Me_3CSbBr_2 + 2\ NaOR \longrightarrow Me_3CSb(OR)_2 + 2\ NaOR$$

(where R was Me or Et)

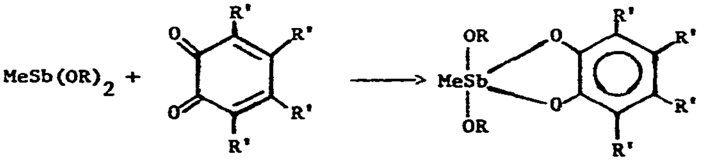
These compounds were extremely sensitive to hydrolysis. They fumed in the air and possessed unpleasant odors. On standing at room temperature they slowly decomposed with the formation of trialkoxystibines. Diethoxy-*tert*-butylstibine underwent exchange reactions with vicinal diols (pinacol, *meso*-2,3-butanediol, or catechol) to give heterocyclic compounds:



(where R was CMe_2CMe_2, CHMeCHMe, or *o*-C_6H_4)

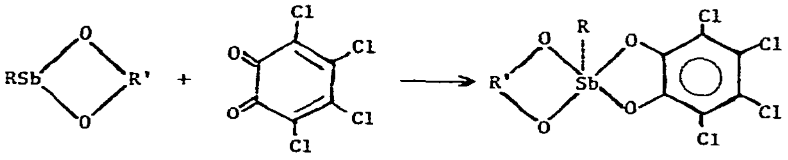
The compounds derived from pinacol and *meso*-2,3-butanediol were soluble in benzene and gave normal molecular weights in this solvent. The catechol derivative, on the other hand, was insoluble in nonpolar solvents and was assumed to be polymeric in the solid state; molecular ions, however, were observed in the mass spectrum.

The reaction of dialkoxyalkylstibines and 1,3,2-dioxastibolanes with *ortho*-benzoquinones has also been investigated [22]. Dialkoxymethylstibines were found to yield organoantimony(V) derivatives:



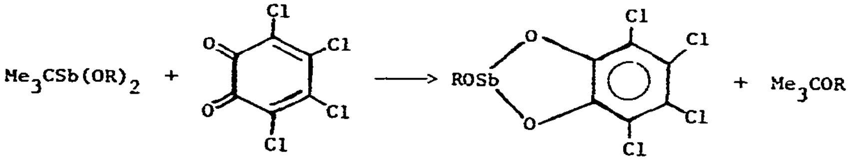
(where R was Me, Et, or $CHMe_2$ and R' was H or Cl)

2-Methyl- or 2-phenyl-1,3,2-dioxastibolanes gave analogous spirocyclic compounds with tetrachloro-*o*-benzoquinone:

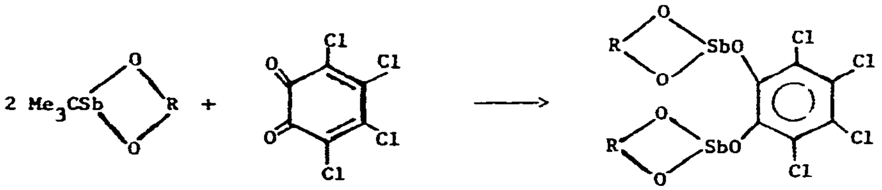


(where R was Me or Me_3C and R' was CMe_2CMe_2, CHMeCHMe, or CHPhCHPh)

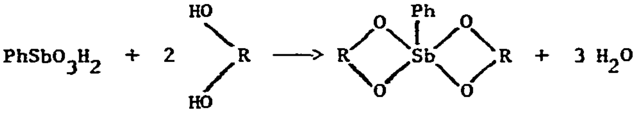
In contrast to these results, the dialkoxy-*tert*-butylstibines and 2-*tert*-butyl-1,3,2-dioxastibolanes did not form adducts with *ortho*-quinones. Instead, the *tert*-butyl group was cleaved from the antimony, and esters of trivalent antimonic acid, $Sb(OH)_3$, were obtained:



(where R was Me or Et)



The fate of the 2-*tert*-butyl group was apparently not determined in the case of the 1,3,2-dioxastibolane reactions. Symmetrical spirocyclic antimony(V) derivatives were prepared by the interaction of phenylstibonic acid and pinacol or *meso*-2,3-butanediol:



(where R was CMe_2CMe_2 or CHMeCHMe)

Catechol, however, was oxidized by phenylstibonic acid to *o*-benzoquinone (which then polymerized to a black substance) while the phenylstibonic acid was reduced to an unspecified antimony(III) derivative.

Methyldibromostibine has been converted to transition metal complexes by means of the following type of reaction [23]:

$$MeSbBr_2 + 2\ Na[M(CO)_nCp] \longrightarrow MeSb[M(CO)_nCp]_2 + 2\ NaBr$$

(where M was Fe, Cr, Mo, or W, Cp was π-cyclopentadienyl, and *n* was 2 for the iron compounds and 3 in the other cases)

It was also possible to obtain complexes in which only one bromine of the methyldibromostibine had been displaced:

$$MeSbBr_2 + Na[M(CO)_3Cp] \longrightarrow MeSb(Br)[M(CO)_3Cp] + NaBr$$

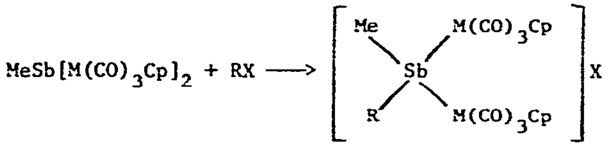
(where M was Mo or W)

These substances could then be converted to heteronuclear species:

$$MeSb(Br)[M(CO)_3Cp] + Na[M'(CO)_3Cp] \longrightarrow MeSb[M(CO)_3Cp][M'(CO)_3Cp] + NaBr$$

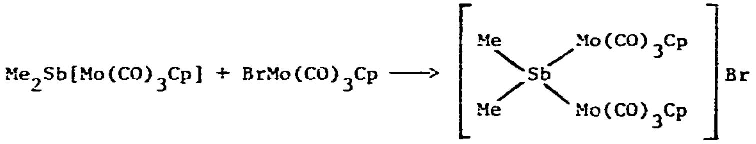
(where M was Mo or W and M' was Cr or Mo)

The antimony-containing complexes could be quaternized by reaction with alkyl halides:

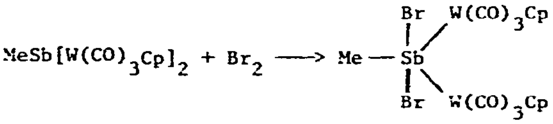


(where RX was MeBr, MeI, EtI, or $PhCH_2Br$ and M was Mo or W)

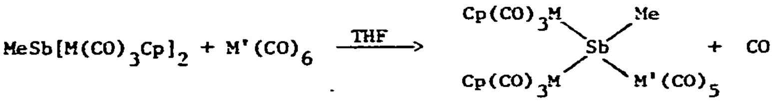
The resulting stibonium compounds were also prepared by the interaction of monometallated stibines and metal halides, *e.g.*:



The trivalent antimony complexes reacted with bromine to give pentacoordinated compounds, *e.g.*:

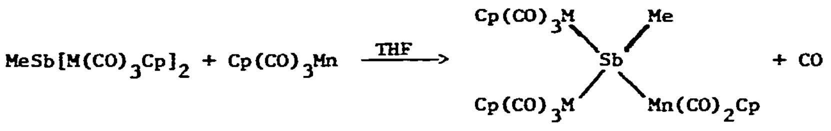


In another paper [24] it was reported that the dimetallated antimony(III) compounds described in the above paragraph underwent photochemical or thermal reactions with chromium, molybdenum, or tungsten hexacarbonyl to yield antimony-bridged trinuclear complexes:

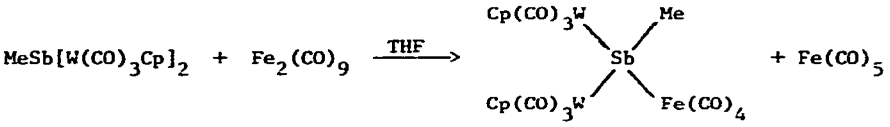


(where M was Cr or W and M' was Cr, Mo, or W)

Cyclopentadienylmanganese tricarbonyl or diiron enneacarbonyl underwent similar reactions with the antimony compounds:



(where M was Cr or W)

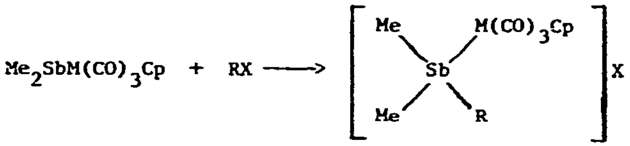


The interaction of dimethylbromostibine and cyclopentadienyl(carbonyl) metal anions was described in a third paper [25]:

$$Me_2SbBr + Na[M(CO)_3Cp] \longrightarrow Me_2SbM(CO)_3Cp + NaBr$$

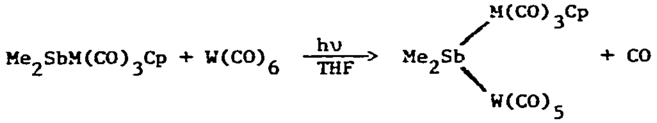
(where M was Cr, Mo, or W)

The metallated stibines thus obtained were quite stable and were unaffected by boiling in tetrahydrofuran or methylcyclohexane. The nucleophilic character of the antimony atom in these stibines was shown by their ready quaternization with alkyl halides:

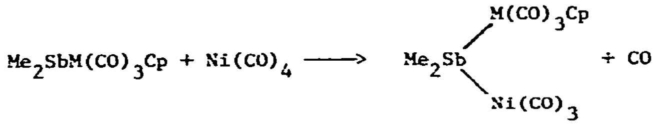


(where M was Mo or W and RX was MeBr, MeI, $CH_2=CHCH_2Br$, or $PhCH_2Br$)

Other reactions gave dinuclear complexes in which the Me_2Sb group was present as a bridging unit:

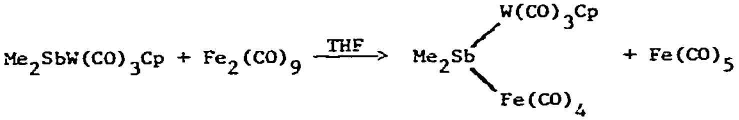


$$\mathrm{Me_2SbM(CO)_3Cp + W(CO)_6 \xrightarrow[THF]{h\nu} Me_2Sb\genfrac{}{}{0pt}{}{\diagup M(CO)_3Cp}{\diagdown W(CO)_5} + CO}$$



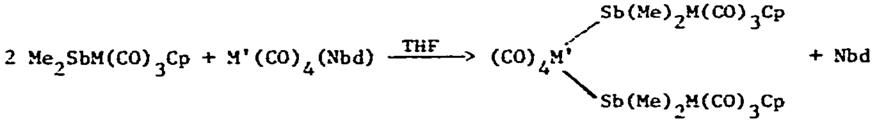
$$\mathrm{Me_2SbM(CO)_3Cp + Ni(CO)_4 \longrightarrow Me_2Sb\genfrac{}{}{0pt}{}{\diagup M(CO)_3Cp}{\diagdown Ni(CO)_3} + CO}$$

(where M was Cr, Mo, or W)



$$\mathrm{Me_2SbW(CO)_3Cp + Fe_2(CO)_9 \xrightarrow{THF} Me_2Sb\genfrac{}{}{0pt}{}{\diagup W(CO)_3Cp}{\diagdown Fe(CO)_4} + Fe(CO)_5}$$

Trinuclear complexes could also be obtained:



$$\mathrm{2\ Me_2SbM(CO)_3Cp + M'(CO)_4(Nbd) \xrightarrow{THF} (CO)_4M'\genfrac{}{}{0pt}{}{\diagup Sb(Me)_2M(CO)_3Cp}{\diagdown Sb(Me)_2M(CO)_3Cp} + Nbd}$$

(where M and M' were Cr, Mo, or W and Nbd was 2,5-norbornadiene)

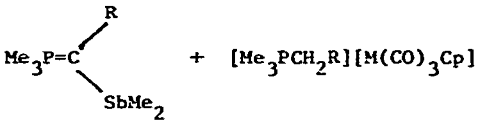
Treatment of the metallated antimony(III) compounds with phosphorus ylids resulted in cleavage of the antimony-metal bond and formation of phosphonium salts:

$$\mathrm{Me_2SbM(CO)_3Cp + Me_3P{=}CHR \longrightarrow [Me_3PCH(R)SbMe_2][M(CO)_3Cp]}$$

(where M was Mo or W and R was H or $SiMe_3$)

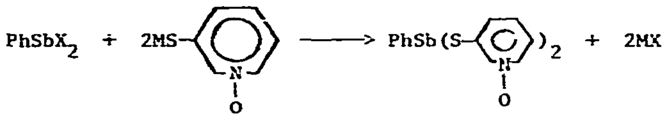
The phosphonium salts thus formed were deprotonated by a second mole of ylid:

$$\mathrm{[Me_3PCH(R)SbMe_2][M(CO)_3Cp] \ + \ Me_3P{=}CHR \longrightarrow}$$



$$\mathrm{Me_3P{=}C(R)(SbMe_2)} + [\mathrm{Me_3PCH_2R}][\mathrm{M(CO)_3Cp}]$$

It has been claimed in the patent literature [26] that bis(1-oxopyridine-2-thiolato)phenylstibine(I) is a highly effective antibacterial and antifungal agent and that it is a desirable component of shampoos, detergent bars, foot powders, cosmetic products, *etc.* The compound was prepared by the following type of reaction:



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(where X was Cl, Br, or I and M was Li, Na, K, or NH_4)

A new chelating agent, *o*-phenylenebis(diphenylstibine), has been synthesized by the following sequence of reactions [27]:

$$o\text{-}\mathrm{BrC_6H_4SbCl_2} + 2\ \mathrm{PhMgBr} \longrightarrow o\text{-}\mathrm{BrC_6H_4SbPh_2} + 2\ \mathrm{MgBrCl}$$

$$o\text{-}\mathrm{BrC_6H_4SbPh_2} + \mathrm{Ph_2SbNa} \xrightarrow[-78°]{\mathrm{NH_3,\ THF}} o\text{-}\mathrm{Ph_2SbC_6H_4SbPh_2} + \mathrm{NaBr}$$

The compound was identified by analysis and mass spectrometry. Attempts to prepare the di-tertiary stibine by the interaction of *o*-dichlorobenzene and sodium diphenylstibide yielded only oxybis(diphenylantimony), $(Ph_2Sb)_2O$, evidently formed by oxidation of tetraphenyldistibine. The same oxy compound was also obtained when sodium diphenylstibide was allowed to react with either *cis*- or *trans*-1,2-dichloroethylene. *o*-Phenylenebis(diphenylstibine) was found to exhibit no reaction with nickel(II) or cobalt(II) salts, even in solvents of very weak donor power, *e.g.*, dichloromethane. The only palladium complexes obtained, even when a considerable excess of ligand was used, were 1:1 adducts of the type $PdLX_2$, where L was the di-tertiary stibine and X was Cl, Br, I, or SCN.

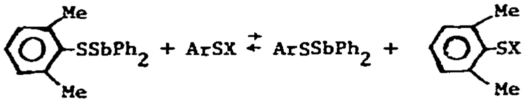
Trimethylenebis(dimethylstibine) has been obtained as a colorless, extremely air-sensitive liquid by the interaction of sodium dimethylstibide and 1,3-dibromopropane in liquid ammonia [28]:

$$2\ Me_2SbNa + BrCH_2CH_2CH_2Br \longrightarrow Me_2SbCH_2CH_2CH_2SbMe_2 + 2\ NaBr$$

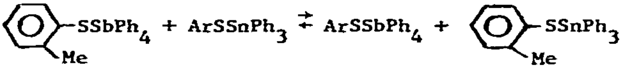
The di-tertiary stibine formed air-stable, purple, diamagnetic nickel(II) complexes of the type $[NiL_2X]ClO_4$ (where L was the stibine and X was Cl, Br, or I) and planar palladium(II) and platinum(II) complexes of the type MLX_2 (where M was Pd or Pt and X was Cl, Br, I, or SCN).

The ^{19}F NMR technique has been used to obtain quantitative information about the ground-state electronic effects of the Ph_2SbS-, Ph_2BiS-, Ph_4SbS-, and Ph_4SbO- groups and about the dependence of these effects on solvent interaction and steric hindrance [29]. The compounds studied in this investigation included the *meta* and *para* isomers of $Ph_2ESC_6H_4F$ (where E was Sb or Bi) as well as $Ph_2SbSC_6H_2Me_2$-2, 6-F-4, $(p\text{-}FC_6H_4)_2SbSPh$, $(p\text{-}FC_6H_4)_2SbSC_6H_4F$-*p*, *p*-$FC_6H_4Sb(SPh)_2$, *p*-$FC_6H_4Sb(SC_6H_4F\text{-}p)_2$, the *meta* and *para* isomers of $Ph_4SbSC_6H_4F$ and $Ph_4SbOC_6H_4F$, and compounds of the type $(p\text{-}FC_6H_4)_2SbX$ (where X was Cl, Br, SPh, or O_2CMe). It was found that the electron-donating effect of the sulfur-containing groups increased in the order $Ph_2SbS < Ph_2BiS < Ph_4SbS$. The *p*-$Ph_4SbO$ group was even more electron-donating than the *p*-Ph_4SbS group, but the *m*-Ph_4SbO group was less electron-donating than the *m*-Ph_4SbS group. The solvent susceptibilities of these electronic effects was studied by noting the change in the ^{19}F NMR chemical shift when a compound was transferred from an inert solvent (benzene) to a proton-donating (chloroform) or a coordinating solvent (pyridine). The solvent susceptibilities of the electronic effects of the Ph_2Sb, Ph_4SbS, and Ph_4SbO groups were negligible, while the chemical shifts of compounds containing the Ph_2BiS group decreased in chloroform and increased in pyridine. It was also noted that steric hindrance had little effect on the electronic effect of the Ph_2SbS group. The ^{19}F NMR chemical shifts observed for the $(p\text{-}FC_6H_4)_2SbX$ compounds in benzene or chloroform showed that the electron-withdrawing effect of the $p\text{-}FC_6H_4SbX$ group increased in the order SPh < O_2CMe < Br < Cl. In pyridine, however, this order was exactly reversed. This reversal was attributed to a specific solvation of the antimony atom. It was concluded that the electronic interactions across the antimony-heteroatom bonds were mainly of inductive character.

The following types of exchange reactions have been studied by means of PMR measurements [30]:



(where X was PhHg, Ph_3Sn, or H)



A comparison of the data obtained in this investigation with the results of earlier studies led to the following conclusions:

(1) the migration ability of organometallic groups of the Ph_nM type in derivatives of thiophenol increased in the order Ph_3Sn < Ph_3Pb ≃ Ph_2Sb < PhHg < Ph_4Sb.

(2) the position of the equilibrium in reactions of the Sb(V) compounds depended greatly on the polar and steric effects of substituents in the thiophenol ring.

(3) The Ph_4SbS group possessed a greater space requirement than the Ph_3SnS, PhHgS, Ph_3PbS, or Ph_2SbS group in nonvalence interactions with the *o*-Me group.

Krommes and Lorberth [31] have prepared dimethylcyclopentadienylstibine and -bismuthine by means of the following reactions:

$$Me_2SbNMe_2 + CpH \xrightarrow[-80°]{Et_2O} Me_2SbCp + Me_2NH$$

$$Me_2BiN(Me)SiMe_3 + CpH \xrightarrow[-80°]{Et_2O} Me_2BiCp + Me_3Si(Me)NH$$

Both compounds were yellow solids that were soluble in degassed, dry, aprotic solvents, such as benzene, toluene, and ether, in which they decomposed to brown-black substances after a short period at room temperature. They could be sublimed in high vacuum onto a cold surface (-80°), but storage at room temperature led to quick decomposition. They were also sensitive to air or moisture. Their PMR spectra indicated a low activation enthalpy (of the order of a few cal/mol) for the rotation of the cyclopentadienyl ring along the metal-carbon axis. The mass spectrum of the stibine was characterized by a very small molecular ion (relative intensity about 0.5%) and a base peak corresponding to $C_5H_6^+$; the antimony-containing fragments present in greatest abundance was $Me_2{}^{121}Sb^+$ (relative intensity 5%). No molecular ion was found in the mass spectrum of the bismuthine. The base peak corresponded to Bi^+, and the relative intensity of the $C_5H_6^+$ ion was 23%. The IR spectra of both the stibine and bismuthine were also analyzed.

In a paper from a different laboratory, Jutzi, Kuhn, and Herzog [32] have described the preparation of dimethylcyclopentadienylstibine by the interaction of lithium cyclopentadienide and dimethylbromostibine:

$$Me_2SbBr + LiCp \longrightarrow Me_2SbCp + LiBr$$

In sharp contrast to the statements noted in the above paragraph, Jutzi and coworkers have asserted that the tertiary stibine was relatively stable. Thus, it was isolated in 49% yield by vacuum distillation (bp 62° at 5 torr), and it could be stored at room temperature for a long time without decomposition. These authors agreed, however, that the stibine was air-sensitive and that it had a fluxional structure. In addition, they prepared a number of other tertiary atibines by the interaction of dimethylbromostibine and the lithium salts of methylcyclopentadiene, trimethylsilylcyclopentadiene, methyltrimethylsilylcyclopentadiene, or bis(trimethylsilyl)cyclopentadiene. These tertiary stibines were also stable enough to be isolated by vacuum distillation. In fact, the presence of a trimethylsilyl group actually increased the thermal stability. The mass spectra of all the tertiary stibines were also determined. The results obtained with dimethylcyclopentadienylstibine were not in agreement with those of Krommes and Lorberth [31]. Thus, Jutzi and coworkers found the fragments formed in greatest abundance (relative intensity, 100%) were $C_5H_5^+$ and $C_6H_8{}^{121}Sb^+$. A number of other antimony-containing fragments were also formed in relatively high abundance. In addition to the tertiary stibines, Jutzi and coworkers prepared and studied cyclopentadienyldichlorostibine. Two different synthetic methods were employed:

$$SbCl_3 + LiCp \longrightarrow CpSbCl_2 + LiCl$$

$$SbCl_3 + Me_3SiCp \longrightarrow CpSbCl_2 + Me_3SiCl$$

Unlike the tertiary stibines, which were clear, yellow liquids, the dichlorostibine was a crystalline, colorless substance. It could be sublimed (at about 70° and 0.05 torr) only with a considerable loss. The PMR spectrum showed that the $SbCl_2$ group (like the Me_2Sb group) underwent sigmatropic rearrangement. The mass spectrum exhibited peaks corresponding to Sb_4^+ and Sb_3^+, presumably formed by thermal decomposition of the dichlorostibine. The IR spectra of all the antimony compounds prepared in this investigation were also studied.

An attempt to prepare dicyclopentadienylmethylstibine by the interaction of bis(dimethylamino)methylstibine and cyclopentadiene at −78° was unsuccessful [33]. Although the elimination of dimethylamine apparently occurred, the desired compound was too unstable to be isolated from the reaction mixture.

Antimony-containing diazo compounds have been prepared by the reaction of (dimethylamino)dimethylstibine with diazomethane, ethyl diazoacetate, or 2-diazo-1-phenylethanone [34]:

$$2\ Me_2SbNMe_2 + CH_2N_2 \xrightarrow[-80^\circ]{Et_2O} (Me_2Sb)_2CN_2 + 2\ Me_2NH$$

$$Me_2SbNMe_2 + CH(N_2)CO_2Et \xrightarrow[-80^\circ]{Et_2O} Me_2SbC(N_2)CO_2Et + Me_2NH$$

$$Me_2SbNMe_2 + CH(N_2)C(O)Ph \xrightarrow[-80^\circ]{Et_2O} Me_2SbC(N_2)C(O)Ph + Me_2NH$$

The stibine obtained from diazomethane had a mp of 7° and at room temperature was a yellow oil that did not explode on impact. It decomposed rapidly in air but only slowly in a nitrogen atmosphere. Short path sublimation in a high vacuum was possible, but led to considerable losses. The stibine obtained from ethyl diazoacetate was an orange oil that was not explosive and could be distilled at 67° at 0.1 torr. In contrast, the stibine obtained from 2-diazo-1-phenylethanone was a reddish substance that was too unstable to be analyzed. Bismuth-containing diazo compounds were prepared by the reaction of [methyl(trimethylsilyl)amino]dimethylbismuthine with diazomethane or ethyl diazoacetate:

$$2\ Me_2BiN(Me)SiMe_3 + CH_2N_2 \xrightarrow[-80^\circ]{Et_2O} (Me_2Bi)_2CN_2 + 2\ Me_3Si(Me)NH$$

$$Me_2BiN(Me)SiMe_3 + CH(N_2)CO_2Et \xrightarrow[-80^\circ]{Et_2O} Me_2BiC(N_2)CO_2Et + Me_3Si(Me)NH$$

The bismuthines thus obtained were yellow or orange solids that were rather unstable. The diazomethane derivative decomposed rapidly at room temperature, while the diazoacetate derivative (mp 35°) decomposed above 40°. Neither compound was explosive on impact. The ^{13}C NMR spectra of the antimony- and bismuth-containing substances indicated that carbon bonded to the diazo group was more nucleophilic in these compounds than in the diazo compounds from which they were derived.

In another paper the interaction of bis(dimethylamino)methylstibine and ethyl diazoacetate was described [35]. The reaction appeared to be complex, and none of the expected antimony-containing diazo compound was isolated from the reaction mixture.

PMR spectroscopy has been used to determine the rates of quaternization of trimethylarsine and trimethylstibine by alkyl halides in methanol or acetonitrile [36]:

$$Me_3E + RX \longrightarrow (Me_3RE)^+X^-$$

(where E was As or Sb and RX was MeI, CD_3I, EtBr, EtI, or PrI)
The results obtained indicated that the reactions were typical S_N2 displacements. Thus, the reactions were first order in alkyl halide and first order in the arsine or stibine, *i.e.*, second order overall. Further, the reactivity of the alkyl halides decreased in the order MeI >> EtI > PrI and EtI > EtBr; there was no significant difference between the reactivity of MeI and CD_3I. The nucleophilic reactivity of trimethylarsine was somewhat greater than that of trimethylstibine, and the rates of quaternization were faster in acetonitrile than in methanol. By employing an equation developed by Kosower for correlating the rates of S_N2 reactions in various protic solvents, it was estimated that the rate constants for the reactions of trimethylarsine and trimethylstibine with methyl iodide in water were 3×10^{-3} and 7×10^{-4} M^{-1} sec^{-1}, respectively.

The reduction of *tert*-butyl hydroperoxide by triphenylarsine or -stibine has been shown to obey second order kinetics [37]:

$$\text{Rate} = k[Ph_3M][Me_3COOH]$$

(where M was As or Sb)

Quantitatively both reactions were fast, but the stibine reacted about 60 times as fast as the arsine and almost as fast as triphenylphosphine. The reactions were only moderately sensitive to the nature of the solvent employed, but were strongly catalyzed by compounds of molybdenum and vanadium. The only products of the interaction of triphenylstibine and the hydroperoxide were *tert*-butyl alcohol and a crystalline antimony compound that was said to have the same characteristics as the oxide produced by the oxidation of the stibine with hydrogen peroxide and believed to be a polymeric Ph_3SbO. Earlier workers [38], however, have reported that the interaction of triphenylstibine and either *tert*-butyl or cumene hydroperoxide yielded an oxide (mp 219°) that was identical to a *monomeric* Ph_3SbO previously described. Further work is needed in order to resolve this discrepancy.

The electrochemical oxidation of triphenylstibine at platinum electrodes in acetonitrile containing small amounts of water has been studied by means of cyclic voltammetry and controlled potential electrolysis [39]. The following overall reaction appeared to account for the results obtained:

$$2\ Ph_3Sb + H_2O \longrightarrow [Ph_3SbOSbPh_3]^{2+} + 2\ H^+ + 4\ e^-$$

The presence of a weak acid in the electrolyzed solution was deduced from acid-base titration data and suggested hydrolysis of the oxybis(triphenylantimony) cation:

$$[Ph_3SbOSbPh_3]^{2+} + H_2O \rightleftharpoons 2\ Ph_3SbOH^+$$

Cathodic reduction of the oxybis(triphenylantimony) cation gave results that were consistent with the following equation:

$$2\ [Ph_3SbOSbPh_3]^{2+} + 2\ e^- \longrightarrow [Ph_3SbOSbPh_3 \cdot Ph_3SbO]^{2+} + Ph_3Sb$$

Perchlorate salts of $[Ph_3SbOSbPh_3 \cdot Ph_3SbO]^{2+}$ and $[Ph_3SbOSbPh_3(Ph_3SbO)_2]^{2+}$ were, in fact, isolated from the reaction mixture. Trace amounts of triphenylstibine oxide were also obtained. This substance was identified by elemental analysis and by its IR spectrum, which was apparently the same as the spectrum of a sample of the oxide prepared by dehydration of triphenylantimony dihydroxide.

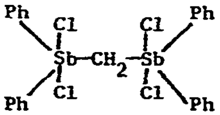
Xenon difluoride has been found to be a mild, selective agent for the oxidative fluorination of aromatic derivatives of trivalent antimony [40]. The reactions were carried out in dichloromethane at room temperature, and the yields of fluorinated products were excellent. Thus, diphenylfluorostibine was converted to diphenylantimony trifluoride in 98% yield, and triphenylstibine to triphenylantimony difluoride in 95% yield:

$$Ph_2SbF + XeF_2 \longrightarrow Ph_2SbF_3 + Xe$$

$$Ph_3Sb + XeF_2 \longrightarrow Ph_3SbF_2 + Xe$$

The interaction of diphenyl(trifluoroacetato)stibine and xenon difluoride led to displacement of the trifluoroacetato group and the formation of diphenylantimony trifluoride. The precise stoichiometry of this reaction was not elucidated.

The reaction of manganese(III) chloride with tertiary phosphines, arsines, stibines, and triphenylbismuthine has been investigated [41]. It was found that triphenylstibine was chlorinated to triphenylantimony dichloride, while methylenebis(diphenylstibine) yielded the following tetrachloride:



Under similar conditions, triphenylbismuthine was degraded to bismuth(III) chloride.

The IR and Raman spectra of tris(pentafluorophenyl)stibine and its dichloride and dibromide have been determined and analyzed [42]. The dichloride was prepared by direct chlorination of the stibine in ethanol, and the dibromide by direct bromination in carbon tetrachloride:

$$(C_6F_5)_3Sb + X_2 \longrightarrow (C_6F_5)_3SbX_2$$

(where X was Cl or Br)

The vibrational modes were classified into eight categories: in-plane C-F deformations, out-of-plane C-F deformations, C-C stretchings, ring breathing, in-plane ring deformation, out-of-plane ring deformation, mass sensitive vibrations, and C-F stretching modes. In addition the Sb-X stretching frequencies of the dihalides were identified. The observed symmetric stretchings in the Raman spectra were at 294 and 188 cm^{-1} for the dichloride and dibromide, respectively. The corresponding asymmetric stretchings in the infrared were at 327 and 240 cm^{-1}.

The direct iodimetric estimation of triphenylstibine in methanol, ethanol, or a mixture of either alcohol with acetic acid has been reported to give excellent results (the maximum standard deviation was 0.7% for 10 mg samples) [43]. The quantity of iodine consumed in the titrations showed that oxidation of antimony(III) to antimony(V) had taken place. Visual, conductometric, or potentiometric techniques were used to detect the end-points of the titrations.

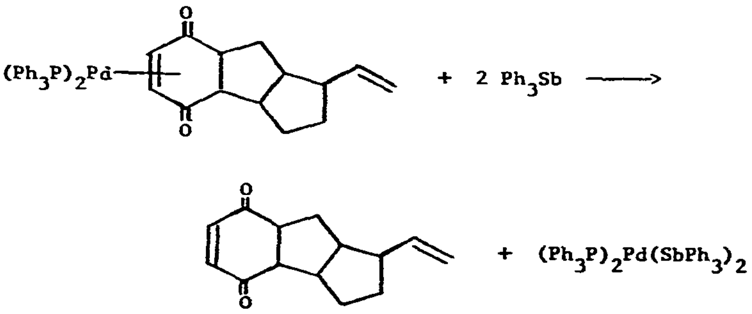
Triphenylstibine has been included in a study of the oxidation of various phosphorus(III), arsenic(III), and antimony(III) compounds in acetic anhydride solution [44]. The results obtained on conductometric titration of triphenylstibine with iodine monochloride suggested the following equilibrium:

$$Ph_3Sb + 2\ ICl \rightleftarrows Ph_3SbI^+ + ICl_2^-$$

When the resulting solution was evaporated under reduced pressure, triphenylantimony dichloride was left behind. It was suggested that the original compound formed by the addition of one mole of the stibine and two moles of iodine monochloride was not very stable and decomposed to triphenylantimony dichloride and molecular iodine.

The reaction between three Lewis bases (trimethylphosphine, -arsine, and -stibine) and five Lewis acids (boron trifluoride, boron trichloride, boron tribromide, diborane, and trimethylborane) has been studied by means of gas-phase calorimetry [45]. In 11 of the 15 reactions, solid adducts of type $Me_3M \cdot BX_3$ were formed. Trimethylborane, however, underwent no reaction with either the arsine or stibine, while both diborane and boron trifluoride reacted anomalously with the stibine. In general, the relative base strengths decreased in the order $Me_3P > Me_3As > Me_3Sb$, and the relative acid strengths decreased in the order $BBr_3 > BCl_3 \simeq BH_3 > BF_3 > Me_3B$. The adducts formed in this study were characterized by PMR, IR, Raman, and mass spectroscopy as well as by conductivity, tensimetric titration, gas-phase displacement reactions, and melting-point determinations [46].

Triphenylstibine has been used to remove a $(Ph_3P)_2Pd$ group that was coordinated to a double bond [47]:



The π-olefin complex had been obtained by the interaction of bis(triphenylphosphine)(p-benzoquinone)palladium(0) and 1,3-butadiene.

The behavior of chlorosulfuric acid solutions of triphenylphosphine, -arsine, -stibine, and -bismuthine has been investigated conductometrically [48]. The phosphine and arsine appeared to be oxidized to the corresponding oxides, which were fully protonated in chlorosulfuric acid. In contrast, the conductance values of the stibine solutions indicated that solvolysis had occurred. The following reaction was suggested:

$$Ph_3Sb + 9\ HSO_3Cl \longrightarrow Sb(SO_3Cl)_3 + 3\ PhSO_3H_2^+ + 3\ SO_3Cl^- + 3\ HCl$$

Triphenylbismuthine was not appreciably soluble in chlorosulfuric acid, and there was only a very slight change in the conductance of the solution.

The reaction of triphenylphosphine, -arsine, or -stibine with activated Raney nickel in a nitrogen atmosphere at 25° has been found to give quantitative yields of benzene [49]. Triphenylamine was practically unaffected under similar conditions. The time required to obtain 50% of the theoretical amount of benzene was 7 minutes for the phosphine, 50 seconds for the arsine, and 10 seconds for the stibine.

Trimethyl-, triethyl-, tributyl-, and trioctylstibines have been found to be effective catalysts for the preparation of alkyltin trihalides by the following type of reaction [50,51]:

$$RX + SnX'_2 \xrightarrow{R_3Sb} RSnXX'_2$$

(where X and X' were Cl or Br)

Diethylbromostibine and triphenylstibine were much less effective catalysts. The catalytic activity of the trialkylstibines decreased markedly with increasing length of the alkyl group, *i.e.*, $Me_3Sb > Et_3Sb > Bu_3Sb > Oct_3Sb$. The rate of the reaction also depended on the nature of the alkyl halide and was again found to decrease as the chain length of the alkyl group increased. Alkyl bromides were more reactive than alkyl chlorides, and stannous bromide was more reactive than stannous chloride. Bromobenzene failed to react with stannous bromide even in the presence of triethylstibine. The mechanism of the trialkylstibine-catalyzed alkylation of stannous halides was not established, but it was suggested that the stibines reversibly formed weak complexes with the alkyl halides and thereby facilitated a carbenoid-like insertion of the stannous halide into the carbon-halogen bond:

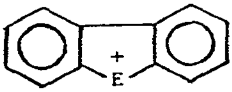
$$R_3Sb + RX \longrightarrow R_3Sb \cdot RX$$

$$R_3Sb \cdot RX + SnX_2 \longrightarrow R_3Sb + RSnX_3$$

A comparative study has been made of the mass spectra of tertiary phosphines, arsines, and stibines of the type Me_2PhE, $MePh_2E$, and MeEtPhE, where E was P, As, or Sb [52]. Also included in this study were the mass spectra of the halo compounds MePhEX, where E was As and X was either Cl or I and where E was Sb and X was Br. The molecular ions, which were observed in the spectra of all of the compounds, were most abundant in the spectra of the phosphorus compounds and least abundant in the spectra of the antimony compounds. The base peak in the spectrum of dimethylphenylstibine was $PhSb^+$. This fragment was also important in the spectra of the other antimony compounds. The spectra of the stibines also exhibited prominent peaks due to the ionized metal atom Sb^+. Analogous ions were not important in the spectra of the other compounds. The dialkylphenylstibines underwent redistribution reactions (possibly in the heated inlet system) and exhibited peaks corresponding to Ph_2MeSb^+ in the spectrum of dimethylphenylstibine and to $PhMe_2Sb^+$ in the spectrum of ethylmethylphenylstibine. Redistribution reactions of this type were not, however, observed in the case of methyldiphenylstibine or the phosphines and arsines.

A study has been reported of the mass spectra of five bidentate chelates of the type o-$C_6H_4(EPh_2)(E'Ph_2)$, where E was P and E' was P, As, or Sb, and where E was As and E' was As or Sb [53]. The fragmentation patterns reflected the effect of the decreasing C–E bond strength as the mass of E increased.

Thus, the relative intensity of the molecular ion M^+ was 73% of the base peak where both E and E' were P but only 14% of the base peak where E was As and E' was Sb. In all five spectra the base peak was a cyclic ion $C_{12}H_8E^+$ of the following structure:



In the case of the mixed bidentates the base peak contained the lighter Group V element. The fragmentation of two di-tertiary stibines $Ph_2Sb(CH_2)_n$-$SbPh_2$, where *n* was 1 or 3, was also studied. In these cases the major fragments were Ph_2Sb^+, $PhSb^+$, and $C_{12}H_{10}^+$.

A reinvestigation of the photoelectron spectra of triphenylamine, -phosphine, -arsine, and -stibine has been reported [54]. The patterns of the observed ionization potentials were discussed in terms of geometric, energetic, and overlap factors. It was concluded that there was extensive mixing of the lone pair of the nitrogen atom with the π-system of the benzene rings but that the importance of this type of mixing decreased as the atomic number of the heteroatom increased. Although *d* orbital participation in phenyl-heteroatom bonding was not entirely ruled out for the phosphorus, arsenic, and antimony compounds, interpreting the photoelectron spectra in terms of this factor alone did not seem to be possible.

The photoelectron spectra of $(Me_3Sn)_3N$, $(Me_3E)_3P$ (where E was C, Si, or Sn), $(Me_3Si)_3As$, and $(Me_3E)_3Sb$ (where E was C, Si, Ge, or Sn) have also been studied [55]. It was found that the ionization potentials of the *n*-hybrid orbitals of N, P, As, and Sb in these compounds were virtually constant. Qualitative MO theory was used to interpret this result as well as possible changes in the hybridization of these orbitals and interactions with the groups bonded to the trivalent atoms.

High-energy photoelectron spectra have been obtained for tributylstibine, triphenylstibine, triphenylstibine oxide, triphenylstibine sulfide, three dibromides of the type R_3SbBr_2 (where R was Me, Bu, or Ph), and a variety of inorganic antimony compounds [56]. In general, the Sb 3*d* binding energies were greater for the Sb(V) than for the Sb(III) oxidation state, but they also depended on other structural features. It was concluded that oxidation states could not, therefore, be assigned on the basis of X-ray photoelectron spectroscopy alone and that, in fact, this type of spectroscopy was not a particularly useful tool for studying structure and bonding in compounds of antimony.

A ^{13}C NMR study has been made of Ph_3Bi, Ar_3Sb (where Ar was Ph, *o*-MeC_6H_4, or *p*-MeC_6H_4), Ph_3BiX_2 (where X was Br, O_2CEt, or O_2CPh), and R_3SbX_2 (where R was Me, Et, Bu, Ph, *o*-MeC_6H_4, *p*-MeC_6H_4 or *p*-ClC_6H_4 and X was Cl, Br, OPh, OC_6H_4Me-*p*, OC_6H_4Cl-*p*, O_2CEt, O_2CPh, or $O_2CC_6H_4Cl$-*p*) [57]. It was found that the antimony or bismuth atom in these compounds had an electron-withdrawing effect. The effect of the metal atom on the ^{13}C NMR of the aromatic ring of the arylcarboxylato or phenolato groups was much smaller than the effect on the directly bonded aromatic rings.

The effect of complex formation upon the ^{13}C NMR spectrum of the ligand has been studied in complexes of the type $LNi(CO)_3$ and $LCr(CO)_5$, where L was Ph_3Sb, Ph_3As, $(PhO)_3P$, Et_3P, or $Ph_{3-n}Me_n$ (n = 0, 1, or 2) [58]. It was concluded among other things that there was a decrease in the resonance interaction of the Group VA atom with the phenyl ring in the order $Ph_3P > Ph_3As > Ph_3Sb$. A study of the ^{13}C NMR chemical shifts of the carbonyl groups in these complexes and in similar ones of the type $LMo(CO)_5$ has also been made [59, 60].

The UV absorption peaks of tris(*o*-methoxyphenyl)stibine have been listed in a paper mainly devoted to the question of 2*p*-3*d* overlap in *o*-methoxyphenyl-substituted tertiary phosphines and phosphonium salts [61]. This stibine exhibited peaks at 257, 271, 279, and 286 nm, while triphenylstibine had a peak only at 256 nm. The extra peaks were attributed to intramolecular charge transfer from the *p* electrons of a methoxy oxygen to a vacant *d* orbital of antimony.

Trimethyl- and triethylstibine have been included in a study of the densities and viscosities of a number of alkyl derivatives of non-transition metals [62]. The experimental data were treated by the method of least squares, and the following equations were fitted:

$$\rho = a + bt$$

$$\log \eta = -A + B/T$$

(where ρ was the density of the liquid in g/cm^3, η was the dynamic viscosity, and t and T were °C and °K, respectively)

The quenching of fluorenone fluorescence in benzene or dimethylformamide by triphenylamine, -phosphine, -arsine, -stibine, or -bismuthine has been examined [63]. The rate for the stibine was higher than for the arsine, but the rates for both the stibine and bismuthine were almost the same. It was concluded that the rate tended to increase with the mass of the central atom and to decrease with a decrease in the availability of the lone electron pair.

Gas chromatography employing sodium dodecylbenzenesulfonate or silicone SKTFV-803 as the stationary phase has been used to separate dimethylselenium, tetramethyltin, trimethylarsine, and trimethylstibine [64]. The temperature dependence of retention by these phases was examined, and the sensitivity of the thermal conductivity detector for the organometallic compounds was estimated.

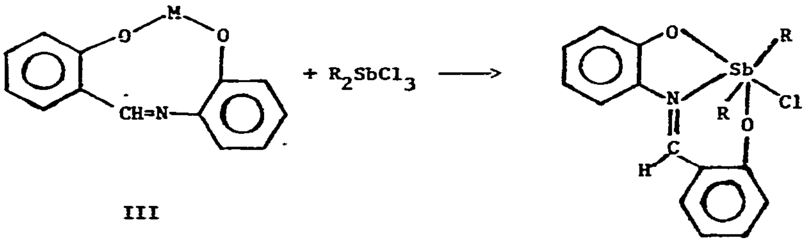
A method has been described for the direct kinetic study of electronically excited antimony atoms [65]. The metastable atoms were generated by the pulsed irradiation of trimethylstibine. Absolute quenching constants for this stibine and for a number of other collision partners were also reported.

A large number of complexes have been described in which tertiary stibines were coordinated to transition metals. The metals bonded to the antimony in these complexes included chromium [58, 60], cobalt [66, 67], gold [68], iridium [69], iron [70-74], manganese [75, 76], molybdenum [25, 60, 77], nickel [28, 58, 59, 78], osmium [79], palladium [27, 28, 47, 80, 81], platinum [28, 82, 83], rhodium [67, 84], ruthenium [79, 85], and tungsten [25].

In continuation of previous work on organoantimony compounds, Bertazzi and coworkers [86] have synthesized a series of salts of phenylantimonic acid. The compounds prepared were salts of $[PhSbF_5]^-$, $[PhSbCl_5]^-$, or $[PhSbBr_5]^-$, where the cation in each case was Me_4N^+ or Me_4As^+. The IR spectra of these compounds were determined and assignments of bands in the region 1100 to 100 cm^{-1} were made.

A series of antimonate salts of the types $[Ph_2SbX_4][Ph_4As]$ and $[Ph_2SbCl_3X][Ph_4As]$ (where X = Cl, Br, N_3, and NCS) have been prepared and their IR spectra reported and assignment of bands in the 80-500 cm^{-1} region made [87,88]. These arsonium salts were compared with the corresponding Me_4N^+ salts. The compounds all behaved as 1:1 electrolytes in acetone solution.

In continuation of previous work on antimony complexes of N-(2-hydroxyphenyl)salicylidenimine, Di Bianca and coworkers [89] have synthesized compounds of the type II by reaction of the antimony or tin compounds III with Me_2SbCl_3 or Ph_2SbCl_3.



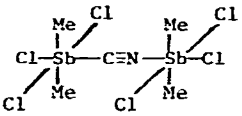
III

II

(where M = Me_2Sn or Me_3Sb, and R = Me or Ph)

The complexes II possessed octahedral geometry.

The pentacovalent antimony compound Me_2SbCl_3 was found to react with both Me_4NF and Me_4NCN to form the complexes $[Me_4N][Me_2SbCl_3FSbCl_3Me_2]$ and $[Me_4N][Me_2SbCl_3CNSbCl_3Me_2]$ [90]. On the basis of IR and Raman spectra the anions were believed to possess bridged structures such as:



From the IR and Raman spectra, assignments of the various bands were made.

The reaction of Me_2SbCl_3 with NaN_3 or with AgNCO led to the formation of dimeric compounds of the type $Me_2Cl_2Sb(X)_2SbCl_2Me_2$ (where X = N_3 or NCO) [91]. The dimeric nature of the compounds was established by mass spectral data. From IR and Raman spectra it was concluded that the N_3 or NCO groups formed the bridging groups of the dimeric structure.

Goel and coworkers [92] have prepared a number of organoantimony compounds of the type $Me_3Sb(O_2CR)_2$ and studied their ^{121}Sb Mössbauer spectra. Most of the carboxylic acids used contained halogens; *e.g.* $ClCH_2CO_2H$, Cl_2CHCO_2H, Cl_3CCO_2H, FCH_2CO_2H, F_2CHCO_2H, F_3CCO_2H, $BrCH_2CO_2H$ and Br_2CHCO_2H. The results of the Mössbauer spectra were compared with those of the corresponding tin compounds and a number of linear correlations were noted. The isomer shift and quadrupole splitting for the antimony acetoxy compounds differed greatly from those of the corresponding Ph_3SbX_2 (X = F, Cl, Br, and I) compounds and explanations for these differences were offered The $Me_3Sb(O_2CR)_2$ compounds were shown to have trigonal bipyramidal geometry with the methyl groups in planar positions.

Ferguson and coworkers [93] have reported on the stereochemistry of the three molecules $(Me_3SbX)_2O$ (where X = ClO_4, N_3, and Cl) which were studied in the solid state by means of X-ray crystallography. These compounds crystallize in the space group Pa3. The molecular symmetry required for this space group is $\bar{3}$; however, the molecules have no symmetry and are severely distorted. The antimony atom in each compound is five-coordinate with distorted trigonal-bipyramidal geometry. The ClO_4 and Cl groups are semicoordinated with rather long Sb–O bond lengths for the perchlorate (2.60A) and long Sb–Cl bond lengths (2.71A) for the chloride.

Kawasaki and Hashimoto [94] have reported on ligand exchange reactions of pentacovalent antimony compounds according to the equation:

$$Me_3Sb(L)X + Me_3Sb'(L)Y \rightleftharpoons Me_3Sb(L)Y + Me_3Sb'(L)X$$

(where LH = oxine or 2-methyl-8-hydroxyquinoline and X, Y = Cl, Br, NO_3, $OC_6H_4NO_2$-*p*, O_2CMe, O_2CCH_2Cl, and O_2CCCl_3)

The technique used for following the exchange reaction was that of line broadening in the ^1H NMR of the methyl groups and the rate constant k, as well as the activation parameters E_a, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ were reported. The syntheses of two of the compounds were reported in detail, and PMR, UV, and IR spectral data and elementary analyses were given for all of the compounds prepared. The rate constant for the exchange reaction was largely determined by the value of $\Delta S^{\neq}$ rather than by E_a, and the lability of the ligands was in the order $O_2CMe \lesssim OC_6H_4NO_2$-*p* $< O_2CCH_2Cl < O_2CCHCl_2 < O_2CCCl_3 < Cl < Br$. A mechanism for the exchange reaction involving a bridging intermediate was suggested to account for the observations.

It has been found [95] that R_2InCl acts as an alkylating agent toward $SbCl_5$, Me_3SbCl_2, and Me_3AsCl_2. Thus with $SbCl_5$ and Et_2InCl, Et_3SbCl_2 was formed which with excess $SbCl_5$ gave the salt $[Et_3SbCl][SbCl_6]$:

$$3\ Et_2InCl + 2\ SbCl_5 \longrightarrow 3\ InCl_3 + 2\ Et_3SbCl_2$$

$$Et_3SbCl_2 + SbCl_5 \longrightarrow [Et_3SbCl][SbCl_6]$$

The compounds Me_3MCl_2 (M = As or Sb) reacted with Me_2InCl in CH_2Cl_2 according to the equation:

$$Me_3MCl_2 + Me_2InCl \longrightarrow [Me_4M][MeInCl_3]$$

The IR and Raman spectra of the compounds prepared were reported, and assignment of bands were made.

The pentacovalent aliphatic antimony compounds R_3SbX_2, where R = Et or Me_2CH and X = F, Cl, Br, and I, have been prepared and their low-frequency IR and Raman spectra determined [96]. The results were best interpreted in terms of C_{3v} symmetry for all of the compounds under study. Known Sb—C stretching frequencies for Me_3SbX_2 (X = F, Cl, and Br) and for Ph_3SbX_2, (X = F and Cl) were compared with those for the Et and Me_2CH compounds. Except for the two benzyl compounds a decrease in frequency in the order $\nu_{Me} > \nu_{Et} > \nu_{Me_2CH}$ where X was constant suggests that this effect is mass dependent.

Mössbauer spectra of six-coordinate tin compounds of the type $R_2SnX_2L_2$ and X_4SnL_2 (where R is an organic group such as Me or Ph, X = Cl, Br, or I, and L is a donor neutral ligand) have not been of particular value in elucidating six-coordinate structures or in studying the effect of various donors because of the small values of the quadrupole splitting. For this reason Bancroft and coworkers [97] turned to compounds of the type $[R_2SnL_4]^{2+}$ and found that the quadrupole splitting had about twice the sensitivity to the ligand L as in the case of $R_2SnCl_2L_2$. This enabled the quadrupole splitting to be readily interpreted in terms of bonding properties of the ligands. A large number of compounds of the type $[R_2SnL_4]^{2+}$ were prepared and their Mössbauer parameters listed. The results were then compared with the Mössbauer parameters for the corresponding antimony compounds of the type $SbCl_5L$

and correlations were found. Thus for ten similar Sb and Sn compounds a correlation between the e^2qQ values with a correlation coefficient of 0.995 was found. Among the organoantimony and organotin complexes compared were the following pairs: Ph_3SbBr_2, $[Ph_3SnBr_2]^-$; Ph_3SbCl_2, $[Ph_3SnCl_2]^-$; Me_3SbBr_2, $[Me_3SnBr_2]^-$; and Me_3SbCl_2, $[Me_3SnCl_2]^-$.

A number of new organoantimony compounds of the type $Ph_3Sb(OCOR)_2$ have been obtained by condensation of triphenylstibine oxide with a carboxylic acid RCO_2H, where R was *p*-HOC_6H_4, *p*-$MeO_2CC_6H_4$, *o*-$MeO_2CC_6Cl_4$, *p*-$MeO_2CC_6Br_4$, *cis*-$MeO_2CCH{=}CH$, *cis*-$MeO_2CCCl{=}CCl$, or *cis*-$MeO_2CCBr{=}CBr$ [98]. PMR and IR frequencies for the carbonyl groups are listed. Attempts to prepare similar compounds from Ph_3SbO and terephthalic, succinic, and sebacic acids resulted in the formation of polymeric products.

Although pentacovalent antimony and bismuth compounds are readily reduced by thiols so that compounds of the type $R_3Sb(SR')_2$ and $R_3Bi(SR')_2$ cannot be readily prepared, Ouchi and coworkers [99] have found that thio acids do not readily reduce the Sb and Bi compounds so that compounds of the type $Ph_3Sb(SSCR)_2$ were readily obtained. Such acids as $MeCS_2H$, $C_6H_5CH_2$-CS_2H, $EtCS_2H$, $PrCS_2H$, and Me_2CHCS_2H were used. Thiobenzoic acid and phenoxyacetic acid formed similar five-covalent Sb and Bi compounds. Elementary analyses and PMR spectral data were given for all of the compounds prepared. Sato and Matsumura [100] have prepared the interesting ditertiary stibine sulfides $[Ph(Me)(S)Sb]_2(CH_2)_3$ and $Ph(Me)(S)SbCH_2Sb(Me)Ph$. The latter compound was obtained as the sole product in the reaction of $[Ph(Me)(Cl_2)Sb]_2CH_2$ with $Na_2S{\cdot}9\ H_2O$ in methanol, whereas the first compound was obtained in a similar reaction of $[Ph(Me)(Cl_2)Sb]_2(CH_2)_3$ and $Na_2S{\cdot}9\ H_2O$ in methanol. Both disulfides, when dissolved in CH_2Cl_2, gave a PMR spectrum which changed with time. Since both compounds were monomeric, it was concluded that the change in the NMR spectrum was due to a change from one diastereomeric form to the other form. By the reaction of Ph_3P with either of the two compounds, they were desulfurized to give $[Ph(Me)Sb]_2CH_2$ and $[Ph(Me)Sb]_2(CH_2)_3$, respectively. With $Ph(Me)(S)SbCH_2Sb(Me)(S)Ph$, addition of Ph_3P to a freshly prepared solution gave exclusively the racemic form of $[Ph(Me)Sb]_2CH_2$, whereas addition of Ph_3P after 1.5 hours gave a mixture of equal amounts of racemic and *meso* forms. From these results the authors concluded that both $Ph(Me)(S)SbCH_2Sb(Me)Ph$ and $[Ph(Me)(S)Sb]_2(CH_2)_3$ crystallized from solution as single diastereomers, but that in solution these diastereomers isomerized to the other diastereomeric form. A mechanism for the isomerization was suggested.

The IR and Raman spectra of Me_3SbO and $(CD_3)_3SbO$ have been studied by Morris, Zingaro, and Laane [101]. The mass spectra of these compounds were also reported. The two compounds were assumed to possess C_{3V} symmetry; a normal coordinate analysis was carried out and an assignment of all of the bands were made. Force constants for the various bonds were given. A polar coordinate linkage was suggested for the Sb—O bond. The authors were unable to obtain single crystals suitable for X-ray structure determinations.

The reactions of dyes, such as Eriochrome Black T, Chrome Dark Blue, and Xylenol Orange (0.05% solutions), with organic compounds of such elements as Si, Ge, Sn, Pb, P, and Sb, have been studied for possible analytical purposes [102]. The Group V compounds Ph_4PBr, Ph_4PI, Ph_4SbOH, Ph_4SbCl, Ph_4SbBr, Ph_3SbCl_2 and $Ph_4SbO_2CHPh_2$ were highly reactive with the dyes, but the Sb compounds gave more intense colors than the P compounds.

The electrical conductivities of the Ph_4M^+ ions (where M = P, As, and Sb) have been measured in aqueous solution [103].

In continuation of previous work on the thermal decomposition of tetraphenylantimony alkoxides, Razuvaev and coworkers [104] have studied the thermal decomposition of both phosphorus and antimony compounds of the type Ph_4POR and Ph_4SbOR. They have prepared a number of new compounds including silicon and germanium compounds of the type $Ph_4SbOSiPh_3$ and $Ph_4SbOGePh_3$. The compound Ph_4SbOCH_2Ph was stable in air, gave Ph_4SbCl and $PhCH_2OH$ when treated with HCl, and decomposed at 180-190° according to the equation:

$$Ph_4SbOCH_2Ph \xrightarrow{\Delta} Ph_3Sb + PhCHO + PhH$$

The synthesis of $Ph_4SbOSiPh_3$ was accomplished according to the equations:

$$Ph_5Sb + Ph_3SiOH \longrightarrow Ph_4SbOSiPh_3 + PhH$$

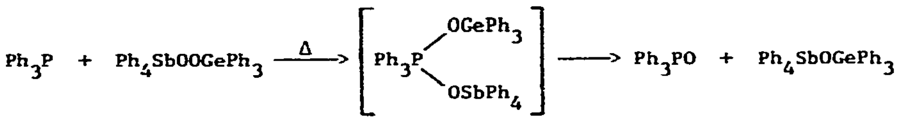
$$Ph_4SbOCH_2Ph + Ph_3SiOH \longrightarrow Ph_4SbOSiPh_3 + PhCH_2OH$$

The siloxy compound decomposed at 250-260° according to the equations:

$$2\ Ph_4SbOSiPh_3 \xrightarrow{\Delta} Ph_3Sb(OSiPh_3)_2 + Ph_5Sb$$

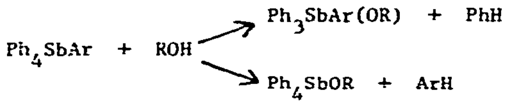
$$Ph_5Sb \longrightarrow Ph_3Sb + Ph\text{-}Ph$$

The product $Ph_3Sb(OSiPh_3)_2$ was stable to air. The stable peroxide $Ph_4SbOOGePh_3$ was found to react with Ph_3P to give an unstable P^V compound which decomposed further:



$$Ph_3P + Ph_4SbOOGePh_3 \xrightarrow{\Delta} \left[Ph_3P\begin{matrix} OGePh_3 \\ OSbPh_4 \end{matrix} \right] \longrightarrow Ph_3PO + Ph_4SbOGePh_3$$

It is well known that pentaarylantimony compounds react with protic solvents with the cleavage of one Sb-C bond and the formation of a tetraarylantimony compound, but the mechanism of this reaction has not been clearly delineated. Lanneau and coworkers [105] have now reported rate constants for the solvolysis of p-$MeC_6H_4SbPh_4$, m-$ClC_6H_4SbPh_4$, and p-$MeOC_6H_4SbPh_4$ with 2-octanol. They were unable to obtain rate data for Ph_5Sb, but, since the other three compounds provided a satisfactory Hammett plot ($\rho = 1.12$) a value for the phenyl group could be readily calculated. Since the three compounds under study were unsymmetrical the solvolysis involved two competing reactions:



$$Ph_4SbAr + ROH \rightarrow Ph_3SbAr(OR) + PhH$$
$$Ph_4SbAr + ROH \rightarrow Ph_4SbOR + ArH$$

Both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the cleavage of a phenyl group and the cleavage of a substituted phenyl group were calculated. From the kinetic data the authors suggested that the reaction involved an S_N1(Sb) reaction, but with strong nucleophilic participation of the solvent. The amounts of benzene *vs.* substituted-benzene formed in the reaction were in accord with this reaction mechanism. The reaction of *p*-$MeOC_6H_4SbPh_4$ with 2-octanol in the presence of the 2-octyl oxide ion was also studied. A second order rate constant was observed which suggested an S_N2(Sb-ate) mechanism for the reaction. The reaction of the other compounds with 2-octanol in the presence of the 2-octyl oxide ion could not be followed quantitatively, but qualitative results indicated that the 2-octyl oxide ion exerted a major influence on the reaction. The syntheses of the three unsymmetrical pentaaryl Sb compounds were described in detail.

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