# ANTIMONY

## ANNUAL SURVEY COVERING THE YEAR 1974

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The chemistry of organoantimony compounds was not extensively reviewed in 1974. There were, however, two short surveys of organoarsenic, -antimony, and -bismuth chemistry [1,2], a review by Noltes and Meinema [3] of their work on organoantimony(V) derivatives of β-diketones, and a comprehensive summary of the synthesis and preparative uses of organoarsenides, -stibides, and - bismuthides [4]. Information about organoantimony compounds has also been given in review articles on biological effects of organometallic compounds [5], organometallic derivatives of hydroxylamines and oximes [6], perfluoroaliphatic compounds [7], bond strengths [8], heat capacity, phase transitions, and thermodynamic functions [9], and vibrational [10,11], NMR [12-13a], NQR [14], and Mössbauer [15] spectroscopy. A review on nitrogen, phosphorus, arsenic, antimony, and bismuth compounds has been published in a new series on molecular structures by diffraction methods [16], and several organoantimony compounds that were subjected to X-ray analysis in 1972 have been listed in Volume 5 of *Molecular Structures and Dimensions* [17]. Organoantimony compounds have been incidentally mentioned in books on organometallic reaction mechanisms [18] and stereochemistry and bonding in inorganic chemistry [19].

Baumann and Wieber [20] have obtained diphenoxy- and dialkoxymethylstibines by the interaction of methyldibromostibine and sodium phenoxide or a sodium alkoxide:

$$\mathrm{MeSbBr_2 + 2NaOR \longrightarrow MeSb(OR)_2 + 2NaBr}$$

$$\text{(where R was Me, Et, } \mathrm{Me_2CH, Me_3C}\text{, or Ph)}$$

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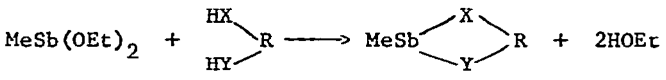
Antimony, Annual Survey covering the year 1973 see J. Organometal. Chem., 89 (1975) 151-182.

All five compounds were extremely sensitive to hydrolysis; they fumed in the air and possessed unpleasant odors. They were shown to be monomeric by means of cryoscopic measurements in benzene. Diethoxymethylstibine underwent exchange reactions with thiols to give almost quantitative yields of sulfur analogs:

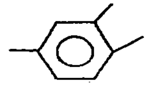
$$\mathrm{MeSb(OEt)_2 + 2HSR \longrightarrow MeSb(SR)_2 + 2HOEt}$$

(where R was Me or $PhCH_2$)

In a similar way ten heterocyclic organoantimony compounds were obtained by the reaction of diethoxymethylstibine with vicinal dithiols (1,2-ethanedithiol or 3,4-dimercaptotoluene), vicinal diols (ethylene glycol, *meso*-2,3-butanediol, pinacol, *meso*-1,2-diphenyl-1,2-ethanediol, catechol, or tetrachlorocatechol), 2-mercaptoethanol, or 2-mercaptophenol:



$$\mathrm{MeSb(OEt)_2 + \begin{matrix}HX\\HY\end{matrix}\!\!>R \longrightarrow MeSb\begin{matrix}X\\Y\end{matrix}R + 2HOEt}$$

(where X and Y were S, R was $CH_2CH_2$ or Me  ; where X and Y were O, R was $CH_2CH_2$, CHMeCHMe, $CMe_2CMe_2$, CHPhCHPh, *o*-$C_6H_4$, or *o*-$C_6Cl_4$; and where X was O and Y was S, R was $CH_2CH_2$ or *o*-$C_6H_4$)

The acyclic antimony-sulfur compounds were soluble in benzene and gave normal molecular weights in this solvent. In contrast, the heterocyclic compounds were either soluble only in polar solvents (such as alcohols, chloroform, or dimethyl sulfoxide) or virtually insoluble in both polar and nonpolar solvents. The insolubility in polar solvents was attributed to polymerization, and it was found that these heterocyclic compounds exhibited no molecular ions in their mass spectra. Molecular ions were present, however, in the mass spectra of the compounds that were soluble only in polar solvents. It was concluded that this latter group of antimony com-

ably existed in the solid state as coordination polymers that were
easily depolymerized.

R spectroscopy has been used to investigate the electronic effects
$_4$SbS group in tetraphenyl(*p*-fluorophenylthio)antimony, the
oup in diphenyl(*p*-fluorophenylthio)stibine and diphenyl(2,6-
-fluorophenylthio)stibine, and the *p*-Ph$_2$BiS group in diphenyl-
enylthio)bismuthine [21]. The Sb(III) and Bi(III) compounds were
om diphenylchlorostibine or -bismuthine:

$$Ph_2MCl + NaSAr \longrightarrow Ph_2MSAr + NaCl$$

ere M was Sb or Bi and Ar was *p*-$FC_6H_4$ or 2,6-$Me_2$-4-$FC_6H_2$)

alent antimony compound was prepared from methoxytetraphenyl-

$$Ph_4SbOMe + p\text{-}FC_6H_4SH \longrightarrow p\text{-}FC_6H_4SSbPh_4 + MeOH$$

al shifts were determined in benzene or pyridine and were compared
orresponding shifts of *p*-fluorothiophenol, *p*-fluorophenyl methyl
nd 2,6-dimethyl-4-fluorophenyl methyl sulfide. It was concluded
-Ph$_2$MS groups were less electron-donating than the *p*-SH and *p*-SMe
ile the *p*-Ph$_4$MS group was more electron-donating. Further, the
ntaining group was somewhat more electron-donating than the corres-
timony-containing group. A comparison of the data for the 2,6-
-fluorophenyl compounds indicated that steric hindrance had a much
fluence on the electronic effect of the *p*-Ph$_2$SbS group than of the
p. The solvation sensitivity of the electronic effects of the
nd *p*-Ph$_4$SbS groups was virtually zero, while the solvation of the
uth compound in pyridine appeared to make the Ph$_2$Bi group more
onating.

pectroscopy has been used to determine the equilibrium constants
lowing types of exchange reaction [22]:

$$YC_6H_4SSbPh_2 + 2,6\text{-}Me_2C_6H_3SHgPh \rightleftharpoons YC_6H_4SHgPh + 2,6\text{-}Me_2C_6H_3SSbPh_2$$

(where Y was H, 2-F, 2-Cl, 2-Br, 3-Cl, 2-$O_2N$, 2-MeO, or 4-$Me_2N$)

Although the equilibria appeared to be quickly established, the reactions were slow on the PMR time scale, and hence the concentrations of the components could be established by PMR techniques. The equilibrium constants were about unity for Y = H, 3-Cl, or 4-$Me_2N$; they increased in the case of the *ortho* substituents in the order F $\sim$ Cl < Br < MeO < $O_2N$. It was also possible to use the PMR method to study the exchange reactions between diphenyl-(2,6-dimethylphenylthio)stibine or diphenyl(*o*-tolythio)stibine and various substituted thiophenols. The results obtained indicated that the equilibrium was only slightly influenced by the polar effects of the substituents. *o*-Halogen substituents decreased the equilibrium constants by a factor of approximately four. It was suggested that this decrease was a consequence of the greater strength of the intramolecular hydrogen bond in *o*-halothiophenols relative to that of the intramolecular coordinate bond involving the $Ph_2Sb$ group. A further decrease in the equilibrium constant was noted with *o*-nitrothiophenol and, presumably, reflected the increasing difference in the strengths of the six-membered chelate rings involving hydrogen and the $Ph_2Sb$ group. On the other hand, the presence of an *o*-methoxy group caused only a slight decrease in the equilibrium constant.

Bis(trifluoromethyl)iodostibine has been used in a study of laser action obtained by the photodissociation of compounds containing iodine bonded to a Group V atom [23]. A UV absorption band near 290 nm was believed responsible for the laser action.

The structure of oxybis(diphenylantimony), $(Ph_2Sb)_2O$, has been investigated by X-ray diffraction [24] and $^{121}Sb$ Mössbauer spectroscopy [25]. The former technique showed that the compound existed as discrete molecules with only a single type of antimony site. The two antimony atoms in each molecule were connected by a bridging oxygen with Sb-O distances of about 1.97 Å and an Sb-O-Sb angle of 122°. Each antimony atom was bonded to two carbons with C-Sb distances of about 2.15 Å. Since the C-Sb-C and C-Sb-O bond angles were only slightly larger than 90°, it was concluded that the antimony lone pair electrons were essentially *s* in character. The $^{121}$Sb Mössbauer spectrum was quite unusual in that it appeared to consist of two distinct absorption peaks. Analysis of the spectrum indicated, however, that the splitting was caused by an extremely large asymmetry parameter ($\eta = 0.90$) and that there were *not* two radically different antimony sites. Independent confirmation of the large value of $\eta$ was sought by NQR measurements, but signals could not be observed.

Azerbaev and coworkers [26] have prepared a number of tertiary stibines of the type $RC{\equiv}CSbPh_2$ by means of the following reaction sequence:

$$RC{\equiv}CH \xrightarrow{EtMgBr} RC{\equiv}CMgBr \xrightarrow{Ph_2SbCl} RC{\equiv}CSbPh_2$$

(where R was $Me_2NCH_2$, $Et_2NCH_2$, $(HOCH_2CH_2)_2NCH_2$, piperidinomethyl, morpholinomethyl, 1-(acetamido)-cyclohexyl, or 1,2,5-trimethyl-4-hydroxy-4-piperidyl)

The tertiary stibines thus obtained were converted to the corresponding antimony(V) dihalides by reaction with chlorine, bromine, or iodine in chloroform. The dihalides showed bactericidal activity at concentrations of 0.5-13.7 mg/liter. Another paper [27] from the same laboratory has described the preparation of two phenylethynyltetraarylantimony compounds by the interaction of diphenyl(phenylethynyl)antimony dichloride and an aryllithium compound in boiling ether:

$$Ph_2(PhC{\equiv}C)SbCl_2 + 2\ ArLi \longrightarrow Ph_2Ar_2(PhC{\equiv}C)Sb + 2\ LiCl$$

(where Ar was Ph or $p$-$MeC_6H_4$)

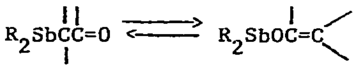
Kato and coworkers [28] have prepared four tertiary stibines by the interaction of *p*-chlorophenyldiiodostibine and Grignard reagents:

$$p\text{-}ClC_6H_4SbI_2 + 2\ RMgX \longrightarrow p\text{-}ClC_6H_4SbR_2 + 2\ MgXI$$

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

Bromination of these stibines yielded the corresponding antimony(V) dihalides.

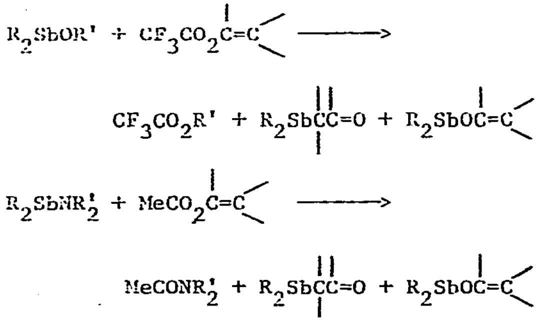
Foss and coworkers have investigated the effect of steric [29] and electronic [30] factors on the tautomeric equilibrium between dialkylstibino-substituted carbonyl and enolate isomers:



$$R_2SbCC{=}O \rightleftharpoons R_2SbOC{=}C<$$

(where R was Et or $Me_3C$)

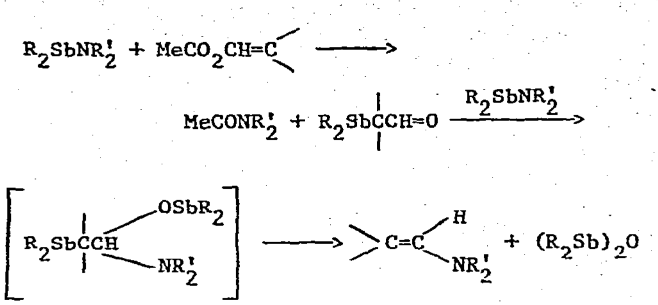
The compounds were synthesized by the interaction of an alkoxydialkylstibine and an enol trifluoroacetate or by the interaction of a dialkylaminodialkylstibine and an enol acetate:



$$R_2SbOR' + CF_3CO_2C{=}C< \longrightarrow CF_3CO_2R' + R_2SbCC{=}O + R_2SbOC{=}C<$$

$$R_2SbNR'_2 + MeCO_2C{=}C< \longrightarrow MeCONR'_2 + R_2SbCC{=}O + R_2SbOC{=}C<$$

Attempts to obtain organoantimony derivatives of aldehydes by the second method resulted in the formation of significant amounts of enamines. This result was explained by assuming that the organoantimony carbonyl compound was able to undergo an addition reaction with the aminostibine:



It was shown, in fact, that the diethylstibino-methylpropanal derivative (which appeared to exist only as an Sb-O isomer) reacted with an aminostibine to give an enamine:

$$Et_2SbOCH{=}CMe_2 + Et_2SbNMe_2 \longrightarrow Me_2C{=}CHNMe_2 + (Et_2Sb)_2O$$

The authors suggested that the aminostibine reacted with the above enolate *via* its C-Sb isomer even though the concentration of the latter compound was too low to be detected by the IR and PMR methods employed. The dialkylstibinoacetaldehyde derivatives appeared to exist exclusively as C-Sb isomers, *i.e.*, as $R_2SbCH_2CH{=}O$. On the other hand, a substituent at the α-carbon atom of the aldehyde produced only Sb-O isomers. Ketones were more likely than aldehydes to give C-Sb isomers; and, indeed, all organoantimony derivatives containing the group $SbCH_2C(O)R$ (where R was an alkyl or aryl group) were stable only as the C-Sb isomers. Replacement of one or both of the hydrogens of the $CH_2$ group by an alkyl group, however, favored the enolate structure. An increase in the size of the alkyl groups attached to the antimony also stabilized the Sb-O isomers. It was concluded, therefore, that steric hindrance associated with either the dialkylstibino or carbonyl component decreased the stability of the C-Sb isomers. Electronic effects were studied by determining the Sb-O isomer content of a number of di-*tert*-butylstibino derivatives of *para*-substituted propiophenones. The composition of these derivatives varied from 16% Sb-O isomer for the *p*-methoxy compound to 41% for the *p*-chloro compound, and the equilibrium constants for the conversion of the C-Sb isomers to the corresponding Sb-O isomers could be correlated with the Hammett σ constants:

$$\log K/K_o = 1.13\sigma$$

It was clear, therefore, that electron-attracting substituents favored the Sb-O isomers. Steric effects, however, appeared to be of greater importance than electronic factors.

A new chelating agent, *o*-phenylenebis(dimethylstibine), has been synthesized in 5-8.7% overall yield from antimony trichloride via the following series of reactions [31]:

$$3\ \mathrm{MeMgI} + \mathrm{SbCl_3} \longrightarrow \mathrm{Me_3Sb} + 3\ \mathrm{MgClI}$$

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

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

$$\mathrm{Me_2SbBr} + 2\ \mathrm{Na} \xrightarrow{\mathrm{NH_3}} \mathrm{Me_2SbNa} + \mathrm{NaBr}$$

$$2\ \mathrm{Me_2SbNa} + o\text{-}\mathrm{BrC_6H_4I} \xrightarrow{\mathrm{NH_3}} o\text{-}\mathrm{Me_2SbC_6H_4SbMe_2} + \mathrm{NaBr} + \mathrm{NaI}$$

The di-tertiary stibine thus obtained was a yellow air-sensitive liquid, bp 124-125° at 0.5 torr. The PMR spectrum showed a sharp singlet at δ 0.98 and a broad multiplet at δ 7.08-7.62 with an intensity ratio corresponding to th methyl and aromatic protons, respectively. The mass spectrum exhibited the molecular ion and a fragmentation pattern similar to that observed in relate *o*-phenylene derivatives [32]. The new ligand appeared to undergo many of th reactions characteristic of di-tertiary bidentates containing other Group V donor atoms. For example, it readily formed 1:1 complexes with compounds of the type $MX_2$ (where M was Pd or Pt and X was Cl, Br, I, or SCN). The complexes were pale-yellow to orange-red solids, which were non-electrolytes in nitrobenzene and which showed the expected downfield PMR shift of the Sb-Me signal (0.65-0.91 ppm) upon coordination.

The reaction of triphenylphosphine, -arsine, and -stibine with chloramine-T in acidified aqueous dioxane has been found to yield triphenylphosphine oxide, triphenylarsenic hydroxychloride, and triphenylantimony dichloride, respectively [33]. In each case one mole of oxidant was consumed per mole of substrate. It was suggested that dichlorides of the type $Ph_3MCl_2$ (where M was P, As, or Sb) were initially formed and, in the phosphorus and arsenic cases, were hydrolyzed to the observed products. The interaction of triphenylbismuthine and chloramine-T in the acid medium employed did not give consistent results and was believed to involve cleavage of the carbon-bismuth bond.

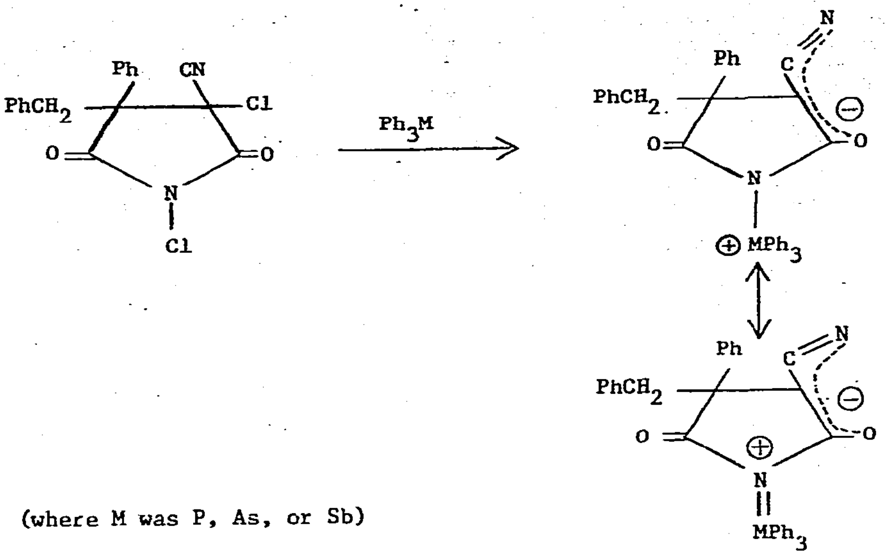
The use of chloramine-T for the oxidimetric determination of triphenylarsine, -stibine, and -bismuthine in aqueous acetic acid has been reported to give excellent results (the error was 0.2-0.8% for 10-15 mg samples) [34]. Excess oxidant was determined by the addition of potassium iodide and titration of the liberated iodine with thiosulfate.

The oxidation of triphenylphosphine, -arsine, and -stibine by copper(II) chloride has also been investigated [35,36]. It was found that triphenylstibine in acetone was immediately converted to triphenylantimony dichloride:

$$Ph_3Sb + 2\ CuCl_2 \longrightarrow Ph_3SbCl_2 + 2\ CuCl$$

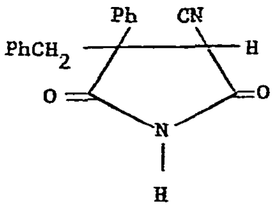
Under similar conditions, the phosphine and arsine formed copper complexes, which then underwent self oxidation-reduction and decomposition. The rate of reduction of copper(II) chloride decreased in the order $Ph_3Sb > Ph_3P > Ph_3As$.

The interaction of a 1,3-dichloro-2,5-pyrrolidinedione and two moles of triphenylphosphine, -arsine, or -stibine in boiling, dry benzene has been found to yield resonance-stabilized betaines [37]:



(where M was P, As, or Sb)

The structure of these stable, crystalline substances was deduced largely from their spectroscopic properties. Hydrolysis of the betaines with hydrogen chloride in warm acetone cleaved the N-M bond and gave the following imide:



Denniston and Martin [38] have prepared and obtained $^{1}H$ and $^{11}B$ NMR data for the 1:1 boron tribromide and triiodide adducts of trimethylstibine. The adducts were white solids that were moisture sensitive and pyrophoric; in addition, the boron triiodide adduct was photosensitive. They appeared, however, to be stable when stored in a dry, inert environment at 0°. At room temperature they slowly decomposed to trimethylantimony dihalides. A similar but more rapid decomposition occurred when the adducts were dissolved in chloroform or acetonitrile.

The preparation of epitaxial layers of indium antimonide through the interaction of triethylindium etherate and trimethylstibine at 300-530° in a hydrogen atmosphere has been investigated [39]. The deposition of the layers was carried out on substrates of indium antimonide, gallium antimonide, gallium arsenide, or germanium arsenide. It was suggested that there was an initial formation of a coordination complex containing an indium-antimony bond:

$$Me_3In{\cdot}OEt_2 + Et_3Sb \longrightarrow Me_3In{\cdot}SbEt_3 + Et_2O$$

A possible scheme for the thermal decomposition of this complex to yield indium antimonide was also proposed.

The reaction of *N,N'*-oxybis[1,1,1,1', 1', 1'-hexafluorodimethylamine] with tris(trifluoromethyl)phosphine or -arsine has been found to yield compounds containing M-N bonds [40]:

$$(CF_3)_2NON(CF_3)_2 + (CF_3)_3M \longrightarrow (CF_3)_2MN(CF_3)_2 + (CF_3)_2NOCF_3$$

(where M was P or As)

In contrast to these results, the main products isolated from the analogous reaction with tris(trifluoromethyl)stibine were $(CF_3)_2NOCF_3$, $CF_3N{=}CF_2$, and $SbF_3$.

Triphenylphosphine and -arsine have been found to react with manganese(II) halides to produce complexes of the type $Mn(OEPh_3)_2X_2$, where E was P or As and X was Cl, Br, or I [41]. A trace of water in the manganous salts was probably the source of the oxygen in these complexes. Triphenylstibine also appeared to be oxidized by the manganese(II) halides, but characterizable complexes could not be isolated. The oxidation of triphenylstibine to triphenylstibine oxide (mp 221°) by the use of bis(trimethylsilyl) peroxide has been observed by Brandes and Blaschette [42] and is discussed in the Arsenic and Bismuth sections. These authors also found that the tertiary stibine was unaffected by refluxing with di-*tert*-butyl peroxide in toluene for 4.5 hours. Rossi and Bunnett [42a] have noted the conversion of triphenylstibine to diphenylstibinic acid. This work is discussed under Bismuth.

De Ketelaere and Van der Kelen [43] have determined and analyzed the IR and Raman spectra of sixteen compounds of the type $(XC_6H_4)_3M$, where M was P, As, Sb, or Bi and X was 3-F, 4-F, 3-Cl, or 4-Cl, over the spectral range 4000 to 100 $cm^{-1}$. They found that *para*-substitution led to absorptions at about 1900, 1780, and 1640 $cm^{-1}$, while *meta*-substitution yielded characteristic bands at about 1940, 1870, 1760, and 1680 $cm^{-1}$. As expected, the nature of the halogen and of the M atom present influenced the positions of the so-called "X-sensitive" bands.

In a second paper the same authors [44] described the NQR spectra for the $^{35}Cl$ nucleus in the chloro compounds mentioned above and for the $^{75}As$, $^{121}Sb$, $^{123}Sb$, and $^{209}Bi$ nuclei in the triaryl compounds $(XC_6H_4)_3M$, where X was H, 4-F, 3-Cl, or 3-F and M was As, Sb, or Bi. The $^{35}Cl$ frequencies were used to calculate Hammett sigma constants for the P, As, Sb, and Bi substituents; these constants were positive for the phosphines and arsines but negative for the stibines and bismuthines. Possible relationships between the NQR data and C-M bonding in these compounds were also discussed.

Elbel and coworkers [45] have compared the photoelectron spectra of trimethylamine, -phosphine, -arsine, and -stibine and concluded that the first ionization potentials (which were assigned to the lone pairs) were the same for the entire series. This result was surprising, since the atomic *s* and *p* ionization potentials were known to decrease in going from nitrogen to antimony. It was suggested that there was a change in hybridization of the lone pairs and an increase in *s* character as the atomic number of the central atom increased. Increasing the *s* contribution lowered the energy of the $sp^x$ hybrid orbital and counteracted the decreasing trend of the original atomic ionization potentials. Thus, the lone pair orbital energies of the trimethyl derivatives tended to remain nearly constant.

The photoelectron spectra of triphenylamine, -phosphine, -arsine, and -stibine have also been studied [46]. The binding energy of the *n* orbital was found to decrease in the order N > Sb > As > P. The relative destabilization of the *n* orbital in the phosphorus, arsenic, and antimony compounds was attributed to a shift of electron density from the phenyl groups toward the heteroatom. Such shifts of electron density were believed to be related to the ability of the heavier heteroatoms to expand their valence shells.

The ionization potentials (and relative ion intensities) of all five triaryl derivatives of nitrogen, phosphorus, arsenic, antimony, and bismuth have been determined by mass spectrometry [47].

Kotlar and Brill [48] have published a spectroscopic evaluation of the possible interaction between hexamethylbenzene and triphenylphosphine. Earlier workers had reported that compound formation occurred at 1:1 stoichiometry between hexamethylbenzene and triphenylphosphine, -arsine, or -stibine and had suggested that bonding between the components probably involved donation of electrons from the hexamethylbenzene to the vacant *d*-orbitals of the hetero atom. In the present study the existence of any interaction between hexamethylbenzene and triphenylphosphine in solution could not be detected by $^{13}C$ and $^{31}P$ NMR, Raman, and UV spectroscopy. Furthermore, the Raman spectrum of a 1:1 mixture melted and then cooled to room temperature was superimposable on the spectra of the pure components. It was concluded, therefore, that any association between hexamethylbenzene and triphenylphosphine was too weak to disturb the spectroscopic parameters of the molecules. Similar conclusions were drawn by extension for any possible interaction between hexamethylbenzene and triphenylarsine or -stibine.

Tertiary stibines have continued to be popular as ligands in transition metal complexes. The metals coordinated to the antimony in these complexes included chromium [49-51], cobalt [52-57], gold [58], iron [52, 59-62], manganese [63], molybdenum [49, 51, 64], nickel [52, 65-67], osmium [68], palladium [69-74], platinum [71, 73-77], rhodium [71, 74, 78-82], ruthenium [83,84], tungsten [49, 51, 64], and vanadium [85].

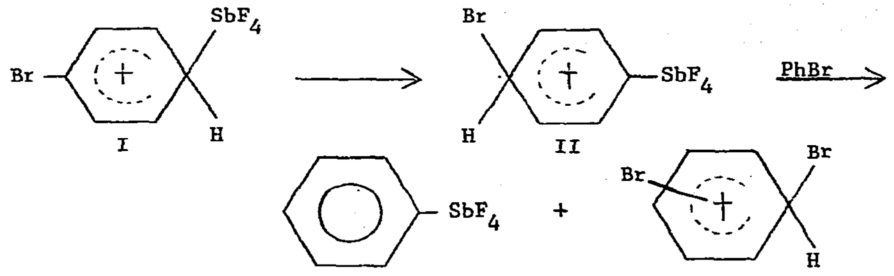
Olah and coworkers [86] have discovered that the reaction of antimony pentafluoride with benzene, halobenzenes, or alkylbenzenes produced compounds containing the C-Sb-F linkage. For example, when antimony pentafluoride was added to benzene, there was a vigorous, strongly exothermic reaction that yielded about 4% of triphenylantimony difluoride and 20% diphenylantimony trifluoride (isolated as a monohydrate or as pyridinium, sodium, or potassium diphenyltetrafluoroantimonate). The mechanism of the reaction appeared to involve the electrophilic attack of antimony pentafluoride on the benzene to yield phenylantimony tetrafluoride as the primary product:

$$\mathrm{PhH + SbF_5 \longrightarrow PhSbF_4 + HF}$$

Attempts to trap the tetrafluoride were, however, unsuccessful. It was concluded, therefore, that it was a strong electrophile and reacted further with benzene to give diphenylantimony trifluoride. The latter compound still possessed Lewis acid character and reacted further with benzene (in a rather slow reaction) to give triphenylantimony difluoride. Further reaction to give pentaphenylantimony was not possible under the reaction conditions employed, since control experiments showed that this substance was cleaved by hydrogen fluoride in benzene:

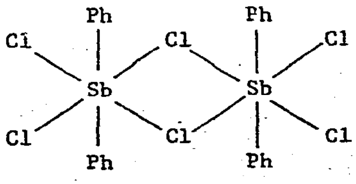
$$\mathrm{Ph_5Sb + 2\ HF \longrightarrow Ph_3SbF_2 + 2\ PhH}$$

The interaction of antimony pentafluoride and toluene, fluorobenzene, or chlorobenzene gave only *para*-substituted diarylantimony trifluorides and triarylantimony difluorides. This fact provided further evidence that antimony pentafluoride reacted as an electrophile, presumably a rather bulky one. The reaction of bromobenzene with antimony pentafluoride gave diphenylantimony trifluoride instead of the expected *para*-substituted derivatives, while *p*-bromotoluene and antimony pentafluoride yielded no organoantimony compounds at all. It was concluded that the σ-complex I (formed from bromobenzene and antimony pentafluoride) rearranged to II that acted as a brominating agent:



Of the three isomeric fluorotoluenes, only *o*-fluorotoluene yielded organoantimony compounds, *viz.* tris(3-fluoro-4-tolyl)antimony difluoride and bis-(3-fluoro-4-tolyl)antimony trifluoride. *o*-Dichlorobenzene and *o*-difluorobenzene also reacted with antimony pentafluoride to yield the expected 3,4-dihalophenyl derivatives.

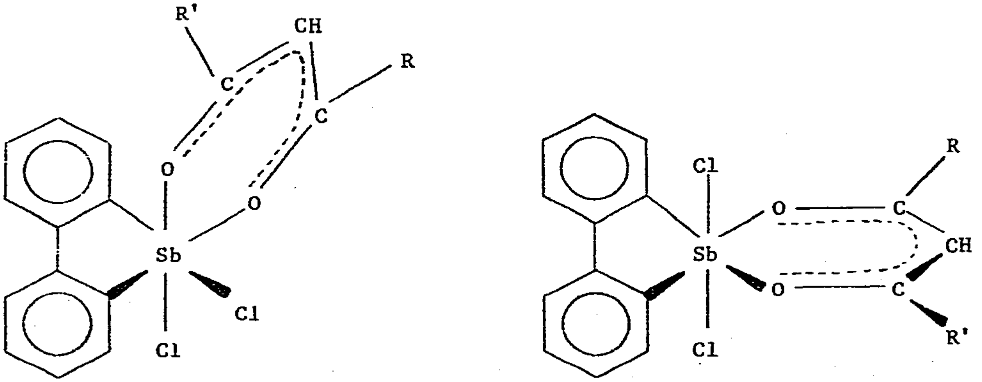
The structure of diphenylantimony trichloride has long been in doubt, in part because authors have often not been clear as to whether they had used the anhydrous substance or the monohydrate, $Ph_2SbCl_3 \cdot H_2O$. The anhydrous material has now unambiguously been shown by means of single-crystal X-ray diffraction studies to exist in the solid state as a chlorine-bridged dimer [87]:



The Sb-Cl bonds in the four-membered ring were appreciably longer than the exocyclic Sb-Cl distances. The Sb-C distance of 2.125(9) Å differed only slightly from the distance of 2.152(11) Å reported for the hexacoordinated Sb-C bond in μ-carbonato-bis(tetraphenylantimony *(vide infra)*.

Several new hexacoordinate organoantimony(V) derivatives, *viz.* $[Me_4N][Ph_2SbCl_3X]$, where X was Cl, Br, or $N_3$, and $[Ph_4As][Ph_2SbCl_3NCS]$, have been prepared by the interaction of diphenylantimony trichloride hydrate and the appropriate tetramethylammonium or tetraphenylarsonium salt [88]. Molar conductivity measurements in acetone indicated that the diphenylantimonates were 1:1 electrolytes. The IR spectra of the compounds was characterized by very intense absorption at 270 $cm^{-1}$, which was assigned to a Sb-Cl stretching frequency. A band at 1985 $cm^{-1}$ in the spectrum of the NCS derivative indicated that this substance contained a Sb-N bond. It was suggested that the phenyl groups in all four compounds had a *trans* configuration.

Meinema and coworkers [89] have investigated the PMR benzene solvent shifts, $\delta(CCl_4)-\delta(C_6D_6)$, of several hexacoordinate dichloro-2,2'-biphenylyleneantimony(V) β-diketonates. These compounds have been shown to exist in *cis*- and *trans*-dichloro forms:



(where R and R' were either Me or $Me_3C$)

The observed solvent shifts were interpreted on the basis of a non-specific tangential approach of the benzene molecules to the electron-deficient sites of the solute. The data were also used to deduce an inductive substitutent constant ($\sigma_1$) of 0.48 for the 2,2'-biphenylylene group.

In connection with their studies of the use of organometallic compounds as analytical reagents, Benmalek and coworkers [90] have prepared a number of radiochemically labelled trialkyl- and triarylstibines by the reaction of Grignard reagents with antimony trichloride containing $^{124}SbCl_3$. The tertiary stibines thus obtained were converted by treatment with chlorine, bromine, or iodine to trialkyl- or triarylantimony dihalides:

$$R_3Sb + X_2 \longrightarrow R_3SbX_2$$

(where X was Cl, Br, or I)

The corresponding difluorides were prepared by dissolving one of the other dihalides in chloroform and extracting the solution with aqueous hydrofluoric acid. After about ten minutes agitation, the layers were separated and the difluoride was isolated by evaporating the chloroform solution to dryness. The yields were over 95%. The solubilities of the dihalides and some of the corresponding dihydroxides in benzene, chloroform, and carbon tetrachloride and the partition coefficients of the dihalides (between water and the organic solvents) were also determined. In addition, equilibrium constants for the following types of hydrolyses were measured:

$$R_3SbX_2 + OH^- \rightleftarrows R_3Sb(X)OH + X^-$$

$$R_3Sb(X)(OH) + OH^- \rightleftarrows R_3Sb(OH)_2 + X^-$$

In two other papers Benmalek and coworkers [91,92] have published a comparative study of the extraction of halide ions by a variety of organic and organometallic compounds. Included in this study were tetraphenyl-arsenic chloride, tetraphenylantimony bromide, triphenylarsenic dihalides, triphenylbismuth dihalides, and a number of triarylantimony dihalides. Although many of the compounds tested were able to extract halide ions selectively and quantitatively under certain conditions, it was concluded that the triphenylantimony derivatives were in general most useful. A fourth paper [93] from the same laboratory has described the selective and quantitative separation of fluoride ion by means of antimony-containing ion exchange resins. These resins were prepared by two methods. The first involved the interaction of triphenylstibine and chloromethylated polystyrene:

$$RCH_2Cl + Ph_3Sb \xrightarrow{AlCl_3} RCH_2Sb(Cl)Ph_3$$

(where R was polystyrene)

In the second method, triphenylstibine was converted to lithium diphenylstibide which was then condensed with the chloromethylated polystyrene:

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

$$RCH_2Cl + Ph_2SbLi \longrightarrow RCH_2SbPh_2 + LiCl$$

In the latter case, the antimony incorporated in the resin was subsequently converted to the Sb(V) state by means of hydrogen peroxide or iodine.

Goel and Ridley [94] have prepared trimethyl- and triphenylantimony diazides and diisocyanates by the metathetical reaction between the corresponding organoantimony dichlorides and sodium azide or silver cyanate. The diazides and diisocyanates were extremely sensitive towards hydrolysis, and stringent precautions to exclude moisture were required during the preparation and manipulation of these compounds. Hydrolysis yielded compounds containing Sb-O-Sb bonds:

$$2\ R_3SbX_2 + H_2O \longrightarrow (R_3SbX)_2O + 2\ HX$$

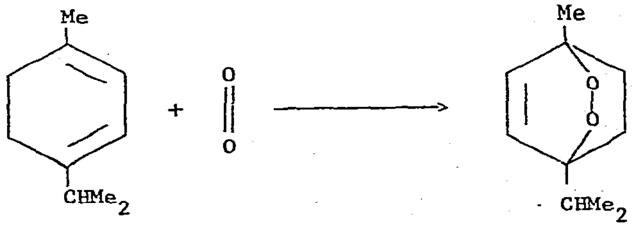
(where R was Me or Ph and X was $N_3$ or NCO)

Molecular weight measurements in benzene showed that the diazides and diisocyanates behaved as monomeric molecular species in this solvent. The molecular nature of the four compounds was further confirmed by electrical conductance measurements in acetonitrile solution. Vibrational (IR and Raman) spectra of the compounds were best interpreted in terms of $D_{3h}$ skeletal symmetry, and it was therefore concluded that the compounds possessed trigonal-bipyramidal coordination around the antimony with planar $SbC_3$ skeletons. Bands in the 300-400 $cm^{-1}$ region were found in the IR and Raman spectra of the four compounds and were attributed to Sb-N stretching vibrations.

Dahlmann and Winsel [95] have reported that the decomposition of peroxybis(triphenylantimony) dibromide in chlorobenzene at 45° proceeded mainly by the following reaction:

$$2\ (Ph_3BrSbO)_2 \longrightarrow 2\ (Ph_3SbBr)_2O + O_2$$

The decomposition was autocatalytic and was accelerated by the oxybis(triphenylantimony) dibromide formed in the reaction; it was not inhibited by the presence of radical traps. The authors suggested that the decomposition of the peroxide generated singlet oxygen. Thus, when the peroxide was allowed to decompose in chlorobenzene to which tetramethylethylene or α-terpinene had been added, there was practically no evolution of oxygen. Instead, the alkene yielded 3-hydroperoxy-2,3-dimethyl-1-butene, while the terpinene gave ascaridole:



Nevett and Perry [96] have derived equations relating the fundamental frequencies of vibration of molecules of the type $R_3SbX_2$ (where R was Me or Ph and X was F, Cl, Br, or I) to the molecular weight and moment of inertia of the molecule and the atomic mass and electronegativity of the halogen. The correlation coefficients of the equations were greater than 0.99. It was also found that the frequencies of the symmetric C-Sb and Sb-X stretching modes were linearly related to their respective asymmetric vibrations.

The $^{121}$Sb Mössbauer spectra of a number of organoantimony(V) derivatives have been determined with the source at 77° K and the absorber at 9° K [97]. Included in this study were compounds of the type $Ph_3SbX_2$ (where X was $ONO_2$, NCS, or $O_2CMe$) and of the type $Ph_4SbX$ (where X was Cl, OH, or NCS) as well as oxybis(triphenylantimony) chromate and diphenylantimony trichloride. The isomers shifts $\delta$ were in the range -4.1 to -7.0 mm/sec (relative to $Ba^{121}SnO_3$). All of the tri- and tetraphenylantimony compounds had negative quadrupole splittings $(e^2qQ)$ and asymmetry parameters $\eta$ not significantly different from zero; these results were best explained by assuming trigonal-bipyramidal geometry for these molecules with the X groups occupying apical positions. By using the data obtained in this investigation and in an earlier study of Long and coworkers [98], it was possible to show for the $Ph_3SbX_2$ compounds that there was an approximately linear correlation between the magnitude of the quadrupole splitting and the isomer shift:

$$\delta = -0.51\ e^2qQ - 16.20 \text{ mm/sec}$$

As the electronegativity of the anionic group X increased, the isomer shift $\delta$ increased (*i.e.* became less negative) and the absolute value of the quadrupole splitting $|e^2qQ|$ also increased. It was concluded that these trends were governed by changes in s-orbital occupancy due primarily to σ-bonding interactions. The Mössbauer parameters for oxybis(triphenylantimony) chromate deviated significantly from the linear relationship given above. This fact was explained by assuming that the presence of dissimilar groups at the apical positions caused a change in the hybridization at antimony. The $Ph_4SbX$ derivatives did not show a linear correlation between $\delta$ and $e^2qQ$, and it was noted that the apical ligands were also unlike in these compounds. There was, however, a general trend to a less negative $\delta$ with increasing electronegativity of X in the tetraphenylantimony compounds. The isomer shift of the hydroxide (-4.1 mm/sec) was, however, less negative than the shift of the fluoride, and the isomer shift of oxybis(triphenylantimony) chromate (-4.3 mm/sec) was less negative than the shifts of any of the $Ph_3SbX_2$ compounds. It was suggested that departures from predicted isomer shift behavior may be characteristic of Sb-O bonding. Two other isomer shift trends were noted: (1) the $\delta$ values of $Ph_3SbX_2$ derivatives were less negative than those of the corresponding $Me_3SbX_2$ compounds and (2) for a given X the isomer shift of $R_4SbX$ was less negative than that of $R_3SbX_2$. It was also possible to devise an additive method of predicting $^{121}Sb$ quadrupole splitting values in trigonal-bipyramidal organoantimony(V) compounds by assigning partial quadrupole splitting parameters to the various ligands. In sharp contrast to all the other compounds discussed in this paragraph, the quadrupole splitting of diphenylantimony trichloride had a large *positive* value (+ 25.9 mm/sec with $\eta$ constrained to zero). As noted above, the trichloride has been shown [87] by X-ray crystallography to be a derivative of hexacoordinate antimony.

Shenoy and Friedt [99] have reinvestigated the $^{121}Sb$ Mössbauer spectrum of trimethylantimony dibromide. They concluded that the previously reported intensity anomalies in the spectrum of this compound were not due to a large Goldanskii-Karyagin effect but arose primarily from absorber-thickness effects. They also showed that the apparent discrepancy between NQR and Mössbauer determinations of the quadrupole coupling constant disappeared if absorber-thickness effects were taken into account in the analysis of the Mössbauer spectrum.

Variations in the isomer shift and in the quadrupole interaction at the $^{121}$Sb nucleus in compounds of the type $Me_nSbX_{3-n}$ (where $n$ was 0, 1, 2, or 3 and X was Cl, Br, or I) have been discussed in terms of geometrical molecular parameters, changes in the ionic character of the antimony-ligand bonds, and varying degrees of intermolecular interactions [100]. Occurrence of such interactions was inferred from $^{127}$I measurements on antimony triiodide and methyldiiodostibine.

The $^{121}$Sb and $^{57}$Fe Mössbauer spectra of the $[(CF_3)_2Sb(Fe(CO)_2Cp)_2]^+$, $[PhSb(Fe(CO)_2Cp)_3]^+$, $[Ph_2Sb(Fe(CO)_2Cp)_2]^+$, $[Ph_3SbFe(CO)_2Cp]^+$, and $[Bu_3SbFe(CO)_2Cp]^+$ cations have been included in a study of a variety of cations containing Fe-Sb bonds [101]. The phenyl, diphenyl, and tri-$n$-butyl derivatives, which had not previously been described, were prepared by the following routes:

$$[PhSbCl_5][PyH] + 3\ NaFe(CO)_2Cp \longrightarrow$$

$$[PhSb(Fe(CO)_2Cp)_3]Cl \xrightarrow{NH_4PF_6} [PhSb(Fe(CO)_2Cp)_3][PF_6]$$

$$Ph_2SbCl_3 + 2\ NaFe(CO)_2Cp \longrightarrow [Ph_2Sb(Fe(CO)_2Cp)_2]Cl$$

$$\xrightarrow{NH_4PF_6} [Ph_2Sb(Fe(CO)_2Cp)_2][PF_6]$$

$$Bu_3Sb + ClFe(CO)_2Cp \longrightarrow [Bu_3SbFe(CO)_2Cp]Cl$$

$$\xrightarrow{NH_4PF_6} [Bu_3SbFe(CO)_2Cp][PF_6]$$

(where Py was pyridine and Cp was π-cyclopentadienyl)

The preparation of a cation containing the bis(trifluoromethyl)stibino group had been reported in an earlier paper [102]:

$$2(CF_3)_2SbI + [Fe(CO)_2Cp]_2 \longrightarrow [(CF_3)_2Sb(Fe(CO)_2Cp)_2][(CF_3)_2SbI_2]$$

The $^{121}$Sb isomer shifts of the organoantimony cations varied from -6.7 to -8.3 mm/sec (relative to a $Ba^{121}SnO_3$ source at 80° K). These values were considered less negative than those usually found for Sb(III) compounds but more negative than for typical Sb(V) compounds. It was concluded that the assignment of a particular oxidation state for antimony in these compounds had little justification. The $^{121}$Sb quadrupole coupling constant data suggested that an asymmetric distribution of electrons in the bonding orbitals made the dominant contribution to the electric field gradient at the antimony nucleus. A comparison of the $^{121}$Sb and $^{57}$Fe isomer shift data with the $^{119}$Sn and $^{57}$Fe shifts found in analogous tin compounds led to the conclusion that π-bonding was of more importance in the Fe-Sb than in the Fe-Sn linkage.

Allyl-substituted tertiary stibines have been cleaved by $FeCp(CO)_2Cl$ to yield compounds containing two Fe-Sb σ-bonds [103]:

$$CH_2{=}CHCH_2SbRR' + FeCp(CO)_2Cl \longrightarrow$$

$$[RR'Sb(Fe(CO)_2Cp)_2]Cl + CH_2{=}CHCH_2Cl + \textit{trans}\text{-}MeCH{=}CHCl$$

(where both R and R' were Me, Ph, or $CH_2{=}CHCH_2$ and where R was $CH_2{=}CHCH_2$ and R' was Me or Ph)

The complex antimony chlorides were yellow unstable compounds, which were readily converted to the corresponding tetraphenylborates. The latter compounds were stable in the solid state and decomposed only slowly in solution. The tertiary stibines used in this study were prepared by the interaction of allylmagnesium bromide and the appropriate secondary halostibine.

Malisch and Panster [104] have converted dimethylbromostibine to stable transition metal complexes by means of the following type of reaction:

$$[Cp(CO)_nM]Na + Me_2SbBr \longrightarrow Cp(CO)_nMSbMe_2 + NaBr$$

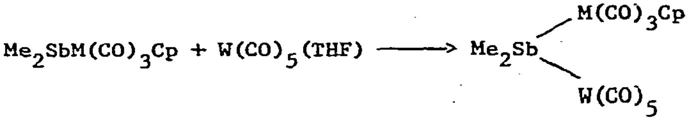
(where Cp was π-cyclopentadienyl, M was Fe, Cr, Mo, or W, and $n$ was 2 in the iron compounds and 3 in the other transition metal compounds)

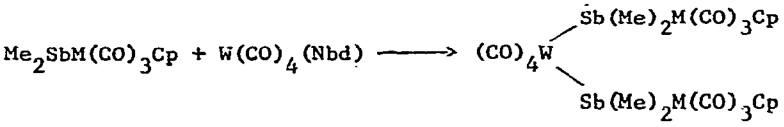
The complexes thus obtained were unexpectedly stable and were not affected by boiling in THF for 48 hours. A characteristic feature of the complexes was their ready reaction with halides to yield tertiary stibine derivatives:

$$RBr + Me_2SbW(CO)_3Cp \longrightarrow [RMe_2SbW(CO)_3Cp]Br$$

(where R was Me, $CH_2$=$CHCH_2$, or $PhCH_2$)

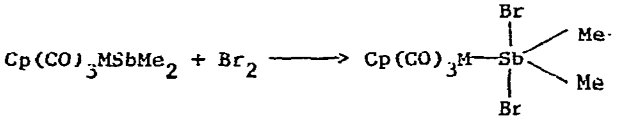
Other reactions gave complexes in which the $Me_2Sb$-group was present as a bridging unit:



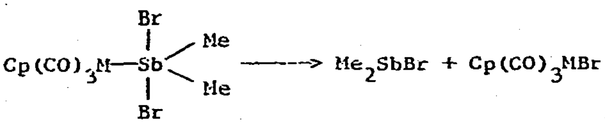


(where M was Cr, Mo, or W and Nbd was 2,5-norbornadiene)

In a second paper Malisch and Panster [105] reported that the mononuclear dimethylantimony complexes described in the above paragraph readily underwent oxidative addition of halogen:

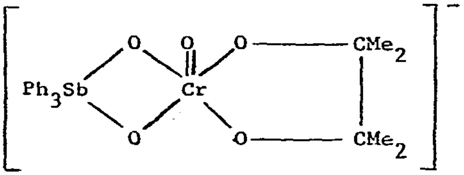


The antimony(V) complexes were monomeric in solution and, according to conductivity measurements, were only insignificantly dissociated. Decomposition under thermal or mass spectrometric conditions led to the elimination of dimethylbromostibine:



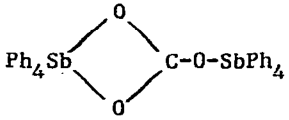
The rate of decomposition depended on the transition metal (Fe>>Mo>Cr>W). The adducts formed from the iron complexes were, in fact, too unstable for complete characterization. It was also possible to prepare bis-metalated antimony(V) dibromides, *e.g.* $MeSb[W(CO)_3Cp]_2Br_2$, but they were much less stable than the mononuclear adducts. The covalent nature of all the antimony(V) complexes depended on the presence of two halogen atoms per molecule. Their successive replacement by methyl or metal-containing groups yielded purely ionic products.

A new antimony-containing complex of chromium(V) has been studied by means of EPR spectroscopy [106]. The spectrum indicated that the complex probably had the following structure:



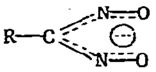
For the first time, additional hyperfine structure from $^{121}Sb$ and $^{123}Sb$ isotopes was observed in the EPR spectrum of a transition metal complex.

The first example of a molecule containing both penta- and hexacoordinated antimony has been reported by Ferguson and Hawley [107]. This substance, *viz.* μ-carbonato-bis(tetraphenylantimony), was obtained in an attempt to prepare a crystalline sample of triphenylantimony dihydroxide, $Ph_3Sb(OH)_2$, by bromination of triphenylstibine and subsequent hydrolysis or by treating triphenylstibine with hydrogen peroxide. Both methods gave material with identical IR spectra and with satisfactory analyses for the dihydroxide. When the material was allowed to recrystallize from chloroform, however, crystals were obtained that were shown to be $(Ph_4Sb)_2CO_3$. X-ray analysis demonstrated that one antimony atom had distorted octahedral coordination while the other antimony was in a slightly distorted trigonal-bipyramidal environment with a carbonato oxygen in an apical position. The two antimony polyhedra were linked by a planar bridging group containing four atoms:



At the hexacoordinate antimony, three of the phenyl carbons and one of the oxygens bonded to the antimony defined a basal plane while the fourth phenyl group and the remaining carbonato oxygen atom occupied the other two coordination sites of the distorted octahedron. The four Sb–C distances did not differ significantly from their mean value of 2.152(11)Å. At the pentacoordinate antimony, the average Sb–C (equatorial) distance of 2.120(11)Å was shorter, but not significantly, than the Sb-C(apical) distance of 2.153-(11)Å.

Kopf, Vetter, and Klar [108] have investigated the structure of the tetramethyl- and tetraphenylantimony derivatives of the 1,1-dinitrosoethane and α,α-dinitrosotoluene anions:



(where R was Me or Ph)

The tetramethylantimony derivatives were blue solids that dissolved in polar solvents to yield blue solutions. The electronic spectra of these solutions indicated that they contained free RC(NO)(NO) anions. In non-polar solvents, however, the tetramethylantimony derivatives gave yellow solutions and apparently existed as covalent, pentacoordinate antimony compounds. The tetraphenylantimony derivatives were yellow or light green even in the solid state and gave yellow solutions in most solvents. In methanol, however, the tetraphenylantimony derivative of the 1,1-dinitrosoethane anion did appear blue and probably was ionized under these conditions. An X-ray diffraction study showed that this derivative consisted in the solid state of discrete molecules in which the antimony had a slightly distorted trigonal-bipyramidal environment with an oxygen atom bonded to one of the apical positions. Its electronic spectra indicated that it had a similar structure when dissolved in benzene or pyridine. In contrast, the tetraphenylantimony derivative of the α,α-dinitrosotoluene anion exhibited electronic spectra (in benzene, chloroform, or methanol) that suggested that each antimony atom was coordinated to *two* oxygens. It was not clear as to whether the anion was behaving in this case as a chelating or bridging ligand.

Tetraphenylantimony bromide has been included in a study of the UV absorption and emission spectra of tetraphenyl derivatives of boron, carbon, silicon, germanium, tin, lead, phosphorus, arsenic, and antimony [109]. The absorption spectrum of the antimony compound in 95% ethanol at room temperature exhibited maxima at 253.7 nm(ε, 1965), 258.5 nm(ε, 2348), 264.1 nm(ε, 2629), and 270 nm(ε, 2011). In common with the absorption spectra of the other compounds, it had a broad, featureless band around 220 nm(ε, ∿30,000). Absorption spectra were also obtained at 77°K in a 5:5:2 mixture of ether, isopentane, and ethanol. The phosphorescence emission of tetraphenylantimony bromide and tetraphenyllead was red shifted from the other compounds by about 0.5 eV, an effect attributed to formation of a triplet excimer.

The dipole moment of triphenylstibonium tetraphenylcyclopentadienylide in benzene at 25° has been found to be only 2.2 D, a value considerably lower than the dipole moments of the arsenic (8.32 D) or phosphorus (7.75 D) analogs [110]. This result was entirely unexpected, since earlier work had suggested that the dipolar character of these ylids increased in the order Sb > As > P.

McEwen and Lin [111] have followed the solvolysis of tetraphenyl-*p*-tolylantimony in methanol, ethanol, and 2-propanol by measuring the rates of formation of benzene and toluene. These hydrocarbons were presumably produced by the following reactions:

$$\begin{tikzcd} & Ph_3(p\text{-}MeC_6H_4)SbOR + PhH \\ Ph_4(p\text{-}MeC_6H_4)Sb + ROH \arrow[ur] \arrow[dr] & \\ & Ph_4SbOR + MeC_6H_5 \end{tikzcd}$$

(where R was Me, Et, or $Me_2CH$)

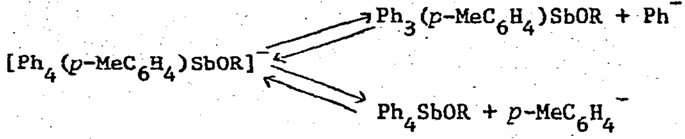
The relative rates of solvolysis in the three alcohols followed the sequence MeOH > EtOH >> $Me_2CHOH$. The ratio of benzene to toluene produced was 5.7 ± 0.3 in the reactions with methanol, 6.3 ± 0.3 with ethanol, and 4.3 ± 0.3 with 2-propanol. The effect of the conjugate bases of the alcohols on the rates of the reactions and on the ratios of the hydrocarbons formed was also investigated. It was concluded that the solvolysis reactions occurred via competing ionic mechanisms somewhat analogous to $S_N1$ and $S_N2$ displacements at carbon. In pure methanol or ethanol, the major reaction sequence appeared to consist of ionization of the tetraphenyl-*p*-tolylantimony and subsequent reactions of the ions with solvent:

$$\begin{tikzcd} & Ph_3(p\text{-}MeC_6H_4)Sb^+,\ Ph^- \arrow[r, "ROH"] & Ph_3(p\text{-}MeC_6H_4)SbOR + PhH \\ Ph_4(p\text{-}MeC_6H_4)Sb \arrow[ur, shift left] \arrow[dr, shift left] & & \\ & Ph_4Sb^+,\ p\text{-}MeC_6H_4^- \arrow[r, "ROH"] \arrow[ul, shift left] & Ph_4SbOR + MeC_6H_5 \end{tikzcd}$$

(where R was Me or Et)

This type of behavior was designated the $S_N1(Sb)$ mechanism. A second pathway, designated the $S_N2$(Sb-ate) mechanism, involved the formation of an "ate" complex and appeared to be important when the solvolysis reactions were carried out in 2-propanol or in the presence of sodium alkoxides:

$$Ph_4(p\text{-}MeC_6H_4)Sb + RO^- \rightleftarrows [Ph_4(p\text{-}MeC_6H_4)SbOR]^-$$



$$[Ph_4(p\text{-}MeC_6H_4)SbOR]^- \rightleftharpoons Ph_3(p\text{-}MeC_6H_4)SbOR + Ph^-$$

$$[Ph_4(p\text{-}MeC_6H_4)SbOR]^- \rightleftharpoons Ph_4SbOR + p\text{-}MeC_6H_4^-$$

The carbanions formed in these reactions subsequently reacted with the alcohol to yield the corresponding alkoxide ion and the aromatic hydrocarbons. The role of radical reactions in the solvolyses was ruled out by showing that the addition of known radical inhibitors had no effect on the rates of formation of the aromatic hydrocarbons.

In a second paper McEwen and Lin [112] have described the reactions of pentaphenylantimony and tetraphenyl-*p*-tolylantimony with carbon tetrachloride. The major products obtained with pentaphenylantimony were tetraphenylantimony chloride (67.3%), chlorobenzene (33.3%), hexachloroethane (21.9%), and biphenyl (21.4%). Other products identified were benzene (8.5%), chloroform (1.7%), and a trace of benzotrichloride. Analogous results were observed with tetraphenyl-*p*-tolylantimony. The aryl halides isolated from these reactions were shown to have been formed via a radical chain process initiated by the generation of a phenyl (or *p*-tolyl) radical from the pentaarylantimony compound. The following chain-propagating steps (for pentaphenylantimony) were suggested:

$$Ph\cdot + CCl_4 \longrightarrow PhCl + \cdot CCl_3$$

$$Ph_5Sb + \cdot CCl_3 \longrightarrow Ph_5(CCl_3)Sb\cdot$$

$$Ph_5(CCl_3)Sb\cdot \longrightarrow Ph_4SbCCl_3 + Ph\cdot$$

Evidence was presented that the tetraphenylantimony chloride was formed by the decomposition, with loss of dichlorocarbene, of the (trichloromethyl)-tetraphenylantimony produced in the third chain-propagating steps given above:

$$Ph_4SbCCl_3 \longrightarrow Ph_4SbCl + CCl_2$$

The formation of hexachloroethane by the interaction of dichlorocarbene and carbon tetrachloride was also demonstrated:

$$CCl_2 + CCl_4 \longrightarrow 2 \cdot CCl_3 \longrightarrow CCl_3CCl_3$$

The rate of formation of benzene from pentaphenylantimony and of benzene plus toluene from tetraphenyl-*p*-tolylantimony was not significantly changed by access of air or light to the reaction mixture or by the presence of diphenylpicrylhydrazyl or dibenzoyl peroxide. It was concluded, therefore, that these hydrocarbons were produced by an ionic process that competed with the radical chain process. The biaryls isolated from the reaction mixtures were apparently formed in at least two ways:

(1) A small amount was the result of one of the chain-terminating steps of the radical process leading to the aryl chlorides.

(2) A larger amount probably resulted from an intramolecular decomposition that did not involve free radicals:

$$Ar_5Sb \longrightarrow Ar_3Sb + Ar\text{-}Ar$$

The tertiary stibines formed by this reaction could not be isolated, and it was suggested that they were consumed by still other reactions.

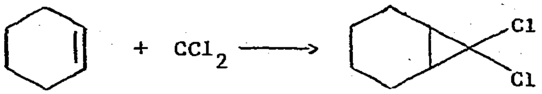
Nesmeyanov and coworkers [113] have also investigated the reaction of pentavalent organoantimony compounds with polyhalomethanes. They reported that the main products of the interaction of penta-*n*-butylantimony and carbon tetrachloride in the presence of cyclohexene at 100° were *n*-butyl chloride, 7,7-dichloronorcarane, and tetra-*n*-butylantimony chloride. Chloroform and tri-*n*-butylantimony dichloride were also isolated from the reaction mixture. It was suggested that the reaction may have proceeded via the following scheme:

$$Bu_5Sb \longrightarrow Bu^{\bullet} + Bu_4Sb^{\bullet}$$

$$Bu^{\bullet} + CCl_4 \longrightarrow BuCl + {}^{\bullet}CCl_3$$

$$Bu_4Sb^{\bullet} + {}^{\bullet}CCl_3 \longrightarrow Bu_4SbCCl_3$$

$$Bu_4SbCCl_3 \longrightarrow Bu_4SbCl + CCl_2$$



Under similar conditions, a mixture of penta-*n*-butylantimony, chloroform, and cyclohexene reacted to give 7,7-dichloronorcarane, tetra-*n*-butylantimony chloride, butane, and traces of tri-*n*-butylantimony dichloride.

In sharp contrast to the square-pyramidal structure of non-solvated pentaphenylantimony, the cyclohexane solvate $Ph_5Sb{\cdot}1/2C_6H_{12}$ has been shown by X-ray data to possess a virtually undistorted trigonal-bipyramidal configuration around the antimony atom [114]. The C-Sb equatorial bond length average (2.14 Å) was significantly shorter than the axial C-Sb average (2.24 Å). The cyclohexane molecule was situated halfway along the *a* axis and made no special contacts with neighboring molecules. It was concluded that variations in lattice energy were responsible for the differences between the structures of solvated and non-solvated pentaphenylantimony.

Kok [115] has carefully examined the IR and Raman spectra of pentaphenylarsenic and pentaphenylantimony both in the solid state and in dichloromethane or dibromomethane solution. Analysis of the phenyl-metal vibrations confirmed the conclusions of an earlier study [116] that the antimony compound possessed square-pyramidal geometry in solution as well as in the solid state while the arsenic compound was trigonal-bipyramidal in both phases.

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