ANTIMONY

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The first supplement to Dub's *Compounds of Arsenic, Antimony, and Bismuth, 1937-1964,* appeared in 1972 and covered the literature from 1965 to 1968 devoted to synthetic methods, physical properties, chemical reactions, and uses of organometallic compounds of the three elements [1]. Crow and Cullen [2], in a chapter of a new series of books on inorganic chemistry, have written a critical review of recent work on organoarsenic, -antimony, and -bismuth compounds. A number of other reviews have been published in which certain aspects of organoantimony chemistry were briefly mentioned. The subjects discussed in these publications included: the preparation of organoantimony compounds via diazonium, iodonium, bromonium, or chloronium salts [3], organoantimony compounds containing Sb-Sn bonds [4], trialkylstibine oxides, sulfides, and selenides [5], the reaction of trialkylstibines with free radicals [6], the conversion of Grignard reagents to tertiary stibines [7], the pyrolysis of trimethylstibine [8], the donor properties of tertiary stibines [9,10], and the use of organic derivatives of antimony as therapeutic agents [11]. Organoantimony compounds have also been discussed in a review by Nesmeyanov [12] of his work in organometallic chemistry.

In continuation of their studies on the addition of organometallic hydrides to suitably substituted alkynes, Nesmeyanov and coworkers [13] have investigated the following reaction:

$$Ph_2SbH + FcC{\equiv}CH \rightarrow FcCH{=}CHSbPh_2$$

(where Fc was ferrocenyl)

The reaction was carried out at 0° and gave a 32% yield of tertiary stibine. The IR spectrum of the reaction product indicated that it was a mixture of *cis* and *trans* isomers.

Laskorin and Yakshin [14] have studied the conjugative interaction of the carbonyl group and the heteroatom in acetyl derivatives of the type R_2ECOMe, where R was Me, CMe_3, or Ph and E was N, P, As, or Sb. The phosphorus, arsenic, and antimony compounds (which were considered analogs of N, N-disubstituted amides) were prepared by the addition of a secondary phosphine, arsine, or stibine to ketene:

$$R_2EH + CH_2=C=O \rightarrow R_2ECOMe$$

The chemical and spectral properties of the acetyl derivatives have been discussed in considerable detail under Arsenic. The formation of a bicyclic tertiary stibine by the addition of hexafluoro-2-butyne to stibabenzene (antimonin) has been described under Bismuth [15].

Becker and Nöth [16] have reported that bis(dimethylamino)chloroborane reacted with lithium diethylstibide (prepared from diethylstibine) to yield a monomeric stibinoborane:

$$(Me_2N)_2BCl + LiSbEt_2 \rightarrow (Me_2N)_2BSbEt_2 + LiCl$$

Monomeric phosphino- and arsinoboranes were obtained in a similar manner. The NMR (^1H and ^{11}B) spectra of the new borane derivatives were recorded and analyzed.

Sodium in liquid ammonia has been used to cleave tertiary stibines of the type Ph_2RSb (where R was Et, Me_2CH, or $PhCH_2$) and PhMeRSb (where R was Me, Et, Me_2CH, or $PhCH_2$) [17]. In every case, alkyl group cleavage was observed, although the reaction of diphenylethylstibine with sodium exhibited both alkyl-antimony and phenyl-antimony cleavage:

$$Ph_2EtSb + 2Na \rightarrow Ph_2SbNa + EtNa$$

and

$$Ph_2EtSb + 2Na \rightarrow PhEtSbNa + PhNa$$

The stibides formed in the cleavage reactions were not isolated but were allowed to react with alkyl halides to form tertiary stibines. In two cases mixtures of tertiary stibines were obtained:

$$Ph_2EtSb \xrightarrow[2.MeCl]{1.Na,NH_3} Ph_2MeSb + PhEtMeSb$$

$$PhEtMeSb \xrightarrow[2.PhCH_2Cl]{1.Na,NH_3} PhEt(PhCH_2)Sb + PhMe(PhCH_2)Sb$$

The cleavage of two di-tertiary stibines was also investigated. The reaction of methylenebis(diphenylstibine) with sodium resulted in cleavage of the CH_2-Sb linkage:

$$Ph_2SbCH_2SbPh_2 \xrightarrow[2.MeCl]{1.Na,NH_3} Ph_2MeSb$$

When trimethylenebis(diphenylstibine) was used, however, one of the phenyl groups attached to each antimony atom was cleaved.

As noted in the above paragraph, alkyl group cleavage was always observed when certain diphenylalkyl- or phenyldialkylstibines were allowed to react with sodium in liquid ammonia. In sharp contrast to these results, the reaction of diphenylmethylstibine resulted in apparently exclusive cleavage of a phenyl group [18]:

$$Ph_2MeSb + 2Na \rightarrow PhMeSbNa + PhNa$$

The stibide obtained in this manner was used to prepare asymmetric tertiary and di-tertiary stibines:

$$\mathrm{PhMeSbNa + RCl \rightarrow PhMeRSb + NaCl}$$

(where R was Et, Me_2CH, or $PhCH_2$)

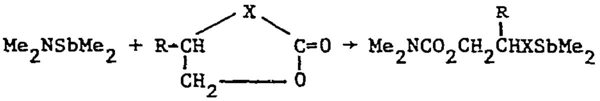
and

$$\mathrm{PhMeSbNa + Cl(CH_2)_{\mathit{n}}Cl \rightarrow PhMeSb(CH_2)_{\mathit{n}}SbMePh}$$

(where n was 1,3, or 4)

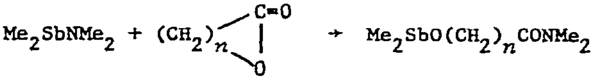
Since pyramidal inversion of trivalent antimony compounds does not occur under ordinary conditions, the PMR spectrum of phenylmethylbenzylstibine showed an AB quartet for the benzyl methylene group. Similarly, the isopropyl methyl groups in phenylmethylisopropylstibine gave two doublets. In methylenebis(phenylmethylstibine) a singlet and an AB quartet were observed for the methylene groups. These signals were attributed to the *racemic* and *meso* forms of the compound, respectively.

Koketsu and co-workers [19] have found that dimethylaminodimethylstibine readily reacted with cyclic carbonates or thiolocarbonates by addition of the Sb-N bond across the oxygen-carbonyl or sulfur-carbonyl bond:



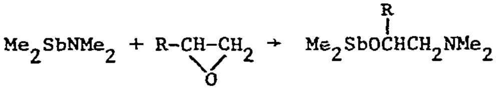
(where R was H or Me and X was O or S)

The reactions took place exothermally at room temperature, and the products were isolated by distillation under reduced pressure. Treatment of the adducts with water gave alcohols or thiols of the type $Me_2NCO_2CH_2CH(R)XH$. The reaction of dimethylaminodimethylstibine with lactones (β-propiolactone or γ-butyrolactone) took place in refluxing ether and yielded insertion products resulting from acyl-oxygen fission:



(where n was 2 or 3)

Epoxides were cleaved by heating with dimethylaminodimethylstibine at 55° for two hours:



$$Me_2SbNMe_2 + R\text{-}\underset{O}{CH\text{-}CH_2} \rightarrow Me_2SbO\overset{R}{C}HCH_2NMe_2$$

(where R was CCl_3 or Ph)

Hydrolysis of the adducts obtained from lactones and epoxides gave the corresponding alcohols. The structures of all of the adducts and their hydrolysis products were confirmed by elementary analyses, IR, and PMR data.

Two new aryldimethylstibines have been prepared by the following sequence of reactions [20]:

$$Me_3Sb + Br_2 \rightarrow Me_3SbBr_2$$

$$Me_3SbBr_2 \xrightarrow[100\ Torr]{105°} Me_2SbBr + MeBr$$

$$ArMgBr + Me_2SbBr \rightarrow ArSbMe_2 + MgBr_2$$

(where Ar was *m*- or *p*-$MeOC_6H_4$)

The tertiary stibines thus obtained were quaternized with methyl iodide and were thoroughly characterized through IR, PMR, and mass spectra.

In an investigation of the chemical properties of silver acetylides, Gol'ding and Sladkov [21] found that silver phenylacetylide reacted smoothly with the trichlorides of phosphorus, arsenic, and antimony in the following manner:

$$3PhC{\equiv}CAg + ECl_3 \rightarrow (PhC{\equiv}C)_3E + 3AgCl$$

(where E was P, As, or Sb)

The reactions were carried out at 50° in a 2:1 mixture of benzene and THF. The yield of tris(phenylethynyl)stibine thus obtained was 52%.

Price and Richard [22] have investigated the pyrolysis of trimethylstibine in a toluene carrier flow system over the temperature range 690-803°K

The progress of the reaction was followed by measuring the amount of methane, ethane, and ethylbenzene formed. In a number of experiments the quantity of undecomposed trimethylstibine was also determined and was found to be in agreement with that expected from the analysis of the other products if it were assumed that three methyl radicals were released for each molecule of trimethylstibine undergoing decomposition. Deuterium labeling led to the conclusion that regeneration of the trimethylstibine was occurring in some experiments:

$$\mathrm{Me} + \mathrm{Me_2Sb} \rightarrow \mathrm{Me_3Sb}$$

This regeneration reaction was effectively suppressed by using toluene pressures greater than 150 mm. Least squares analysis of the results obtained under such conditions gave the following relationship:

$$\log_{10}k/\mathrm{s}^{-1} = 15.33 - (55{,}900 \pm 1{,}000)/2.3RT$$

It was concluded that the observed activation energy was a good approximation of $D[\mathrm{Me_2Sb{-}Me}]$ and that the main steps in the decomposition of trimethylstibine could be represented by the following equations:

$$(1)\ \mathrm{Me_3Sb} \rightarrow \mathrm{Me_2Sb} + \mathrm{Me}$$

$$(2)\ \mathrm{Me_2Sb} \rightarrow \mathrm{MeSb} + \mathrm{Me}$$

$$(3)\ 2\mathrm{MeSb} \rightarrow \mathrm{Me_2Sb} + \mathrm{Sb}$$

A coordination compound of trimethylgallium and triethylstibine has been prepared by direct reaction of the components at room temperature [23]:

$$\mathrm{Me_3Ga} + \mathrm{Et_3Sb} \rightarrow \mathrm{Me_3Ga{\cdot}SbEt_3}$$

The reaction was exothermic and led to a virtually quantitative yield of the product. The coordination compound was considerably less reactive than the starting materials. Thus, it was stable in air and only weakly hydrolyzed by water and acids.

The ^{121}Sb and ^{123}Sb NQR spectra of trimethylstibine, *trans*-tris(2-chlorovinyl)stibine, bis(diphenylstibino)acetylene, and diphenylchlorostibine have been determined at 77°K [24]. The latter two compounds were found to have larger quadrupole splittings than the symmetrical tertiary stibines and much larger asymmetry parameters. These results were explained by assuming that the presence of unlike substituents bonded to the antimony caused a highly asymmetric electron distribution around the antimony atom.

Brill and Long [25] have recorded the arsenic, antimony, chlorine, and bromine NQR spectra of a number of triarylarsines and -stibines. The antimony compounds included tris(pentafluorophenyl)stibine and compounds of the type $(XC_6H_4)_3Sb$, where X was H, *o*-Me, *m*-Me, *p*-Me, *p*-F, *p*-Cl, or *p*-CF_3. The arsenic NQR data indicated that interaction between the arsenic atom and the π-system of the rings was significant and was an efficient mechanism for the transmission of the electronic effects of the substituents. In the antimony compounds, however, both the σ and π networks appeared to be important in the transmission of substituent effects. These results have been discussed more fully under Arsenic. We have also mentioned under Arsenic papers containing information on the vibrational spectra of tri-1-propynylstibine [26] and tris(trifluoromethyl)stibine [27], the mass spectra of tertiary stibines [28,29], the proton-accepting properties of trivalent organoantimony compounds in hydrogen bonding [30], a quantum mechanical analysis of the chemical and optical properties of triphenylstibine [31], and a method for the microdetermination of antimony in organoantimony compounds [32].

The interaction of methylenebis(dichlorostibine) and *p*-tolylmagnesium bromide in the presence of N,N,N',N'-tetramethylethylenediamine has been used to prepare a new di-tertiary stibine [33]:

$$(Cl_2Sb)_2CH_2 + 4p\text{-}MeC_6H_4MgBr \rightarrow [(p\text{-}MeC_6H_4)_2Sb]_2CH_2 + 4MgBrCl$$

This compound, as well as methylenebis(diphenylstibine), reacted with chromium, molybdenum, and tungsten hexacarbonyls to give monosubstituted complexes of the type $M(CO)_5(Ar_2Sb)_2CH_2$, where M was Cr, Mo, or W and Ar was Ph or p-MeC_6H_4. Similarly, the reaction of methylenebis(diphenylstibine) and iron pentacarbonyl gave $Fe(CO)_4(Ph_2Sb)_2CH_2$. In contrast to these results methylenebis(dimethylstibine) gave the complexes $[M(CO)_5]_2(Me_2Sb)_2CH_2$ (where M was Mo or W) and $[Fe(CO)_4]_2(Me_2Sb)_2CH_2$. From molecular weight, PMR, and IR data, it was concluded that the methylenebis(diarylstibines) behaved as monodentate ligands in these complexes, while methylenebis(dimethylstibine) appeared to be a bridging ligand.

Baracco and McAuliffe [34] have synthesized the quadridentate ligand tris(*o*-dimethylarsinophenyl)stibine (sbtas) by means of the following reaction sequence:

$$o\text{-}Me_2AsC_6H_4Br + BuLi \rightarrow o\text{-}Me_2AsC_6H_4Li + BuBr$$

$$3o\text{-}Me_2AsC_6H_4Li + SbCl_3 \rightarrow (o\text{-}Me_2AsC_6H_4)_3Sb + 3LiCl$$

The ligand thus obtained was a white solid, the PMR spectrum of which exhibited a single methyl resonance at $\tau 8.80$. It formed pentacoordinate, trigonal-bipyramidal complexes of the type [Pd(sbtas)X]Y, where X was Cl, Br, I, or SCN and Y was Cl, CNS, or BPh_4.

Bowen, Garrou, and Long [35] have investigated the ^{121}Sb and ^{57}Fe Mössbauer spectra of two triphenylstibine-substituted iron carbonyls, *viz.* $Ph_3SbFe(CO)_4$ and $(Ph_3Sb)_2Fe(CO)_3$. They found that there was a large increase in the ^{121}Sb isomer shift when triphenylstibine was converted to these complexes. It was concluded that the observed increase in isomer shift was consistent with the removal of about 0.26 5*s* electron from the antimony atom. The shift upon complexing was in fact large enough to correspond to a change from Sb(III) to Sb(V). The ^{57}Fe Mössbauer results agreed with the conclusion that the Fe-Sb linkage in the complexes was probably a sigma bond.

There were numerous papers published that described the use of tertiary stibines as ligands in transition metal complexes. The metals coordinated to the antimony in these complexes included chromium [33,36], cobalt [37,38], gold [39], iron [33,35,40,41], manganese [42], molybdenum [33,36], nickel [43] osmium [44], palladium [34,45], platinum [46], rhenium [47], rhodium [48,49], ruthenium [50, 51], vanadium [52], and tungsten [33,36].

A Japanese patent [53] has claimed that the conversion of a mixture of bis(hydroxyethyl) terephthalate and terephthalic acid to transparent, heat-stable poly(ethylene terephthalate) was aided by small amounts of a trialkylstibine. A German patent [54] has similarly reported the use of triphenylstibine or triphenylbismuthine as a catalyst for the condensation of azelaic acid and bis(*p*-aminophenyl) sulfone to a polyamide copolymer. The production of fibers containing onium groups by the treatment of brominated poly(vinyl alcohol) fibers with triethylstibine, triethylphosphine, trimethylamine, or bis(2-hydroxyethyl) sulfide has been described in the Russian literature [55].

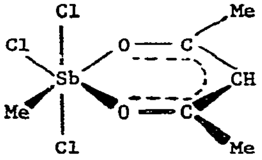
Meinema and coworkers [56] have studied the stereochemistry of (acetylacetonato)organoantimony(V) complexes of the type $R_nSbCl_{4-n}Acac$, where R was Me, Et, or Ph and n was 1,2,3, or 4. The previously unknown triphenylantimony derivative was prepared by the reaction of acetylacetone and methoxychlorotriphenylantimony in benzene:

$$MeCOCH_2COMe + Ph_3SbClOMe \rightarrow Ph_3SbClAcac + MeOH$$

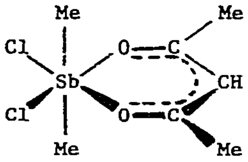
It could also be obtained by the interaction of the sodium salt of acetylacetone with triphenylantimony dichloride:

$$NaAcac + Ph_3SbCl_2 \rightarrow Ph_3SbClAcac + NaCl$$

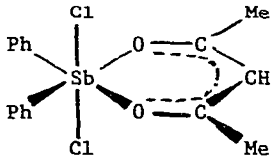
Attempts to prepare (acetylacetonato)chlorotrimethylantimony by a similar procedure were, however, unsuccessful. The presence of a bidentate Acac ligand in every complex was shown by the absence of a free carbonyl absorption in the IR spectrum. Since the complexes had been found to be monomeric in benzene, it was concluded that the antimony was hexacoordinate in these compounds. (The previously reported [57] presence of a C=O absorption in the IR spectrum of Ph_2SbCl_2Acac was, presumably, due to an impurity.) The PMR spectra of the $RSbCl_3Acac$ compounds exhibited two distinct Acac-Me signals and hence suggested the following octahedral geometry:



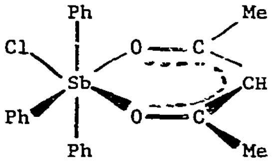
Dipole moment data were consistent with the presence of two axial chloro substituents in these complexes. The presence of only one singlet due to the Acac-Me protons in the PMR spectrum of Me_2SbCl_2Acac showed that this complex had a symmetrical configuration. Since IR spectral data suggested the presence of *cis*-dichloro groups, the following structure was proposed:



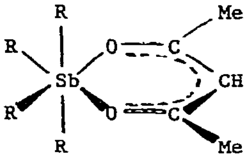
This structure was further corroborated by the relatively high dipole moment of 6.4D observed in benzene solution. In contrast with the results obtained with Me_2SbCl_2Acac, the PMR spectrum of Ph_2SbCl_2Acac showed two sets of singlets (with an intensity ratio of 5:2) for the Acac-CH and Acac-Me protons This observation was explained by assuming the presence of two isomers, each of which possessed a symmetric structure. It was concluded from dipole moment data that the more abundant isomer had a *trans*-diphenyl configuration (analogous to the dimethyl compound illustrated above) and that the less abundant isomer had the following *cis*-diphenyl configuration:



(In a later paper discussed below, Meinema and Noltes [58] reported that the PMR spectrum of a freshly prepared benzene solution of Ph_2SbCl_2Acac showed only the signals of the *trans*-diphenyl isomer. In addition, two groups of workers [59,60] have established by three-dimensional X-ray diffraction analysis that crystalline Ph_2SbCl_2Acac had the *trans*-diphenyl configuration.) The PMR spectrum of $Ph_3SbClAcac$ displayed only one Acac-CH signal and indicated, therefore, the presence of only one configuration. At room temperature only one Acac-Me signal was also observed. Below 5°, however, the Me singlet was transformed into a doublet with 4.2 Hz separation. Accordingly, it was concluded that this compound existed in the following asymmetric configuration:

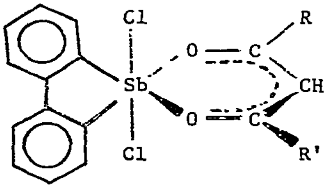


PMR analysis of $R_4SbAcac$ (where R was Me or Ph) showed the presence of two axial and two equatorial R groups:



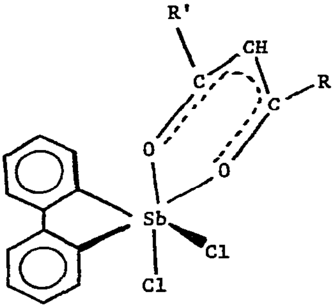
Nishii and Okawara [61] have prepared and investigated the stereochemistry of a series of dihalodiaryl(acetylacetonato)antimony(V) compounds of the type $(p\text{-}YC_6H_4)_2SbX_2Acac$, where X was F, Cl, or Br and Y was O_2N, Cl, H, Me, or MeO. The IR absorption bands due to the acetylacetonato groups were characteristic of chelated metal acetylacetonates. In addition, the presence of a strong Sb-O band at a similar position for the both the solid state and in chloroform solution and the monomeric nature of these compounds in chloroform clearly indicated that the antimony atom was hexacoordinated in both states. The PMR spectra of the compounds showed that each of them existed in a variety of solvents as a mixture of two isomers, both with chelated hexacoordinated configurations. The equivalence of both acetylacetonato methyl groups in every case showed that both isomers possessed symmetric structures. It was concluded that one isomer had a *trans*-diaryl configuration while the other isomer had a *cis*-diaryl configuration. Equilibrium between the two isomers was readily established. A line-shape analysis indicated that the two isomers of Ph_2SbF_2Acac isomerized above 100° in 1,1,2,2-tetrachloroethane at a rate which was rapid on the PMR time scale. The intensity ratio of the higher field Acac-Me proton resonance to that at lower field was found to increase with the polarity of the solvent. Since the *trans*-diphenyl isomer was thought to be more polar than the *cis*-diphenyl isomer, the higher field resonance was attributed to the *trans* compound. Meinema and coworkers [56], it should be noted, have come to similar conclusions.

As discussed in the above paragraphs the existence of geometric isomers of Ar_2SbX_2Acac has been demonstrated in two laboratories by PMR techniques. Meinema and Noltes [58] have also published preliminary information on the related diphenyl complexes Ph_2SbCl_2Dpm and Ph_2SbCl_2Pac (where Dpm was $Me_3CCOCHCOCMe_3$ and Pac was $Me_3CCOCHCOMe$) as well as the corresponding 2,2'-biphenylylene complexes of Acac, Dpm, and Pac. All complexes were shown to be monomeric in benzene and to contain bidentate β-diketonate ligands. The PMR spectrum of Ph_2SbCl_2Dpm in deuterochloroform showed two sets of signals (with an intensity ratio of 18:1) for the *tert*-butyl and the ring CH protons of the Dpm ligand. By analogy with the results obtained with Ph_2SbCl_2Acac, it was assumed that two isomers were present and that the more abundant isomer had the *trans*-diphenyl configuration while the less abundant isomer had the *cis*-diphenyl configuration. When the chloroform solution of Ph_2SbCl_2Dpm was heated for one minute or allowed to stand at room temperature for an hour, an equilibrium mixture was obtained in which the ratio of *trans*-diphenyl to *cis*-diphenyl isomer was about 5:4. A freshly prepared solution of Ph_2SbCl_2Dpm in benzene-d_6 showed only the presence of the *trans*-diphenyl isomer. Heating for 1-2 minutes at 80° or allowing to stand for 24 hours gave an equilibrium mixture in which the ratio of *trans* to *cis* was about 2:3. Analogous results were obtained with Ph_2SbCl_2Pac. It was concluded that Ph_2SbCl_2Dpm and Ph_2SbCl_2Pa adopted the *trans*-diphenyl configuration in the crystalline state but showed geometrical isomerism in solution. The 2,2-biphenylylene complexes were also shown to exhibit geometrical isomerism. In freshly prepared benzene-d_6 solutions of the Acac and Dpm complexes, only the following *trans*-dichloro configuration was present:



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

Isomerization was rapid, however, and led to an equilibrium mixture which contained the above *trans*-dichloro isomer and the following *cis*-dichloro isomer:



Aged solutions of the 2,2'-biphenylene complex of Pac showed three CH, three Me, and three Me_3C signals and hence contained three isomers. One isomer (which was present alone in freshly prepared solutions) had a *trans*-dichloro configuration in which R was Me and R' was Me_3C. The other two isomers had a *cis*-dichloro configuration in which R was Me and R' was Me_3C or R was Me_3C and R' was Me.

Mackor and Meinema [62] have measured PMR benzene solvent shifts ($\Delta^{CCl_4}_{C_6D_6}$ and $\Delta^{CDCl_3}_{C_6D_6}$) for the acetylacetonato protons of $SbCl_4Acac$, $RSbCl_3Acac$ (where R was Me, Et, or Ph), R_2SbCl_2Acac (where R was Me, Et, or Ph), $Ph_3SbClAcac$, and $R_4SbAcac$ (where R was Me or Ph). The observed values correlated better with the inductive effect of the groups bonded to the antimony atom than with the molecular dipole moments of the compounds. Steric influences on the benzene solvent shifts were also demonstrated. Thus, successive replacement of the Acac-Me groups in Ph_2SbCl_2Acac by *tert*-butyl groups led to decreasing accessibility of the Acac-CH proton and hence to a striking reduction in its solvent shift.

Meinema and Noltes [63] have prepared a series of thermally stable dialkylantimony(V) compounds of the type R_2SbX_3, where R was Me, Et, Pr, or Bu and X was OMe, OEt, or OCOMe. The trialkoxy derivatives were obtained by converting the appropriate dialkylbromostibine to a tribromide and then adding a sodium alkoxide:

$$R_2SbBr + Br_2 \xrightarrow{-20° \text{ to } -40°} R_2SbBr_3$$

$$R_2SbBr_3 + 3NaOR' \xrightarrow{-20° \text{ to } -40°} R_2Sb(OR')_3 + 3NaBr$$

This procedure gave the trimethoxy compounds in yields up to 70%. The triethoxy compounds, however, were more conveniently prepared by exchange between the trimethoxy compounds and excess ethanol:

$$R_2Sb(OMe)_3 + 3EtOH \rightarrow R_2Sb(OEt)_3 + 3MeOH$$

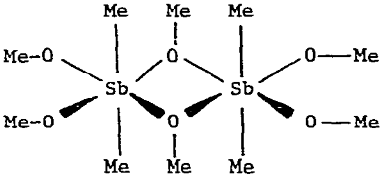
The triacetoxy compounds were obtained by the addition of an excess of acetic acid to the trimethoxy compounds:

$$R_2Sb(OMe)_3 + 3MeCO_2H \rightarrow R_2Sb(O_2CMe)_3 + 3MeOH$$

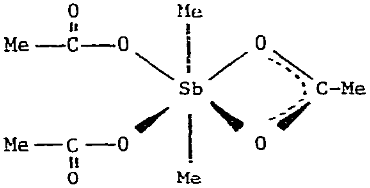
The trialkoxy and triacetoxy compounds were unaffected by atmospheric oxygen but were extremely sensitive towards moist air. Hydrolysis of the trialkoxy compounds gave almost quantitative yields of the hitherto virtually unexplored dialkylstibinic acids:

$$R_2Sb(OR')_3 + 2H_2O \rightarrow R_2SbO_2H + 3R'OH$$

Cryoscopic measurements in benzene gave normal molecular weights for the triacetoxy compounds. The trimethoxydialkylantimony compounds, however, showed some tendency toward association. For the diethyl compounds the degree of association varied from 1.1-1.4 within the concentration range 0.4-1.1%. The dimethyl compound behaved like a dissociating dimer; thus, its degree of association increased from 1.4 to 1.9 as the concentration increased from 0.4 to 1.5%. The PMR spectrum of the dimethyl compound at 25° showed a sharp singlet for the methoxy group protons. At -80°, however, the spectrum exhibited two methoxy signals in a ratio of 2:1. The Raman spectrum of the crystalline compound indicated a *trans* disposition for the two methyl groups bonded to antimony. It was concluded from the molecular weight and spectral data that the compound possessed the following dimeric octahedral structure both in the solid state and in concentrated solution:



Spectral investigation of monomeric triacetoxydimethylantimony indicated that it had a hexacoordinate structure in which there was one bidentate and two monodentate acetoxy ligands:



Keck and Klar [64] have prepared a number of dihalides derived from tris(*p*-dimethylaminophenyl)phosphine, -arsine, -stibine, and -bismuthine. The dichlorides were obtained by the reaction of the corresponding tertiary phosphine, arsine, stibine, or bismuthine with iodobenzene dichloride:

$$Ar_3E + PhICl_2 \rightarrow Ar_3ECl_2 + PhI$$

(where Ar was p-$Me_2NC_6H_4$ and E was P,As,Sb, or Bi)

Bromine and iodine dissolved in chlorinated hydrocarbons were used to obtain the dibromides and diiodides:

$$Ar_3E + X_2 \rightarrow Ar_3EX_2$$

(where E was P,As, or Sb and X was Br or I)

Tris(*p*-dimethylaminophenyl)antimony difluoride was prepared by the metathetica reaction between the dibromide and potassium fluoride in aqueous ethanol:

$$Ar_3SbBr_2 + 2KF \rightarrow Ar_3SbF_2 + 2KBr$$

Cryoscopic measurements in 1,2-dibromoethane gave normal molecular weights for the antimony and bismuth compounds. The other dihalides were not soluble enough in this solvent for molecular weights to be determined. Reaction of the antimony dichloride or dibromide with *p*-dimethylaminophenyllithium gave pentakis(*p*-dimethylaminophenyl)antimony:

$$Ar_3SbX_2 + 2ArLi \rightarrow Ar_5Sb + 2LiX$$

(where X was Cl or Br)

In contrast to these results, the interaction of the diiodide and the aryllithium compound involved oxidation-reduction and gave the tertiary stibine and N,N,N',N'-tetramethylbenzidine:

$$Ar_3SbI_2 + 2ArLi \rightarrow Ar_3Sb + Ar\text{-}Ar + 2LiI$$

The UV spectra of the various dichlorides and dibromides prepared in this study differed only slightly from one another; each compound exhibited an absorption band ($\log\varepsilon = 4.8$) in the region 36,000 to 34,000 cm^{-1}. The diiodides had an additional band ($\log\varepsilon = 3.8$) at 27,500-27,000 cm^{-1}. The PMR spectra of all the dihalides were determined in deuterochloroform, and it was concluded that the chemical shifts were related to the electronegativity and the principal quantum number of the valence electrons of the central atom.

In a second paper, Keck and Klar [65] reported that the arsenic and antimony dichlorides discussed in the above paragraph reacted with antimony pentachloride or aluminum trichloride to give deep blue cations in which the Group V atom had an oxidation state of +5 and a coordination number of 3:

$$Ar_3ECl_2 + 2SbCl_5 \rightarrow [Ar_3E][SbCl_6]_2$$

and

$$Ar_3ECl_2 + 2AlCl_3 \rightarrow [Ar_3E][AlCl_4]_2$$

(where E was As or Sb)

The electronic and PMR spectra of these salts suggested that the structure of the cations was similar to that of the isoelectronic cation of Crystal Violet. The authors were unable to obtain a pure compound by the interaction of tris(*p*-dimethylaminophenyl)bismuth dichloride and antimony pentachloride.

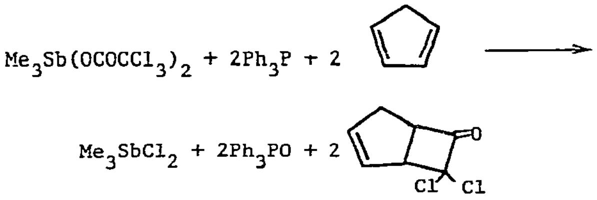
Kustan, Smith, and coworkers [66] have found that the reaction of equimolar amounts of triphenylstibine and thionyl chloride (or sulfur dichloride) at about 10° gave triphenylantimony dichloride:

$$2Ph_3Sb + 2SOCl_2 \rightarrow 2Ph_3SbCl_2 + S + SO_2$$

$$Ph_3Sb + SCl_2 \rightarrow Ph_3SbCl_2 + S$$

It was noted that triphenylstibine did not react with either sulfur dioxide or sulfur under these conditions. The reaction of triphenylarsine with thionyl chloride and sulfur dichloride has been discussed under Arsenic.

Okada and Okawara [67] have reported that the interaction of triphenylphosphine and certain organometallic haloacetates produced a dihaloketene, which could be trapped by 1,3-cyclopentadiene. Thus, trimethylantimony bis(trichloroacetate) reacted with triphenylphosphine in the presence of the diene to give a 33% yield of 7,7-dichlorobicyclo[3.2.0]hept-2-ene-6-one:



Trimethylantimony bis(trichloroacetate) was prepared by the reaction of trimethylstibine sulfide with an excess of trichloroacetic acid.

The interaction of antimony pentafluoride and vinylidene fluoride in liquid sulfur dioxide has been found to yield an addition product [68]:

$$3CF_2{=}CH_2 + SbF_5 \rightarrow (CF_3CH_2)_3SbF_2$$

When the reaction mixture was poured onto ice, crystals were obtained which could be recrystallized from carbon tetrachloride. The product was characterized by NMR (^{1}H and ^{19}F) and mass spectrometry.

Halide exchange involving dimethylantimony trichloride has been studied by Kustes, Moreland, and Long [69]. It was found by PMR measurements that this compound readily exchanged with antimony tribromide in chloroform:

$$Me_2SbCl_3 + SbBr_3 \rightleftarrows Me_2SbBr_3 + SbCl_3$$

The downfield shift of the methyl signal reached a limit when a large excess of antimony tribromide was used; at 30° this limit was at δ = 3.34 ppm. Methyl PMR shifts were also determined for a number of mixtures of dimethylantimony trichloride and trimethylantimony dibromide. The results obtained indicated that there was at 30° a random exchange of halide between the dimethylantimony and trimethylantimony moieties. At -65°, the trimethylantimony signal was split into two components when the ratio of trimethylantimony dibromide to dimethylantimony trichloride was 4:3 or larger. The upfield signal (δ = 2.36-2.40) corresponded essentially to trimethylantimony dichloride, which was undergoing little or no exchange. The lower field component (δ = 2.56-2.61) represented an average between trimethylantimony dibromide and trimethylantimony chloride bromide; the δ value of this peak increased as the ratio of trimethylantimony dibromide to dimethylantimony trichloride in the mixture was increased.

Moreland and Long [70] have extented their earlier work on redistrbibution reactions of the type:

$$R_3SbX_2 + R_3SbY_2 \rightleftarrows 2R_3SbXY$$

(where X and Y were F,Cl,Br, or I and R was Me,$PhCH_2$, or Ph)

The equilibrium constants, which were obtained from PMR and ^{19}F NMR data, ranged from 1.0 (where X,Y were F,I and R was Ph) to 10.0 (where X,Y was F,Cl and R was Ph); *i.e.,* the constants were not greatly different from the statistical value of 4. Equilibria were also investigated for cases involving the reactions of trimethylantimony dihalides with tribenzyl- or triphenylantimony dihalides:

$$Me_3SbX_2 + R_3SbY_2 \rightleftharpoons Me_3SbY_2 + R_3SbX_2$$

(where X was F,Cl, Br, or I,Y was F,Cl, or Br, and R was $PhCH_2$ or Ph) The range of equilibrium constants was from 2.7 (where X was Br,Y was Cl, and R was $PhCH_2$) to 600 (where X was F,Y was Cl or Br, and R was Ph). Where R was $PhCH_2$, the equilibrium favored the tribenzylantimony dihalide in which the halide had the lower electronegativity; *i.e.*, the stability for the tribenzylantimony dihalides increased in the order I>Br>Cl>F. On the other hand, where R was Ph, the stability for the triphenylantimony dihalides increased with increasing electronegativity of halide; *i.e.*, $F \gg Cl \sim Br$. It was suggested that a steric effect (in the case of the triphenyl compounds) favored the small fluorine atom.

Moreland and Beam [71] have investigated the kinetics of exchange reactions involving compounds of the type Me_3SbClX, where X was ONO_2,F, or Br. The PMR spectrum of a nitrobenzene solution of trimethylantimony dichloride and dinitrate showed that the following redistribution reaction occurred:

$$Me_3SbCl_2 + Me_3Sb(ONO_2)_2 \rightleftharpoons 2Me_3Sb(Cl)(ONO_2)$$

Integration of the three methyl resonances permitted calculation of the equilibrium constant, which was approximately 20 at 32°. The methyl resonance for the dinitrate was a sharp singlet which did not shift over the temperature range 20-80°. On the other hand, exchange between the dichloride and the chloride nitrate broadened their signals significantly. NMR line shape analysis made it possible to determine the specific rate constants and the activation parameters for the exchange reaction. It was concluded that only the nitrate group of the chloride nitrate was directly involved in the exchange with the dichloride. Similarly, it was concluded that fluoride was the labile group in exchanges involving trimethylantimony chloride fluoride and that chloride was only slightly more labile than bromide in trimethylantimony chloride bromide.

Chermette and coworkers [72,73] have used triphenylantimony dichloride for the separation of fluoride ion (in the concentration range of 10^{-8} to 10^{-1} M) from complex aqueous media. The solution was adjusted to a pH between 4 and 6.5 with phosphate buffer, and 1,2-diaminocyclohexanetetracetic acid was added to prevent interference from aluminum, zirconium(IV), ferric, and uranyl ions. It was then extracted with a carbon tetrachloride solution of the organoantimony compound. In this step over 99% of the fluoride ion entered the organic phase as triphenylantimony hydroxyfluoride. Treatment of the organic phase with aqueous ammonia converted the hydroxyfluoride to triphenylantimony dihydroxide and extracted the fluoride ion into the aqueous layer. The dihydroxide was then removed by extraction with carbon tetrachloride, and the fluoride ion in the aqueous phase was determined by means of a fluoride electrode.

In connection with their studies of the use of organoantimony compounds as analytical reagents, Chermette and coworkers [74] have employed solvent extraction methods for the determination of the equilibrium constants for the formation of triphenylantimony dihydroxide, difluoride, dichloride, and diiodide:

$$Ph_3Sb^{2+} + 2X^- \rightleftarrows Ph_3SbX_2$$

(where X was OH,F,Cl, or I)

The logarithms of these constants were 19.5, 7.0, 2.5, and 1.1, respectively. The logarithms of the partitions coefficients of these compounds (between benzene and water) were 4.0, 4.7, 5.0 and 4.9, respectively. The partition coefficients for the carbon tetrachloride-water system were somewhat smaller.

Goel and Ridley [75] have prepared and studied the physical properties of twenty-one compounds of the type $R_3Sb(O_2CR')_2$, where R was Me or Ph and

R' was CF_3, CF_2H, CFH_2, CCl_3, CCl_2H, $CClH_2$, CBr_2H, $CBrH_2$, Me, CD_3, or CH_2CN. All of the compounds were white crystalline solids, which were stable at room temperature and unaffected by atmospheric moisture. Conductivity measurements showed that the bis(trifluoroacetates) were slightly ionized in pyridine, while the other compounds were essentially non-electrolytes in this solvent. Molecular weight determinations by vapor osmometry showed that all the compounds were monomeric, molecular substances in benzene. The IR spectra of the compounds suggested that they possessed trigonal-bipyramidal coordination around the antimony. The carbonyl stretching frequency was found to decrease linearly with an increase in the pK_a of the carboxylic acid from which the compound had been derived. The antimony-methyl proton chemical shift (δ) was also found to decrease linearly with an increase in the pK_a of the parent acid; presumably, therefore, the Me_3Sb protons were progressively deshielded with an increase in the electronegativity of the R' group in $Me_3Sb(O_2CR')_2$.

Goel and Prasad [76] have reinvestigated the preparation and structure of the diperchlorates $(R_3SbOSbR_3)(ClO_4)_2$, where R was Ph or Me. A dihydrate of the phenyl compound was formed by the interaction of triphenylantimony dichloride or oxybis(triphenylantimony) dichloride with silver perchlorate in ethanol. Anhydrous oxybis(triphenylantimony) diperchlorate was obtained by treating the dihydrate with triethyl orthoformate. Oxybis(trimethylantimony) diperchlorate did not form a hydrate and was most conveniently prepared by the metathetical reaction of the corresponding dichloride with silver perchlorate. The IR spectrum of the dihydrate of oxybis(triphenylantimony) diperchlorate in the solid state suggested that the compound contained ionic perchlorate groups. The IR spectra of both anhydrous diperchlorates indicated, however, that they were non-ionic compounds in the solid state and that the perchlorate groups acted as monodentate ligands. Conductance and IR measurements showed that both the hydrated and anhydrous oxybis(triphenylantimony) diperchlorates existed as either ion pairs or nonionic species in dichloromethane. In nitromethane, however, these compounds behaved as 1:2 electrolytes. Oxybis(trimethylantimony) diperchlorate was also largely dissociated in nitromethane. Treatment of the diperchlorates with O-donor bases resulted in the formation of cationic complexes of the type $[(R_3SbL)_2O](ClO_4)_2$, where R was Me or Ph and L was one of the following ligands: N,N-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), diphenyl sulfoxide (DPSO), pyridine N-oxide (pyO), triphenylphosphine oxide, and triphenylarsine oxide. The complexes were white crystalline substances and were soluble in polar organic solvents. Complexes of DMA, DMSO, and pyO were sensitive to atmospheric moisture, while the other compounds could be handled in the air. The DMA complex of oxybis(trimethylantimony) diperchlorate was explosive, and several explosions occurred during the handling and attempted analysis of this compound. The IR spectra of the complexes clearly showed the presence of ionic perchlorate groups and cations of the type $[(R_3SbL)_2O]^{2+}$ in which the antimony atoms were five-coordinate. Conductance measurements showed that the complexes behaved as 1:2 electrolytes in nitromethane. In dichloromethane, however, the molar conductance values were lower in some cases (particularly for the pyO and Ph_3PO complexes) than anticipated for 1:2 electrolytes. It was suggested that the low values resulted from the following type of equilibrium:

$$(R_3SbL)_2O^{2+} + 2ClO_4^- \rightleftharpoons [R_3Sb(ClO_4)]_2O + 2L$$

In accordance with this hypothesis, the conductance of dichloromethane solutions of $[Me_3Sb(pyO)]_2O(ClO_4)_2$ and $[Me_3Sb(Ph_3PO)]_2O(ClO_4)_2$ increased markedly upon addition of pyO or Ph_3PO.

The reaction of trimethylstibine sulfide with indium trichloride, methylindium dichloride, or a dialkylindium halide in methanol at 0° has been found to give 1:1 adducts [77]. The IR spectra of the adducts indicated that the coordination occurred through the sulfur atom, since the Sb-S stretching frequencies were about 30 cm^{-1} lower in the complexes. The values of these shifts increased in the following order, which paralleled the expected order of acceptor strength of the indium atom:

$$R_2InX < MeInCl_2 < InCl_3$$

The proton resonances of the methyl groups attached to antimony were shifted to lower fields in the same order. When trimethylstibine sulfide and one of the organoindium halides were refluxed for several hours, a tetraalkylantimony halide was obtained. For example, the interaction of the sulfide and dimethylindium chloride for four hours in boiling methanol yielded a precipitate of methylindium sulfide and a solution from which tetramethylantimony chloride was obtained:

$$Me_3SbS + Me_2InCl \rightarrow Me_4SbCl + MeInS$$

The use of indium trichloride gave trimethylantimony dichloride:

$$Me_3SbS + InCl_3 \rightarrow Me_3SbCl_2 + InSCl$$

Indium(III) sulfide was also isolated from the reaction mixture.

Investigations of two substances corresponding to the formula Ph_3SbO were reported in 1972. McEwen and coworkers [78] studied one of these substances which melted at 221.5 - 222.0° and could be prepared by the thermal decomposition of hydroxytetraphenylantimony at about 60° or by the hydrolysis of dimethoxytriphenylantimony. This substance gave the correct elemental analyses for triphenylstibine oxide, and its molecular weight (in refluxing benzene) showed that it was monomeric. The chemical properties of this compound also supported the conclusion that it was triphenylstibine oxide. Thus, it reacted with triphenylantimony dichloride in benzene to give the known oxybis-(chlorotriphenylantimony) in quantitative yield:

$$Ph_3SbO + Ph_3SbCl_2 \rightarrow (Ph_3SbCl)_2O$$

Treatment with concentrated hydrochloric acid in acetone gave the dichloride:

$$Ph_3SbO + 2HCl \rightarrow Ph_3SbCl_2 + H_2O$$

The IR spectrum of the oxide in carbon disulfide or in a nujol mull exhibited a strong band at 664 cm^{-1} attributable to the Sb=O group. The nujol mull spectrum also showed broad peaks at 450 and 478 cm^{-1}. It was suggested that the 478 cm^{-1} peak should be assigned to a Sb-O single bond stretching frequency and that triphenylstibine oxide was partially associated in the solid state. Air oxidation of triphenylstibine oxide in refluxing *p*-xylene gave diphenylstibinic anhydride, $(Ph_2SbO)_2O$. Small amounts of benzene and oxybis(phenoxytriphenylantimony), $(Ph_3SbOPh)_2O$, were also isolated from the reaction mixture. Identification of diphenylstibinic anhydride was based on elemental analyses and the fact that it could be converted to diphenylantimony trichloride:

$$(Ph_2SbO)_2O + 6HCl \rightarrow 2Ph_2SbCl_3 + 3H_2O$$

Furthermore, the anhydride was independently synthesized from oxybis(dichlorodiphenylantimony):

$$(Ph_2SbCl_2)_2O \xrightarrow[2.\ H_2O]{1.\ NaOMe,MeOH} (Ph_2SbO)_2O$$

Incidental to this work, an improved synthesis of oxybis(dichlorodiphenylantimony) was devised:

$$Ph_2SbCl_3 \xrightarrow[2.\ KOH]{1.\ MeOH} (Ph_2SbCl_2)_2O$$

A homolytic chain mechanism for the air oxidation of triphenylstibine oxide was also suggested. The UV absorption spectrum of the oxide contained four bands of moderate intensity in the "benzenoid" region (λ_{max} 251nm,ε = 1.12 x 10^3; λ_{max} 257nm,ε=1.23 x 10^3; λ_{max} 263nm,ε = 1.34 x 10^3; λ_{max}269nm,ε=0.950 x 10^3). Photolysis in dioxane at 253.7nm gave benzene and an intractable solid of mp > 320°. The very low carbon and hydrogen content of the solid showed that more than one phenyl-antimony bond had been cleaved. Pyrolysis of triphenylstibine oxide at 230-260° in an evacuated system gave biphenyl, benzene, and an unidentified residue.

Razuvaev and coworkers [79] have reported the preparation of triphenylstibine oxide (identical to the material described in the above paragraph) by the interaction of triphenylstibine and either *tert*-butyl or cumene hydr peroxide:

$$Ph_3Sb + ROOH \rightarrow Ph_3SbO + ROH$$

(where R was Me_3C or $PhMe_2C$)

When the initial molar ratio of triphenylstibine to hydroperoxide was 1:3, the main product was a peroxy antimony compound:

$$Ph_3Sb + 3ROOH \rightarrow Ph_3Sb(OOR)_2 + ROH + H_2O$$

The reaction of triphenylstibine with one equivalent of *tert*-butyl hydroperoxide and two equivalents of triphenylsilyl hydroperoxide yielded a diperoxide that contained both antimony and silicon:

$$Ph_3Sb + Me_3COOH + 2Ph_3SiOOH \rightarrow Ph_3Sb(OOSiPh_3)_2 + Me_3COH + H_2O$$

The same compound was obtained from triphenylantimony dichloride:

$$Ph_3SbCl_2 + 2Ph_3SiOOH + 2Et_3N \rightarrow Ph_3Sb(OOSiPh_3)_2 + 2Et_3NHCl$$

Thermal decomposition of the diperoxide at 100° yielded oxygen:

$$Ph_3Sb(OOSiPh_3)_2 \rightarrow O_2 + Ph_3Sb(OSiPh_3)_2$$

The structure of the antimony compound thus obtained was ascertained by the following independent synthesis:

$$Ph_3SbCl_2 + 2Ph_3SiOH + 2NH_3 \rightarrow Ph_3Sb(OSiPh_3)_2 + 2NH_4Cl$$

Treatment with hydrogen chloride in alcohol yielded triphenylantimony dichloride and triphenylsilanol:

$$Ph_3Sb(OSiPh_3)_2 + 2HCl \rightarrow Ph_3SbCl_2 + 2Ph_3SiOH$$

The reaction of triphenylstibine and triphenylsilyl hydroperoxide (in a 1:1

ratio) did *not* give triphenylstibine oxide. Instead, a hydroxy derivative of Sb(V) was formed when the temperature of the reaction mixture was kept at 5-6°:

$$Ph_3Sb + Ph_3SiOOH \rightarrow Ph_3Sb(OH)OSiPh_3$$

When the reaction mixture was not cooled, the product lost water:

$$2Ph_3Sb(OH)OSiPh_3 \rightarrow (Ph_3SbOSiPh_3)_2O + H_2O$$

Treatment of the anhydride with hydrogen chloride resulted in cleavage of the SbOSb and SbOSi bonds:

$$(Ph_3SbOSiPh_3)_2O + 4HCl \rightarrow 2Ph_3SbCl_2 + 2Ph_3SiOH + H_2O$$

Glacial acetic acid, however, cleaved only the SbOSb bonds:

$$(Ph_3SbOSiPh_3)_2O + 2MeCO_2H \rightarrow 2Ph_3Sb(OSiPh_3)O_2CMe + H_2O$$

Venezky and coworkers [80] have also investigated a substance corresponding to the formula Ph_3SbO. This material (mp180-181°) was prepared by the hydrogen peroxide oxidation of triphenylstibine in acetone or the hydrolysis of triphenylantimony dichloride with alcoholic potassium hydroxide. The mass spectrum of this substance exhibited weak peaks at m/e 368 and 370, which were assigned to Ph_3SbO^+. Peaks at higher m/e values were, however, also observed. Thus, there were *inter alia* intense peaks at m/e 428, 430, and 432 (assigned to $Ph_2Sb_2O_2^+$) and weak peaks at m/e 659, 661, and 663 (assigned to $Ph_5Sb_2O_2^+$). It was concluded that the material melting at 180-181° was a polymer and should be designated poly(triphenylstibine oxide). This material was also subjected to solubility, IR, Raman, thermal (DTA and TGA), and X-ray powder measurements. The data obtained were believed to corroborate the polymeric nature of the oxide.

McEwen and Chupka [81] have made a thorough study of the thermal decomposition of hydroxytetraphenylantimony at about 60°. When the decomposition was carried out in *p*-xylene, small amounts of 4,4'-dimethylbibenzyl and 2,5-dimethylbiphenyl were formed in addition to the major products, benzene and triphenylstibine oxide. These minor products were apparently formed via the reaction of *p*-xylene with phenyl radicals derived from the primary decomposition of the hydroxy compound. Evidence was also obtained that indicated that at least some of the benzene and triphenylstibine oxide was produced by a free radical chain reaction. Thus, the rate of formation of benzene was markedly enhanced by the addition of di-*tert*-butylnitroxide to the reaction mixture. The following initiation and propagation steps were suggested:

$$Ph_4SbOH + (Me_3C)_2NO\cdot \rightarrow Ph_4SbO\cdot + (Me_3C)_2NOH$$

$$Ph_4SbO\cdot \rightarrow Ph\cdot + Ph_3SbO$$

$$Ph_4SbOH + Ph\cdot \rightarrow Ph_4SbO\cdot + PhH$$

In the absence of di-*tert*-butylnitroxide, phenyl radicals were probably produced by thermolysis of hydroxytetraphenylantimony and set the chain reaction in motion. The presence of oxygen caused a decrease in the rate of formation of benzene, both in the presence and absence of di-*tert*-butylnitroxide. It was suggested that oxygen inhibited the chain reaction by reacting with one or both of the chain carriers, $Ph\cdot$ and $Ph_4SbO\cdot$. More evidence that the decomposition of hydroxytetraphenylantimony involved phenyl radicals was obtained by the use of carbon tetrachloride at 60° as the solvent. Under these conditions the decomposition yielded chlorobenzene, chloroform, and hexachloroethane in addition to benzene and triphenylstibine oxide. These results were explained by assuming that a phenyl radical produced in the primary decomposition reaction abstracted a chlorine atom from the solvent to give chlorobenzene plus a trichloromethyl radical. Dimerization of the latter radical then yielded hexachloroethane. In the presence of mercury the decomposition of hydroxytetraphenylantimony in carbon tetrachloride produced phenylmercuric chloride as one product of the reaction

Some of the phenyl radicals produced in the decomposition were, presumably, captured by the mercury:

$$Ph\cdot + Hg \rightarrow PhHg\cdot \xrightarrow{CCl_4} PhHgCl + Cl_3C\cdot$$

Razuvaev and Osanova [82] have studied the thermal decomposition of methoxy-, isopropoxy-, and phenoxytetraphenylantimony. The latter compound was prepared by the interaction of pentaphenylantimony and phenol in dioxane:

$$Ph_5Sb + PhOH \rightarrow Ph_4SbOPh + PhH$$

Thermal decomposition of the phenoxy compound at 200° resulted in the formation of diphenyl ether:

$$Ph_4SbOPh \rightarrow Ph_3Sb + PhOPh$$

Methoxytetraphenylantimony under similar conditions, however, yielded only a small amount (10%) of anisole:

$$Ph_4SbOMe \rightarrow Ph_3Sb + PhOMe$$

The principal decomposition route gave benzene and formaldehyde:

$$Ph_4SbOMe \rightarrow Ph_3Sb + PhH + CH_2O$$

Isopropoxytetraphenylantimony decomposed rapidly within a half hour at 150-160° to yield benzene and acetone:

$$Ph_4SbOCHMe_2 \rightarrow Ph_3Sb + PhH + Me_2CO$$

Kok and Morris [83] have investigated the aqueous electrochemistry of a series of quaternary ions of the type $Me_nPh_{4-n}Sb^+$ (where n was 1-4) by means of polarography, cyclic voltammetry, and controlled potential electrolysis. Tetramethylantimony ion was found to undergo a single two-electron reduction to trimethylstibine and methane:

$$Me_4Sb^+ + H^+ + 2e^- \rightarrow Me_3Sb + MeH$$

The other three quaternary ions were reduced in two one-electron steps. The first electron transfer produced an organoantimony radical:

$$Me_nPh_{4-n}Sb^+ + e^- \rightarrow Me_nPh_{4-n}Sb\cdot$$

By reaction with the mercury electrode used, the radical could yield a tertiary stibine and an organomercury radical:

$$Me_nPh_{4-n}Sb\cdot + Hg \rightarrow Me_nPh_{3-n}Sb + PhHg\cdot$$

or

$$Me_nPh_{4-n}Sb\cdot + Hg \rightarrow Me_{n-1}Ph_{4-n}Sb + MeHg\cdot$$

The organomercury radical formed in this reaction then underwent rapid disproportionation:

$$2RHg\cdot \rightarrow R_2Hg + Hg$$

(where R was Ph or Me)

The second electron transfer involved direct reduction of the organoantimony radical to give a tertiary stibine and benzene or methane:

$$Me_nPh_{4-n}Sb\cdot + H^+ + e^- \rightarrow Me_nPh_{3-n}Sb + PhH$$

or

$$Me_nPh_{4-n}Sb\cdot + H^+ + e^- \rightarrow Me_{n-1}Ph_{4-n}Sb + MeH$$

Phenyltrimethylantimony ion lost only phenyl groups in the course of its reduction; *i.e.*, trimethylstibine was the only organoantimony compound formed. In contrast, the reduction of diphenyldimethylantimony ion yielded a mixture of phenyldimethylstibine and diphenylmethylstibine. Similarly, triphenylmethylantimony ion gave both triphenylstibine and diphenylmethylstibine.

Tsentovskii and coworkers [84] have investigated the electrical conductivity of tetraphenylantimony bromide in acetone, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) and of tetraphenylantimony iodide in acetone, nitromethane, DMF, DMSO, 1-propanol, 1-butanol, and acetonitrile. The iodide was found to be weakly associated in all seven solvents. The bromide was weakly associated in DMSO but strongly associated in acetone and DMF. The authors used their data to calculate the limiting mobilities of the Ph_4Sb^+ ion and the Stokes ionic radii ($r_s^{\pm}$). The relationship between the values of $r_s^{\pm}$ and the dielectric constants of the solvents was also analyzed.

The tetraphenylantimony compound $[Ph_4Sb]_2[Re_2Cl_8]$ has been included in a study of the preparation and properties of some new derivatives of the octahalodirhenate(III) ion [85]. Reflectance spectra of the solid compounds were obtained in the 250–2500 nm region, and absorption spectra in acidified methanol were also determined. Magnetic measurements showed that the octahalodirhenate(III) ion was not paramagnetic. The IR spectrum of the antimony compound had a band at $430 cm^{-1}$ that was assigned to C-Sb stretching.

Dahlmann and Winsel [86] have reported in an East German patent that the reaction of haloimides with tertiary arsines, stibines, or bismuthines yielded imido derivatives of arsonium, stibonium, or bismuthonium halides:

$$R_3E + R'_2NX \rightarrow [R_3ENR'_2]X$$

(where R was Me or Ph, E was As, Sb, or Bi, R'_2NH was succinimide or phthalimide, and X was Cl or Br)

In another patent the same authors [87] claimed that the imido group in the stibonium or bismuthonium halides could be displaced by a wide variety of reagents including alcohols, silanols, acids, hydrogen peroxide, and hydrogen sulfides. The following examples were given in which R_2NH was succinimide:

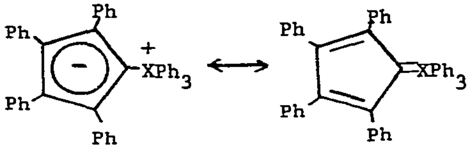
$$[Ph_3SbNR_2]Br + Me_3SiOH \rightarrow [Ph_3SbOSiMe_3]Br + R_2NH$$

$$[Ph_3SbNR_2]Br + Me_3COH \rightarrow [Ph_3SbOCMe_3]Br + R_2NH$$

$$2[Ph_3SbNR_2]Br + H_2O_2 \rightarrow [Ph_3SbOOSbPh_3]Br_2 + 2R_2NH$$

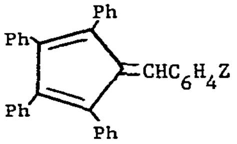
It was also stated that triphenyl(8-quinolinyloxy)stibonium chloride and triphenyl(8-quinolinyloxy)bismuthonium bromide were prepared in a similar manner.

Freeman, Lloyd, and Singer [88] have interpreted the physical and chemical properties of tetraphenylcyclopentadienylides of phosphorus, arsenic, antimony, and bismuth in terms of the relative contributions made by the following canonical forms:



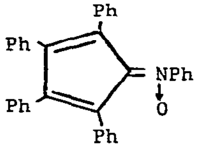
(where X was P, As, Sb, or Bi)

It was concluded that the dipolar and nucleophilic character of the ylids increased and their stability decreased as one descended the periodic table. With increasing contributions from the dipolar form, the electronic spectra exhibited absorption maxima at longer wavelengths. In particular there was a striking difference between the triphenylbismuthonium ylid and the other ylids. The bismuth compound was dark blue-purple and exhibited solvatochromism, while the other ylids were yellow and showed only small solvent shifts. It was concluded that the contribution of the "covalent" (*i.e.*, non-dipolar) form to the structure of the bismuth compound was minimal, presumably because the large, diffuse 6*d*-orbitals of bismuth could not effectively overlap the p_π-orbitals of the anionic ring. The bismuthonium ylid appeared to be a very unstable compound. Thus, it was rapidly attacked and decomposed by alkali or by dilute or concentrated mineral acids. The stibonium ylid was also destroyed by alkali, and it was quickly decomposed by boiling ethanol into tetraphenylcyclopentadiene and triphenylstibine oxide. It was possible, however, to convert the stibonium ylid into a crystalline perchlorate. Although both the salt and the ylid hydrolyzed rapidly in 95% ethanol, rapid measurements indicated that the pK_a of the perchlorate in this solvent was >7.6. The pK_a's of the corresponding arsenic and phosphorus compounds were 7.6 and 5.3, respectively. Thus, the order of the basicity of the ylids (Sb>As>P) agreed with inferences made from their spectra and relative stabilities. The arsonium and stibonium ylids reacted with benzaldehyde and *p*-nitrobenzaldehyde to give the following fulvenes:



(where Z was H or *p*-NO_2)

Triphenylarsine oxide or triphenylstibine oxide was also isolated. The phosphonium ylid did not react with either aldehyde and was recovered quantitatively after the mixture of ylid and aldehyde was refluxed in carbon tetrachloride for 18 hours. A similar pattern of reactivity was observed in the interaction of the ylids with nitrosobenzene. Thus, the stibonium compound reacted in 10 minutes to give an 80% yield of the following anil oxide:



The arsonium ylid required four hours to give a 48% yield of the anil oxide and a 35% yield of the corresponding anil. The phosphonium ylid gave neither anil nor anil oxide even after 18 hours in refluxing benzene and was in fact recovered quantitatively. No fulvenes, anil, or anil oxide could be obtained by the interaction of the bismuthonium ylid with aldehydes or nitrosobenzene; in these cases decomposition of the ylid apparently occurred. Attempts to prepare a dichlorofulvene by the reaction of the phosphonium, arsonium, or stibonium ylids with dichlorocarbene were unsuccessful. The phosphonium and arsonium compounds gave largely unchanged ylid; the stibonium compound was converted to 1,2,3,4-tetraphenylcyclopentadiene.

The square-pyramidal structure of pentaphenylantimony in the solid state has long been attributed to "crystal packing forces". During 1972, it was concluded that this compound was also a square pyramid in dichloromethane or dibromomethane [89]. This judgement was based on a low frequency IR and Raman study, which showed close agreement of solution and solid-state spectra Polarization measurements in the Raman were also consistent with the assumption of square-pyramidal geometry. The ^{13}C NMR spectrum of pentaphenylantimony in carbon disulfide at room temperature showed three sharp lines, indicating that the rings were effectively magnetically equivalent. The three lines were assigned to the *ortho, para,* and *meta* carbon atoms. The resonance of the carbon atoms directly attached to antimony was not observed. The apparent equivalence of the rings was attributed to the fluxional nature of the molecule. PMR measurements on pentaphenylantimony that had been fully deuteriated in the *meta* and *para*- positions showed only a single line down to -142°, although below -100° broadening and some asymmetry appeared.

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