ANTIMONY

ANNUAL SURVEY COVERING THE YEAR 1973

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No book or critical review devoted exclusively to organoantimony chemistry was published in 1973. A review on organoarsenic, -antimony, and -bismuth compounds was included, however, in the second volume of The Chemical Society's Specialist Periodical Reports on organometallic compounds [1]. Organoantimony compounds have been briefly mentioned in review articles on sigma-bonded organometallic compounds [2], the mass spectrometry of compounds containing the representative Group V elements [3], ^{121}Sb Mössbauer spectroscopy [4], NQR in organic and organometallic chemistry [5], and the electrochemistry of onium compounds [6]. The donor properties of tertiary stibines have been discussed in several books [7-9], and the relatively few organoantimony compounds that were subjected to X-ray analysis in 1971 and 1972 have been listed in Volume 4 of *Molecular Structures and Dimensions* [10].

Meinema and coworkers [11] have discovered that the interaction of a trialkylstibine and sodium in liquid ammonia resulted in the cleavage of one alkyl-antimony bond:

$$R_3Sb + 2Na \rightarrow R_2SbNa + RNa$$

As these reactions proceeded, the dark blue color of the ammoniacal sodium solutions changed to the dark red color of the dialkylstibides. The cleavage of trimethylstibine by sodium was so fast that the color change occurred within a few minutes. A noticeable color change required about 10-15 minutes for triethylstibine and 4-5 hours for tripropylstibine, whereas with tributylstibine hardly any reaction took place even after 8 hours. It was concluded that the rate of cleavage depended on the stability of the carbanion formed. When the solution obtained by the reaction of triethylstibine with sodium in liquid ammonia was treated with *n*-butyl bromide, a new tertiary stibine was formed:

$$Et_3Sb + 2Na \rightarrow Et_2SbNa + EtNa \xrightarrow{BuBr} Et_2SbBu$$

Reaction of this stibine with sodium in liquid ammonia resulted in cleavage of an ethyl group and made possible the synthesis of an asymmetric trialkylstibine, which was quaternized to an asymmetric tetraalkylantimony iodide:

$$Et_2SbBu + 2Na \rightarrow EtBuSbNa + EtNa \xrightarrow{PrBr} EtPrSbBu$$

$$EtPrSbBu + MeI \rightarrow MeEtPrBuSbI$$

The sodium dialkylstibides in liquid ammonia were also used for the preparation of di-tertiary stibines:

$$R_3Sb + 2Na \rightarrow R_2SbNa + RNa \xrightarrow{NH_4Br} R_2SbNa + RH + NaBr + NH_3$$

$$2R_2SbNa + CH_2Cl_2 \rightarrow (R_2Sb)_2CH_2 + 2NaCl$$

(where R was Me, Et, or Pr)

The reaction of the sodium dialkylstibides with 1,2-dichloroethane yielded tetraalkyldistibines:

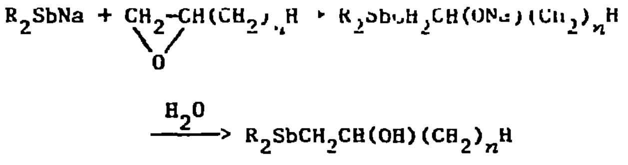
$$2R_2SbNa + ClCH_2CH_2Cl \rightarrow R_2SbSbR_2 + CH_2{=}CH_2 + 2NaCl$$

The latter compounds could be converted to dialkylchlorostibines or dialkylantimony trichlorides:

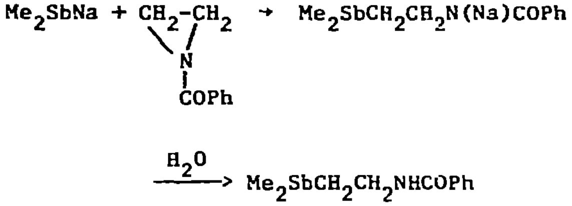
$$R_2SbSbR_2 + SO_2Cl_2 - 2R_2SbCl + SO_2$$

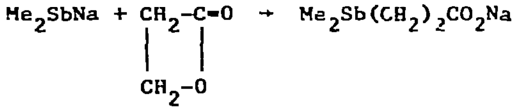
$$R_2SbSbR_2 + 3SO_2Cl_2 \rightarrow 2R_2SbCl_3 + 3SO_2$$

Reaction of the sodium stibides with epoxides, N-benzoylethylenimine, or β-propiolactone led to the formation of functionally substituted tertiary stibines:



(where R was Me, Et, Pr, Bu or Ph and *n* was 0 or 1)

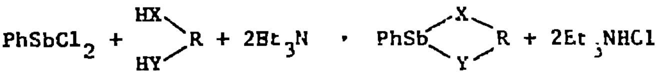


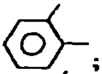
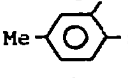


The antimony-containing alcohols were not isolated as such, but were converted into the corresponding antimony(V) dibromides by treatment with bromine in carbon tetrachloride. Meinema and coworkers have enhanced the importance of the work described in their paper by showing that the easily handled trialkylantimony dichlorides reacted with sodium in liquid ammonia to yield sodium dialkylstibides:

$$Me_3SbCl_2 + 4Na \rightarrow Me_2SbNa + MeNa + 2NaCl$$

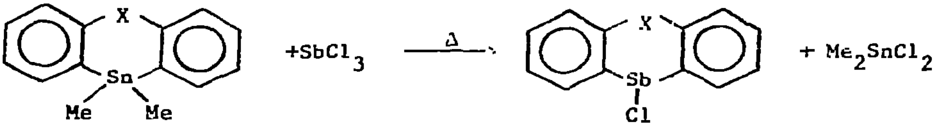
Wieber and Baumann [12] have prepared five heterocyclic organoantimony compounds by the reaction of phenyldichlorostibine with vicinal diols(pinacol and catechol), vicinal dithiols (1,2-ethanedithiol and 3,4-dimercaptotoluene), and 2-mercaptoethanol:



(where X and Y were O, R was $-Me_2CCMe_2-$ or  ;
where X and Y were S, R was $-CH_2CH_2-$ or  ;
and where X was O and Y was S, R was $-CH_2CH_2-$)

The two dithia compounds thus obtained had relatively low melting points and were quite soluble in most organic solvents; they were shown to be monomeric by cryoscopic measurements in benzene. In contrast, the two dioxa compounds decomposed at 280° and were insoluble in both polar and non-polar organic solvents. It was suggested that the dioxa compounds were associated by intermolecular coordination of oxygen lone-pair electrons with empty *d*-orbitals of the antimony. The heterocyclic compound prepared from 2-mercaptoethanol melted at 160-162° and was soluble enough in dimethyl sulfoxide to have its PMR spectrum recorded; no information about its molecular weight was given.

In 1971 Jutzi [13] reported that the interaction of 5,5-dimethyl-5,10-dihydrodibenzo[*b*,*e*]stannin and antimony trichloride yielded 5-chloro-5,10-dihydrodibenz[*b*,*e*]antimonin. Meinema and coworkers [14] have repeated this reaction and extended it to the preparation of other heterocyclic chlorostibines:



(where X was O, S, SO_2, CH_2, or CH_2CH_2)

The compounds were isolated in 50-70% yields as colorless, crystalline solids, which were found to be monomeric in benzene. The PMR spectra of the antimony compounds in which X was CH_2 or CH_2CH_2 exhibited (in deuterochloroform solution) methylene and ethylene proton resonances as broadened singlets at δ4.32 and δ3.24 ppm, respectively. In carbon tetrachloride, carbon disulfide, and benzene solutions, the ethylene proton resonances appeared as a well resolved AA'BB' spectrum.

The photoelectron spectra of phosphorin (phosphabenzene), arsenin (arsabenzene), and antimonin (stibabenzene) have been determined, and *ab initio* calculations have been carried out to aid in the assignment of the observed bands [15]. This work has been discussed under Arsenic. Calculation of the electron configuration of triphenylphosphine, -arsine, -stibine, and -bismuthine has been described in the Russian literature[16].

Azerbaev and coworkers have synthesized a large number of organoantimony compounds containing the carbon-carbon triple bond. Hydroxyalkynyldiphenylstibines of the type $Ph_2SbC\equiv CC(OH)(R)R'$ were prepared by reaction of the corresponding acetylenic alcohol $HC\equiv CC(OH)(R)R'$ with two moles of ethylmagnesium bromide and subsequent treatment of the resulting reaction mixture with diphenylchlorostibine [17]. The tertiary stibines thus obtained were converted to antimony(V) dihalides by reaction with iodine, bromine, or copper(II) chloride. The Grignard reaction was also used to prepare (dialkylaminopropynyl)diphenylstibines [18]:

$$Ph_2SbCl + BrMgC\equiv CCH_2NR_2 \rightarrow Ph_2SbC\equiv CCH_2NR_2 + MgBrCl$$

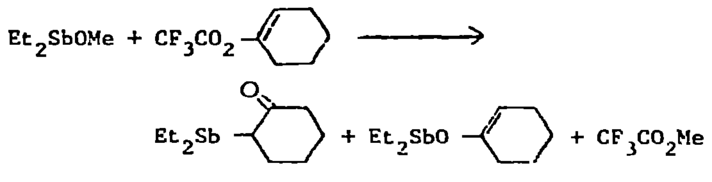
[where R_2N was dialkylamino, bis(hydroxyalkylamino),
morpholino, or piperidino]

Interaction of these compounds with halogens also gave antimony(V) dihalides. Acetylenic alkoxides of the type Ar_2SbOR (where R was an alkynyl or hydroxyalkynyl group) were prepared by metathesis [19]:

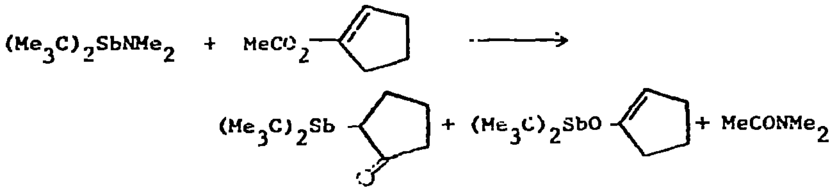
$$Ar_2SbX + MOR \rightarrow Ar_2SbOR + MX$$

(where X was a halogen and M was an alkali metal)

Foss and coworkers [20] have found that the interaction of alkoxydialkylstibines and enol trifluoroacetates resulted in the formation of dialkylstibino-substituted ketones. 1-Cyclohexen-1-yl trifluoroacetate was found to yield a tautomeric mixture of organoantimony compounds:



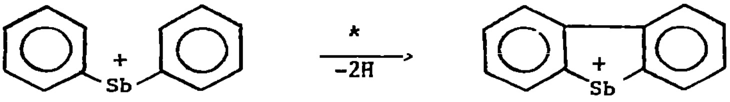
The PMR spectrum of the tautomeric mixture showed that the C- and O-isomers were rapidly interconverted; as the temperature was raised the concentration of O-isomer increased. An attempt to distill the mixture in a high vacuum resulted in decomposition at a bath temperature of 90-100°. Dimethylaminodialkylstibines were found to react even with vinyl esters of unsubstituted acetic acid When 1-cyclopenten-1-yl acetate was used, a tautomeric mixture was again obtained:



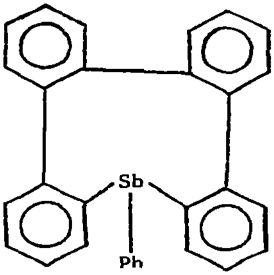
In this case, the rate of interconversion of the isomers was lower, and the PMR signals of the protons of the C- and O-isomers were not averaged out. As in the tautomeric equilibrium discussed above, the content of O-isomer increased with temperature. After two slow vacuum distillations, a non-equilibrium mixture containing as much as 80% of the O-isomer could be obtained. On standing for about a day, equilibrium was reestablished. The equilibrium mixture contained 20% of the O-isomer at 20° and 30% at 113°.

Nesmeyanov and coworkers [21] have reported a comparative ^{19}F NMR study of symmetrical and unsymmetrical compounds of the type *m*-$FC_6H_4MAr_2$ and *p*-$FC_6H_4MAr_2$, where M was CH,N,Sb, or Bi and Ar was Ph, *m*-FC_6H_4, or *p*-FC_6H_4. The symmetrical stibines and bismuthines were prepared by the interaction of *m*- or *p*-fluorophenylmagnesium bromide and antimony(III) or bismuth(III) chloride, while the unsymmetrical stibines and bismuthines were obtained by the reaction of the Grignard reagents with diphenylchlorostibine or -bismuthine. The chemical shifts were measured (relative to internal fluorobenzene) in cyclohexane, chloroform, pyridine and in several cases in anisole or phenol. It was found that a change in solvent from cyclohexane to chloroform had little influence (<0.3 ppm) on the ^{19}F chemical shift of any of the triaryl compounds. A change to phenol also had little effect. It was concluded that the lone-pair electrons of triarylamines, -stibines, and -bismuthines are inert to hydrogen bond formation with chloroform or phenol. The use of pyridine as a solvent produced a significant change only for tris(*m*-fluorophenyl)- and tris(*p*-fluorophenyl)bismuthine. The chemical shift of the *meta* compound changed from -1.76 ppm in cyclohexane to -1.05 ppm in pyridine, while the change for the *para* compound was from -0.48 ppm in cyclohexane to 0.16 ppm in pyridine. As a general rule, therefore, the triaryl compounds appeared to be incapable of coordinating to the molecules of strongly solvating solvents despite the possession of vacant orbitals by the metal atoms. The data also showed that the introduction of Ar_2Sb or Ar_2Bi groups into aromatic rings led, as a rule, to a decrease in the fluorine shielding at the *meta* and *para* positions. The Ph_2Bi group was an exception in that it caused a slight increase in the fluorine shielding at the *para* position. In order to obtain quantitative estimates of the electronic effects of the substituents studied, the σ_I and σ_R^o values of the Ph_2CH, Ph_2N, Ph_2Sb, and Ph_2Bi groups were calculated from the Taft correlation equations. In all cases, the σ_I values were small and positive, while the σ_R^o values were small and negative. The electronic effect of the Ph_2Sb and Ph_2Bi groups was almost entirely inductive. The electron-withdrawing inductive effect of the antimony and bismuth groups was virtually the same as that of the Ph_2N substituent and larger than the almost nil inductive effect of the Ph_2CH group. The small σ_R^o values for the Ph_2Sb(-0.01) and Ph_2Bi(-0.04) groups suggested the absence of any perceptible electron-withdrawing effect due to d_π-p_π conjugation between the π-electrons of the aromatic ring and the vacant orbitals of the metal atom. There was apparently also no significant electron-releasing effect associated with p_π-p_π conjugation between the metal lone-pair electrons and the aromatic ring. In contrast, both the Ph_2CH and Ph_2N groups exerted a definitely perceptible electron-releasing conjugative effect.

In a paper on the mass spectra of a variety of trivalent and pentavalent organic derivatives of phosphorus, arsenic, antimony, and bismuth, Hellwinkel and coworkers [22] have included triphenylstibine, 5-phenyl-, 5-methyl-, and 5-o-biphenylyldibenzostibole, pentaphenylantimony, and 5-phenyl-5,5'-spirobis(dibenzostibole). The most intense peak in the spectrum of triphenylstibine was the $PhSb^+$ ion, while the molecular ion was the second most intense peak. The other antimony-containing fragments were (in order of relative intensity) Ph_2Sb^+, $C_6H_4Sb^+$, $(Ph_2Sb-2H)^+$, Sb^+, and Ph_3Sb^{2+}. The $(Ph_2Sb-2H)^+$ fragment was believed to be a dibenzoheterocyclic ion formed by loss of two hydrogen atoms from the Ph_2Sb^+ ion:



Not surprisingly, this heterocyclic ion was prominent in the spectra of the trivalent dibenzostibole derivatives. It was the most intense peak in the spectrum of 5-methyldibenzostibole and the second largest antimony-containing peak for 5-phenyl- and 5-o-biphenylyldibenzostibole. The most intense peak in the spectra of the latter two compounds corresponded to the molecular ion. The molecular ion was very weak in the spectrum of pentaphenylantimony. The most intense peak was for the Ph_4Sb^+ ion, and there was a somewhat weaker peak for $PhSb^+$. There were rather weak peaks for Ph_3Sb^+, Ph_2Sb^+, $(Ph_2Sb-2H)^+$, $C_6H_4Sb^+$, Sb^+, and $(Ph_5Sb-H)^+$. As was the case for triphenylstibine, the $(Ph_2Sb-2H)^+$ fragment was formed from Ph_2Sb^+ and presumably had the heterocyclic structure noted above. By far the most prominent fragment in the spectrum of 5-phenyl-5,5'-spirobis(dibenzostibole) was formed by loss of a phenyl group from the molecular ion. Interpretation of this spectrum was complicated by the possibility of the thermal rearrangement of the spiro compound to a tertiary stibine containing a nine-membered heterocyclic ring:



Lemmon and Jackson [23] have prepared and studied the IR, Raman, and ^{19}F NMR spectra of tris(3,3,3-trifluoro-1-propynyl)phosphine, -arsine, and -stibine. The compounds were obtained by the following reaction sequence:

$$CF_3C{\equiv}CH + BuLi \xrightarrow[Et_2O]{-30^\circ} CF_3C{\equiv}CLi + BuH$$

$$3CF_3C{\equiv}CLi + MCl_3 \xrightarrow[Et_2O]{-30^\circ} (CF_3C{\equiv}C)_3M + 3LiCl$$

(where M was P, As, or Sb)

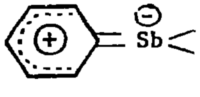
Several attempts to prepare tris(3,3,3-trifluoro-1-propynyl)bismuthine by the same general procedure met with uncertain success. The IR spectra used to monitor the reaction products indicated that the bismuthine had been formed in minute amounts, but the authors were unable to purify a sufficient quantity to permit characterization. The vibrational spectra of the phosphine, arsine, and stibine were satisfactorily explained by C_{3v} selection rules, and it was concluded that the molecular framework was that of a trigonal pyramid. The ^{19}F NMR spectra at 34° showed that the nine fluorines in each molecule were magnetically equivalent and provided no evidence for hindered rotation of the CF_3 groups.

Asano and coworkers [24] have reported that the interaction of triphenylphosphine, -arsine, -stibine, or -bismuthine with styrene in the presence of palladium(II) acetate led to cleavage of the carbon-heteroatom bond and formation of *trans*-stilbene:

$$Ph_3M + PhCH{=}CH_2 \xrightarrow[MeCO_2H,\ Dioxane]{Pd(O_2CMe)_2} \textit{trans}\text{-}PhCH{=}CHPh$$

The reactions were carried out by refluxing equimolar amounts of the triphenyl compound, styrene, and palladium(II) acetate in a mixture of acetic acid and dioxane. With respect to the formation of *trans*-stilbene, the reactivity of the triphenyl compounds was in the order $Ph_3As > Ph_3Sb > Ph_3P > Ph_3Bi$. Thus, triphenylarsine gave a 99% yield of *trans*-stilbene, while triphenylbismuthine gave only 3%. (Yield data were based on palladium(II) acetate.) In addition to *trans*-stilbene, biphenyl was isolated from the reactions of the arsine, stibine, and bismuthine; the latter two compounds yielded 108% biphenyl, while the arsine yielded 14% biphenyl. Triphenylbismuthine also gave 11% *trans*, *trans*-1,4-diphenylbutadiene, and triphenylphosphine gave 22% methyldipnenylphosphine oxide. The origin of the methyl group of the latter compound was not elucidated. Triphenylamine was also found to react with styrene and palladium(II) acetate, but no *trans*-stilbene was obtained in this case; instead, a 41% yield of *trans*-*p*-diphenylaminostilbene was recovered from the reaction mixture. When the reaction of triphenylbismuthine with styrene was carried out in the absence of the palladium compound, benzene and biphenyl were the only organic products isolated.

The ^{121}Sb Mössbauer spectra at 4°K and the ^{121}Sb and ^{123}Sb NQR spectra at 300°K of di-tertiary stibines of the type $Ph_2Sb(CH_2)_nSbPh_2$, where n was 1,4, or 10, have been compared with analogous data obtained with trimethyl- and triphenylstibine [25]. All of the compounds exhibited little or no asymmetry in the electric field gradient about the antimony nucleus. (In contrast to this result, earlier workers [26] had found very large asymmetry parameters for diphenylchlorostibine and bis(diphenylstibino)acetylene and had suggested that the presence of unlike substituents bonded to the antimony atom caused a highly asymmetric electron distribution around it.) The isomer shift for trimethylstibine was −0.22 mm/sec (relative to InSb), and the shifts for the other compounds were in the narrow range -0.50 to -0.69 mm/sec. The quadrupole coupling constants for the five stibines were quite similar to one another. The lower negative value for the isomer shift of trimethylstibine suggested that the antimony in this compound had slightly less s-electron density. The presence of phenyl substituents in the other compounds apparently allowed a small amount of back-donation of electrons from the aromatic π-systems; *i.e.*, the over-all bonding picture probably included a small contribution of the following type:



The di-tertiary stibines used in this study were synthesized by the interaction of sodium diphenylstibide (obtained by the cleavage of triphenylstibine with sodium in liquid ammonia) and the appropriate dihaloalkane:

$$2Ph_2SbNa + X(CH_2)_nX \rightarrow Ph_2Sb(CH_2)_nSbPh_2 + 2NaX$$

(where X was Cl or Br)

Gukasyan and coworkers [27] have used Mössbauer spectroscopy at about 80°K to investigate the structure of five antimony(V) dihalides (Ph_3SbF_2 and R_3SbCl_2, where R was Ph, *o*-$MeOC_6H_4$, *cis*-ClCH=CH, or *trans*-ClCH=CH), diphenylantimony trichloride, tetraphenylantimony bromide and tetrafluoroborate, and three triarylstibines (Ar_3Sb, where Ar was Ph, *p*-ClC_6H_4, or *p*-$MeOC_6H_4$). The isomer shifts for all the organoantimony(V) compounds were in the range 2.3 to 4.1 mm/sec (relative to InSb). These values are considerably less the isomer shifts found for inorganic antimony(V) compounds such as antimony pentachloride (5.8 mm/sec) and antimony pentafluoride (11.1 mm/sec). It was concluded that the lower electron accepting ability of the organic groups led to relatively greater s-electron density at the antimony nucleus. The organoantimony(V) dihalides exhibited large negative quadrupole splittings, suggesting that the *p*-electron density in the equatorial plane of these trigonal-bipyramidal molecules was greater than along the axis of the apical bonds. This result was attributed to the occupation of the apical positions by the more electronegative groups (the halogen atoms) and to the presence of conjugated π-systems. In contrast to these findings, the quadrupole splitting for diphenylantimony trichloride was large and *positive*. Assuming trigonal-bipyramidal geometry for this compound, the authors suggested that the three halogen atoms probably occupied equatorial positions. The two tetraphenylantimony compounds exhibited little or no quadrupole splitting. It was concluded that the tetrafluoroborate was an ionic compound containing the tetrahedral Ph_4Sb^+ cation. The authors were reluctant to come to a similar conclusion about tetraphenylantimony bromide, since earlier work [28] from another laboratory had indicated that the Sb-Br bond in this compound was covalent. The isomers shifts found for the triarylstibines were in the range 0 to -0.8 mm/sec and were less negative than the values characteristic of inorganic antimony(III) compounds; hence, the *s*-electron density at the antimony nucleus appeared to be lower for the organic compounds. The quadrupole splittings for the triarylstibines were large and positive and suggested excess *p* electron density along the threefold rotational axis of the molecule.

Several organoantimony compounds have been included in a study of the theoretical interpretation of antimony Mössbauer effects [29]. A value of $(\delta R/R)_{Sb} = -(9.8\pm0.4)\times 10^{-4}$ was obtained by combining molecular orbital estimates of the population of valence electron states with the results of atomic Hartree-Fock calculations. The deuteron quadrupole frequency of triphenylstibine-d_{15} at 77°K has been observed at 135.3±0.5 kHz [30]. The deuteron coupling constant was 180.4±0.7, and the asymmetry parameter was 0.044.

The ^{115}In, ^{75}As, ^{121}Sb, and ^{123}Sb NQR parameters of the 1:1 complexes of trimethylindium with trimethylamine, -phosphine, -arsine, and -stibine have been compared with like data obtained for an analogous series of trimethylaluminum complexes [31]. It was concluded that there was a small amount of (*d*-*d*)π bonding in the indium complexes of trimethylphosphine and its heavier congeners. Tsvetkov and coworkers [32] have determined the enthalpies of mixing triethyl- or tri-*n*-propylgallium with triethylamine, -arsine, or -stibine. The results obtained were discussed in terms of the donor-acceptor complexes formed by the two mixed compounds. A group of Russian workers [33] have also measured the heats of fusion and the heat capacities (between 60 and 298°) of trimethylgallium, triethylindium, and triethylstibine. Other Russian papers have described the behavior (including R_f values) of organoantimony compounds during thin-layer chromatography on alumina [34]and the use of IR spectroscopy to determine the amounts of *p*- and π-complexing between phenol and triphenylamine, -phosphine, -arsine, or -stibine [35].

Beall and Houk [36] have studied the thermal reaction of the Group VIB metal carbonyls $M(CO)_6$, where M was Cr, Mo, or W, with the potentially bidentate ligand methylenebis(diphenylstibine), $Ph_2SbCH_2SbPh_2$ (Dpsm). The initial evolution of carbon monoxide produced a pentacarbonyl derivative in which Dpsm functioned as a monodentate ligand:

$$M(CO)_6 + Dpsm \rightarrow M(CO)_5(Dpsm) + CO$$

More drastic conditions led to the formation of tetracarbonyl dimers:

$$2M(CO)_5(Dpsm) \rightarrow [M(CO)_4(Dpsm)]_2 + 2CO$$

Larger yields of these dimers were obtained by taking advantage of the facile replacement of 2,5-norbornadiene(Nbd) or N,N,N',N'-tetramethyl-1,3-propanediamine(Tmpa) from their metal carbonyls:

$$2Cr(CO)_4(Nbd) + 2Dpsm \rightarrow [Cr(CO)_4(Dpsm)]_2 + 2Nbd$$

$$2Mo(CO)_4(Nbd) + 2Dpsm \rightarrow [Mo(CO)_4(Dpsm)]_2 + 2Nbd$$

$$2W(CO)_4(Tmpa) + 2Dpsm \rightarrow [W(CO)_4(Dpsm)]_2 + 2Tmpa$$

Monomeric $Mo(CO)_4(Dpsm)$ was prepared in low yield by ultraviolet irradiation of a hexane solution of $Mo(CO)_6$ and Dpsm. A tricarbonyl complex of molybdenum was obtained by heating $Mo(CO)_5(Dpsm)$ with additional ligand at 130° for 13 days or by using a complex of 1,3,5-cyclohexatriene (Cht):

$$Mo(CO)_3(Cht) + 2\ Dpsm \rightarrow Mo(CO)_3(Dpsm)_2 + Cht$$

The molecular structure of the various Dpsm complexes prepared in this work was investigated by means of molecular weight measurements and NMR and IR spectral studies.

Fukumoto, Matsumura, and Okawara [37] have also prepared di-tertiary stibine complexes of Group VIB metal carbonyls. The reaction of Dpsm or the related methylenebis(di-*p*-tolylstibine) with the dienyl derivatives $M(CO)_4L$, where M was Cr or Mn and L was 1,5-cyclooctadiene or Nbd, gave the tetracarbonyl dimers $[M(CO)_4(Ar_2SbCH_2SbAr_2)]_2$, where Ar was Ph or p-MeC_6H_4. Monomeric complexes of the type $M(CO)_4(Ph_2SbCH_2CH_2CH_2SbPh_2)$ were obtained, however, by the interaction of trimethylenebis(diphenylstibine) and $M(CO)_6$, where M was Cr, Mo, or W.

Cardaci [38] has investigated the kinetics of the following reaction in toluene solution:

$$Fe(CO)_4(CH_2{=}CHX) + Ph_3Sb \rightarrow Fe(CO)_4(SbPh_3) + CH_2{=}CHX$$

(where X was OEt, Ph, Bu, Cl, Br, CO_2Me, or CN)

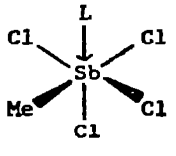
The reaction was found to occur by a dissociative mechanism in which $Fe(CO)_4$ was produced as an intermediate. Analysis of the effect of the substituent X on the stability of the complexes led to the conclusion that π-backbonding between the iron atom and the olefinic ligand was the major cause of the Fe-olefin bond strength.

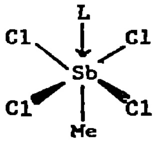
In addition to the papers discussed in the above three paragraphs, there were numerous other articles published in 1973 that described the use of tertiary stibines as ligands in transition metal complexes. The metals coordinated to the antimony in these complexes included cadmium [39], cobalt [40], gold [41,42], iron [43-46], manganese [47-49], mercury [50], nickel [51], osmium [52], palladium [53-55], platinum [56-58], rhodium [59,60], ruthenium [61], and silver [62].

Nishii, Hashimoto, and Okawara [63] have described the preparation and spectral properties of adducts of the type $RSbCl_4L$, where R was Me,Ph, or *p*-MeC_6H_4 and L was one of the following oxygen donors: hexamethylphosphoric triamide (HMPT), pyridine N-oxide (PyO), α-picoline N-oxide (4-MePyO), or dimethyl sulfoxide (DMSO). The adducts were obtained by reaction of the appropriate dichlorostibine with sulfuryl chloride at -70° and subsequent addition of the ligand:

$$RSbCl_2 \xrightarrow{SO_2Cl_2} RSbCl_4 \xrightarrow{L} RSbCl_4L$$

Unlike uncomplexed organoantimony(V) tetrahalides, the adducts were found to be stable in the solid state at room temperature. A lowering of the IR frequency of the P-O, N-O, or S-O stretching vibration (compared to the free ligand) indicated that oxygen was the donor atom; and cryoscopic measurements in nitrobenzene showed that the adducts were monomeric, molecular species. It was concluded, therefore, that the adducts were derivatives of hexacoordinated antimony. The PMR spectrum of $MeSbCl_4$·4-MePyO exhibited a pair of signals due to the Sb-Me protons and a second pair due to the C-Me protons. The observed doubling was attributed to the existence in solution of *cis* and *trans* isomers:





As the temperature of a solution of $MeSbCl_4$·4-MePyO in nitrobenzene was raised above 70°, the intensities of the Sb-Me and C-Me signals began to decrease, and two new signals appeared, which were assigned to the protons of methyl chloride and $SbCl_3 \cdot$4-MePyO. This change was shown to be irreversible and was obviously due to decomposition:

$$MeSbCl_4 \cdot 4\text{-}MePyO \rightarrow SbCl_3 \cdot 4\text{-}MePyO + MeCl$$

The adducts $MeSbCl_4 \cdot PyO$ and $MeSbCl_4 \cdot HMPT$ similarly decomposed in solution above 70°. In fact, the latter adduct gradually decomposed even at room temperature.

Pligina [64] has studied the precipitation of twenty-three alkaloids and fifty-eight synthetic organic nitrogen bases by arylpentabromoantimonate anions of the type $[YC_6H_4SbBr_5]^-$. The number of bases precipitated by a specific anion depended on the substituent Y and increased in the following order: *m*-Cl>*m*-Me>H>*p*-Me>*o*-Cl>*o*-Me.

Doak and Summy [65] have prepared a series of unsymmetrical diarylantimony trichlorides of the type $PhArSbCl_3$ (where Ar was a phenyl group containing a *p*-CH_3,*p*-O_2N,*p*-Cl, *m*-Cl, or *p*-F substituent) by the interaction of an arenediazonium tetrafluoroborate and phenyldichlorostibine. Diphenylantimony trichloride was obtained by treatment of diphenylstibinic acid with an excess of hydrochloric acid:

$$Ph_2SbO_2H + 3HCl \rightarrow Ph_2SbCl_3 + 2H_2O$$

The stibinic acid in turn was prepared by using alkaline hydrogen peroxide to cleave a phenyl group from triphenylstibine. Attempts were made to convert the diarylantimony trichlorides to oxides of the type $(PhArSbCl_2)_2O$:

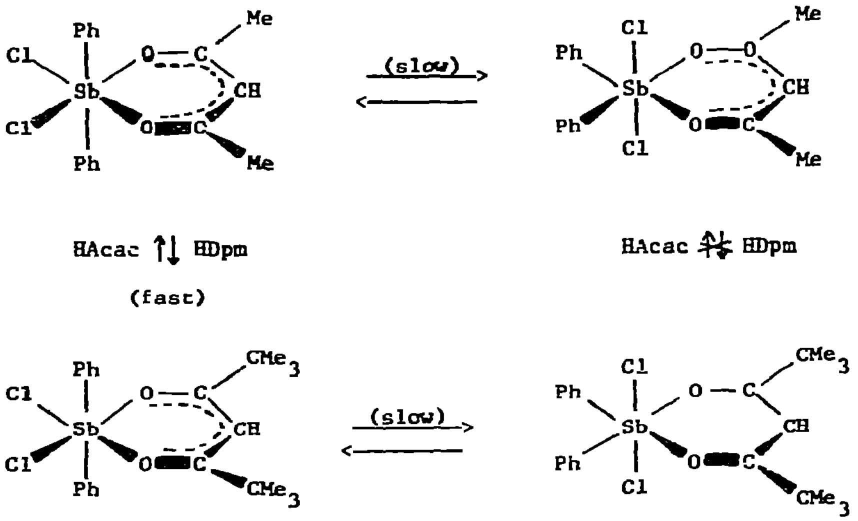
$$2PhArSbCl_3 + H_2O \rightleftarrows (PhArSbCl_2)_2O + 2HCl$$

μ-Oxo-bis(dichlorodiphenylantimony) was obtained in 84% yield by refluxing a methanol solution of diphenylantimony trichloride in a Soxhlet apparatus and removing the hydrogen chloride by allowing the condensate to drip through solid sodium carbonate in the Soxhlet thimble. This procedure, unfortunately, was not successful with the unsymmetrical diarylantimony trichlorides. It was found possible, however, to prepare μ-oxo-bis(phenyl-

p-tolyldichloroantimony) in 93% yield by allowing a methanol solution of phenyl-*p*-tolylantimony trichloride and sodium methoxide to stand at room temperature for 48 hours. The PMR spectrum of this oxide at 27° exhibited a single sharp peak for the methyl group at τ 7.6. When the temperature was lowered the signal broadened, and at -90° there were two peaks (separation 10Hz at 100 MHz) in a ratio of 1:2.5. The two peaks were attributed to the presence of *dl* and *meso* forms, which underwent rapid stereomutation at room temperature. μ-Oxo-bis(phenyl-*p*-fluorophenyldichloroantimony) was obtained by the same method used for the tolyl derivative. The fluoro compound was contaminated, however, with μ-oxo-bis(diphenyldichloroantimony) and μ-oxo-bis(di-*p*-fluorophenyldichloroantimony). The latter compound was removed by fractional crystallization to yield a mixture containing 77% of the desired unsymmetrical oxide and 23% μ-oxo-bis(diphenyldichloroantimony). The ^{19}F NMR spectrum of this mixture gave a single peak at room temperature. As the temperature was lowered, the signal broadened and was split into two peaks (δ106.2 and 113.2 referred to fluorotrichloromethane) at -60°. It was concluded, therefore, that μ-oxo-bis(phenyl-*p*-fluorophenylantimony) also existed in *dl* and *meso* forms, which underwent rapid stereomutation at room temperature.

Meinema and Noltes [66] have employed PMR spectroscopy to study the influence of stereochemistry on β-diketonate exchange in organoantimony(V) complexes of the type R_2SbCl_2Acac and R_2SbCl_2Dpm (where R was Ph or Me, Acac was $CH_3COCHCOCH_3$, and Dpm was $Me_3CCOCHCOCMe_3$) as well as in the corresponding 2,2'-biphenylylene complexes. As illustrated below for the Ph_2SbCl_2Acac + HDpm and the Ph_2SbCl_2Dpm + HAcac systems, there was fast β-ketonate exchange only when the two aryl (or methyl) groups were *trans* to one another; the corresponding *cis* isomers, in fact, appeared to be inert to exchange with free β-diketone.

The occurrence of a slow isomerization process did lead, however, to a



mixture of *cis*-diphenyl and *trans*-diphenyl isomers of Ph_2SbCl_2Acac and Ph_2SbCl_2Dpm. Fast β-diketonate exchange was also observed when HDpm was added to a solution of Me_2SbCl_2Acac (which had been shown to exist only in the *trans*-dimethyl form) and led to an equilibrium mixture of Me_2SbCl_2Acac, Me_2SbCl_2Dpm, HAcac, and HDpm. The 2,2'-biphenylylene complexes (which are capable of existing only in *cis*-diaryl configurations) did not react at all with the free β-diketones. It was concluded that this investigation has provided the first examples of the influence of geometric configuration on ligand stabilization in octahedral main group organometallic complexes.

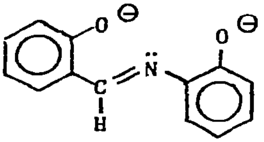
Beattie and coworkers [67] have investigated the vibrational spectra of a number of chloro and methylchloro derivatives of cadmium, indium, tin, antimony, tellurium, and iodine. Included in this study were trimethylantimony dichloride, dimethylantimony trichloride, and an adduct of the latter compound with tetraethylammonium chloride. The adduct was prepared by mixing equimolar ammounts of the reactants in thionyl chloride:

$$Me_2SbCl_3 + Et_4NCl \rightarrow [Et_4N][Me_2SbCl_4]$$

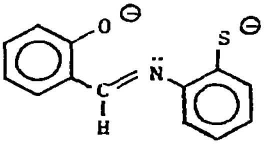
The spectral data suggested that the Me_2SbCl_4 anion in the adduct had a octahedral structure in which the four Sb-Cl bonds were in the same plane. The spectra of the uncharged organoantimony species were, as expected, consistent with trigonal-bipyramidal structures in which the methyl groups occupied only equatorial positions.

An X-ray crystal structure determination of μ-oxo-bis(triphenylazidoantimony), $(Ph_3SbN_3)_2O$, has been completed by Ferguson and Ridley [68]. The compound was shown to be a non-ionic derivative of pentacoordinated antimony. Each metal atom was in a slightly distorted trigonal-bipyramidal environment with the bridging oxygen at one apex and an azido group at the group at the other. The O-Sb-N angle was 178.3(3)°. The N-N-N angle was also nearly linear. The three phenyl carbon atoms bonded to each antimony atom were in a plane slightly below the antimony (with respect to the bridging oxygen) so that the mean O-Sb-C angle was 92.9(3)°. The Sb-O bond length, 1.985(3)Å, was significantly shorter than values reported in tetraphenylantimony hydroxide, methoxytetraphenylantimony, and dimethoxytriphenylantimony; it was, however, very similar to the Sb-O distance in $Me_3POSbCl_5$, in which theoretical calculations suggested that there was equal attraction of electrons on both sides of the bridging oxygen. The Sb-O-Sb angle, 139.8(4)°, was much larger than tetrahedral as a consequence of steric interactions between phenyl groups in the two halves of the molecule. The mean C-Sb bond length, 2.115(9)Å, was similar to the mean values found for other equatorial C-Sb bonds. The C-Sb-C angles ranged from 115.8 to 125.6°; the deviations from 120° were attributed to steric interactions of the three phenyl groups attached to the antimony atom.

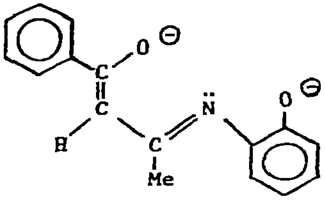
Di Bianca and coworkers [69,70] have investigated the synthesis and structure of organoantimony(V) compounds of the type R_3SbL, where R was Me or Ph and L was a potentially tridentate Schiff base dianion that contained ONO or ONS donor atoms:



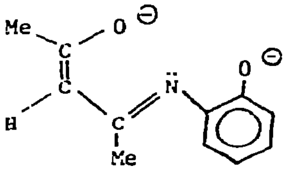
(SAB^{2-})



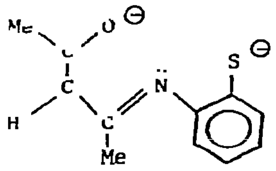
(SAI^{2-})



(BAH^{2-})



(AAH^{2-})



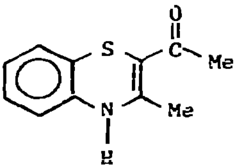
(AAI^{2-})

The complexes were prepared by using the free ligand or its disodium salt:

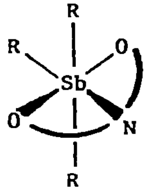
$$R_3Sb(OMe)_2 + H_2L \xrightarrow{PhH} R_3SbL + 2MeOH$$

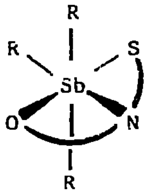
$$R_3SbCl_2 + Na_2L \xrightarrow{MeOH} R_3SbL + 2NaCl$$

Attempts to prepare Me_3SbBAH and Me_3SbAAH resulted in the formation of viscous oils of unknown structure. Complexes of the type R_3SbAAT could not be isolated as a result of their spontaneous decomposition to a tertiary stibine and 2-acetyl-3-methyl-4H-1,4-benzothiazine:



The other six complexes appeared to be relatively stable, although Me_3SbSAT decomposed in about a month at room temperature. Molecular weight determinations at 37° showed that these complexes were non-dissociating monomers. Their UV and IR spectra suggested the following hexacoordinate structures:





PMR spectroscopy indicated that the trimethylantimony complexes had non-rigid structures in solution. Thus, the Sb-Me protons of Me_3SbSAB in carbon tetrachloride at 25° gave only one sharp singlet, indicating a rapid exchange of equatorial and axial methyl groups. In toluene-d_8 at -65°, however, the signal was split into two peaks with the expected 2:1 intensity ratio. Me_3SbSAT was more rigid and give two broad peaks (2:1 intensity) at 25°; at -20° the peaks became sharp singlets. An X-ray structure determination revealed that the antimony atom in Me_3SbSAB was indeed hexacoordinate and possessed a distorted octahedral geometry.

Goel and Prasad [71] have described pentacoordinate cationic complexes of the type $[R_3SbL_2](ClO_4)_2$, where R was Me or Ph and L was dimethyl sulfoxide (DMSO), diphenyl sulfoxide (DPSO), triphenylphosphine oxide, or triphenylarsine oxide. The complexes were prepared by methathesis:

$$R_3SbCl_2 + 2L + 2AgClO_4 \rightarrow [R_3SbL_2](ClO_4)_2 + 2AgCl$$

The cations were readily hydrolyzed to form the oxygen-bridged $[(R_3SbL)_2O]^{2+}$ species and were therefore much more difficult to isolate than the corresponding bismuth cations, which have been found to be unaffected by moisture. A violent explosion occurred during one preparation of $[Me_3Sb(DMSO\text{-}d_6)_2](ClO_4)_2$, and the authors warned that the other complexes should also be considered as potentially explosive. The IR spectra of the solid complexes clearly showed the presence of ionic perchlorate groups and also suggested that the antimony atoms were bonded to the oxygen atoms of the ligands. It was concluded that the configuration around antimony was trigonal-bipyramidal with the methyl or phenyl groups in equatorial positions. Conductance measurements showed that all of the complexes behaved as 1:2 electrolytes in nitromethane, and IR measurements in dichloromethane or nitromethane indicated that the complex cations did not dissociate in these solvents. PMR spectra of the trimethylantimony complexes in nitromethane showed that the resonances due to the methyl groups depended markedly on the nature of the ligand L; the shielding of the Sb-Me protons increased in the order DMSO $<$ Ph_3PO $<$ Ph_3AsO.

Reinert [72] has prepared diphenyl(*p*-dimethylaminophenyl)antimony dibromide by the following sequence of reactions:

$$Ph_3SbBr_2 \xrightarrow{\Delta} Ph_2SbBr + PhBr$$

$$Ph_2SbBr + p\text{-}Me_2NC_6H_4Li \rightarrow p\text{-}Me_2NC_6H_4SbPh_2 + LiBr$$

$$p\text{-}Me_2NC_6H_4SbPh_2 + Br_2 \rightarrow Ph_2(p\text{-}Me_2NC_6H_4)SbBr_2$$

Triphenylantimony dichloride has been obtained by the interaction of triphenylstibine and copper(II) chloride in acetone [73]:

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

In methanol solution, the reaction gave triphenylantimony dichloride plus an adduct of triphenylstibine and copper(I) chloride, which was not further investigated. In agreement with other studies, an analysis of the far IR, Raman, and ^{19}F NMR spectra of tribenzylarsenic and -antimony dichlorides and difluorides has supported the conclusion that the geometry about the arsenic and antimony atoms in these compounds was trigonal-bipyramidal (slightly distorted in the solid state) [74]. The work has been discussed in more detail under Arsenic. In a paper dealing mainly with reactions of tertiary arsines, Ang and Lien [75] have reported that bis(trifluoromethyl) nitroxide added to trimethylstibine:

$$Me_3Sb + 2(CF_3)_2NO \rightarrow Me_3Sb[ON(CF_3)_2]_2$$

Treatment of the pentacovalent antimony compound with hydrogen chloride cleaved the Sb–O bonds and gave quantitative yields of the products:

$$Me_3Sb[ON(CF_3)_2]_2 + 2HCl \rightarrow Me_3SbCl_2 + 2(CF_3)_2NOH$$

A U.S. government report [76] has described the preparation of organoantimony(V) compounds of the type $Ph_3Sb(O_2CXCO_2Me)_2$, where X was not defined.

Sato, Matsumura, and Okawara [77] have described the first preparation of an optically-active quaternary antimony compound, *viz*. dextrorotatory methylethylisopropylphenylantimony iodide. The racemic iodide was obtained by the quaternization of methylisopropylphenylstibine with triethyloxonium tetrafluoroborate and subsequent treatment with potassium iodide:

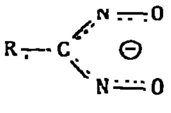
$$\begin{tikzcd}
Me(Me_2CH)(Ph)Sb+[Et_3O][BF_4] \arrow[r] & {[Me(Et)(Me_2CH)(Ph)Sb][BF_4]+Et_2O} \arrow[d, "KI"] \\
 & {[Me(Et)(Me_2CH)(Ph)Sb]I}
\end{tikzcd}$$

The same racemic iodide could also be prepared by the interaction of methylisopropylphenylstibine sulfide and diethylindium iodide:

$$Me(Me_2CH)(Ph)SbS + Et_2InI \rightarrow [Me(Et)(Me_2CH)(Ph)Sb]I + EtInS$$

Treatment of the quaternary iodide with silver hydrogen (-)-dibenzoyltartrate and subsequent recrystallization from ethyl acetate gave a laevorotatory antimony hydrogen (-)-dibenzoyltartrate. Potassium iodide in methanol then converted the latter compound to the dextrorotatory antimony iodide.

Vetter and Klar [78] have prepared quaternary nitrogen, phosphorus, arsenic, and antimony derivatives of the 1,1-dinitrosoethane and α,α-dinitrostoluene anions:



(where R was Me or Ph)

The nitrogen, phosphorus, and arsenic compounds were deep blue, crystalline substances, which exhibited salt-like behavior. Thus, they were soluble in polar solvents such as water, alcohols, hexamethylphosphoric triamide, or pyridine and insoluble in non-polar solvents like diethyl ether, benzene, or petroleum ether. The intense blue color of the solutions was attributed to the free RC(NO)(NO) anions. Molecular weight determinations in solution gave half the formula weight; *i.e.*, each mole of compound yielded two moles of ions. In contrast to these observations, the antimony compounds (the tetramethyl- and tetraphenylantimony derivatives of both anions) did not behave like salts under all conditions. Thus, although the tetramethylantimony derivatives were blue solids and dissolved in polar solvents to yield blue solutions, they were also soluble in non-polar solvents and gave yellow solutions. The tetraphenylantimony derivatives were yellow or yellow-green even in the solid state and gave yellow solutions in most solvents. In methanol or ethanol, however, the tetraphenylantimony derivative of the 1,1-dinitrosoethane anion did appear blue. Molecular weight determinations showed that the antimony compounds were covalent in the yellow solutions but 1:1 electrolytes in the blue solutions. It was concluded that the tetramethylantimony compounds had a greater tendency to be ionic substances, while the tetraphenylantimony compounds were more covalent. The authors also suggested that the antimony atom in the covalent complexes was probably hexacoordinate.

Kok and coworkers [79] have used pulsed NMR spectroscopy to investigate magnetic relaxation of the ^{121}Sb nucleus in tetramethylantimony iodide, tetraphenylantimony sulfate, fluoride, and chloride. The magnetic relaxation time T_2 obtained with tetramethylantimony iodide in aqueous solution (which has been shown to contain the tetrahedral tetramethylantimony cation) was about 200μsec and was dependent on both concentration and temperature. An Arrhenius plot of the longitudinal relaxation rate gave a value of 3.8 kcal/mol. A decrease in T_2 with increasing concentration was observed and was attributed to ion pairing which tended to distort the tetrahedral symmetry of the tetramethylantimony cation. Ion pairing was also invoked to explain the small T_2 value (70μsec) of this cation in methanolic solution.

Aqueous solutions of tetraphenylantimony sulfate and methanolic solutions of tetraphenylantimony fluoride and chloride were also studied, but signals were not observed because of extremely short T_2 values (∿10μsec) in these solutions. It was concluded that these results showed that the geometry of the tetraphenylantimony cation in water or methanol deviated significantly from tetrahedral.

In a paper devoted largely to quaternary arsenic compounds, Schiemenz [80] has described some molecular weight and PMR measurements on triphenylmethylantimony tetrafluoroborate and tetraphenylborate. It was concluded that these antimony compounds existed as contact ion pairs in solutions of chloroalkanes. In the tecrophenylborate, the aromatic ring current of the phenyl groups of the anion caused the PMR signal of the methyl protons to move upfield by about 0.7 ppm. The ion pairs were short-lived so that the tetraphenylborate anion had the characteristic properties of an NMR shift reagent. It has been claimed in the patent literature [81] that anion exchangers containing quaternary arsonium or stibonium groups were prepared by treating chloromethylated divinylbenzene-styrene copolymers with trimethylarsine or -stibine.

Schmidbaur and coworkers [82] have reported that tetramethylantimony fluoride, which previously had been prepared by the interaction of pentamethylantimony and trimethyltin fluoride, could be more readily obtained by the use of hydrogen fluoride or potassium bifluoride:

$$Me_5Sb + HF \rightarrow Me_4SbF + MeH$$

$$Me_5Sb + KHF_2 \rightarrow Me_4SbF + MeH + KF$$

The mass spectrum of tetramethylantimony fluoride was determined and compared with that of the analogous phosphorus compound. Corresponding peaks in the two spectra often appeared with quite different relative intensities. For example, the relative intensities of the ylid-like ions $Me_3SbCH_2^+$ and $Me_3PCH_2^+$ were 10% and 26%, respectively. The spectrum of the phosphorus compound exhibited only one fluorine-containing fragment (Me_3PF^+, relative intensity 100%), while the antimony compound yielded Me_3SbF^+ (100%), Me_2SbF^+ (15%), $MeSbF^+$ (25%), and SbF^+ (8%). It was concluded that the greater lability of the P-F bond tended to favor formation of the ylid-like ion mentioned above. The affinity of antimony for fluorine was also illustrated by the following addition reactions:

$$Me_4SbF + Me_4PF \rightarrow [Me_4P][Me_4SbF_2]$$

$$Me_4SbF + MeBu_3PF \rightarrow [MeBu_3P][Me_4SbF_2]$$

The infrared spectrum of the adduct formed in the first reaction suggested that the compound was composed of Me_4P^+ cations and $Me_4SbF_2^-$ anions. The ^{31}P NMR spectrum of the other adduct exhibited a signal at δ -32.0 ppm (with reference to 85% phosphoric acid). This chemical shift was considered to be in the range expected for tetracoordinated phosphonium cations. No P-F coupling was observed even at -80°.

The interaction of tri-*n*-butylantimony dibromide and methylmagnesium iodide has been found to yield a mixture of pentaalkylantimony compounds [83]. The mixture, which was analyzed by PMR spectroscopy, contained 75% of the expected tri-*n*-butyldimethylantimony, 20% di-*n*-butyltrimethylantimony, 4% *n*-butyltetramethylantimony, and 1% pentamethylantimony. The following reaction sequence (possibly involving hexacoordinate antimony intermediates of the type $[Bu_{5-n}SbMe_{n+1}]^-$) was suggested:

$$2MeMgI + Bu_3SbBr_2 \rightarrow Bu_3SbMe_2 \xrightarrow{MeMgI} Bu_2SbMe_3$$

$$\xrightarrow{MeMgI} BuSbMe_4 \xrightarrow{MeMgI} Me_5Sb$$

Similarly, the interaction of trimethylantimony dibromide and *n*-butylmagnesium bromide gave a mixture containing 66% of the expected di-*n*-butyltrimethylantimony in addition to 17% tri-*n*-butyldimethylantimony and 17% *n*-butyltetramethylantimony. Vacuum distillation of the reaction products failed to yield pure compounds. The PMR spectra of the mixtures showed that an increase in the number of *n*-butyl groups in a molecule of the type Bu_nSbMe_{5-n} led to an upfield shift in the methyl proton signal. It was concluded that the donor effect of the *n*-butyl group probably caused an increase in the electron density on the methyl hydrogen atoms.

Unlike pentaphenylantimony, which has long been known to exist as square-pyramidal molecules, penta-*p*-tolylantimony has been shown by X-ray data to exhibit the more common trigonal-bipyramidal structure [84]. The C-Sb equatorial bond length average (2.16Å) was significantly shorter than the axial C-Sb average (2.26Å). Two of the equatorial C-Sb-C bond angles (113°, 130°) differed considerably from the ideal value of 120°, but the other angles around antimony were normal. Preliminary results on the cyclohexane solvate of pentaphenylantimony, $Ph_5Sb\cdot\frac{1}{2}C_6H_{12}$, in the solid state indicated a virtually undistorted trigonal-bipyramidal configuration around the antimony atom. The NMR spectrum of penta-*p*-tolylantimony in carbon disulfide showed rapid intramolecular exchange of axial and equatorial groups at temperatures down to -100°C. It was concluded that pentaaryl-antimony derivatives consisted of highly flexible molecules and that relatively small variations in crystal packing energy could be responsible for important structural changes in the solid state.

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