a crystal radius of 0.98 A. Of course one must view such point-charge estimates with much skepticism.

Returning again to Table I, it will be found that S_1 and S_3 are much lower for the ultraviolet bands than for the infrared bands whereas experiment shows these absorptions to be of more nearly comparable intensity even when generous allowance is made for experimental uncertainty. We note, however, that when account is taken of the $\bar{\nu}$ factor in eq 13 and the fact that the excited states of the ultraviolet bands are much nearer the admixed opposite-parity states than are the excited states of the infrared bands, then the discrepancy between estimated and observed relative intensities is not so large.

It was noted previously[3] that under special conditions a weak shoulder is observed near 12,700 cm^{-1}, which is of uncertain origin. Let us suppose that this band belongs to the normal spectrum of the Bi$^+$ complex and see how this influences our theoretical analysis. What we find is that by changing F_2, λ, and B_0^2 slightly (to 960, 5100, and 8200 cm^{-1}, respectively) and increasing $|B_2^2|$ substantially (to 5700 cm^{-1}) we can still fit the spectrum reasonably well but by no means as

well as the fit presented in Table I. The band energies deviate from the measured value by larger amounts in this fitting as compared with the previous one, and the calculated relative values of S_1 and S_3 for the 12,700-cm^{-1} band are much larger than one would expect from the measured oscillator strength. Under this new scheme the ultraviolet bands are assigned to ligand field components of the free-ion $^3P_0 \rightarrow {}^1D_2$ transition, the weak infrared bands at 11,100 and 12,700 cm^{-1} are assigned to ligand field components of the free-ion $^3P_0 \rightarrow {}^3P_1$ transition, while the relatively strong bands at 14,400, 15,200, and 17,100 cm^{-1} are assigned to components of the free-ion $^3P_0 \rightarrow {}^3P_2$ transition. These new assignments are not greatly different from those achieved by neglecting the 12,700-cm^{-1} band.

We have not computed best parameters for the Bi$^+$ complex in ZnCl$_2$–KCl but quite clearly the band assignments and even the ligand field parameters are much the same as for Bi$^+$ in AlCl$_3$–NaCl. Differences between the spectra of Bi$^+$ in these two media are attributed to differences in the ligands, presumed to be chloroaluminate ions in one case and chlorozincate ions in the other.

The Chloramination of Some Substituted Stibines

By ROBERT L. McKENNEY and HARRY H. SISLER

Trimethyl-, triethyl-, tri-*n*-propyl-, tri-*n*-butyl-, and triphenylstibines react with ammonia-free chloramine or an ammonia–chloramine mixture to produce compounds of the type [R$_3$Sb(Cl)]$_2$NH (I). These compounds readily hydrolyze to [R$_3$Sb(Cl)]$_2$O (II). Further reactions of II are also described. Infrared and proton magnetic resonance studies were carried out on compounds of types I and II and on a variety of other antimony compounds. Qualitative assignments of infrared bands are given.

In earlier communications[1-3] it was reported that trialkylamines, trialkylphosphines, and trialkylarsines react with chloramine to produce the corresponding 1,1,1-trialkylhydrazinium, trialkylaminophosphonium, and trialkylaminoarsonium chlorides. Also, the formation of compounds of the type R$_3$Sb(OH)Cl has been reported,[4,5] leading one to believe that the corresponding R$_3$Sb(NH$_2$)Cl might be obtained by the chloramination of the trialkylstibine. However, other work[6-9] has

shown that partial hydrolysis of trialkyl- and triaryldichlorostibanes gives the anhydride-like compounds [R$_3$Sb(Cl)]$_2$O and not the hydroxy chlorides. This communication describes the results of the reaction of chloramine with various trialkylstibines and triphenylstibine. The hydrolysis of these products and their reaction with either aqueous or gaseous hydrogen chloride are also described.

Experimental Section

Materials.—Tri-*n*-butyl- and triphenylstibines were purchased from M & T Chemicals, Inc. The former was redistilled and the latter was recrystallized before use. All solvents used were reagent grade and were dried and stored over calcium hydride.

The gaseous mixture of chloramine and ammonia was produced by the gas-phase reaction of excess ammonia with chlorine in a generator similar to that described by Sisler and Omietanski.[10] The solution was freed of ammonia by the method of Gilson and

(1) G. Omietanski and H. Sisler, *J. Am. Chem. Soc.*, **78**, 1211 (1956).

(2) H. Sisler, A. Sarkis, H. Ahuja, R. Drago, and N. Smith, *ibid.*, **81**, 2982 (1959).

(3) C. Stratton and H. Sisler, *Inorg. Chem.*, **5**, 2003 (1966).

(4) G. Morgan, F. Micklethwait, and G. Whitby, *J. Chem. Soc.*, **97**, 34 (1910).

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(9) G. Doak, G. Long, and L. Freedman, *J. Organometal. Chem* (Amsterdam), **4**, 82 (1965).

(10) H. Sisler and G. Omietanski, *Inorg. Syn.*, **5**, 91 (1957).

Sisler[11] and additional contact with moisture was avoided by using vacuum line technique.

Analyses.—Elementary analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; Crobaugh Laboratories, Charleston, W. Va.; and Galbraith Laboratories, Inc., Knoxville, Tenn. Chloride analyses were usually carried out in this laboratory by the Volhard technique. Melting points were obtained on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Molecular weights were determined by the cryoscopic method using benzene as a solvent. Analytical and melting point data are listed in Table II.

Infrared Spectra.—Infrared spectra were obtained on a Beckman Model IR 10 spectrophotometer. The spectra of most of the products were obtained using Nujol or Kel-F mulls. The spectra of all the trialkylstibines were obtained using thin films. The infrared spectral absorptions are listed in Table IV and discussed in a later section.

Proton Magnetic Resonance Spectra.—The proton magnetic resonance spectra were obtained with a Varian Model V-4300-2 high-resolution nuclear magnetic resonance spectrometer, provided with field homogeneity control, magnet insulator, and field stabilizer, operating at 56.4 Mc or with a Varian Model A-60A nuclear magnetic resonance analytical spectrometer. The spectra were obtained by sweeping slowly through the field and interchanging the reference with the sample being studied. Usually acetaldehyde or tetramethylsilane was used as reference. Nmr data are listed in Table III.

Synthesis of Trialkylstibines.—Trimethyl-, triethyl-, and tri-*n*-propylstibines were prepared by the novel method of Stamm and Breindel,[12] who, however, did not report the preparation of the trimethyl- or tri-*n*-propylstibines. Trimethylstibine was distilled from the reaction products as a hexane solution and was then treated with a carbon tetrachloride solution of bromine.[13] The resulting trimethyldibromostibane was obtained in 76% yield; mp 185–186.5° dec (lit.[14] mp 200°). This compound was then reduced to trimethylstibine by the method of Morgan and Yarsley,[15] bp 80–81° (763 mm). Tri-*n*-propylstibine was obtained in 41% yield; bp 93–95° (15.5 mm) [lit.[16] bp 113° (39 mm) and 100° (25 mm)].

Procedure for Chloramination Reactions.—The anhydrous ether solution of ammonia-free chloramine was introduced into a vacuum line and distilled into a special flask equipped with a syringe cap. A 1-ml sample was taken and the chloramine concentration was determined.[11] The appropriate amount of stibine was then placed in the vacuum line and diluted with ether, and the once distilled chloramine solution was transferred into the reaction flask at liquid nitrogen temperature. Since the chloramine concentration in the residue is greatly increased during the distillation and the stability of such solutions is sometimes low, it is recommended that a drop or two of residue be left to avoid possible decomposition. A freshly distilled ethereal solution of ammonia-free chloramine can be redistilled to dryness with excellent recovery of chloramine in the distillate. The experimental details for the various chloramination reactions are summarized in Table I. Tri-*n*-butylstibine was allowed to react with the gaseous effluent of the chloramine generator,[10] since the use of ammonia-free chloramine and vacuum line technique gave a mixture from which the product could not be separated. The reaction of trimethyl- and triphenylstibines with ammonia-free chloramine gave side reactions in which trimethyldichloro- and triphenyldichlorostibanes were produced in variable yields.

Hydrolysis of Chloramination Products.—In most cases the imino compounds obtained in the chloramination reactions were exposed to the atmosphere until ammonia evolution ceased. Dry iminobis(triphenylchlorostibane) was placed in boiling

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(12) W. Stamm and A. Breindel, *Angew. Chem. Intern. Ed. Engl.*, **3**, 1 (1964).

(13) G. Morgan and G. Davies, *Proc. Roy. Soc.* (London), **A110**, 523 (1926).

(14) T. Lowry and J. Simons, *Ber.*, **63B**, 1595 (1930).

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(16) W. Dyke. W. Davies, and W. Jones, *ibid.*, 463 (1930).

TABLE I

REACTION CONDITIONS FOR THE CHLORAMINATION OF VARIOUS STIBINES

Compound	Product	Yield, %
$(CH_3)_3Sb$	$[(CH_3)_3Sb(Cl)]_2NH^a$	71 (10.2)^b
	$(CH_3)_3SbCl_2$	16
$(C_2H_5)_3Sb$	$[(C_2H_5)_3Sb(Cl)]_2NH^c$	87
$(n\text{-}C_3H_7)_3Sb$	$[(n\text{-}C_3H_7)_3Sb(Cl)]_2NH^d$	76.5
$(n\text{-}C_4H_9)_3Sb$	$[(n\text{-}C_4H_9)Sb(Cl)]_2NH^e$	51
$(C_6H_5)_3Sb$	$[(C_6H_5)_3Sb(Cl)] NH^f$	55–71
	$(C_6H_5)_3SbCl_2{}^g$	25–43

^{a} $(CH_3)_3SbCl_2$ was extracted from the imino product with boiling toluene. ^{b} Obtained as a mixture with a small amount of the imino product after allowing the toluene to cool to room temperature. ^{c} Product washed with hot cyclohexane, but can be recrystallized from hot benzene. ^{d} Product recrystallized from ether at low temperature. ^{e} Crude semisolid product was ground between porous plates until a flaky solid was obtained. ^{f} $(C_6H_5)_3$-$SbCl_2$ was removed from the imino product by washing with small portions of CCl_4 at room temperature; however, the imino product can be recrystallized from hot benzene. ^{g} $(C_3H_5)_3SbCl_2$ removed from the residue obtained upon evaporation of the toluene by treating with boiling alcohol.

wet acetone until ammonia evolution ceased. Generally the yields were approximately quantitative. Analytical and melting point data are given in Table II.

Reaction of the Anhydrides with Hydrogen Chloride.—Oxybis(trimethylchlorostibane) and oxybis(triphenylchlorostibane) react with concentrated hydrochloric acid and gaseous hydrogen chloride, respectively, to give the corresponding dichlorostibanes in excellent yield.

Preparation of the Nitrato Anhydrides.—The oxybis(trialkylnitratostibanes) were prepared by mixing an aqueous solution of the corresponding chloro compound with aqueous silver nitrate. Oxybis(triphenylnitratostibane) was prepared by allowing an alcoholic solution of triphenyldichlorostibane to react with alcoholic silver nitrate and recrystallizing the product from boiling water.[4] Trimethyldinitratostibane was prepared by allowing an aqueous solution of trimethyldibromostibane to react with aqueous silver nitrate until the precipitation of silver bromide was complete.[8] Analytical and melting point data are given in Table II.

Pyrolyis of Oxybis(trimethylchlorostibane).—Oxybis(trimethylchlorostibane), 2.02 mmoles, was placed in a small flask equipped with a take-off head and receiver. The apparatus was thoroughly evacuated and then brought to atmospheric pressure with dry nitrogen. The flask was slowly heated until a maximum temperature of 260° was reached and held for 0.5 hr. During this time a liquid distilled. A total of 0.32 g of distillate was obtained and identified as trimethylstilbine by vapor pressure measurements;[17] yield 71.4% of theory. The solid residue, 0.18 g, was identified as antimony(III) oxide by comparison of its infrared spectrum with that of an authentic sample of the compound;[18] yield 92.6% of theory. Methyl chloride is assumed to be the other product but was not measured in this experiment. The reaction is believed to proceed according to the equation

$$3[(CH_3)_3Sb(Cl)]_2O \xrightarrow{\Delta} Sb_2O_3 + 4(CH_3)_3Sb + 6CH_3Cl$$
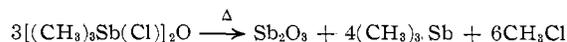
Preparation of Tri-*n*-butyldichlorostibane.[19-21]—Resublimed antimony(III) chloride, 0.137 mole, was dissolved in 100 ml of dry benzene and slowly added to tri-*n*-butylstibine, 0.204 mole, with vigorous stirring in a dry nitrogen atmosphere. The colorless liquid clouded and turned yellow, then orange, then brown, and finally black. The mixture was stirred overnight and then

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TABLE II

ANALYTICAL AND MELTING POINT DATA

Compound	Bp, °C (mm) or Mp, °C	%C Calcd	%C Found	%H Calcd	%H Found	%N Calcd	%N Found	%Sb Calcd	%Sb Found	%Cl Calcd	%Cl Found
$[(CH_3)_3Sb(Cl)]_2NH$	>200 dec[a]	17.17	18.13	4.56	4.79	3.34	3.69	58.03	58.81	16.90	17.14
$[(C_2H_5)_3Sb(Cl)]_2NH$	128–129.5	28.61	28.81	6.20	6.12	2.78	2.75	48.33	48.16	14.08	14.31
$[(n-C_3H_7)_3Sb(Cl)]_2NH$	83–85	36.77	36.58	7.37	7.22	2.38	2.17	41.42	42.13	12.06	11.99
$[(n-C_4H_9)_3Sb(Cl)]_2NH$	49–50	42.88	42.72	8.25	8.13	2.08	1.80	36.23	36.24	10.55	10.51
$[(C_6H_5)_3Sb(Cl)]_2NH$	219–220.5	54.59	54.26	3.94	4.13	1.77	1.81			8.95	9.15
$[(CH_3)_3Sb(Cl)]_2O$[b]	>200 dec[c]									16.85	16.66
$[(C_2H_5)_3Sb(Cl)]_2O$[d]	179–180	28.54	28.92	5.99	5.92					14.04	14.18
$[(n-C_3H_7)_3Sb(Cl)]_2O$[e]	98–100	36.71	36.75	7.19	7.16			41.34	41.39	12.04	11.75
$[(n-C_4H_9)_3Sb(Cl)]_2O$[f]	52–54	42.83	43.03	8.09	8.11					10.54	10.60
$[(CH_3)_3Sb(ONO_2)]_2O$[g]	262 dec	15.21	15.20	3.83	3.90	5.91	5.98				
$[(C_2H_5)_3Sb(ONO_2)]$[g]	233 dec	25.83	26.45	5.42	5.78						
$[(C_6H_5)_3Sb(ONO_2)]_2O$[g]	226 dec	51.10	51.00	3.57	3.64	3.31	3.31				
$(CH_3)_3Sb(ONO_2)_2$[g]	149–150	12.39	12.25	3.12	3.22	9.63	9.44				
$(n-C_4H_9)_3SbCl_2$	120–125 (0.14)	39.59	39.59	7.48	7.36					19.48	19.32
$(n-C_4H_9)_2SbCl$	121–123 (10)										

[a] Product decomposes to a metallic gray solid and a volatile reactive liquid. [b] Product recrystallized from alcohol. [c] Product decomposes to a white solid and a volatile reactive liquid. [d] Product recrystallized from hot cyclohexane. [e] Product recrystallized from hot *n*-hexane. [f] Product ground between porous plates until a flaky solid obtained. [g] Product recrystallized from hot alcohol.

TABLE III

¹H NMR SPECTRAL DATA[a]

Compound	CH₃	CH₂	C₆H₅	Solvent[b]
$[(CH_3)_3Sb(Cl)]_2NH$	7.57, 7.82, 7.97			
$[(CH_3)_3Sb(Cl)]_2O$	7.92			H_2O
	7.65, 7.97, 8.05			
$[(CH_3)_3Sb(ONO_2)]_2O$	7.95			H_2O
	8.03, 8.10, 8.45			
$[(C_2H_5)_3Sb(Cl)]_2NH$[c]	8.45	7.63		
$[(C_2H_5)_3Sb(Cl)]_2O$	8.39	7.37		H_2O
	8.55[c]	7.85		C_6H_6
$[(n-C_3H_7)_3Sb(Cl)]_2NH$	8.97	7.24–8.53		
$[(n-C_3H_7)_3Sb(Cl)]_2O$	8.97	7.43–8.55		CCl_4
$[(n-C_4H_9)_3Sb(Cl)]_2NH$	8.88	7.05–8.9		
$[(C_6H_5)_3Sb(Cl)]_2NH$			1.96–2.80	
$[(C_6H_5)_3Sb(Cl)]_2O$			2.08–2.80	
$[(C_6H_5)_3Sb(ONO_2)]_2O$			2.06–2.74	
$(CH_3)_3Sb(ONO_2)_2$	7.83			
$(CH_3)_3SbCl_2$	7.56			
$(CH_3)_3SbBr_2$	7.28			
$(C_6H_5)_3Sb$			2.44–2.96	
$(C_6H_5)_3SbCl_2$			1.54–1.90, 2.24–2.62	
$(C_6H_5)_3SbO \cdot 0.3H_2O$			1.85–2.28, 2.28–2.76	

[a] External standards were used unless otherwise indicated. [b] CDCl₃ was used as a solvent unless otherwise indicated. [c] Internal standard was used (C₆H₆).

heated to 50° for 2 hr. During this time the black solid turned metallic gray. The liquid was filtered in a drybox, the benzene was removed under reduced pressure, and the higher boiling liquid residue was distilled under vacuum; yield 61.8 g (83% of theory).

Tri-*n*-butyldichlorostibane is a colorless, mobile liquid which slowly hydrolyzes when exposed to the atmosphere. It decomposes to an orange, high-boiling liquid and a low-boiling liquid when heated over 200° at 200 mm pressure. Since compounds of the type R_2SbX are commonly prepared by heating the corresponding R_3SbX_2,[5,13] it is probable that the orange liquid is di-*n*-butylchlorostibine. No analytical data were obtained since the orange compound partially decomposed upon standing with the deposition of a black solid. The yield was 89% of theory.

Discussion

The generality of the reaction of ammonia-free chloramine with trialkylstibines and triphenylstibine has been clearly established. Side reactions are observed in some cases in which trialkyldichlorostibanes are obtained in variable yields. The chloramination is thought to proceed in accordance with the equations

$$R_3Sb + NH_2Cl \longrightarrow R_3Sb(NH_2)Cl \quad (1)$$

$$2R_3Sb(NH_2)Cl \longrightarrow [R_3Sb(Cl)]_2NH + NH_3 \quad (2)$$

and in some cases

$$2R_3Sb(NH_2)Cl \longrightarrow R_3SbCl_2 + R_3Sb + \tfrac{1}{3}N_2 + \tfrac{4}{3}NH_3 \quad (3)$$

or

$$R_3Sb(NH_2)Cl + NH_2Cl \longrightarrow R_3SbCl_2 + \tfrac{1}{3}N_2 + \tfrac{4}{3}NH_3 \quad (4)$$
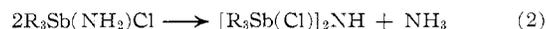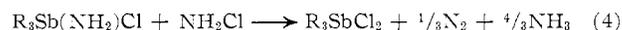
The reaction sequence postulated above is reasonable since step 1 has been shown to be the primary reaction in the case of trialkyl- and triarylphosphines and -arsines and step 2 would be expected because of the demonstrated stability of the imino product. The side reaction, which occurs in the case of trimethyl- and triphenylstibines, is an unusual reaction in which chloramine acts as a chlorinating agent. The reaction is postulated to be in accordance with eq 3 or 4. The factors which control the side reaction are not known at present.

TABLE IV[a]

INFRARED SPECTRAL DATA (CM^{-1})

[(CH$_3$)$_3$Sb(Cl)]$_2$NH

3225 m	2420 vw	2330 vw	2055 vw
1800 vw	1750 vw	1645 vw, b	1408 m
1238 vw, sh	1209 w	1098 vw	1055 vw
861 vs	741 vs	580 s	533 w

[(CH$_3$)$_3$Sb(ONO$_2$)]$_2$O

3010 m	2730 vw	2440 vw, d	2010 vw, d
1795 w, b	1720 w, b	1480–1380 vs, b	
1310–1275 vs, b		1238 w	1222 w
1018 vs	860 s	815 vs, sh	788 vs, b
715 vs	578 s	530 m	260 vw

(C$_2$H$_5$)$_3$Sb

2960 vs	2920 vs	2880 s	2835 w
2740 vw	1465 m	1428 w	1380 m
1235 vw	1185 m	1025 m	965 w, b
700 m	685 m, sh	655 w, sh	500 m

[(C$_2$H$_5$)$_3$Sb(Cl)]$_2$NH

3162 m, b	1670 vw, b	1284 vw	1212 m, sh
1193 s	1026 s	972 s	758 vs
704 vs	538 m, sh	528 m	497 w

[(C$_2$H$_5$)$_3$Sb(Cl)]$_2$O

2760 vw	2166 vw	1404 m	1200 s
1063 w, sh	1025 m	971 m	768 s, b
713 s, b	647 m, sh	545 m	498 vw
300 w, b	265 w		

[(C$_2$H$_5$)$_3$Sb(ONO$_2$)]$_2$O

2285 vw	1715 vw	1480–1420 vs, b	
1285 vs	1220 w, sh	1208 m	1095 w
1025 s, sh	1013 vs	980 m	815 s, sh
792 vs	702 vs	546 m	498 w

(n-C$_3$H$_7$)$_3$Sb

2960 vs	2936 vs	2905 s	2870 s
2820 w, sh	1460 m, sh	1455 m	1415 vw
1373 w	1332 w	1275 w	1190 vw
1170 w, sh	1155 w	1068 w	1020 vw
995 vw	800 vw	720 vw, b	680 vw, b
655 w, sh	585 w	500 w	

[(n-C$_3$H$_7$)$_3$Sb(Cl)]$_2$NH

3142 m	1657 vw, b	1417 w	1337 vw
1242 vw	1202 w	1174 m	1164 w, sh
1076 s	1012 s	815 w	752 vs
692 s	665 vw, sh	613 w	595 vw
516 vw	422 w		

[(n-C$_3$H$_7$)$_3$Sb(Cl)]$_2$O

2960 m	2930 m	2870 m	1455 m
1413 w	1373 w	1335 w	1278 w
1167 s	1075 s	1017 vw, sh	1008 s
802 vw, sh	754–734 s, d		696 s
628 w	607 w	522 w	395 w
300 m	285 m, sh	260 m	

(n-C$_4$H$_9$)$_3$Sb

2960 vs	2930 vs	2880 s	2860 s
2753 vw	1460 s	1420 w	1378 m
1360 vw	1351 w	1294 w	1250 w
1178 w	1148 w	1080 w	1050 vw
1022 vw	1005 w	961 w	876 w, b
770 vw	745 vw	686 w, b	590 w
500 w			

(n-C$_4$H$_9$)$_2$SbCl

2965 vs	2930 vs	2880 s	2870 s
2740 vw	1463 s	1412 w	1380 m
1360 vw	1344 w	1295 w	1250 w
1180 w	1152 w	1082 w	1050 vw
1025 vw	1005 vw	965 w	868 w, b
850 vw, sh	772 vw	748 vw	678 w, b
590 w	505 w		

[(n-C$_4$H$_9$)$_3$Sb(Cl)]$_2$NH

3162 m	2181 w	1582 w, b	1395 s
1252 w, b	1164 s	1082 s	1030 m
1002 w, sh	962 vw	883 m	768 vs
736 vs	698 vs	615 vw	511 vw

[(n-C$_4$H$_9$)$_3$Sb(Cl)]$_2$O

2965 vs	2930 vs	2870 s	1572 vw, b
1405 m	1343 m	1294 m	1253 vw
1181 s	1165 s	1081 m	1028 m
994 w, sh	885 s	855 m, sh	770 vs
743 vs	693 vs	620 w	562 w
524 w	460 vw, b	400 w	260 w

[(C$_6$H$_5$)$_3$Sb(Cl)]$_2$NH

3140 w	3070 vw, sh	3040 m	1570 m
1475 s	1430 vs	1329 m	1302 m
1268 vw	1180 m	1157 m	1090 vw
1061 s	1019 s	995 vs	985 w
975 w	969 w	915 m	880 vw, sh
850 w	840 vw, sh	765 vs	735 vs
690 vs	662 m, sh	655 w, sh	612 w
454 vs, sh	447 vs	385 vw	365 vw, sh
302 w, sh	285 m		

[(C$_6$H$_5$)$_3$Sb(Cl)]$_2$O

3044 w	1968 vw	1891 vw	1824 vw
1780 vw	1659 vw	1578 w	1482 s
1444 s, sh	1436 vs	1334 w	1307 w
1244 vw	1177 m	1153 w	1058 m
1018 m	966 s		913 w
851 vw	840 vw	768 vs	744 s
731 vs	690 vs	661 vw	653 vw
611 w		456 s	
448 s	388 vw	305 w, sh	290 m

[(C$_6$H$_5$)$_3$Sb(ONO$_2$)]$_2$O

3045 w	2240 w	1950 vw	1885 vw
1815 vw	1660 vw	1575 w	1510 m, sh
1492 vs	1475 m	1432 s	1335 w
1305 w, sh	1280 vs	1183 w	1160 vw
1064 m	1020 m	995 s	975 vs
915 vw	840 vw	802 w	740 vs
708 vs	690 vs	455 vs	455 s, sh
380 m; 300 w, sh;			
280 w, b			

(n-C$_4$H$_9$)$_3$SbCl$_2$

2970 vs	2940 vs	2880 s	2740 vw
1468 s	1410 m	1388 m	1350 w
1295 w	1255 m	1170 m	1095 m
1048 w	1005 vw	960 vw	890 m
860 w	760 w	712 m	615 vw
512 vw			

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; b, broad; d, doublet.

Iminobis(trialkylchlorostibanes) have been shown to readily hydrolyze to give the corresponding anhydride, [R$_3$Sb(Cl)]$_2$O, and ammonia. Hydrolysis occurs according to the equation

$$[R_3Sb(Cl)]_2NH + H_2O \longrightarrow [R_3Sb(Cl)]_2O + NH_3$$

The phenyl analog is, as might be expected, more difficult to hydrolyze.

Some of the oxybis(chlorostibanes) have been shown to react with either aqueous or gaseous hydrogen chloride to give the corresponding dichlorostibanes. This in accordance with the reports[5,8] that various oxides, R$_3$SbO, and their hydrates, R$_3$SbO·H$_2$O, react with hydrochloric acid to give the dichlorostibanes.

That the chloramination and hydrolysis products are truly imino and anhydride species is clearly established by infrared spectra, proton magnetic resonance data, and elemental analyses (Tables II–IV). Infra-

red spectra show the N–H stretching absorption in the 3225–3140 cm^{-1} (medium broad to weak) region and no deformation mode; the >N–H deformation absorption is very weak and normally not observed in solid-state spectra. Also, no absorption resulting from the O–H stretching vibration is found in the spectra of the hydrolysis products. This is in complete agreement with the proposed structures. Both aryl and alkyl compounds exhibit absorptions in or very near the frequency ranges commonly assigned to C–H and C–C stretching and deformation modes.

All of the alkyl compounds exhibit weak to strong absorptions in the 591–500 cm^{-1} region. Previous work[8,22] has clearly established that absorptions in this region result from antimony–carbon asymmetrical stretching vibrations. The lower-molecular-weight analogs also exhibit a medium to very weak absorption in the region of 534 cm^{-1} and below. Since this weaker absorption does not appear in the spectra of the dihalostibines, one might conclude that it results from the antimony–carbon symmetrical stretching vibration which is made infrared active by the reduced symmetry of the imino and oxy compounds.

The antimony–carbon asymmetrical stretching frequency for aryl compounds, such as triphenylstibine and triphenyldichlorostibane, must occur close to 450 cm^{-1}.[9,22] As a result, it is overlapped by the phenyl out-of-plane ring bending by quadrant vibration and occurs as a strong singlet. Imino- and oxybis(triphenylchlorostibane) both exhibit a strong sharp doublet in the 450 cm^{-1} region which is attributable to partial resolution of the above overlapping.

All of the oxyalkyl compounds currently under discussion exhibit a medium to weak broad band in the 285–300 cm^{-1} region followed by a sharp absorption at 265 cm^{-1}. The former band is ill-defined in some cases and is accompanied with shoulders. This is the general region of the spectrum in which one would expect the bond corresponding to the antimony–chlorine stretching vibration to occur. However, neither of the above-mentioned absorptions can be assigned to this vibration with any degree of certainty without further investigation in this region and below.

The corresponding aryl imino and oxy compounds exhibit a medium broad peak in the 270–300 cm^{-1} region. Triphenyldichloro- and triphenyldibromostibanes, oxybis(triphenylnitratostibane), and triphenylstibine oxide also exhibit an absorption in this region. It is therefore concluded that this peak must be char-

acteristic of pentavalent antimony compounds containing phenyl groups and it probably overlaps the antimony–chlorine absorption.[9]

The very strong absorption in the 788–736 cm^{-1} region, which occurs in all of the imino and oxy compounds, is assigned to the Sb–NH–Sb and Sb–O–Sb vibrations. Long[8] made a tentative assignment for the latter vibration, and Doak[9] verified it by studying a number of phenyl-containing compounds. Other data[18,23] are available that show infrared data for antimony–oxygen compounds. All are consistent with the above assignment.

The nitrato compounds prepared in this study exhibit the characteristic absorptions observed in the chloro compounds. They also exhibit strong absorptions in the 1505–1380 cm^{-1} (ν_4) and 1310–1275 cm^{-1} (ν_1) regions which are indicative of the covalent nitrate group[24] (C_{2v} symmetry). The degree of splitting between ν_4 and ν_1, which has been suggested to be a measure of covalent character,[24] decreases as we proceed from the phenyl compound to the methyl compound. These compounds also exhibit absorptions in the 1025–975 cm^{-1} (ν_2), 815–805 cm^{-1}, (ν_6), and 715–708 cm^{-1} (ν_3 or ν_5) regions. The infrared spectrum of trimethyldinitratostibane indicates the presence of covalent nitrato groups,[25] which is consistent with the other nitrato compounds.

Proton magnetic resonance spectra of these new compounds are somewhat complex, but are consistent with the proposed structures. The only exception is the spectrum of iminobis(trimethylchlorostibane), from which no conclusions could be drawn. Chemical shift values for a variety of compounds are listed in Table III.

The splitting which occurs in the phenyl absorption has also been observed in a number of phosphorus compounds and is in no way inconsistent with the postulation of equivalent phenyl groups.

Elementary analyses agree quite closely with the proposed formulas, particularly with respect to the per cent nitrogen, which would undergo the greatest change in a deviation from the imino structure. Molecular weight data are also in close agreement with the formulas.

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