are completely exchanged for silver ions which in turn are replaced by gallium ions on a mole for mole basis without altering the β-alumina structure. The mean valence state of the gallium in gallium(I) β-alumina is +1. The possibility of gallium existing in a mixed valence state (Ga^{3+},$2Ga^{0}$) in the aluminum oxide lattice seems improbable because two-thirds of the gallium would be Ga^{0} atoms which are not expected to be stable while dispersed in an oxide and would therefore separate into a metallic Ga phase leaving the crystals opaque. The gallium(I) β-alumina can be prepared as transparent, colorless single crystals. It is concluded that the gallium exists as Ga^{+} ions in the β-alumina lattice.

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Reactions of Triphenylgermyl Bromide with Ammonia and of Tri-*n*-propyltin Chloride with Ammonia and Sodium Amide

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We have noted that the report of the synthesis of tris(triphenylgermyl)amine by Kraus and Wooster[1] in 1930 continues to be listed in recent reviews.[2-4] No other report of the synthesis of this compound appears in the literature. We have found that the "calculated" percentage of nitrogen for $[(C_6H_5)_3Ge]_3N$ given by Kraus and Wooster in their paper is incorrect, and have repeated their procedure with results which indicate that the product obtained is not $[(C_6H_5)_3Ge]_3N$, but rather is $[(C_6H_5)_3Ge]_2NH$. Since the reaction of triphenylgermanium bromide and ammonia has been shown to yield bis(triphenylgermyl)amine instead of tris(triphenylgermyl)amine, it can now be observed that this reaction is analogous to the reaction of trialkylgermanium halides with ammonia or sodium amide[5,6] in that the secondary rather than the tertiary amine is formed.

Only three tris(trialkylstannyl)amines have been reported: $[(CH_3)_3Sn]_3N$,[7] $[(C_2H_5)_3Sn]_3N$,[8] and $[(n\text{-}C_3H_7)_3Sn]_3N$.[8] There is no reason to doubt the identification of the first compound, since Lehn[9] confirmed it by molecular weight determination in 1964. However, since no molecular weight determinations have been made on the remaining two compounds, their identification must be subject to some doubt, since the expected elemental analyses of corresponding tertiary and secondary compounds, such as $[(n\text{-}C_3H_7)_3Sn]_3N$ and $[(n\text{-}C_3H_7)_3Sn]_2NH$, are very similar. We have repeated the procedures of Sisido and Kozima[8] and have isolated two compounds, $[(n\text{-}C_3H_7)_3Sn]_2NH$ and $[(n\text{-}C_3H_7)_3Sn]_3N$, instead of one as previously reported. This is the first report of a distannyl-substituted amine having an NH bond. No attempt was made to maximize the yield of either product. We suggest that the compound isolated by Sisido and Kozima may have been $[(n\text{-}C_3H_7)_3Sn]_2NH$, rather than $[(n\text{-}C_3H_7)_3Sn]_3N$ as claimed by them; however, this suggestion is based solely on comparison of boiling points, since this was the only property given in their report. It should be recognized that comparison of boiling points obtained under reduced pressure is often not reliable. However, regardless of boiling point considerations, the fact remains that two distinct compounds were obtained when only one was previously reported.

Experimental Section

Elemental analysis of the germanium compound was carried out by Galbraith Laboratories, Inc., Knoxville, Tenn., and of the tin compounds by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points (uncorrected) were obtained using a Thomas-Hoover capillary melting point apparatus. Infrared spectra were obtained with a Beckman IR-10 spectrophotometer using potassium bromide disks. Mass spectral data were obtained using a Hitachi Perkin-Elmer RMU-6E mass spectrometer at an ionizing voltage of 70 eV, calibrated at $m/e = 200$. Proton magnetic resonance spectra were obtained with a Varian A-60A instrument.

Triphenylgermanium bromide was prepared from tetraphenylgermane according to the procedure of Kraus and Foster[10] (mp 136–139°, lit.[10] mp 138.7°). Tri-*n*-propyltin chloride was used as purchased from Alfa Inorganics, Inc. Reagent grade solvents were dried by storing over calcium hydride in the inert atmosphere box. All operations such as transfers, filtrations, and preparation of samples for determination of their infrared and nuclear magnetic resonance spectra were carried out in the inert atmosphere box, Dri-Lab Model HE-43 with Dri Train HE-93B, from Vacuum Atmospheres, Inc.

Reaction of Triphenylgermanium Bromide with Ammonia.—A procedure, analogous to the reported procedure of Kraus and Wooster,[1] was used. Ammonia was introduced into a solution of 3.07 g of triphenylgermanium bromide in 50 ml of carbon tetrachloride until no further reaction was noted at room temperature and the mixture was left to stand for 24 hr. It was filtered and the solvent was removed from the filtrate by distillation under reduced pressure. It was warmed to 205° for 4 hr and then held under reduced pressure to remove the ammonia. The liquid solidified upon cooling. It was recrystallized from hot petroleum

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ether in a drybox. The reported melting point for $[(C_6H_5)_3Ge]_3N$ is 163–164° (corrected).[1] The melting point of the solid isolated in this experiment, after recrystallization, was 156–157° (uncorrected). Molecular weight, spectra, and analysis, however, support the contention that the solid is $[(C_6H_5)_3Ge]_2NH$. The yield was 77% based on the initial amount of triphenylgermanium bromide and the equation

$$2(C_6H_5)_3GeBr + 3NH_3 \rightarrow [(C_6H_5)_3Ge]_2NH + 2NH_4Br$$

The molecular weight was determined cryoscopically in benzene (Table I) in our laboratory and is supported by the mass spectrum of the solid (Table II). Analytical results are shown in Table I. A broad absorption at −50 Hz, in addition to the phenyl proton absorptions (centered at −440 Hz), was detected in the proton magnetic resonance spectrum of a solution of the solid in chloroform-*d* with respect to tetramethylsilane as an internal standard. The relative area ratio between the two absorptions was appropriate for the assumption that the absorption at −50 Hz is due to the NH proton (found, 1.0 to 30.0; calcd, 1 to 30).

The infrared spectrum of the solid in the form of a Halocarbon mull did not exhibit an absorption in the NH stretching region (3500–3300 cm^{-1}); however, the spectrum of a solution of the solid in dry carbon tetrachloride, prepared and sealed in the inert atmosphere box, exhibited an absorption at 3480 cm^{-1}. The absence of the NH absorption in the mull spectrum can be attributed to the inferior quality of mull spectra compared with that of solution spectra.

TABLE I

	% C	% H	% N	% Ge	mol wt
Calcd for $[(C_6H_5)_3Ge]_3N$ (ref 1)	. . .	. . .	1.98	. . .	. . .
Found (ref 1)	. . .	. . .	1.94	. . .	. . .
Calcd for $[(C_6H_5)_3Ge]_3N$	70.06	4.90	1.51	23.52	926
Calcd for $[(C_6H_5)_3Ge]_2NH$	69.42	5.02	2.25	23.31	623
Found	68.71	5.27	2.39	23.19	570 ± 80

TABLE II

MASS SPECTRA—PARENT AND PRINCIPAL PEAKS DUE TO SINGLY CHARGED IONS CONTAINING THE MOST ABUNDANT ISOTOPE OF THE GROUP IV ELEMENT[a]

$[(C_6H_5)_3Ge]_2NH$

$[(C_6H_5)_3Ge]_2NH$ (625), 49; $(C_6H_5)_5Ge_2NH$ (548), 63; $(C_6H_5)_4Ge_2NH$ (471), 20; $(C_6H_5)_3Ge_2NH$ (394), 15; $(C_6H_5)_3Ge_2$ (379), 20; $(C_6H_5)_3GeNH$ (320), 30; $(C_6H_5)_3Ge$ (305), 100; $(C_6H_5)_2GeNH$ (243), 20; $(C_6H_5)_2Ge$ (228), 30; C_6H_5Ge (151), 60; Ge (74), 20

$[(n\text{-}C_3H_7)_3Sn]_2NH$

$[(C_3H_7)_3Sn]_2NH$ (513), 2; $(CH_3Sn)_2NH$ (285), 24; $(C_3H_7)_3Sn$ (249), 76; Sn_2 (240), 24; $(C_2H_5)_3Sn$ (207), 100; $(CH_3)_3Sn$ (165), 85; Sn (120), 58

$[(n\text{-}C_3H_7)_3Sn]_3N$

$[(C_3H_7)_3Sn]_3N$ (761), 1; $(C_3H_7)_3(C_2H_5)_3Sn_2N$ (470), 91; $[(C_2H_5)_3Sn]_2N$ (428), 66; $(C_2H_5)_3(CH_3)_3Sn_2N$ (386), 39; $[(CH_3)_3Sn]_2N$ (344), 52; $CH_3SnNSnC_2H_5$ (298), 36; $(CH_3Sn)_2N$ (284), 54; Sn_2N (254), 81; $(C_3H_7)_3Sn$ (249), 47; $C_3H_7(C_2H_5)_2Sn$ (221), 54; $(C_2H_5)_3Sn$ (207), 47; $C_2H_5(CH_3)_2Sn$ (179), 17; $(CH_3)_3Sn$ (165), 100; CH_3Sn (135), 37; Sn (120), 53

[a] The mass number is given in parentheses, followed by the relative intensity which is based on peak height.

TABLE III

INFRARED SPECTRA[a]

$[(C_6H_5)_3Ge]_2NH$ (mulls, except as noted)

3480 m (CCl_4 soln), 3080 w, 3060 w, 3010 w, 1490 m, 1440 s, 1310 w, 1270 w, 1190 s, 1170 m, 1100 s, 1030 w, 1000 w, 975 w, 915 w, 850 w, 820 s, 735 s, 700 s, 675 m, 460 m

$[(n\text{-}C_3H_7)_3Sn]_2NH$ (pure liquid)

3350 w (CCl_4 soln), 2950 s, 2920 s, 2900 s, 2860 s, 2810 m, 2720 w, 1450 m, 1410 m, 1370 m, 1330 m, 1270 w, 1190 w, 1170 w, 1150 w, 1060 s, 1015 w, 985 m, 790 s, b, 710 s, 685 m, 650 m, 580 m, 490 m

$[(n\text{-}C_3H_7)_3Sn]_3N$ (pure liquid)

2950 s, 2925 s, 2900 s, 2860 s, 2805 m, 2715 w, 1450 s, 1410 m, 1370 m, 1330 m, 1275 w, 1200 w, 1170 w, 1150 w, 1060 s, 1020 m, 980 m, 780 m, 705 s, 680 s, sh, 650 m, sh, 580 m, 490 m

[a] s, strong; m, medium; w, weak; b, broad; sh, shoulder.

Reaction of Tri-*n*-propyltin Chloride with Ammonia and Sodium Amide.—The reported procedure A of Sisido and Kozima[5] was followed, except that the reaction mixture was held at 0° for 20 hr instead of at −50° for 2 hr. A fraction, boiling at 124° (0.20 mm), was obtained, which appears to correspond to the reported boiling point of 143–145° (0.6 mm) for tris(tri-*n*-propylstannyl)amine. However, this fraction was identified as bis(tri-*n*-propylstannyl)amine, $[(n\text{-}C_3H_7)_3Sn]_2NH$, by its elemental analysis and mass spectrum (Table II). The yield was 46%, based on the initial amount of tri-*n*-propyltin chloride. *Anal.* Calcd for $[(n\text{-}C_3H_7)_3Sn]_2NH$: C, 42.31; H, 8.48; N, 2.74; Sn, 46.46. Found: C, 41.95; H, 8.47; N, 2.54; Sn, 46.45. No absorption corresponding to an NH proton was detected in the proton magnetic resonance spectrum of a chloroform-*d* solution of the liquid, which is not unexpected, in view of the usual quadrupole broadening of an NH absorption.[11] The infrared spectrum of the pure liquid (Table III) did not exhibit an absorption in the NH stretch region, which agrees with the observation of Sisido and Kozima. However, a carbon tetrachloride solution of the liquid did exhibit a very weak absorption at 3350 cm^{-1}.

The temperature dropped after the first liquid had distilled and then it increased until a second liquid boiling at 161° at 0.20 mm distilled. This was identified as tris(tri-*n*-propylstannyl)amine, $[(n\text{-}C_3H_7)_3Sn]_3N$, by its mass spectrum (Table II) and elemental analysis. The yield was 20%, based on the initial amount of tri-*n*-propyltin chloride. The infrared spectrum of the pure liquid is tabulated in Table III. A carbon tetrachloride solution of the liquid did not exhibit an absorption in the NH stretching region. *Anal.* Calcd for $[(n\text{-}C_3H_7)_3Sn]_3N$: C, 42.79; H, 8.38; N, 1.85; Sn, 46.98. Found: C, 43.11; H, 8.59; N, 2.08; Sn, 46.90.

The absence of the NH absorption in the spectrum of bis(tri-*n*-propylstannyl)amine in the pure liquid state may be the result of intermolecular hydrogen bonding which could cause the absorption to be shifted, perhaps to a point where it is overlapped by CH absorptions. Hydrogen bonding in organo amines has been investigated and shifts of the NH stretching absorption to lower frequencies have been observed (up to 375 cm^{-1}).[12] The shift has been shown to be greater if the base strength of the species involved in the hydrogen bond is greater.[12,13] Assuming that this observation holds for the series of group IV substituted amines and in view of the fact that stannyl-substituted amines are more basic than organo amines,[14] the NH stretching fre-

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quency could be shifted more when the hydrogen is bonded with a stannyl-substituted amine than with an organo amine. This conjecture is supported by observations that the CD[15,16] and OH[17] stretching frequencies do undergo a much greater shift upon hydrogen bonding with a stannyl-substituted amine than with an organo amine. Therefore, it is probable that the NH stretching frequency in bis(tri-*n*-propylstannyl)amine could be shifted to the region of the CH absorptions (400 cm^{-1} shift) and escape detection by overlap with the CH absorptions.

The NH absorption observed for the solution appeared to be unusually weak, which is in agreement with the observation that the intensity of the NH absorption is much less when the base is stronger,[18] assuming that this observation for organo amines can be extended to group IV substituted amines. It will be interesting to compare other secondary or primary tin- or lead-substituted amines when they are reported.

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The Gas-Phase Synthesis and Some Reactions of Bromamine and Dimethylbromamine

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The gas-phase synthesis of chloramine has been known for some time[1] but there has been no previously published work on the gas-phase synthesis of bromamine, NH_2Br, and dimethylbromamine, $(CH_3)_2NBr$. Bromamine has been synthesized at low temperatures by mixing ethereal solutions of bromine and ammonia,[2,3] and more recently there have been investigations of the formation and stability of aqueous solutions of bromamine by Johannesson[4] and Morris.[5]

In this study bromamine and dimethylbromamine have been formed in a generator similar to that used in the gas-phase synthesis of chloramine,[1] but in much smaller yields. The reaction of bromine with ammonia to produce bromamine can be represented by

$$Br_2(g) + 2NH_3(g) \rightarrow NH_2Br(g) + NH_4Br(s)$$

however, the actual yield of bromamine is subject to side reactions such as

$$8NH_3(g) + 3Br_2(g) \rightarrow N_2(g) + 6NH_4Br(s)$$

Reported in this paper are $[H_2NP(C_6H_5)_3]Br$, $[(CH_3)_2NP(C_6H_5)_3]Br$, and $[(CH_3)_2NP(C_4H_9)_3]Br$ which were synthesized by allowing the appropriate phosphine to react with bromamine or dimethylbromamine.

Experimental Section

Materials.—The bromine, ammonia, and dimethylamine used were of reagent grade and were used without further purification. Triphenylphosphine and tri-*n*-butylphosphine were obtained from Eastman Organic Chemicals and Carlisle Chemical Works respectively, and were used without further purification.

The gases introduced into the generator were metered by flow meters which were calibrated with nitrogen gas. Gaseous bromine was obtained by bubbling nitrogen through liquid bromine.

In the work with dimethylbromamine all reactions were carried out under nitrogen and the products were then transferred to a glove bag because of the hygroscopic nature of the compounds.

Apparatus.—Infrared spectra were obtained with a Perkin-Elmer Model 137 Infracord spectrometer. The infrared spectral data are presented in Table I. The pmr spectra were obtained with either a Varian A-60A spectrometer or a Varian HA-100 spectrometer. The spectra were run on precalibrated chart paper at either 500- or 1000-cps sweep width with tetramethylsilane as the internal reference. In Table II are reported the pmr spectral parameters for the compounds synthesized.

TABLE I[a]

INFRARED DATA IN NUJOL (CM^{-1})

$[H_2NP(C_6H_5)_3]Br$

3330 sh, 2900 vs, 2840 sh, 1590 m, 1553 m, 1481 sh, 1466 s, 1433 s, 1400 sh, 1372 s, 1364 sh, 1333 w, 1310 w, 1186 w, 1156 w, 1120 s, 1110 sh, 1028 w, 992 w, 980 sh, 966 s, 756 s, 749 m, 720 s, 691 s

$[(CH_3)_2NP(C_6H_5)_3]Br$

2900 vs, 2840 sh, 1590 w, 1464 s, 1445 sh, 1380 s, 1370 sh, 1300 w, 1164 m, 1116 m, 1110 sh, 1066 w, 1005 sh, 995 sh, 985 m, 766 w, 738 sh, 725 s, 694 sh, 686 m

$[(CH_3)_2NP(C_4H_9)_3]Br$

2900 vs, 2450 w, 2137 w, 1653 w, 1600 w, 1493 sh, 1470 vs, 1440 sh, 1418 m, 1385 m, 1350 w, 1305 s, 1253 m, 1238 m, 1215 m, 1170 s, 1104 sh, 1090 s, 1078 sh, 1053 w, 1026 sh, 994 vs, 917 s, 911 sh, 900 sh, 873 w, 825 m, 805 m, 763 bw, 740 m, 729 sh, 714 sh

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; b, broad.

Bromamine.—Bromamine was synthesized in the gas phase by introducing nitrogen, gaseous bromine, and a large excess of ammonia into the generator. As indicated previously, ammonium bromide is formed along with the bromamine. Table III shows the per cent yield of bromamine obtained during each change in the $Br_2/NH_3/N_2$ ratio. The concentration of bromamine (or dimethylbromamine) in the effluent gases was determined by bubbling the gases from the generator into a potassium iodide solution for a timed interval. The solution was then acidified and a known excess of 0.100 *N* $S_2O_3^{2-}$ was added to reduce the iodine present to iodide ion. The solution was then back-titrated with 0.100 *N* iodine.

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