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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Table II

Proton Magnetic Resonance Data in $CDCl_3$

Compound	τ,[a] ppm, from TMS: C_6H_5[b]	NH_2	$N-CH_3$	$P-CH_2$	$-CH_2-$	$-CH_3$
$[H_2NP(C_6H_5)_3]Br$	2.25 m	2.89 b				
$[(CH_3)_2NP(C_6H_5)_3]Br$	2.22 m		6.96 d (10.2)			
$[(CH_3)_2NP(C_4H_9)_3]Br$			7.13 d (9.8)	7.43 m	8.46 m	9.01 m

[a] Abbreviations: m, multiplet; d, doublet; b, broad. Coupling constants in cps are in parentheses. [b] The chemical shift values of the phenyl peaks were obtained by measuring to the highest part of the peak.

Table III

Yield Data from the Synthesis of Bromamine

$Br_2/NH_3/N_2$, mol/hr	Approx ratio	Mol of NH_2Br/hr	Total mol/hr	% yield
0.014/1.57/1.73	1/112/124	0.0021	3.31	15.0
0.020/1.57/1.78	1/79/90	0.0019	3.37	8.0
0.010/1.57/1.57	1/157/157	0.0013	3.15	13.4
0.016/1.57/1.59	1/98/99	0.0017	3.18	11.0
0.033/1.57/1.66	1/48/50	0.0026	3.26	7.9
0.069/1.57/1.53	1/23/22	0.0011	3.17	1.6
0.020/1.57/1.04	1/79/52	0.0014	2.63	7.0
0.020/1.57/0.685	1/79/34	0.00091	2.27	4.6
0.020/1.57/0.250	1/79/13	0.00042	1.84	2.1
0.047/1.57/2.31	1/33/49	0.0023	3.93	4.9
0.047/1.57/1.57	1/33/33	0.0017	3.19	3.7
0.047/1.57/1.22	1/33/26	0.00085	2.84	1.8
0.158/1.42/1.22	1/9/8	0.0033	2.80	2.1

Dimethylbromamine.—Substituting dimethylamine for ammonia in the reaction mixture of gases in the generator produces gaseous dimethylbromamine and dimethylammonium bromide. Table IV shows the per cent yield of dimethylbromamine obtained during each change in the $Br_2/(CH_3)_2NH/N_2$ ratio. The generator was heated to 50° to retard condensation of the reaction mixture.

Table IV

Yield Data from the Synthesis of Dimethylbromamine

$Br_2/(CH_3)_2NH/N_2$, mol/hr	Approx ratio	Mol of $(CH_3)_2NBr$/hr	Total mol/hr	% yield
0.019/1.84/1.88	1/97/99	0.0058	3.74	31
0.022/1.84/1.88	1/84/85	0.0070	3.75	32
0.033/1.60/1.43	1/49/43	0.0073	3.06	22
0.038/1.60/1.44	1/43/38	0.0077	3.08	20
0.043/1.60/1.45	1/37/34	0.0072	3.09	17
0.026/1.18/1.22	1/45/47	0.0072	2.43	28
0.032/1.18/1.17	1/37/37	0.0068	2.38	22
0.042/1.18/1.25	1/28/30	0.0070	2.47	17
0.052/1.18/1.28	1/23/25	0.0072	2.51	14
0.064/1.18/1.31	1/18/20	0.0068	2.56	11
0.078/1.18/1.35	1/15/17	0.0066	2.61	9
0.102/1.18/1.45	1/12/14	0.0092	2.73	9

$[H_2NP(C_6H_5)_3]Br$.—Bromamine was generated in the gas phase and bubbled for 20 min into 50 ml of toluene containing 1 g of triphenylphosphine. The reaction mixture was allowed to stand for 2 hr to permit the excess ammonia to escape. The solvent was then removed and the product was separated from NH_4Br with chloroform. Recrystallization was affected by the addition of a small amount of ether. The white crystalline product was the previously unreported aminotriphenylphosphonium bromide with a melting range of 247–249 °

$$(C_6H_5)_3P + NH_2Br \rightarrow [H_2NP(C_6H_5)_3]Br$$

The yield, based on bromamine in the above equation, is essentially 100%. The identity of this compound was verified by ir, pmr, and elemental analyses. *Anal.* Calcd for $[H_2NP(C_6H_5)_3]Br$: C, 60.36; H, 4.79; Br, 22.31; N, 3.91; P, 8.65. Found: C, 60.33; H, 4.88; Br, 22.09; N, 3.93; P, 8.74.

$[(CH_3)_2NP(C_6H_5)_3]Br$.—Using 35 ml of hexane as a solvent in the reaction vessel, dimethylbromamine was generated and the effluent gases from the generator were bubbled through the solvent for 30 min. At the end of this time the reaction mixture separated into a yellow liquid and a white precipitate, dimethylammonium bromide. The mixture was allowed to stand for 2 hr to allow the excess dimethylamine to evaporate and was then filtered. The filtrate was transferred to a dropping funnel and was then added dropwise, with stirring, to 50 ml of hexane in which 2 g of triphenylphosphine had been dissolved. A white precipitate formed which was collected after being washed with two portions of hexane and one of ether. The resulting hygroscopic white crystalline solid had a melting range of 145–146 °. The weight of product indicated a quantitative yield based on an addition reaction. Purification attempts by recrystallization and sublimation were unsuccessful. A sample of this material was hydrolyzed with base in a vacuum line and the products of the reaction were the expected dimethylamine and triphenylphosphine oxide. The pmr spectrum, Figure 1, and the elemental analyses indicate that there is an impurity present in a small amount which is probably dimethylammonium bromide. The infrared spectrum contains a very weak N–H absorption which adds weight to this assumption. *Anal.* Calcd for $[(CH_3)_2NP(C_6H_5)_3]Br$: C, 62.19; H, 5.48; N, 3.63; Br, 20.69; P, 8.02. Found: C, 59.81; H, 5.61; N, 3.75; Br, 22.05; P, 8.37.

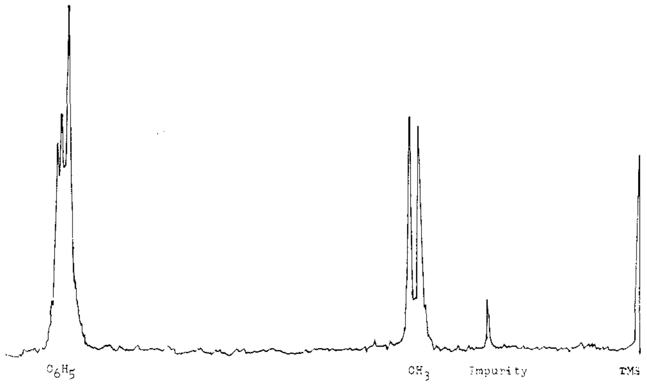

Figure 1.—Proton magnetic resonance spectrum of $[(CH_3)_2NP(C_6H_5)_3]Br$ showing the impurity.

$[(CH_3)_2NP(C_4H_9)_3]Br$.—Using the above procedure 2 g of tri-*n*-butylphosphine was allowed to react with dimethylbromamine to form a white crystalline solid that had a melting range of 131–136°. The yield was essentially quantitative based on an addition reaction. The pmr spectrum and the elemental analyses indicate that the product is dimethylaminotri-*n*-butylphosphonium bromide. *Anal.* Calcd for $[(CH_3)_2NP(C_4H_9)_3]Br$: C, 51.53; H, 10.18; N, 4.29; P, 9.49; Br, 24.49. Found: C, 51.17; H, 9.83; N, 4.45; P, 9.86; Br, 24.39.

Discussion

The experiments above allow the following conclusions to be drawn.

(1) Bromamine, NH_2Br, can be synthesized in the gas phase by the reaction between bromine and ammonia, but the yield in moles per hour is quite low. The low concentrations are, however, in accord with the findings of Coleman, *et al.*,[6] concerning their inability to obtain high concentrations of bromamine in ether solution. They report yields varying from 0.042 to 0.054 mol/l.

The formation of bromamine in the gas phase was confirmed by comparing the absorption spectra of the product in ethereal and aqueous solutions with the 284- and 278-mμ peaks reported by Johannesson[4] and Morris[5] and by the synthesis and characterization of aminotriphenylphosphonium bromide.

Table III shows the effect of changes in the $Br_2/NH_3/N_2$ ratio on the yield of bromamine. The table indicates that the Br_2/NH_3 ratio is one factor controlling the yield. Generally a small ratio or a large excess of ammonia gives the best yield. Another factor is the total number of moles of gas passing through the generator. A rapid flow through the reaction zone would sweep the bromamine out of the hot zone before it could decompose by

$$3NH_2Br + 2NH_3 \rightarrow 3NH_4Br + N_2$$

The rapid flow is achieved by increasing the nitrogen flow through the system.

(2) Dimethylbromamine, $(CH_3)_2NBr$, can also be synthesized in the gas phase by an analogous reaction using bromine and dimethylamine. Because of the difficulties encountered in attempts to purify reaction products, the effluent gases from the generator were bubbled into a nonhydrogen-bonding solvent and then the mixture was allowed to stand to allow the excess dimethylamine to escape. As the concentration of dimethylamine is reduced, the dissolved dimethylammonium bromide crystallizes out. This procedure is followed because the phosphorus-containing reaction products could not be recrystallized and, therefore, could not be separated from the dimethylammonium bromide.

Table IV indicates that a large excess of dimethylamine is necessary to obtain a reasonable yield of dimethylbromamine. The yields of dimethylbromamine are considerably higher than the yields of bromamine: 0.0092 mol/hr as compared to 0.0033 mol/hr for the highest yields in the two reactions.

(3) Bromamine reacts with triphenylphosphine in a manner similar to that of chloramine to produce the expected aminotriphenylphosphonium bromide, $[H_2NP(C_6H_5)_3]Br$. The infrared spectrum of this material was noted to be essentially the same as the infrared spectrum of the chloride analog.

(4) Dimethylbromamine reacts with triphenylphosphine and tri-*n*-butylphosphine to produce dimethylaminotriphenylphosphonium bromide, $[(CH_3)_2NP(C_6H_5)_3]Br$, and dimethylaminotri-*n*-butylphosphonium bromide, $[(CH_3)_2NP(C_4H_9)_3]Br$, respectively.

The pmr spectra of the compounds synthesized compare favorably with the spectra of similar known compounds. The spectrum of $[H_2NP(C_6H_5)_3]Br$ gives the chemical shift for the NH_2 protons as 2.89 ppm relative to the TMS peak, compared with 2.68 ppm for the chemical shift of the NH_2 protons in $[H_2NP(C_6H_5)_3]Cl$.[7] The spectra of $[(CH_3)_2NP(C_6H_5)_3]Br$ and $[(CH_3)_2NP(C_4H_9)_3]Br$ give the chemical shifts for the N–CH_3 protons as 6.96 and 7.13 ppm, respectively. These values compare favorably with the reported values of 6.96 ppm for $[((CH_3)_2N)_3PBr]Br$[8] and 7.05 ppm for $[(C_6H_5)_2P(N(CH_3)_2)NH_2]Cl$.[7]

The magnitude of the coupling constants J_{PNCH} is in accord with the value of 10.6 ± 1.1 cps reported by earlier workers for a variety of phosphonium compounds.[7] The chemical shifts of $(CH_3)_2N$ protons are reported to be constant (τ 7.11 ± 0.06),[7] being almost unaffected by other substituents on the phosphorus atom. These protons in dimethylaminotriphenylphosphonium bromide, $[(CH_3)_2NP(C_6H_5)_3]Br$, have a chemical shift which is outside the reported range by 0.09 τ unit. However, the $(CH_3)_2N$ protons in the dimethylaminotri-*n*-butylphosphonium bromide are well within the reported range.

Infrared spectra of the new aminophosphonium bromides given in Table I are similar to spectra reported by other workers.

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A New Series of Rare Earth Garnets $Ln^{3+}{}_3M_2Li^+{}_3O_{12}$ (M = Te, W)[1]

BY H. M. KASPER

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The preparation of tellurate garnets $\{A^{2+}{}_3\}[Te_2]\cdot(B^{2+}{}_3)O_{12}$, with A = Ca or Cd and B = Zn or Co, was recently reported.[2] This suggests the possibility of

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[2] H. M. Kasper, *Mater. Res. Bull.*, **3**, 765 (1968).