CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA 32601

The Reaction of Chloramine and Dimethylchloramine with Tris(trimethylsilyl)phosphine and Some Silyl-, Germyl-, and Stannylamines

BY RONALD E. HIGHSMITH AND HARRY H. SISLER

Chloramine has been found to cleave the metal–nitrogen bonds in dimethyl(trialkylsilyl)amines, certain germylamines, and stannylamines to produce a trialkylmetal halide, nitrogen, and ammonia or dimethylamine. Dimethylchloramine cleaves the tin–nitrogen bond in dimethyl(tri-n-butylstannyl)amine to produce tri-n-butyltin chloride and other unidentified products. Certain silylamines, particularly those with two or more silyl groups attached to the nitrogen, were found to be inert toward chloramine and dimethylchloramine. Chloramine and dimethylchloramine cleave all of the silicon–phosphorus bonds in tris(trimethylsilyl)phosphine to produce aminophosphines and trimethylchlorosilane. Reaction between chloramine and dimethyl(trialkylstannyl)amines can produce pure 2,2-dimethyltriazanium chloride in high yields.

Introduction

The initial purpose of this work was to determine whether certain silyl-, germyl-, and stannylamines and phosphines react with chloramine to form addition compounds analogous to the well-established reactions of chloramine with amines[1,2] and phosphines.[3] No stable addition compounds were found; instead, cleavage of the metal to nitrogen or phosphorus bond was found in all cases where reaction occurred.

Many silylamines have been prepared.[4] However, few germylamines and stannylamines were known prior to 1960[5] and only a few of their reactions have been reported. It has been found in this laboratory that one germylamine and one stannylamine, previously reported in the literature, may be incorrectly identified.[6] Two previously unreported compounds—dimethyl-(tri-n-butylsilyl)amine and dimethyl(triethylgermyl)-amine—were prepared.

Experimental Section

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were obtained on samples in sealed capillaries and are reported uncorrected. Infrared spectra were obtained with a Beckman IR-10 spectrophotometer, using potassium bromide disks to support thin films of pure liquids or mulls. When the region from 250 to 400 cm^{-1} was of concern, cesium iodide disks were used. Proton magnetic resonance spectra were obtained with a Varian A-60A instrument and reported with respect to tetramethylsilane (TMS) in the solvent specified in the text. Since almost all of the compounds studied are extremely sensitive to moisture, they were handled in an inert-atmosphere box, Dri-Lab Model HE-43 with Dri-Train HE-93B manufactured by Vacuum Atmospheres, Inc. All solvents were dried by mixing with powdered calcium hydride.

Chloramine was prepared by the method of Mattair and Sisler.[7] Anhydrous ammonia-free solutions of chloramine were prepared by the method of Gilson and Sisler.[8] Dimethylchloramine was prepared by the method of Berg[9] (bp 45°, lit.[9] bp 46° (760 mm)). Its proton magnetic resonance spectrum consisted of a singlet at −171 Hz (no solvent).

Two methods of carrying out the reactions were used.

Method A.—This method consisted of transferring the chloramine solution into a flask containing the other reactant on a conventional Pyrex-glass vacuum system by distillation and condensation at liquid nitrogen temperature. The chloramine solution was first dried by passing it through a column of anhydrous copper sulfate and distilling it from a small amount of anhydrous copper sulfate. The mixture was allowed to warm to room temperature and magnetically stirred with a Teflon-covered stirring bar.

Method B.—This method consisted of adding the dried chloramine solution dropwise to a stirred solution of the other reactant under atmospheric pressure.

Reaction of Tris(trimethylsilyl)phosphine with Chloramine.—Tris(trimethylsilyl)phosphine, [(CH$_3$)$_3$Si]$_3$P, was prepared by the method of Parshall and Lindsay[10] (bp 242°, lit.[10] bp 242–243°). One mmol of tris(trimethylsilyl)phosphine dissolved in 10 ml of diethyl ether was mixed, by method B, with 3.54 mmol of

(1) G. M. Omietanski and H. H. Sisler, *J. Am. Chem. Soc.*, **78**, 1211 (1956).
(2) G. M. Omietanski, A. D. Kelmers, R. W. Shellman, and H. H. Sisler, *ibid.*, **78**, 3874 (1956).
(3) H. H. Sisler, A. Sarkis, M. S. Ahuja, R. J. Drago, and N. L. Smith, *ibid.*, **81**, 2982 (1959).
(4) R. Fessenden and J. Fessenden, *Chem. Rev.*, **61**, 361 (1961).
(5) J. G. A. Luijten, F. Rijkens, and G. J. M. van der Kerk, *Advan. Organometal. Chem.*, **2**, 397 (1965).
(6) R. E. Highsmith and H. H. Sisler, *Inorg. Chem.*, **8**, 996 (1969).

(7) R. Mattair and H. H. Sisler, *J. Am. Chem. Soc.*, **73**, 1619 (1951).
(8) I. Gilson and H. H. Sisler, *Inorg. Chem.*, **4**, 273 (1965).
(9) A. Berg, *Ann. Chim. Phys.*, **3**, 314 (1894).
(10) G. Parshall and R. Lindsay, *J. Am. Chem. Soc.*, **81**, 6273 (1959).

chloramine in 20 ml of ether. The mixture was filtered after 24 hr at room temperature and the yellow solid obtained was shown to contain a large percentage of ammonium chloride by its X-ray powder diffraction pattern and its infrared spectrum. Complete separation of the yellow phosphorus-containing compound from the ammonium chloride could not be obtained by solvent extraction or vacuum sublimation. The phosphorus-containing compound appeared to react with water. Destructive vacuum sublimation at 500°, analogous to that described by Dubrisay[11] for the preparation of P_4N_6 from $(NH_2)_3P$, produced a tan solid whose composition approached that of P_4N_6. Other workers, since the time of Dubrisay's work, have found that there exists a series of amorphous phosphorus nitrides having an N:P mole ratio ranging from 0.9 to 1.7.[12] The color of some of these phosphorus nitrides varies from tan to dark brown.[12] A sample from each of two separate experiments during this investigation was analyzed and the N:P mole ratio was found to be 1.38 for one sample and 1.70 for the other. The weight of phosphorus nitride in this experiment accounted for 50% of the total amount of phosphorus which was originally in the form of tris(trimethylsilyl)phosphine. *Anal.* Calcd for P_4N_6: N, 40.4; P, 59.6. Found (sample 1): N, 34.1; P, 54.8. Found (sample 2): N, 39.2; P, 51.2. The proton magnetic resonance spectrum of the filtrate indicated the presence of trimethylchlorosilane and a smaller amount of hexamethyldisilazane (-22 and -3 Hz, respectively). The filtrate was acidic with respect to wet litmus, indicating a larger amount of trimethylchlorosilane. The relatively small amount of these materials compared to the large quantity of solvent (diethyl ether) could not be isolated by distillation, but a 100% yield of hexamethyldisiloxane was obtained when the filtrate was hydrolyzed with concentrated sodium hydroxide solution. The initial reaction involves the cleavage of the Si–P bond, presumably according to the equation

$$[(CH_3)_3Si]_3P + 3NH_2Cl \longrightarrow 3(CH_3)_3SiCl + (NH_2)_3P$$
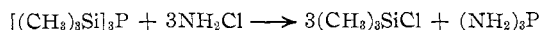
yielding phosphorus triamide which would condense yielding some ammonia.[11] The trimethylchlorosilane could then react with the ammonia to produce the observed hexamethyldisilazane.

Reaction of Tris(trimethylsilyl)phosphine with Dimethylchloramine.—A solution of 19.5 mmol of dimethylchloramine in 5 ml of ether was mixed, by method B, with 0.97 g (3.9 mmol) of tris(trimethylsilyl)phosphine. Tris(dimethylamino)dichlorophosphorane, $[(CH_3)_2N]_3PCl_2$, in 92% yield, was obtained by filtration of the mixture after 15 hr at room temperature; mp 258°, lit.[13] mp 252–254°. *Anal.* Calcd for $C_6H_{18}Cl_2N_3P$: N, 17.9; Cl, 30.3. Found: N, 17.4; Cl, 28.4.

The filtrate was acidic with respect to wet litmus and its proton magnetic resonance spectrum indicated the presence of trimethylchlorosilane (single nmr peak at -22 Hz). It has previously been reported by the authors that tris(dimethylamino)phosphine reacts with dimethylchloramine to produce tris(dimethylamino)dichlorophosphorane,[14] $[(CH_3)_2N]_3PCl_2$. Therefore, the initial reaction is apparently cleavage of the Si–P bonds

$$[(CH_3)_3Si]_3P + 3(CH_3)_2NCl \longrightarrow [(CH_3)_2N]_3P + 3(CH_3)_3SiCl$$
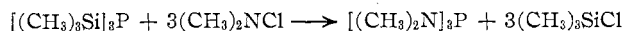
Reaction of Tris(trimethylsilyl)amine with Chloramine.—Tris(trimethylsilyl)amine was prepared by the procedure of Goubeau and Jimenez-Barbera[15] (mp 69–70°, lit.[15] mp 70–71°). No reaction was observed when the effluent gases of the chloramine generator[7] were passed through the molten amine at 70–90°, and the amine was quantitatively recovered. Similar re-

sults were obtained with benzene solutions of the amine at room temperature.

Reaction of Hexamethyldisilazane with Chloramine.—Hexamethyldisilazane, $[(CH_3)_3Si]_2NH$, was purchased from Peninsular ChemResearch, Inc., and distilled (bp 126°, lit.[16] bp 126°). No reaction between hexamethyldisilazane and chloramine was detected at room temperature or even at temperatures up to 126°. Although part of the chloramine decomposed to ammonium chloride, the hexamethyldisilazane was quantitatively recovered. The infrared N–H stretching frequency of hexamethyldisilazane in the presence of an equimolar amount of chloramine in toluene was found to be the same as that of hexamethyldisilazane in the same solvent with no chloramine present.

Preparation of Dimethyl(tri-*n*-butylsilyl)amine.—Tri-*n*-butylchlorosilane was used as obtained from Peninsular ChemResearch. The procedure consisted of passing dimethylamine through an ether solution of the chlorosilane at room temperature until no further reaction was observed. The mixture was filtered and the filtrate was distilled after tests showed that it was basic. Dimethyl(tri-*n*-butylsilyl)amine, $(n\text{-}C_4H_9)_3SiN(CH_3)_2$, distilled at 90° at 0.22 mm. Its infrared spectrum exhibited absorptions at the following frequencies (cm^{-1}): 2960 s, 2920 s, 2880 s, 2860 s, 1460 s, 1410 m, 1380 m, 1340 m, 1290 s, 1200 s, 1180 s, 1140 w, 1080 m, 1050 m, 1025 m, 990 s, 965 m, 890 m, 850 w, 790 m, 760 m, 720 s. Its proton magnetic resonance spectrum in chloroform-*d* consists of many close-spaced absorptions between -30 and -90 Hz, attributed to butyl protons, and a sharp singlet at -148 Hz, attributed to the dimethylamino protons. The area ratio between the two types of absorptions was 4.5 (calcd, 4.5). *Anal.* Calcd for $C_{14}H_{33}NSi$: C, 69.07; H, 13.65; N, 5.75; Si, 11.53. Found: C, 69.04; H, 13.69; N, 5.76; Si, 11.31.

Reaction of Dimethyl(tri-*n*-butylsilyl)amine with Chloramine.—Two grams of the amine (8.2 mmol) (prepared according to the preceding method) was mixed, by method B, with 100 ml of 0.175 *M* chloramine solution (17.5 mmol) in ether. A mixture of dimethylammonium chloride and ammonium chloride was obtained upon filtration of the reaction mixture after 48 hr of reaction.

The mixture of ammonium chlorides was separated by dissolving the dimethylammonium chloride in chloroform and recrystallizing it (mp 170°). The insoluble ammonium chloride was identified by its infrared spectrum. The filtrate was distilled yielding ether which contained 0.6 mmol of dimethylamine (identified by addition of anhydrous HCl and subsequent identification of the hydrochloride), 11.6 mmol of unreacted chloramine, 1.2 mmol of unreacted dimethyl(tri-*n*-butylsilyl)amine, and 1.40 g of liquid boiling at 136–144° (0.08 mm). The infrared and proton magnetic resonance spectra and the analysis of the liquid indicated that it was hexa-*n*-butyldisilazane. The yield was 95% based on the amount of unrecovered dimethyl-(tri-*n*-butylsilyl)amine. *Anal.* Calcd for $C_{24}H_{55}NSi_2$: C, 69.96; H, 13.39; Si, 13.57; N, 3.38. Found: C, 69.44; H, 13.15; Si, 13.60; N, 3.48. An independent experiment, conducted on the vacuum line, showed that a gas, noncondensable at $-196°$, is a product of the reaction.

Analogous results were obtained from the reaction of dimethyl(trimethylsilyl)amine with chloramine although the silicon-containing product was not identified. No reaction occurs between dimethyl(trimethylsilyl)amine and dimethylchloramine under similar conditions.

Reaction of Bis(triethylgermyl)amine with Chloramine.—Bis(triethylgermyl)amine was prepared by the reaction of triethylgermanium iodide (purchased from Strem Chemicals, Inc.) with sodium amide in a procedure analogous to that given by Mironov, *et al.*[17] By method A, 89 ml of 0.40 *M* chloramine solution in ether was mixed with 1.61 mmol of bis(triethylgermyl)-amine and the mixture was stirred for 18 hr. It was then allowed to evaporate into a series of traps: 0, -46, and $-196°$ (liquid

(11) R. Dubrisay, "Nouveau Traité de Chimie Minérale," Vol. X, P. Pascal, Ed., Masson and Co., Paris, 1956, p 881.

(12) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958, p 328.

(13) H. Nöth and H. Vetter, *Ber.*, **98**, 1981 (1965).

(14) S. R. Jain, L. K. Krannich, R. E. Highsmith, and H. H. Sisler, *Inorg. Chem.*, **6**, 1058 (1967).

(15) J. Goubeau and J. Jimenez-Barbera, *Z. Anorg. Allgem. Chem.*, **303**, 317 (1960).

(16) R. O. Sauer, *J. Am. Chem. Soc.*, **66**, 1707 (1944).

(17) V. F. Mironov, E. S. Sobolev, and L. M. Antipin, *Zh. Obshch Khim.*, **37**, 1707 (1967); *Chem. Abstr.*, **68**, 13112 (1968).

nitrogen cooled). Ether and 1.7 mmol of ammonia were found in the $-196°$ trap. The ammonia was identified by addition of anhydrous HCl and identification of the resulting white solid as ammonium chloride from its infrared spectrum. A noncondensable gas was observed which was assumed to be nitrogen. A liquid (0.14 g), found in the $-46°$ trap, was identified as triethylgermanium chloride by comparison of its infrared and proton magnetic resonance spectra with those of a known sample of triethylgermanium chloride. Ammonium chloride (0.04 g) and an unidentified liquid (0.31 g) remained in the reaction flask.

Preparation of Dimethyl(triethylgermyl)amine.—Five grams of triethylgermanium iodide (17 mmol) in 25 ml of hexane was added dropwise to a vigorously stirred slurry of 0.92 g of lithium dimethylamide in hexane. The mixture was stirred for 24 hr and then filtered. Dimethyl(triethylgermyl)amine distilled at $152-156°$ under atmospheric pressure. Its proton magnetic resonance spectrum in chloroform-d consisted of the typical group of close-spaced peaks attributed to ethyl groups on germanium ($-44-85$ Hz), and the sharp singlet attributed to the dimethylamino group (-153 Hz). The area ratio of the two absorptions was 2.58 (calculated, 2.50). Its infrared spectrum consisted of absorptions at the following frequencies (cm^{-1}): 2950 s, 2930 s, 2910 s, 2870 s, 2840 m, 2820 m, 2770 s, 1460 s, 1425 m, 1375 w, 1250 m, 1175 s, 1060 w, 1015 m, 950 s, 850 w, 690 s, 565 s. The yield was 67%. *Anal.* Calcd for C_8H_{21}-GeN: C, 47.14; H, 10.38. Found: C, 46.79; H, 10.57.

Reaction of Dimethyl(triethylgermyl)amine with Chloramine.—Dimethyl(triethylgermyl)amine (5.8 mmol) was mixed, by method A, with 5.8 mmol of chloramine in 97 ml of ether. After 24 hr, the mixture was allowed to evaporate into a series of two traps: one at $-46°$ and the other at $-196°$. A noncondensable gas was observed which was assumed to be nitrogen and was pumped from the system. Ether and 3.8 mmol of dimethylamine were found in the $-196°$ trap. The dimethylamine was identified by addition of anhydrous HCl and identifying the resulting dimethylammonium chloride. Triethylgermanium chloride (36% yield) was found in the $-46°$ trap. The residue in the reaction flask consisted of a liquid identical in all respects with the unidentified liquid from the reaction of bis(triethylgermyl)amine and chloramine.

It was found that under similar conditions, dimethylchloramine does not react with dimethyl(triethylgermyl)amine.
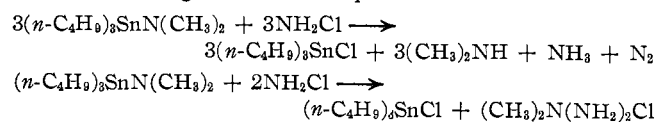
Reactions of Bis(triphenylgermyl)amine with Chloramine.—Bis(triphenylgermyl)amine was prepared by the reaction of triphenylgermanium bromide with ammonia.[6] It had previously been reported that tris(triphenylgermyl)amine is the product of this reaction.[18]

The effluent gases of the chloramine generator[7] were passed through a solution of 0.45 g of bis(triphenylgermyl)amine (0.72 mmol) in 50 ml of benzene until 25 mmol of chloramine had passed through the solution. After 4 hr, the solution was filtered free of ammonium chloride and the benzene was removed from the filtrate by distillation under reduced pressure. The white solid residue was recrystallized from hot petroleum ether (bp $20-40°$); mp $156-157°$, lit.[6] mp $156-157°$. The amount of recovered bis(triphenylgermyl)amine was 91% of the initial amount.

Reaction of Dimethyl(tri-n-butylstannyl)amine with Chloramine.—Dimethyl(tri-n-butylstannyl)amine was prepared by the procedure given by Jones and Lappert.[19,20] Dimethyl(tri-n-butylstannyl)amine (7.33 mmol) was mixed, by method A, with 95 ml of 0.080 M chloramine solution in ether and stirred for 20 hr. A noncondensable gas was found when the flask was opened. The volatile materials were distilled leaving a relatively nonvolatile yellow liquid and a white solid. The infrared spectrum, the decomposition point ($138-139°$), and the analysis of the white solid were identical with those of 2,2-dimethyltri-

azanium chloride, $(CH_3)_2N(NH_2)_2Cl$.[21,22] The white solid did not require purification other than washing with ether, followed by drying under reduced pressure. As part of this investigation, it was found that it could be easily recrystallized from hot acetonitrile. The yield was 21% based on the amount of chloramine. Other experiments demonstrated that the yield could be increased to as high as 90% by varying the mole ratio of reactants and the concentration of chloramine.

The nonvolatile, yellow liquid was shown to be tri-n-butyltin chloride (bp $87°$ (0.07 mm)) by comparison of its boiling point and infrared and proton magnetic resonance spectra with those of a known sample of tri-n-butyltin chloride. The yield was 89% based on the amount of starting stannylamine. The volatile products were found to consist of ammonia and dimethylamine, which were separated and identified by addition of anhydrous hydrogen chloride and isolation of the respective ammonium chlorides. The yields of ammonia and dimethylamine corresponded to 100% of the calculated amount based on the first equation and after subtracting the amount of chloramine used to produce the observed quantity of 2,2-dimethyltriazanium chloride according to the second equation.

$$3(n\text{-}C_4H_9)_3SnN(CH_3)_2 + 3NH_2Cl \longrightarrow$$
$$3(n\text{-}C_4H_9)_3SnCl + 3(CH_3)_2NH + NH_3 + N_2$$
$$(n\text{-}C_4H_9)_3SnN(CH_3)_2 + 2NH_2Cl \longrightarrow$$
$$(n\text{-}C_4H_9)_3SnCl + (CH_3)_2N(NH_2)_2Cl$$

Analogous results were obtained from the reaction of dimethyl(trimethylstannyl)amine and chloramine under similar conditions, except that the expected trimethyltin chloride was not isolated in a pure state.

Reaction of Dimethyl(tri-n-butylstannyl)amine with Dimethylchloramine.—Dimethyl(tri-n-butylstannyl)amine (6.9 mmol) in 20 ml of ether was mixed, by method B, with 19 ml of 0.37 M dimethylchloramine solution in ether. The mixture was refluxed for 4 hr and then stirred at room temperature for 2 days. The mixture was distilled yielding ether (bp $34-37°$) containing a basic substance which was not identified and 5.2 mmol (75%) of tri-n-butyltin chloride which was identified by its boiling point and infrared and proton magnetic resonance spectra. The basic substance was not identified because of the difficulty in separation from the solvent. It was apparently not tetramethylhydrazine, since many attempts at preparation of methyl iodide or hydrogen chloride addition compounds yielded unstable white solids. The addition compounds of tetramethylhydrazine and methyl iodide or hydrogen chloride are stable white solids.[23,24] However, it should be noted that the presence of unreacted dimethylchloramine might interfere with the formation of the expected addition compounds.

Reaction of Bis(tri-n-propylstannyl)amine with Chloramine.—Bis(tri-n-propylstannyl)amine was prepared by the reaction of tri-n-propyltin chloride with sodium amide.[6] Bis(tri-n-propylstannyl)amine (3.48 mmol) was mixed, by method A, with 81 ml of 0.043 M chloramine solution (3.48 mmol) in ether. After 12 hr, the mixture was distilled. A noncondensable gas was present but no solid was noted. Two fractions in addition to ether were obtained. The one boiling at $59-63°$ (0.10 mm) was shown to be tri-n-propyltin chloride by its boiling point and infrared and proton magnetic resonance spectra. Similarly, the second fraction was shown to be unreacted bis(tri-n-propylstannyl)amine (1.35 mmol recovered). The ether was found to contain 2.9 mmol of ammonia which corresponds to 100% of the expected amount based on the initial amount of chloramine and the equation

$$[(n\text{-}C_3H_7)_3Sn]_2NH + 2NH_2Cl \longrightarrow$$
$$2(n\text{-}C_3H_7)_3SnCl + {}^5/_3NH_3 + {}^2/_3N_2$$
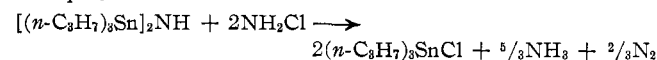
The amount of tri-n-propyltin chloride isolated corresponded to 70% of the calculated amount based on the equation and the amount of chloramine.

(18) C. Kraus and C. Wooster, *J. Am. Chem. Soc.*, **52**, 372 (1930).
(19) K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 358 (1962).
(20) K. Jones and M. F. Lappert, *J. Chem. Soc.*, 1944 (1965).

(21) K. Utvary and H. H. Sisler, *Inorg. Chem.*, **5**, 1835 (1966).
(22) K. Utvary and H. H. Sisler, *ibid.*, **7**, 698 (1968).
(23) R. T. Beltrami and E. R. Bissell, *J. Am. Chem. Soc.*, **78**, 2467 (1956).
(24) H. Nöth, *Z. Naturforsch.*, **15b**, 327 (1960).

An analogous reaction apparently occurs between tris(tri-*n*-propylstannyl)amine and chloramine, since tri-*n*-propyltin chloride was isolated as a product from their interaction.

Results and Discussion

This report shows that chloramine cleaves the metal to nitrogen bonds in dimethyl(trialkylsilyl)amines, germylamines, and stannylamines apparently according to the following equations, where R = alkyl and M = Si, Ge, or Sn

$$3R_3MN(CH_3)_2 + 3NH_2Cl \longrightarrow$$
$$3R_3MCl + 3(CH_3)_2NH + NH_3 + N_2$$
$$3(R_3M)_2NH + 6NH_2Cl \longrightarrow 6R_3MCl + 5NH_3 + 2N_2 \quad (M \neq Si)$$

The trialkylsilicon chlorides could not be isolated because of their rapid reaction with ammonia. It should be noted that $[(n\text{-}C_4H_9)_3Si]_2NH$ was isolated instead of the expected $(n\text{-}C_4H_9)_3SiCl$ in the reaction of $(n\text{-}C_4H_9)_3$-$SiN(CH_3)_2$. In the case of the germanium compounds, small yields of trialkylgermanium chlorides were isolated which may be the result of the relatively slow rates of reaction of trialkylgermanium chlorides with ammonia. In the case of the tin compounds, nearly quantitative yields of the trialkyltin chlorides were obtained because of their inertness toward ammonia under these conditions.

Tris(trimethylsilyl)amine and bis(trimethylsilyl)amine do not react with chloramine, but corresponding trialkylgermanium and trialkyltin compounds react readily with chloramine. It is tempting to propose an explanation for the inertness of these two silylamines toward chloramine in terms of reduced basicity caused by the silyl groups reducing the electron density on the nitrogen atoms through $d\pi$–$p\pi$ bonding. However the complexity of the phenomena observed in this investigation cannot easily be reconciled with such a simple interpretation. Other factors, such as bond strengths, reaction rates, and steric factors, may be important; however, large steric effects are not immediately apparent when, for example, the reactivity of $[(n\text{-}C_3H_7)_3Sn]_2NH$ and the reactivity of $[(CH_3)_3Si]_2$-NH are considered.

It was observed that chloramine readily cleaves the metal to nitrogen bonds in all three $R_3MN(CH_3)_2$ compounds where M = Si, Ge, or Sn, but the dimethylchloramine cleaves only the tin–nitrogen bond.

The nonreactivity of bis(triphenylgermyl)amine compared to the reactivity of the corresponding bis(triethylgermyl)amine with chloramine could be the result of an inductive effect of the phenyl groups.

All three silicon to phosphorus bonds in tris(trimethylsilyl)phosphine are cleaved by chloramine or dimethylchloramine.

The reaction of chloramine with dimethyl(trialkylstannyl)amines to produce 2,2-dimethyltriazanium chloride is of interest, since the product can be obtained in high yield in a pure state by simple filtration of the reaction mixture. A method for purification, which is more convenient than the previously reported method,[22] is recrystallization from hot acetonitrile.

Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida 32601

Reactions of Chloramine, Dimethylchloramine, and Chlorine with Arsine, Primary Arsines, and Secondary Arsines

By LARRY K. KRANNICH and HARRY H. SISLER

Chloramine and dimethylchloramine abstract hydrogen from As–H bonds, converting arsine, primary arsines, and secondary arsines to elemental arsenic, diarsines, and tetrasubstituted cyclopolyarsines, respectively. When used in less than stoichiometric quantities and in the presence of an HCl acceptor, free chlorine yields similar products. Secondary arsines react with aminoarsines of the type R_2AsNH_2 to yield tetrasubstituted diarsines. Several possible mechanisms for the chloramination reactions are discussed.

Introduction

During the past decade, the chloramination of amines, phosphines, and arsines has been extensively investigated in this laboratory.[1-8] Such chloramination has been shown to result, in the cases previously studied, in the formation of hydrazines or hydrazinium salts, aminophosphonium salts, and aminoarsonium salts, respectively. Trialkylstibines have been shown to react with chloramine to produce compounds of the type $[R_3Sb(Cl)]_2NH$.

(1) H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Am. Chem. Soc.*, **81**, 2982 (1959).
(2) W. A. Hart and H. H. Sisler, *Inorg. Chem.*, **3**, 617 (1964).
(3) D. F. Clemens and H. H. Sisler, *ibid.*, **4**, 1222 (1965).
(4) S. R. Jain, W. S. Brey, Jr., and H. H. Sisler, *ibid.*, **6**, 515 (1967).
(5) H. H. Sisler and S. R. Jain, *ibid.*, **7**, 104 (1968).
(6) H. H. Sisler and C. Straton, *ibid.*, **5**, 2003 (1966).
(7) S. R. Jain, L. K. Krannich, R. E. Highsmith, and H. H. Sisler, *ibid.*, **6**, 1058 (1967).
(8) R. L. McKenney and H. H. Sisler, *ibid.*, **6**, 1178 (1967).