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Dehydrohalogenation and Cleavage Reactions in Silicon-Nitrogen-Boron Systems

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Two sets of reaction conditions have been found where a dehydrohalogenation reaction occurred when triethylamine-boron trichloride adduct was allowed to react with hexamethyldisilazane. In one case both dehydrohalogenation and cleavage occurred, resulting in the formation of a novel unsymmetrical N-silyl-substituted aminohalogenoborane. Under the other set of conditions an N-silyl-substituted aminodihalogenoborane was produced as a result of only dehydrohalogenation.

Introduction

One of the well-known and quite thoroughly documented reactions in the chemistry of silicon-nitrogen compounds is the cleavage of the silicon-nitrogen bond by boron halides.¹⁻⁵ In the past a variety of silylamines have been allowed to react with various boron halides and as a result many boron-nitrogen and silicon-nitrogen-boron-containing compounds have been prepared. Thus, it has been reported that hexamethyldisilazane reacts with boron trichloride, and, depending on the conditions used, one isolates either $(\text{CH}_3)_3\text{SiNHBCl}_2$ ^{4,6} or $(\text{BClNH})_3$.⁵ On the other hand, it is also well known that a wide variety of organic amines having hydrogen bonded to nitrogen will undergo dehydrohalogenation reactions with boron trichloride;⁹ however, no report has been made concerning the possibility of analogous silylamines or disilazanes undergoing a similar dehydrohalogenation reaction. In view of this, it seemed appropriate to initiate a study of dehydrohalogenation reactions involving silicon amines. By carefully controlling the reaction conditions, it has been found possible to achieve dehydrohalogenation. The results of an initial study of reactions involving triethylamine-boron trichloride with hexamethyldisilazane are reported in this paper.

Experimental Section

Materials and Apparatus.—Hexamethyldisilazane was purchased from Columbia Organic Chemicals Co., Inc., Columbia, S. C., and boron trichloride, CP grade, was purchased from Matheson Co., East Rutherford, N. J. Triethylamine-boron trichloride adduct was prepared¹⁰ and purified¹¹ according to procedures previously reported. Infrared spectra were obtained using Perkin-Elmer 137 or 237 spectrophotometers. Proton nuclear magnetic resonance spectra were obtained using a Varian

A-60 spectrometer. Mass spectra were obtained using a Bendix Model 14 time-of-flight mass spectrometer. All reactions were carried out in systems that were set up to exclude moisture.

Preparation of $[(\text{CH}_3)_3\text{Si}]_2\text{NBClNHSi}(\text{CH}_3)_3$, I.—Triethylamine-boron trichloride adduct (57.05 g, 0.261 mole) was placed in a 1000-ml, three-neck, round-bottom flask equipped with an addition funnel, a Tru-bore stirrer, and a Friedrich condenser with a drying tube. The adduct was dissolved in 300 ml of benzene which had been distilled from calcium hydride. Hexamethyldisilazane (109 ml, 0.522 mole) in 100 ml of dry benzene was added quickly to the stirred solution at room temperature. The reaction mixture was refluxed for 3 hr, cooled, and then stirred at room temperature for 12 hr. A small amount of white solid formed immediately on mixing the reactants; during the application of heat and the refluxing period, more solid was precipitated. The reaction mixture was filtered under nitrogen, and the solid product was identified as triethylamine hydrochloride (35.61 g, yield 99.4%), mp 255°, lit.¹² 253–254°. After removing the solvent and trimethylchlorosilane from the filtrate, I was distilled as a colorless liquid (49.48 g, 64.3% yield), bp 76–77° (2.3 mm). Trimethylchlorosilane was identified in the solvent fraction by gas chromatography. A brown liquid residue remained in the distillation flask after I was removed.

*Anal.*¹³ Calcd for $\text{C}_9\text{H}_{25}\text{BClN}_2\text{Si}_3$: C, 36.66; H, 9.57; B, 3.67; Cl, 12.02; N, 9.50; Si, 28.58; mol wt, 294.9. Found: C, 36.60; H, 9.81; B, 4.25, 4.17; Cl, 11.19, 10.83; N, 9.48; Si, 27.27; mol wt, 300 (cryoscopically in benzene), 294 (mass spectrum).

The infrared spectrum of I contained the following characteristic absorption bands (cm^{-1}): 3400, m (N-H); 2965, s (C-H); 2910, m (C-H); 2490, w; 1943, w; 1885, w; 1405, m, sh ($\text{B}^{10}\text{-N}$); 1380, s ($\text{B}^{11}\text{-N}$); 1265, m, sh $[(\text{CH}_3)_3\text{Si}]$; 1257, s $[(\text{CH}_3)_3\text{Si}]$; 1216, m; 1115, s; 1050, w; 938, s; 890, m, sh; 845, s $[(\text{CH}_3)_3\text{Si}]$; 797, m; 760, m $[(\text{CH}_3)_3\text{Si}]$; 740, w, sh; 680, m; 727, m.

The pmr spectrum of I (neat) contained two peaks, one very broad at $\delta = 2.83$ ppm (N-H proton) and the other very sharp at $\delta = 0.04$ ppm (CH_3) (TMS = 0). The ratio of the amine hydrogen to the methyl hydrogens is: calcd, 1:27; found from pmr integration, 1:29.

Table I contains mass spectral data for compound I. Only the major peaks from the mass spectrum are given. These data further support the molecular formula, and the fragmentation pattern is consistent for compound I.

Preparation of $[(\text{CH}_3)_3\text{Si}]_2\text{NBCl}_2$, II.¹⁴—The same apparatus setup as described previously for the preparation of I was used in this preparation. Triethylamine-boron trichloride adduct (83.60 g, 0.383 mole) was added to the reaction flask and dissolved in 300 ml of dry benzene; then excess triethylamine (53.8 ml, 0.383 mole) was added by a syringe. This solution

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TABLE I
 MASS SPECTRA OF $[(\text{CH}_3)_3\text{Si}]_2\text{NBClNH}(\text{CH}_3)_3$, I, AND $[(\text{CH}_3)_3\text{Si}]_2\text{NBCl}_2$, II

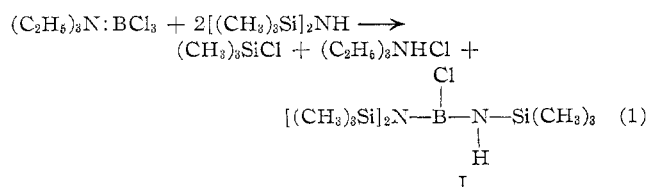
Compound I			Compound II		
<i>m/e</i>	Rel intens	Assignment	<i>m/e</i>	Rel intens	Assignment
294	16	$[(\text{CH}_3)_3\text{Si}]_2\text{NBClNH}(\text{CH}_3)_3^+(\text{P})$	241	7	$[(\text{CH}_3)_3\text{Si}]_2\text{NB}^{39}\text{Cl}_2^+(\text{P})$
279	100	$\text{P} - \text{CH}_3$	230	9	$[(\text{CH}_3)_3\text{Si}]_2[(\text{CH}_3)_2\text{Si}]\text{NB}^{37}\text{Cl}_2^+$
171	22	$[(\text{CH}_3)_3\text{Si}]_2\text{NB}^+$	228	37	$[(\text{CH}_3)_3\text{Si}]_2[(\text{CH}_3)_2\text{Si}]\text{NB}^{35}\text{Cl}^{37}\text{Cl}^+$
146	46	$[(\text{CH}_3)_3\text{Si}][(\text{CH}_3)_2\text{Si}]\text{N}^+ + \text{H}$	226	51	$[(\text{CH}_3)_3\text{Si}][(\text{CH}_3)_2\text{Si}]\text{NB}^{35}\text{Cl}_2^+$
130	45	$[(\text{CH}_3)_3\text{Si}][(\text{CH}_3)_2\text{Si}]\text{N}^+$	146	40	$[(\text{CH}_3)_3\text{Si}][(\text{CH}_3)_2\text{Si}]\text{N}^+ + \text{H}$
98	23	$(\text{CH}_3)_3\text{SiNB}^+$	118	89	$(\text{CH}_3)_2\text{SiNBCl}^+$
73	62	$(\text{CH}_3)_3\text{Si}^+$	98	84	$(\text{CH}_3)_3\text{SiNB}^+$
45	22	$\text{CH}_3\text{Si}^+ + 2\text{H}$	93	22	$(\text{CH}_3)_2\text{SiCl}^+$
			73	100	$(\text{CH}_3)_3\text{Si}^+$

was heated to reflux and then hexamethyldisilazane (80.0 ml, 0.383 mole), dissolved in 150 ml of dry benzene, was added dropwise to the refluxing solution over a period of 75 min; a white precipitate was formed during the addition. After the addition was completed, the reaction mixture was refluxed for 4 hr and then allowed to cool to room temperature. The mixture was vacuum filtered under dry nitrogen to remove the solid triethylamine hydrochloride (52.1 g, yield 99%). The solvent and excess triethylamine were removed by distillation, leaving a brown viscous liquid. From this viscous liquid it was possible to distill the colorless liquid II (19.22 g, yield 20.8%), bp 49° (2.2 mm), lit.¹⁴ 82° (11 mm) (extrapolated to 760 mm, 200° and 205°, respectively), mp 6–7°, lit.¹⁴ 5–6°; pmr $\delta = 0.23$ ppm, lit.¹⁴ $\delta = 0.3$ ppm (TMS = 0). The fragmentation pattern observed in the mass spectrum of II is consistent for the compound (Table I).

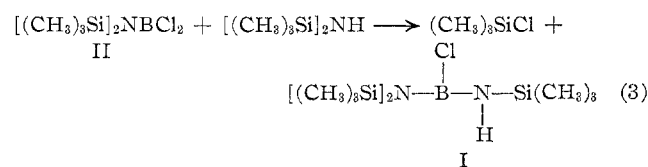
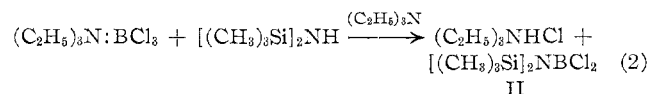
Reaction of $[(\text{CH}_3)_3\text{Si}]_2\text{NBCl}_2$, II, with $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$.—To a 25-ml round-bottom flask equipped with a stirring bar and reflux condenser was added II (3.07 g, 0.0127 mole) and hexamethyldisilazane (2.70 ml, 0.0127 mole) in 10 ml of dry benzene. The reaction mixture was stirred and refluxed for 2 hr. Fractional distillation of the reaction mixture allowed the separation of trimethylchlorosilane (yield 82.5%, estimated from gas chromatogram) and compound I (3.72 g, yield 87%), bp 75–77° (2.2 mm); the infrared spectrum was identical with that of an authentic sample.

Results and Discussion

Under the proper conditions, it has been found that both dehydrohalogenation and silicon–nitrogen bond cleavage occur when hexamethyldisilazane is allowed to react with triethylamine–boron trichloride adduct. The occurrence of both reactions in this system allows the isolation of a novel unsymmetrical N-silyl-substituted aminohalogenoborane, bis(trimethylsilyl)aminotrimethylsilylaminochloroborane, I (eq 1). The



compound bis(trimethylsilyl)aminodichloroborane, II, previously prepared by Rochow,¹⁴ *et al.*, by the reaction of sodium bis(trimethylsilyl)amide with boron trichloride, was not isolated under the conditions that allowed the formation of I; however, by varying the reaction conditions it was possible to prepare II, with the almost complete exclusion of I (eq 2). Also, it was observed that compound II reacts readily with hexamethyldisilazane to yield I (eq 3).



The unsymmetrical N-silyl-substituted aminohalogenoborane, I, is easily hydrolyzed, but was readily characterized by elemental analyses, molecular weight data, and the infrared, pmr, and mass spectra (Table I) of the compound.

Although the silicon–nitrogen bond is easily cleaved by boron halides, it appears that the presence of 1 mole of triethylamine for each mole of hexamethyldisilazane in our reaction system resulted in dehydrohalogenation as the initial step in the formation of I. When there was an additional mole of hexamethyldisilazane present, the dehydrohalogenation step was followed by a cleavage reaction and compound I was formed (eq 1). On the other hand, in the reaction of 1 mole of hexamethyldisilazane with 1 mole of triethylamine–boron trichloride adduct and using an excess of triethylamine, it was possible to isolate the dehydrohalogenation product II (eq 2). When this dehydrohalogenation product was isolated and then allowed to react with hexamethyldisilazane, it was found that I was formed in high yields. The results of the latter two reactions (eq 2 and 3) support the reaction sequence of dehydrohalogenation followed by cleavage in the preparation of I from triethylamine–boron trichloride adduct and hexamethyldisilazane in a mole ratio of 1:2 (eq 1).

The results of this investigation indicate that dehydrohalogenation reactions may well find use in the preparation of other new silicon–nitrogen–boron compounds. This type of reaction, when used in conjunction with cleavage and transamination reactions, should lead to other heretofore unreported silicon–nitrogen–boron compounds.

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