[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, AND THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Interaction of Diborane with Silyl Cyanides[1]

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RECEIVED OCTOBER 30, 1958

The interaction of diborane with silyl cyanide or trimethylsilyl cyanide results in the formation of the adducts $H_3SiCN \cdot BH_3$ and $(CH_3)_3SiCN \cdot BH_3$, respectively. When these are heated the corresponding silyl hydrides are eliminated and the polymeric compound $(BH_2CN)_x$ is formed.

Diborane and acetonitrile combine readily forming the adduct $CH_3CN \cdot BH_3$, from which a portion of the diborane and acetonitrile may be recovered by heating *in vacuo*. However, most of the adduct undergoes a rearrangement during the heating process. Two hydrogen atoms apparently shift from the boron to the carbon of the cyanide group to form an N-substituted borazene and higher polymers, as illustrated in the equation[2]

$$CH_3CN \cdot BH_3 \longrightarrow (CH_3CH_2NBH)_x$$

Somewhat different results are reported for the interaction of acetonitrile with decaborane which proceeds according to the equation[3]

$$B_{10}H_{14} + 2CH_3CN \longrightarrow B_{10}H_{12} \cdot 2CH_3CN + H_2$$

This research was undertaken with the view of investigating the reaction of diborane with the simplest silicon analog of acetonitrile, namely, silyl cyanide, in an endeavor to prepare N-silylborazene. The reaction involving trimethylsilyl cyanide was also studied.

Experimental

Apparatus and Materials.—All studies were carried out in a Stock type vacuum system wherever necessary. Commercial diborane[4] was used after suitable purification. Silyl cyanide (vapor pressure at 0°, found, 42.0 mm., literature value[5] 41.4 mm.) was prepared by treating SiH_3I with AgCN.[6] The former was prepared from SiH_4 and HI.[6] Although $(CH_3)_3SiCN$ previously has been prepared by the reaction of $(CH_3)_3SiI$[7] and also $(CH_3)_3SiBr$[7,8] with AgCN an attempt was made in this research to prepare it from $(CH_3)_3SiCl$ which is more readily obtainable than the iodo- and bromotrimethylsilanes. Eaborn[8] investigated the reaction of $(CH_3)_3SiCl$ with AgCN but was unable to isolate the desired product from the reaction mixture. Limited success has been reported by McBride and Beachell[7] using $(CH_3)_3SiCl$ and AgCN, and most recently,[9] 38% yields of $(CH_3)_3SiCN$ based on the amount of AgCN used have been reported by heating $(CH_3)_3SiCl$ and AgCN in a bomb at 125° and then distillation of the reaction mixture after filtration.

In the present research it has been found that if distillation is attempted directly from the reaction mixture the $(CH_3)_3SiCN$ partly recombines with the AgCl to re-form $(CH_3)_3SiCl$ since the latter compound has the lower boiling point and is therefore the first substance to be removed from the reaction vessel. This presents an explanation of the low yields obtained by Eaborn[8] and McBride and Beachell.[7] When the AgCl is removed before distillation, the yields approach 90%.

A typical preparation follows: $(CH_3)_3SiCl$[10] (55 g.) and AgCN (26 g.) were combined in a round-bottomed flask equipped with a mercury seal stirrer and were stirred at room temperature for 71 hours. The liquid was then decanted and the solid was extracted with three 20-ml. portions of anhydrous ether. The liquid product was fractionated in an 18″ × 1/4″ column packed with glass helixes. About 20 ml. of xylene, previously dried over P_2O_5, was added to assist the removal of the last traces of $(CH_3)_3SiCN$, which was collected in the boiling point range 117.9–118.2°. A total of 16.5 g. of pure product was obtained. This corresponded to an 86% yield based on the amount of AgCN used.

Some of the $(CH_3)_3SiCN$ used in the research also was prepared by the following method: a mixture of $(CH_3)_3SiCl$ and HCN[11] in diethyl ether was added dropwise to a lithium dispersion in petroleum ether which was contained in a round-bottomed flask equipped with a mercury seal stirrer. The reaction vessel was cooled in an ice-bath during the four hour period in which the $(CH_3)_3SiCl$–HCN solution was added. The reaction vessel then was allowed to stand at room temperature for 17 hours and the mixture was then distilled. Dry xylene was added to assist the complete removal of all the products. A typical preparation using 380 ml. of $(CH_3)_3SiCl$, 20 g. of Li[12] and 400 ml. of HCN produced approximately 250 ml. of $(CH_3)_3SiCN$ which was collected in the boiling point range 116–117°.

The cyanosilanes have been described in the literature as being the iso- rather than the normal cyanides. This interpretation was based largely on inference: both the method of preparation[5,7,8,13] and certain chemical properties[7,13] as well as a similarity to the infrared spectra of carbon analogs[7] suggest the iso-configuration. Early infrared[7] and Raman[14] data had not been successful in differentiating between the two possible structures. However, recent infrared studies[15] have indicated that these compounds probably possess the normal cyanide structures, although other investigations indicate that the compounds may exist as equilibrium mixtures of the normal and iso-cyanides.[9]

The infrared spectrum of the $(CH_3)_3SiCN$ from the AgCN preparation shows a band at 4.57 μ while that from the Li preparation shows one at 4.54 μ and another considerably weaker band at 4.78 μ. This differs slightly from the data of McBride and Beachell[7] who report a band at 4.61 μ and a weak band at 4.78 μ. Linton and Nixon[15] report a $-C \equiv N$ stretching frequency at 4.54 μ while Bither, *et al.*,[9] conclude that a band observed at 4.58 μ is the normal $-C \equiv N$ stretching frequency and attribute a weaker band at 4.76 μ to the $-N \equiv C$ stretching frequency.

Vapor Pressure of $(CH_3)_3SiCN$.—The vapor pressure of a sample of tensiometrically pure $(CH_3)_3SiCN$ (m.p. found 11.4°, lit. value[7] 10.5–11.5°) was measured at a series of temperatures. The results are given in Table I.

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[1] This research was supported in part by the Office of Naval Research, Contract No. Nonr-551(21). Reproduction in whole or in part is permitted for any purpose of the United States Government. Certain of these results were presented at the Second Delaware Valley Regional Meeting of the American Chemical Society, February, 1958.

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TABLE I

VAPOR PRESSURE OF $(CH_3)_3SiCN$

T, °C.	0.0	37.7	43.3	49.75	54.9	61.2	67.15	72.35	81.1	91.25
P_{mm}, obsd.	3.7	37.3	48.6	65.1	81.7	106.7	135.7	166.8	229.4	327.8
P_{mm}, calcd.	..	37.2	48.6	65.2	81.7	106.6	135.6	165.9	229.7	328.2

The vapor pressure equation is $\log P_{mm} = -1539.0/(231.9 + t) + 7.2788$. The extrapolated boiling point is 118.0°, the heat of vaporization, 8.8 kcal./mole and Trouton's constant, 22.5. The $(CH_3)_3SiCN$ had undergone no decomposition during the experiment as was evidenced by *the fact that its melting point* (11.5°) *was the same as that* of the starting material.

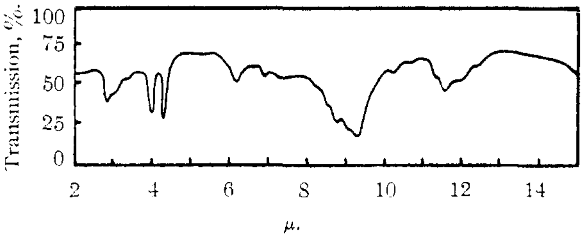

Fig. 1.—Infrared absorption spectrum of BH_2CN.

Reaction of SiH_3CN with B_2H_6.—SiH_3CN (3.05 mmoles) and B_2H_6 (4.01 mmoles) were combined at −196°. The vessel was warmed to room temperature, then cooled to −126°, and the volatile material was removed. This was found to be excess B_2H_6 (2.47 mmoles; vapor pressure at −126 ± 1° found, 61 mm., literature value[16] 66 mm.). No other volatiles were obtained up to 0°. The SiH_3CN/BH_3 ratio in the solid was calculated to be 1.00. Consequently, under the conditions of this experiment, B_2H_6 and SiH_3CN combine to form a solid adduct according to the equation

$$2SiH_3CN + B_2H_6 \longrightarrow 2SiH_3CN{\cdot}BH_3 \quad (1)$$

Thermal Decomposition of $SiH_3CN{\cdot}BH_3$.—$SiH_3CN{\cdot}BH_3$ (3.05 mmoles) was heated gradually on a water-bath for one hour. Melting and bubbling commenced at 35°; all signs of reaction ceased after the temperature was raised to 70° during a period of 15 minutes. The temperature was raised to 100° to ensure complete decomposition. The volatiles were removed, together with a small amount of hydrogen, and on fractionation yielded only SiH_4 (2.93 mmoles; mol. wt. found, 31.1, calcd., 32.1; confirmed by infrared spectrum[17]). A yellowish, clear, glassy solid remained which had the empirical formula BH_2CN as calculated from the quantities of reactants and the products involved. It may be concluded therefore that $SiH_3CN{\cdot}BH_3$ decomposes readily below 100° as shown by the equation

$$SiH_3CN{\cdot}BH_3 \longrightarrow BH_2CN + SiH_4 \quad (2)$$

Hydrolysis of $SiH_3CN{\cdot}BH_3$.—$SiH_3CN{\cdot}BH_3$ (2.12 mmoles) was treated in a closed vessel with 20 ml. of water at room temperature and then at 100° for a short time. H_2 (5.48 mmoles; mol. wt. found 2.2) and a volatile compound was produced. The latter, probably $(H_3Si)_2O$, was returned to the hydrolysis vessel to which a few pellets of KOH had been added. An extremely vigorous reaction occurred and more H_2 (7.09 mmoles) was produced. Total H_2 liberated was 12.6 mmoles or 99.0% of that required by the equation

$$H_3SiCN{\cdot}BH_3 + 4KOH + H_2O \longrightarrow K_2SiO_3 + KBO_2 + 6H_2 + KCN \quad (3)$$

Reaction of $(CH_3)_3SiCN$ with B_2H_6.—Diborane (5.28 mmoles) and trimethylsilyl cyanide (1.98 mmoles) were combined at −196° and brought successively to −126°, −78° and room temperature. White solid mixed with a little liquid was observed. Distillation at −78° yielded B_2H_6 (4.43 mmoles; vapor pressure at −126°, found 64 mm., literature value[16] 66 mm.). Distillation at room temperature gave $(CH_3)_3SiCN$ (0.220 mmole; mol. wt. found 98.2, calcd. 99.2). A white crystalline solid remained which was barely sublimable *in vacuo* at room temperature. The $(CH_3)_3SiCN/BH_3$ ratio in the solid was calculated to be 1.03. It therefore appears that $(CH_3)_3SiCN$ and B_2H_6 combine at low temperatures to form a non-volatile solid of gross composition $(CH_3)_3SiCN{\cdot}BH_3$ as indicated by the equation

$$2(CH_3)_3SiCN + B_2H_6 \longrightarrow 2(CH_3)_3SiCN{\cdot}BH_3 \quad (4)$$

Subsequent preparations of $(CH_3)_3SiCN{\cdot}BH_3$ were carried out in essentially the same manner, diborane always being present in excess. In some cases, depending on minor variations in experimental conditions, no unreacted $(CH_3)_3SiCN$ was found. In one experiment, when the condensed reactants were allowed to come to room temperature rapidly, the reaction vessel became slightly warm to the touch indicating that the reaction was exothermic. The solid products contained $(CH_3)_3SiCN$ and BH_3 in ratios which varied between 0.98 and 1.05.

TABLE II

VAPOR PRESSURE OF SOLID $(CH_3)_3SiCN{\cdot}BH_3$

T, °C.	26.8	34.6	44.6	54.5	64.3	69.3
P, mm.	0.2	0.5	0.9	1.9	3.4	5.3

The compound melted sharply at 69–69.3° to a clear colorless liquid. At 69.3° *the pressure increased steadily* from 5.3 to 8.1 mm. in 20 minutes. Since the pressure at 69.3°, obtained by extrapolation of the sublimation data, using the data at lower temperatures, is 5.0 mm., decomposition was proceeding rapidly at this temperature.

Thermal Decomposition of $(CH_3)_3SiCN{\cdot}BH_3$.—A sample of freshly prepared $(CH_3)_3SiCN{\cdot}BH_3$ (3.70 mmoles) was heated at 100° for 10 hours. Dry nitrogen was present in the vessel at about 400 mm. pressure to prevent the adduct from subliming from the hot zone. $(CH_3)_3SiH$ (3.59 mmoles; vapor pressure at −78°, found 6.5–7.0 mm., literature value[18] 6.6 mm.) was evolved. Heating at 100° for an additional 6 hours produced only 0.02 mmole of gas. The residue was a clear, glassy solid. Its composition calculated from the stoichiometry was BH_2CN. This was confirmed by analysis[19]: Calcd.: B, 27.85; H, 5.19; C, 30.91; N, 36.05.[19] Found: B, 27.72, 28.22; H, 5.36, 5.55; C, 31.09, 30.88; N, 35.55, 35.84. Decomposition had therefore proceeded according to the equation

$$(CH_3)_3SiCN{\cdot}BH_3 \longrightarrow BH_2CN + (CH_3)_3SiH \quad (5)$$

In an additional experiment carried out in petroleum ether approximately equivalent amounts of $(CH_3)_3SiCN$ (1.301 mmoles) and B_2H_6 (0.648 mmole) were combined at −196° in a vessel containing 5 ml. of petroleum ether. A white solid formed during warming to room temperature. Warming the mixture to 40–60° caused complete solution of the adduct which precipitated again on cooling. The solution was refluxed for four hours at 50–60°. An infrared spectrum of the solution was found to contain the strongest lines of the $(CH_3)_3SiH$ spectrum, hence some decomposition of the adduct had occurred. A Perkin-Elmer Model 21 spectrophotometer with a sodium chloride prism was used. The spectrum was made on a sample in a KBr disk.

The frequencies observed were interpreted as follows: 2.9 μ, medium, N–H stretch; 4.05 μ, strong, B–H stretch; 4.33 μ, strong, —C≡N; 6.15 μ, medium, cyclic C=N or N–H bending; 9.35 μ, very strong; 11.35 μ, medium. The spectra of BH_2CN prepared from $H_3SiCN{\cdot}BH_3$ and $(CH_3)_3SiCN{\cdot}BH_3$ were identical.

Hydrolysis of $(CH_3)_3SiCN{\cdot}BH_3$.—To a sample of freshly prepared $(CH_3)_3SiCN{\cdot}BH_3$ (2.53 mmoles) was added 70.50 mmoles of degassed water. Hydrogen (4.11 mmoles; mol. wt. found 2.1) was liberated immediately. The reaction vessel then was allowed to stand at room temperature and hydrogen was removed daily. After seven days hydro-

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[19] Galbraith Laboratories, Knoxville, Tenn.

gen evolution had ceased and a total of 5.68 mmoles of H_2 (74.8%)[20] was obtained. On distilling the aqueous mixture through a trap filled with magnesium perchlorate, which previously had been brought to constant weight by heating and pumping, it was found that 6.58 mmoles of H_2O (75.5%)[20] had been consumed by the reaction. Fractionation of the anhydrous products yielded hexamethyldisiloxane (0.553 mmoles, 43.7%[20]; vapor pressure at 4.5° found 12.7 mm., literature value[21] 12.5 mm.) and HCN (1.907 mmoles, 75.4%[20]; vapor pressure at −18.5° found 103.0 mm., lit. value[22] 100.0 mm.). The solid residue in the hydrolysis vessel gave a neutral solution in water and consumed 1.925 mmoles NaOH (76.1%)[20] in the presence of mannitol.

The low recovery of hexamethyldisiloxane in this experiment may have been due to absorption in Dow Silicone Vacuum Grease. When Apiezon N grease was substituted in a second experiment, 1.05 mmoles of adduct yielded 0.385 mmole of hexamethyldisiloxane (73.5%).[20] This second experiment was carried out in the same manner as the above except that KOH was present in the hydrolysis mixture. The results with respect to hydrogen evolution and titration for H_3BO_3 in the solid residue were essentially the same as in the first experiment (H_2, 2.26 mmoles, 71.6%[20]; H_3BO_3, 0.794 mmole, 75.6%[20]). It therefore appears that hydrolysis of $(CH_3)_3SiCN \cdot BH_3$ proceeds in a more complex manner than indicated by equation 6

$$2(CH_3)_3SiCN \cdot BH_3 + 4KOH + H_2O \longrightarrow [(CH_3)_3Si]_2O + 2KBO_2 + 2KCN + 6H_2 \quad (6)$$

This may be compared with the quantitative yields of hydrogen from $SiH_3CN \cdot BH_3$ on hydrolysis. This difference in behavior probably is related to the fact that the rate of hydrolysis of the trimethyl compound is much slower than that of the parent silyl compound; consequently side reactions can occur more readily with the former substance.

Reaction of $(CH_3)_3SiCN \cdot BH_3$ with HCl.—$(CH_3)_3SiCN \cdot BH_3$ (0.469 mmole) and HCl (0.491 mmole) were held at −78° for 41.5 hours; the reaction vessel then was opened and all volatile material removed. The principal product was hydrogen (0.33 mmole). Fractionation of the volatiles yielded what appeared to be HCl (0.13 mmole) and $(CH_3)_3SiCl$ (0.18 mmole; vapor pressure at −22.4° found 21–24 mm., lit. value[23] 21 mm.). The residue remaining in the reaction vessel was allowed to warm to room temperature. The pressure rose for 1 hour and then was constant for 12 hours. The volatile material was found to be $(CH_3)_3SiCl$ (0.16 mmole; vapor pressure at −22.4° found 21 mm.; lit. value[23] 21 mm.).

In the above experiment the $(CH_3)_3SiCN \cdot BH_3$ and HCl did not react in exactly equimolar ratios, presumably because of the heterogeneous nature of the system. The reaction products suggest that at low temperatures reaction (7) occurs

$$(CH_3)_3SiCN \cdot BH_3 + HCl \longrightarrow (CH_3)_3SiCN \cdot BH_2Cl + H_2 \quad (7)$$

and that raising the temperature causes decomposition as indicated in equation 8

$$(CH_3)_3SiCN \cdot BH_2Cl \longrightarrow (CH_3)_3SiCl + BH_2CN \quad (8)$$

This hypothesis is supported by the fact that the reaction of $(CH_3)_3N \cdot BH_3$ with HCl may be expressed by an equation analogous to equation 7 above,[24] *viz.*

$$(CH_3)_3N \cdot BH_3 + HCl \longrightarrow (CH_3)_3N \cdot BH_2Cl + H_2$$

Reaction of $(CH_3)_3SiCN \cdot BH_3$ with $(CH_3)_3N$.—$(CH_3)_3N$ (0.495 mmole) was added to $(CH_3)_3SiCN \cdot BH_3$ (0.33 mmole) and the reaction vessel was left for 12 days at room temperature. A liquid and white crystals (presumed to be $(CH_3)_3N \cdot BH_3$) were observed. The volatiles were removed from the white crystals at −30°, at which temperature $(CH_3)_3N \cdot BH_3$ distils only very slowly. The former consisted of $(CH_3)_3SiCN$ (0.20 mmole; vapor pressure at 0° found 3.5–4.0 mm., Table I, 3.7 mm.) and a mixture of $(CH_3)_3N$ and $(CH_3)_3SiH$ (identified by comparison with published infrared spectra of $(CH_3)_3N$[25] and $(CH_3)_3SiH$.[26]

HCl (0.33 mmole) was added to this mixture and the volatile material remaining then was distilled from the white solid (presumably $(CH_3)_3N \cdot HCl$) which had formed. The volatile material (0.136 mmole) was fractionated in order to separate the excess HCl (0.114 mmole) from the $(CH_3)_3SiH$ (0.022 mmole). Hence 0.274 mmole of $(CH_3)_3N$ had reacted.

The principal reaction occurring at room temperature between $(CH_3)_3SiCN \cdot BH_3$ and $(CH_3)_3N$ appears, therefore, to be represented by the equation

$$(CH_3)_3SiCN \cdot BH_3 + (CH_3)_3N \longrightarrow (CH_3)_3N \cdot BH_3 + (CH_3)_3SiCN \quad (9)$$

Thermal Decomposition of $(CH_3)_3SiCN \cdot BH_3$ in the Presence of $(CH_3)_3SiCN$.—$(CH_3)_3SiCN \cdot BH_3$ was prepared by mixing B_2H_6 (0.558 mmole) with a large excess of $(CH_3)_3SiCN$ (2.96 mmoles) and then heating at 100°. Fractionation of the volatiles yielded $(CH_3)_3SiH$ (1.12 mmoles; vapor pressure at −82° found 5–6 mm., lit. value[18] 7.8 mm.) and $(CH_3)_3SiCN$ (0.817 mmole; vapor pressure at 0° found 4–6 mm., Table I, 3.7 mm.). The residue in the reaction vessel was a light yellow liquid which had a vapor pressure of 0.2 mm. at 20°. These results indicate that the new compound $(CH_3)_3SiCN \cdot BH_2CN$ was formed according to the equation

$$(CH_3)_3SiCN \cdot BH_3 + (CH_3)_3SiCN \longrightarrow (CH_3)_3SiCN \cdot BH_2CN + (CH_3)_3SiH \quad (10)$$

Hydrolysis of BH_2CN.—Water was added to a sample of BH_2CN (3.70 mmoles). Very little reaction was observed during four days at room temperature. Refluxing at 60–80° for 1.5 hours each day for four days yielded H_2 (1.233 mmoles; mol. wt. found, 3.5). Refluxing at 90–95° for 4 to 5 hours each day for three days caused further hydrogen evolution and complete dissolution of the sample. A total of 5.951 mmoles of H_2 was obtained. HCN (2.06 mmoles; identified by infrared spectrum[27]) was separated by fractionation. The aqueous solution was acidic and reduced Ag_2O in NH_4OH to metallic Ag. A qualitative test for the CN^- ion was negative. Titration with NaOH showed the presence of approximately one milliequivalent of strong acid and, after addition of mannitol, approximately 2 mmoles of H_3BO_3. The hydrolysis is therefore more complex than the expected reaction given in equation 11

$$BH_2CN + 3H_2O \longrightarrow H_3BO_3 + HCN + 2H_2 \quad (11)$$

since only 80% of the hydrogen and 60% of the H_3BO_3 and HCN calculated from equation 11 are formed.

Thermal Decomposition of BH_2CN.—A freshly prepared sample of BH_2CN (3.14 mmoles) was subjected to a gradual increase in temperature in an evacuated vessel connected to a trap cooled in liquid nitrogen. After two hours at 200° the material turned coppery in color, but was still transparent and glassy. A very small amount of a white sublimate formed, together with 0.16 mmole of hydrogen. On raising the temperature to 300° for four hours another 0.055 mmole of hydrogen was formed. Additional heating at 350 ± 10° for 11 hours caused no further change and produced only 0.034 mmole of hydrogen. The total yield of hydrogen (0.305 mmole) represents only 9.4% of the hydrogen in the compound. The brownish resinous residue was stable in air. It dissolved in boiling water and liberated ammonia. The infrared spectrum of the sublimate, like that of the original material, showed strong B–H and C≡N absorption bands, while that of the resin showed N–H and C–H but no B–H bands. Hence it appears that heating causes reduction of the C≡N linkage.

In a second experiment, BH_2CN (1.01 mmoles) yielded 0.472 mmole of non-condensable gas when heated to approximately 500° for several hours. The non-condensable gas was heated over copper oxide at 310° for 3.5 hours and at 280° for 5 hours; 0.058 mmole of gas was not converted to a condensable product. The condensable product consisted of 0.085 mmole which was volatile at −78° and 0.32 mmole of H_2O (vapor pressure at 0° found 5 mm., lit. value[28]

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[20] Percentage of theoretical yield according to equation 6.

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4.6 mm.). It therefore appears that approximately 64% of the original non-condensable product was hydrogen. 0.825 mmole of water was added to the residue. On warming to room temperature the black solid began to turn white. The mixture was allowed to stand at room temperature for three weeks. The only volatile product obtained by distilling at −78° was NH_3 (0.21 mmole; vapor pressure at −80° found 37 mm., lit. value[21] 39 mm.).

On rapid heating above 200° BH_2CN often decomposed with explosive violence.

Results and Discussion

Diborane reacts with silyl cyanides at low temperatures according to the general equation

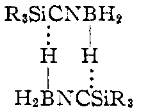
$$2R_3SiCN + B_2H_6 \longrightarrow 2R_3SiCN\cdot BH_3 \qquad (12)$$

where R = H or CH_3. Available chemical evidence indicates that a borine adduct is formed. This is suggested by the reactions of $(CH_3)_3SiCN\cdot BH_3$ with HCl and $(CH_3)_3N$ as given in equations 7, 8 and 9.

Of considerable interest is the irreversible thermal decomposition of the adducts to the corresponding silane and a solid whose composition corresponds to BH_2CN, *viz.*

$$R_3SiCN\cdot BH_3 \longrightarrow R_3SiH + BH_2CN \qquad (13)$$

The fact that silicon has available vacant 3d orbitals would suggest that a transfer of hydrogen from the boron to the silicon could occur readily by the means of an intermediate complex of the type



followed by the elimination of silane. This is consistent with the observation that hydrogen migration from the boron occurs more readily with the silicion derivatives than with the carbon analogs, as evidenced by the fact that some unchanged CH_3CN and B_2H_6 can be obtained on heating $CH_3CN\cdot BH_3$. Since the B–H hydrogen can presumably form a linkage more readily to the silicon in an intermediate complex than to the carbon of the CN group, it is understandable why the H migrates to the Si and not to the carbon as is the case in the formation of $(CH_3CH_2NBH)_x$ from $CH_3CN\cdot BH_3$. Reduction of the cyanide carbon only occurs on heating BH_2CN to higher temperatures.

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[CONTRIBUTION NO. 549 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

B^{11} Magnetic Resonance Study of Boron Compounds

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RECEIVED APRIL 17, 1959

B^{11} chemical shifts are presented for representative examples of most classes of boron-containing compounds. B^{11}–H^1 coupling constants are given for the boron hydrides and borane adducts. Some qualitative conclusions regarding bonding in these compounds are derived from observed chemical shifts and coupling constants. Temperature dependences of the B^{11} spectra of $B_2H_5\cdot N(CH_3)_2$ and $B_{10}H_{14}$ are presented and discussed.

Introduction

The B^{11} magnetic resonance spectra of several boron-containing compounds already have been reported[1–10] and discussed, usually in connection with proofs of structure. However, with the exception of the work of Onak, *et al.*,[10] no systematic study of the nuclear magnetic resonances of this important class of compounds has been made. In the present study, boron chemical shifts and B^{11}–H^1 coupling constants for most types of boron-containing compounds are given, from which some qualitative conclusions regarding electronic structures are made. In addition, some temperature dependences of the B^{11} spectra of $B_{10}H_{14}$ and $B_2H_5\cdot N(CH_3)_2$ are reported and discussed.

Results and Discussion

I. B^{11} Chemical Shifts.—An example of a B^{11} magnetic resonance spectrum is that of $B_2H_5\cdot N(CH_3)_2$ shown in Fig. 1. The three main triplet components centered around 237, 367 and 497 c.p.s., arise from nuclear spin coupling between boron atoms and the two "terminal" hydrogen atoms bonded to each boron. The single "bridge" hydrogen atom splits each of the triplet components into doublets of spacing 29 c.p.s. Because of the low nuclear moment and probably weak coupling to the B^{11} nuclei, the "bridge" N^{14} nucleus with a spin of $I = 1$ only contributes to the breadth of the B^{11} resonance through spin-spin coupling. The B^{11} nucleus has a nuclear spin of 3/2 and a non-zero electric quadrupole moment; and in general, because of quadrupole relaxation effects, it exhibits resonance line widths considerably greater than those observed for hydrogen and fluorine. For this reason, coupling constants between boron and hydrogen separated by more than one bond length have not been observed. Indeed line widths of boron resonances are such that only in a few in-

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