Studies of Boron–Nitrogen Compounds. IX. Synthesis and Properties of Some Substituted Trimethylboranes

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Reaction of chloromethyldimethylborane with lithium azide yields azidomethyldimethylborane, which upon hydrogenation yields aminomethyldimethylborane. Molecular weight and n.m.r. spectral studies indicate that aminomethyldimethylborane exists in a monomer-polymer equilibrium. Dissociation studies with ammonia and trimethylborane suggest that monomeric aminomethyldimethylborane is a weaker Lewis acid and Lewis base than corresponding monofunctional derivatives. The acid–base character and the n.m.r. spectral study suggest that monomeric aminomethyldimethylborane may exist as a metastable three-membered ring. The reactions of chloromethyldimethylborane with water, ammonia, and 2,4,6-trimethylpyridine are described. The thermal decomposition of azidomethyldimethylborane is described.

Introduction

Recently Zeldin and Girardot reported the synthesis of chloromethyldimethylborane by direct chlorination of trimethylborane.[1] This discovery opens the way to a new phase of research on the chemistry of the alkyl group of trialkylboranes. By analogy to S_N2 displacements of α-halo ketones, it was thought possible that chloromethyldimethylborane might undergo displacement of chloride ion by other nucleophiles. In support of this postulate it has been recently shown that α-bromoalkaneboronic esters undergo displacement of bromide ion.[2,3] The proximity of the boron atom and a substituent on the carbon should result in interesting chemical and physical properties for any new substituted trimethylboranes.

Experimental

Apparatus and Materials. All reactions were carried out using vacuum techniques similar to those described by Sanderson.[4] The n.m.r. spectra were determined by use of a Varian DP 60 high resolution spectrometer operating at 60 Mc. for ^1H spectra and 19.3 Mc. for ^{11}B spectra. The ^{11}B chemical shift values are relative to $BF_3 \cdot O(C_2H_5)_2 = 0$ p.p.m. The integrals were obtained using a Varian Model V-3521 integrator. The infrared spectra were measured with Perkin-Elmer Infracord Models 137 and 137G. The infrared samples were confined in a 5-cm. gas cell with sodium chloride windows. The mass spectra were measured with a

Consolidated Engineering Corp. Model 21-620 mass spectrometer.

Trimethylborane was prepared in a manner similar to that described by Brown.[5] 2,6-(N,N-Dimethyl)xylidine was prepared by the method of Brown and Grayson.[6] The product was vacuum distilled in the presence of a small amount of acetic anhydride, b.p. 48–49° (2 mm.). 2,4,6-Trimethylpyridine (White Label) was obtained from Eastman Kodak and purified by distillation, b.p. 164–165° (740 mm.). Lithium azide was prepared and purified by the method of Hofman-Bang and stored in a desiccator.[7] B-Trimethyl-N-triethylborazine was prepared by the method Haworth and Hohnstedt used to prepare similar borazines.[8] Ammonia was dried over sodium and a middle fraction, sublimed at −80°, was collected.

Table I. ^1H and ^{11}B N.m.r. Chemical Shift Values

Compound	^1H chemical shift,[a] p.p.m.	Assignment	^{11}B chemical shift,[b] p.p.m.
$(CH_3)_2BCH_2Cl$	−0.9 (s)	–CH_3	−84.1
(no solvent)	−3.4 (s)	–CH_2–	
$(CH_3)_2BCH_2N_3$	−0.6 (s)	–CH_2–	− 6.1
(CS_2 as solvent)	−1.0 (s)	–CH_3–	−62.8
$(CH_3)_2BCH_2NH_2$	−0.23 (s)	–CH_2–	− 0.3
(no solvent)	−0.85 (s)	–CH_3	−48.4
	−3.55 (t)	–NH_2	
	(J = 54 c.p.s.)		
$(CH_3)_2BCH_2OH$	−0.34 (s)	–CH_2–	−55.3
(no solvent)	−0.89 (s)	–CH_3	
	−6.56 (s)	–OH	

[a] Tetramethylsilane (internal) = 0 p.p.m.; s = singlet, t = triplet. [b] $BF_3 \cdot O(C_2H_5)_2 = 0$ p.p.m.

Chlorination of Trimethylborane. The procedure described below is similar to that used by Zeldin and Girardot.[1] In a typical preparation, chlorine gas (40.0 mmoles) was slowly added to trimethylborane (40.0 mmoles) in a 1-l. flask at −95° and the reaction allowed to proceed at −95° for 1 hr. The unchanged chlorine was separated by several passes through a −142° trap and condensation in a −196° trap. Trimethylborane (22.0 mmoles) was recovered by several passes through a −112° trap and condensation in a −142° trap. The remaining material was separated on a low temperature fractionation column. The purified chloromethyldimethylborane (I) (12.4 mmoles) had a vapor tension of 36.5 mm. at 0°. The material balance of the reaction determined is shown in eq. 1.

(1) L. Zeldin and P. R. Girardot, Abstracts of the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961, p. 15N.
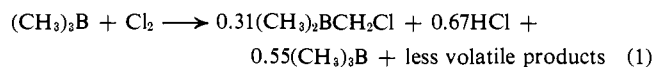
(2) D. S. Matteson and J. D. Liedtke, Chem. Ind. (London), 1241 (1963).

(3) D. S. Matteson and R. W. H. Mah, J. Am. Chem. Soc., 85, 2599 (1963).

(4) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(5) H. C. Brown, J. Am. Chem. Soc., 67, 374 (1945).

(6) H. C. Brown and M. Grayson, ibid., 75, 20 (1953).

(7) N. Hofman-Bang, Acta Chem. Scand., 11, 581 (1957).

(8) D. T. Haworth and L. F. Hohnstedt, J. Am. Chem. Soc., 82, 3860 (1960).

Table II. Mass Spectra of Some Substituted Alkylboranes

m/e	Relative intensity	m/e	Relative intensity	m/e	Relative intensity	m/e	Relative intensity
Chloromethyl-dimethylborane		Azidomethyl-dimethylborane		Aminomethyl-dimethylborane		Hydroxymethyl-dimethylborane	
10	1.24	10	2.5	10	0.6	10	0.4
11	4.7	11	10.2	11	2.4	11	1.8
12	1.3	12	5.3	12	1.2	12	0.7
13	3.7	13	13.1	13	3.4	13	1.1
14	2.1	14	9.4	14	0.6	14	1.1
15	12.4	15	24.2	15	1.9	15	7.5
16	13.0	24	0.7	16	0.3	25	0.9
17	0.1	25	3.5	24	0.1	26	3.6
24	0.2	26	17.2	25	0.6	27	9.4
25	1.1	27	42.0	26	2.2	28	6.5
26	4.4	28	11.4	26.5	0.4	29	25.6
27	10.3	29	11.2	27	10.7	37	0.7
28	0.55	30	0.5	28	25.2	38	0.4
29	0.8	31	1.3	29	1.44	39	1.2
35	0.8	31.5	0.8	30	0.1	40	1.0
36	2.3	36	1.1	32	0.4	41	3.6
37	3.9	37	3.5	36	0.3	42	27.0
38	3.3	38	3.1	37	0.8	43	*100*
39	10.5	39	6.4	38	0.7	44	1.5
40	27.0	40	6.4	39	2.3	45	0.7
41	*100*	41	8.0	40	6.4	52	0.4
42	3.2	42	8.4	41	31.0	53	1.5
43	1.9	43	64.0	42	*100*	54	1.5
44	0.2	44	2.5	43	5.2	55	4.8
45	0.6	45	4.5	44	0.1	56	3.5
46	3.0	49	0.6	49	0.2	57	16.7
47	12.8	50	1.2	50	0.3	69	0.5
48	1.7	51	1.8	51	0.6	71	3.0
49	12.3	52	1.5	52	0.7	72	2.1
50	0.8	53	5.3	53	0.5		
51	2.7	54	16.7	54	1.1		
52	0.1	55	17.4	55	3.7		
53	0.7	56	1.3	56	10.8		
54	1.5	57	12.2	57	7.8		
55	6.5	58	0.7	70	1.0		
56	0.8	59	1.9	71	5.5		
57	2.5	66	0.3				
58	0.0	67	25.5				
59	0.4	68	*100*				
60	0.9	69	4.9				
61	1.3	71	9.2				
62	0.4	74	2.3				
63	1.4	82	5.5				
65	0.2	83	1.0				
71	0.5	96	5.5				
72	0.1	97	11.5				
73	0.4						
74	0.6						
75	2.4						
76	0.1						
77	0.6						
84	2.4						
86	1.4						
90	0.3						
92	0.0						

$(CH_3)_3B + Cl_2 \longrightarrow 0.31(CH_3)_2BCH_2Cl + 0.67HCl +$

$$0.55(CH_3)_3B + \text{less volatile products} \quad (1)$$

The infrared spectrum of I (pressure, 40 mm.) contained bands at 3.36 and 3.43 (C–H), 7.7 (CH$_3$ deformation), 8.6 (B–C), 9.1, 10.65, and 13.4 (C–Cl). The ^{1}H and ^{11}B chemical shifts and the mass spectral data are given in Tables I and II.

Preparation of Azidomethyldimethylborane. Dry, finely divided lithium azide (7.7 mmoles) and 2 ml. of 2,6-(N,N-dimethyl)xylidine were placed in a 50-ml. flask, and I (6.7 mmoles) was condensed into the flask at −196°. As the mixture warmed to 0°, a vigorous

exothermic reaction occurred. The mixture was stirred at 0° for 0.5 hr. and then fractionated. The amine solvent was removed by condensing it in a 0° trap through which the remaining material passed. Separation of the azidomethyldimethylborane (II, 5.09 mmoles) was accomplished by several passes through a −22.8° trap and condensation in a −50° trap. The vapor tension of II was 4 mm. at 0°. A vapor phase molecular weight of II was obtained. Calculated for C$_3$H$_8$BN$_3$: mol. wt., 96.8. Found: mol. wt., 110. The salts remaining in the reaction flask were treated with dilute nitric acid and boiled to expel any azide present as hydrazoic acid and then analyzed for chlo-
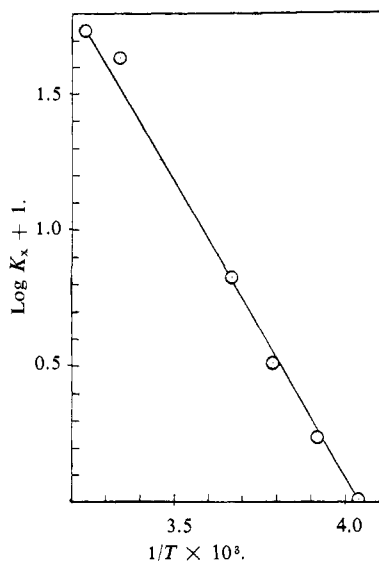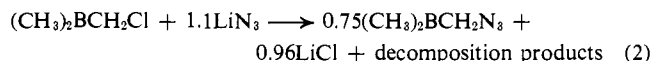
Figure 1. Log K_x vs. $1/T$ for aminomethyldimethylborane.

ride content by titration with silver nitrate using di-chlorofluorescein as indicator. The material balance determined is given in eq. 2. The infrared spectrum

$$(CH_3)_2BCH_2Cl + 1.1LiN_3 \longrightarrow 0.75(CH_3)_2BCH_2N_3 +$$
$$0.96LiCl + \text{decomposition products} \quad (2)$$

of II (pressure, 20 mm.) contained bands at 3.3 and 3.4 (C–H), 4.7 (N_3), 7.7 (CH_3 deformation), and 8.9 (B–C). The ^1H and ^{11}B chemical shift values and the mass spectral data for II are given in Tables I and II. The relative size of the two peaks in the ^{11}B n.m.r. spectrum was temperature dependent. At lower temperatures the peak at +14.2 p.p.m. increased and the peak at −15.5 p.p.m. decreased in size relative to their size at room temperature.

Preparation of Aminomethyldimethylborane. Platinum(II) oxide (100 mg.) was reduced with hydrogen and the water formed removed *in vacuo.* The solvent, 1 ml. of 2,6-(N,N-dimethyl)xylidine, and 4.5 mmoles of II were then condensed into the flask containing the catalyst at −196°. Dry hydrogen (1 atm.) was introduced and the mixture was stirred for 0.5 hr. at room temperature. The solvent was removed by condensing it in a 0° trap through which the remaining material passed. The aminomethyldimethylborane (III) was purified by several passes through a −80° trap and condensations in a −112° trap. The amount of III obtained was 2.25 mmoles (50% yield). The infrared spectrum of III (pressure, 30 mm.) contained bands at 2.84 and 2.91 (N–H), 3.39 and 3.64 (C–H), 6.2 (NH₂ deformation), 7.5 (CH₃ deformation), and 8.5 (B–C). The mass spectral data for III are given in Table II.

Vapor Tension Data for Aminomethyldimethylborane. Saturated vapor tension measurements were made by starting with III completely in the vapor phase at room temperature (except for the measurement made at 30°) and cooling to the desired temperature. Measurements of the vapor tension were made after a minimum of 2 hr. to enable the sample to approach an equilibrium pressure. The measurements were reproducible to ±0.2 mm. Table III gives the vapor tension data. A plot of log p vs. $1/T$ resulted in a slightly curved line.

Table III. Vapor Tension Data for Aminomethyldimethylborane

Temp., °C.	Pressure, mm.	Temp., °C.	Pressure, mm.
30	364	−30.6	15.2
0	89.5	−36.0	11.9
−11.9	38.9	−45.0	7.8
−22.8	17.9	−63.5	3.0

Molecular Weight of Aminomethyldimethylborane. Aminomethyldimethylborane (78.1 mg.) was placed in a tensimeter having two calibrated volumes (V_1 = 243.6 ml.: V_2 = 257.9 ml.). The molecular weight was determined at several temperatures and the data are given in Table IV. The calculated molecular weight for $C_3H_{10}BN$ is 70.84.

Table IV. Molecular Weight Data for Aminomethyldimethylborane

Volume	Temp., °C.	Pressure, mm.	Observed mol. wt.
V_1	0.8	70.30	76.12
	4.5	74.45	72.84
	8.6	77.65	70.87
	14.8	79.60	70.65
V_2	27.0	79.50	71.10
	41.8	83.95	70.72
	49.6	86.20	70.53
	60.0	89.15	70.46
	66.0	90.90	70.34
	75.1	93.40	70.31

Temperature-Dependent N.m.r. Spectra of Aminomethyldimethylborane. A. ^{11}B N.m.r. Spectra. The room temperature spectrum of a neat sample of III, containing an internal capillary of boron trichloride as reference, was measured. Two peaks at −48.4 and −0.3 ± 1 p.p.m. were observed. The areas of the two peaks were integrated at various fixed temperatures between +35 and −25°. Assuming that the low-field peak was due to monomer and the high-field peak due to dimer, the data were used to calculate a per cent dimerization. The equilibrium constant, K_x, was calculated assuming an ideal solution. The quantities of monomer and dimer were expressed as mole fractions. To assure that saturation of the observed signal was not occurring, one value was checked at a lower power setting. The two values agreed within 0.7%. The per cent dimerization and equilibrium constants for the various temperatures are given in Table V. The plot of log K_x vs. $1/T$ is given in Figure 1. The heat of dimerization was calculated to be 8.98 kcal./mole.

Table V. Summary of Data from ^{11}B N.m.r. Spectrum of Aminomethyldimethylborane

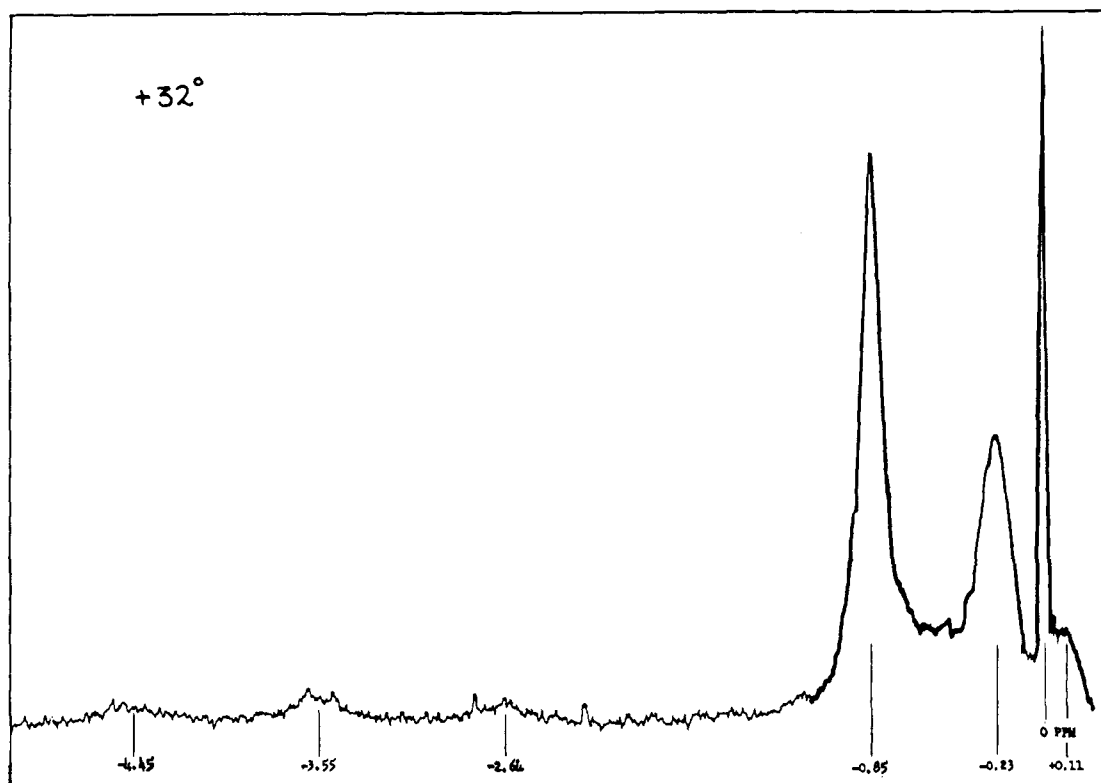| Temp., °C.	Dimer, %[a]	K_x
35.25	24.3	5.379
26.75	28.2	4.260
− 0.50	62.4	0.660
− 9.25	72.4	0.325
−18.00	79.6	0.172
−25.30	84.3	0.101

[a] Values reproducible to with ±4%.

Figure 2a. ¹H n.m.r. spectrum of aminomethyldimethylborane at +32°.

B. ¹H N.m.r. Spectra. The proton n.m.r. spectra of IV were taken at +32, −14.5, and −45° and are shown in Figures 2a and 2b.

Dissociation Studies. A. The Aminomethyldimethylborane–Ammonia Complex. Equal quantities of gaseous aminomethyldimethylborane (approximately 0.30 mmole) and ammonia were measured out. The two volumes of gas were matched to within 1 part in 760. The mixture was completely vaporized in the tensimeter and the pressure measured as a function of the temperature. The average deviation in the pressure measurements was ±0.05 mm. The degree of dissociation, α, and the equilibrium constant, K_p', were calculated for each temperature. The method of approximations described by Brown and Gerstein was used to obtain a straight-line plot of log K_p' vs. $1/T$.[9] The pressure

Figure 2b. ¹H n.m.r. spectra of aminomethyldimethylborane at −14.5 and −45°.

Table VI. Actual Data for the Dissociation of the Aminomethyldimethylborane–Ammonia Complex

Temp., °C.	—Pressure, mm.— Obsd.	Calcd.[a]	Degree of dissociation (α)	K_p', atm.
29.3	44.40	23.41	0.896	0.239
42.3	46.80	24.42	0.916	0.3222
49.8	48.25	24.99	0.930	0.410
59.9	49.80	25.78	0.931	0.430
70.0	51.25	26.56	0.929	0.423
80.1	52.91[b]	27.34	0.935	0.485
90.0	54.40[b]	28.11	0.935	0.498

[a] Pressure of aminomethyldimethylborane or ammonia at 29.5° is 23.43 mm. [b] A correction for the vapor pressure of mercury at these temperatures was applied since the tensimeter used did not have a ground-glass mercury seal.

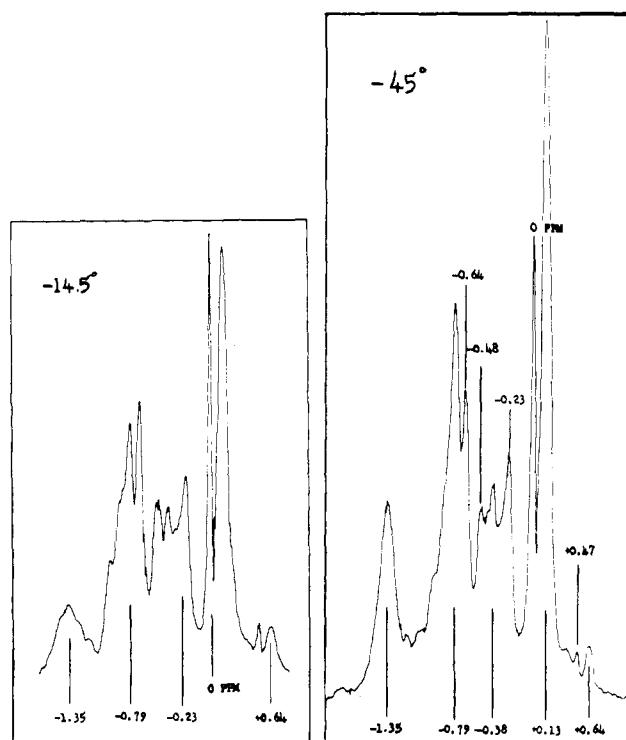(9) H. C. Brown and M. Gerstein, *J. Am. Chem. Soc.*, **72**, 2923 (1950).

measurements and the resulting calculations are given in Tables VI and VII.

B. The Aminomethyldimethylborane–Trimethylborane Complex. Equal quantities of the two pure boranes were measured out. The two volumes of gas were matched to within 1 part in 726. The mixture

Table VII. Data Obtained Using the Approximation Method for the Dissociation of the Aminomethyldimethylborane–Ammonia Complex

Temp., °C.	—Pressure, mm.—		Degree of dissociation (α)	K_p', atm.
	Obsd.	Calcd.[a]		
29.3	44.40	22.68	0.957	0.644
42.3	46.80	23.65	0.978	1.402
49.8	48.25	24.22	0.992	3.948
59.9	49.80	24.97	0.994	5.679
70.0	51.25	25.73	0.991	4.042
90.0	54.40	27.23	0.997	15.486

[a] The pressure of aminomethyldimethylborane or ammonia at 29.5° is 22.70 mm.

was completely vaporized in the tensimeter and the pressure measured as a function of temperature. The pressure measurements and the degree of dissociation are given in Table VIII.

Table VIII. Data for the Dissociation of the Aminomethyldimethylborane–Trimethylborane Complex

Temp., °C.	——Pressure, mm.——		Degree of dissociation
	Obsd.	Calcd.[a]	
30.8	41.30	20.52	1.01
0.0	34.40	17.43	0.973

[a] The pressure of either borane at 30° is 20.47 mm.

Hydrolysis of Chloromethyldimethylborane. Equivalent quantities of chloromethyldimethylborane and water reacted vigorously while warming to room temperature. The products were condensed into a −95° trap. The material which passed the −95° trap was identified as hydrogen chloride by its vapor tension, 124 mm. at −112°, and its infrared spectrum. The remaining hydrogen chloride was removed by treatment of the products with 2,6-(N,N-dimethyl)-xylidine. The recovered chloride was titrated with silver nitrate and 86% of the theoretical chloride was found. Most of the remaining material passed a −36° trap and condensed in a −45° trap. The vapor tension of this new tensiometrically homogeneous material, tentatively assigned the structure of hydroxymethyldimethylborane (IV), was 16.2 mm. at 0°. The infrared spectrum of IV contained bands at 2.9 (C–H), 3.3 and 3.4 (C–H), 7.6 (CH₃ deformation), and 3.5 (B–C). The ¹H and ¹¹B chemical shift values and the mass spectral data for IV are given in Tables I and II.

Reaction of 2,4,6-Trimethylpyridine with Chloromethyldimethylborane. Chloromethyldimethylborane reacted rapidly with an excess of 2,4,6-trimethylpyridine as the mixture warmed to room temperature. After removal of the excess 2,4,6-trimethylpyridine, a white nonvolatile solid remained. The solid dissolved readily in chloroform and upon exposure to the air the solution underwent several color changes from yellow to blue. The white solid was exposed to the atmosphere for several days. This material was then chromatographed on Giulini alumina (neutral, activity grade I). The major fraction was eluted with chloroform. The material obtained was slightly yellow and crystalline and gave a negative boron flame test. The proton n.m.r.

spectra of the chromatographed material and of an authentic sample of 1,2,4,6-tetramethylpyridinium iodide were run in deuteriochloroform as solvent. The chromatographed material had peaks at −7.65, −4.35, −2.96, and −2.57 p.p.m., and the 1,2,4,6-tetramethylpyridinium iodide had peaks at −7.74, −4.26, −2.93, and −2.59 p.p.m. The peak areas in both spectra were 2:3:6:3, respectively.

The Thermal Decomposition of Azidomethyldimethylborane. Azidomethyldimethylborane (9.25 mmoles) was sealed in a 1-l. flask and allowed to stand at ambient temperature for 136 days. The flask was opened and the gases not condensable at −196° were measured with a Toepler pump. There was 6.41 mmoles of gas measured. The mass spectrum of the gas indicated that it was nitrogen. The other volatile materials were passed into a −112° trap. The material passing this trap was trimethylborane as indicated by its mass spectrum. The vapor tension and infrared spectrum indicated that the remaining volatile material was recovered II (1.25 mmoles). There remained in the reaction flask a large quantity of much less volatile liquid which was partly transferred from the reaction flask to the vacuum line by pumping at room temperature for 15 hr. Vapor phase chromatography of this colorless liquid on a 6-ft. column of 5% DC silicon oil 550 on Haloport F at 175° indicated the presence of several components. The largest peak had a retention time of 3.6 min. A programmed temperature chromatogram from 100 to 180° at 2°/min. further resolved this mixture, indicating the presence of at least three components. The retention time determined under identical conditions for B-trimethyl-N-triethylborazine was 3.6 min. The ¹¹B n.m.r. spectrum of the mixture contained a broad peak at −37.7. The ¹H n.m.r. spectrum of the mixture in carbon tetrachloride solution was measured and is shown in Figure 3. Spin decoupling of the protons in the −1-p.p.m. region caused a collapse of the quartet in the −3.3-p.p.m. region. Conversely, spin decoupling of the protons in the −3.3-p.p.m. region caused collapse of the fine structure in the 1-p.p.m. region. The ¹H n.m.r. spectrum of B-trimethyl-N-triethylborazine was measured in carbon tetrachloride solution and contained a quartet, doublet, and singlet centered at −3.45, −1.07, and −0.53 p.p.m., respectively.

Results and Discussion

Displacement Reactions. Chloromethyldimethylborane (I) was found to undergo vigorous exothermic reactions with several nucleophilic reagents. Thus I and lithium azide gave a 75% yield of azidomethyldimethylborane (II), and the nonvolatile salts remaining after reaction contained 96% of the expected chloride. The reaction of I with water produced a good yield of hydroxymethyldimethylborane (IV) and hydrogen chloride. A nonvolatile solid was formed when I was mixed with 1 equiv. of ammonia in 2,6-(N,N-dimethyl)-xylidine as solvent or with 2 equiv. of ammonia in the gas phase. The reaction of I with 2,4,6-trimethylpyridine produced a nonvolatile solid. After the nonvolatile solid was exposed to moist air for several days, there was obtained a 1,2,4,6-tetramethylpyridinium salt. A comparison of the proton n.m.r. spectra of the final product and of an authentic sample of

1,2,4,6-tetramethylpyridinium iodide served to determine the structure.

In several reactions 2,6-(N,N-dimethyl)xylidine was used as solvent and in no instance was reaction observed with this base.

From the few examples presented above, it appears that chloride ion displacement from I should occur with a large variety of nucleophiles. The success of such reactions will probably depend largely on the use of a solvent which permits a homogeneous reaction but which itself will not react with the substituted trimethylborane. All the displacement reactions studied thus far were much faster than expected for analogous alkyl halides. This supports the hypothesis that the neighboring boron atom may aid the displacement reaction by a *coordinative assistance* of the incoming nucleophile.

The lack of reaction in the case of 2,6-(N,N-dimethyl)xylidine is possibly due to its lower base strength, the lack of assistance from the boron atom because of the hindered approach, and the probable internal steric strain that would be present in the product.

Aminomethyldimethylborane. Catalytic hydrogenation of II gave aminomethyldimethylborane (III). Vapor phase molecular weight measurements indicated 13.8% association at 0° and essentially no association above 40°. The ^{11}B n.m.r. spectrum of III contained two peaks at -48.4 and -0.3 p.p.m. whose relative intensities were temperature dependent. The peak at -48.4 p.p.m. was assumed to arise from the monomer since resonances of trigonally substituted boron compounds are found in this region. A variable temperature ^{11}B n.m.r. study indicated that the percentage of monomer III in the liquid phase decreased from 75.7% at 35° to 15.7% at $-25°$. With the assumption that the polymeric form of III is a dimeric six-membered ring, a straight line plot of log K_x vs. $1/T$ for the temperature-dependent ^{11}B n.m.r. data was obtained and is shown in Figure 1. The heat of dimerization of III was calculated to be 8.98 kcal./mole. The heat of dimerization of the similar aminodimethylborane determined by Wiberg and co-workers was approximately 10 kcal./mole.[10]

The proton n.m.r. spectrum of III was measured at -32, 14.5, and $-45°$ and is shown in Figure 2. The spectrum contains a triplet centered at -3.55 p.p.m. ($J = 54$ c.p.s.) attributed to the protons of the amino group and two singlets at -0.85 and -0.23 p.p.m. assigned to the methyl and methylene protons, respectively. In addition there appear to be two smaller peaks at -0.67 and $+0.11$ p.p.m. which are due to the small percentage of polymers present. The proton n.m.r. spectrum at $-45°$ consists of at least nine peaks and the peaks are much sharper. The complex nature of this spectrum is probably due to spin coupling of magnetically nonequivalent amino, methylene, and possibly methyl protons in the polymeric form of aminomethyldimethylborane.

Dissociation Studies of Aminomethyldimethylborane. The degree of dissociation of a 1:1 complex of III and ammonia was studied. The data were treated by the method of approximations described by Brown and Gerstein.[9] The complex was found to be approxi-

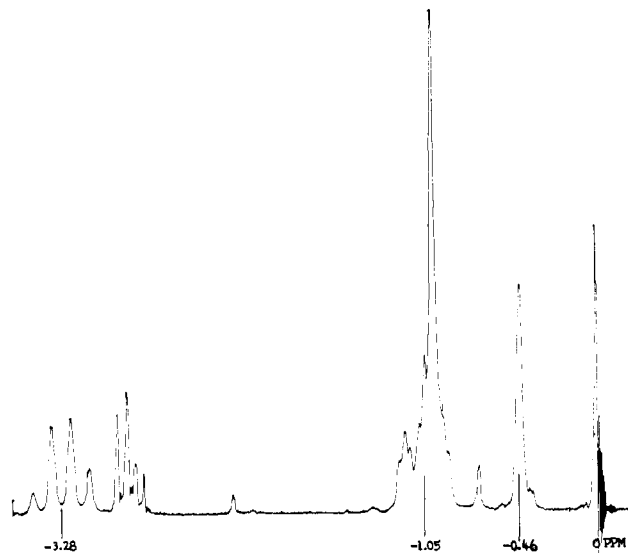(10) E. Wiberg, K. Hertwig, and A. Bolz, *Z. anorg. allgem. Chem.*, **256**, 177 (1948).

Figure 3. ^{1}H n.m.r. spectrum of decomposition products of azidomethyldimethylborane.

mately 95% dissociated at 29.3°. The heat of dissociation was calculated to be 11.4 ± 1.7 kcal./mole. The large probable error is assumed because of the extremely difficult region ($\alpha = 0.95$ to 0.99) in which the dissociation was measured.

The degree of dissociation of a 1:1 complex of III and trimethylborane was studied. At 30.8° there was no association detected, and at 0° the complex was 97% dissociated. The dissociation values of III with ammonia and trimethylborane are considered to be only approximate values. However, these values suggest that III is both a weaker Lewis acid and Lewis base than corresponding monofunctional derivatives. The dissociation data are summarized in Table IX.

Table IX. Summary of Dissociation Data

Compounds	Degree of dissociation	Temp., °C.	Ref.
$(CH_3)_2BCH_2NH_2-NH_3$	0.95	29.3	This work
$(CH_3)_3B-NH_3$	0.90	54.8	11
$(CH_3)_2BCH_2NH_2-B(CH_3)_3$	1.01	30.8	This work
$CH_3CH_2CH_2NH_2-B(CH_3)_3$	0.58	94.9	12
$CH_3CH_2CH(CH_3)NH_2-B(CH_3)_3$	0.78	79.9	13

The Thermal Decomposition of Azidomethylborane. Azidomethyldimethylborane was observed to decompose slowly at room temperature and much more rapidly at 125°. In an attempt to avoid further thermal changes to the products, samples of II were allowed to decompose at ambient temperature for several months. The products were nitrogen, recovered II, and a slightly volatile oil. A vapor phase chromatogram of the oil indicated the presence of three components, the largest of which had a retention time of 3.6 min. The infrared spectrum of the oil contained a peak at 7.1 suggesting
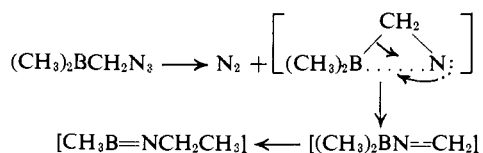
(11) H. C. Brown, J. Bartholomay, Jr., and M. D. Taylor, *J. Am. Chem. Soc.*, **66**, 435 (1944).
(12) H. C. Brown, M. D. Taylor, and S. Sujishi, *ibid.*, **73**, 2464 (1951).
(13) H. C. Brown and G. K. Barbaras, *ibid.*, **75**, 6 (1953).

the presence of boron–nitrogen bonds. The ^{11}B n.m.r. spectrum contained a broad peak at -37.7, in the region where borazines are found. The proton n.m.r. of the oil is shown in Figure 3. There is a quartet centered at -3.3 p.p.m. and a less well-defined triplet centered at -1.0 p.p.m. Proton spin decoupling of each of these multiplets led to collapse of the other multiplet to a single peak. An authentic sample of B-trimethyl-N-triethylborazine was prepared. The proton n.m.r. spectrum of the borazine contained a quartet, triplet, and singlet with chemical shift values similar to those obtained for the decomposition products of II (see Table I). A vapor phase chromatogram of the authentic borazine under the same conditions used for the decomposition products of II gave a retention time of 3.6 min.

The evidence obtained on the decomposition products of II strongly supports but does not prove the hypothesis that a major product is B-trimethyl-N-triethylborazine. The following scheme is offered as a speculated mechanism for the formation of the borazine from II.

$$(CH_3)_2BCH_2N_3 \longrightarrow N_2 + \left[(CH_3)_2B \overset{CH_2}{\underset{N:}{\diagup \diagdown}} \right]$$

$$[CH_3B{=}NCH_2CH_3] \longleftarrow [(CH_3)_2BN{=}CH_2]$$

Comments on the N.m.r. Data. The ^{11}B chemical shift values of the monomeric substituted trimethylboranes show a gradual shift to higher field as the electron-donating ability of the substituent group increases. Thus, the chemical shift of chloromethyl-dimethylborane is very close to that of trimethylborane

(-86.3), but the chemical shift of aminomethyldimethylborane is 35.7 p.p.m. upfield from chloromethyldimethylborane, near the chemical shift of boron trichloride. This suggests that the electron density on the boron atom in aminomethyldimethylborane is greater than that of a simple trialkylborane. This is further evidence of some intramolecular interaction in aminomethyldimethylborane.

It is interesting to note that although the proton chemical shifts of the methyl groups in the substituted trimethylboranes are relatively invariant (-0.84 to -1.0 p.p.m.), the chemical shifts of the methylene protons undergo a dramatic change from -3.4 p.p.m. for chloromethyldimethylborane to -0.24 p.p.m. for aminomethyldimethylborane. The proton resonance of cyclopropane is also found at unusually high field (0.20 p.p.m.). However, it is not clear whether this similarity is caused by the same electronic phenomenon. The chemical and physical evidence suggest that monomeric III may exist in a metastable three-membered configuration which would be isoelectronic and isosteric with 1,1-dimethylcyclopropane.[14]

(14) NOTE ADDED IN PROOF. Subsequent to the acceptance of this paper, work has appeared describing the preparation of an isomer of III [N. E. Miller and E. L. Muetterties, *Inorg. Chem.*, 3, 1196 (1964)]. It is interesting to note that this isomer [H$_2$BCH$_2$N(CH$_3$)$_2$] appears to exist primarily in the dimeric form (although the molecular weight reported is nearly 10% low for the dimer). Enhancement of both the acid strength of the boron and the base strength of the nitrogen on transfer of the methyl groups is of course not unexpected. Further comparison of the two isomers is clearly necessary.