

CONTRIBUTION FROM THE SCHOOL OF CHEMICAL ENGINEERING,  
GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA, GEORGIA 30332**Cryochemical Preparation of Monomeric Aminoborane<sup>1a</sup>**By C. T. KWON<sup>1b</sup> AND H. A. MCGEE, JR.\*

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Borazine vapor was subjected to a radiofrequency discharge in a low-pressure, fast-flow system followed by an immediate quench to  $-196^\circ$ . Unidentified solid products were deposited in the discharge tube, and all gaseous products except nitrogen and hydrogen were trapped by the cryoquench. Upon slow warming of the trap, diborane, aminoborane ( $H_2BNH_2$ ), unreacted borazine, and probably borazanaphthalene and diborazinyll were evolved at  $-170$ ,  $-160$ ,  $-130$ ,  $-40$ , and  $-30^\circ$ , respectively. Aminoborane was identified by (a) its relative volatility, (b) its mass spectrometric fragmentation pattern, (c) its ionization potential,  $I(H_2^{11}BNH_2) = 11.0 \pm 0.1$  eV, which was unchanged when observing the compound in the effluent from the discharge, in the cold subliming vapor or over the purified solid product, and (d) its infrared spectrum at various temperatures down to  $4.2^\circ K$ . Mass spectrometric data were obtained using cryogenic inlet techniques to prevent premature loss of reactive or unstable species. Solid aminoborane begins to polymerize between  $-196$  and  $-155^\circ$  to yield an inert, white material. However, this reaction does not rapidly go to completion since the mass spectrum of  $H_2BNH_2$  is continuously observed during warming the polymerizing material from  $-155$  to  $-64^\circ$  over an approximately 100-min period.

**I. Introduction**

Isoelectronic arguments involving BN and CC have implied the probable existence of an inorganic analog of organic chemistry, and a large number of "organic-like" compounds have, in fact, been prepared and characterized.<sup>2</sup> Better understanding of the bonding and reactivity of both the conjectured and the observed BN compounds would be aided by the isolation and study of the simplest olefin analog, aminoborane,  $H_2BNH_2$ . This new physical understanding, together with the availability of the borane itself, would both suggest and allow many interesting syntheses.

The ethylene-like molecule has been neither isolated nor characterized, but rather all experiments have led to heavier condensation products. Only two recent reports have yielded reasonably convincing observations of even the transitory existence of aminoborane. When gaseous cyclodiborazane, the BN analog of cyclobutane, is subjected to pyrolysis at  $135^\circ$  followed by condensation of the products at  $-78^\circ$ , convincing evidence has been obtained for the presence of  $H_2BNH_2$  in the vapor evolved upon subsequently warming the trap to room temperature.<sup>3</sup> These studies also suggested that aminoborane was reasonably stable below  $-78^\circ$ . The very low-pressure equilibrium vapor over subliming ammonia-borane at  $20^\circ$  evidently contains  $H_2BNH_2$  as has been reported from molecular beam, mass spectrometric experiments.<sup>4</sup>

Hence, it seemed reasonable that the new techniques of cryochemistry might permit the successful synthesis, purification, and characterization of this very interesting and elusive species.

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(2) W. L. Jolly, Ed., "Preparative Inorganic Reactions," Vol. 3, Wiley, New York, N. Y., 1966, pp 123-227.

(3) K. W. Bøddeker, S. G. Shore, and R. K. Bunting, *J. Amer. Chem. Soc.*, **88**, 4396 (1966).

(4) P. M. Kuznesof, D. F. Shriver, and F. E. Stafford, *ibid.*, **90**, 2557 (1968).

**II. Experimental Section**

These experiments consist essentially of subjecting a suitable parent substance to either a pyrolysis or a radiofrequency discharge in a fast-flow, low-pressure system followed by a rapid quench usually to  $-196^\circ$ . The cold composite solid was then processed in various ways and studied by low-temperature infrared spectroscopy and by mass spectrometric techniques utilizing a cryogenically cooled inlet agreement.

**Materials.**—Borazine was the only parent compound used in this particular series of experiments. Commercial *B*-trichloroborazine was reduced with sodium borohydride in diglyme as a solvent.<sup>5</sup> The product was distilled from the reaction solution under vacuum, using a reflux condenser packed with glass helices and cooled to  $-20^\circ$  to ensure a more complete separation of solvent and product. The borazine was initially purified further using a high-efficiency spinning-band column, but this operation was later omitted when the mass spectrum was noted as being equivalent to an earlier report<sup>6</sup> and to be unchanged by this final distillation procedure.

**Pyrolysis.**—Fast-flow, low-pressure pyrolyses of borazine were conducted using 2-mm i.d. Pyrex, stainless steel, or alumina furnace tubes, having a 4-cm heated length. These furnace tubes could also be packed with a bundle of four stainless steel small-bore tubes, 4 cm in length, to obtain a greater heat-transfer area. The furnace was mounted near the ion source of a Bendix Model 12-107 time-of-flight mass spectrometer with the ionizing electron beam essentially tangent to the exhaust port of the furnace. Either this or equivalent arrangements have allowed the detection of many intermediates and transitory species both in this laboratory and in many others.

**Electric Discharge.**—Regardless of the subsequent processing, each discharge-initiated experiment involved an inductively coupled electrodeless discharge produced in borazine vapor by a 17 cm long coil of 70 turns of no. 14 enameled copper wire. The coil was wound on a 25-mm o.d. Pyrex tube which was mounted concentrically with the 10-mm o.d. Pyrex discharge tube. Compressed air was gently blown through the annulus between the coil and the discharge tube which was thereby maintained at essentially room temperature. The discharge was self-igniting, and the coil was energized through an impedance matching network which allowed the VSWR to be turned to approximately unity. Power was supplied by a 3.5-MHz oscillator capable of a maximum output of about 350 W.

Two general types of fast-flow radiofrequency discharge reac-

(5) G. H. Dahl and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **12**, 380 (1960).

(6) API Research Project 44, "Selected Mass Spectral Data," Serial No. 1346 (BaN<sub>3</sub>H<sub>6</sub>).

tor-inlet configurations were used in conjunction with the T-O-F mass spectrometer: (1) for direct analysis of the discharge effluent and (2) for cold analysis of the products at cryogenic temperatures. In sampling the gases pumped from the discharge with the mass spectrometer, it was necessary to place the axis of the discharge coil at a right angle to the center line of the sample inlet port of the ion source and to impose an 83-V bias over a 10-cm length perpendicular to the flow of ions from the discharge were to be neutralized before reaching the ion source. Ions from the discharge entering the source make spectrometer operation impossible. Therefore, the discharge plasma could be no closer to the ionizing electron beam than about 30 cm (compare the essentially zero separation in the pyrolysis experiments), but by moving the discharge coil still further back down the discharge tube, the effect of a longer reaction or relaxation time could be explored. The second discharge arrangement involved a straight-line flow from the coil to a cryogenically thermostated trap through a total of about 38 cm of 10-mm o.d. Pyrex and Monel tubing. This apparatus, which also permits mass spectrometric analysis at cryogenic temperatures, is schematically shown in Figure 1.

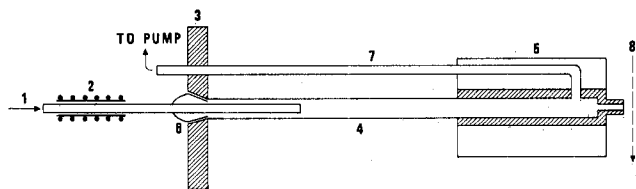


Figure 1.—Schematic diagram of radiofrequency discharge and mass spectrometric inlet apparatus for the cryoquench production and characterization of aminoborane. The entire apparatus projects into the mass spectrometer high-vacuum space from the main header (3). A suitable parent substance enters at (1) and is discharged at (2), and the products are quenched or thermostated at any very low temperature at (5). The cold sample from this trap is injected directly into the ionizing electron beam (8).

**Purification.**—The effluent gases from the radiofrequency discharge were pumped through two conventional vacuum traps maintained at  $-130$  and  $-168^\circ$ . Unreacted borazine, which was by far the most abundant species, and heavier condensation products condensed in the first trap, while aminoborane, a small fraction of the diborane product, and traces of borazine were condensed at  $-168^\circ$ . Both the recovery of the unreacted borazine and the final purification of the aminoborane product required only simple vacuum distillation because of the wide difference in volatilities of the several species. For example,  $B_2H_6$  could be distilled from  $H_2BNH_2$  by pumping on the solid mixture thermostated at  $-155^\circ$ . At this temperature, loss of  $H_2BNH_2$  due to evaporation was slight, but the product was however slowly lost to polymerization. Aminoborane is itself conveniently distillable near  $-130^\circ$ , but there is now at the higher temperature, a much faster loss of monomer to polymer. The increased distillation rate with increasing temperature must be balanced against the increased polymerization rate in any practical situation.

**Infrared Spectroscopy.**—A 4 mm thick  $\times$  4 cm  $\times$  2 cm NaCl plate was mounted in a copper block designed such that the plate was effectively "immersed" in copper on all four sides. This block was soldered to the bottom of the liquid helium dewar of a conventional double-dewar optical system,<sup>7</sup> where it was cooled by direct contact with boiling liquid helium or with whatever other refrigerant was placed in the inner dewar. The salt plate must have been very near refrigerant temperature, but its temperature was never actually measured. The sample inlet tube was mounted perpendicularly to the salt plate so as to allow the deposition of aminoborane in a well-defined elliptical spot of about 4-mm diameter. The helium dewar was then rotated  $90^\circ$  *in vacuo* to place the deposit on its NaCl substrate within the

infrared beam of a Perkin-Elmer Model 221 spectrophotometer. All windows and optics were also NaCl.

The spectrum was recorded at liquid helium temperature, at liquid nitrogen temperature, and at  $-155^\circ$  by merely pouring the warmer refrigerant into the inner dewar just as the colder refrigerant had almost evaporated. Precooled 2-methylpentane was used at  $-155^\circ$ , and this refrigerant may be used conveniently to thermostat the sample at any temperature up to room temperature where the liquid still exerts a vapor pressure of only 200 Torr.

**Mass Spectrometry.**—Figure 1 suggests schematically the simple way in which mass spectrometric analyses may be performed on species stable only at very low temperatures. One merely provides an inlet channel which is maintained at the same low temperature as the sample reservoir and which exhausts the sample vapor directly into the ionizing electron beam. In the apparatus of Figure 1, the electron beam (8) makes grazing, tangential contact with the cold sample inlet port. A refrigeration system permits thermostating and automatic control of this reservoir and inlet arrangement (5) at any temperature down to  $-218^\circ$ . Such arrangements, or equivalent apparatus or technique, are necessary in cryochemistry to prohibit the premature decomposition or loss of excessively labile or reactive substances.<sup>8</sup>

### III. Results

Pyrolysis of borazine vapor in both clear and packed furnace tubes at about 0.2 Torr (borazine vapor pressure at  $-78^\circ$ ) and at temperatures of up to  $600^\circ$  produced no iron intensity enhancement at  $m/e$  28 and 29, the parent ion masses of aminoborane. The fast-inlet mass spectrometric technique employed here would have revealed these species, had they been present. Minor ions heavier than borazine did appear, suggesting condensation reactions in the furnace.

Discharge of borazine vapor at about 1.5 Torr (vapor pressure at  $-60^\circ$ ) using fast-inlet mass spectrometry with one stage of differential pumping yielded spectra with essential features as summarized in Table I. The intensities at a number of values of  $m/e$  par-

TABLE I  
PARTIAL MASS SPECTRA OF BORAZINE AND OF THE EFFLUENT  
FROM THE RADIOFREQUENCY DISCHARGE OF BORAZINE  
VAPOR AT 50 eV

$m/e$	Intensity		Assignment <sup>b</sup>
	Borazine <sup>a</sup>	Effluent	
1		5.9	H <sup>+</sup>
2	0.66	212.7	H <sub>2</sub> <sup>+</sup>
10	1.49	5.4	<sup>10</sup> B <sup>+</sup>
11	5.42	20.2	<sup>11</sup> B <sup>+</sup> , <sup>10</sup> BH <sup>+</sup>
12	0.97	6.2	<sup>11</sup> BH <sup>+</sup> , <sup>10</sup> BH <sub>2</sub> <sup>+</sup>
13	1.06	5.4	<sup>11</sup> BH <sub>2</sub> <sup>+</sup>
14	0.23	4.0	N <sup>+</sup>
15	0.08	3.0	NH <sup>+</sup>
16	0.09	4.4	NH <sub>2</sub> <sup>+</sup>
24	0.37	21.7	<sup>10</sup> BN <sup>+</sup>
25	0.12	22.2	<sup>11</sup> BN <sup>+</sup> , <sup>10</sup> BNH <sup>+</sup>
26	0.96	71.6	<sup>11</sup> BNH <sup>+</sup> , <sup>10</sup> BNH <sub>2</sub> <sup>+</sup>
27	2.62	163.0	<sup>11</sup> BNH <sub>2</sub> <sup>+</sup> , <sup>10</sup> BNH <sub>3</sub> <sup>+</sup>
28	4.45	137.4	<sup>11</sup> BNH <sub>3</sub> <sup>+</sup> , <sup>10</sup> BNH <sub>4</sub> <sup>+</sup> , N <sub>2</sub> <sup>+</sup>
29		37.5	<sup>11</sup> BNH <sub>4</sub> <sup>+</sup>
80	100.00	100.0	Parent

<sup>a</sup> Reference 6; also independently confirmed in this laboratory.

<sup>b</sup> Ions from  $B_2H_6$  also contribute to the indicated intensities at many values of  $m/e$ , but these obvious assignments have been omitted here for simplicity.

(8) H. A. McGee, Jr., T. J. Malone, and W. J. Martin, *Rev. Sci. Instrum.*, **37**, 561 (1966); J. Holzhauser and H. A. McGee, Jr., *Anal. Chem.*, **41** (11), 24A (1969).

(7) H. M. Hersh, *Phys. Rev.*, **105**, 1158 (1957).

tially arise from diborane, but, for simplicity, these assignments have been omitted from the table. These data were recorded at a lower than normal electron voltage due to an unavoidably high sample input rate to the source. The significant structure at  $m/e$  26–29 is either absent or only a minor contributor (less than 5% of the principal ion at  $m/e$  80) to the mass spectrum of borazine itself. The volatile products consisted of  $H_2$ ,  $N_2$ ,  $B_2H_6$ ,  $H_2BNH_2$ , and unreacted borazine, but a solid was also deposited on the walls of the discharge tube. The relative amounts of the several gaseous products depended upon the discharge tube pressure, the power level of the discharge, and the length of 10-mm tubing (relaxation time) between the plasma and the sampling port into the mass spectrometer. The intensities at  $m/e$  27, 28, and 29, as well as their ratios, varied greatly with pressure, flow rate, and discharge power level. Reasonably optimum conditions, *i.e.*, conditions which seemed roughly to maximize  $m/e$  27, 28, and 29, employed a borazine reservoir temperature of  $-50$  to  $-60^\circ$  or discharge pressures of approximately 1–3 Torr, discharge power levels of about 40 W, and minimum separation between the discharge coil and the mass spectrometer inlet port. Expectedly, the amount of free  $N_2$  and  $H_2$  and the rate of solid deposition in the plasma region increased with increasing discharge power levels. To reduce this solid deposition and to allow for free passage of gases through the discharge for extended periods of time, the borazine reservoir temperature was usually maintained at about  $-70^\circ$ . This lower pressure operation also greatly reduced the yield of aminoborane. The solid deposit in the discharge tube seemed composed of a white powder and a transparent material, but neither of these substances was studied.

In the discharge and quench experiments using the apparatus of Figure 1, the discharge and flow conditions were adjusted to their optimum values as determined from the discharge experiments. The gases passing the  $-196^\circ$  trap (5) of Figure 1 were continuously monitored, and labile species stable only at cryogenic temperatures would have been readily detected. However, only  $H_2$  and  $N_2$  were observed during typically 90-min runs. Upon subsequent controlled warming of this trap, the composite solid slowly evolved its constituent species in the order of their decreasing volatility. Only  $B_2H_6$  and  $H_2BNH_2$  were more volatile than the unreacted parent.

The mass spectrum of diborane was observed in the sublimate at  $-170^\circ$ . In separate experiments designed for a more complete identification of this most volatile product, the subliming vapor at  $-170^\circ$  was trapped at  $-196^\circ$ , and after subsequently warming to room temperature, its mass spectrum and infrared spectrum were both found to agree with earlier characterizations of diborane.<sup>9,10</sup> The mass spectra of this separated product were also equivalent at  $-170^\circ$  and at room temperature.

(9) W. J. Lehmann, J. F. Ditter, and I. Shapiro, *J. Chem. Phys.*, **29**, 1248 (1958).

(10) J. L. Margrave, *J. Phys. Chem.*, **61**, 38 (1957).

Ions at  $m/e$  28 and 29 from aminoborane were first observed at about  $-160^\circ$ , and their rate of growth with temperature was very fast.

Close observation of the mass spectra revealed that no other ions heavier than  $m/e$  29 appeared on heating the composite solid to  $-130^\circ$ . The unreacted parent compound began to appear above  $-130^\circ$ , followed by  $m/e$  128–133 ( $B_5N_5H_8$ , probably borazanaphthalene) at  $-40^\circ$  and then structure at  $m/e$  98–105 and 154–160 ( $B_6N_6H_{10}$ , probably diborazinyl) at  $-30^\circ$ . No heavier compounds were observed. The structure at  $m/e$  98–105 was not identified but it is probably fragment ions from borazanaphthalene. These heavier BN compounds could be formed during the heating of the discharge products, and some reports have appeared on the formation of such compounds from borazine.<sup>11–13</sup> Interestingly, these heavy products appeared in our experiments only if the composite cold solid was slowly warmed. In rapid warm-ups, the unreacted borazine parent was the heaviest observed species.

The mass spectrum of  $H_2BNH_2$  is observed using the cold-inlet system at  $-160^\circ$  or using conventional fast-inlet techniques wherein the sample is warmed to room temperature prior to its ionization. That is, aminoborane withstands short-term exposures to room temperature. This characteristic enables its purification by simple trap-to-trap distillation. The mass spectrum of such purified aminoborane was observed beginning at about  $-160^\circ$ , and it continued unchanged with increasing temperature up to about  $-64^\circ$ . This warming of approximately  $100^\circ$  occurred in approximately 100 min. In another series of experiments, the mass spectrum of pure  $H_2BNH_2$  was observed for at least 3 hr with the solid sample thermostated at  $-155^\circ$ . The mass spectrum of pure aminoborane is presented in Table II.

TABLE II  
MASS SPECTRUM OF AMINOBORANE AT 70 eV

$m/e$	Intens	Assignment
1	0.25	$H^+$
2	0.15	$H_2^+$
10	1.27	$^{10}B^+$
11	5.40	$^{11}B^+$ , $^{10}BH^+$
12	1.84	$^{11}BH^+$ , $^{10}BH_2^+$
13	1.08	$^{11}BH_2^+$ , $^{10}BNH_2^{2+}$
13.5	0.30	$^{11}BNH_2^{2+}$
14	0.84	$N^+$
15	0.61	$NH^+$
16	1.43	$NH_2^+$
24	0.29	$^{10}BN^+$
25	2.53	$^{11}BN^+$ , $^{10}BNH^+$
26	13.83	$^{11}BNH^+$ , $^{10}BNH_2^+$
27	56.20	$^{11}BNH_2^+$ , $^{10}BNH_3^+$
28	100.00	$^{11}BNH_3^+$ , $^{10}BNH_4^+$
29	38.83	$^{11}BNH_4^+$

The infrared spectrum of solid aminoborane was observed as a function of temperature, and the data

(11) A. W. Laubengayer, P. C. Moews, Jr., and R. F. Porter, *J. Amer. Chem. Soc.*, **83**, 1337 (1961).

(12) G. Mamantov and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **20**, 348 (1961).

(13) A. W. Laubengayer and O. T. Beachley, Jr., *Advan. Chem. Ser.*, **No. 42**, 281 (1964).

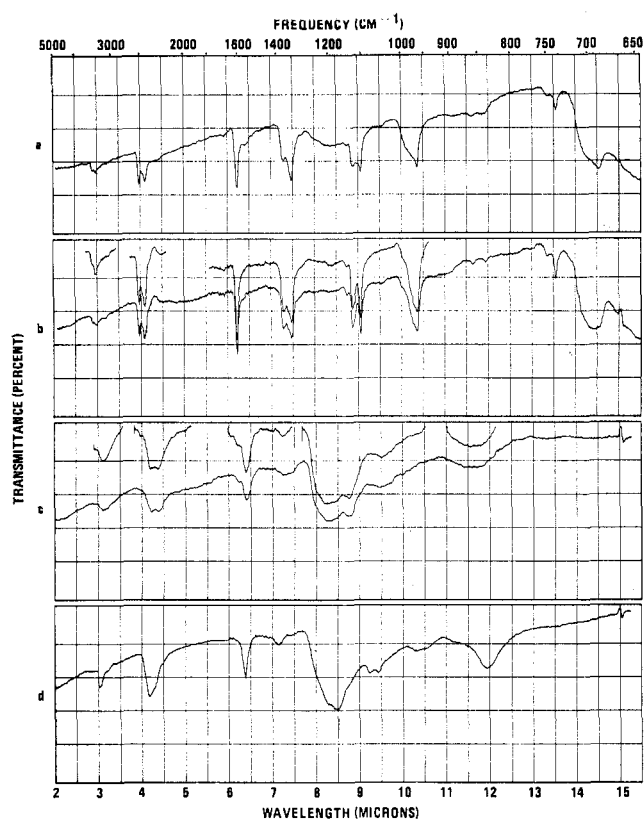


Figure 2.—Infrared spectrum of aminoborane at various temperatures: (a) at 4.2°K; (b) at 77°K; (c) at 118°K; (d) at room temperature after exposure to the atmosphere for 1 week.

are summarized by the selected spectra reproduced in Figure 2. The spectra at liquid helium and at liquid nitrogen temperatures are equivalent as are the spectra at and above  $-155^{\circ}$ . The unreacted aminoborane was, of course, pumped out of the sample at  $-155^{\circ}$  before recording the spectrum of Figure 2c. Onset of this self-destructive reaction occurred between  $-196$  and  $-155^{\circ}$ , and it yielded a white polymeric product inert upon long-term exposure to the atmosphere. After exposure of this product to the atmosphere for 1 month, its spectrum remained equivalent to that of Figure 2d.

The ionization potential of aminoborane was determined from a number of independent sets of ionization efficiency data in each of three experimental ar-

rangements.  $I(\text{H}_2^{11}\text{BNH}_2)$  was  $11.0 \pm 0.1$  eV in the effluent gas from the discharge, in the subliming vapor over the quenched composite solid at  $-152^{\circ}$ , and in the subliming vapor over the purified product at  $-150^{\circ}$ . These critical potentials were determined by the linear extrapolation method using ionization efficiency curves recorded directly from the electrometer using a Hewlett-Packard (Model 7001 AR) X-Y plotter. The above ionization potential of aminoborane may be compared with the value of 10.5 eV<sup>14</sup> for its isoelectronic analog, ethylene.

#### IV. Discussion

The identification of the low-temperature reactive species as aminoborane rests upon mass spectral, infrared, and energetic data. The  $^{10}\text{B}/^{11}\text{B}$  ratio of 19.6/80.4 or 0.244 may be used to interrelate the data of Table II. Assuming  $m/e$  29 to arise from  $^{11}\text{BNH}_4^+$ , one can calculate a monoisotopic mass spectrum and predict the intensity at  $m/e$  24, *i.e.*,  $^{10}\text{BN}^+$ . Similar calculations can interrelate the BH structure at  $m/e$  10–13. The predicted and experimental intensities agree well, and therefore the entire spectrum must be due to  $\text{H}_2\text{BNH}_2$  alone. The equivalence of the ionization potential at  $m/e$  29,  $\text{H}_2^{11}\text{BNH}_2^+$ , confirms that the same species is being observed from the discharge, in the quenched composite solid, and in the purified product. The N–H stretching band in aminoborane is clearly resolved into its components at 2.89 and 3.0  $\mu$  as is also the B–H band at 3.96 and 4.09  $\mu$ . The polymeric product is very stable and very inert at room temperature.

The appearance of product species heavier than the unreacted parent borazine depended upon the time-temperature history of the initially quenched composite solid. These larger products do not appear on warming purified aminoborane through its polymerization region, and therefore they must arise from the interaction of borazine and aminoborane in the cold composite solid. It is necessary only to warm the composite at a rate such that the aminoborane does not all evaporate before it has time to react.

We may expect the rapid unfolding of much interesting chemistry using this new reagent.

(14) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, p 253.