

1,6-Bis-(*o*-hydroxyphenyl)-2,4-di-aza-hexane-zinc(II).—Zinc dust (30 g.) and acetic acid (100 ml.) were added to a hot, vigorously stirred solution of ethylenediamine (6 g.) in 95% ethanol (300 ml.). A solution of salicylaldehyde (24 g.) in ethanol (150 ml.) was slowly added over a period of 90 minutes. Zinc dust (70 g.) and acetic acid (200 ml.) were added in small amounts at intervals over a period of 3 hr. and the mixture allowed to stand overnight. The zinc acetate and unchanged zinc were filtered and the excess alcohol and acetic acid removed by distillation under reduced pressure. The residual syrup was dissolved in water and on adding excess sodium hydroxide solution a pale cream precipitate of the zinc complex of VIII separated. This was obtained pure on recrystallization from aqueous dimethylformamide solution.

Anal. Calcd. for $[C_{16}H_{18}N_2O_2Zn]$: C, 57.3; H, 5.4; Zn, 19.4. Found: C, 57.2; H, 5.5; Zn, 19.6.

Reduction of the Polymeric Schiff Base from Diethylene-triamine and 5,5'-Methylene-bis-salicylaldehyde.—5,5'-Methylene-bis-salicylaldehyde (5.12 g.) in hot glacial acetic acid (100 ml.) was added to a hot, stirred solution of diethylenetriamine (2.06 g.) in glacial acetic acid (50 ml.). Heat was generated and the solution became brown. It was stirred and gently heated for 75 minutes. After cooling, the solution was subjected to hydrogenation, using platinum dioxide as catalyst and a pressure of 1,000 p.s.i. for 24 hr. After this time the acetic acid was removed by distillation under

reduced pressure. The dark brown, syrupy residue was diluted with water and distillation repeated three more times to remove as much of the acetic acid as possible. Finally the residue was dissolved in ethanol. This solution was filtered and the filtrate evaporated by distillation at atmospheric pressure. When as much of the ethanol as possible had been removed in this manner the residual syrup was dried *in vacuo*. It rapidly foamed and ultimately became brittle and resinous. The material is very hygroscopic and was stored *in vacuo*.

Anal. Calcd. for $(C_{19}H_{25}N_3O_2)_n$: C, 69.7; 7.7; N, 12.8. Calcd. for $(C_{19}H_{25}N_3O_2 \cdot 2CH_3COOH \cdot C_2H_5OH)_n$: C, 60.7; H, 8.0; N, 8.5. Found: C, 60.3; H, 8.0; N, 8.2.

Coordination of Reduced Schiff's Base Polymer with Chromium.—A suspension of trichloro-tris-(pyridine)-chromium(III) (0.79 g.) in dimethylformamide (20 ml.) was added to a warm, stirred solution of the above polymer (0.66 g.) in dimethylformamide (20 ml.). Soon after mixing, the $[Crpy_3Cl_3]$ dissolved and a light violet solution was obtained. The mixture was stirred and gently refluxed for three days. The solution slowly became blue and a dark violet, almost black, amorphous precipitate gradually separated. This was washed with dimethylformamide and ethanol and dried *in vacuo*.

Anal. Calcd. for $(CrCl_3 \cdot H_{23}N_3O_2Cl \cdot 1.5H_2O)_n$: C, 51.8; H, 6.0; N, 9.6. Found: C, 51.9; H, 6.0; N, 9.9.

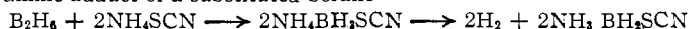
[CONTRIBUTION NO. 640 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE]

Chemistry of Boranes. I. Reactions of Boron Hydrides with Metal and Amine Salts

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RECEIVED SEPTEMBER 16, 1960

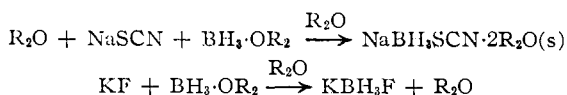
Diborane, tetraborane and decaborane react readily with certain metal salts, *e.g.*, NaCN, to form substituted borohydride salts (NaH_3BCNBH_3 , NaB_4H_7CN and $NaB_{10}H_{12}CN$) which are generally isolated as etherates. Ammonium and amine salts with diborane initially form substituted borohydrides, but at 0–25° hydrogen loss is spontaneous and the final product is an ammonia or amine adduct of a substituted borane



Introduction

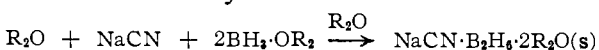
The behavior of boron hydrides as electrophilic reagents is well characterized.¹ One class reaction within this chemistry is complex formation with H^- to form borohydride anions; however, apparently few other anions have been investigated with the boranes.¹ We have found that a variety of inorganic and organic anions react with boranes to form substituted borohydride anions.

Diborane.—Borane (BH_3) in the form of an ether complex reacts with metal thiocyanates and fluorides



The B^{11} spectrum of BH_3SCN^- (or BH_3NCS^-) consists of a quadruplet which is consistent with a monosubstituted borohydride anion structure. Hydrolytic stability of BH_3F^- is poor in neutral solution whereas that of the thiocyanate derivative appears to be comparable to BH_4^- .

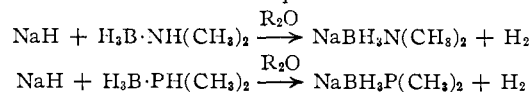
Sodium cyanide and diborane do not follow the above stoichiometry but react as



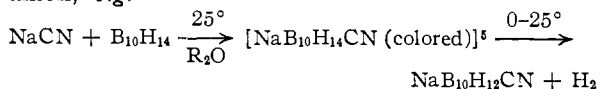
(1) For review see F. G. A. Stone, *Quart. Rev. (London)*, **9**, 174 (1955); D. T. Hurd, "Chemistry of the Hydrides," John Wiley and Sons, Inc., New York, N. Y., 1952; "Gmelins Handbuch der Anorg. Chemie," BOR 13, Verlag Chemie, GMBH, Weinheim, 1954; R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

The B^{11} spectrum of this product consists of two quadruplets of equal intensity, and the only reasonable structure consistent with this is $(H_3BCNBH_3)^-$.² Hydrolytic stability of this salt is comparable to $NaBH_4$. Sodium cyanide and tetraborane also form NaH_3BCNBH_3 plus a second product believed to be NaB_3H_7CN .³ Pentaborane is apparently not cleaved by cyanide ion and a simple salt, NaB_5H_9CN , is obtained.

Another new, simple route to substituted borohydride etherates is the protolysis of sodium hydride and borane-base complexes



Decaborane.—We have found a characteristic reaction of decaborane with metal salts and ammonium salts in which the anion displaces a mole of hydrogen from decaborane to give a $B_{10}H_{12}X^-$ anion,⁴ *e.g.*



(2) One quadruplet was slightly broadened. This probably represents the boron atom bonded to a nitrogen atom since the latter nucleus has a quadrupole moment that would affect the relaxation time.

(3) It has been established that tetraborane can be cleaved symmetrically to effectively yield BH_3 and B_3H fragments. *Cf.* R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

(4) Decaborane and H^- form $B_{10}H_{12}^-$. *Cf.* W. V. Hough and L. J. Edwards, paper presented before the Division of Inorganic

TABLE I
 SUBSTITUTED DECABOROHYDRIDE SALTS

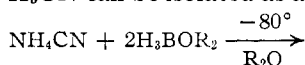
Compound ^c	Yield, %	Analytical											
		-N-		-B-		-C-		-H-		-X-			
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
NaB ₁₀ H ₁₂ CN·2(C ₂ H ₅) ₂ O	80	7.2	7.2	34.1	35.7	34.1	33.0	10.2	9.9	4.4(N)	4.3		
NaB ₁₀ H ₁₂ NCO·2.5C ₆ H ₅ O ₂	55	5.7	6.1	26.7	27.4	32.6	32.1	8.0	8.1	3.5(N)	3.6		
(CH ₃) ₄ NB ₁₀ H ₁₂ -SCN	^a	42.8	41.6	23.8	24.0	9.6	10.1	11.1(N)	11.1	12.7(S)	12.7
NaB ₁₀ H ₁₂ OCH ₃ ·C ₄ H ₉ O ₂	75	8.8	8.8	41.2	40.1	22.9	21.3	8.8	8.5				
(CH ₃) ₄ NB ₁₀ H ₁₂ -C(CN) ₃	^b	38.9	38.5	14.1	15.1	3.5	3.9				

^a See Experimental for procedure. ^b Reaction of KC(CN)₃ and B₁₀H₁₄; (CH₃)₄NCl added to aqueous solution of reaction product; (CH₃)₄N⁺ salt has a strong band at 2260 cm.⁻¹ characteristic of covalently bound C(CN)₃ and a weak band at 2180 cm.⁻¹ indicative of a trace impurity of a cyanoforn salt. ^c All compounds are crystalline and homogeneous; the X-ray patterns are unique and devoid of lines characteristic of starting materials.

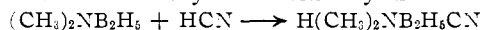
Examples of the substituted decaborohydrides isolated in this study are listed in Table I. These salts are recovered from ethereal reaction media as etherates. Solvent-free salts are obtained by recrystallization from water, *e.g.*, (CH₃)₄NB₁₀H₁₂SCN.

The structure of the B₁₀H₁₂X⁻ anion was not established. B¹¹ spectra are too complicated due to overlapped resonances and solvent dependency for a unique interpretation.⁶ We suggest that the X⁻ group either bridges the 6,9 boron atoms or is terminally attached to one of these boron atoms,⁷ and we favor the latter alternative.

Diborane-Ammonium Salt Reactions.—An ethereal slurry of ammonium cyanide absorbs diborane at -80° with dissolution of the salt. On warming to 0°, one mole of hydrogen per mole of salt is evolved, and from the solution H₃NB₂H₅CN can be isolated as an etherate.



The same chemistry prevails for CH₃NH₃CN and (CH₃)₂NH₂CN, but (CH₃)₃NHCN gives H₃BN-(CH₃)₃. Dimethylaminodiborane and hydrogen cyanide yield the same product as obtained from diborane and dimethylammonium cyanide



The B¹¹ spectra of the above cyanide reaction products consist of a diffuse triplet on the low-field side of a considerably sharper quadruplet. This is indicative of a BH₂ and a BH₃ group, respectively. The diffuse triplet suggests the BH₂ group is directly bonded to a nitrogen atom and conversely the sharp quadruplet suggests the BH₃ group is not directly bonded to a nitrogen atom. Thus, structure I would appear to be more likely than II.



The CN absorption in the infrared spectra of these compounds is at ~2250 cm.⁻¹ which is characteristic of covalently bound cyanide. All of these data are thus consistent with structure I.

Chemistry, National Meeting of the American Chemical Society, San Francisco, California, April, 1958.

(5) Not isolated.

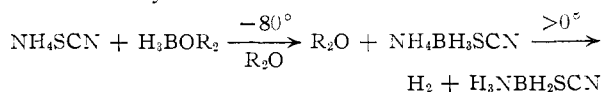
(6) Cf. W. H. Knoth and E. L. Muetterties, *Chemistry of Boranes II*, to be published, for more detailed discussion of this point.

(7) In B₁₀H₁₂·2CHCN, the base ligands are bonded to the 6,9 boron atoms. Thus, nucleophilic attack appears to take place preferentially at these positions. J. M. Reddy and W. N. Lipscomb, *J. Am. Chem. Soc.*, **81**, 754 (1959).

In water, the cyanide complexes slowly evolve hydrogen and the solutions become acidic (*pH* ~3-4) and conductive. The rate of hydrogen evolution is greatly accelerated by addition of base. This behavior is in rather sharp contrast to that of simple amine borane complexes.

These cyanoboranes effect an unusual reductive amination of acetone. The initial products, water-insoluble liquids of unknown structures, hydrolyze to give isopropylamines. Diisopropylamine and dimethylisopropylamine were obtained from H₃BCNBH₂NH₂ and H₃BCNBH₂NH(CH₃)₂, respectively.

Other ammonium salts react with diborane in a fashion formally similar to the cyanides but the stoichiometry is different



The B¹¹ spectra of nonaqueous solutions of the thiocyanate derivative consist of a triplet indicating two hydrogen atoms bound directly to the boron atom. In the infrared spectrum of the solid, there is a band at 2130-2165 cm.⁻¹ characteristic of covalently bound thiocyanate (compare Na⁺SCN⁻ at 2040 cm.⁻¹, C₆H₅NCS at 2035 cm.⁻¹ and C₆H₅SCN at 2160 cm.⁻¹). These data give strong support to the structure H₃N·BH₂SCN but do not exclude the structure H₃N·BH₂NCS.

Aqueous solutions of the thiocyanate product slowly evolve hydrogen and are initially poorly conducting (comparable to (CH₃)₂NH·BH₃) and acidic (*pH* = 3.4-4.3). The specific resistivity of a 0.1 molar solution drops from an initial 705 to 490 ohms in 20 minutes and to 24.5 ohms (*pH* = 2.3) in three days. Fresh solutions give an immediate test for SCN⁻ with ferric ion, although the red color slowly fades due to reduction of Fe⁺³ to Fe⁺². The B¹¹ spectra of aqueous solutions of the compound show that a new boron species forms at the expense of H₃N·BH₂SCN. The peak representing the new species is somewhat broad and no fine structure, if present, was resolved. The thiocyanate derivative, like the cyanide derivatives, is more rapidly decomposed by base than by acid. A cationic BH species may be generated in water which would account for the facile protolysis in basic solution.

Experimental

Materials and Method.—Callery Chemical Company diborane was purified by bulb-to-bulb distillation to remove

hydrogen and traces of higher boranes. Tetraborane and pentaborane were obtained by fractionation of the high boiling impurities in the diborane. American Potash decaborane was purified by recrystallization from methylecyclohexane. Most of the inorganic salts were reagent materials and were vacuum dried before use. Ammonium and amine cyanides were prepared directly from hydrogen cyanide and anhydrous ammonia or amine. Ether solvents were distilled from lithium aluminum hydride and stored over sodium.

All of the diborane, tetraborane and pentaborane experiments were effected in vacuum systems and conventional techniques were employed to follow the stoichiometries of these reactions. Vacuum technique was not always necessary for decaborane reactions; many of these were satisfactorily carried out in open Erlenmeyer flasks.

In some cases, particularly for carbon and alkali-metals, precision analyses could not be obtained. Inspection of Table I shows that good analyses were often obtained for most of the elements in a given compound but one or two elemental analyses were at variance. It is not possible to give precision values to our analytical procedures because of the widely varying types of compounds examined here. Alternatively, the analytical procedures are given: Alkali metals were determined by flame photometric methods (low precision) and the carbon-hydrogen determinations were based on a modified Pregl micro combustion procedure (samples were covered with a mixture of CuO and WO₃). For nitrogen, micro Kjeldahl or Dumas methods were used depending on the nature of the nitrogen group present. The remaining elemental analyses were preceded by a Parr bomb peroxide decomposition. Boron was analyzed, after ion-exchange removal of cationic species, by titration as the boric acid-mannitol complex. Fluorine was distilled (Willard and Winter) and titrated with standard thorium nitrate solution.

Synthesis of MBH₃SCN.—Sodium thiocyanate (0.146 mole, which had been dried to <1 μ at 90°) was dissolved in glycol dimethyl ether (100 ml.). This solution rapidly absorbed 1/2 mole of diborane per mole of thiocyanate at 25°. Addition of dioxane to the solution gave a white precipitate which was collected, washed with dioxane and dried at room temperature under vacuum to give 22.3 g. of a crystalline white solid (56%). It darkens at 330°.

Anal. Calcd. for NaBH₃SCN·2C₄H₈O₂: Na, 8.49; B, 3.99; H, 7.06; S, 11.8; C, 39.8; N, 5.16; Hydrol. H₂, 248 cc./g. Found: Na, 8.50; B, 3.51; H, 7.28; S, 11.7; C, 39.9; N, 5.33; Hydrol. H₂, 248 cc./g.

The X-ray pattern is strong and sharp, unique and devoid of lines characteristic of starting material. The B¹¹ spectrum of an aqueous solution is a quadruplet consistent with a BH₃SCN anion structure. The infrared spectrum shows in addition to the characteristic dioxane bands a B-H stretch at 2380–2300 cm.⁻¹ and -SCN or -NCS absorption at 2175 and 2085 cm.⁻¹.

LiSCN behaved similarly. Addition of dioxane to the reaction mixture caused separation of an oil which solidified on treatment with fresh dioxane. Elemental analysis approximated the composition LiBH₃SCN·1.5C₄H₈O₂. The B¹¹ and infrared spectra were essentially identical to the spectra of the NaSCN product. Barium thiocyanate also gave a BH₃SCN⁻ salt.

Preparation of KBH₃F.—Analytical reagent grade KF·2H₂O was dried on the vacuum train at 90° to <1 μ vapor pressure. The dried salt (24.8 g., 0.427 mole) was suspended in about 250 ml. of dimethoxyethane. Diborane (0.25 mole) was added to the stirred slurry at room temperature. About 0.15 mole of diborane was absorbed rapidly, then slow absorption continued until a total of 0.20 moles had been consumed. The suspended solid was collected on a filter in a nitrogen atmosphere, washed with ether and dried to yield 31.0 g. of product as compared with 30.3 g. of starting materials (24.8 g. KF plus 5.5 g. of diborane).

Anal. Calcd. for KBH₃F: K, 54.4; B, 15.05; F, 26.4; hyd. H₂, 938 cc./g. Found: K, 52.7; B, 14.59; F, 26.21; hyd. H₂, 869 cc./g.

The crystals have a density of 1.5197 and a unique X-ray powder pattern. The pattern is devoid of lines characteristic of KF, KBF₄ and KH. Some of the lines of this pattern are coincident with those of KBH₄. The infrared absorption spectrum (KBr wafer) show B-H stretching as a strong

2230, 2400 cm.⁻¹ doublet with a shoulder at about 2380 cm.⁻¹. Broad, strong absorption is present in the 1020–1078 cm.⁻¹ region with a maxima at 1082 and 1023 cm.⁻¹ and a shoulder at 1030 cm.⁻¹.

Synthesis of NaH₃BCNBH₃.—Sodium cyanide (0.2 mole) was suspended in 50 ml. of ethylene glycol dimethyl ether and diborane was then introduced in small portions at room temperature. The diborane was rapidly absorbed and cooling was necessary to keep the temperature below 30°. A total of about 1 mole of diborane was absorbed per mole of the sodium cyanide. During the addition of the diborane, the sodium cyanide dissolved. The resulting solution was first filtered and then about 250 ml. of dioxane was added to the filtrate to give a copious precipitate of a white solid which was dried at room temperature to give 41.53 g. of product.

Anal. Calcd. for NaH₃BCNBH₃·2C₄H₈O₂: Na, 9.1; H, 8.8; B, 8.6; C, 42.8; N, 5.5; hydrol. H, 532 cc./g. Found: Na, 9.9; H, 8.8; B, 8.6; C, 43.0; N, 5.3; hydrol. H, 572 cc./g.

The infrared spectrum consists of bands characteristic of dioxane, of B-H at 2355 cm.⁻¹ and of C≡N at 2248 cm.⁻¹. The density of this compound is 1.648 at 25° and the X-ray powder pattern is unique. There is no evidence for the presence of sodium cyanide, sodium borohydride or sodium borates.

Cadmium cyanide was reacted with diborane in a fashion similar to that described above. The product was an oil that could not be freed of excess ether because decomposition occurred at 35°.

Anal. Calcd. for Cd(H₃BCNBH₃)₂·3.7C₄H₈O₂: Cd, 20.31; B, 7.8; N, 5.1; hydrol. H, 490 cc./g. Found: Cd, 20.23; B, 8.1; N, 5.1; hydrol. H, 490 cc./g.

Preparation of NaBH₃N(CH₃)₂.—A solution of dimethylamine borane (30 g., 0.5 mole) in 100 ml. of dry glyme was added slowly to a stirred suspension of excess sodium hydride (24 g., 1.0 mole) in about 50 ml. of glyme under a blanket of N₂. Hydrogen was evolved slowly at room temperature. From the heat of the reaction, the temperature rose to 35° whereupon hydrogen evolved rapidly and smoothly. The rate of dimethylamine borane addition was controlled to hold the temperature of the reaction mixture between 35 and 45° and this temperature was maintained with external heating (for 1 hr.) after the addition was complete until no more hydrogen was formed. On standing, the excess sodium hydride settled and the clear supernatant solution was decanted. The solution was concentrated under reduced pressure until crystals began to separate. The solution was then diluted to a volume of 250 ml. with dry dioxane. A white solid separated which was collected, washed with dioxane and dried to <1 μ at room temperature to give 32 g. of a crystalline dioxanate of NaBH₃N(CH₃)₂. The X-ray pattern is unique.

Anal. Calcd. for NaBH₃N(CH₃)₂·0.5C₄H₈O₂: Na, 18.4; B, 8.7; H, 10.5; N, 11.2; C, 38.5; hydrol. H, 538 cc./g. Found: Na, 18.1; B, 9.5; H, 10.3; N, 11.1; C, 36.9; hydrol. H, 514 cc./g.

The B¹¹ spectrum is a quadruplet consistent with the structure [H₃BN(CH₃)₂]⁻.

A similar procedure was followed with NaH and (CH₃)₂PH·BH₃.

Anal. Calcd. for NaBH₃P(CH₃)₂·1/2C₄H₈O₂: Na, 16.2; B, 7.6; P, 21.8. Found: Na, 17.2; B, 7.4; P, 21.2.

The X-ray pattern is unique.

Reaction of B₄H₁₀ and NaCN.—Approximately 0.05 mole of B₄H₁₀ was added to a slurry (at -80°) of 2.3 g. (0.047 mole) of dry sodium cyanide in 70 ml. of dimethoxyethane. When the mixture was allowed to warm from -80°, a gentle, exothermic reaction set in at room temperature or a little below. The sodium cyanide dissolved but only a small amount of hydrogen was formed (0.0032 mole). Addition of dioxane to the filtrate gave a solid and an oily phase. The solid was collected on a funnel, most of the oil was sucked out of the solid, and the rest removed with ether. The solid (5.7 g.) (Fraction A) was dried to less than 1 μ at room temperature. By evaporating the filtrate to smaller and smaller volumes and adding more dioxane, two fractions of additional (5.7 g.) solid material were obtained. The last fraction (B, 1.2 g.) was obtained by evaporating the final filtrate to dryness.

X-Ray powder pattern of Fraction A showed the absence of sodium cyanide, the presence of $\text{NaB}_2\text{H}_6\text{CN}\cdot 2\text{C}_4\text{H}_{10}\text{O}_2$ as a major component and a second component. Elemental analysis showed a 4/1 B/N ratio (B, 10.48%, N, 3.51%). Although a 4/1 B/N ratio would be expected for the product, $\text{NaB}_4\text{H}_{10}\text{CN}$, the presence of a major amount of the 2/1 B/N compound $\text{NaB}_2\text{H}_6\text{CN}$, as shown by X-ray, requires the presence of material having a B/N ratio greater than 4. Elemental analysis of Fraction B checked very well for $\text{NaB}_3\text{H}_7\text{CN}\cdot\text{C}_4\text{H}_{10}\text{O}_2$.

Anal. Calcd. for $\text{NaB}_3\text{H}_7\text{CN}\cdot\text{C}_4\text{H}_{10}\text{O}_2$: B, 18.38; N, 7.93; C, 34.00; H, 8.56. Found: B, 18.81; N, 8.16; C, 34.24; H, 8.12.

Synthesis of Decaborane Salts.—Two procedures were employed in this investigation for the preparation of the decaborane salts. In one, a vacuum-train was used and in the other an open Erlenmeyer flask. In all cases an ether was employed as a reaction medium. Either procedure may be used satisfactorily but the latter is preferred for its simplicity. Given below are two representative examples of these two procedures.

In a vacuum-train, ~50 ml. of tetrahydrofuran was distilled into a reaction flask that contained 0.04 mole decaborane. To this solution, 0.04 mole of NaCN was added through a side arm. The mixture was stirred and, in the course of 4 hr., 0.04 mole of hydrogen was evolved. The tetrahydrofuran was removed from the reaction mixture at reduced pressure to leave a yellow oil. This oil dissolved in diethyl ether, was filtered and on evaporation yielded 6.2 g. of white solid. The analytical data for this compound are given in Table I. The pertinent features of the infrared spectrum of the solid compound are a B-H band at 2532 cm^{-1} and a CN band at 2247 cm^{-1} .

To an Erlenmeyer flask containing 25 ml. of dimethoxyethane were added 0.024 mole of decaborane and 0.2 mole of ammonium thiocyanate. An immediate yellow color developed which was accompanied by heat and hydrogen evolution. The reaction was complete in about 3 hr. as evidenced by diminution in rate of hydrogen evolution. The solution was added to excess water and a concentrated solution of tetramethylammonium chloride was added to the solution. A yellow precipitate was obtained which was recrystallized from warm water. The product was a yellow solid that analyzed for $(\text{CH}_3)_4\text{NB}_3\text{H}_7\text{CN}$. The analytical data are in Table I. The pertinent features of the infrared spectrum of this solid compound are a B-H band at 2525 cm^{-1} and an SCN or NCS absorption at 2160 cm^{-1} .

Reaction of Ammonium and Amine Cyanides with Diborane.—Into about 150 ml. of dimethoxyethane cooled to -80° was condensed 0.1 mole of dry hydrogen cyanide and 0.1 mole of dry ammonia to obtain a slurry of white crystals. To this slurry was added 0.1 mole of diborane. At -80° , the diborane was absorbed and all of the solid dissolved. On warming, hydrogen evolution began about 0° and a total 0.091 mole of hydrogen was collected. Complete removal of solvent to a vapor pressure of less than 1μ at room temperature left a clear, fluid liquid. In successive experiments the weight of nonvolatile residue per mole of reactant varied from 82 to 134 g. as compared with theory for $\text{H}_3\text{NB}_2\text{H}_6\text{CN}$ of 69.7 g. This indicates that the solvent was not removed reproducibly and this was confirmed by analysis of various samples.

Anal. Calcd. for $\text{NH}_3\text{B}_2\text{H}_6\text{CN}\cdot 3/4\text{C}_4\text{H}_{10}\text{O}_2$: N, 20.4; H, 11.4; B, 15.8; C, 35.0; hydrol. H, 823 cc./g. Found: N, 20.6; H, 11.4; B, 15.7; C, 35.3; hydrol. H, 766 cc./g.

Anal. Calcd. for $\text{H}_3\text{NB}_2\text{H}_6\text{CN}\cdot 0.21\text{C}_4\text{H}_{10}\text{O}_2$: N, 31.6; H, 11.5; B, 24.4; C, 25.0; O (diff.), 7.6; hydrol. H, 1260 cc./g. Found: N, 31.8; H, 11.7; B, 24.4; C, 24.9; O (diff.), 7.3; hydrol. H, 1085 cc./g.

At 90° , under high vacuum, ether is removed but at the same time 1 mole of hydrogen is lost per $\text{H}_3\text{NB}_2\text{H}_6\text{CN}$ unit. The nonvolatile material is a liquid of nonrational elemental analysis.

The infrared absorption spectrum of $\text{H}_3\text{NB}_2\text{H}_6\text{CN}\cdot n\text{-C}_4\text{H}_{10}\text{O}_2$ consists of a broad peak at 2355 cm^{-1} in the B-H region, a sharp nitrile peak at 2248 cm^{-1} ($\text{C}\equiv\text{N}$ absorption occurs at 2062 cm^{-1} in NaCN and 2222 cm^{-1} in $\phi\text{C}\equiv\text{N}$) and NH absorption as a broad peak at 3230 cm^{-1} and a weak peak at 1612 cm^{-1} .

A similar procedure with methylammonium cyanide yielded a non-volatile liquid.

Anal. Calcd. for $\text{CH}_3\text{NH}_2\text{B}_2\text{H}_6\text{CN}\cdot 0.125\text{C}_4\text{H}_{10}\text{O}_2$: C, 28.6; H, 12.2; B, 23.9; N, 30.9; hydrol. H, 1230 cc./g. Found: C, 28.3; H, 11.2; B, 24.1; N, 31.2; hydrol. H, 1028 cc./g.

In the infrared spectrum of this compound there is no absorption typical of the ether which was presumed to be present to a slight degree from the elemental analyses. There is NH absorption at 3230 cm^{-1} and 1600 cm^{-1} , saturated CH at 2940 and 2985 cm^{-1} , BH at 2355 cm^{-1} and CN at 2248 cm^{-1} .

A similar procedure was followed with dimethylammonium cyanide to give a liquid product.

Anal. Calcd. for $(\text{CH}_3)_2\text{NHB}_2\text{H}_6\text{CN}\cdot 0.075\text{C}_4\text{H}_{10}\text{O}_2$: C, 37.9; H, 12.3; N, 26.8; B, 20.7; hydrol. H, 1065 cc./g. Found: C, 37.2; H, 12.0; N, 26.6; B, 20.5; hydrol. H, 897 cc./g.

The infrared absorption spectrum of this material consists of a NH absorption at 3230 cm^{-1} , CH at 2940 and 3030 cm^{-1} , BH at 3280 and 2440 cm^{-1} and a sharp 2275 cm^{-1} absorption believed to be associated with CN.

Into about 100 ml. of dimethoxyethane was condensed 0.03 mole of dimethylaminodiborane followed by an equivalent amount of hydrogen cyanide. The cold mixture was allowed to warm to room temperature and then stirred for 90 minutes. No hydrogen was generated. Removal of volatile material gave a liquid whose infrared spectrum was essentially identical to that of the product from dimethylammonium cyanide except for the relative intensity of the cyanide band (2275 cm^{-1}). The 2275 cm^{-1} absorption in the products from dimethylammonium cyanide, ammonium cyanide and even sodium cyanide was usually stronger than the BH absorption. Such was not the case for this product of dimethylaminodiborane. On the other hand, this product showed elemental composition, solubility behavior, hydrolytic stability and reactivity with carbonyl compounds similar to that described above for the product from dimethylammonium cyanide.

A sample of $\text{NH}_3\cdot\text{B}_2\text{H}_6\cdot\text{CN}\cdot 0.21\text{C}_4\text{H}_{10}\text{O}_2$ was dissolved in 49.8 g. of acetone. An exothermic reaction occurred causing the acetone to reflux and releasing 0.024 mole of hydrogen. Removal of all volatile material on the vacuum train left 17.7 g. of oil which was readily soluble in 25 ml. of acetone. The solution was poured into 100 ml. of water. An oil separated which was isolated from the aqueous phase by ether extraction. The extract was washed with water, dried and evaporated under vacuum to leave 5.5 g. of amber oil which partially crystallized on standing at room temperature. Attempts to find a suitable recrystallization solvent were unsuccessful. Analysis of the crude oil suggested elemental ratios of approximately $\text{C}_3\text{H}_6\text{N}(\text{BH}_2)_6$. Hydrolysis of a portion of the oil (2.43 g.) in dilute sulfuric acid gave 0.1 mole of hydrogen. Upon distillation of the hydrolyzate after addition of excess alkali, a low boiling foreshot ($72\text{--}73^\circ$) was obtained. This was dried over KOH and redistilled to give 1.5 ml. of liquid identified as diisopropylamine by its boiling point (84°) and infrared spectrum.

Synthesis of $\text{H}_3\text{NBH}_2\text{SCN}$.—Ammonium thiocyanate (0.52 mole) was dissolved in 200 ml. of dimethoxyethane. The solution was cooled to -80° and 0.263 mole of diborane was added. On warming, 0.588 mole of hydrogen was evolved. The solvent was then removed at reduced pressure to leave a nonvolatile residue which crystallized on standing to give 49.7 g. of solid. This residue was taken up in 400 ml. of dry ether and filtered; addition of petroleum ether to the filtrate gave a crystalline solid. The X-ray pattern is unique.

Anal. Calcd. for $\text{H}_3\text{NBH}_2\text{SCN}$: H, 5.7; N, 31.8; B, 12.3; S, 36.4; C, 13.7; hydrol. H, 510 cc./g.; mol. wt., 87.9. Found: H, 5.3; N, 31.7; B, 12.3; S, 34.3; C, 13.4; hydrol. H, 412 cc./g.; mol. wt. 112 (dioxane, f.pt.).

This compound melts with decomposition at 119° . The infrared spectrum consists of a band at 2130–2165 cm^{-1} , assigned to the SCN or NCS group, a BH absorption at 2410 cm^{-1} , NH absorption at 2700–3330 cm^{-1} and at 1575, 1600 and 1640 cm^{-1} .