complex appears to have an important influence upon the redox behavior of the molecule. In a cyclic voltammetry study the $(B_9H_9CHPCH_3)_2Co$ species (*i.e.*, the 1,2 and 1,7 derivatives) contained reversible oxidation and reduction waves as seen in Table IV. However, the $(B_9H_9CHP)_2Co^-$ species (*i.e.*, the 1,2 and 1,7 derivatives) show no oxidation or reduction waves between +1.5 and −1.0 V (*vs.* sce). The reversible redox reaction [Co(II)–Co(III)], observed by cyclic voltammetry for $(1,2\text{-}B_9H_9CHPCH_3)_2Co$ at +0.43 V (*vs.* sce), suggests that the cationic Co(III) complex might be isolable. Attempts to date have not been successful.

The effective magnetic moments of the cobalt(II) complexes are given in Table V. The average value is 1.79 BM which compares well with the magnetic moment for cobaltocene and corresponds to a spin-only formulation of one unpaired electron.

Reaction of $(1,7\text{-}B_9H_9CHP)_2Co^-$ with methyl iodide in tetrahydrofuran solution gave a 56% yield of orange, sublimable $(1,7\text{-}B_9H_9CHPCH_3)Co(1,7\text{-}B_9H_9CHP)$. The proton nmr spectrum contains two $P\text{–}CH_3$ and two carborane C–H resonances indicating that the above compound is a mixture of two isomers as expected.

The electronic spectra of the phosphacarbollylcobalt derivatives are presented in Table I without interpretation. The ^1H nmr data of the cobalt complexes are given in Table III. Both ^{11}B and ^1H nmr spectral data of the paramagnetic cobalt(II) complexes were difficult to obtain because of the insolubility of the compounds in suitable solvents and the broadness of the resonance lines. The ^1H nmr spectrum of $(1,2\text{-}B_9H_9CHPCH_3)_2Co$ and $(1,7\text{-}B_9H_9CHPCH_3)_2Co$ (isomer I) (acetone-d_6) contained an intense, broadened singlet at τ 6.76 and 7.25, respectively, which may be due to the methyl group attached to phosphorus. The carborane C–H could not be detected.

Phosphacarbollylmanganese Tricarbonyl Derivatives.—Reaction of $7,9\text{-}B_9H_9CHPCH_3^-$ or $7,9\text{-}B_9H_9CHP^{2-}$ with 1 equiv of $BrMn(CO)_5$ at reflux in tetrahydrofuran resulted in carbon monoxide evolution over a 2-hr period and produced low yields of $(1,7\text{-}B_9H_9CHPCH_3)Mn(CO)_3$ and $(1,7\text{-}B_9H_9CHP)Mn(CO)_3^-$, respectively. The infrared spectrum of $(1,7\text{-}B_9H_9CHP)Mn(CO)_3^-$ (acetonitrile solution) contains A and E carbonyl stretching modes at 2025 and 1955 cm^{-1}, respectively. The infrared spectrum of $(1,7\text{-}B_9H_9CHPCH_3)Mn(CO)_3$ (CS_2 solution) contains a carbonyl band (A mode) at 2045 cm^{-1}. However, the E mode predicted for C_{3v} local symmetry is apparently no longer degenerate but is split into two bands at 1984 and 1963 cm^{-1}. The ^1H nmr spectrum ($CDCl_3$ solution) of $(1,7\text{-}B_9H_9CHPCH_3)Mn(CO)_3$ contained a sharp doublet at τ 7.82 ($J = 13$ Hz) and a broad singlet at τ 8.2 assigned to the methyl group on phosphorus and the carborane C–H, respectively. The ^{11}B nmr spectra of these two compounds extended over approximately 30 ppm but were uninterpretable.

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CONTRIBUTION FROM THE ROHM AND HAAS COMPANY,
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1,2,4,5-Tetraaza-3,6-diborinane Monomers and Dimers

BY JOHN J. MILLER AND FREDERIC A. JOHNSON

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The thermal decomposition of hydrazine–*t*-butylborane has been examined and the product has been identified as a polyhedral "cage" compound, a dimer of 3,6-di-*t*-butyl-1,2,4,5-tetraazadiborinane (VIII). Nuclear magnetic resonance data for this compound and its derivatives with methyl isocyanate are presented and discussed in relation to their structures. Proton-exchange studies of VIII and its derivatives were monitored by nmr. Attempts to dimerize 3,6-diphenyl-1,2,4,5-tetraaza-3,6-diborinane (I, R = C_6H_5) provided the same product as thermal decomposition of hydrazine–phenylborane. This product is not a polyhedral cage compound.

Introduction

Initial attempts at the preparation of hydrazinoboranes[1,2] were unsuccessful and it was not until 1961 that the first compound of this type, diborylhydrazine, $H_2B\text{–}NH\text{–}NH\text{–}BH_2$, was reported; it was prepared by the pyrolysis of a diborane–hydrazine adduct.[3] Alkylated compounds of similar structure were obtained by treatment of tetraalkyldiboranes with hydrazine at 100–150°.[4] Formation of compounds of type I from the reaction of bis(amino)boranes with hydrazine have been reported[5,6] and this type of ring structure

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[1] H. J. Emeléus and F. G. A. Stone, *J. Chem. Soc.*, 840 (1951).

[2] J. Steindler and H. I. Schlesinger, *J. Am. Chem. Soc.*, **75**, 756 (1953).

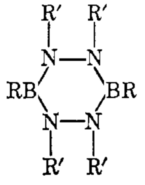
[3] J. Goubeau and E. Ricker, *Z. Anorg. Allgem. Chem.*, **310**, 123 (1961).

[4] H. Noth, *Z. Naturforsh.*, **16b**, 471 (1961).

[5] K. Niedenzu, H. Beyer, and J. W. Dawson, *Inorg. Chem.*, **1**, 738 (1962).

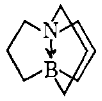
[6] H. Noth and W. Regnet, "Boron–Nitrogen Chemistry," Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 166.

can also be obtained by reduction of azobenzene with diborane (R = H, R′ = C_6H_5) or by reaction of phenylboron dichloride with dilithiodiphenylhydrazine (R = R′ = C_6H_5).[6]



I

Bicyclic[7] and tricyclic[8,9] compounds containing boron and nitrogen, such as II, have previously been reported but no materials containing a polyhedral boron–nitrogen structure are known. This paper[10] describes in detail the preparation and pyrolysis of hydrazine–*t*-butylborane and the isolation and proof of structure of a polyhedral, boron–nitrogen cage product.

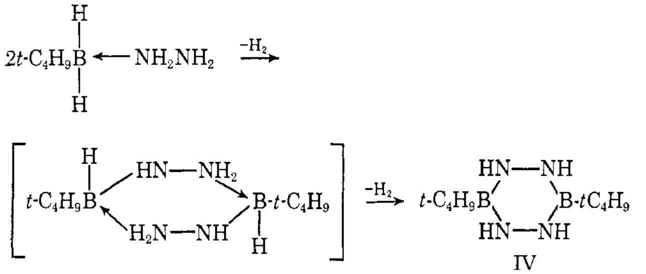


II

Results and Discussion

Hydrazinolysis of trimethylamine–*t*-butylborane gives an excellent yield of the expected hydrazine–*t*-butylborane (III) as evidenced by analytical, infrared, and ^{11}B nuclear magnetic resonance data. Thermal decomposition of III was examined. Previous studies of thermal decomposition of hydrazine–boranes suggested the possibility of cleavage of the nitrogen–nitrogen bond with the formation of a borazole,[11] while the production of a tetraazadiborinane (IV) by the following scheme also appeared plausible.

$$t\text{-}C_4H_9BH_2\leftarrow N(CH_3)_3 + NH_2NH_2 \longrightarrow \underset{\text{III}}{t\text{-}C_4H_9BH_2\leftarrow NH_2NH_2} + N(CH_3)_3$$



$$2t\text{-}C_4H_9\overset{H}{\underset{H}{B}}\leftarrow NH_2NH_2 \xrightarrow{-H_2} \left[t\text{-}C_4H_9\overset{H}{B}\begin{matrix}\leftarrow HN\text{—}NH_2\rightarrow\\ \leftarrow H_2N\text{—}NH\leftarrow\end{matrix}\underset{H}{B}\text{-}t\text{-}C_4H_9\right] \xrightarrow{-H_2} t\text{-}C_4H_9B\begin{matrix}HN\text{—}NH\\ HN\text{—}NH\end{matrix}B\text{-}tC_4H_9$$

IV

The product of the decomposition (compound A) was a white, crystalline solid, mp 161–163°. Based on the elemental analysis and on the amount of hydrogen evolved in the decomposition, the product has the empirical formula $C_4H_{11}BN_2$. Determination of the molecular weight by thermal tensimetry indicated that the material is a tetramer of the empirical composition. This, of course, mitigated against either a borazole or a simple tetraazadiborinane as the product. The molecular weight was confirmed by the mass spectrum; the parent peak at *m/e* 392 is small compared to the largest peak at *m/e* 196. The boron isotope distribution pattern at *m/e* 392 is consistent with the presence of four boron atoms and the pattern at *m/e* 196 shows two borons. A peak is also present at *m/e* 98.

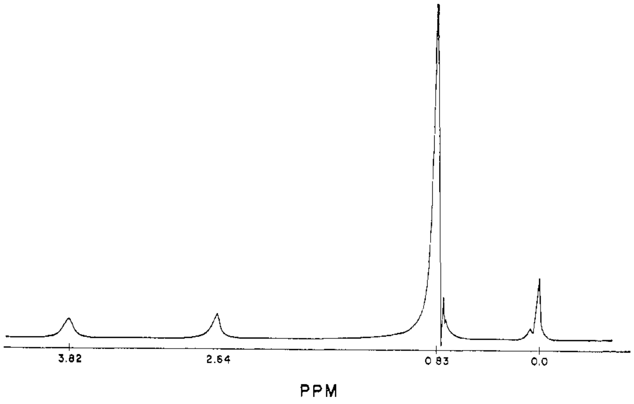


Figure 1.

The infrared spectrum of compound A has no absorption in the 2500-cm^{-1} region, thus indicating the absence of a B–H bond in the product. The sharp N–H absorption at 3320 cm^{-1} is affected by treatment of a methylene chloride solution of the compound with D_2O; the NH band is reduced in intensity as a band at 2460 cm^{-1} appears for the resulting N–D. Complete removal of the N–H peak by repeated exchange with D_2O was not possible. A very strong absorption at 1470 cm^{-1} in compound A is most probably due to a B–N stretching vibration.[12] No absorption appears in the ultraviolet spectrum of the compound. The proton nuclear magnetic resonance spectrum (Figure 1) is strikingly simple; a single absorption at δ 0.83 ppm is apparent for the hydrogens of the methyl groups on the *t*-butyls. Only two other absorptions, which are equal in area, appear at δ 2.64 and 3.82 ppm and are due to hydrogens on nitrogen. The spectrum of the D_2O-exchanged product indicates that the hydrogens of the upfield peak exchange faster than those of the downfield peak but that some exchange occurs with both types. A more thorough study of proton exchange was carried out employing *t*-butyl alcohol and trifluoroacetic acid. Addition of *t*-butyl alcohol causes a shift and broadening of the upfield resonance without affecting the downfield peak as can be seen in Table I. Addition of trifluoroacetic acid causes a strong downfield shift and broadening of the upfield peak while the downfield peak also shifts slightly but does not broaden. These data confirm that the N–H protons responsible for the upfield

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[7] J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Am. Chem. Soc.*, **89**, 3148 (1967).

[8] N. N. Greenwood, J. H. Morris, and J. C. Wright, *J. Chem. Soc.*, 4753 (1964).

[9] H. C. Brown and E. A. Fletcher, *J. Am. Chem. Soc.*, **73**, 2808 (1951).

[10] Preliminary accounts of this work have appeared: J. J. Miller and F. A. Johnson, *ibid.*, **90**, 218 (1968). Paper presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[11] H. J. Emeléus and G. J. Videla, *J. Chem. Soc.*, 1306 (1959).

[12] H. J. Becher and H. T. Baechle, ref 6, p 71.

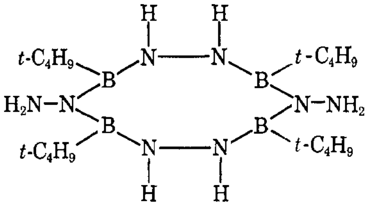
TABLE I

[t-C_4H_9OH]/ [compd A]	Upfield peak δ, ppm	Upfield peak Width, cps	Downfield peak δ, ppm	Downfield peak Width, cps
0	2.64	3.0	3.82	4.0
$^1/_4$	2.57	8.9	3.82	4.0
$^2/_1$	2.46	10.9	3.82	4.0

peak exchange much more rapidly than the downfield N–H groups.

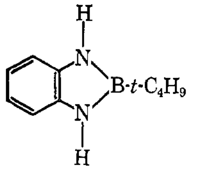
The ^{11}B nmr spectrum of compound A exhibits a singlet.

Consideration of the above data led to rejection of a number of postualted ring structures. A ten-membered ring, V, could not be discarded by the above data but formation of a large ring was questionable.



V

Hydrolysis of compound A in aqueous acid provided t-butylboronic acid and hydrazine. The boronic acid was isolated as its o-phenylenediamine derivative (VI) and the hydrazine was derivatized with benzaldehyde to give VII. Isolation of these products demonstrates that no boron–carbon or nitrogen–nitrogen cleavage occurred during the thermal decomposition.



VI

$C_6H_5CH{=}N{-}N{=}CHC_6H_5$

VII

Preparation of derivatives of compound A appeared feasible through use of the amino functionality. Reaction of compound A with isocyanates led to the formation of a series of compounds which provided enough information to propose structures with some confidence. Reaction with excess methyl isocyanate in methylene chloride solution under mild conditions provided a new material, mp 184–185°. The infrared spectrum contains an absorption at 1610 cm^{-1}, which was assigned to an amide carbonyl, and N–H absorptions other than those due to the amide. Elemental analyses and molecular weight data, both mass spectral and ebullioscopic, indicate that the product is composed of 1 equiv of compound A and 2 equiv of the isocyanate. The proton magnetic resonance spectrum of this new compound, Figure 2, was quite revealing. The most interesting portion of the spectrum is that due to the absorptions from the methyl groups of the t-butyls. As can be seen there are four different absorptions indicating that the t-butyl groups are all nonequivalent. Examination of 40- and 60-Mc spectra demonstrated that the separation of methyl absorptions is due to differences in chemical shifts and not coupling.

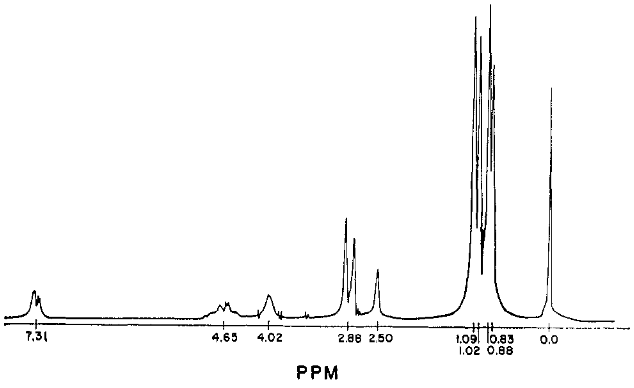
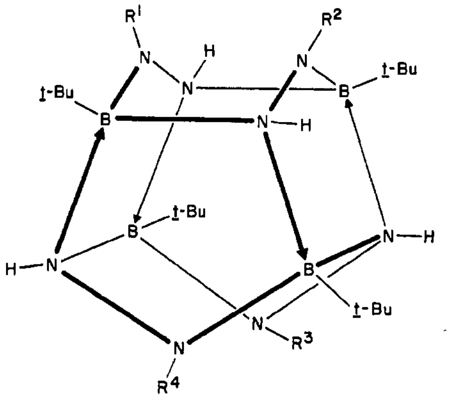


Figure 2.

Consideration of this spectrum and that of compound A (Figure 1) led to rejection of structure V and postulation of a novel structure (VIII) for compound A.



VIII

The structure is composed of two six-membered rings of the tetraazadiborinane type (I, R = t-C_4H_9, R′ = H) bonded to each other through four coordinate covalent nitrogen–boron bonds such that four five-membered rings are formed. Only conventional kinds of bonds and bond angles are required and maximum coordination of boron and nitrogen is achieved. Examination of this structure shows that there are two types of N–H present in the molecule; one is trigonal and the other tetrahedral. The trigonal nitrogens have a free electron pair and thus have a low-energy mechanism; *i.e.*, protonation of the lone pair, for proton exchange. These, then, should be the protons seen in the upfield portion of the nmr spectrum (Figure 1). The tetrahedral nitrogens share their electrons with a neighboring boron atom through a coordinate covalent bond and thus the protons on nitrogen are deshielded and appear at lower field in the spectrum.

Because of the presence of a pair of electrons on the trigonal nitrogens, attack of an isocyanate should occur at these positions. In no instance have we been able to isolate a product from reaction of only 1 equiv of an isocyanate with the boron compound. Use of an excess of the boron compound with methyl isocyanate gives the disubstituted derivative and unreacted starting material. There are two possibilities

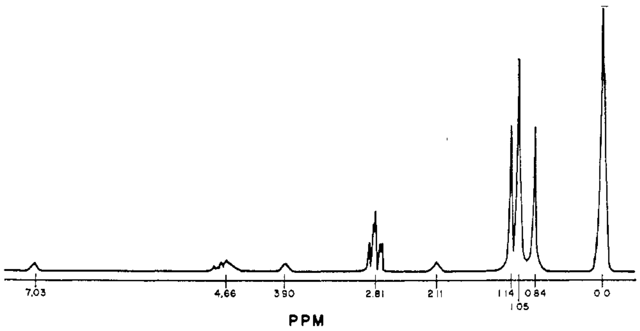


Figure 3.

for the structure of the disubstituted derivative. One is that in which both trigonal nitrogens in one six-membered ring have been attacked (VIII, $R^1 = R^2 =$ RNHC(=O)–, $R^3 = R^4 =$ H) and the other is that in which a trigonal nitrogen in each ring has been attacked (VIII, $R^1 = R^3 =$ RNHC(=O)–, $R^2 = R^4 =$ H). The most likely possibility is the latter and this is the only structure which fits the nmr data. Scrutiny of the latter structure indicates that one should indeed expect four separate absorptions for the *t*-butyl groups as they are all in different electronic environments on a nearest neighbor, next nearest neighbor basis. Further examination of structure VIII indicates that substitution at the trigonal positions in a stepwise manner should influence the chemical shift of the protons on the *t*-butyl groups bonded to boron. Table II, which examines only nearest and next nearest neighbors, is an analysis of this effect.

Table II

No. of trigonal nitrogens substituted	Boron atoms nearest neighbor[a]	Boron atoms next nearest neighbor	Expected bands for CH_3 of *t*-C_4H_9
1	2 N^4 1 NCO	. . .	
	2 N^4 1 N^3	1 NCO	3 (or 4)
	2 N^4 1 N^3	. . .	
	2 N^4 1 N^3	1 NCO	
2	2 N^4 1 NCO	. . .	
	2 N^4 1 N^3	2 NCO	4 (Figure 2)
	2 N^4 1 N^3	1 NCO	
	2 N^4 1 NCO	1 NCO	
3	2 N^4 1 NCO	1 NCO	
	2 N^4 1 NCO	2 NCO	3 (or 4) (Figure 3)
	2 N^4 1 N^3	2 NCO	
	2 N^4 1 NCO	1 NCO	
4 (4)	2 N^4 1 NCO	2 NCO	1 (Figure 4)

[a] N^3 is trigonal; N^4 is tetrahedral.

If one extends the analysis to atoms more distant than next nearest neighbors, four bands might be expected for both the mono- and trisubstituted materials. The differences in these cases are small enough, however, that separation of nmr bands might not be observed and one may see only three bands. Maximum separation of bands should be obtained with the disubstituted material and four bands are observed in both the products from methyl and phenyl isocyanate. The above analysis predicts that further reaction of the disubstituted compound with isocyanate should change the nmr in the *t*-butyl region and that complete reaction of isocyanate at all trigonal positions would cause the *t*-butyls to appear again as a single absorption just as they did in the unsubstituted material due to a return to the original S_4 symmetry.

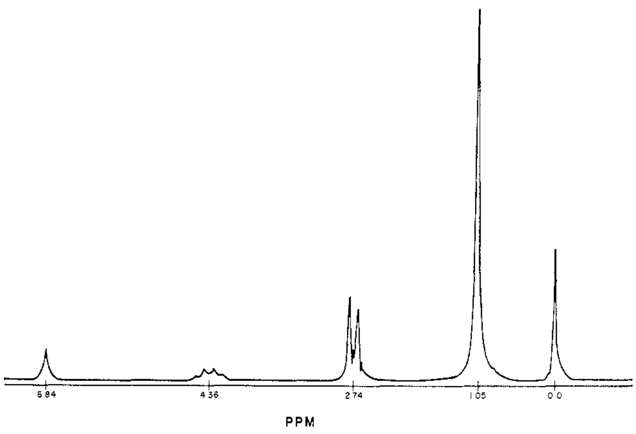


Figure 4.

Refluxing excess methyl isocyanate with the unsubstituted boron compound gave a good yield of a new compound, mp 232° dec, which exhibits an elemental analysis consistent with the trisubstituted derivative. Three absorptions are present in the *t*-butyl region of the ^1H nmr spectrum (Figure 3) and the remainder of the spectrum is as expected.

Heating excess methyl isocyanate and compound A in a sealed tube for 2 days gave a mixture of the trisubstituted derivative and a new material, mp 300–302° dec. All of the analytical data obtained are in agreement with formulation of this compound as the tetrasubstituted derivative (VIII, $R^1 = R^2 = R^3 = R^4 =$ –C(=O)$NHCH_3$), and the nmr spectrum (Figure 4) shows only a single absorption for the *t*-butyl groups indicating that they are identical and that the molecule has returned to S_4 symmetry. Structure VIII uniquely fits all of the data presented and confirmation of this structure by X-ray crystallography has recently been published.[13]

An effort was made to extend the synthetic scope of the thermal decomposition to the phenyl-substituted tetraazadiborinane (I, R = C_6H_5, R′ = H), which has been previously prepared and does not spontaneously dimerize[5,6] but does behave in an unusual manner on melting. The material partially melts at 155–160° and then resolidifies and melts again at 257–258°[4] thus suggesting that dimerization might occur. The high melting point and poor solubility characteristics of this material suggest that it is not a cage dimer, however. Hydrazine–phenylborane was prepared and subjected to thermal decomposition. Slightly more than the expected amount of gas, presumed to be hydrogen, was evolved and a product melting at 258–261°, which is identical with the high-melting material from the thermal decomposition (melting point determination) of diphenyltetraazadiborinane (I, R = C_6H_5), was obtained. This new material was too insoluble to obtain an nmr spectrum; the infrared spectrum is quite

[13] P. C. Thomas and I. C. Paul, *Chem. Commun.*, 1130 (1968).

different from the monomeric tetraazadiborinane. Titration with perchloric acid in acetic acid gave an equivalent weight of 186. The cage *t*-butyl dimer equivalent weight is 98 [$^1/_4$(MW)] and diphenyl tetraazadiborinane(I) is 120 [$^1/_2$(MW)]. Although the structure of this compound remains to be determined, it is not a cage dimer. Either the *t*-butyl dimer is not formed by dimerization of a tetraazadiborinane or steric and/or electronic factors control the dimerization.[13a]

Experimental Section

***t*-Butylboronic Anhydride.**—The Grignard reagent prepared from 28 g (2 g-atom) of magnesium in 100 ml of ether and 274 g (2 mol) of *t*-butyl bromide was added in dropwise fashion to 400 g (2.75 mol) of triethyl borate in 2 l. of ether at 0°. The mixture was stirred for 30 min after addition under a blanket of nitrogen. The mixture was cooled in ice, and 500 ml of 1:1 concentrated hydrochloric acid–water was added to dissolve the solid. The ether was removed by vacuum stripping after separation from the water layer. The residue from the stripping was dissolved in 600 ml of toluene and water was azeotroped from the mixture under a nitrogen blanket. The toluene was distilled from the mixture under nitrogen on a spinning-band column and the residue was distilled under vacuum and nitrogen to give 51 g of *t*-butylboronic anhydride, bp 62–65° (4 mm) (lit. bp[14] 66–68° (5 mm)).

Trimethylamine–*t*-Butylborane.[15]—In a three-necked, 1-l. flask equipped with a mechanical stirrer, dropping funnel, and Dry Ice condenser with drying tube was placed 7.6 g (0.2 mol) of lithium aluminum hydride in 250 ml of dry ether and the mixture was heated at reflux and stirred for 30 min. The mixture was then cooled to room temperature and 30 ml (18 g, 0.3 mol) of trimethylamine was added by distillation. A solution of 16.8 g (0.2 mol) of *t*-butylboronic anhydride in 50 ml of ether was added in dropwise fashion and then the mixture was heated at the reflux temperature for 2 hr. After cooling the system in an ice bath, 13 g of water was added very cautiously. The mixture was allowed to warm to room temperature after addition of water and was filtered through filter aid. The ether solution was dried over calcium chloride and was then stripped to provide 22 g (86% yield) of trimethylamine–*t*-butylborane. This material is unstable and must be stored in Dry Ice.

Hydrazine–*t*-Butylborane.—To a suspension of 6.48 g (0.202 mol) of hydrazine in 250 ml of ether was added 25.84 g (0.2 mol) of trimethylamine–*t*-butylborane in dropwise fashion. The dropping funnel was flushed with 50 ml of ether and the mixture was then heated at the reflux temperature for 17 hr. The mixture was allowed to cool to room temperature and was filtered. Evaporation of the filtrate gave 19.1 g (94% yield) of hydrazine–*t*-butylborane. Recrystallization from low-boiling petroleum ether (bp 30–60°) gave a white solid, mp 92.5–93°. *Anal.* Calcd for $C_4H_{15}BN_2$: C, 47.10; H, 14.82; N, 27.47; B, 10.61. Found: C, 47.29; H, 14.88; N, 27.45; B, 11.11. The infrared spectrum shows B–H bands at 2175–2300 cm^{-1} as well as NH bands and the ^{11}B nuclear magnetic resonance spectrum exhibits a triplet.

3,6-Di-*t*-butyl-1,2,4,5-tetraazadiborinane Dimer (**Compound A**), **VIII.**—A 10-g (0.1-mol) sample of hydrazine–*t*-butylborane was put into a round-bottomed flask fitted with a condenser which was connected to a wet-test meter. The flask was immersed in an oil bath and the oil was gradually heated to 140°. This temperature was maintained for 3 hr during which time 4.45 l. of gas was evolved. The flask was cooled and weighed, and 9.7 g of a white solid was obtained. Addition of ether dissolved most of the product. The ether solution was filtered and evaporated. Recrystallization of the product from low-boiling petroleum ether gave white crystals, mp 161–163°. *Anal.* Calcd for $(C_4H_{11}BN_2)_4$: C, 49.04; H, 11.32; N, 28.60; B, 11.04. Found: C, 49.08; H, 11.60; N, 28.67; B, 10.90. The infrared spectrum shows a sharp NH absorption at 3250 cm^{-1}; no B–H band is present. The proton nuclear magnetic resonance spectrum shows one sharp absorption for the methyls of the *t*-butyl groups at 0.83 ppm and two different types of hydrogen on nitrogen at 2.64 and 3.82 ppm. Molecular weight by thermal tensimetry is 385; calculated, 392. The mass spectrum shows a peak at *m/e* 392; the cracking pattern shows largest peak at *m/e* 196. The boron isotope distribution pattern is as follows: *m/e* 392—4 borons, 1:16:96:256:256 for $^{10}B_4$:$^{10}B_3{}^{11}B$:$^{10}B_2{}^{11}B_2$:$^{10}B^{11}B_3$:$^{11}B_4$; *m/e* 196—2 borons, 1:8:16 for $^{10}B_2$:$^{10}B^{11}B$:$^{11}B_2$.

Hydrolysis of Compound A.—A mixture of 50 ml of 6 *N* hydrochloric acid and 0.5 g of compound A was heated at the reflux temperature overnight. No gas was liberated. A white solid which had sublimed into the condenser was collected and weighed, 0.35 g, mp 106–108° (68% yield). (The melting point of *t*-butylboronic acid is 113°.[14,16]) Rather than recrystallize this material, 0.2 g was dissolved in benzene and treated with *o*-phenylenediamine. A small amount (0.1 g) of *t*-butyldihydrobenzoboradiazole was isolated. The ir spectrum was identical with that of an authentic specimen.[15]

The aqueous acid solution from the hydrolysis was neutralized with sodium hydroxide and a gas was evolved. To the rapidly stirred, neutralized solution was added 10 ml of 28% ammonium hydroxide and 2.65 g of benzaldehyde. The yellow solid which formed was collected on a filter. Recrystallization from 95% ethanol provided 1.81 g of benzalazine (20% yield), mp 92–92.5° (lit. mp 93°), identical with an authentic sample.

Reaction of Compound A with Methyl Isocyanate. (a) **Mild Reaction.**—To a solution of 1.95 g (0.005 mol) of 3,6-di-*t*-butyl-1,2,4,5-tetraazadiborinane dimer (VIII) in 25 ml of methylene chloride was added 2.28 g (0.04 mol) of methyl isocyanate. The solution immediately became slightly cloudy and a very mild exotherm was noted. The excess methyl isocyanate and methylene chloride were removed by distillation on a steam bath. Addition of ether to the residue caused precipitation of a white solid which was collected on a filter and recrystallized from methanol–water to give 2.5 g (94.5% yield) of white crystals, mp 184–185°. *Anal.* Calcd for $C_{20}H_{50}N_{10}B_4O_2$: C, 47.48; H, 9.96; N, 27.69; B, 8.55. Found: C, 47.34; H, 9.80; N, 27.35; B, 8.57. Infrared analysis shows a urea type of carbonyl absorption at 1610 cm^{-1}; N–H absorptions are also apparent. The proton nuclear magnetic resonance spectrum shows four absorptions for the methyls of the *t*-butyl groups at 0.83, 0.88, 1.02, and 1.09 ppm. The $CH_3NHC(=O)$– system appears as a 2.88-ppm doublet and a 4.65-ppm quartet. Peaks at 7.31 and 3.82 ppm are assigned to protons on quaternary nitrogens with those at low field adjacent to trigonal nitrogens which have attacked isocyanate. Molecular weight by thermal tensimetry was 497 and from mass spectral analysis was 506. The calculated molecular weight is 506.

(b) **Reflux Procedure.**—To a solution of 1.95 g (0.005 mol) of VIII in 25 ml of methylene chloride was added 5 g (0.088 mol) of methyl isocyanate. The mixture was heated at the reflux temperature for 7 hr and allowed to stand overnight at room temperature. The excess methyl isocyanate and methylene chloride were removed by distillation and the solid product was redissolved in methylene chloride and the cloudy solution was filtered. Removal of the solvent from the filtrate left 2.8 g (96% yield) of a white crystalline solid. Two recrystallizations from methanol–water gave a product melting at 232° dec. *Anal.* Calcd for $C_{22}H_{53}N_{11}B_4O_3$: C, 46.93; H, 9.49; N, 27.37; B, 7.69. Found: C, 46.78; H, 9.28; N, 27.58; B, 7.64. The nulcear magnetic resonance spectrum contains three bands for the methyls on the *t*-butyl groups at 0.84, 1.05, and 1.14 ppm in a 1:2:1 ratio. The product is substituted at three trigonal positions by isocyanate.

(13a) NOTE ADDED IN PROOF.—Tetra- and octamethyl-substituted derivatives of structure VIII have recently been described by Noth [H. Noth and W. Regnet, *Chem. Ber.*, **102**, 167 (1969); H. Noth and W. Regnet, *ibid.*, **102**, 2241 (1969)].

(14) J. R. Johnson, M. G. VanCampen, and O. Grummitt, *J. Am. Chem. Soc.*, **60**, 111 (1938).

(15) M. F. Hawthorne, *ibid.*, **83**, 831 (1961).

(16) D. T. Hurd, *ibid.*, **70**, 2053 (1948).

(c) **Vigorous Reaction.**—A 1-g (0.0025-mol) sample of VIII was dissolved in 25 ml of methylene chloride and the solution was placed in a 3-oz pressure tube. Addition of 6 g of methyl isocyanate caused the solution to become cloudy. The tube was sealed and the mixture was heated at 95° behind a shield for 42.5 hr. After cooling, the tube was vented and the cloudy solution was distilled to dryness on a steam bath. The residue was dissolved in methylene chloride and the cloudy solution was filtered. This solution shows two spots on thin layer chromatography. The spot due to the trisubstituted compound, mp 232° dec, is minor. The methylene chloride solution was washed with two 50-ml portions of 6 *N* hydrochloric acid and then dried and evaporated to give 1.3 g (82% yield) of product. Thin layer analysis shows only a very slight trace of trisubstituted material present. The product was recrystallized from a small volume of methylene chloride at low temperature to give a product melting at 300–302° dec. *Anal.* Calcd for $C_{24}H_{56}N_{12}B_4O_4$: C, 46.49; H, 9.10; N, 27.11; B, 6.98. Found: C, 45.97; H, 9.36; N, 27.02; B, 7.01.

Thin layer chromatography of the methyl isocyanate substituted derivatives of VIII using a silica gel substrate, methylene chloride solvent, and development with potassium permanganate gave the R_f values: 0.757, disubstituted compound; 0.686, trisubstituted compound; 0.615, tetrasubstituted compound.

Trimethylamine–Phenylborane.—A fresh sample of phenylboronic anhydride was prepared by heating phenylboronic acid under vacuum at 100° for 5 hr. To a suspension of 2.2 g (0.058 mol) of lithium aluminum hydride in 100 ml of ether was added 5.7 g of trimethylamine by distillation. A suspension of 6 g (0.0575 mol) of phenylboronic anhydride in 50 ml of ether was added in portions and the mixture was then heated at the reflux temperature for 2 hr. The reaction vessel was cooled in an ice bath and a large excess of water was added. Addition must be carried out cautiously at first. The mixture was filtered through filter aid and the layers were separated. After drying the ether layer over calcium chloride, the solvent was removed to provide 7.7 g (90% yield) of trimethylamine–phenylborane, mp 75–75.5°. Analysis was conducted without purification. *Anal.* Calcd for $C_9H_{16}BN$: C, 72.52; H, 10.82; N, 9.40; B, 7.26. Found: C, 73.15; H, 11.30; N, 9.77; B, 7.51. Infrared analysis shows BH absorptions and ^{11}B nmr shows a triplet. Attempted recrystallization caused some decomposition.

Hydrazine–Phenylborane and Its Decomposition.—Trimethylamine–phenylborane, 6.6 g. (0.045 mol), was dissolved in 50 ml of ether which was added dropwise to a suspension of 1.42 g (0.045 mol) of hydrazine in 100 ml of ether. The mixture was heated at the reflux temperature for 10 hr during which time trimethylamine was evolved. The cloudy solution was cooled, filtered, and evaporated to give 5.4 g (99% yield) of hydrazine–phenylborane. The oily product had B–H and N–H absorptions in the infrared spectrum. This product was immersed in an oil bath and the temperature was raised slowly to 140°. At about 100°, hydrogen began to come off; a total of 2.05 l. (slightly greater than expected) was evolved after the mixture had been at 120–140° for 1 hr. The mixture was cooled and 5.0 g of a white solid product was isolated, mp 258–261°. Infrared analysis shows N–H but no B–H. Because of the insolubility of the material, no nmr data were obtained.

3,6-Diphenyl-1,2,4,5-tetraaza-3,5-diborinane (I).—The method of Niedenzu, Beyer, and Dawson[5] was employed. A solution of 18.7 g (0.0106 mol) of bis(dimethylaminophenyl)borane in 30 ml of dry *n*-hexane was added slowly to a stirred mixture of 3.5 g (0.011 mol) of hydrazine in 25 ml of *n*-hexane cooled in a Dry Ice bath. No apparent reaction occurred. The mixture was allowed to warm to room temperature and after a few minutes a white solid began to precipitate. The mixture was stirred vigorously for 1.5 hr and then filtered. The white solid product was dried overnight under vacuum at room temperature to give 11.5 g (92% yield) of I. The material partially melted at about 150° and then resolidified and melted at 258–260°. Titration with perchloric acid in acetic acid gives an equivalent weight of 120.

Thermal Decomposition of I.—A 0.25-g sample of I was put into a small vial and immersed in an oil bath at 170° for 10 min. The sample was then removed and the infrared spectrum was examined; it is quite different from that of the unheated material (I) and is identical with that from the thermal decomposition of hydrazine–phenylborane. Titration with perchloric acid in acetic acid gives an equivalent weight of 186. Analytical data show a definite loss of nitrogen content on decomposition.

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