CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Boron–Nitrogen Compounds. VI.[1,2] Amino-phenylboranes

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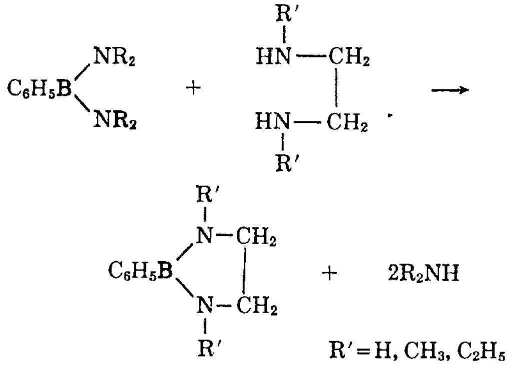
Chlorodiphenylborane is conveniently prepared by the interaction of dichlorophenylborane with triphenylborane. Dichlorophenylborane reacts with secondary amines in *n*-hexane to give high yields of bis-(dialkylamino)-phenylborane. Reactions of the latter with boron trichloride, ethylenediamines, and hydrazines are described. Some reactions of (amino)-diphenylboranes are reported. The X-ray powder pattern of (diphenylamino)-diphenylborane is compared with that of tetraphenylethylene. Infrared absorption determinations on aminoboranes are reinforced by isotope studies.

The interaction of boron trichloride with tetraphenyltin in benzene solution recently has been shown to be a convenient method for preparing dichlorophenylborane, $Cl_2BC_6H_5$.[3] The reaction of dichlorophenylborane with triphenylborane has now been found to afford chlorodiphenylborane, $ClB(C_6H_5)_2$, in a smooth reaction.

Dichlorophenylborane reacts with ammonia or primary amines to yield B-triphenylborazines[4–6]; bis-(primary amino)-phenylboranes have been isolated as intermediates.[5,6]

On treating dichlorophenylborane with an excess of diethylamine in ether a 14% yield of bis-(diethylamino)-phenylborane has been reported.[5] In the present work, in *n*-hexane, yields up to 90% of bis-(dialkylamino)-phenylboranes have been obtained.

Boron–nitrogen bonded materials are easily prepared by transamination.[7–11] This type of reaction was used to synthesize 2-phenyl-1,3,2-diazaborolidines through the interaction of bis-(dialkylamino)-phenylboranes with ethylenediamines.



(1)

1,3,2-Diazaborolidines are not well known. The B-methyl derivative has been obtained through thermal decomposition of the addition product of ethylenediamine with trimethylborane[12] and also has been prepared recently through transamination, although no experimental details are reported.[11] It adds two moles of hydrogen chloride rapidly at room temperature.[12] In a similar manner 2-phenyl-1,3,2-diazaborolidines add two moles of boron trichloride at low temperatures. The solid addition compounds decompose near room temperature with cleavage of the original B–N linkages. The acyclic bis-(dialkylamino)-phenylboranes undergo an analogous reaction; dichlorophenylborane and aminodichloroborane have been isolated and identified as reaction products.

$$C_6H_5B(NR_2)_2 + 2BCl_3 \longrightarrow C_6H_5BCl_2 + 2R_2N\text{–}BCl_2 \qquad (2)$$

Hydrazinolysis of bis-(dimethylamino)-phenylborane with an excess of unsymmetrical dimethylhydrazine afforded bis-(N,N-dimethylhydrazino)-phenylborane. On treating a 1:1 molar ratio of bis-(dimethylamino)-phenylborane and anhydrous hydrazine, a diphenyl derivative of hexahydro-1,2,4,5-tetraza-3,6-diborine (I) was obtained. Such compounds have been mentioned briefly in

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[1] Boron–Nitrogen Compounds, V, *J. Chem. Soc.*, in press.

[2] Supported by the U. S. Army Research Office (Durham).

[3] K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **82**, 4223 (1960).

[4] W. L. Ruigh and co-workers, WADC Technical Report 55-26, Part II, 1956, p. 38.

[5] B. M. Mikhailov and P. M. Aronovich, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1146 (1957).

[6] B. M. Mikhailov, A. N. Blokhina, and T. V. Kostroma, *J. Gen. Chem. USSR*, **29**, 1483 (1959).

[7] H. Nöth, *Angew. Chem.*, **72**, 40 (1960).

[8] W. D. English, A. L. McCloskey, and H. Steinberg, *J. Am. Chem. Soc.*, **83**, 2122 (1961).

[9] K. Niedenzu, D. H. Harrelson, and J. W. Dawson, *Chem. Ber.*, **94**, 671 (1961).

[10] K. Niedenzu and J. W. Dawson, *Angew. Chem.*, **73**, 433 (1961).

[11] H. Nöth, *Z. Naturforsch.*, **16b**, 470 (1961).

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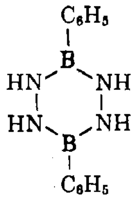

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the literature[13] but no additional data are available.

(Amino)-diphenylboranes have been accorded increased attention only recently.[14–16] Their preparation has been reported through: (a) the interaction of chlorodiphenylborane with amines[14] or lithium amides[15] and (b) a Grignard reaction of (amino)-dichloroboranes with phenylmagnesium bromide.[3]

The ultraviolet spectrum of (diphenylamino)-diphenylborane was found to be similar in general appearance to that of tetraphenylethylene, and the infrared spectra of these two isoelectronic compounds are nearly identical.[15] It therefore appears of interest to compare their X-ray powder patterns, since occasionally isoelectronic compounds have been found to be isomorphous.[17,18] Debye patterns and patterns taken on a Guinier focusing camera, however, clearly demonstrate that (diphenylamino)-diphenylborane and tetraphenylethylene are not isomorphous. (Dimethylamino)-diphenylborane was treated with boron trichloride. In analogy with bis-(dimethylamino)-phenylborane, a clean rupture of the B-N linkage occurred and (dimethylamino)-dichloroborane and chlorodiphenylborane were recovered.

When (dimethylamino)-diphenylborane was treated with an excess of unsymmetrical dimethylhydrazine, a good yield of (N,N-dimethylhydrazino)-diphenylborane was obtained; the same reaction using an excess of anhydrous hydrazine afforded (hydrazino)-diphenylborane. The latter had been prepared previously by Nöth[11] through direct interaction of chlorodiphenylborane with hydrazine.

Experimental

Dichlorophenylborane, $Cl_2BC_6H_5$, was prepared, as previously reported, through the interaction of boron trichloride with tetraphenyltin in benzene solution.[3]

Chlorodiphenylborane, $ClB(C_6H_5)_2$.—Ten grams (0.0414 mole) of triphenylborane was covered with 7.94 g. (0.05 mole) of dichlorophenylborane in a dry nitrogen atmosphere. The mixture was slowly heated to reflux over a period of 3 hr. and kept at that temperature for 15 min. Vacuum distillation of the reaction product afforded 12.8 g. (77%) of chlorodiphenylborane, b.p. 106–108° (3–4 mm.) (lit.[19] 98° (0.1 mm.)).

Bis-(dimethylamino)-phenylborane, $[(CH_3)_2N]_2BC_6H_5$.—One hundred grams (2.22 moles) of anhydrous dimethylamine was dissolved in 1200 cc. of dry hexane and the solution was cooled to Dry Ice–methanol temperature. A mixture of 79.4 g. (0.5 mole) of dichlorophenylborane and 300 cc. of dry hexane was added with stirring over a period of 30 min. The cooling bath was removed and the mixture was stirred until it reached room temperature. The solid precipitate (dimethylamine hydrochloride) was filtered off and the solvent evaporated. Distillation of the residue under vacuum yielded 77 g. (87.5%) of pure bis-(dimethylamino)-phenylborane, b.p. 59° (3 mm.). *Anal.* Calcd. for $BN_2C_{10}H_{17}$: B, 6.1; N, 15.9; C, 68.3; H, 9.7. Found: B, 6.3; N, 15.3; C, 68.7; H, 10.0.

Bis-(diethylamino)-phenylborane, $[(C_2H_5)_2N]_2BC_6H_5$, was prepared in a 72% yield using the same technique and molar ratios as described above; b.p. 70° (2 mm.) (lit.[5] 70–72° (0.2 mm.)).

Bis-(N,N-dimethylhydrazino)-phenylborane, $[(CH_3)_2N–NH–]_2BC_6H_5$.—Thirty-six grams (0.6 mole) of unsymmetrical dimethylhydrazine was diluted with 100 cc. of dry benzene and a solution of 44 g. (0.25 mole) of bis-(dimethylamino)-phenylborane in 50 cc. of benzene was slowly added at room temperature. The mixture was heated to boiling over a period of 1 hr. and the solvent and the excess dimethylhydrazine were removed. The residue was distilled under vacuum, yielding 39 g. (76%) of bis-(N,N-dimethylhydrazino)-phenylborane, b.p. 80° (2 mm.). *Anal.* Calcd. for $BN_4C_{10}H_{19}$: B, 5.2; N, 27.2; C, 58.3; H, 9.3. Found: B, 5.5; N, 27.3; C, 58.5; H, 9.3.

1,2,4,5-Tetrahydro-3,6-diphenyl-1,2,4,5-tetraaza-3,6-diborine, $(–BC_6H_5–NH–NH–)_2$.—A solution of 18.7 g. (0.106 mole) of bis-(dimethylamino)-phenylborane in 30 cc. of *n*-hexane was slowly added to a vigorously stirred mixture of 3.5 g. (0.110 mole) of anhydrous hydrazine and 25 cc. of *n*-hexane under cooling with Dry Ice–acetone. After warming to room temperature, the white precipitate was filtered off, washed with hexane, and dried under vacuum at 50°; 12.2 g. (95%) of product, m.p. 156°, was obtained and analyzed without further purification. *Anal.* Calcd. for $(BN_2C_6H_7)_2$: B, 9.15; N, 23.8; C, 61.1; H, 6.0. Found: B, 9.1; N, 23.9; C, 61.2; H, 6.2.

Although the analysis of this compound clearly substantiates the empirical formula, molecular weight determinations indicate the possible inclusion of a trace of higher polymeric material. In addition, even though the reaction was run in a large excess of hydrazine, no bis-(hydrazino)-phenylborane was found. This would appear to confirm the six-membered ring structure as the preferred reaction product.

1,3-Dimethyl-2-phenyl-1,3,2-diazaborolidine, $(–CH_2–NCH_3–)_2BC_6H_5$.—A solution of 27.6 g. (0.15 mole) of

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(13) H. Nöth, Abstr. of Papers, XVIIth Intern. Congress of Pure and Applied Chemistry, Vol. I (Inorganic Chemistry), 1959, p. 44.

(14) B. M. Mikhailov and N. S. Fedotov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1511 (1956).

(15) G. E. Coates and J. G. Livingstone, *J. Chem. Soc.*, 1000 (1961).

(16) G. E. Coates and J. G. Livingstone, *ibid.*, 4904 (1961).

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(18) M. Goehring and K. Niedenzu, *Chem. Ber.*, **89**, 1771 (1956).

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bis-(dimethylamino)-phenylborane in 400 cc. of dry benzene was added to a solution of 13.2 g. (0.15 mole) of N,N'-dimethylethylenediamine in 1000 cc. of benzene. The mixture was refluxed for 5 hr. and the solvent was removed. Distillation of the residue under vacuum afforded 18.5 g. (83%) of 1,3-dimethyl-2-phenyl-1,3,2-diazaborolidine, b.p. 73° (3 mm.). *Anal.* Calcd. for $BN_2C_{10}H_{15}$: B, 6.2; N, 16.1; C, 68.9; H, 8.7. Found: B, 6.5; N, 16.2; C, 68.8; H, 8.7.

1,3-Diethyl-2-phenyl-1,3,2-diazaborolidine, $(-CH_2-NC_2H_5-)_2BC_6H_5$, was prepared in an analogous procedure n 53% yield; b.p. 95° (8 mm.). *Anal.* Calcd. for $BN_2C_{12}H_{19}$: B, 5.4; N, 13.9; C, 71.3; H, 9.5. Found: B, 5.2; N, 13.8; C, 71.4; H, 9.8.

(Diphenylamino)-diphenylborane, $(C_6H_5)_2N-B(C_6H_5)_2$, was prepared utilizing the techniques previously described[8] through interaction of phenylmagnesium bromide with (diphenylamino)-dichloroborane. The yield was 58% and the sample was identical with one prepared according to Coates and Livingstone.[15]

(Dimethylamino)-diphenylborane, $(CH_3)_2N-B(C_6H_5)_2$, b.p. 104° (2 mm.) (lit.[15] 102–104° (0.05 mm.)) was prepared by the interaction of chlorodiphenylborane with an excess of anhydrous dimethylamine in *n*-hexane; yield, 81%.

(N,N-Dimethylhydrazino)-diphenylborane, $(CH_3)_2N-NH-B(C_6H_5)_2$, was prepared utilizing the procedure of transamination as described above through the interaction of (dimethylamino)-diphenylborane with an excess of unsymmetrical dimethylhydrazine in hexane. An 89% yield of liquid material, b.p. 123° (3 mm.) was obtained. *Anal.* Calcd. for $BN_2C_{14}H_{17}$: B, 4.8; N, 12.5; C, 74.9; H, 7.6. Found: B, 4.9; N, 12.2; C, 75.6; H, 7.7.

(Hydrazino)-diphenylborane, $H_2N-NH-B(C_6H_5)_2$.—The hydrazinolysis of (dimethylamino)-diphenylborane was effected in hexane. Details of this procedure are described above; yield, 94%; m.p. 145–147° (lit.[11] 147°).

Interaction of Aminoboranes with Boron Trichloride (Typical Experiment).—A solution of 10.5 g. (0.045 mole) of bis-(diethylamino)-phenylborane in 100 cc. of dry hexane was added slowly at Dry Ice temperature to a solution of 18 g. (0.15 mole) of boron trichloride in 50 cc. of dry hexane. The resultant white precipitate gave an analysis corresponding to the formula $C_6H_5B[N(C_2H_5)_2]_2 \cdot 2BCl_3$. On warming the product to room temperature an exothermic reaction occurred and the precipitate disappeared. Rectification of the reaction product yielded both dichlorophenylborane and (diethylamino)-dichloroborane in nearly theoretical yield.

Discussion

The preparation of dichlorophenylborane by interaction of boron trichloride with tetraphenyltin in benzene solution was reported in a previous paper.[3]

Based upon eq. 3

$$Sn(C_6H_5)_4 + 2BCl_3 \longrightarrow 2C_6H_5BCl_2 + Cl_2Sn(C_6H_5)_2 \quad (3)$$

experimental results would make it appear that yields exceeding the theoretical were possible. An analysis of the reaction by-products confirmed the existence of substantial amounts of diphenyltin dichloride along with some triphenylborane. Therefore the mechanism described by Gerrard and co-workers[20] (eq. 4 and 5) does not appear to obtain in benzene solution, although extremely small amounts of phenyltin trichloride have been detected.

$$Sn(C_6H_5)_4 + 3BCl_3 \longrightarrow 3C_6H_5BCl_2 + C_6H_5SnCl_3 \quad (4)$$

$$Sn(C_6H_5)_4 + 4BCl_3 \longrightarrow 4C_6H_5BCl_2 + SnCl_4 \quad (5)$$

Actual yields of about 85–90% of purified dichlorophenylborane are obtained if calculations are based on another reaction mechanism (eq. 6), which also would explain the formation of triphenylborane. However, no appreciable amounts of tin tetrachloride could be isolated from the reaction mixture.

$$2Sn(C_6H_5)_4 + 4BCl_3 \longrightarrow 5C_6H_5BCl_2 + B(C_6H_5)_3 + 2SnCl_4 \quad (6)$$

The interaction of boron trichloride with trialkylboranes has been investigated by McCusker and co-workers.[21] By variation of the experimental conditions, all possible members of the series R_nBCl_{3-n} for a given alkyl group (R) can be obtained in good yield.[22] In conformance with eq. 7, substantial amounts of dichlorophenylborane are formed on reaction of triphenylborane

$$B(C_6H_5)_3 + 2BCl_3 \longrightarrow 3C_6H_5BCl_2 \quad (7)$$

with boron trichloride. However, attempts to prepare chlorodiphenylborane by altering the stoichiometry of the equation gave unsatisfactory results. On the other hand chlorodiphenylborane can be obtained in good yield by the reaction illustrated in eq. 8.

$$C_6H_5BCl_2 + B(C_6H_5)_3 \longrightarrow 2(C_6H_5)_2BCl \quad (8)$$

Although triphenylborane was obtained as a by-product of the preparation of dichlorophenylborane *via* interaction of boron trichloride with tetraphenyltin in benzene, the formation of chlorodiphenylborane was never observed. It therefore appears that triphenylborane may be formed during the processing of the mentioned reaction mixture. Possible mechanisms of such formation might involve a disproportionation of dichlorophenylborane or a Friedel-Crafts reaction in the presence of aryltin halides. The latter seems

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(20) J. E. Burch, W. Gerrard, M. Howarth, and E. F. Mooney, *J. Chem. Soc.*, 4916 (1960).

(21) P. A. McCusker, G. F. Hennion, and E. C. Ashby, *J. Am. Chem. Soc.*, **79**, 5192 (1957).

(22) K. Niedenzu, D. H. Harrelson, W. George, and J. W. Dawson, *J. Org. Chem.*, **26**, 3037 (1961).

more likely since the formation of some hydrogen chloride in the reaction of boron trichloride with tetraphenyltin in benzene suggests a possible interaction of boron halide with the solvent. The possibility of a Friedel-Crafts reaction is supported by evidence that boron–carbon bonds indeed can be formed by this mechanism.[23,24] Such occurrence then might very well account for the unusually high yields of dichlorophenylborane and the formation of triphenylborane. However, no definite conclusions with regard to the reaction mechanism can be drawn at present. The interaction of boron trichloride with tetraaryltin compounds in aryl solvents is under investigation; the results will be published later.

The 1300-1600 cm.$^{-1}$ region of the infrared spectra of aminoboranes shows a number of strong absorptions, one of which should definitely belong to the asymmetric B–N stretching frequency. However, unequivocal assignments cannot easily be made. On hydrolysis of aminoboranes, the B–N linkage is ruptured. Evidence of new infrared absorptions of the hydrolysis products should be restricted to N–H and B–O linkages, or possibly those of amine–borane systems. As a rule none of the new bands should interfere with the range reported for most aminoborane B–N absorptions. By comparing the spectra of the original compounds with those of their hydrolysis products, assignment of the B–N stretching frequency can be attempted.

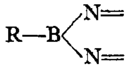
The characteristic B-phenyl absorption of bis-(dimethylamino)-phenylborane was found at 1440 cm.$^{-1}$. The two strongest infrared bands, however, were recorded at 1512 and 1384 cm.$^{-1}$ and they both disappeared on hydrolysis. This could suggest that both bands are related to the B–N linkage, since similar observations have been made on other bis-(amino)-phenylboranes.

It is well recognized that strong aromatic C–H vibrations usually occur near 1600 and 1500 cm.$^{-1}$, although the latter is not consistently observed. (For instance, dichlorophenylborane shows only a very weak aromatic absorption near 1500 cm.$^{-1}$.) An attempt to relate an absorption at 1500 cm.$^{-1}$ with the B–N grouping appears unreasonable if this value is compared with the B–N stretching frequency reported for most aminoboranes.

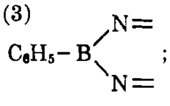
However, bis-(dialkylamino)-alkylboranes exhibit their B–N absorption in the 1500 cm.$^{-1}$ region.[25] In addition, 1,3-dimethyl-2-phenyl-1,3,2-diazaborolidine, a typical representative of the heterocyclic system formed on reaction of bis-(dialkylamino)-phenylboranes with ethylenediamines, was found to exhibit two extremely strong infrared absorptions, at 1503 and 1408 cm.$^{-1}$; they both disappeared on hydrolysis of the compound.

Comparison of the spectra of the following types of boron–nitrogen compounds demonstrates

(1) $=B-N=$ (II): absorption in the 1300–1500 cm.$^{-1}$ region

(2) 
$\mathrm{R{-}B}\left\langle\begin{matrix}\mathrm{N{=}}\\ \mathrm{N{=}}\end{matrix}\right.$ (III): absorption in the 1300–1450 cm.$^{-1}$ region and near 1500 cm.$^{-1}$, even when R = alkyl

(3)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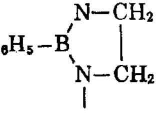
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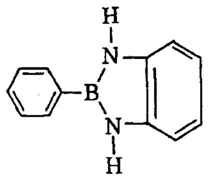
VI

absorption in the 1300–1450 cm.$^{-1}$ region, near 1440 cm.$^{-1}$, and near 1500 and at 1600 cm.$^{-1}$

On hydrolysis of these compounds the absorptions at 1300–1450 and at 1500 cm.$^{-1}$ disappear, but those at 1600 cm.$^{-1}$ are retained where aromatic C–H bonds are present and the 1440 cm.$^{-1}$ band is retained where B-phenyl linkages are present.

This leads to the tentative assumption that not only is the absorption at 1300–1450 cm.$^{-1}$ associated with the asymmetric B–N stretch, but the band at 1500 cm.$^{-1}$ normally associated with aromatic C–H vibrations is in truth rather a manifestation of a B–N absorption.

In order to confirm this conclusion several B^{10}-enriched borimidazolidines (VI) were investigated. The infrared spectra of those compounds when compared with the B^{11} analog showed a shift of about 15–20 cm.$^{-1}$ in the following absorptions

(a) 1340–1370 cm.$^{-1}$ (asymmetric B–N stretch)
(b) 1410–1440 cm.$^{-1}$ (B-phenyl absorption)
(c) 1480–1520 cm.$^{-1}$

There was no shift whatever of the aromatic absorption at 1600 cm.$^{-1}$.

On the basis of these findings it is concluded that, in compounds of type III–VI, B–N absorption occurs not only in the 1300–1450 cm.$^{-1}$ region but also near 1500 cm.$^{-1}$ and implies a difference in the bonding between the two B–N linkages.

Molecular weight determinations of bis-(dialkylamino)-phenylboranes and 1,3,2-diazaborol-

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[23] E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 2597 (1959).

[24] K. Niedenzu and J. W. Dawson, *Angew. Chem.*, **71**, 651 (1959).

[25] J. K. Ruff, private communication.

idines by the cryoscopic method in benzene indicated the existence of the monomeric species only.

A more detailed study of (amino)-diphenylboranes has been reported recently.[15]

The infrared spectra were recorded on a Perkin-Elmer Model 21 double beam spectrophotometer using sodium chloride optics. Only mulls were used for the present investigation, since it was observed that the preparation of KBr pellets caused a slight shift and change of intensity of absorptions in several cases.

Melting points were taken in sealed tubes on a Mel-Temp block.

Analyses reported herein were furnished by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

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Thermal Rearrangement of 1-Alkylpentaboranes: A One-Step Synthesis of 2-Alkylpentaboranes from Pentaborane

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1-Alkylpentaboranes were found to rearrange to 2-alkylpentaboranes at *ca.* 200°. Possible mechanisms for the rearrangement are considered. A procedure has been developed for a one-step synthesis of 2-alkylpentaboranes from pentaborane.

Various pentaborane-9 derivatives previously have been reported to give rearranged products in the presence of a catalyst.[1,2] In the presence of 2,6-dimethylpyridine 1-alkylpentaboranes were shown to rearrange to 2-alkylpentaboranes at ambient temperature.[1] We wish to report a conversion of 1-alkylpentaboranes to 2-alkylpentaboranes at an elevated temperature (*ca.* 200°) in the absence of a Lewis-base catalyst. Furthermore, this thermal conversion is the basis upon which a one-step synthesis of 2-alkylpentaboranes from pentaborane can be effected through a "Friedel-Crafts" alkylation.

When 1-methylpentaborane was heated at 190–200° for 18 hr., a methylpentaborane fraction was isolated which analyzed for *ca.* 90% 2-methylpentaborane; the remainder underwent extensive decomposition to give hydrogen and unidentified non-volatile boron hydrides.

The results of this thermal rearrangement suggested that the methylpentaborane obtained from the alkylation of pentaborane would greatly depend upon the reaction temperature. When the alkylation of pentaborane with excess methyl chloride in the presence of aluminum chloride was carried out at 100° for 3 hr., an excellent yield of 1-methylpentaborane was obtained; however, when the temperature of the reaction mixture was raised to 200° for an overnight period the principal methylpentaborane isolated was 2-methylpentaborane. Again, extensive decomposition occurs at the higher temperature with *ca.* 35% yield of the 2-methylpentaborane realized. No detectable amount of methyl chloride remained after the reaction at 200° and yet only traces of higher alkylated pentaboranes were formed. It is probable that most of the excess methyl chloride had been consumed in some side reactions(s) before an appreciable amount of 2-methylpentaborane was formed. It is unlikely that the excess methyl chloride reacted with the rearranged monoalkylated pentaborane since this would have led to higher alkylated pentaboranes; for example, the reaction of 2-methylpentaborane with methyl

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(2) R. N. Grimes and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 496 (1962).