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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(1) T. P. Onak, *J. Am. Chem. Soc.*, **83**, 2584 (1961).

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

chloride was shown to produce 1,2-dimethylpentaborane.

As in the above methyl- series, 1-ethylpentaborane was prepared from pentaborane and ethylene in the presence of aluminum chloride at 100°.[3] However, after subjecting the same reaction mixture to an overnight period at 200°, we found 2-ethylpentaborane to be the principal alkylated pentaborane formed.

Whereas the rearrangement catalyzed by 2,6-dimethylpyridine[1] may involve an intramolecular hydrogen migration[2,4] or "symmetrical" cleavage[5] mechanism, intermolecular hydrogen exchange may well play an important role in the thermal rearrangement. Shapiro and Keilin found that no boron exchange occurred between isotopically-normal pentaborane and B^{10}-enriched pentaborane at temperatures up to 250° in the gas phase; however, hydrogen exchange between deuteriopentaborane and pentaborane was observed at 200°, but not at room temperature.[6] It is not unreasonable to expect the alkylpentaboranes to undergo a similar intermolecular hydrogen exchange at these elevated temperatures.

The results of the thermal rearrangement lead to the conclusion that the 2-alkylpentaboranes are thermodynamically more stable than the corresponding 1-alkylpentaboranes. If solvation effects can be ignored, this same conclusion can be reached from the results of the 2,6-dimethylpyridine-catalyzed rearrangement.[1]

Experimental

Chemicals.—Methyl chloride and ethylene were obtained from the Matheson Company, Inc.; pentaborane, from Olin Mathieson Chemical Co.; and aluminum chloride, from J. T. Baker Chemical Co. All of the chemicals were handled in the high vacuum line. Methyl chloride and ethylene were fractionated through a −80° trap to remove traces of moisture.

Gas chromatography was used for final purification of the boron hydrides. A 6 m. × 8 mm. 30% Kel-F column on firebrick (30 mesh) operated at 60° was attached to a high vacuum system in order to provide facile transfer of the sample to the column and of the effluent to an infrared or n.m.r. cell for further examination. Up to 0.25 ml. of sample could be chromatographed with appreciable separation of components if $\Delta R_V \geq 0.2$. The retention volumes (relative to *n*-hexane = 1.0) at 60° for the various materials encountered are given in Table I.

TABLE I

Substance	R_V
Methyl chloride	0.31
Ethylene	.31
Pentaborane	.84
1-Methylpentaborane	1.2
2-Methylpentaborane	1.6
1,2-Dimethylpentaborane	2.6
1-Ethylpentaborane	2.8
2-Ethylpentaborane	3.2

B^{11} Nuclear Magnetic Resonance.—B^{11} n.m.r. spectra were measured with a Varian V-4300 high resolution n.m.r. spectrometer operating at 12.83 Mc. The following δ regions and J values[7] were found for pentaborane and pentaborane derivatives: apical B–H, $\delta = +49$ to $+52$, $J \cong 170$ c.p.s.; apical B–R, $\delta = +39$ to $+43$; basal B–H, $\delta = +12$ to $+19$, $J \cong 160$ c.p.s.; basal B–R, $\delta = -2$ to $+1$. Precise δ and J values for a number of substituted pentaboranes are presently being gathered and will be reported shortly.

1-Ethylpentaborane.—The adopted procedure for the preparation of 1-ethylpentaborane is similar to that reported by Blay, *et al.*[3b] Aluminum chloride (*ca.* 0.1 mmole) was freshly sublimed into the main body of a 1-l. reaction flask from a side arm which subsequently was sealed off. Pentaborane (7 mmoles) and ethylene (8 mmoles) were distilled into the flask which then was sealed off from the vacuum line. After heating the mixture at 100° for 3 hr. the flask was opened to the line and fractionated through traps at −80 and −190°. A gas chromatogram of the material trapped at −80° gave 3.5 mmoles of 1-ethylpentaborane (50% yield). The 1-ethylpentaborane was identified by infrared[3a] and B^{11} n.m.r.[3a] spectra (*vide supra*).

1-Methylpentaborane.—Using methyl chloride for the alkylating agent instead of ethylene, essentially the same procedure as described above for the preparation of 1-ethylpentaborane was used for the preparation of 1-methylpentaborane. After a gas chromatogram of the products an 80% yield of the purified 1-methylpentaborane was isolated and identified by infrared[3a] and B^{11} n.m.r.[3a] spectra (*vide supra*).

2-Methylpentaborane from 1-Methylpentaborane.—1-Methylpentaborane (4.8 mmoles) was sealed in a flask and heated at 190–200° for 18 hr. The flask was opened into the high vacuum line and fractionated through traps at −80 and −190°. A considerable amount of non-condensable gas was present (H_2 and/or CH_4) as well as light yellow non-volatile solids. Only a trace of 1-methylpentaborane was present in the −190° trap as indicated by its infrared spectrum.[3a] The material trapped at −80° (2.1 mmoles) was shown by an infrared spectrum to consist of 2-methylpentaborane[8] (*ca.* 90%) and 1-methylpentaborane[3a] (*ca.* 10%). The two compounds were conveniently separated by gas chromatography (*vide supra*).

2-Methylpentaborane from Pentaborane.—Pentaborane (15 mmoles), methyl chloride (45 mmoles), and freshly sublimed aluminum chloride (*ca.* 0.1 mmole) were sealed

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(3) (a) B. N. Figgis and R. L. Williams, *Spectrochim. Acta*, 331 (1959); (b) N. J. Blay, I. Dunstan, and R. L. Williams, *J. Chem. Soc.*, 430 (1960).

(4) R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961); also see ref. 1.

(5) R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

(6) I. Shapiro and B. Keilin, *ibid.*, **77**, 2663 (1955).

(7) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

(8) J. H. Lamneck and S. Kaye, National Advisory Committee for Aeronautics, Research Memorandum E58E12, September, 1958.

in a 2-l. flask and heated at 110° for 12 hr. and then at 190–200° for 12 hr. The contents of the flask were fractionated through traps at −80 and −190°. A considerable amount of non-condensable gas (H_2 and/or CH_4) was present as well as yellow non-volatile solids. The material trapped at −190° (*ca.* 20 mmoles) consisted largely of unidentifiable compounds as well as traces of 1-methylpentaborane. No detectable amount of methyl chloride was present as determined by infrared. The material trapped at −80° (6 mmoles) was identified as a mixture of 2-methylpentaborane (*ca.* 85%) and 1-methylpentaborane (*ca.* 15%) by infrared[3a,8] and B^{11} n.m.r. spectra (*vide supra*).

2-Ethylpentaborane from Pentaborane.—Using ethylene (15 mmoles) for the alkylating agent instead of methyl chloride, the same reaction conditions, amounts of materials, and work-up procedure were used as described above for the preparation of 2-methylpentaborane from pentaborane. A gas chromatogram of the products trapped at −80° gave 2-ethylpentaborane, $R_V = 3.2$, (1 mmole) with no evidence of 1-ethylpentaborane. The infrared spectrum of 2-ethylpentaborane is very similar to that of 2-methylpentaborane.[8] The B^{11} n.m.r. spectrum consisted of a low field singlet, a low field doublet, and a high field doublet in an estimated area ratio of 1:3:1 (*vide supra*).

1,2-Dimethylpentaborane.—A sealed flask containing 2-methylpentaborane (2 mmoles), methyl chloride (2 mmoles), and freshly sublimed aluminum chloride (*ca.* 0.1 mmole) was heated for 4 hr. at 100°. After fractionating the contents of the flask through −90 and −190° baths the material trapped at −90° was gas chromatographed on the Kel-F column. About 0.4 mmole (20% yield) of 1,2-dimethylpentaborane, m.p. −80° to −78°, and 0.25 mmole of unreacted 2-methylpentaborane were isolated. The infrared spectrum of 1,2-dimethylpentaborane appeared to be nearly a composite of 1-methylpentaborane[3a] and 2-methylpentaborane.[8] The B^{11} n.m.r. spectrum consisted of a low field singlet, low field doublet, and high field singlet in an estimated area ratio of 1:3:1 (*vide supra*).

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Boron Heterocycles. I. Preparation and Properties of 1,3,2-Dioxaborolane

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1,3,2-Dioxaborolane, $(CH_2O)_2BH$, has been prepared through the reaction of $HOCH_2CH_2OH$ with B_2H_6 in $(C_2H_5)_2O$. It is essentially monomeric in the vapor phase. In the liquid state it is a viscous material which is rapidly converted to a non-volatile, glassy solid at room temperature. In the vapor phase disproportionation occurs reversibly.

$$(CH_2O)_2BH(g) \rightleftharpoons \frac{1}{6}\, B_2H_6(g) + \frac{1}{3}\, (CH_2O)_2BOCH_2CH_2OB(OCH_2)_2(s)$$

The equilibrium constant at 25° is 25 ± 3. This boron heterocycle is a weak Lewis acid.

Introduction

The general tendency for mixed alkoxyboranes to disproportionate to form more symmetrical species is well known. Mixed trialkoxyboranes, $(RO)_2BOR'$, equilibrate so rapidly with disproportionation products that they cannot be isolated in the pure state in general.[1] Dialkoxyboranes also disproportionate, though less readily. The disproportionation of dimethoxyborane is an example.[2]

$$(CH_3O)_2BH(g) \rightleftharpoons \frac{1}{6}\, B_2H_6(g) + \frac{2}{3}\, B(OCH_3)_3(g) \quad (1)$$

Since the heterocyclic analogs of the acyclic alkoxyboranes have been reported to show less tendency to disproportionate,[1] it is of interest to know the properties of the cyclic counterpart of dimethoxyborane, 1,3,2-dioxaborolane, $(CH_2O)_2BH$. The only reference to this compound in the available literature appears as a very brief description given by Schlesinger and Burg,[3] who synthesized it through the reaction of ethylene glycol with diborane.

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(1) J. A. Blau, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 4116 (1957).

(2) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **55**, 4020 (1933).

(3) H. I. Schlesinger and A. B. Burg, *Chem. Rev.*, **31**, 1 (1942).