TABLE III

DECOMPOSITION OF DIMETHYL ETHER TRIBORANE-7

$$0.24(CH_3)_2O{-}B_3H_7 \longrightarrow \mathit{0.16}B_2H_4 + \mathit{0.16}(CH_3)_2O{-}BH_3 \qquad (1a)$$

$$\longrightarrow \mathit{0.10}B_3H_7 + \mathit{0.10}(CH_3)_2O \qquad (1b)$$

$$\mathit{0.120}B_2H_4 \longrightarrow \mathit{0.040}B_6H_{12}{}^{\ddagger} \longrightarrow 0.024B_6H_{12} \qquad (2a)$$

$$\longrightarrow 0.016B_5H_9 + \mathit{0.016}BH_3 \qquad (2b)$$

$$\mathit{0.055}B_3H_7 + \mathit{0.027}B_2H_6 \longrightarrow 0.055B_4H_{10} \qquad (3)$$

$$\mathit{0.043}B_3H_7 + \mathit{0.043}B_2H_4 \longrightarrow 0.043B_5H_{11} \qquad (4)$$

Reactions from Dimethyl Ether Triborane-7
and Boron Trifluoride

$$1.246(CH_3)_2O{-}B_3H_7 + BF_3 \longrightarrow \mathit{1.246}B_3H_7 + \mathit{1.246}(CH_3)_2O{-}BF_3 \qquad (5)$$

$$\mathit{0.474}B_3H_7 \longrightarrow B_6H_{14}{}^{\ddagger} \longrightarrow 0.134B_5H_{11} + \mathit{0.134}BH_3 \qquad (6a)$$

$$\longrightarrow \mathit{0.103}B_4H_8 + \mathit{0.103}B_2H_6 \qquad (6b)$$

$$\mathit{0.103}B_3H_7 + \mathit{0.103}B_4H_8 \rightarrow B_7H_{15}{}^{\ddagger} \longrightarrow 0.087B_6H_{12} + \mathit{0.087}BH_3 \qquad (7a)$$

$$\longrightarrow 0.016B_5H_9 + \mathit{0.016}B_2H_6 \qquad (7b)$$

$$\mathit{0.557}B_3H_7 + \mathit{0.278}B_2H_6 \longrightarrow 0.557B_4H_{10} \qquad (8)$$

$$\mathit{0.093}B_3H_7 \longrightarrow \mathit{0.093}(BH)_n + \mathit{0.093}B_2H_6 \qquad (9)$$

between eq 2–4 and others involving the dimethyl ether adducts of the same reacting species. Neither is it presently possible to choose unambiguously more than one or two reactions for obtaining the same product. In the equations the coefficients in Roman type are the observed quantities found in Table II; those in italic type are values calculated from the required material balances. The equations were selected from an intuitively[11] contrived set of all possible reactions. The ones chosen were those which collectively gave the most consistent stoichiometry. A more detailed examination of these reactions is in progress from which it is expected that more criteria for mechanism will emerge.

CONTRIBUTION FROM THE OLIN MATHIESON RESEARCH CENTER,
NEW HAVEN, CONNECTICUT 06504

Synthesis of B-Vinylpentamethylborazine

BY A. J. KLANICA AND J. P. FAUST

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Alkylborazine derivatives are among the more stable boron compounds and borazine-based linear polymers may have application where high thermal stability is a necessity. Hexamethylborazine, for example, can be exposed to a temperature of 475° for 3 hr with no decomposition.[1]

Numerous trifunctional borazine derivatives have been described in the literature but difunctional borazine derivatives needed to prepare linear polymers are more difficult to synthesize and only a limited number have been described. The difunctional derivative B-perfluorovinylpentamethylborazine had been prepared[2] but the corresponding B-vinylpentamethylborazine was not known. Pellon, Diechert, and Thomas[3] had prepared B-trivinyl-N-triphenylborazine but attempts to polymerize this polyfunctional derivative were not successful. They attributed this decrease in olefinic reactivity to the steric effect of the bulky phenyl groups. One would expect that methyl groups, being less bulky, would alleviate this situation.

We, therefore, chose to prepare B-vinylpentamethylborazine since this compound was expected to exhibit good thermal and hydrolytic stability due to the stabilizing influence of the methyl groups. N-Methyl groups function as election donors and decrease the tendency of the nitrogen atoms to retain localization of their unshared electrons, and consequently aromatic character is imparted to the borazine nucleus. In addition, the boron–carbon bond is electron rich so that hydrolytic and thermal stability should be high.

We were successful in the preparation and isolation of B-vinylpentamethylborazine. This new difunctional borazine derivative was stable to 460° and the compound could be handled openly in moist air with no evidence of hydrolytic decomposition.

Experimental Section

Preparation of B-Vinylpentamethylborazine.—The following reaction was used to prepare the difunctional borazine derivative described above

$$CH_2{=}CHMgBr + (CH_3N)_3(BCH_3)_2BCl \longrightarrow (CH_3N)_3(BCH_3)_2BCH{=}CH_2 + MgBrCl$$

In a typical preparation, a Pyrex, 500-ml, round-bottom, three-neck flask was fitted with a closed 125-ml Pyrex addition funnel and a 300-ml cold finger condenser.

The thoroughly dried reactor assembly was evacuated and filled to atmospheric pressure with dry N_2 gas and the cold finger condenser was filled with a Dry Ice–acetone slurry (−78°). $(CH_3B)_2(NCH_3)_3BCl$ (2 g) prepared by the reaction of $(CH_3N)_3(BCH_3)_2BH$ and HCl by the method of Wagner and Bradford[4] was dissolved in 15 ml of tetrahydrofuran (THF) previously distilled over $LiAlH_4$, and the solution was added to the reactor. Vinyl Grignard solution (2.2 g of $CH_2{=}CHMgBr$ in 10 ml of THF) was placed in the addition funnel. The reactor contents were stirred vigorously and heated to 40°. The Grignard solution was then added dropwise to the borazine solution. Addition was completed in about 30 min. The resulting mixture was stirred for 16 hr at 25°.

The reactor contents were then placed in a clean, dry 500-ml Pyrex round-bottom flask which was attached to a high-vacuum line, and the more volatile THF was vaprorized off at reduced pressure (3 mm) and 25° leaving a light brown solid wetted with a high-boiling liquid in the reactor. This high-boiling liquid was vaporized at 0.3 mm and 200° and the vapors were condensed in a trap cooled to −78°. About 2 ml of a colorless liquid (theoretical yield, 1.98 g) was collected, which melted in the range 5.2–8.0°.

The clear liquid was fractionated on an F & M Model 500 vapor fractometer with a 2-m long, $^3/_{16}$-in. diameter aluminum column packed with Carbowax 20M on Chromosorb W, 80–100 mesh. The temperature was programmed from 60 to 125° at 8°/min. The purified product was identified as B-vinylpentamethylborazine by mass spectrometry, nuclear magnetic resonance, infrared spectrophotometry, and element analysis.

Mass spectrometric analysis revealed the presence of fragments postulated for the structure B-vinylpentamethylborazine. A parent ion was observed at m/e 177 (mol wt 176.7).

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[2] A. J. Klanica, J. P. Faust, and C. S. King, *Inorg. Chem.*, **6**, 840 (1967).

[3] J. Pellon, W. D. Diechert, and W. M. Thomas, *J. Polymer Sci.*, **55**, 153 (1961).

[4] R. I. Wagner and J. R. Bradford, *Inorg. Chem.*, **1**, 93 (1962).

The 60-MHz nmr spectrum showed the presence of two CH_3–B, 0.57 ppm, and three CH_3–N, 2.97 ppm, groups relative to tetramethylsilane. Other proton resonances were observed in the 5.3–6.8-ppm region which were attributed to the vinyl grouping (85 mol %). The ^{11}B nmr spectrum contained one broad low-field peak, −15 ppm, relative to external trimethyl borate, which is characteristic of the borazine ring. All nmr data were in agreement with the postulated structure, B-vinylpentamethylborazine.

The infrared spectrum was obtained as a thin liquid film between sodium chloride plates on a Perkin-Elmer Model 137 spectrophotometer. The observed vibrational frequencies (cm^{-1}) are: 2941 (m), C—H str; 1610 (w), C=C str; 1462 (vs), asym CH_3 def; 1449 (vs), B—N def; 1389 (vs), sym CH_3 def; 1290 (m), 1266 (m), 1099 (m), N—CH_3 def; 1015 (m), 940 (m), C—H out-of-plane def of vinyl group; 880 (m), B—CH_3 def; 685 (w), B—N def.

The element analysis was consistent with the theoretical values. *Anal.* Calcd for $C_7H_{18}B_3N_3$: B, 18.36; N, 23.78; C, 47.59; H, 10.27. Found: B, 18.27; N, 23.91; C, 47.36; H, 10.00.

A sample of B-vinylpentamethylborazine purified by vapor phase chromatography was heated to 600° in a closed system and the pressure was monitored during the heating cycle. There was no evidence of decomposition up to 460°. Above this temperature, decomposition occurred as evidenced by gas evolution. This gas was identified by mass spectrometric analysis as primarily methane and small amounts of hydrogen and ethane.

It was observed that B-vinylpentamethylborazine was more stable thermally and hydrolytically than B-perfluorovinylpentamethylborazine. B-Perfluorovinylpentamethylborazine undergoes thermal decomposition at 370° and hydrolyzes readily in moist air.[2]

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA 92502

An Improved Synthesis of 1,7-$C_2B_6H_8$

BY GARY B. DUNKS AND M. FREDERICK HAWTHORNE

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The preparation of the 1,7-$C_2B_6H_8$ carborane system has been previously described.[1-4] The structure of the C,C′-dimethyl derivative has been determined by Hart and Lipscomb[5] and has been shown to be essentially that which had been initially proposed.[1,2]

Previously, 1,7-$C_2B_6H_8$ and its C-methyl derivatives were obtained in moderate yield by the pyrolysis of dicarbanonaborane(13),[6] $C_2B_7H_{13}$, or its C-methyl derivatives in diphenyl ether. The yields approached 30% for the B_6 system.[2-4]

In this work, the slow, low-pressure pyrolysis of $C_2B_7H_{13}$ or the appropriate C-methyl derivatives formed, as major products, 2,4-$C_2B_5H_7$,[7-9] 1,7-$C_2B_6H_8$, 1,7-$C_2B_7H_9$, and 1,6-$C_2B_8H_{10}$ or their corresponding C-methyl derivatives together with diborane and hydrogen.

In another study, 1,7-$C_2B_6H_8$ was allowed to stand at room temperature for 4 weeks in the presence of excess diborane. The products of this reaction are 1,7-$C_2B_7H_9$ and 1,6-$C_2B_8H_{10}$ which are formed in approximately 30 and 10% yields, respectively. These data, plus the fact that the addition of diborane during the pyrolysis of $C_2B_7H_{13}$ in diphenyl ether gives enhanced yields of 1,6-$C_2B_8H_{10}$[2] and very little 1,7-$C_2B_6H_8$, suggest that the thermal decomposition of $C_2B_7H_{13}$ yields diborane, hydrogen, and 1,7-$C_2B_6H_8$. This step may be followed by progressive recombination of 1,7-$C_2B_6H_8$ and diborane to yield 1,7-$C_2B_7H_9$, 1,6-$C_2B_8H_{10}$, and hydrogen. The direct reaction of $C_2B_7H_{13}$ and diborane to yield 1,6-$C_2B_8H_{10}$ may also occur

$$C_2B_7H_{13} \longrightarrow 0.5B_2H_6 + C_2B_6H_8 + H_2$$

$$C_2B_6H_8 + 0.5B_2H_6 \longrightarrow C_2B_7H_9 + H_2$$

$$C_2B_7H_9 + 0.5B_2H_6 \longrightarrow C_2B_8H_{10} + H_2$$

$$C_2B_7H_{13} + 0.5B_2H_6 \longrightarrow C_2B_8H_{10} + 3H_2$$

The yields of 1,7-$C_2B_6H_8$ obtained in the present study are about double (see Table I) those obtained previously,[2,3] and conversion is substantially complete.

TABLE I

Starting compound	Products	Yield,[a] %
$C_2B_7H_{13}$	2,4-$C_2B_5H_7$	1.4
	1,7-$C_2B_6H_8$	62.7
	1,7-$C_2B_7H_9$	6.6
	1,6-$C_2B_8H_{10}$	5.9
$CH_3C_2B_7H_{12}$	2,4-$CH_3C_2B_5H_6$	2.4
	1,7-$CH_3C_2B_6H_7$	57.2
	1,7-$CH_3C_2B_7H_8$	9.5
	1,6-$CH_3C_2B_8H_9$	6.1
$(CH_3)_2C_2B_7H_{11}$	2,4-$(CH_3)_2C_2B_5H_5$	4.6
	1,7-$(CH_3)_2C_2B_6H_6$	54.0
	1,7-$(CH_3)_2C_2B_7H_7$	11.0
	1,6-$(CH_3)_2C_2B_8H_8$	4.0

[a] Yield based on starting material consumed.

Experimental Section

The apparatus for the pyrolysis consisted of a 50-ml flask fitted with a ground-glass joint to a 25-mm o.d., 350-mm medium-walled Pyrex tube, packed with 6-mm Pyrex beads and attached to a standard high-vacuum line. The tube was maintained at 360° by the use of a 1 in. × 4 ft heating tape[10] wrapped about the tube and a thermometer. The temperature was controlled by a Thermo-O-Watch.[11]

In a typical experiment, 2.4245 g (21.5 mmol) of $C_2B_7H_{13}$ was placed in a flask which was maintained at 48° with an oil bath and attached to the bottom of the vertical hot tube. The entire

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(1) R. E. Williams and F. J. Gerhart, *J. Am. Chem. Soc.*, **87**, 3513 (1965).

(2) F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *ibid.*, **88**, 609 (1966).

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(4) The 1,7-$C_2B_6H_8$, 1,7-$C_2B_7H_9$, and 1,6-$C_2B_8H_{10}$ carboranes and their C-methyl derivatives have been prepared and completely characterized and will appear in a subsequent publication.

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(8) T. Onak, F. J. Gerhart, and R. E. Williams, *ibid.*, **85**, 3378 (1963).

(9) The $CH_3C_2B_5H_6$ carborane obtained in this work was identical with an authentic sample prepared by T. Onak and G. Dunks from the pyrolysis of $CH_3C_2B_4H_7$ and identified as the 2-methyl derivative.

(10) Briscoe Mfg. Co., Columbus, Ohio.

(11) Instruments for Research and Industry, Cheltenham, Pa.