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]

Acknowledgment.—The authors are indebted to Mr. W. W. Harple for the infrared data, to Mrs. Linda Allen for the vpc work, and to Mr. G. D. Vickers for the nmr analysis.

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

Received December 18, 1967

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

---

(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).

(3) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *ibid.*, **90**, 869 (1968).

(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.

(5 H. V. Hart and W. N. Lipscomb, *J. Am. Chem. Soc.*, **89**, 4220 (1967).

(6) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *ibid.*, **88**, 607 (1966).

(7) T. Onak, G. B. Dunks, R. A. Beaudet, and R. L. Poynter, *ibid.*, **88**, 4622 (1966).

(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.

system was maintained under high vacuum. The off-gases were trapped at liquid-nitrogen temperature which allowed the hydrogen to be continuously removed. The contents of the trap were separated by fractional condensation,[12] through traps at 0, −80, and −196°. The 0° trap contained 0.0675 g (0.6 mmol) of unreacted $C_2B_7H_{13}$, and the −196° trap contained 0.5 mmol of B_2H_6, both identified by infrared spectra. The −80° (Dry Ice, 2-propanol) trap contained 1.7689 g of a semisolid, white material. A 0.5-ml portion of *n*-pentane was added to liquefy the −80° fraction and the resulting solution was then passed through a vpc[13] in 0.5-ml increments. Four major fractions were collected in traps maintained at −80°. The products were identified by infrared and nmr spectra.[2,3,6–9]

Derivative and reaction chemistry is currently under study on the 1,7-$C_2B_6H_8$ and the 1,7-$C_2B_7H_9$ systems.

Acknowledgment.—This research was supported in part by the Office of Naval Research.

---

[12] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[13] Aerograph Model A350-B, equipped with a 0.25 × 10 ft Apiezon L on Chromosorb P column operating at 135° with flow rate 60 cc of helium/min.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
SAINT LOUIS UNIVERSITY, ST. LOUIS, MISSOURI 63103

The Alcoholysis of Carbon Monoxide Borane

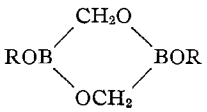
BY LEO J. MALONE

Received December 20, 1967

We have recently reported that the reaction of H_3BCO and water yields not only $B(OH)_3$, CO, and H_2 but also hydroxymethylboronic acid.[1] We now report that analogous reactions occur between H_3BCO and alcohols

$$H_3BCO + 3ROH \longrightarrow B(OR)_3 + CO + 3H_2 \qquad (1)$$

$$H_3BCO + 2ROH \longrightarrow \underset{\text{I}}{(RO)_2BCH_2OH} + H_2 \longrightarrow$$



(2)

II

Although reaction 1 accounts for most of the products at 0°, reaction 2 occurs exclusively at −78°. This is consistent with the suggestion that reaction 1 occurs as a result of the initial dissociation of H_3BCO and subsequent solvolysis of the diborane formed.[1] At −78° dissociation of H_3BCO would be negligible and thus account for the absence of reaction 1 at low temperatures.

The hydroxymethylboronic esters (I) could not be isolated as such but eliminate alcohol to form the dimeric cyclic esters (II). A similar cyclic boronic acid anhydride has been reported previously.[2] In the present work concrete evidence for ring structure II was provided by the rapid hydrolysis of the cyclic esters in moist air to yield the dimeric hydroxymethylboronic acid anhydride.[1] This facile hydrolysis is inconsistent with the other possible dimeric structure involving a four-membered B–O ring.[3]

We also prepared an ester (II) in high yield by reaction of HCl with ethanolic solutions of $K^+H_3BC(O)OC_2H_5^-$ at 0°.

Experimental Section

Standard vacuum procedures and Ŧ apparatus were used throughout.

Materials.—The H_3BCO used was generated as needed by the action of 85% phosphoric acid on an appropriate amount of potassium boranocarbonate.[1,4] The $K^+H_3BC(O)OC_2H_5^-$ (potassium O-ethylboranocarbonate) was prepared in a manner similar to that for $(K^+)_2H_3BCO_2{}^{2-}$. It was found in this study that the initial product in the reaction of H_3BCO and ethanolic KOH at −78° is $K^+H_3BC(O)OC_2H_5^-$. If the ethanolic KOH solution containing this compound is warmed, the $K^+H_3BC(O)OC_2H_5^-$ reacts with the hydroxide to precipitate $(K^+)_2H_3BCO_2{}^{2-}$. If, however, an equal amount of diethyl ether cooled to −78° is added to the cold solution of $K^+H_3BC(O)OC_2H_5^-$, the compound precipitates and can be isolated by filtration and washed with a cold 1:1 ether–alcohol mixture. The yield is about 75% based on the initial amount of diborane[5] used. *Anal.* Calcd for $K^+H_3BC(O)OC_2H_5^-$: C, 28.5; H, 6.34; K, 31.1. Found: C, 27.6; H, 6.11; K, 31.8. The equivalent weight was determined by titration of an aqueous solution with standard HCl: calcd, 125.9; found, 121.6.

The Reaction of Gaseous H_3BCO and Alcohol.—The procedures for the reactions of H_3BCO and methyl, ethyl, and isopropyl alcohols were similar to that described for the reaction of gaseous H_3BCO and water.[1] When 2.15 mmol of H_3BCO and 10 ml of absolute ethanol were allowed to react at −78° for 10 days, 1.80 mmol of hydrogen had evolved but no carbon monoxide. When the reaction mixture was allowed to warm slowly to room temperature an additional 0.90-mmol quantity of hydrogen and carbon monoxide evolved. When the ethanol solution remaining was allowed to pass through a trap at −23° the dimeric ethyl ester[6] (II) (mp 1°) condensed in this trap. From the total amount of noncondensable gas evolved, it was determined that reaction 2 accounted for about 92% of the products under these conditions. *Anal.* Calcd for $(C_2H_5OBCH_2O)_2$: C, 41.8; H, 8.16; B, 12.6. Found: C, 40.5; H, 8.27; B, 12.5. The molecular weight was determined cyroscopically in benzene: calcd for the dimer, 171.6; found, 173.1. This reaction was also carried out so that the H_3BCO and ethanol were allowed to warm rapidly to 0° and stand at this temperature for 2 days. In this case the yield of the ester was 20%.

The reactions of H_3BCO and methyl and isopropyl alcohols were carried out by allowing the reactants to stand at −78° for 1 day and then to warm slowly to room temperature over a 1-day period. Under these conditions the methyl ester was formed in 50% yield (reaction 2). The solid dimeric methyl ester was separated by distillation of the methanol solution through a −23° trap. *Anal.* Calcd for $(CH_3OBCH_2O)_2$: C, 33.4; H, 6.95; B, 15.0. Found: C, 34.4; H, 6.70; B, 14.6. Molecular weight: calcd for the dimer, 143.6; found, 141.0. Under the same conditions the isopropyl ester was prepared in 95% yield. This ester (mp 6°) was separated from the isopropyl alcohol by distillation through a trap at 0°. *Anal.* Calcd for $(C_3H_7OBCH_2O)_2$: C, 48.1; H, 9.02. Found: C, 47.5; H, 9.03. Molecular weight: calcd for the dimer, 199.8; found, 195.0.

Reaction of HCl and Ethanolic $K^+H_3BC(O)OC_2H_5^-$.—In a

---

[1] L. J. Malone and M. R. Manley, *Inorg. Chem.*, **6**, 2260 (1967).

[2] D. S. Matteson and G. D. Schaumberg, *J. Org. Chem.*, **31**, 726 (1966).

[3] R. T. Hawkins, W. J. Lennarz, and H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 3053 (1960).

[4] L. J. Malone and R. W. Parry, *Inorg. Chem.*, **6**, 817 (1967).

[5] G. F. Freegard and L. H. Lang, *Chem. Ind.* (London), **11**, 471 (1965).

[6] 1,4-Diethoxy-1,4-diboro-2,5-dioxacyclohexane.