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Dimethyl Ether Triborane-7[1]

BY W. R. DEEVER AND D. M. RITTER[2]

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This is a report on the preparation and decomposition of dimethyl ether triborane-7. It has proved useful in a number of syntheses where its reactivity was advantageous and the after and side effects of the weakly basic ether were minimal. The preparative result is consistent with earlier observations on similar adducts.[3,4]

Experimental Section

Vacuum line operations were those developed essentially by Stock[5] and by Schlesinger and his co-workers and described by Sanderson[6] and by Jolly.[7]

Melting points were determined at the site of sample formation by visual observation of the temperatures for first appearance of liquid and last appearance of solid.

Tetraborane was prepared by dropping tetramethylammonium triboronate-8 into polyphosphoric acid[8] containing 85% P_2O_5. Dimethyl ether was used directly from a cylinder[9] because it was found free from other substances by glpc analysis.

According to the preferred preparative method tetraborane-10 and dimethyl ether were condensed together at −196°. Then they were warmed to room temperature for 5 min while the vessel was agitated to accomplish thorough mixing. Thereafter the mixture was swiftly cooled to −80°. During the next 2–3 min (depending upon the heat drain) there formed from the liquid a white solid phase, presumably the adduct. Then the temperature was raised to −45°, where it was kept while whatever could be vaporized was removed by high-vacuum pumping during the next 5 hr. The material collected was unreacted tetraborane-10, dimethyl ether, and diborane-6. When instead the reactants were first mixed at −45°, formation of the solid adduct required as long as 2.5 hr. Otherwise the procedure was unchanged. The solid adduct developed negligible vapor pressure (<0.5 mm) until the melting point. The apparent decomposition pressure followed the van't Hoff isochore and reached 29 mm at 24°. Because the processes accompanying vaporization are ill defined, the values[10] have only limited thermochemical use.

Complete decomposition of the adduct (0.24 mmol) occurred within 1 hr at room temperature in a static volume. The products were separated by glpc using mineral oil supported on 80-mesh ground firebrick.

Reaction of boron trifluoride (1.57 mmol) with dimethyl ether triborane-7 (1.25 mmol) was carried out at −16°. Initially there was visible only the solid, but after 30 min there were two liquid phases. Three hours later the products were separated by glpc.

Results

The material balances found in Table I support the belief that the reaction observed was the formation of the 1:1 adduct between dimethyl ether and triborane-7

$$B_4H_{10} + (CH_3)_2O \longrightarrow (H_3C)_2O{-}B_3H_7 + {}^1/_2B_2H_6$$

That an essentially pure solid phase was obtained was attested by the melting range, 10.5–11.1°.

TABLE I
STOICHIOMETRY OF DIMETHYL ETHER TRIBORANE-7 FORMATION

B_4H_{10}			$(CH_3)_2O$			B_2H_6
Added[a]	Recovered	Net	Added	Recovered	Net	Recovered
1.51[b]	0.33	1.18	2.13	0.85	1.28	0.59
2.65[c]	0.20	2.45	5.17	2.62	2.45	1.24

[a] All quantities are given in millimoles. [b] Mixed at ≈25°; adduct formed at −80° in 11 ml. [c] Mixed and allowed to react at −45° in 216 ml.

The substances found after decomposition of the adduct and following its reaction with boron trifluoride are to be found in Table II. Other reactions known, but reserved for description elsewhere,[11] are those with diborane and methyldiboranes to give tetraborane and its methyl derivatives and that with trifluorophosphine[12] to give trifluorophosphine diborane-4.

TABLE II
PRODUCTS FROM REACTIONS OF TRIBORANE-7–DIMETHYL ETHER ADDUCT

Substance	Decomposition[a,b]	Reaction with BF_3[a,c]
B_2H_6	0.043	0.000
B_4H_{10}	0.055	0.557
B_5H_9	0.016	0.016
B_5H_{11}	0.043	0.134
B_6H_{12}	0.024	0.087
$(CH_3)_2O$	0.234	0.000
Boron recovered as volatile hydrides	0.744	3.510

[a] Quantities in millimoles. [b] From 0.24 mmol of adduct. [c] From 1.25 mmol of adduct, 1.57 mmol of BF_3.

As significant as any substance found is the absence of hydrogen as a product in any of these cases.

In Table III are listed series of reactions suggested to account for the data in Table II. The information presently available does not permit a unique selection from among all reactions possibly contributing to the products. For example, no choice can be made

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[1] Assistance given through NSF Grants GP-3459 and GP-6078 is gratefully acknowledged.

[2] To whom correspondence should be addressed.

[3] L. J. Edwards, W. V. Hough, and M. D. Ford, *Congr. Intern. Chim. Pure Appl., 16e, Paris 1957, Mem. Sect. Chim. Minerale,* 475 (1958).

[4] R. W. Parry, R. W. Rudolph, and D. F. Shriver, *Inorg. Chem.,* **3**, 1479 (1964), item (4), p 1480.

[5] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p 77 ff.

[6] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1958.

[7] W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1960.

[8] D. F. Gaines and R. Schaeffer, *Inorg. Chem.,* **3**, 438 (1964).

[9] Supplied by the Matheson Co., Inc., East Rutherford, N. J.

[10] W. R. Deever, Doctoral Thesis, University of Washington, Seattle, Wash., 1967.

[11] Forthcoming publication.

[12] W. R. Deever and D. M. Ritter, *J. Am. Chem. Soc.,* **89**, 5073 (1967).

TABLE III

DECOMPOSITION OF DIMETHYL ETHER TRIBORANE-7

$$0.24(CH_3)_2O\text{–}B_3H_7 \longrightarrow \mathit{0.16}B_2H_4 + \mathit{0.16}(CH_3)_2O\text{–}BH_3 \tag{1a}$$

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

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

$$\longrightarrow 0.016B_5H_9 + \mathit{0.016}BH_3 \tag{2b}$$

$$\mathit{0.055}B_3H_7 + \mathit{0.027}B_2H_6 \longrightarrow 0.055B_4H_{10} \tag{3}$$

$$\mathit{0.043}B_3H_7 + \mathit{0.043}B_2H_4 \longrightarrow 0.043B_5H_{11} \tag{4}$$

Reactions from Dimethyl Ether Triborane-7
and Boron Trifluoride

$$1.246(CH_3)_2O\text{–}B_3H_7 + BF_3 \longrightarrow \mathit{1.246}B_3H_7 + \mathit{1.246}(CH_3)_2O\text{–}BF_3 \tag{5}$$

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

$$\longrightarrow \mathit{0.103}B_4H_8 + \mathit{0.103}B_2H_6 \tag{6b}$$

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

$$\longrightarrow 0.016B_5H_9 + \mathit{0.016}B_2H_6 \tag{7b}$$

$$\mathit{0.557}B_3H_7 + \mathit{0.278}B_2H_6 \longrightarrow 0.557B_4H_{10} \tag{8}$$

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

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.

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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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[1] H. C. Newsom, W. D. English, A. T. McCloskey, and W. D. Woods, *J. Am. Chem. Soc.*, **83**, 4134 (1961).

[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).