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Task No. NR 052-481

TECHNICAL REPORT NO. 3

An Improved Synthesis of 1,7-C<sub>2</sub>B<sub>6</sub>H<sub>6</sub>

by

Gary B. Dunks and M. Frederick Hawthorne

Prepared for Publication

in

Inorganic Chemistry

The University of California  
Department of Chemistry  
Riverside, California 92502

15 December 1967

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## An Improved Synthesis of 1,7-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>

The preparation of the 1,7-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub> carborane system has been previously described<sup>1, 2, 3, 4</sup>. The structure of the C-C' dimethyl

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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, J. Am. Chem. Soc., **88**, 609 (1966).

(3) F. N. Tebbe, P. M. Garrett and M. F. Hawthorne, J. Am. Chem. Soc., **89**, 0000 (1967).

(4) The 1,7-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>, 1,7-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub> and 1,6-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> carboranes and their C-methyl derivatives have been prepared and completely characterized and will appear in a subsequent publication.

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derivative has been determined by Hart and Lipscomb<sup>5</sup> and

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

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shown to be essentially that which had been initially proposed<sup>1, 2</sup>.

Previously, 1,7-C<sub>2</sub>B<sub>6</sub>H<sub>8</sub> and its C-methyl derivatives were obtained in moderate yield by the pyrolysis of dicarbanonaborane(13)<sup>6</sup>,

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(6) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, J. Am. Chem. Soc., 88, 607 (1966).

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C<sub>2</sub>B<sub>7</sub>H<sub>13</sub>, or its C-methyl derivatives in diphenyl ether. The yields approached 30% for the B<sub>6</sub> system<sup>2, 3, 4</sup>.

The slow, low pressure pyrolysis of C<sub>2</sub>B<sub>7</sub>H<sub>13</sub>, or the appropriate C-methyl derivatives, formed as major products, 2,4-C<sub>2</sub>B<sub>6</sub>H<sub>7</sub><sup>7, 8, 9</sup>, 1,7-C<sub>2</sub>B<sub>6</sub>H<sub>8</sub>, 1,7-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub> and 1,6-C<sub>2</sub>B<sub>6</sub>H<sub>10</sub>, or their

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(7) T. Onak, G. B. Dunks, R. A. Beaudet and R. L. Poynter, J. Am. Chem. Soc., 88, 4622 (1966).

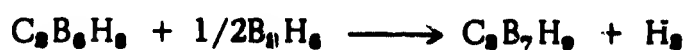
(8) T. Onak, F. J. Gerhart and R. E. Williams, J. Am. Chem. Soc., 85, 3378 (1963).

(9) The CH<sub>3</sub>C<sub>2</sub>B<sub>6</sub>H<sub>8</sub> carborane obtained in this work was identical to an authentic sample prepared by T. Onak and G. Dunks from the pyrolysis of CH<sub>3</sub>C<sub>2</sub>B<sub>4</sub>H<sub>7</sub> and identified as the 2-methyl derivative.

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corresponding C-methyl derivatives together with diborane and hydrogen.

In another study, 1,7-C<sub>2</sub>B<sub>8</sub>H<sub>8</sub> was allowed to stand at room temperature for four weeks in the presence of excess diborane. The products of this reaction are 1,7-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub> and 1,6-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> 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<sub>2</sub>B<sub>7</sub>H<sub>13</sub> in diphenyl ether gives enhanced yields of 1,6-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub><sup>2</sup> and very little 1,7-C<sub>2</sub>B<sub>8</sub>H<sub>8</sub>, suggest that the thermal decomposition of C<sub>2</sub>B<sub>7</sub>H<sub>13</sub> yields diborane, hydrogen and 1,7-C<sub>2</sub>B<sub>8</sub>H<sub>8</sub>. This step may be followed by progressive recombination of 1,7-C<sub>2</sub>B<sub>8</sub>H<sub>8</sub> and diborane to yield 1,7-C<sub>2</sub>B<sub>7</sub>H<sub>9</sub>, 1,6-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> and hydrogen. The direct reaction of C<sub>2</sub>B<sub>7</sub>H<sub>13</sub> and diborane to yield 1,6-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub> may also occur.



The yields of 1,7-C<sub>2</sub>B<sub>8</sub>H<sub>8</sub> obtained from this new procedure are significantly higher than those obtained from other reported methods.

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TABLE I

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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. x 350 mm med. walled pyrex tube, packed with 6 mm pyrex beads and attached to a standard high-vacuum line. The tube was maintained at 360<sup>o</sup> by the use of a 1 in. x 4 ft heating tape<sup>10</sup> wrapped about the tube

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

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and a thermometer. The temperature was controlled by a Thermo-O-Watch<sup>11</sup>.

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

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In a typical experiment, 2.4245 g (21.5 mmoles) of C<sub>2</sub>B<sub>7</sub>H<sub>13</sub> was placed in a flask which was maintained at 48<sup>o</sup> with an oil bath and attached to the bottom of the vertical hot tube. The entire 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<sup>12</sup>, through traps at

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(12) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds", J. Wiley, New York, New York, 1948.

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0°, -80°, -196°. The 0° trap contained .0675 g (0.6 mmoles) of unreacted C<sub>2</sub>B<sub>7</sub>H<sub>13</sub>, and the -196° trap contained 0.5 mmoles of B<sub>2</sub>H<sub>6</sub>, both identified by infrared spectra. The -80° (Dry-ice, isopropanol) trap contained 1.7689 g of a semi-solid white material. A 0.5 ml portion of n-pentane was added to liquify the -80° fraction and the resulting solution was then passed through a vpc<sup>13</sup> in 0.5 ml increments. Four major fractions

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(13) Aerograph Model A350-B, equipped with a 0.25' x 10' Apiezon-L on chromosorb-P column operating at 135° with flow rate 60 cc/min of helium.

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were collected in traps maintained at -80°. The products were identified by infrared and nmr spectra<sup>2, 3, 6, 7, 8, 9</sup>.

Derivative and reaction chemistry is currently under study on the 1,7-C<sub>2</sub>B<sub>8</sub>H<sub>8</sub> and the 1,7-C<sub>2</sub>B<sub>7</sub>H<sub>8</sub> systems.

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

TABLE I

<u>Starting Compound</u>	<u>Products</u>	<u>Yield<sup>a</sup>%</u>
$C_2B_7H_{13}$	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- $C_2B_5H_{10}$	5.9
$CH_3C_2B_7H_{13}$	2, 4- $CH_3C_2B_5H_8$	2.4
	1, 7- $CH_3C_2B_6H_7$	57.2
	1, 7- $CH_3C_2B_7H_8$	9.5
	1, 6- $CH_3C_2B_5H_9$	6.1
$(CH_3)_2C_2B_7H_{11}$	2, 4- $(CH_3)_2C_2B_5H_8$	4.6
	1, 7- $(CH_3)_2C_2B_6H_7$	54.0
	1, 7- $(CH_3)_2C_2B_7H_7$	11.0
	1, 6- $(CH_3)_2C_2B_5H_8$	4.0

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(a) Yield based on starting material consumed.



UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) The University of California Department of Chemistry Riverside, California 92502	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
	2b. GROUP Not Applicable

3. REPORT TITLE  
  
AN IMPROVED SYNTHESIS OF 1,7-C<sub>2</sub>B<sub>6</sub>H<sub>8</sub>

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)  
Technical

5. AUTHOR(S) (First name, middle initial, last name)  
M. Frederick Hawthorne  
Gary B. Dunks

6. REPORT DATE 15 December 1967	7a. TOTAL NO. OF PAGES seven	7b. NO. OF REFS 13
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8a. CONTRACT OR GRANT NO. Nonr 4443(00)	9a. ORIGINATOR'S REPORT NUMBER(S) Technical Report No. 3
b. PROJECT NO. Nr 052-481	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
c.	
d.	

10. DISTRIBUTION STATEMENT  
Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Chemistry Branch Office of Naval Research Washington, D. C. 20360
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13. ABSTRACT  
Pyrolysis of B<sub>7</sub>C<sub>2</sub>H<sub>13</sub> and its C-methyl derivatives at low pressures in a flow apparatus operating at 360° affords the corresponding B<sub>6</sub>C<sub>2</sub>H<sub>8</sub> carborane derivative in 50-60% yield.

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