CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CALIFORNIA STATE COLLEGE AT LOS ANGELES, LOS ANGELES, CALIFORNIA

Studies on 2,3-Dicarbahexaborane(8)[1] and Related Compounds

BY THOMAS ONAK, ROGERS P. DRAKE, AND GARY B. DUNKS

Received June 22, 1964

The reaction between alkynes and pentaborane at elevated temperatures was studied. Increasing the number of alkyl groups about the triple bond of the alkyne enhanced the reactivity toward pentaborane and resulted in increased yields of the corresponding 2,3-dicarbahexaborane(8). Attempts to effect a "direct" conversion of alkynes and pentaborane to the appropriate 2,4-dicarbaclovoheptaborane(7) were unsuccessful. The decomposition of 2,3-dicarbahexaborane(8) in a silent electric discharge apparatus has given improved yields of 1,5-dicarbaclovopentaborane(5) and 1,2-dicarbaclovohexaborane(6). Earlier findings are rationalized in terms of the thermal stabilities of the latter two compounds.

Although various C-alkylated-2,3-dicarbahexaboranes(8) have been prepared in satisfactory yield (*ca.* 40%) from the 2,6-lutidine-catalyzed reaction between pentaborane and substituted acetylenes,[2] a similar base-catalyzed synthesis of the parent compound, $C_2B_4H_8$, has been somewhat disappointing. A procedure for the preparation of $C_2B_4H_8$ in the absence of a base catalyst has been reported[3]; however, the yield of purified product was found to be less than that experienced from the base-catalyzed reaction.[4]

Ryschkewitsch, Mezey, Altwicker, Sisler, and Garrett[5] recently reported that the relative reactivities of the various olefins toward pentaborane at 150° are in accord with a mechanism of nucleophilic attack by the olefin. The formation of a 2,3-dicarbahexaborane(8) from pentaborane may also involve an initial nucleophilic attack by the alkyne. This suggests that 2-butyne might react more readily with pentaborane at elevated temperatures to form the C,C′-dimethyl derivative than does acetylene to form the parent compound. In the present study experimental support is given to this suggestion and, in addition, an improved procedure for preparing 2,3-dicarbahexaborane(8) is described. The improved preparation of 2,3-dicarbahexaborane(8) has paved the way for the examination of several earlier predictions.[6]

Experimental

Gas Chromatography.—A 30% Kel-F on firebrick[7] column operated at 60° was used. Retention volumes (relative to pentaborane = 1.00) are: 1,5-dicarbaclovopentaborane(5), 0.33; 1,6-dicarbaclovohexaborane(6), 0.53; 1,2-dicarbaclovohexaborane(6), 0.76; 2,4-dicarbaclovoheptaborane(7), 1.27; 2,3-dicarbahexaborane(8), 1.36; C-methyl-2,3-dicarbahexaborane(8), 1.63. See ref. 6 for g.l.c. data on related compounds.

Nuclear Magnetic Resonance Data.—B^{11} n.m.r. spectra were taken with a Varian V-4300 high resolution spectrometer operating at 12.83 Mc. (Table I). H^1 n.m.r. spectra were taken with a Varian A-60 spectrometer (Table II).

Preparation of 2,3-Dicarbahexaborane(8). (a) From Acetylene and Pentaborane in the Presence of 2,6-Lutidine.—A mixture of acetylene (20 mmoles), pentaborane (10 mmoles), and 2,6-lutidine (35 mmoles)[8] was sealed into a 500-ml. flask and subsequently shaken for 7 hr. at room temperature. The volatiles were vacuum fractionated through traps at −50 and −190°. The contents of the −190° trap were gas chromatographed yielding, in addition to small quantities of unreacted acetylene and pentaborane, 0.70 mmole (7%) of 2,3-dicarbahexaborane (8).

(b) From Acetylene and Pentaborane at 215°.—Acetylene (9.8 mmoles) and pentaborane (1.21 mmoles) were sealed into a 30-ml. flask equipped with a 5-mm. diameter tube for taking n.m.r. spectra. The lowest temperature at which the disappearance of pentaborane and the appearance of 2,3-dicarbahexaborane(8) occurred at a reasonable rate was *ca.* 215°. This was determined by analyzing H^1 n.m.r. spectra after each 18-hr. heating period. The volatile products were separated by gas chromatography, and there was obtained 3.1 mmoles of recovered acetylene (contaminated with some ethylene), 0.26 mmole of recovered pentaborane, and 0.36 mmole (38% yield based on pentaborane consumed) of 2,3-dicarbahexaborane(8). In addition to the above materials, about 0.1 mmole of noncondensables was formed during the pyrolysis as well as a considerable quantity of dark brown solids. When $C_2B_4H_8$ was prepared on a larger scale, it was found convenient to extend the heating period to 3 days. Using the longer heating period reduced the amount of unreacted pentaborane which in turn made the purification of the dihydrocarborane somewhat easier.

Preparation of C-Methyl-2,3-dicarbahexaborane(8). (a) From Propyne and Pentaborane in the Presence of 2,6-Lutidine.—A mixture of propyne (20 mmoles), pentaborane (5 mmoles), and 2,6-lutidine[8] (15 mmoles) was sealed into a 500-ml. flask and subsequently shaken for 10 hr. at room temperature. The volatile products were separated from the reaction mixture by a high vacuum distillation through a −190° trap. After adding 5 ml. of boron trifluoride etherate to the −190° trap and stirring for 15 min. at room temperature, the resulting heterogeneous mixture was vacuum fractionated through traps at −50, −80, and −190°. A gas chromatogram of the contents in the −50° trap gave 0.42 mmole (8.4%) of C-methyl-2,3-dicarbahexaborane(8).

(b) From Propyne and Pentaborane at 175°.—Propyne (5.1 mmoles) and pentaborane (0.45 mmole) were sealed in a 25-ml. flask equipped with a 5-mm. diameter tube for taking n.m.r. spectra. The minimum conditions required for the disappear-

---

(1) Nomenclature adopted for $C_2B_4H_8$ which, previously, was called "dihydrocarborane"[2]: R. Adams, *Inorg. Chem.*, **2**, 1087 (1963). Other adopted names for compounds mentioned in this article are: $C_2B_3H_5$, 1,5-dicarbaclovopentaborane(5); *sym*-$C_2B_4H_6$, 1,6-dicarbaclovohexaborane(6); *unsym*-$C_2B_4H_6$, 1,2-dicarbaclovohexaborane(6); $C_2B_5H_7$, 2,4-dicarbaclovoheptaborane(7). At times it will be convenient to use the term carborane in a generic sense covering the above clovo carbon–boron hydrides with skeletal carbon atoms.

(2) T. Onak, R. E. Williams, and H. G. Weiss, *J. Am. Chem. Soc.*, **84**, 2380 (1962).

(3) H. G. Weiss and I. Shapiro, U. S. Patent 3,086,996.

(4) H. G. Weiss, private communication.

(5) G. E. Ryschkewitsch, E. J. Mezey, E. R. Altwicker, H. H. Sisler, and A. B. Garrett, *Inorg. Chem.*, **2**, 893 (1963).

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

(7) T. Onak and F. Gerhart, *Inorg. Chem.*, **1**, 742 (1962).

(8) Purified according to the procedure described by H. C. Brown, S. Johnson, and H. Podall, *J. Am. Chem. Soc.*, **76**, 5556 (1954).

TABLE I

B^{11} N.M.R. CHEMICAL SHIFT VALUES AND COUPLING CONSTANTS[a]

1,5-Dicarbaclovopentaborane(5) $C_2B_3H_5$[c]	$B^{2,3,4}$–H	δ^b −1.4;	J = 183 c.p.s.
1,2-Dicarbaclovohexaborane(6) *unsym*-$C_2B_4H_6$[c]	$B^{3,5 \text{ or } 4,6}$–H	δ^b +1.6;	J = 178 c.p.s.
	$B^{4,6 \text{ or } 3,5}$–H	δ^b +15.3;	J = 194 c.p.s.
2,3-Dicarbahexaborane(8) $C_2B_4H_8$	B^1–H	δ^b +54.0;	J = 179 c.p.s.
	$B^{4,5,6}$–H[d]	δ^b +3.0;	J = 158 c.p.s.
C-Phenyl-2,3-dicarbahexaborane(8) C_6H_5—$C_2B_4H_7$	B^1–H	δ^b +49.3;	J = 175 c.p.s.
	$B^{4,5,6}$–H[d]	δ^b +5.1;	J = *ca.* 150 c.p.s.
C-Isopropenyl-2,3-dicarbahexaborane(8) CH_2═$C(CH_3)$—$C_2B_4H_7$	B^1–H	δ^b +50.6;	J = 175 c.p.s.
	$B^{4,5,6}$–H[d]	δ^b +3.0;	J = *ca.* 155 c.p.s.

[a] The B^{11} chemical shift values and coupling constants for 1,6-dicarbaclovohexaborane(6), 2,4-dicarbaclovoheptaborane(7), C-methyl-2,3-dicarbahexaborane(8), and C,C′-dimethyl-2,3-dicarbahexaborane(8) have been reported previously.[2,6] [b] δ, p.p.m. relative to boron trifluoride etherate. [c] See ref. 15. [d] The $B^{4,6}$–H doublet and B^5–H doublet are nearly superimposable. In a reinterpretation of the 2,3-dicarbahexaborane(8) B^{11} n.m.r.[2] [R. E. Williams and T. Onak, *J. Am. Chem. Soc.*, **86**, 3159 (1964)] the low-field region consists of a broad doublet (B^5–H) which is superimposed on a larger doublet ($B^{4,6}$–H) with resolved splitting due to coupling to a single bridge hydrogen. The H_{bridge}–$B^{4,6}$ coupling constant is 43 c.p.s. in 2,3-dicarbahexaborane(8) but not well enough defined in C-phenyl-2,3-dicarbahexaborane(8) and C-isopropenyl-2,3-dicarbahexaborane(8) to be measured.

TABLE II

H^1 N.M.R. CHEMICAL SHIFTS AND COUPLING CONSTANTS[a] (δ,[b] $J_{H-^{11}B}$, c.p.s.)

	H–B^1	H–$B^{4,5,6}$	H_{bridge}	H–C_{skeletal}	Other
2,3-Dicarbahexaborane(8) $C_2B_4H_8$	+1.13, 181	−3.44, 158	+2.6 (estd.)	−6.32	
C-Methyl-2,3-dicarbahexaborane(8) CH_3—$C_2B_4H_7$	+0.81, 179	−3.45, 158	+2.3 (estd.)	−6.16	CH_3–, −2.27
C-Phenyl-2,3-dicarbahexaborane(8) C_6H_5—$C_2B_4H_7$	+1.08,[c] 182	−3.05,[c] 168	+2.6 (estd.)[c]	−5.75[c]	H–phenyl, −6.53[c]
C-Isopropenyl-2,3-dicarbahexaborane(8) CH_2═$C(CH_3)$—$C_2B_4H_7$	+0.76, 180	−3.53, 158	+2.2 (estd.)	−6.27	CH_3–, −1.93; CH_2═, −5.06 and −5.38
1,5-Dicarbaclovopentaborane(5) $C_2B_3H_5$	H–$B^{2,3,4}$, −2.93,[c] 188			−4.65[c]	
1,2-Dicarbaclovohexaborane(6) *unsym*-$C_2B_4H_6$	H–$B^{3,5;4,6}$, −1.82,[d] 178			−2.87	
1,6-Dicarbaclovohexaborane(6) *sym*-$C_2B_4H_6$	H–$B^{2,3,4,5}$, −1.92, 187			−3.14	
2,4-Dicarbaclovoheptaborane(7) $C_2B_5H_7$	H–$B^{1,7 \text{ or } 5,6}$, −0.15, 177	H–$B^{5,6 \text{ or } 1,7}$, −4.00, 171	H–B^3, −4.75, 183	−5.50	

[a] H^1 chemical shift values and coupling constants for C,C′-dimethyl-2,3-dicarbahexaborane(8) have been previously reported.[6] [b] δ, p.p.m. relative to tetramethylsilane; negative values are to low field. [c] Not corrected for bulk susceptibility. [d] Represents an average chemical shift for the two types of B–H hydrogens. High-field members of the quartet were broader than low-field members; the degree of overlap prevents an accurate chemical shift determination of the component quartets.

ance of pentaborane and the appearance of C-methyl-2,3-dicarbahexaborane(8), as followed by H^1 n.m.r., were 175° for 18 hr. A gas chromatogram of the volatile fraction gave 2.3 mmoles of unreacted propyne, 0.19 mmole of pentaborane, and 0.19 mmole (54% yield based on pentaborane consumed) of C-methyl-2,3-dicarbahexaborane(8).

Preparation of C,C′-Dimethyl-2,3-dicarbahexaborane(8).—2-Butyne (33 mmoles) and pentaborane (8.3 mmoles) were sealed in a 1-l. flask and heated at 165° for 18 hr. This was the lowest temperature at which a reasonable rate of reaction occurred as determined by the method outlined above for the preparation of 2,3-dicarbahexaborane(8) at elevated temperatures. A gas chromatogram of the volatile fraction gave 14 mmoles of unreacted 2-butyne, 3.4 mmoles of unreacted pentaborane, and 2.6 mmoles (53% yield based on pentaborane consumed) of C,C′-dimethyl-2,3-dicarbahexaborane(8).

Conversion of 2,3-Dicarbahexaborane(8) to 2,4-Dicarbaclovoheptaborane(7).—One mmole of 2,3-dicarbahexaborane(8) was sealed into a 25-ml. flask equipped with a 5-mm. diameter tube for taking n.m.r. spectra. The lowest temperature at which 2,3-dicarbahexaborane(8) disappeared at a reasonable rate was 295°. After an 18-hr. heating period at 295° the inside of the flask was coated with tan-colored solids. A gas chromatogram of the volatile fraction gave 0.28 mmole (27%) of 2,4-dicarbaclovoheptaborane(7), 0.02 mmole of 1,5-dicarbaclovopentaborane(5), and 0.01 mmole of 1,6-dicarbaclovohexaborane(6).

Attempted "Direct" Preparation of 2,4-Dicarbaclovoheptaborane(7) from Acetylene and Pentaborane.—Pentaborane (1.0 mmole) and acetylene (10 mmoles) were sealed in a 25-ml. flask equipped with a 5-mm. tube for taking n.m.r. spectra. After heating the mixture at 210° fo 20 hr. the H^1 n.m.r. spectrum indicated that a considerable quantity of 2,3-dicarbahexaborane(8) had formed. The flask and its contents were next heated at 300° for an additional 20-hr. period. A gas chromatogram of the volatile fraction (0.24 mmole) gave no detectable quantity of 2,4-dicarbaclovoheptaborane(7).

Attempted "Direct" Preparation of C,C′-Dimethyl-2,4-dicarbaclovoheptaborane(7) from 2-Butyne and Pentaborane.—2-Butyne (1.25 mmoles) and pentaborane (0.32 mmole) were sealed in a 25-ml. flask equipped with a 5-mm. tube for taking n.m.r. spectra. After heating the mixture at 165° for 18 hr. the B^{11} n.m.r. spectrum indicated that a considerable quantity of C,C′-dimethyl-2,3-dicarbahexaborane(8) had formed. The flask was subsequently heated to 285° for an 18-hr. period. The B^{11} n.m.r. pattern was not recognizable in terms of known compounds[6]; however, a very large single peak at δ −9 is indicative of alkylated boron atoms that are part of a pyramidal framework. A gas chromatogram of the volatile fraction followed by an infrared examination of each fraction indicated that at least six volatile compounds containing B–H and C–H bonds (infrared analysis) had been formed in very small quantities. None of the fractions contained the expected C,C′-dimethyl-2,4-dicarbaclovoheptaborane(7).

Preparation of C-Phenyl-2,3-dicarbahexaborane(8).—To 5 ml. of 2,6-lutidine[8] were added 10 mmoles of pentaborane and 10 mmoles of freshly distilled phenylacetylene. After stirring the mixture for 4 hr. at room temperature the volatile components were vacuum fractionated through traps at 0 and −190°. The contents of the 0° trap were vacuum fractionated an additional two times using the same bath temperatures in order to remove traces of 2,6-lutidine. The last 0° fraction contained 1.1 mmoles (11% yield) of C-phenyl-2,3-dicarbahexaborane(8). The ultraviolet spectrum exhibits λ_{max} at 247 mμ, ϵ 7500.

Preparation of C-Isopropenyl-2,3-dicarbahexaborane(8). (a) From Isopropenylacetylene and Pentaborane in 2,6-Lutidine.—A mixture of 10 mmoles of pentaborane, 20 mmoles of isopropenylacetylene, and 10 ml. of 2,6-lutidine[8] was stirred for 48 hr. at room temperature. To the dark brown product mixture was added, with continued stirring, 25 ml. of boron trifluoride etherate over a 15-min. period. The volatile fraction was vacuum fractionated through traps at −15, −65, and −190°, and the contents of the −65° trap subsequently was gas chromatographed to give 0.31 mmole (3% yield) of C-isopropenyl-2,3-dicarbahexaborane(8), vapor pressure 7 mm. at 24°.

(b) Attempted Synthesis from Isopropenylacetylene and Pentaborane at Elevated Temperatures.—Isopropenylacetylene (1.95 mmoles) and pentaborane (0.52 mmole) were sealed in a 25-ml. flask and heated for a series of 18-hr. runs at 70, 140, 160, and 170°. The course of the reaction was followed by taking an H^1 n.m.r. spectrum after each heating period. At 140° a small amount of tan solid material appeared on the walls of the flask; however, the H^1 n.m.r. spectrum did not show any appreciable decrease in either reactant. After the 160° treatment the quantity of solids increased and the n.m.r. spectrum indicated that *ca.* 30% of the isopropenylacetylene had disappeared. Over 90% of the alkyne disappeared after the 170° run; however, the amount of pentaborane appeared not to have changed either by H^1 or B^{11} n.m.r. spectra. There was no evidence in either the H^1 or the B^{11} n.m.r. spectra that C-isopropenyl-2,3-dicarbahexaborane(8) was present.

Carboranes from the Electric Discharge of 2,3-Dicarbahexaborane(8). Apparatus.—A silent discharge apparatus with an annular spacing of *ca.* 1.5 mm. between two coaxial Pyrex tubes (8 and 13 mm. o.d.) 85 cm. in length was employed. A 15,000-v. luminous tube transformer[9] which was regulated with a variable transformer served as a high voltage source between the outside tube covered with copper foil and the inner tube filled with copper sulfate solution. The electric discharge unit was part of a closed system with a 10-l. capacity to which was attached an all-glass magnetically operated pump with a displacing capacity of 30 cc. The pump was normally operated at 25 r.p.m. which, for this system, represents a 13-min. circulating time.

Procedure.—In a typical experiment 2.5 mmoles of 2,3-dicarbahexaborane(8) and sufficient helium to give a total pressure of 25 mm. were precirculated for *ca.* 1 hr. A high voltage discharge (*ca.* 5.2 kv.) was then passed through the mixture for a period of 4 hr. after which the condensable products were gas chromatographed. Isolated from the chromatographed mixture were 1.17 mmoles of recovered 2,3-dicarbahexaborane(8), 0.06 mmole of 1,5-dicarbaclovopentaborane(5), 0.06 mmole of 1,6-dicarbaclovohexaborane(6), and 0.07 mmole of 1,2-dicarbaclovohexaborane(6). The amount of 2,4-dicarbaclovoheptaborane(7) could not be determined since it was swamped with the large quantity of unreacted 2,3-dicarbahexaborane(8) as it emerged from the column. The results for a number of discharge experiments are given in Table III.

TABLE III

SILENT ELECTRIC DISCHARGE OF 2,3-DICARBAHEXABORANE(8)

2,3-Dicarbahexaborane(8), mmoles	Time of discharge, hr.	Recovered 2,3-dicarbahexaborane(8), mmoles	1,2-Dicarbaclovohexaborane(6) isolated, mmoles (%)[a]
2.50	1.0	1.37	Trace
2.50	4.0	1.17	0.07 (5)
2.50	6.8	0.59	0.04 (2)
5.00	6.8	0.72	0.11 (3)
2.50	8.0	0.32	0.02 (1)

[a] Based on 2,3-dicarbahexaborane(8) consumed. The yields of the other isolated carboranes, 1,5-dicarbaclovopentaborane(5) and 1,6-dicarbaclovohexaborane(6), were generally the same as the yield of 1,2-dicarbaclovohexaborane(6) for a given run.

Carboranes from the Electric Discharge of Pentaborane–Acetylene Mixtures.—A number of pentaborane–acetylene mixtures (Table IV) were subjected to a silent electric discharge using the apparatus described in the previous section. Both 1,5-dicarbaclovopentaborane(5) and 1,6-dicarbaclovohexaborane(6) could be separated from the product mixture by gas chromatography; however, the overlap of the relatively large quantity of unreacted pentaborane with both the 1,2-dicarbaclovohexaborane(6) and 2,4-dicarbaclovoheptaborane(7) made the isolation of the latter two compounds difficult by this method. The latter two carboranes could be separated from the mixture by complexing the pentaborane with trimethylamine and subsequently vacuum fractionating using traps at −40 and −190°. After adding diborane to the contents of the −190° trap in order to complex the excess trimethylamine the entire mixture was fractionated again through traps at −40 and −190°. The contents of the last −190° trap were chromatographed and analyzed for 1,2-dicarbaclovohexaborane(6) and 2,4-dicarbaclovoheptaborane(7). The results of three runs are summarized in Table IV.

Thermal Instability. (a) 1,5-Dicarbaclovopentaborane(5).—A 50-μmole quantity of 1,5-dicarbaclovopentaborane(5) was sealed in a 3-mm. o.d. Pyrex tube 4 cm. in length. The minimum set of conditions at which the carborane disappeared (as followed by B^{11} n.m.r.) was 150° for 20 hr. In addition to a considerable quantity of tan solids, 12 μmoles of noncondensables and 6.5 μmoles of condensable volatiles (trapped at −190°) were found. The contents of the −190° trap exhibited the infrared spectrum of the starting material; however, a mass spectrum indicated that it was contaminated with small quantities of one or both of the dicarbaclovohexaboranes(6) and butane.

(b) 1,2-Dicarbaclovohexaborane(6).—A 30-μmole quantity of 1,2-dicarbaclovohexaborane(6) was sealed in a 4-mm. o.d. Pyrex tube 6 cm. in length. The B^{11} n.m.r. spectrum did not show a significant change until the sample was heated at 250° for 20 hr. At this temperature the B^{11} n.m.r. signal changed from the pattern of 1,2-dicarbaclovohexaborane(6) to that of 1,6-dicarbaclovohexaborane(6). Very little solid material had formed; 7 μmoles of noncondensables was found in addition to 27 μmoles of condensables that analyzed by infrared for *ca.* 90% 1,6-dicarbaclovohexaborane(6) and 10% 1,2-dicarbaclovohexaborane(6).

Results and Discussion

The ease with which C-substituted 2,3-dicarbahexaboranes(8) are formed from pentaborane and alkynes at elevated temperatures increases with increasing number of alkyl groups about the alkyne. The temperatures required to effect a reasonable rate of reac-

---

(9) Obtained from Jefferson Electric Co., Bellwood, Ill., No. 721-111.

TABLE IV

ELECTRIC DISCHARGE OF PENTABORANE–ACETYLENE MIXTURES

Starting materials, mmoles		Time of discharge, hr.	Recovered starting materials, mmoles		Carboranes, mmoles (%)[a]			
B_5H_9	C_2H_2		B_5H_9	C_2H_2	$C_2B_3H_5$	*sym*-$C_2B_4H_6$	*unsym*-$C_2B_4H_6$	$C_2B_5H_7$
5.60	5.60	2.75	0.44	Trace	Trace	Trace	Trace	Trace
52	83	4.50	4.7	0.5	0.05 (0.07)	0.35	0.20 (0.26)	0.10
76	107	24	2.5	Trace	. . .	0.03	0.13 (0.18)	0.02

[a] Based on pentaborane consumed.

tion are *ca.* 165, 175, and 215° using 2-butyne, propyne, and acetylene, respectively. The yield of the corresponding 2,3-dicarbahexaborane(8) drops from slightly above 50% to 30%, which might be explained by the relative instability of pentaborane at the higher temperatures. Application of elevated temperatures for the formation of C-isopropenyl-2,3-dicarbahexaborane(8) from isopropenylacetylene and pentaborane was unsuccessful although a low yield was effected by the use of 2,6-lutidine as a catalyst at room temperature. Attempts to effect a "direct" synthesis of 2,4-dicarbaclovoheptaborane(7) derivatives from pentaborane and alkynes *via* an intermediate 2,3-dicarbahexaborane(8)[6] failed. After first raising the temperature of the pentaborane–alkyne mixture to that required for the formation of the 2,3-dicarbahexaborane(8), a further temperature increase resulted in the formation of a complex multicomponent mixture in which none of the desired 2,4-dicarbaclovoheptaborane(7) could be detected. These results appear to be consistent with the previously reported preparation of $C_2B_4H_8$[3] in very low yield[4] from acetylene and pentaborane at a preferred temperature range of 240–260°.[3] Above 210° 2,3-dicarbahexaborane(8) probably reacts with one of the components of the reaction mixture to give rise to "undesirable" side products.

Pyrolysis of chromatographically pure $C_2B_4H_8$ gives $C_2B_5H_7$ in a manner similar to that experienced for the alkyl derivatives.[6] Microwave spectroscopic studies[10] made on $C_2B_5H_7$ have confirmed the assignment of two carbons nonadjacent in the base of a pentagonal bipyramid.[6] It has already been established by X-ray diffraction methods[11] that the C,C′-dimethyl derivative of $C_2B_4H_8$[2,6] contains two adjacent carbons in the base of a pentagonal pyramid. The H^1 n.m.r. spectrum of C^{13}-labeled $C_2B_4H_8$ gives a measured $J_{^{13}C-H}$ of 160 c.p.s., which is in the region found for carbon in an sp^2 bonding environment.[12–14] This is in agreement with Streib, Bohr, and Lipscomb's localized bond description for the derivative of $C_2B_4H_8$.[11]

Carboranes from Silent Electric Discharge Reactions.—2,4-Dicarbaclovoheptaborane(7) and 1,6-dicarbaclovohexaborane(6) derivatives can now be obtained in preparative amounts[6]; however, the two remaining small carboranes, 1,5-dicarbaclovopentaborane(5) and 1,2-dicarbaclovohexaborane(6), can only be found in very low yield from the silent electric discharge of a pentaborane–acetylene mixture.[15] On repeating the previous work we have also found the yield of carboranes to be extremely low (*e.g.*, 1,5-dicarbaclovopentaborane(5), less than 0.1%; 1,2-dicarbaclovohexaborane(6), less than 0.3%). In an effort to improve on this route to the less available carboranes, advantage was taken of an earlier suggestion[6] when it was found that $C_2B_4H_8$ could be synthesized in preparative yield. On subjecting $C_2B_4H_8$ to a silent electric discharge, 1,5-dicarbaclovopentaborane(5) and 1,2-dicarbaclovohexaborane(6) were isolated in yields up to *ca.* 5%. Although this is far from quantitative it represents a marked improvement over the direct electric discharge of pentaborane–acetylene mixtures. The requirement of an extra synthetic step is offset by the ease with which the desired carboranes can be removed from the unreacted $C_2B_4H_8$ by gas chromatography.

Thermal Stabilities of the Carboranes.—Williams[15] and, independently, Hoffmann and Lipscomb[16] have suggested that 1,2-dicarbaclovohexaborane(6) might rearrange to the more stable[17] 1,6-dicarbaclovohexaborane(6) at elevated temperatures. On subjecting 1,2-dicarbaclovohexaborane(6) to a series of thermal instability tests no appreciable reaction is observed below *ca.* 250°, and at this temperature a nearly quantitative conversion to the 1,6- isomer is observed. In retrospect, it is not surprising that only 1,6- isomers were obtained from the pyrolysis of 2,3-dicarbahexaborane(8) derivatives in the presence of trimethylamine, for temperatures above 250° were generally required.[6]

1,5-Dicarbaclovopentaborane(5) is stable up to *ca.* 150°, at which it slowly decomposes to tan-colored solids. Although very small quantities of one or both of the dicarbaclovohexaboranes(6) and butane are found in the recovered 1,5-dicarbaclovopentaborane(5), they may have been present in trace amounts prior to the heat treatment. The thermal instability of 1,5-dicarbaclovopentaborane(5) above 150° provides an answer for the observed absence of major quantities of C-alkylated 1,5-dicarbaclovopentaborane(5) derivatives in the volatile carborane mixture from the pyrolysis of C-alkylated-2,3-dicarbahexaboranes(8).[6]

The accumulation of H^1 n.m.r. data for a number of 2,3-dicarbahexaborane(8) derivatives (Table II and ref. 6) permits the establishment of a number of reason-

---

(10) R. A. Beaudet and R. L. Poynter, *J. Am. Chem. Soc.*, **86**, 1258 (1964).

(11) W. E. Streib, F. P. Boer, and W. N. Lipscomb, *ibid.*, **85**, 2331 (1963).

(12) P. C. Lauterbur, *J. Chem. Phys.*, **26**, 217 (1957).

(13) N. Muller and D. E. Pritchard, *ibid.*, **31**, 768, 1471 (1959).

(14) J. N. Shoolery, *ibid.*, **31**, 1427 (1959).

(15) R. E. Williams, C. D. Good, I. Shapiro, and B. Keilin, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961, p. 14N; *J Am. Chem. Soc.*, **84**, 3837 (1962); *ibid.*, **85**, 3167 (1963); R. E. Williams, private communication.

(16) R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963).

(17) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962).

ably reliable generalizations. Apical protons are found 0.7 to 1.2 p.p.m. to higher field than tetramethylsilane, whereas basal B–H protons are located 3.6 to 3.0 p.p.m. to lower field. Bridge hydrogens and skeletal C–H protons are found in the regions +2.3 to +2.6 p.p.m. and −6.4 to 5.7 p.p.m., respectively. Approximate "effective" shielding constants[18] for the various carborane groups bonded at a skeletal carbon atom to an alkyl group are: 2,3-dicarbahexaboranyl(8)-, 1.8; 1,6-dicarbaclovohexaboranyl(6)-, 1.1; 2,4-dicarbaclovoheptaboranyl(7)-, 1.8.

Acknowledgments.—The authors wish to express their gratitude to the Office of Naval Research for financial support to this research. They also thank Drs. R. E. Williams and J. Spielman for stimulating and helpful discussions.

---

[18] B. P. Dailey and J. N. Shoolery, Varian Technical Information Bulletin, **2**, No. 3, 4 (1959); *J. Am. Chem. Soc.*, **77**, 3977 (1955).

CONTRIBUTION NO. 993 FROM THE CENTRAL RESEARCH DEPARTMENT,
EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON 98, DELAWARE

Chemistry of Boranes. XXI.[1] Icosaborane-16[2,3]

BY N. E. MILLER, J. A. FORSTNER, AND E. L. MUETTERTIES

Received July 30, 1964

A new volatile boron hydride, icosaborane-16 ($B_{20}H_{16}$), has been synthesized by catalytic pyrolysis of decaborane-14. Icosaborane-16 reacts irreversibly on dissolution in water and in alcohol to form the $B_{20}H_{16}(OH)_2^{2-}$ and $B_{20}H_{16}(OC_2H_5)_2^{2-}$ ions, respectively. Formally related to these dianions is a class of adducts of the type $B_{20}H_{16}\cdot$2base which are formed in the reaction of icosaborane-16 with Lewis bases.

Preparation of Icosaborane-16.—Pyrolysis of decaborane-14 at 350° in the presence of methylaminodimethylborane catalyst yields hydrogen, nonvolatile materials, and the icosaborane-16, $B_{20}H_{16}$. Synthesis conditions are quite critical. Short contact times are necessary and oxygen in trace amounts inhibits icosaborane-16 formation. Our best conversions and yields have been in the range of 10 and 15%, respectively, which is superior to the discharge synthesis.[3]

Icosaborane-16 was purified by repeated vacuum sublimation. A rigorous purification was effected by a gas chromatographic procedure. The melting point of icosaborane-16 is 196–199°.

Characterization of Icosaborane-16.—As reported in the original communication,[2] the composition of this new hydride was uniquely determined by a combination of analytical and spectroscopic data. This was an independent solution to the unique characterization provided by the complete crystal structure determination.[3,4] The molecular weight was established fairly precisely from the mass spectrum, unit cell dimensions and density, and isopiestic studies. The B:H ratio was determined precisely from analysis, hydrolytic hydrogen, and B^{11} n.m.r. data. The basic arguments for the characterization were presented[2] earlier, and the complete data are in the Experimental section of this paper.

All of our spectroscopic data[2] suggest the structure presented in Fig. 1, and this is the unique solution obtained from the crystal structure analysis.[3,4]

Derivatives of Icosaborane-16.—Icosaborane-16 dissolves in water with reaction to generate an acidic solution that titrates as a strong acid and gives a neutral equivalent one-half the molecular weight of icosaborane-16. This reaction is irreversible. Removal of solvent water at 25° under vacuum gave $B_{20}H_{16}\cdot 4H_2O$. Attempts to dehydrate this species led to degradation of the B_{20} cage. The tetrahydrate is formulated as the hydronium salt of $B_{20}H_{16}(OH)_2^{2-}$ since neutralization with tetraalkylammonium hydroxide gave the corresponding salts of $B_{20}H_{16}(OH)_2^{2-}$. These salts behave as strong 2:1 electrolytes. The $B_{20}H_{16}(OH)_2^{2-}$ anion slowly hydrolyzes in water; a 0.04 *N* aqueous solution was 3% decomposed in 2 weeks time.

The structure of the $B_{20}H_{16}(OH)_2^{2-}$ ion has not been established. However, the strong acceptor properties of icosaborane-16 unquestionably originate at the four unique boron atoms (IV in Fig. 1) which are not bonded to hydrogen. These should be the sites of nucleophilic attack, and it is reasonable to presume that in $B_{20}H_{16}(OH)_2^{2-}$ the OH groups are bonded to two of these boron atoms, probably to *trans* boron atoms. The B^{11} n.m.r. spectrum of $B_{20}H_{16}(OH)_2^{2-}$ solutions is a broad multiplet centered at about +33 p.p.m. This multiplet shifts to higher fields on addition of acid, and the general contour changes slightly. Because of the small chemical shifts, no structural conclusions can be made from these data, nor from the proton-decoupled B^{11} spectra.

Icosaborane-16 reacts with ethanol in an analogous fashion to that with water. From these solutions,

---

[1] Paper XX: H. C. Miller, N. E. Miller, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1456 (1964).

[2] This chemistry was first described in a communication: N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **85**, 3506 (1963).

[3] Icosaborane-16 was prepared independently by L. F. Friedman, R. D. Dobrott, and W. N. Lipscomb, *ibid.*, **85**, 3505 (1963).

[4] R. D. Dobrott, L. F. Friedman, and W. N. Lipscomb, *J. Chem. Phys.*, **40**, 866 (1964).