

CONTRIBUTION FROM THE RESEARCH LABORATORIES, ORGANICS DIVISION,  
OLIN MATHIESON CHEMICAL CORPORATION, NEW HAVEN, CONNECTICUT

## A New Series of Organoboranes. I. Carboranes from the Reaction of Decaborane with Acetylenic Compounds<sup>1</sup>

BY T. L. HEYING, J. W. AGER, JR., S. L. CLARK, D. J. MANGOLD,  
H. L. GOLDSTEIN, M. HILLMAN, R. J. POLAK, AND J. W. SZYMANSKI

Received June 14, 1963

Decaborane and certain of its derivatives reacted with acetylenic compounds in the presence of Lewis bases to produce members of a new class of organoboranes. The parent compound 1,2-dicarboclovododecaborane(12) has the formula  $B_{10}C_2H_{12}$  and various C and B substituted derivatives are reported. Unlike other higher boranes, this nucleus is quite impervious to attack by compounds containing active hydrogen and it does not attack reducible groups such as carbonyl or nitrile.

### Introduction

The reactions of decaborane with a variety of compounds of Lewis base classification have been described. One type of product from such reactions is the simple adduct,<sup>2</sup> while a second variety is typified by the compounds bis-(diethyl sulfide)-decaborane<sup>3</sup> and bis-(chlorodiphenylphosphine)-decaborane,<sup>4</sup> which are formed with the accompanying elimination of a molecule of hydrogen.

The reaction products from pentaborane and various Lewis bases have been studied,<sup>5</sup> and recently, members of a novel series of organoboranes of the general empirical formula  $B_nC_2H_{n+2}$  have been prepared by the reaction of pentaborane with acetylene.<sup>6</sup>

Consideration of these latter reactions along with the preparation and structure advanced<sup>7,8</sup> for the anion and  $B_{12}H_{12}^{-2}$  prompted interest in the reactions of decaborane and its various derivatives with acetylenic compounds.

Longuet-Higgins and Roberts<sup>9</sup> had demonstrated that the icosahedral structure as proposed for the  $B_{12}H_{12}^{-2}$  ion requires 26 bonding electrons aside from those participating in B-H bonds. The dodecaborate nucleus itself can contribute 24 such electrons and in the case in point, the twenty-fifth and twenty-sixth electrons are those present because of the double negative charge of the anion. A neutral  $B_{12}H_{12}$  species, therefore, is precluded by these considerations. It was postulated that if decaborane could react with acetylene, a stable entity similar to  $B_{12}H_{12}^{-2}$  might

form since the triple bond of acetylene could supply those electrons necessary for an icosahedral molecule.

### Discussion

The reactions of decaborane and suitable derivatives with acetylenic compounds were investigated employing a variety of conditions. The formation of a new entity was first observed from the reactions of bis-(acetonitrile)-decaborane with acetylene in refluxing benzene.<sup>10</sup> Upon further examination we determined that hydrogen was evolved and the material which was isolated had a chemical analysis which agreed with the empirical formula  $B_{10}C_2H_{12}$ . The fact that this was the composition of the molecule was proven by cryoscopic molecular weight determinations and detailed mass spectral analysis. Examination of the infrared and proton n.m.r. spectra as well as subsequent chemistry supported but did not unequivocally prove a closed icosahedral structure as in  $B_{12}H_{12}^{-2}$  where two of the adjacent boron atoms have been substituted for by carbon atoms. <sup>11</sup>B n.m.r. evidence also supporting this structure is presented elsewhere.<sup>11</sup> A detailed discussion and representation of such structures has been published.<sup>12</sup>

Reactions 1 and 2 which define the chemical steps can be conveniently combined and in practice conducted as indicated by reaction 3 without isolating the  $B_{10}H_{12}$ -(ligand)<sub>2</sub> intermediate. Further study of reaction 3 indicated that it would proceed when as little as 0.1 mole of Lewis base per mole of decaborane was present. The use of 0.9 mole of base has proven to be quite satisfactory for many syntheses since this ratio seems to afford good yields in a relatively short reaction period.

Types of Lewis bases other than acetonitrile including amines, dialkyl sulfides, and the cyclic ethers tetrahydrofuran and dioxane have been used with decaborane to effect this reaction. Reactions where the sul-

(1) Presented in part at the Conference on Current Trends in Organometallic Chemistry, University of Cincinnati, June, 1963.

(2) (a) A. Stock and E. Pohland, *Ber.*, **62B**, 90 (1929); (b) W. H. Hill and M. S. Johnson, *Anal. Chem.*, **27**, 1300 (1955); S. J. Fitch and A. W. Laubengayer, *J. Am. Chem. Soc.*, **78**, 3546 (1956).

(3) B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *ibid.*, **83**, 2669 (1961).

(4) H. A. Schroeder, J. R. Reiner, and T. L. Heying, *Inorg. Chem.*, **1**, 618 (1962).

(5) A. B. Burg, *J. Am. Chem. Soc.*, **79**, 2129 (1957); G. W. Campbell and L. Johnson, *ibid.*, **81**, 3800 (1959).

(6) R. E. Williams, C. D. Good, and I. Shapiro, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961; T. P. Onak, R. E. Williams, and H. G. Weiss, *J. Am. Chem. Soc.*, **84**, 2830 (1962); I. Shapiro, C. D. Good, and R. E. Williams, *ibid.*, **84**, 3837 (1962).

(7) A. R. Pitochelli and M. F. Hawthorne, *ibid.*, **82**, 3228 (1960).

(8) J. A. Wunderlich and W. N. Lipscomb, *ibid.*, **82**, 4427 (1960).

(9) H. C. Longuet-Higgins and M. deV. Roberts, *Proc. Roy. Soc. (London)*, **A230**, 110 (1955).

(10) M. Fein, private communication.

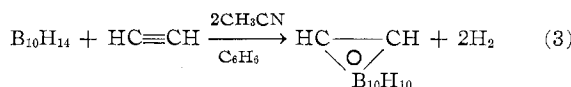
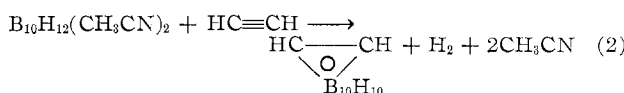
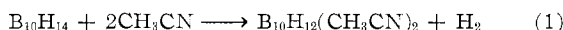
(11) Refer to paper II of this series: H. Schroeder, T. L. Heying, and J. R. Reiner, *Inorg. Chem.*, **2**, 1092 (1963).

(12) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962); R. Grimes, F. E. Wang, R. Lewin, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **47**, 996 (1961).

TABLE I  
 CARBORANYL HYDROCARBONS MADE BY DIRECT SYNTHESIS

	R	R'	R''	M.p., °C. <sup>a</sup>	Yield, %	B.p., °C. (mm).
I	H	H	H	320	65-77	...
II	CH <sub>3</sub>	H	H <sup>c</sup>	114-115	...	...
III	CH=CH <sub>2</sub>	H	H	78-79	65-70	...
	CH <sub>3</sub>					
IV	C=CH <sub>2</sub>	H	H <sup>c</sup>	45-46	70	...
V	<i>n</i> -C <sub>6</sub> H <sub>7</sub>	H	H <sup>c</sup>	62	...	...
VI	<i>n</i> -C <sub>4</sub> H <sub>7</sub>	H	H <sup>c</sup>	...	...	75(0.01)
VII	(CH <sub>2</sub> ) <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	H	H <sup>c</sup>	33	23	...
VIII	C <sub>6</sub> H <sub>5</sub>	H	H	66-67	27	...
IX	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	H	H <sup>c</sup>	...	...	101-102(0.5)
X	(CH <sub>2</sub> ) <sub>3</sub> C	H	H <sup>c</sup>	355-357	...	...
	CH					
	B <sub>10</sub> H <sub>10</sub>					
XI	H	H	C <sub>2</sub> H <sub>5</sub>	...	77	<sup>b</sup>

<sup>a</sup> Melting points were achieved on a Fisher-Johns apparatus and are uncorrected. <sup>b</sup> Consult Experimental section. <sup>c</sup> Mass spectral identification.



rides and ethers functioned both as the base and the solvent were successful but usually a solvent such as benzene, diethyl ether, or di-*n*-propyl ether was used. Since the reaction does not proceed at a reasonable rate below 70°, the reactions were conducted in an autoclave when a low boiling solvent was used. (The use of dioxane is not recommended since solutions of decaborane in it are shock sensitive.)

In addition to carborane itself, many C-alkyl and C-alkenyl derivatives were prepared by using the appropriate, substituted acetylene. Some symmetrical acetylenes such as 2-butyne or 3-hexyne would not react although unsymmetrical substituted acetylenes usually gave high yields of the corresponding carboranes. A summary showing the carboranyl hydrocarbons prepared by direct reaction of an acetylene with decaborane is given in Table I. Some products derived from boron-substituted decaboranes<sup>13,14</sup> are also included.

This reaction of decaborane also occurred with many functionally substituted acetylenic compounds, but compounds such as propargyl alcohol or acetylenedicarboxylic acid preferentially led to the destruction of the borane structure rather than producing the desired carborane. Table II lists the preparations of those substituted carboranes which were achieved by the direct reaction of decaborane with the corresponding substituted acetylene.

## Experimental

**Reagents.**—Unless specified to the contrary, reagents were used as received from various commercial sources. Decaborane was from the Olin Mathieson Chemical Corporation.

**Analyses.**—The elemental analysis of the carboranes by standard techniques sometimes produced results which were not quite acceptable. Boron analyses (Parr Bomb method) were usually 1-2% lower than theoretical and this was found to be due to boron carbide formation. Carbon analyses were sometimes 1-2% higher than theoretical, but the cause of this has not been ascertained. By employing cumbersome techniques, accurate analyses could be obtained and are herein reported for the fundamental compounds for which they were obtained.<sup>15</sup> It was found that mass spectrometric analysis of the reaction mixtures and products coupled with infrared analysis afforded an accurate means of identifying the carboranes and of establishing any impurities which were present. The method(s) of analysis in each instance is noted.

**Carborane (I).**—In a typical reaction, a 1-l., three-necked flask is equipped with an efficient paddle stirrer, an inlet tube reaching as near to the bottom of the flask as possible, and an adapter for installing a second gas inlet and a water-cooled condenser. An acetylene source is connected to a purification train consisting of first a tower containing granular alumina, next a scrubber of concentrated sulfuric acid, then a tower of solid sodium hydroxide, and finally the line is split to be attached in parallel to the two gas inlet tubes of the reaction vessel. In the flask a solution of 200 g. of decaborane in 225 ml. of di-*n*-propyl ether and 225 ml. of diethyl sulfide is prepared. The flask and contents are heated at 40 ± 5° for at least 12 hr. and then heated to 90 ± 5°, at which temperature acetylene is admitted at a rapid rate for 24 hr. The mixture is cooled and the volatile materials are removed under reduced pressure. The solvents may be collected and reused in succeeding preparations. The residue is dissolved by adding individually three 250-ml. portions of methanol and each portion is quickly poured into a 3-l., three-necked flask equipped with a magnetic stirrer, a water-cooled condenser, and an addition funnel. Provisions for cooling as needed are made. The mixture is stirred until the vigorous reaction has subsided (about 10 min.) and cooling may be necessary. Concentrated hydrochloric acid (200 ml.) is slowly added, with cooling to control the reaction, and the mixture allowed to stir for 30 min. Next, 100 ml. of acetone is added.

(13) R. L. Williams, I. Dunstan, and N. J. Blay, *J. Chem. Soc.*, 5006 (1960).

(14) E. R. Altwicker, A. B. Garrett, and E. A. Weilmuenster, U. S. Patent 2,999,117.

(15) Recently a new elemental analytical procedure has been reported which has proven very satisfactory for such compounds and was used in papers II and IV of this series: R. C. Rittner and R. Culmo, *Anal. Chem.*, **35**, 1268 (1963).

TABLE II  
 FUNCTIONALLY SUBSTITUTED CARBORANES PREPARED BY DIRECT SYNTHESIS

	R	R'	Yield, %	M.p., °C.	B.p., °C. (mm.)
XII	CH <sub>2</sub> Br	H <sup>a</sup>	70	30	...
XIII	COOCH <sub>3</sub>	H <sup>a</sup>	35	73	...
XIV	CH <sub>2</sub> Cl	CH <sub>2</sub> Cl <sup>a</sup>	74	119-120	...
XV	CH <sub>2</sub> OOCCH <sub>3</sub>	H <sup>a</sup>	83	42-43	82-84 (0.2)
XVI	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	Br <sup>a</sup>	66	44-45	107 (1)
XVII	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	Br <sup>b,e</sup>	37	...	85-90 (0.5)
XVIII	(CH <sub>2</sub> ) <sub>2</sub> OOCCH <sub>2</sub>	H	72	61-63	146 (1.6)
XIX	CH(OOCCH <sub>3</sub> )CH <sub>3</sub>	H <sup>a</sup>	66	...	85-95 (0.2)
XX	CH <sub>2</sub> N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	H <sup>a</sup>	(4) <sup>d</sup>	33-35	...
XXI	CH <sub>2</sub> OOCCH <sub>3</sub>	CH <sub>2</sub> OOCCH <sub>3</sub> <sup>a</sup>	89	43-44	...
XXII	COOCH <sub>3</sub>	COOCH <sub>3</sub>	54	66-67	...

<sup>a</sup> *n*<sup>21</sup>D 1.5291. <sup>b</sup> *n*<sup>23</sup>D 1.5500. <sup>c</sup> Hydrochloride m.p. >300°. <sup>d</sup> >50%, but not all was recovered. <sup>e</sup> Mass spectral identification.

A very vigorous reaction occurs initially but subsides after about 20 ml. has been added. The resulting mixture is allowed to stir overnight.

The mixture is poured into approximately 16 l. of water (80-85°) and after 30 min. the yellow precipitate which has accumulated on the surface is removed and allowed to drain. The wet solid is next dissolved in 800 ml. of methanol and a solution of 40 g. of sodium hydroxide, dissolved in a minimum amount of water, is added with vigorous stirring. This solution is quickly poured into 3 l. of cold water, and the resulting precipitate is removed by filtration, washed with cold water, and allowed to air-dry for 24 hr.

The product is ground to a powder and mixed with an equal amount of anhydrous calcium chloride and placed in a large Soxhlet thimble for extraction with 1 l. of pentane for 24 hr. The pure white product crystallizes in the pentane extract. When the extraction is complete, the pentane may be decanted and used in succeeding preparations or evaporated to completely recover the product. By this procedure 153-180 g. of pure white carborane (65-77% yield) is obtained.

*Anal.* Calcd. for B<sub>10</sub>C<sub>2</sub>H<sub>12</sub>: C, 16.7; H, 8.3; B, 75.0; mol. wt., 144. Found: C, 16.9; H, 8.4; B, 74.9; mol. wt., 147, 145 (cryoscopic in benzene); *m/e* 144.

Through many experiments it has been found that carborane can be obtained in highest yield and purity suitable for any synthesis purpose by utilizing the method described. Smaller quantities may be purified by vacuum sublimation after the treatment with hydrochloric acid in methanol and acetone. Other less cumbersome modes of purification have resulted in poorer recovery and the product contained impurities which interfered with some subsequent reactions.

**1-Vinylcarborane (III).**—In a typical experiment a 5-l., 3-necked flask is equipped with a 500-ml. graduated dropping funnel, a nitrogen inlet tube, and a straight bore water condenser topped by a Dry Ice condenser which is vented through a Nujol-filled trap. Agitation is achieved *via* a magnetic stirrer and the reactor is warmed by use of a suitable heating mantle. Decaborane (454 g.), ethyl sulfide (360 ml. or 0.9 mole/mole of decaborane), and toluene (2700 ml.) are mixed thoroughly in the reactor and allowed to stand overnight under nitrogen. This mixture is then heated with stirring (to 80-90°) for 1 hr. and the temperature is adjusted to 85°, whereupon 450 ml. of a cold solution of vinylacetylene in xylene (1:1 by weight) is added dropwise. The addition usually requires 1.5-2 hr. to maintain the reaction temperature between 90 and 100°. After the addition is complete, reflux is maintained for 1.5-2 hr. and the mixture is allowed to cool and stand overnight. The apparatus is then arranged so that the bulk of the solvent may be evaporated with the aid of a water aspirator and this is continued until the volume becomes less than 1 l. The solvents may be recovered and reused. The remainder is transferred to a 1-l. flask fitted with a Claisen head to which is attached a series of detachable glass bulbs in which the product condenses and is

collected. The mixture is distilled at 0.5-1.0 mm. pressure until the flask temperature reaches 135-140°. 1-Vinylcarborane distills at 75-80° at 0.5 mm. pressure. Yields of 65-70% of theoretical are obtained. The product as recovered is suitable for many synthesis purposes but can be further purified as follows. The solid is dissolved in methanol and distilled water is added until, with gentle warming, solution is maintained. The solution is then cooled to 0° and the precipitated product is removed. If the filtrate is treated with additional water and the cooling repeated, essentially quantitative recovery of the product is achieved. 1-Vinylcarborane treated in this manner melts at 78-79°.

*Anal.* Calcd. for B<sub>10</sub>C<sub>4</sub>H<sub>14</sub>: C, 28.2; H, 8.2; B, 63.8; mol. wt., 170. Found: C, 28.6; H, 8.5; B, 63.6; mol. wt., 172 (cryoscopic).

**1-Phenylcarborane (VIII).**—Phenylacetylene (3 g.) and bis-(acetonitrile)-decaborane (5 g.) in 50 ml. of benzene were refluxed for 2 hr. After cooling and filtering, the filtrate was treated with trimethylamine and the resulting mixture was also filtered. On evaporation of the filtrate and recrystallization of the residue from pentane, 1-phenylcarborane was obtained in 27% yield.

*Anal.* Calcd. for B<sub>10</sub>C<sub>8</sub>H<sub>16</sub>: C, 43.6; H, 7.3; B, 49.2. Found: C, 44.4; H, 7.9; B, 48.7.

**B-Ethylcarborane (XI).**—The preparation of B-ethylcarborane from monoethyldecaborane containing two isomers (60% 2- and 40% 1-substitution) was conducted in at least twenty different manners. In all cases the product varied only in the ratio of the isomeric B-ethylcarboranes obtained. This could be ascertained through infrared and mass spectrometric analysis and was reflected in slight differences in refractive index. In general, di-*n*-butyl ether was found to be the best solvent for this reaction and di-*n*-propyl sulfide, di-*n*-butyl sulfide, and *n*-butyl methyl sulfide were the desired Lewis bases. With these materials, yields ranged from 70 to 83%. A typical experiment giving 77% yield is described.

A solution of 100 g. of ethyldecaborane in 84.4 g. of *n*-butyl methyl sulfide in 114.7 g. of di-*n*-butyl ether is placed in a 1-l., 3-necked flask equipped with a high speed, turbine-drive stirrer (5000 r.p.m.), a water-cooled condenser, and a sintered glass gas delivery tube reaching to near bottom of the flask. An oil bath is provided. The stirred mixture is slowly heated to 110° and acetylene, purified as in the preparation of I, is admitted at a rate of 90 cc./min. for 8 hr. Initially, the reaction foams vigorously but after 2-3 hr. subsides as the color changes from light yellow to burnt orange.

The mixture is cooled and the volatile materials are removed under reduced pressure. The residue is transferred to a 250-ml. flask and, using a modified Claisen-type still head having a cold-finger condenser and liquid fractionating take-off, is distilled under reduced pressure. Distillation is allowed to proceed until the overhead temperature has risen from 70° (0.3 mm.) to 110° (2.5 mm.). The distillation is stopped to avoid decomposition of the sulfur-containing residue. The pot temperature is not

allowed to go above 150°. Redistillation gives 89.1 g. of product distilling at 70° (0.3 mm.) (*i.e.*,  $n_D^{25}$  1.5375) while the bath temperature is maintained below 170°.

By infrared, mass spectra, and  $^{11}\text{B}$  n.m.r. analysis the product is identified as a mixture of two isomers of B-ethylcarborane. In addition, values of 62.7 and 62.8% boron (theory for  $\text{B}_{10}\text{C}_4\text{H}_{17}$  is 62.8) were found.

**1-( $\beta$ -Acetoxyethyl)-carborane (XVIII).**—A solution of 4.0 g. (0.0327 mole) of decaborane, 4.5 g. (0.0402 mole) of 3-butyn-1-yl acetate, and 1.5 g. (0.037 mole) of acetonitrile in 30 ml. of benzene was refluxed for 103 hr. The solvent was removed and 5.17 g. (71.7%) of liquid which solidifies to a white solid distilled at 108–118° (0.3 mm.). Mass spectrometric and infrared analysis showed it to be essentially pure 1-( $\beta$ -acetoxyethyl)-carborane.

*Anal.* Calcd. for  $\text{B}_{10}\text{C}_8\text{H}_{18}\text{O}_2$ : C, 31.2; H, 7.9. Found: C, 31.7; H, 7.9.

**1-( $\alpha$ -Acetoxyethyl)-carborane (XIX).**—A solution of 4.0 g. (0.0327 mole) of decaborane, 4.5 g. (0.0402 mole) of 3-butyn-2-yl acetate, and 1.5 g. (0.0366 mole) of acetonitrile in 30 ml. benzene was refluxed for 95 hr. The benzene was removed and the residue was distilled at 85–95° (0.15–0.2 mm.) to recover 4.75 g. (65.7%) of a slightly yellow liquid,  $n_D^{25}$  1.5291. Mass spectrometric and infrared examination indicated it to be essentially pure 1-( $\alpha$ -acetoxyethyl)-carborane.

*Anal.* Calcd. for  $\text{B}_{10}\text{C}_8\text{H}_{18}\text{O}_2$ : C, 31.2; H, 7.88. Found: C, 33.0; H, 7.81.

**1-(N,N-Dimethylaminomethyl)-carborane (XX).**—A solution of 6.1 g. of decaborane and 5.5 g. of N,N-diethylamino-2-propyne in 50 ml. of benzene was refluxed for 7.5 hr. After cooling, the mixture was filtered and the filtrate was extracted with dilute hydrochloric acid. The acid was neutralized and the amine which is released was recovered in ether. Isolation and recrystallization from pentane gives a waxy, white solid.

*Anal.* Calcd. for  $\text{B}_{10}\text{C}_7\text{H}_{28}\text{N}$ : C, 36.7; H, 10.1; B, 47.2; N, 6.1. Found: C, 37.1; H, 9.8; B, 45.8; N, 6.4.

**Other Compounds Reported.**—A number of compounds herein

reported which are merely other examples of the fundamental reaction type were identified by a combination of infrared and detailed mass spectral analysis. The parent spectral peak (accounting for the normal isotopic distribution of boron) and the breakdown pattern were very characteristic and conclusively identified the compounds as well as indicating and often establishing minor impurities which would then have to be removed to obtain the pure product.

Compounds which were so identified are indicated in Tables I and II. They can be prepared from decaborane and the corresponding acetylenic compound by adapting one of the techniques above.

**Dimethyl Carborane-1,2-dicarboxylate (XXII).**—A mixture of 18.0 g. of bis(acetonitrile)-decaborane, 15 g. of dimethyl acetylenedicarboxylate, and 50 ml. of toluene was refluxed for 22 hr. The toluene was removed under reduced pressure and the residue was treated with pentane to extract the product. Recrystallization from pentane gave 12.5 g. (53.6%) of dimethyl carborane-1,2-dicarboxylate.

*Anal.* Calcd. for  $\text{B}_{10}\text{C}_8\text{H}_{16}\text{O}_4$ : C, 27.7; H, 6.1; B, 41.7. Found: C, 28.0; H, 6.3; B, 41.6.

**Acknowledgments.**—This research was supported in large part by the United States Air Force under Contract AF 33(616)-5934 monitored by the Propulsion Laboratories, Air Force Flight Test Center, Edwards Air Force Base, California, and partly by the Office of Naval Research. The authors are grateful for the assistance of Dr. J. H. Norman, who interpreted the mass spectra, through which many of the compounds were initially identified, and who contributed many helpful suggestions. R. P. Alexander and J. A. Reid contributed experimental data.

CONTRIBUTION FROM THE ORGANICS DIVISION,  
OLIN MATHIESON CHEMICAL CORPORATION, NEW HAVEN, CONNECTICUT

## A New Series of Organoboranes. II. The Chlorination of 1,2-Dicarboclovododecaborane(12)<sup>1</sup>

BY HANSJUERGEN SCHROEDER, THEODORE L. HEYING, AND JOSEPH R. REINER

Received January 2, 1963

A detailed investigation of the chlorination of a new series of organoboranes derived from decaborane-14 resulted in the stepwise formation of a number of chlorocarboranes containing from two to eleven chlorine atoms per molecule. Some of their chemical characteristics are described; a detailed  $\text{B}^{11}$  n.m.r. treatment of the parent carborane ( $\text{B}_{10}\text{H}_{10}\text{C}_2\text{H}_2$ ),  $\text{B}_{10}\text{Cl}_{10}\text{C}_2\text{H}_2$ , and  $\text{B}_{10}\text{Cl}_9\text{C}_2\text{HCl}$  as related to structural considerations is presented.

Semiorganic derivatives of higher boron hydrides have become of considerable interest because of their peculiar structure and the theoretical and chemical consequences which could be envisioned for them. Products derived from reactions of pentaborane-9 and acetylenes have been described in the literature,<sup>2</sup> but unfortunately, the parent compounds (carboranes)  $\text{B}_n\text{C}_2\text{H}_{n+2}$  can be obtained only in very small amounts

by means of complicated techniques.

These considerations prompted us to investigate another member of this series derived from decaborane-14 and which may be prepared in substantial quantities. A general method for synthesis of higher carborane derivatives of the formula  $\text{B}_{10}\text{H}_{10}\text{C}_2\text{R}_2$ , the parent compound of which is 1,2-dicarboclovododecaborane(12) ( $\text{B}_{10}\text{H}_{10}\text{C}_2\text{H}_2$ ),<sup>3</sup> has been reported in detail.<sup>4</sup>

(1) Presented in part at the conference on Current Trends in Organometallic Chemistry, University of Cincinnati, June, 1963.

(2) R. E. Williams, C. D. Good, and I. Shapiro, 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961; T. P. Onak, R. E. Williams, and H. G. Weiss, *J. Am. Chem. Soc.*, **84**, 2830 (1962); I. Shapiro, C. D. Good, and R. E. Williams, *ibid.*, **84**, 3837 (1962).

(3) For brevity, in this series of publications the term carborane is used for 1,2-dicarboclovododecaborane(12).

(4) Paper I of this series: T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963).