The color then became green due to the blue color caused by a small amount of excess sodium. The ammonia was evaporated to leave a yellow solid that decomposed violently in water and less rapidly in air.

Reaction with Lithium in Liquid Ammonia.—In a similar fashion 0.058 g.-atom of lithium added to 0.015 mole of the alkenylcarborane. At the first addition a red color appeared which persisted through subsequent addition until the total quantity had been added. The color than became dark green. Evaporation of the ammonia resulted in a product with properties as described above.

Reaction of 1-Isopropylcarborane with Sodium.—With the technique used above for the isopropenylcarborane–sodium reaction, it was found that 0.0449 g.-atom of sodium caused a lasting green color with 0.0223 mole of 1-isopropylcarborane. The product reacted violently with water.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, REACTION MOTORS DIVISION,
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Carboranes. II.[1] The Preparation of 1- and 1,2-Substituted Carboranes

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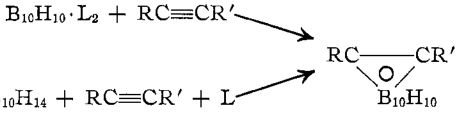
The broad applicability of the conversion of mono- and disubstituted acetylenes to carboranes by treatment with decaborane and Lewis bases is demonstrated. The resultant carboranes may then be treated as typically organic, covalent products and, by usual synthetic procedures, converted to other carboranes. The formation of typical Grignard reagents from haloalkylcarboranes is reported.

Introduction

The formation of carboranes by treatment of acetylenic compounds with decaborane–Lewis base (L) mixtures, or by treatment with $B_{10}H_{12}\cdot L_2$ compounds, has been reported in the previous paper of this series.[1]



This investigation was undertaken to better define R and R′ and to study some of the chemical transformations made possible by the stability of the carborane nucleus.

Results and Discussion

A wide variety of terminal and internal mono- and diacetylenes were treated with 6,9-bis-(acetonitrile)-decaborane, 6,9-bis-(diethyl sulfide)-decaborane, or decaborane in the presence of these ligands. The carboranylation reaction was universal for compounds of the type RC≡CH except when the group R contained a functionality capable of destroying the borane precursor, *e.g.*, $-CH_2OH$ and $-CO_2H$. Esterification of these reactive groups followed by treatment with 6,9-bis-(acetonitrile)-decaborane resulted in normal conversion of RC≡CH to the corresponding carborane. In Table I are presented those 1-substituted carboranes which were prepared by direct treatment of the acetylenic precursor; also included are experimental data, analytical results, and physical properties.

After a sufficient number of the 1-substituted carboranes had been prepared, the characteristic infrared absorption bands were established for monosubstituted carboranes and in several cases identification was established by infrared spectroscopy. Thus, conversion of 1-pentyne to 1-*n*-propylcarborane proceeded as expected to form a solid product, which was identified as a 1-*n*-alkylcarborane by infrared spectroscopy. Comparison of the spectra of 1-ethyl-, 1-hexyl- and 1-isopropylcarborane helped to establish the identity of the 1-*n*-propyl derivative; elemental analysis was not deemed essential.

Conversion of RC≡CR′ to carborane derivatives also proceeded smoothly to give varying yields of the desired products. The lowest yields were obtained when R and R′ were alkyl groups, and the products of this type (from 2-butyne and 2-pentyne) were obtained in trace quantities. Evidence for their formation was obtained by infrared analysis of the incompletely purified products. Thus, in the case of 2-pentyne, trace quantities of 1-methyl-2-ethylcarborane were obtained under conditions which resulted in greater than 50% yield of 1-propylcarborane from 1-pentyne. When R and R′ were alkenyl, as in diisopropenylacetylene, somewhat higher yields (15%) were obtained. In other cases (haloalkyl, esters) the yields were sigficantly higher. The internally acetylenic alcohols and acids also decomposed the borane precursors, and, as was the case with the terminal acetylenes, it was necessary to esterify the –OH and $-CO_2H$ functionali-

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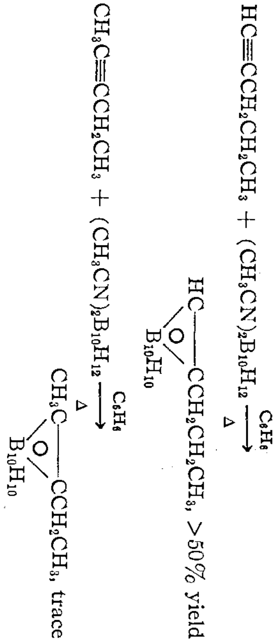
[1] For paper I see M. Fein, *et al.*, *Inorg. Chem.*, **2**, 1111 (1963).

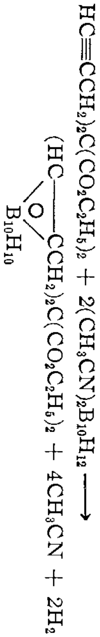


$$HC\equiv CCH_2CH_2CH_3 + (CH_3CN)_2B_{10}H_{12} \xrightarrow[\Delta]{C_6H_6} \underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{HC\text{——}CCH_2CH_2CH_3}, >50\% \text{ yield}$$

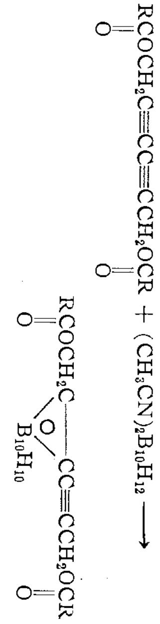
$$CH_3C\equiv CCH_2CH_3 + (CH_3CN)_2B_{10}H_{12} \xrightarrow[\Delta]{C_6H_6} \underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{CH_3C\text{——}CCH_2CH_3}, \text{ trace}$$

ties. For example, the direct treatment of 2-butyne-1,4-diol with 6,9-bis-(acetonitrile)-decaborane resulted in a highly exothermic reaction followed by combustion, whereas similar treatment of the esterified diol 1,4-diacetoxy-2-butyne proceeded smoothly to give the anticipated carborane derivative. The compounds prepared by direct treatment of RC≡CR′ are presented in Table II as well as the necessary supporting data.

The preparation of biscarboranyl compounds by the treatment of selected diacetylenes was also attempted (Table III). Conversion of 1,6-heptadiyne to the biscarboranyl propane has been discussed.[1] Treatment of diethyl dipropargyl malonate with $(CH_3CN)_2B_{10}H_{12}$ resulted in the preparation of the dicarborane product, diethyl bis-(1-carboranylmethyl)-malonate, in good yield. By contrast, treatment of diacetylenes such as the dibenzoate and diacetate esters of 2,4-hexadiyne-1,6-diol resulted in the formation of the monocarborane as the major product along with traces of the dicarborane, despite the use of a significant excess of 6,9-bis-(acetonitrile)-decaborane



$$(HC\equiv CCH_2)_2C(CO_2C_2H_5)_2 + 2(CH_3CN)_2B_{10}H_{12} \longrightarrow (\underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{HC\text{——}CCH_2})_2C(CO_2C_2H_5)_2 + 4CH_3CN + 2H_2$$



$$R\underset{\underset{O}{\|}}{C}OCH_2C\equiv CC\equiv CCH_2O\underset{\underset{O}{\|}}{C}R + (CH_3CN)_2B_{10}H_{12} \longrightarrow R\underset{\underset{O}{\|}}{C}OCH_2\underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{C\text{——}C}C\equiv CCH_2O\underset{\underset{O}{\|}}{C}R$$

R = CH_3, C_6H_5

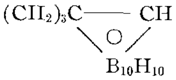
The resistance of the carborane nucleus to solvolysis or chemical degradation[1] made it apparent that many of the compounds prepared by direct conversion of the acetylenes to carboranes could be further treated to prepare new mono- and difunctional carboranes.

Treatment of 1-bromomethylcarborane under typical Grignard conditions resulted in the formation of 1-carboranylmethylmagnesium bromide. The ease with which this Grignard reagent is formed differs markedly from the reaction of iododecaborane with magnesium.[2] The carboranyl Grignard reagent entered into the standard reactions; condensations with ketones, allyl halides, and alkyl halides proceeded with ease. The chemistry of these reactions is presented in subsequent papers.[3,4] Hydrolysis of the Grignard with water resulted in the formation of 1-methylcarborane,

TABLE I

1-SUBSTITUTED CARBORANES PREPARED FROM RC≡CH

R[a]	Method of syn.[b]	Solvent	Time at reflux, hr.	m.p., °C.	B.p., °C. (mm.)	Analytical								n^{25}D
						Calculated				Found				
						C	H	B	Hal.	C	H	B	Hal.	
CH_3CH_2	A	$C_6H_5CH_3$	12	. . .	75–80 (0.5)	27.87	9.36	62.77	. . .	27.58	9.48	62.36	. . .	. . .
$CH_3CH_2CH_2$	B	C_6H_6	3	68–69	. . .	Identified by infrared analysis								
$CH_3(CH_2)_4CH_2$	A	$C_6H_5CH_3$	12.5	. . .	101–102 (0.5)	42.05	10.59	47.36	. . .	41.28	11.08	47.18	. . .	1.5211
$CH_2{=}CH$	C	$C_6H_5CH_3$	3	76–77	. . .	28.20	8.28	63.52	. . .	28.71	8.37	63.68	. . .	. . .
C_6H_5	A	CH_3CN	18	69.5–70	. . .	43.59	7.32	49.09	. . .	43.72	7.45	49.18	. . .	. . .
$BrCH_2CH_2$	A	CH_3CN	5	114–115	. . .	19.12	6.02	43.06	31.81	18.67	6.01	42.33	31.95	. . .
$ClCH_2$	A	CH_3CN	7	83–85	. . .	18.69	6.80	56.12	. . .	18.84	7.09	56.32	. . .	. . .
$ClCH_2CH_2$	B	$C_6H_5CH_3$	7	80–82	. . .	23.23	7.31	52.32	17.14	23.17	7.40	53.60	17.78	. . .
$ClCH_2CH_2CH_2$	A	CH_3CN	16	53–55	170 (10)	27.39	7.76	48.99	16.06	27.06	7.68	48.47	15.90	. . .
$CH_3C({=}O)OCH_2$	B	$C_6H_5CH_3$	27	48–48.5	110 (0.5)	27.75	7.45	50.01	. . .	27.81	7.56	51.20	. . .	. . .
$CH_2{=}CHC({=}O)OCH_2$	B	$C_6H_5CH_3$	20	. . .	98 100 (0.2)	31.55	7.06	47.37	. . .	31.5	7.64	48.3	. . .	1.5390
$(CH_3C({=}O)OCH_2)_2CHCH_2$	B	$C_6H_5CH_3$	18	. . .	180–184 (0.3)	37.95	7.64	34.19	. . .	38.46	7.98	32.62	. . .	. . .
$(CH_3CH_2OC({=}O))_2CHCH_2$	B	$C_6H_4(CH_3)_2$	3	. . .	144–148 (0.2)	37.95	7.64	34.19	158.2[c]	39.	7.95	34.7	157.3[c]	. . .
$(CH_3CH_2OC({=}O))_2C(CH_3)CH_2$	B	C_6H_6	10	. . .	164 (0.5)	39.97	7.93	32.74	. . .	40.68	7.31	32.93	. . .	1.5131



[a] For R = H, CH_3, CH_2Br, $C(CH_3){=}CH_2$, and $\underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{(CH_2)_3C\text{——}CH}$; see ref. 1. [b] Preparation A, $B_{10}H_{14} + CH_3CN + RC\equiv CH$; B, $(CH_3CN)_2B_{10}H_{12} + RC\equiv CH$; C, $B_{10}H_{14} + (C_2H_5)_2S + RC\equiv CH$. [c] Saponification equivalent.

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[2] B. Siegel, J. L. Mack, J. U. Lowe, and J. Gallaghan, *J. Am. Chem. Soc.*, **80**, 4523 (1958).

[3] D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *Inorg. Chem.*, **2**, 1120 (1963).

[4] N. Schwartz, S. Karlan, E. O'Brien, and M. M. Fein, to be published.

TABLE II

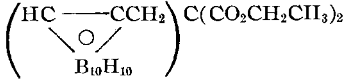
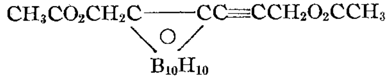
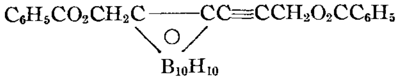
1,2-DISUBSTITUTED CARBORANES PREPARED FROM $RC{\equiv}CR'$

							Analytical							
							Calculated				Found			
R[a]	R′	Method of syn.[b]	Solvent	Time at reflux, hr.	M.p., °C.	B.p., °C. (mm.)	C	H	B	Hal.	C	H	B	Hal.
$\underset{\underset{CH_3}{\vert}}{CH_2{=}C}$	$\underset{\underset{CH_3}{\vert}}{C{=}CH_2}$	B	$C_6H_5CH_3$	24	82–83	. . .	42.81	8.98	48.21	. . .	41.50	9.17	48.28	. . .
$ClCH_2$	CH_2Cl	B	$ClCH_2C{\equiv}CCH_2Cl$	. .[c]	114–115	. . .	19.99	5.85	44.84	29.39	20.48	5.98	44.3	29.02
$\underset{\underset{O}{\Vert}}{CH_3OC}$	$\underset{\underset{O}{\Vert}}{COCH_3}$	B	$C_6H_5CH_3$	18	52–54	108 (0.5)	27.67	6.19	41.47	130.2[d]	27.73	6.52	42.11	132.8[d]
CH_3	CH_2Br	A	CH_3CN	4	125–127	. . .	19.12	6.02	43.06	31.80	19.73	6.18	43.83	30.70

For R = R′ = C_6H_5, $\underset{\underset{O}{\Vert}}{CH_3COCH_2}$, $BrCH_2$, see ref. 1. [b] Preparation A, $B_{10}H_{14} + CH_3CN + RC{\equiv}CR'$; B, $(CH_3CN)_2B_{10}H_{12} + RC{\equiv}CR'$. [c] Two min. at 60°. [d] Saponification equivalent.

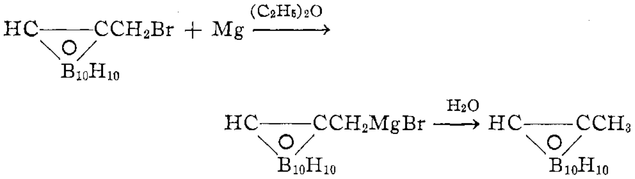
TABLE III

CARBORANES PREPARED FROM DIACETYLENES,[a] $RC{\equiv}CR'$

R	H	$CH_3CO_2CH_2$	$C_6H_5CO_2CH_2$
R′	$CH_2C(CO_2C_2H_5)_2CH_2C{\equiv}CH$	$C{\equiv}CCH_2O_2CCH_3$	$C{\equiv}CCH_2O_2CC_6H_5$
Product	 $\left(\underset{B_{10}H_{10}}{\overset{HC\text{——}CCH_2}{\diagdown O \diagup}}\right)C(CO_2CH_2CH_3)_2$	 $\underset{B_{10}H_{10}}{\overset{CH_3CO_2CH_2C\text{——}CC{\equiv}CCH_2O_2CCH_3}{\diagdown O \diagup}}$	 $\underset{B_{10}H_{10}}{\overset{C_6H_5CO_2CH_2C\text{——}CC{\equiv}CCH_2O_2CC_6H_5}{\diagdown O \diagup}}$
Method[b]	B	B	B and C
Solvent	$C_6H_5CH_3$	$C_6H_5CH_3$	CH_3CN-$C_6H_5CH_3$
Time at reflux, hr.	26	19	5 and 17
Melting point, °C.	198–199	. . .	250
Analytical		Structure confirmed by infrared analysis; product used for conversion to the corresponding diol	Structure confirmed by infrared analysis; product used for conversion to the corresponding diol
C (Calcd.)	33.02		
C (Found)	33.09		
H (Calcd.)	7.67		
H (Found)	8.02		
B (Calcd.)	45.77		
B (Found)	45.38		

[a] For R = H and R′ = $(CH_2)_3C{\equiv}CH$, see ref. 1. [b] Preparation B, $(CH_3CN)_2B_{10}H_{12} + RC{\equiv}CR'$; C, $[(C_2H_5)_2S]_2B_{10}H_{12} + RC{\equiv}CR'$.

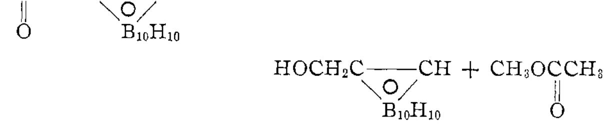
identical with the product prepared from propyne and 6,9-bis-(acetonitrile)-decaborane.



$$\underset{B_{10}H_{10}}{HC\text{—}CCH_2Br} + Mg \xrightarrow{(C_2H_5)_2O} \underset{B_{10}H_{10}}{HC\text{—}CCH_2MgBr} \xrightarrow{H_2O} \underset{B_{10}H_{10}}{HC\text{—}CCH_3}$$

The other haloalkylcarboranes presented in Table I also entered into Grignard formation and transformations.

The various esters of the carborane alcohols were readily transesterified with methanol and hydrogen chloride to the alcohols; 1-acetoxymethylcarborane was thus converted to 1-hydroxymethylcarborane.

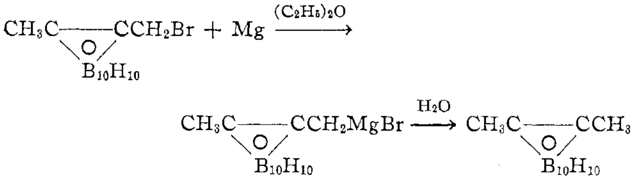


$$\underset{B_{10}H_{10}}{CH_3\overset{}{\underset{\|O}{C}}OCH_2C\text{—}CH} + CH_3OH \xrightarrow{HCl} \underset{B_{10}H_{10}}{HOCH_2C\text{—}CH} + CH_3O\underset{\|O}{C}CH_3$$

The co-existence of a $-CH_2OH$ group and a boron hydride group in the same molecule is once again evidence of the stability of the carborane nucleus.

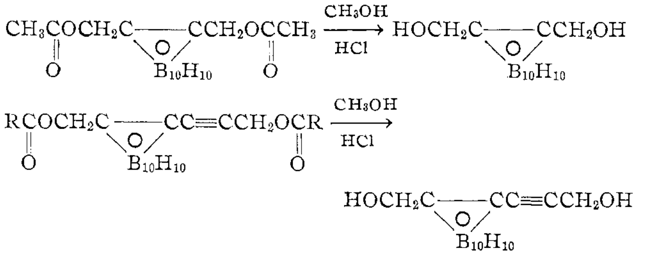
The saponification of the esters of the carboranylcarboxylic acids was effected with somewhat greater difficulty. The saponifications are discussed in a subsequent paper.[3]

The 1,2-disubstituted carboranes tabulated in Table II, as well as those presented in the previous paper,[1] underwent reactions similar to those of their 1-substituted analogs. Thus, 1-bromomethyl-2-methylcarborane formed a Grignard reagent which entered into the usual reactions and which could be hydrolyzed to 1,2-dimethylcarborane.



$$\underset{B_{10}H_{10}}{CH_3C\text{—}CCH_2Br} + Mg \xrightarrow{(C_2H_5)_2O} \underset{B_{10}H_{10}}{CH_3C\text{—}CCH_2MgBr} \xrightarrow{H_2O} \underset{B_{10}H_{10}}{CH_3C\text{—}CCH_3}$$

The transesterification of diesters of the 1,2-carboranediols proceeded with the same ease as that of 1-acetoxymethylcarborane.



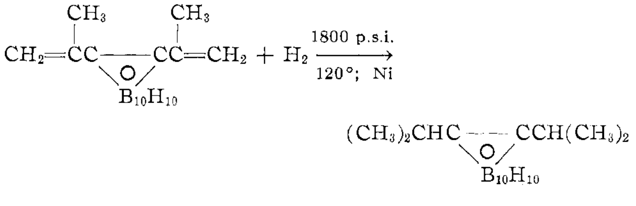
$$\underset{B_{10}H_{10}}{CH_3\underset{\|O}{C}OCH_2C\text{—}CCH_2O\underset{\|O}{C}CH_3} \xrightarrow[HCl]{CH_3OH} \underset{B_{10}H_{10}}{HOCH_2C\text{—}CCH_2OH}$$

$$\underset{B_{10}H_{10}}{R\underset{\|O}{C}OCH_2C\text{—}CC{\equiv}CCH_2O\underset{\|O}{C}R} \xrightarrow[HCl]{CH_3OH} \underset{B_{10}H_{10}}{HOCH_2C\text{—}CC{\equiv}CCH_2OH}$$

$R = CH_3, C_6H_5$

Transesterification of 1,2-bis-(acetoxymethyl)-carborane resulted in high conversion to 1,2-bis-(hydroxymethyl)-carborane. 1-Hydroxymethyl-2-(γ-hydroxy-α-propynyl)-carborane was formed from the acetylenic carborane diesters.

The reduction of 1,2-diisopropenylcarborane proved to be considerably more difficult than that of the monoisopropenyl derivative. Whereas 1-isopropenylcarborane was reduced readily with hydrogen at 50 p.s.i.[1] in the presence of nickel catalysts, the conditions required for reduction of the disubstituted product were considerably more stringent (1800 p.s.i.). In fact, quantitative recovery of 1,2-diisopropenylcarborane resulted when nickel (50 p.s.i.) or Pt-charcoal (50 p.s.i.) was used.



$$\underset{B_{10}H_{10}}{CH_2{=}\overset{CH_3}{C}C\text{—}C\overset{CH_3}{C}{=}CH_2} + H_2 \xrightarrow[120°;\ Ni]{1800\ p.s.i.} \underset{B_{10}H_{10}}{(CH_3)_2CHC\text{—}CCH(CH_3)_2}$$

Experimental[5]

Reagents.—The decaborane used in this work was obtained from Callery Chemical Corp., American Potash and Chemical Corp., and Olin Mathieson Chemical Corp. and was recrystallized from heptane prior to use. The majority of the acetylenic materials were obtained from General Aniline and Film Corp., Air Reduction Co., Inc., and E. I. du Pont Co., Inc., and were used as received. Others were prepared in this laboratory by conventional techniques, as noted below.

All yield figures are based upon the boron hydride charged in the reaction. Melting points are uncorrected.

Instrumentation.—Infrared data were obtained on a Perkin-Elmer Model 21 recording spectrophotometer.

Preparation of 1- and 1,2-Substituted Carboranes.—Since the compounds listed in Tables I, II, and III were prepared according to the same general reaction and by similar techniques, a complete preparative description of each compound is not given. To avoid unnecessary repetition, only selected preparations illustrative of the general methods are described. Key reaction conditions for the other carborane derivatives are listed in Tables I, II, and III.

1-Chloromethylcarborane.—Propargyl chloride, 0.2 mole, was added to a refluxing solution of 0.1 mole of decaborane in 100 ml. of acetonitrile. After 18 hr. at reflux, the reaction mixture was cooled and filtered, and the acetonitrile was removed from the filtrate by distillation. The residue was dissolved in methanol, and after gas evolution ceased, the solution was concentrated and the residue extracted with hot hexane. The hexane was removed by distillation, and the residue, a yellow oil, was purified by sublimation (twice) to give 12.5 g. (64%) of white crystals, m.p. 83–85°.

Anal. Calcd. for $C_3H_{13}B_{10}Cl$: C, 18.69; H, 6.80; B, 56.12. Found: C, 18.84; H, 7.09; B, 56.32.

1-Vinylcarborane.—A mixture of 0.46 mole of decaborane, 0.44 mole of diethyl sulfide, and 350 ml. of toluene was heated at 80–85° for 1 hr. A small amount of di-*t*-butylcatechol was then added, followed by the addition of 80 ml. of a nominal 50% xylene solution of vinylacetylene over a period of 45 min. After this addition was complete, heating (at 80–85°) was continued for 3 hr. The mixture was cooled, then treated with trimethylamine for 30 min. and filtered, and the solvents were removed by distillation. The residue was distilled *in vacuo* and a 40-g. fraction collected (51% yield), b.p. 75–77° (0.5 mm.). Recrystallization from methanol–water followed by drying over phosphorus pentoxide yielded a white solid product, m.p. 76–77°.

Anal. Calcd. for $C_4H_{14}B_{10}$: C, 28.20; H, 8.28; B, 63.52. Found: C, 28.71; H, 8.37; B, 63.68.

1,2-Dimethylcarboranyldicarboxylate.—A mixture of 0.69 mole of $(CH_3CN)_2B_{10}H_{12}$, 0.70 mole of dimethylacetylene dicarbox-

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(5) We are grateful to Mr. Lawrence G. Adlum for spectral data, to Mr. Frederick G. Hoffman and Mr. Frank J. Billovits for elemental analyses, and to Mr. Andrew F. Lum for physical constants.

ylate, and 500 ml. of toluene was heated at reflux for 18 hr. After cooling to room temperature, the mixture was filtered and the filtrate concentrated by distillation. The residue was extracted with pentane and the pentane stripped from the resultant solution. The residue was distilled *in vacuo* and a fraction, b.p. 108° (5 mm.), collected (59.8 g., 33% yield). This material melted at 52–54°.

Anal. Calcd. for $C_6H_{16}O_4B_{10}$: C, 27.67; H, 6.19; B, 41.47; sapon. equiv., 130.2. Found: C, 27.73; H, 6.52; B, 42.11; sapon. equiv., 132.8.

1-Bromomethyl-2-methylcarborane.—The 1-bromo-2-butyne required for this reaction was prepared by the method of Petrov and Nikishin.[6] A solution of 0.125 mole of this compound and 0.125 mole of decaborane in 125 ml. of acetonitrile was refluxed for 4 hr., the acetonitrile was removed by distillation, and the residue was distributed between 500 ml. of 10% sodium hydroxide and 250 ml. of hexane. The hexane layer was separated and dried, and the solvent was removed by distillation under reduced pressure, leaving 13.2 g. of a yellow solid. Crystallization from ethanol–water (5:1) yielded 11.3 g. (36%) of white crystals, m.p. 125–127°.

Anal. Calcd. for $C_4H_{15}B_{10}Br$: C, 19.12; H, 6.02; B, 43.07; Br, 31.80. Found: C, 19.73; H, 6.18; B, 43.83; Br, 30.70.

Diethyl 2,2-Bis-(1-carboranylmethyl)-malonate.—Diethyl 2,2-dipropargylmalonate was prepared from diethyldisodio malonate and propargyl chloride by standard techniques. This compound (0.5 mole), 1.0 mole of 6,9-bis-(acetonitrile)-decarborane, and 1200 ml. of benzene were heated at reflux for 22 hr., during which time 7.7 l. of gas was evolved. After cooling to room temperature, the reaction mixture was filtered, and the solvents were distilled from the filtrate. The residue was suspended in *n*-hexane, absolute ethanol was added slowly with accompanying gas evolution, and the mixture finally was heated at reflux until gas evolution had ceased. The hexane was removed by distillation while adding additional ethanol. A total of 2375 ml. of ethanol was used. On cooling to room temperature, 127.5 g. (53% yield) of white solid, m.p. 198–199°, was obtained.

Anal. Calcd. for $C_{13}H_{36}O_4B_{20}$: C, 33.02; H, 7.67; B, 45.77. Found: C, 33.09; H, 8.02; B, 45.38.

1-Carboranylmethylmagnesium Bromide.—Magnesium, 0.5 g.-atom, and anhydrous ether, 400 ml., were charged to a 1-l. flask. A portion of a solution of 0.50 mole of 1-bromomethylcarborane in 125 ml. of anhydrous ether was added to the flask and the contents were heated to reflux to initiate the reaction. The remainder of the solution was added over a 1-hr. period, at a rate sufficient to maintain gentle reflux, after which time reflux was continued for an additional 3 hr. The resulting solution was drawn into another flask through a filter stick. Unreacted magnesium, 1.6 g., was recovered.

1-Methylcarborane.—To a solution of 1-carboranylmethylmagnesium bromide prepared from 0.50 mole of 1-bromomethylcarborane was added excess dilute hydrochloric acid dropwise, while maintaining the temperature at 10–15°. The ether layer was separated and evaporated to dryness to yield 69.3 g. of a solid, which was recrystallized from pentane to yield 58.0 g. (73% yield) of white crystals, m.p. 214–217°. No depression of melting point was observed with a mixture of this product and the 1-methylcarborane prepared by the interaction of propyne and $(CH_3CN)_2B_{10}H_{12}$.

1-Hydroxymethylcarborane.—1-Acetoxymethylcarborane, 0.64 mole, was dissolved in 500 ml. of methanol and the solution brought to reflux. Hydrogen chloride was passed through for a 2-hr. period after which heating was continued for an additional 2 hr. The methanol–methyl acetate azeotrope was removed (55°), followed by the remainder of the methanol. The residue was recrystallized from hexane to yield 80 g. (72% yield) of a white, crystalline product, m.p. 220–222°.

Anal. Calcd. for $C_3H_{14}OB_{10}$: C, 20.67; H, 8.09; B, 61.06. Found: C, 20.87; H, 8.46; B, 61.21.

1-Hydroxymethyl-2-(γ-hydroxy-α-propynl)-carborane.—A solution of 0.027 mole of the dibenzoate ester of 1-hydroxymethyl-2-(γ-hydroxy-α-propynyl)-carborane in 150 ml. of methanol was cooled to 0° and saturated with hydrogen chloride, then refluxed for 18 hr., followed by removal of the methanol by distillation. The pasty residue was filtered and the filter cake recrystallized from ethanol–water, then chloroform–petroleum ether. The product, 3 g. (49%), melted at 163–164°.

Anal. Calcd. for $C_6H_{16}O_2B_{10}$: C, 31.55; H, 7.06; B, 47.38. Found: C, 31.35; H, 7.74; B, 49.65.

1,2-Bis-(hydroxymethyl)-carborane.—1,2-Bis-(acetoxymethyl)-carborane, 1.55 moles, was dissolved in 750 ml. of absolute methanol and heated for 3 hr. at reflux while hydrogen chloride was passed through the solution. The methanol–methyl acetate constant boiling mixture was slowly distilled from the reaction mixture, followed by the remainder of the methanol. A white solid (322.5 g.) was obtained, which was then dissolved in 350 ml. of hot toluene at 90–95° and filtered while hot. The filtrate was cooled to 0–5°, and the product was filtered and washed with two portions of cold toluene and then pentane. A white granular product was isolated, 306 g. (96%).

Anal. Calcd. for $C_4H_{16}B_{10}$: OH number, 16.64. Found: OH number, 16.83.

1,2-Diisopropylcarborane.—A solution of 0.047 mole of diisopropenylcarborane in 50 ml. of cyclohexane was charged to a 300-ml. pressure reactor, 3.0 g. of a reduced nickel catalyst (54% Ni on Kieselguhr) was added, and the reaction was pressurized to 1800 p.s.i. with hydrogen and heated, with shaking, overnight at 120°. After cooling, the reactor was vented and the solution filtered and concentrated. The residue was sublimed to yield 7.0 g. (65%) of a white solid, m.p. 104–105°. The infrared spectrum of this material indicated the absence of unsaturation.

Anal. Calcd. for $C_8H_{24}B_{10}$: C, 42.43; H, 9.79; B, 47.78. Found: C, 42.12; H, 10.42; B, 48.7.

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[6] A. D. Petrov and G. J. Nikishin, *Dokl. Akad. Nauk SSSR*, **93**, 1049 (1953); *Chem. Abstr.*, **49**, 841*c* (1955).