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A New Series of Organoboranes. III. Some Reactions of 1,2-Dicarbaclovododecaborane(12) and its Derivatives[1]

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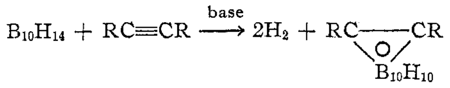
The general participation of carborane and its derivatives in standard organic chemical transformations has been established. Reactions of carborane and some functionally substituted derivatives are described. Differences in the reactivity of the hydrogen atoms attached to carbon atoms of carborane from those attached to the boron atoms have been demonstrated.

Introduction

The reaction of decaborane and certain decaborane derivatives with acetylenic compounds to produce 1,2-dicarbaclovododecaborane(12) (carborane) derivatives

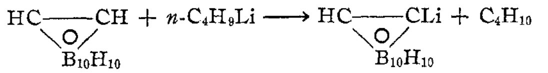


$$B_{10}H_{14} + RC{\equiv}CR \xrightarrow{\text{base}} 2H_2 + \underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{RC\text{---}CR}}$$

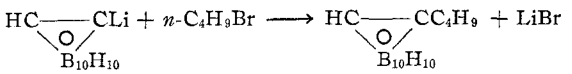
has been reported.[2] The parent compound where R = H was found to undergo chlorination readily[3] and it was of interest to explore further chemical behavior of this novel structure.[3] Since there was no reported species to which a reasonable analogy might be drawn, this investigation was conducted to determine the variety of transformations that could occur.

Discussion

Initial interest was concerned with determining the chemical nature of the hydrogen atoms of the carborane structure and whether reactions other than chlorination at these sites could be conducted without causing disruption of the nucleus itself. Carborane was found to react readily with a variety of organometallic compounds to produce monosubstituted and disubstituted derivatives which in turn would undergo many of the reactions common to organometallics. The alkyllithium reagents proved to be generally most useful in this respect, but in some instances use of Grignard reagents was advantageous. Reactions 1, 2, 3, and 4 illustrate such transformations.



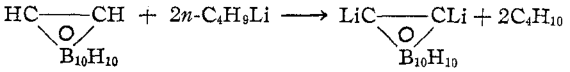
$$\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{HC\text{---}CH}} + n\text{-}C_4H_9Li \longrightarrow \underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{HC\text{---}CLi}} + C_4H_{10} \quad (1)$$



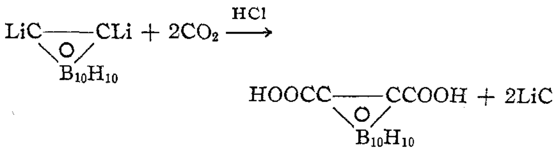
$$\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{HC\text{---}CLi}} + n\text{-}C_4H_9Br \longrightarrow \underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{HC\text{---}CC_4H_9}} + LiBr \quad (2)$$

I

The 1-butylcarborane prepared by reaction 2 was found to be identical with that prepared by the direct reaction of decaborane with hexyne-1.[2]



$$\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{HC\text{---}CH}} + 2n\text{-}C_4H_9Li \longrightarrow \underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{LiC\text{---}CLi}} + 2C_4H_{10} \quad (3)$$



$$\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{LiC\text{---}CLi}} + 2CO_2 \xrightarrow{HCl} \underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{HOOCC\text{---}CCOOH}} + 2LiCl \quad (4)$$

II

Subsequent conversion of II to its dimethyl ester, as discussed later, and comparison of this ester to that prepared by the direct reaction of decaborane with dimethyl acetylenedicarboxylate[2] proved that the materials were identical. These reactions establish the fact that hydrogen atoms attached to the carbon atoms of the carborane nucleus are relatively more acidic that those attached to the boron atoms and attack of organometallics occurs preferentially at these points. The corresponding hydrogen atoms of octachloro- and decachlorocarborane were found to be extremely acidic.[3]

Initial investigations of the chemistry of carborane-1,2-dicarboxylic acid and its derivatives gave unusual results. For example, it was found that dimethyl carboranedicarboxylate, prepared by direct synthesis,[2] could not be hydrolyzed to the free diacid, nor could the diacid be esterified by any method attempted. The ester could neither be transesterified nor converted to the diamide *via* ammonolysis. The diacid could be titrated giving the expected neutralization equivalent and formed the diammonium, dihydrazinium, dianilinium, and bis-(diethylammonium) salts readily; however none of these compounds could be converted to the corresponding diamide. Heating these salts with phosphorus pentoxide gave carborane as the major boron-containing product. Attempts to prepare the diacid dichloride by standard procedures gave either no reaction or the anhydride was formed. In fact, very good yields of carborane-1,2-dicarboxanhydride were achieved by treating the diacid with thionyl chloride in the presence of sodium carbonate. The anhydride could be converted to the diacid dichloride

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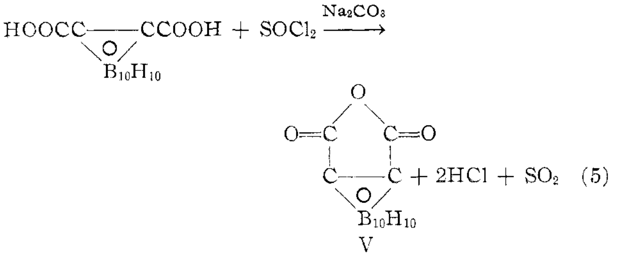
(1) Presented in part at the Conference on Current Trends in Organometallic Chemistry, University of Cincinnati, June, 1963.

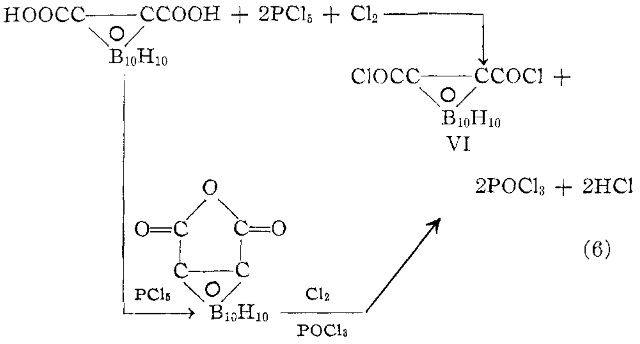
(2) Paper I of this series: T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963).

(3) Paper II of this series: H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, **2**, 1092 (1963).



$$\underset{B_{10}H_{10}}{\text{HOOCC—CCOOH}} + SOCl_2 \xrightarrow{Na_2CO_3} \underset{\text{V}}{\text{(O=C–O–C=O)}\underset{B_{10}H_{10}}{\text{C—C}}} + 2HCl + SO_2 \quad (5)$$

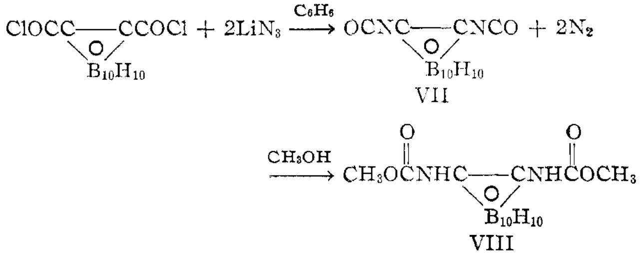
VI by refluxing it in phosphorus oxychloride in a chlorine atmosphere. Subsequently, it was found that the diacid could be converted directly, in excellent yield, combining these steps.



$$\underset{B_{10}H_{10}}{\text{HOOCC—CCOOH}} + 2PCl_5 + Cl_2 \longrightarrow \underset{\text{VI}}{\underset{B_{10}H_{10}}{\text{ClOCC—CCOCl}}} + 2POCl_3 + 2HCl \quad (6)$$

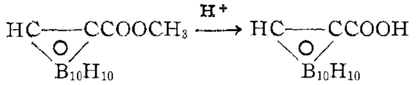
The diacid dichloride would react with alcohols to give the esters (the dimethyl ester so prepared was identical with that from decaborane and dimethyl acetylenedicarboxylate[2]), and would hydrolyze to the diacid, but in reactions with ammonia or amines did not give products which could be established as the amides.

Treatment of carborane-1,2-dicarboxyl dichloride in benzene with lithium azide,[4] in anticipation of preparing the diisocyanate, gave 98% of the theoretical quantity of nitrogen in every attempt. The infrared spectrum of the resulting solution showed the -NCO absorption at 4.45 μ and the mass spectrum showed a characteristic pattern with a cut-off peak at m/e = 228. All attempts to isolate the diisocyanate led to an intractable semisolid which no longer exhibited the -NCO absorption. The benzene solution of the diisocyanate VII gave reactions characteristic of this compound as exemplified by its reaction with methanol, giving a high yield of carborane-1,2-bis-(methylurethane) (VIII).



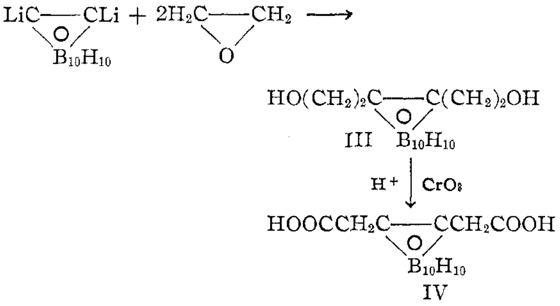
$$\underset{B_{10}H_{10}}{\text{ClOCC—CCOCl}} + 2LiN_3 \xrightarrow{C_6H_6} \underset{\text{VII}}{\underset{B_{10}H_{10}}{\text{OCNC—CNCO}}} + 2N_2 \xrightarrow{CH_3OH} \underset{\text{VIII}}{\underset{B_{10}H_{10}}{\text{CH}_3\text{O}\overset{O}{\overset{\|}{C}}\text{NHC—CNH}\overset{O}{\overset{\|}{C}}\text{OCH}_3}}$$

Since the unusual behavior of carborane-1,2-dicarboxylic acid had been observed, other carboranyl acids were prepared for study. Methyl carborane-1-carboxylate, prepared directly from decaborane,[2] could be easily hydrolyzed to the free acid by normal means.



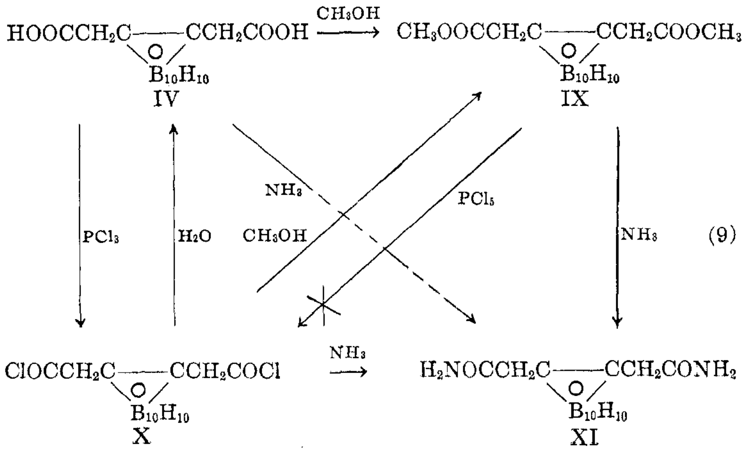
$$\underset{B_{10}H_{10}}{\text{HC—CCOOCH}_3} \xrightarrow{H^+} \underset{B_{10}H_{10}}{\text{HC—CCOOH}} \quad (7)$$

This acid in turn could be converted to the acid chloride or the amide or reconverted to the ester by common procedures. 1,2-Bis-(carboxymethyl)-carborane (IV) was prepared in very good yields *via* reaction 8.



$$\underset{B_{10}H_{10}}{\text{LiC—CLi}} + 2\underset{O}{H_2\text{C—CH}_2} \longrightarrow \underset{\text{III}}{\underset{B_{10}H_{10}}{\text{HO(CH}_2)_2\text{C—C(CH}_2)_2\text{OH}}} \xrightarrow{H^+,\ CrO_3} \underset{\text{IV}}{\underset{B_{10}H_{10}}{\text{HOOCCH}_2\text{C—CCH}_2\text{COOH}}} \quad (8)$$

This compound also underwent the conversions expected of a dicarboxylic acid. It was readily esterified in high yield by treatment with alcohols in the presence of an acid catalyst. Reaction of the diacid with phosphorus pentachloride readily gave the expected diacid dichloride although the latter compound could not be formed from the diester. Appropriate treatment of the diacid, its dimethyl ester, and the diacid dichloride gave the same product in each case and is believed to be the diamide. (The carbon analyses were somewhat higher than theoretical, but all other elemental analyses and the infrared spectrum indicate the diamide.)



$$\begin{tikzcd}
\underset{\text{IV}}{\underset{B_{10}H_{10}}{\text{HOOCCH}_2\text{C—CCH}_2\text{COOH}}} \arrow[r, "CH_3OH"] \arrow[d, shift right, "PCl_3"'] \arrow[dr, dashed, "NH_3"] & \underset{\text{IX}}{\underset{B_{10}H_{10}}{\text{CH}_3\text{OOCCH}_2\text{C—CCH}_2\text{COOCH}_3}} \arrow[d, "NH_3"] \arrow[dl, "PCl_5", "\times"'] \\
\underset{\text{X}}{\underset{B_{10}H_{10}}{\text{ClOCCH}_2\text{C—CCH}_2\text{COCl}}} \arrow[u, shift right, "H_2O"'] \arrow[ur, "CH_3OH"] \arrow[r, "NH_3"] & \underset{\text{XI}}{\underset{B_{10}H_{10}}{\text{H}_2\text{NOCCH}_2\text{C—CCH}_2\text{CONH}_2}}
\end{tikzcd} \quad (9)$$

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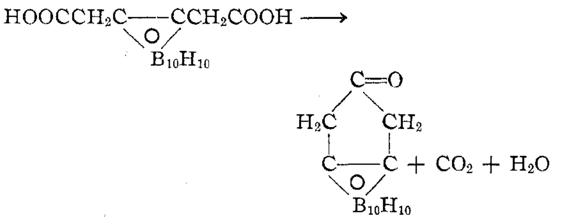
(4) N. Hofman-Bang, *Acta Chem. Scand.*, **2**, 581 (1957).

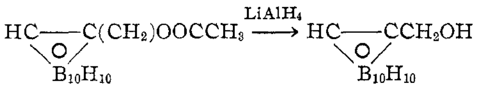
On heating 1,2-bis-(carboxymethyl)-carborane under vacuum, it showed similarity to adipic acid by forming the cyclic ketone XII.


(10)

XII

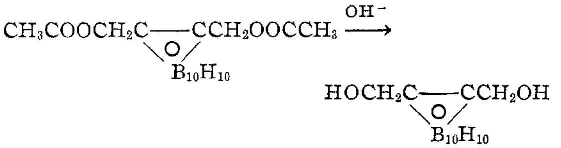
Thus, the Blanc observation is upheld in this homologous series.

The two esters, 1-acetoxymethylcarborane and 1,2-bis-(acetoxymethyl)-carborane, had been prepared,[2] and it was found that they could be saponified to the corresponding alcohols. The same result, in higher yield, was achieved by lithium aluminum hydride reduction.



(11)

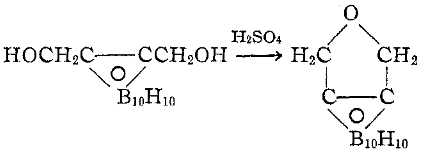
XIII



(12)

XIV

Attempts to prepare the latter compound by the reaction of dilithiocarborane with formaldehyde failed. Compound XIV was treated under many conditions to prepare a diether unsuccessfully, but it was found that on treatment with hot, concentrated sulfuric acid, the tetrahydrofuran analog XV was formed.

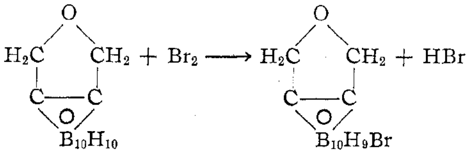


(13)

XV

1,2-Bis-(hydroxymethyl)-carborane (XIV) readily reacted with active metals such as sodium in inert solvents to produce the dimetallo alcoholates. These salts, however, were quite unreactive except toward hydrolysis.

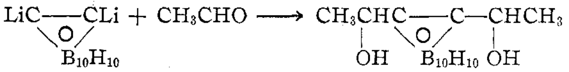
1,2-(2′-Oxapropylene)-carborane (XV) resisted change in all reactions attempted. No reaction occurred in the presence of Friedel–Crafts type catalysts often useful in opening tetrahydrafuran rings.[5] Halogenation was generally unsuccessful, but on treatment with bromine in sunlight and in the presence of benzoyl peroxide, a good yield of a monobromo derivative was formed. It was shown by mass spectrometric and nuclear magnetic spectrometric determinations that the bromine atom was attached to a boron atom rather than a carbon atom as occurred in the chlorinations described previously.[3]



XVI

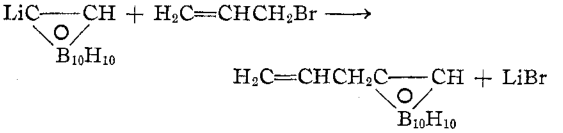
No reaction of B-bromo-1,2-(2′-oxapropylene)-carborane (XVI) with ethylmagnesium bromide occurred.

1-(α and β-acetoxyethyl)-carborane were prepared by direct synthesis[2] and could be hydrolyzed to the alcohols. However, the compounds were viscous oils which could not be purified and decomposed slowly on standing. The reaction of dilithiocarborane with acetaldehyde gave moderate yields of 1,2-bis-(α-hydroxyethyl)-carborane. This high melting diol contrasted markedly with the unstable alcohol 1-(α-hydroxyethyl)-carborane.


(14)

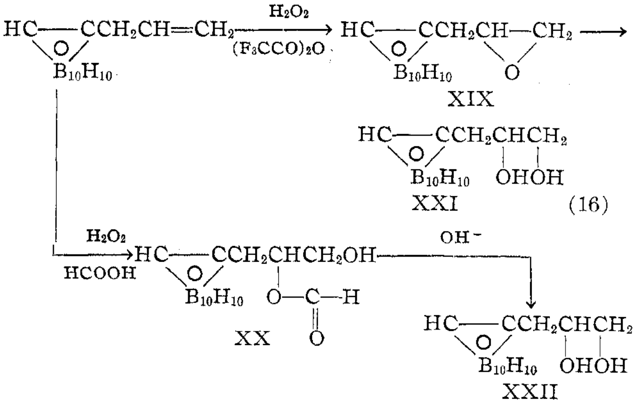
XVII

Treatment of monolithiocarborane with allyl halides produced good yields of 1-allylcarborane.


(15)

XVIII

This compound was converted to 1-(β-γ-dihydroxypropyl)-carborane by (1) conversion to the epoxide followed by ring opening and (2) conversion to the hydroxyformyl compound which was subsequently hydrolyzed.



(16)

Elemental and infrared analyses showed the products to be identical. However, XXI melted at 88–89°, while XXII melted at 93° and on mixing there was a 15–20° depression in melting point. This suggests that two different stereoisomers had been synthesized, which could be expected from the difference in mechanisms of the two routes employed.

Bis-carboranylmethyl methanol had been reported[6] and was readily acetylated in ethyl acetate using acetic anhydride and a trace of perchloric acid (eq. 17). This ester, as well as 1-(α-acetoxyethyl)-carborane and

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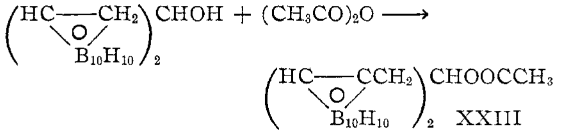
(5) K. Hamann, *Angew. Chem.*, **63**, 236 (1951).

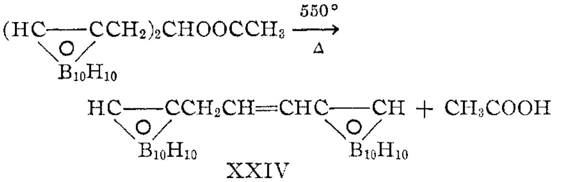
(6) M. F. Hawthorne, *et al.*, private communication.



$$\left(\underset{B_{10}H_{10}}{HC\text{—}CH_2}\right)_2CHOH + (CH_3CO)_2O \longrightarrow \left(\underset{B_{10}H_{10}}{HC\text{—}CCH_2}\right)_2CHOOCCH_3 \quad (17)$$

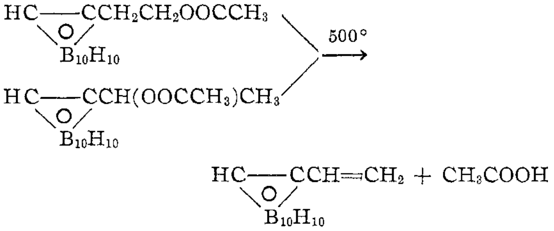
XXIII

1-(β-acetoxyethyl)-carborane, was found to undergo elimination of acetic acid at temperatures above 500° to form 1,3-dicarboranylpropene (XXIV) and 1-vinylcarborane (XXV), respectively, in good yield as illustrated in reactions 18 and 19. The fact that the carborane nucleus withstood such treatment contrasts with the behavior of the parent compound, decaborane, which is completely decomposed at much lower temperatures.



$$(\underset{B_{10}H_{10}}{HC\text{—}CCH_2})_2CHOOCCH_3 \xrightarrow[\Delta]{550°} \underset{B_{10}H_{10}}{HC\text{—}CCH_2}CH{=}CH\underset{B_{10}H_{10}}{C\text{—}CH} + CH_3COOH \quad (18)$$

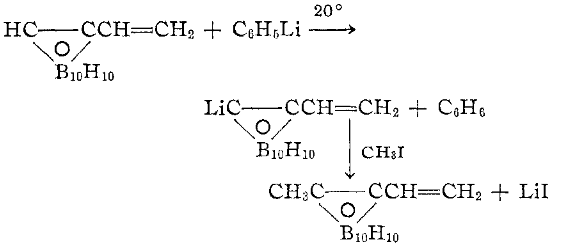
XXIV



$$\left.\begin{array}{l}\underset{B_{10}H_{10}}{HC\text{—}CCH_2CH_2OOCCH_3}\\ \underset{B_{10}H_{10}}{HC\text{—}CCH(OOCCH_3)CH_3}\end{array}\right\} \xrightarrow{500°} \underset{B_{10}H_{10}}{HC\text{—}CCH{=}CH_2} + CH_3COOH \quad (19)$$

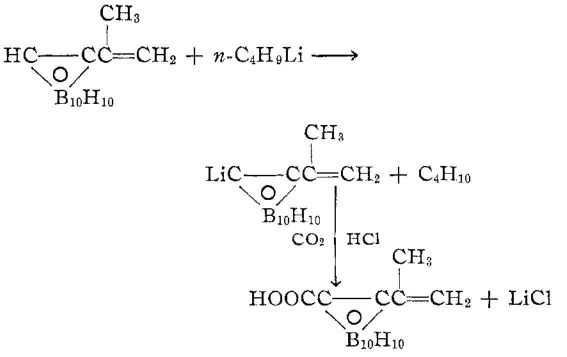
XXV

Syntheses involving the reaction of metal derivatives of carborane as described above need not be restricted to carborane itself. Monosubstituted carboranes will undergo similar reactions as exemplified by the synthesis of 1-methyl-2-vinylcarborane and 1-isopropenylcarborane-2-carboxylic acid.



$$\underset{B_{10}H_{10}}{HC\text{—}CCH{=}CH_2} + C_6H_5Li \xrightarrow{20°} \underset{B_{10}H_{10}}{LiC\text{—}CCH{=}CH_2} + C_6H_6 \xrightarrow{CH_3I} \underset{B_{10}H_{10}}{CH_3C\text{—}CCH{=}CH_2} + LiI \quad (20)$$

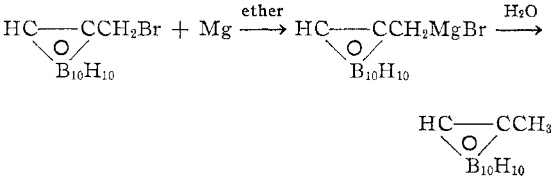
XXVI



$$\underset{B_{10}H_{10}}{HC\text{—}C}\overset{CH_3}{C}{=}CH_2 + n\text{-}C_4H_9Li \longrightarrow \underset{B_{10}H_{10}}{LiC\text{—}C}\overset{CH_3}{C}{=}CH_2 + C_4H_{10} \xrightarrow{CO_2,\ HCl} \underset{B_{10}H_{10}}{HOOCC\text{—}C}\overset{CH_3}{C}{=}CH_2 + LiCl \quad (21)$$

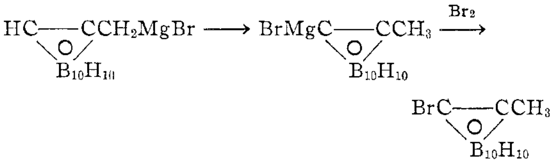
XXVII

The chemistry of C-halogenated carborane derivatives was studied to some extent. It was discovered that 1-bromomethylcarborane[2] would readily form a Grignard derivative, but this compound was exceedingly sluggish in reactions with simple aldehydes and ketones. Hydrolysis was vigorous to produce good yields of 1-methylcarborane and this method of preparing the methyl compound was usually used in this laboratory in preference to the direct preparation from methylacetylene and decaborane. Treatment



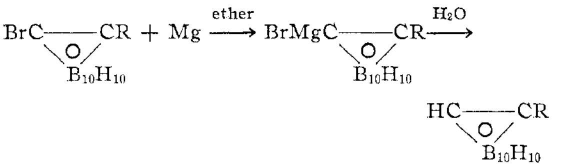
$$\underset{B_{10}H_{10}}{HC\text{—}CCH_2Br} + Mg \xrightarrow{ether} \underset{B_{10}H_{10}}{HC\text{—}CCH_2MgBr} \xrightarrow{H_2O} \underset{B_{10}H_{10}}{HC\text{—}CCH_3} \quad (22)$$

of the Grignard compound with bromine gave a compound which by elementary and mass spectral analysis showed a composition identical with that of 1-bromomethylcarborane but was not the same compound. This suggests the possibility indicated in reaction 23.



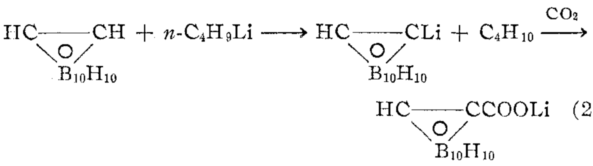
$$\underset{B_{10}H_{10}}{HC\text{—}CCH_2MgBr} \longrightarrow \underset{B_{10}H_{10}}{BrMgC\text{—}CCH_3} \xrightarrow{Br_2} \underset{B_{10}H_{10}}{BrC\text{—}CCH_3} \quad (23)$$

This possibility is in agreement with the following observations. 1-Bromo-2-*n*-propylcarborane and 1-bromo-2-*n*-butylcarborane[2] each formed a Grignard compound on reaction with magnesium, but these intermediates were found not to react with aldehydes or ketones. They did give the parent alkylcarborane on hydrolysis. Also, in attempts to prepare carborane-

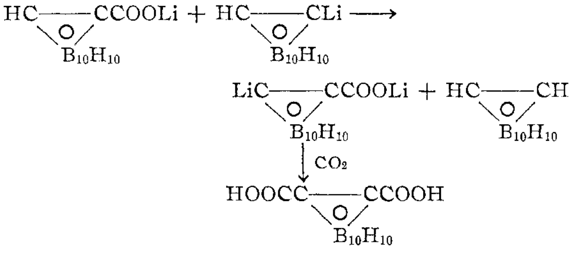


$$\underset{B_{10}H_{10}}{BrC\text{—}CR} + Mg \xrightarrow{ether} \underset{B_{10}H_{10}}{BrMgC\text{—}CR} \xrightarrow{H_2O} \underset{B_{10}H_{10}}{HC\text{—}CR} \quad (24)$$

carboxylic acid by the carbonation of lithiocarborane only carboranedicarboxylic acid was recovered (in good yield). This probably involves the exchange of a lithium atom as indicated in reactions 25 and 26. This transfer must be influenced by the presence of the carboxyl group since, in contrast, lithiocarborane reacts with alkyl or alkenyl and silyl halides to give monosubstituted carboranes in good yield.



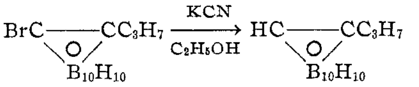
$$\underset{B_{10}H_{10}}{HC\text{—}CH} + n\text{-}C_4H_9Li \longrightarrow \underset{B_{10}H_{10}}{HC\text{—}CLi} + C_4H_{10} \xrightarrow{CO_2} \underset{B_{10}H_{10}}{HC\text{—}CCOOLi} \quad (25)$$



$$\underset{B_{10}H_{10}}{HC\text{—}CCOOLi} + \underset{B_{10}H_{10}}{HC\text{—}CLi} \longrightarrow \underset{B_{10}H_{10}}{LiC\text{—}CCOOLi} + \underset{B_{10}H_{10}}{HC\text{—}CH} \xrightarrow{CO_2} \underset{B_{10}H_{10}}{HOOCC\text{—}CCOOH} \quad (26)$$

1,2-Bis-chloromethylcarborane formed a di-Grignard reagent by reaction in the standard manner. The solution of the di-Grignard was red in color and this color was discharged on shaking the solution in air. The color re-formed on standing. The compound was rather unreactive but formed dimethylcarborane on hydrolysis.

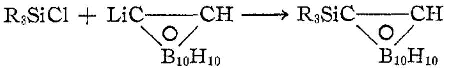
In general none of the 1-halo derivatives could be converted to the corresponding alcohols on treatment with base. One exception was observed when 1-bromo-2-propylcarborane was carefully treated with potassium hydroxide in methanol–water; a compound identified, mass spectrometrically, as hydroxypropylcarborane was isolated. Usually, treatment of bromopropylcarborane or bromobutylcarborane with bases such as sodium hydroxide or potassium cyanide in ionizing solvents led to replacement of the bromine by hydrogen. The path of these reactions has not been established.



$$\underset{\mathrm{B_{10}H_{10}}}{\underset{\diagdown O \diagup}{\mathrm{BrC{-}{-}CC_3H_7}}} \xrightarrow[\mathrm{C_2H_5OH}]{\mathrm{KCN}} \underset{\mathrm{B_{10}H_{10}}}{\underset{\diagdown O \diagup}{\mathrm{HC{-}{-}CC_3H_7}}} \qquad (27)$$

1-Bromomethylcarborane and 1,2-bis-chloromethylcarborane reacted similarly with organic bases such as diethylamine or pyridine. In all cases evidence for the breaking of the carbon–halogen bond was obtained, but products identifiable as the quaternary salts or substituted amines could not be isolated.

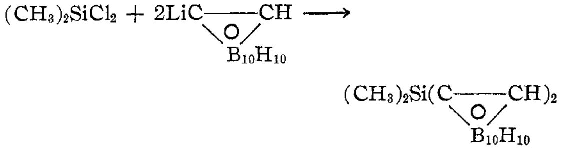
The metallo carboranes were useful in synthesizing several silylcarboranes, as illustrated in reactions 28 through 31.



$$\mathrm{R_3SiCl} + \underset{\mathrm{B_{10}H_{10}}}{\underset{\diagdown O \diagup}{\mathrm{LiC{-}{-}CH}}} \longrightarrow \underset{\mathrm{B_{10}H_{10}}}{\underset{\diagdown O \diagup}{\mathrm{R_3SiC{-}{-}CH}}} \qquad (28)$$

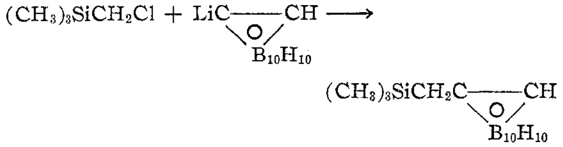
XXVIII

a, R = CH_3; b, R = C_6H_5



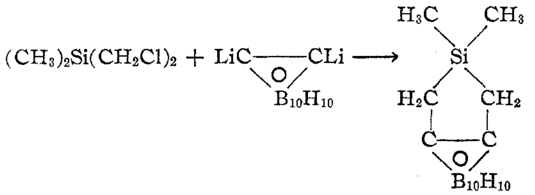
$$\mathrm{(CH_3)_2SiCl_2} + 2\underset{\mathrm{B_{10}H_{10}}}{\underset{\diagdown O \diagup}{\mathrm{LiC{-}{-}CH}}} \longrightarrow \mathrm{(CH_3)_2Si}(\underset{\mathrm{B_{10}H_{10}}}{\underset{\diagdown O \diagup}{\mathrm{C{-}{-}CH}}})_2 \qquad (29)$$

XXIX



$$\mathrm{(CH_3)_3SiCH_2Cl} + \underset{\mathrm{B_{10}H_{10}}}{\underset{\diagdown O \diagup}{\mathrm{LiC{-}{-}CH}}} \longrightarrow \underset{\mathrm{B_{10}H_{10}}}{\underset{\diagdown O \diagup}{\mathrm{(CH_3)_3SiCH_2C{-}{-}CH}}} \qquad (30)$$

XXX



$$\mathrm{(CH_3)_2Si(CH_2Cl)_2} + \underset{\mathrm{B_{10}H_{10}}}{\underset{\diagdown O \diagup}{\mathrm{LiC{-}{-}CLi}}} \longrightarrow \qquad (31)$$

XXXI

It is of interest to note that the heterocyclic silane XXXI is the fourth example of compounds in which the carbon atoms of a carborane nucleus participate in a five-membered ring (*cf.* compounds V, XII, and XV).

Experimental

1-*n*-Butylcarborane (I).—*n*-Butyllithium (0.035 mole) in 50 ml. of ether was added at 0° to a solution of 5.0 g. (0.035 mole) of carborane in 50 ml. of ether. The mixture was gradually warmed to reflux temperature. *n*-Butyl bromide (5.6 g., 0.041 mole) was added to the refluxing solution and heating was continued for 3 hr. The mixture was treated with water and the ether layer was separated, dried over magnesium sulfate, and filtered and the ether was removed. The residue was distilled (40° (0.3 mm.)), giving 4.5 g. (69.0%) of *n*-butylcarborane ($n^{25}\mathrm{D}$ 1.5298; for *n*-butylcarborane by direct preparation[2] 1.5301), identical in infrared and mass spectrum with that prepared for decaborane and hexyne-1.

Carborane-1,2-dicarboxylic Acid (II).—Carborane (15 g., 0.104 mole) in 75 ml. of ether was added at 0° to a stirred solution of 0.231 mole of *n*-butyllithium contained in 80 ml. of ether. The addition required only 10 min. but stirring was continued at 0–15° for 5 hr. Gaseous carbon dioxide was passed into the solution rapidly for 0.5 hr., after which the mixture was treated with dilute hydrochloric acid. The product was isolated in the ether, which was dried over magnesium sulfate and filtered; the ether then was removed. The slightly yellow product was recrystallized from toluene, giving 21.0 g. (86.5%) of carborane-1,2-dicarboxylic acid (m.p. 232°).[7]

Anal. Calcd. for $B_{10}C_4H_{12}O_4$: C, 36.3; H, 9.1; B, 46.8; mmoles of base to neutralize 0.0733 g., 1.109. Found: C, 36.6; H, 9.4; B, 46.6; mmoles of base, 1.099.

This preparation was conducted many times at the 3-mole scale with equally good results. It was found that when the addition of the carborane to the butyllithium and the carbonation were conducted as fast as possible, slightly higher yields were obtained.

1,2-Bis-(β-hydroxyethyl)-carborane (III).—Carborane (55.0 g., 0.382 mole) in 100 ml. of ether was added at 0° to 0.852 mole of *n*-butyllithium in 600 ml. of ether. After 0.5 hr. at 0° the mixture was cooled to −20° and 57.7 g. of liquid ethylene oxide[8] was slowly added. When the addition was complete the reaction mixture was allowed to warm to 0°, whereupon cold water was added and the mixture hydrolyzed. The ether layer was removed, dried over magnesium sulfate, filtered, and poured into an equal volume of *n*-pentane, whereupon the crude product separated and was removed and recrystallized from ether–pentane; 89 g. of bis-β-hydroxyethylcarborane (m.p. 124–125°), as white needles, was obtained.

Anal. Calcd. for $B_{10}C_6H_{20}O_2$: C, 31.0; H, 8.6. Found: C, 31.3; H, 8.8.

1,2-Bis-(carboxymethyl)-carborane (IV).—In a typical preparation, 19 g. of bis-(β-hydroxyethyl)-carborane is dissolved in 320 ml. of commercial acetone and cooled in an ice–water bath. While stirring, 160 ml. of 6 *N* chromic anhydride in 12 *N* sulfuric acid is added slowly (about 30–45 min.). Stirring is continued for an additional 45 min.; 500 ml. of water is then added and the resulting mixture is extracted several times with ether. The combined ethereal solution is extracted with potassium carbonate solution, from which solution, on acidification with hydrochloric acid, bis-(carboxymethyl)-carborane precipitates with 20–21 molecules of water. The solid is taken up in ether, dried over magnesium sulfate, and filtered. Removal of the ether gave 17.7 g. (83%) of the white diacid (m.p. 203–205°).

Anal. Calcd. for $B_{10}C_6H_{16}O_4$: C, 27.5; H, 6.9; B, 41.2. Found: C, 26.9; H, 6.6; B, 41.0.

The **dimethyl ester IX** was obtained by refluxing a solution of 12.0 g. of bis-(carboxymethyl)-carborane in 20 ml. of absolute methanol containing 0.5 ml. of sulfuric acid for 17 hr. An equal volume of ether was added and this solution was extracted with

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[7] Melting points were obtained using a Fisher–Johns apparatus and are uncorrected.

[8] It was found that the purity of the ethylene oxide was an important factor in obtaining high yields in a controllable reaction. Generally if the liquid oxide was water white, smooth reactions and good yields were obtained. Use of oxide that is yellow or cloudy should be avoided.

two 10-ml. portions of water. The organic layer was dried over magnesium sulfate and filtered, and the volatiles were evaporated, leaving 12.1 g. (91%) of crude product which was distilled at 140–148° (0.5 mm.) to give 8.9 g. (67%) of a clear liquid which solidified on standing (m.p. 47–48°).

Anal. Calcd. for $B_{10}C_8H_{20}O_4$: C, 33.3; H, 6.9; B, 37.5. Found: C, 33.4; H, 7.4; B, 37.8.

The **diethyl ester** was obtained in an identical manner in 87% yield (m.p. 40°).

1,2-Bis-(chlorocarboxymethyl)-carborane (X).—Bis-(carboxymethyl)-carborane (0.5 g.) was heated at 60–80° with excess phosphorus pentachloride for 40 hr. The phosphorus oxychloride formed was removed under reduced pressure and the liquid residue was extracted with pentane. The pentane solution was cooled and the yellow solid which precipitated was removed and recrystallized from pentane; 4.1 g. of bis-(chlorocarboxymethyl)-carborane was recovered and identified *via* its mass and infrared spectra.

Anal. Calcd. for $B_{10}C_6H_{14}Cl_2O_2$: C, 24.2; H, 4.7; B, 36.5; Cl, 23.9. Found: C, 24.5; H, 4.9; B, 36.3; Cl, 23.9.

Carborane-1,2-dicarboxanhydride (V).—Carboranedicarboxylic acid (10 g.) and 10.0 g. of sodium carbonate were ground together in a mortar. The mixture was transferred to a round-bottomed flask and 17.5 ml. of thionyl chloride was added while stirring. When the vigorous gas evolution subsided, the mixture was refluxed for 4 hr., after which 50 ml. of *n*-heptane and some activated charcoal were added and the excess thionyl chloride was distilled off. The remaining solution was filtered, cooled to −78°, and the precipitated anhydride was removed by filtration. Recrystallization afforded 7.1 g. (77% yield) of carboranedicarboxanhydride (m.p. 180°).

Anal. Calcd. for $B_{10}C_4H_{10}O_3$: C, 22.45; H, 4.71. Found: C, 22.60; H, 4.52.

Carborane-1,2-dicarboxylyl Dichloride (VI).—In a typical preparation 10 g. of carboranedicarboxylic acid, 24.0 g. of phosphorus pentachloride, and 10 ml. of phosphorus oxychloride are heated at 90° for 2 hr. Chlorine is then passed through the solution while this temperature is maintained. The phosphorus oxychloride is removed by distillation at water-aspirator pressure and the residue is dissolved in 150 ml. of *n*-pentane and filtered. Mass spectral analysis of this solution indicated that only the diacid dichloride and the solvent were present. The pentane was removed and the residue was sublimed under reduced pressure to give 8.5 g. (74% yield) of pure carboranedicarboxylyl chloride (m.p. 69–70°). Mass spectral analysis indicated that only the diacid dichloride was present.

Anal. Calcd. for $B_{10}C_4H_{10}Cl_2O_2$: C, 17.8; H, 3.7; B, 40.2; Cl, 26.4. Found: C, 18.1; H, 3.9; B, 40.0; Cl, 26.2.

The compound is moisture and probably light sensitive, and after standing for several weeks will turn black. Resublimation affords a pure product with very little loss of material.

Carborane-1-carboxylic Acid.—Methyl carboranecarboxylate (52.8 g.) was stirred in 1500 ml. of 0.5 *N* sodium hydroxide to which 300 ml. of methanol had been added. Stirring was continued for 3 days and the solution was acidified. The precipitated acid was removed, dried, and recrystallized from pentane, giving 40 g. of carboranecarboxylic acid (m.p. 150°). On titration with sodium hydroxide a molecular weight of 187–191 was obtained (theory 190.5).

Refluxing of carboranecarboxylic acid with excess thionyl chloride followed by removal of the unreacted thionyl chloride gave a white solid (m.p. 70°) in essentially quantitative yield, the mass spectrum of which indicated it to be pure carborane-1-carboxylyl chloride. Treatment with aniline afforded the **anilide** (m.p. 132–133°).

Anal. Calcd. for $B_{10}C_9H_{17}NO$: C, 41.1; H, 6.5; B, 41.2; N, 5.3. Found: C, 41.2; H, 6.7; B, 41.0; N, 5.1.

Carborane-1,2 Diisocyanate (VII).—Carboranedicarboxylyl dichloride (2.5 g.) was dissolved in 25 ml. of benzene and 1.5 g. of lithium azide was added. The mixture was warmed to reflux temperature as nitrogen was evolved. Heating was continued until gas evolution ceased; 438 ml. of nitrogen was evolved (theory 448 ml.). The amber solution was filtered. The infrared spectrum of this solution showed a strong absorption at 4.55 μ characteristic of the isocyanate group and its mass spectrum was indicative of carborane diisocyanate.

Treatment of the benzene solution with excess methanol followed by refluxing led to the precipitation of a white solid which was recrystallized from methanol and analyzed correctly for carborane-1,2-bis-(methylurethane) (VIII) (m.p. 257–258°).

Anal. Calcd. for $B_{10}H_{18}C_6N_2O_4$: C, 24.8; H, 6.2; B, 37.2. Found: C, 24.8; H, 6.4; B, 37.2.

1,2-(2′-Oxopropylene)-carborane (XII).—A typical synthesis is described. 1,2-Bis-(carboxymethyl)-carborane and barium carbonate (5:1 weight ratio) are mixed and placed in a suitable sublimation apparatus. Vacuum is applied and the solids are warmed to 210° and maintained at this temperature until no more material sublimes from the melt. The sublimate is resublimed, giving 1,2-(2′-oxopropylene)-carborane melting at 170°.

Anal. Calcd. for $B_{10}C_5H_{14}O$: C, 30.3; H, 7.1. Found: C, 30.1; H, 7.1. **2,4-Dinitrophenylhydrazone:** Calcd. for $B_{10}C_{11}H_{18}N_4O_4$: C, 35.0; H, 4.8; B, 28.6. Found: C, 36.0; H, 5.3; B, 28.3.

1-Hydroxymethylcarborane (XIII).—Lithium aluminum hydride (15 g.) and 650 ml. of ether were placed in a 2-l., 3-necked flask fitted with a stirrer, reflux condenser, and nitrogen inlet. After refluxing under nitrogen for 0.5 hr., 93 g. of 1-acetoxymethylcarborane in 30 ml. of ether was added at a rate sufficient to maintain refluxing (about 1 hr.). When the addition was complete, the mixture was refluxed for another hour. After cooling to room temperature, 100 ml. of methanol was added followed by 300 ml. of water. Next, concentrated hydrochloric acid was added until the solid dissolved. The ethereal layer was removed and the aqueous layer was extracted three times with additional portions of ether. The combined ethereal solution was dried over magnesium sulfate, filtered, and the ether was removed, leaving a slightly pink solid which was recrystallized from pentane, giving 66.1 g. of white hydroxymethylcarborane (m.p. 225°).

Anal. Calcd. for $B_{10}C_3H_{14}O$: C, 20.7; H, 8.1. Found: C, 20.8; H, 8.2.

1,2-Bis-(hydroxymethyl)-carborane (XIV).—A solution of 27 g. of potassium hydroxide in 30 ml. of water was added to 200 ml. of methanol. This solution was cooled to 20° and 27 g. of bis-(acetoxymethyl)-carborane was added. The mixture was stirred for 1.5 hr. at room temperature and then poured into 1 l. of water. This solution was neutralized with hydrochloric acid and the resulting precipitate was washed well with water and dried under vacuum. The product was recrystallized from heptane–toluene to give 18.0 g. (99%) of white needles of bis-(hydroxymethyl)-carborane (m.p. 303–304°).

Anal. Calcd. for $B_{10}C_4H_{16}O_2$: C, 23.5; H, 7.9. Found: C, 23.9; H, 8.1.

1,2-(2′-Oxapropylene)-carborane (XV).—Bis-(hydroxymethyl)-carborane (5.8 g.) and 50 ml. of concentrated sulfuric acid were placed in a sublimation apparatus and heated under vacuum at 110° for 6 hr. The sublimate was dissolved in pentane, separated from insoluble material, and dried over magnesium sulfate. After filtering, the solvent was removed and the residue was resublimed to give 4.4 g. of white 1,1-(2′-oxapropylene)-carborane. The tendency of this material to sublime prevented obtaining an accurate melting point. It was readily identified by its mass spectrum (*m/e* value), and the nuclear magnetic resonance spectrum indicated 4 C–H/10 B–H.

B-Bromo-1,2-(2′-oxapropylene)-carborane (XVI).—A satisfactory procedure consisted of dissolving 1,2-(2′-oxapropylene)-carborane in a solution prepared by dissolving 10 equivalents of bromine in a 10% solution of benzoyl peroxide in carbon tetrachloride. The solution was exposed to sunlight for 5 hr., during which time hydrogen bromide was evolved. The solution was treated with sodium hydroxide solution to decompose the peroxide and remove excess bromine. The carbon tetrachloride solution was dried over magnesium sulfate and filtered, and the solvent was removed. Sublimation readily removed the remaining starting material and recrystallization from pentane gave B-bromo-1,2-(2′-oxapropylene)-carborane, which melted at 127–129°, in 70–75% yield. The mass spectrum verified the molecular formula (*m/e* value), and integration of the proton n.m.r. spectrum showed a ratio of 4 C–H to 9 B–H groups, indicating attachment of the bromine to a boron atom.

1,2-Bis-(α-hydroxyethyl)-carborane (XVII).—Carborane (15 g.) in 50 ml. of ether was added to 0.276 mole of *n*-butyllithium in 120 ml. of ether. The resulting solution was cooled to −50° and when 30 ml. of acetaldehyde was slowly added, a vigorous reaction occurred. The solution was allowed to warm to 0° and poured into water. The resulting mixture was acidified with hydrochloric acid, the ether was separated, and the aqueous portion was extracted with more ether. The combined ethereal solution was dried over anhydrous magnesium sulfate. The ether was evaporated until the volume was about one-third of the original. An equal volume of pentane was added and a precipitate formed; this was removed and recrystallized from ether–pentane. The bis-(α-hydroxyethyl)-carborane (8.0 g. or 31.3%) did not melt below 400°.

Anal. Calcd. for $B_{10}H_{20}C_6O_2$: C, 31.0; H, 8.6. Found: C, 31.1; H, 8.8.

1-Allylcarborane (XVIII).—This material has been prepared many times in amounts varying from 10 to 600 g. A generalized procedure is given. The desired quantity of carborane is dissolved in ether (50 g. of carborane/150 ml. of ether) in a three-necked flask which has been fitted with an addition funnel, air driven stirrer, and low temperature thermometer. The solution is cooled to −10° and a stoichiometric amount of phenyllithium[9] is added at a fairly rapid rate while keeping the temperature at −10°. After the addition, the temperature is allowed to rise to 0° and maintained there for 15 min., whereupon the temperature is again lowered to −10° when an equimolar plus 15% quantity of 3-bromopropene dissolved in an equal volume of ether is added dropwise. After completion the reaction mixture is allowed to warm to 10° for 15 min. and treated with 20% hydrochloric acid, sufficient to dissolve the lithium bromide formed. The ethereal layer is separated, dried over calcium chloride, and filtered, and the ether is removed under reduced pressure. Any unreacted carborane will sublime out by holding the material at 100° (0.1 mm.). The still head is changed and distillation of the residue is conducted, collecting the fraction distilling at 65–85° (0.05–0.1 mm.) in about 70% yield. Mass spectral analysis identified the product and readily informs one of the quantity of by-product diallylcarborane present, if any. Use of phenyllithium rather than *n*-butyllithium greatly lowers the tendency for forming diallylcarborane. Diallylcarborane can be removed by fractionation. 1-Allylcarborane will solidify on standing and melts at 63–65°.

Anal. Calcd. for $B_{10}C_5H_{16}$: C, 32.5; H, 8.7; B, 58.8. Found: C, 32.7; H, 8.9; B, 58.5.

Epoxy-1-allylcarborane (XIX).—A solution of 1.25 ml. of 90% hydrogen peroxide (0.045 mole) in 65 ml. of methylene chloride was prepared and cooled in an ice bath and to this was added 7.5 ml. (0.054 mole) of trifluoroacetic anhydride. This was stirred and allowed to come to room temperature over a 45-min. period. This solution was then added to a stirred slurry of 19.15 g. (0.134 mole) of disodium hydrogen phosphate and 5.0 g. of allylcarborane in 50 ml. of methylene chloride. When the addition was complete, the solution was refluxed for 1 hr., cooled, and filtered. The methylene chloride was removed from the filtrate under reduced pressure, leaving a yellow solid which was refluxed in petroeum ether (30–60°), filtered, and cooled in Dry Ice. The resulting precipitate was removed and recrystallized from petroleum ether to give 2.8 g. (51.5%) of epoxyallylcarborane (m.p. 68°), which had an infrared spectrum indicating the presence of an epoxide link and the usual carborane absorption and a mass spectrum also consistent with this structure. Conversion to the diol (XXI) also confirms this structure.

1-(**β,γ-Dihydroxypropyl)-carborane (XXI). A.**—Epoxyallylcarborane (1.5 g.) was refluxed for 16 hr. in 50 ml. of 5% sulfuric acid. After cooling, the mixture was extracted with ether which had been dried over magnesium sulfate and filtered, and the ether was removed. The resulting solid was transferred to the thimble of a Soxhlet extractor and extracted with *n*-heptane for 8 hr. Cooling the extract and filtering gave 1.4 g. (86%) of white β,γ-dihydroxypropylcarborane (m.p. 89–90°).

Anal. Calcd. for $B_{10}C_5H_{18}O_2$: C, 27.5; H, 8.3; B, 49.7. Found: C, 27.3; H, 8.5; B, 49.5.

B.—Allylcarborane (24 g.) was dissolved in 75 ml. of formic acid (98 + %) and 4.0 ml. of hydrogen peroxide (98 + %) was added. The cloudy mixture was warmed at 55–60° for 20 hr. (After about 2.5 hr. the solution had become clear and the reaction was probably complete at this time). The solution was poured into 350 ml. of 20% sodium hydroxide solution. This was extracted with ether, dried over magnesium sulfate, and filtered, and the ether was removed leaving a yellowish solid (m.p. 65–80°) which was probably impure hydroxyformyl allylcarborane. This was dissolved in a minimum of absolute ethanol (∼60 ml.) and to this was added sufficient ethanolic potassium hydroxide (∼10% solution) to contain 0.20 mole of the base. The resulting solution was stirred at room temperature for 2 hr. and poured into 200 ml. of water. This mixture was extracted with ether, which was dried over magnesium sulfate and filtered, and the ether was removed leaving a white solid which was recrystallized with difficulty from refluxing *n*-heptane, giving 14.9 g. (52.7%) of white, crystalline β,γ-dihydroxypropylcarborane (m.p. 92–93°). The infrared spectrum of this compound was identical with that of the product formed in A, but a mixture of the two materials melted over the range 65–80°.

Anal. Found: C, 27.1; H, 8.5.

Bis-(carboranylmethyl) Methyl Acetate (XXIII).—In a typical preparation, a solution of 1 g. of bis-(carboranylmethyl) methanol in a mixture of 10 ml. of ethyl acetate and 5 ml. of acetic anhydride is treated with 2 drops of perchloric acid. The temperature immediately rises about 15°. After 0.5 hr. the solvents are removed under reduced pressure and the residue is washed well with a solution of sodium bicarbonate. The solid is dissolved in ether, dried over magnesium sulfate, and filtered, and the ether is removed. The residue is recrystallized twice from heptane–toluene to give the ester in 47% yield (m.p. 206–207.5°). It is believed that the second recrystallization is not necessary, and if it is omitted, yields above 90% are obtained.

Anal. Calcd. for $B_{20}C_9H_{30}O_2$: C, 28.0; H, 7.8. Found: C, 28.1; H, 8.0.

1,3-Dicarboranylpropene (XXIV).—Bis-(carboranylmethyl) methyl acetate (53 g., 0.137 mole) was dissolved in 125 ml. of ethyl acetate and placed in a dropping funnel mounted atop a glass tube (24 in. long by 29 mm. o.d.) which was filled with glass helices and heated along most of its length to 550°. A 250-ml. round-bottomed flask with an outlet to a bubble-off was at the bottom. After flushing with nitrogen, the solution was allowed to drop in slowly. After about one-half had been added, the tube became plugged near the bottom. The reactor was cooled and washed out with ether and the reaction was resumed. After all of the solution had been added, the reactor was cooled and again washed out with ether. The combined ethereal solution was washed three times with water and three times with sodium bicarbonate solution, dried over magnesium sulfate, and filtered. The ether was removed and the white, solid residue was recrystallized from *n*-heptane, giving 27.5 g. (61%) of 1,3-dicarboranylpropene, which did not melt below 300°.

Anal. Calcd. for $B_{20}C_7H_{26}$: C, 25.7; H, 8.0; B, 66.3. Found: C, 25.9; H, 8.2; B, 66.3.

1-Vinylcarborane (XXV).—This preparation is typical of many in which either α- or β-acetoxyethylcarborane was used. β-Acetoxyethylcarborane (6.16 g., 0.0268 mole) is dissolved in 15 ml. of glacial acetic acid. (The α isomer is a liquid and may be used directly.) The solution is placed in an addition funnel and allowed to drop through a column (*cf.* preparation of 1,3-dicarboranylpropene (XXIV)) heated to 500 ± 5° in a slow stream of nitrogen. After cooling, the column is washed out with pentane and added to the product collected in the receiver. The

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[9] H. Gilman and L. S. Miller, *Org. Reactions*, **6**, 353 (1951).

organic solution is washed several times until the acetic acid has been removed. The solution is dried over magnesium sulfate, filtered, and chilled to precipitate unconverted ester, which is removed. The solvent is removed and the product may be distilled or sublimed to give vinylcarborane melting at 76–77°. Occasionally, one recrystallization of the distilled material from methanol–water was required to give this melting point. The material is identical in every respect with that prepared by the direct reaction of vinylacetylene and decaborane[2] (Table I).

TABLE I

SUMMARY OF PREPARATIONS

Starting matl.	Amt., g.	Yield, g.	Yield, %
α-Acetoxyethylcarborane	5.0	3.4	98.8
	8.6	4.4	74.1
β-Acetoxyethylcarborane	15.0	9.8	95.2
	13.0	7.1	78.9
	10.4	5.0	69.5
	12.8	6.7	76.2

1-Methyl-2-isopropenylcarborane (XXVI).—1-Isopropenylcarborane (7.2 g., 0.04 mole) in 25 ml. of ether was treated with an equimolar quantity of phenyllithium as prepared in ether; 6.3 g. of methyl iodide was added and the reaction mixture was refluxed for 2 hr., then poured into water. The ethereal solution was recovered, washed with water, and dried over magnesium sulfate. After filtration, the ether was removed and the residue was distilled, collecting the fraction boiling at 77–82° (0.3 mm.). Methylisopropenylcarborane was identified through its mass spectrum, which showed no other materials to be present except a trace of biphenyl.

1-Isopropenylcarborane-2-carboxylic Acid (XXVII).—Isopropenylcarborane (7.2 g., 0.04 mole) in 75 ml. of ether was treated with a commercially available solution (containing 0.04 mole) of *n*-butyllithium. Carbon dioxide was passed rapidly through the resulting solution and a precipitate formed. The mixture was treated with an equal volume of water and the water layer was separated. Acidification of the aqueous layer freed the product, which was recovered and recrystallized from ether–pentane, giving 8.8 g. (79%) of isopropenylcarboranecarboxylic acid (m.p. 175°).

Anal. Calcd. for $B_{10}C_6H_{16}O_2$: C, 31.6; H, 7.1; mol. wt., 228. Found: C, 32.1; H, 7.3; mol. wt., 231 (cryoscopic).

Reactions of Carboranylmethylmagnesium Bromide. Preparation of the Reagent.—Magnesium turnings (0.4 g.) were slurried in 25 ml. of ether. After flushing the apparatus with nitrogen, a solution of 4.0 g. of 1-bromomethylcarborane in 25 ml. of ether was added very slowly. A crystal of iodine was used to initiate the reaction. After the addition was complete ($\sim$3 hr.) the mixture was refluxed for 1 hr. Solutions such as this were used in the following reactions.

Reaction with Water.—Carboranylmethylmagnesium bromide from 4.0 g. of bromomethylcarborane was poured into 25 ml. of cold, saturated ammonium chloride solution. The ethereal layer was recovered, dried over magnesium sulfate, and filtered, and the ether was removed leaving a tan solid. The mass spectrum of this material showed it to be methylcarborane containing a small quantity of bromomethylcarborane. Recrystallization from pentane gave 2.0 g. (75%) of methylcarborane identical with that prepared by the reaction of methylacetylene with decaborane.[2]

Reaction with Bromine.—Carboranylmethylmagnesium bromide was prepared from 4.0 g. of bromomethylcarborane. A solution of bromine in ether was added until the orange color was no longer discharged. The solution was hydrolyzed and the ethereal layer was recovered, washed with sodium thiosulfate solution, dried over magnesium sulfate, and filtered, and the ether was removed leaving 3.5 g. of white solid melting over the range 70–75°. This was not purified further, but its mass spectrum showed the *m/e* cut-off expected for a bromomethylcarborane, although the breakdown peaks indicated the presence of a methyl group and not a bromomethyl group.

Reaction of 1,2-Bis-(chloromethyl)-carborane with Magnesium.—A micro resin kettle was fitted with a reflux condenser (sodium hydroxide drying tube as outlet), a stirrer, and a distillation apparatus so arranged that tetrahydrofuran could be directly distilled into the resin kettle. Bis-(chloromethyl)-carborane (1.0 g.) and magnesium turnings (2.0 g.) were placed in the flask. Approximately 30 ml. of tetrahydrofuran was distilled from sodium hydride into the reactor. A small crystal of iodine was added and reaction was observed. The mixture was heated to reflux and after about 45–60 min. all of the magnesium had dissolved and an intense red solution had formed.

Hydrolysis of this solution yielded a semisolid which was identified by its mass spectrogram as chiefly dimethylcarborane, although no further characterization was made.

Reaction of 1-Bromo-2-propylcarborane with Potassium Cyanide.—A solution of 0.5 g. of 1-bromo-2-propylcarborane, 12 ml. of acetone, 6 ml. of water, and 0.2 g. of potassium cyanide was refluxed for 42 hr. A clear, yellow solution resulted. The acetone was distilled from the mixture and replaced with water. On cooling, a tan solid formed, which was removed. This material melted at 60–62° without purification and its mass spectrum and infrared spectra were identical with those for 1-propylcarborane, the former indicating the presence of a trace of bromopropylcarborane.

1-Trimethylsilylcarborane (XXVIIIa).—Trimethylchlorosilane (1.52 g., 0.014 mole) was added dropwise to 37.1 ml. of a previously prepared solution containing 2.2 g. (0.014 mole) of lithiocarborane. An instantaneous reaction occurred with the precipitation of lithium chloride. When the addition was complete, the mixture was refluxed for 6 hr., cooled, and treated with 50 ml. of cold, dilute hydrochloric acid. The ethereal layer was separated, dried over calcium chloride, and filtered, and the solvent was removed. The residue was dissolved in 100 ml. of pentane, and the solution was filtered and cooled in a Dry Ice bath. The precipitated product was recovered and sublimed under vacuum at 90° to give pure trimethylsilylcarborane (m.p. 94–95°).

Anal. Calcd. for $B_{10}C_5H_{20}Si$: C, 27.8; H, 9.3; B, 50.0; Si, 12.9. Found: C, 28.0, 28.0; H, 9.4, 9.6; B, 59.8, 59.5; Si, 13.0.

1-Triphenylsilylcarborane (XXVIIIb).—The procedure as described for XXVIIIa was repeated using 12.7 ml. of an ethereal solution of 0.74 g. of lithiocarborane and 1.4 g. of triphenylchlorosilane. The triphenylsilylcarborane melted at 165–167°.

Anal. Calcd. for $B_{10}C_{20}H_{26}Si$: C, 59.9; H, 6.5; B, 26.9. Found: C, 61.0, 62.3; H, 6.5, 6.4; B, 27.1, 27.1.

Dimethyldicarboran-1-ylsilane (XXIX).—The procedure as described for XXVIIIa was repeated using 106 ml. of an ethereal solution of 2.1 g. of lithiocarborane and 10.74 g. of dimethyldichlorosilane. The dimethyldicarboranylsilane melted at 195–196.5°.

Anal. Calcd. for $B_{20}C_6H_{28}Si$: C, 21.0; H, 8.2; B, 62.2; Si, 8.6; mol. wt., 345. Found: C, 21.5, 21.2; H, 8.3, 8.3; B, 62.5, 62.8; Si, 8.9; mol. wt., 349 (cryoscopic).

Trimethyl-(carboran-1-ylmethyl)-silane (XXX).—The procedure as described for XXVIIIa was repeated using 127 ml. of an ethereal solution of 0.72 g. of lithiocarborane and 5.95 g. of trimethylchloromethylsilane. The trimethyl-(carboranylmethyl)-silane melted at 52 although it appeared to soften at 42°.

Anal. Calcd. for $B_{10}C_6H_{22}Si$: B, 47.0. Found: B, 46.4, 46.6.

1,2-(2′,2′-Dimethyl-2′-silapropylene)-carborane (XXXI).—An ethereal solution (56 ml.) of 3.1 g. (0.02 mole) of dilithiocarborane was allowed to react with 1.65 g. (0.01 mole) of dimethyldichloromethylsilane as described for XXVIIIa. After recovering the product from ether it was recrystallized from pentane, giving white crystals melting at 149–150°.

Anal. Calcd. for $B_{10}C_6H_{20}Si$: C, 31.6; H, 8.9; B, 47.4;

mol. wt., 228. Found: C, 32.8, 32.9; H, 9.4, 9.3; B, 46.8, 46.9; mol. wt., 232.

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

A New Series of Organoboranes. IV. The Participation of the 1,2-Dicarbaclovododecaborane(12) Nucleus in Some Novel Heteratomic Ring Systems.

BY STELVIO PAPETTI AND T. L. HEYING

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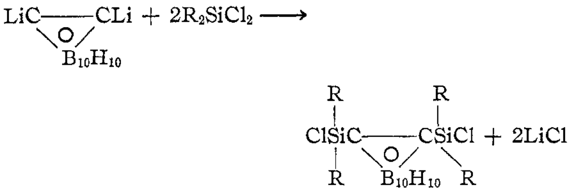
Various chlorosilylcarborane derivatives were prepared. In subsequent reactions with amines or water a marked propensity for the formation of five-membered disilaazane and disilaoxane rings was exhibited. In reactions with dilithiocarborane, novel disilacyclohexane analogs were formed.

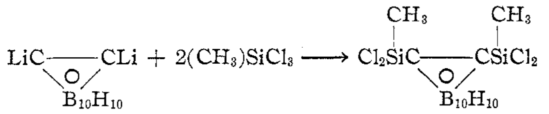
In the preceding paper[1] several examples of the synthesis of mono- and disilylcarboranes were given. Utilization of the same general preparative procedures has proven quite satisfactory for the preparation of 1,2-bis-(chlorosilyl)-carboranes in good yield as indicated in reaction 1.



(1)

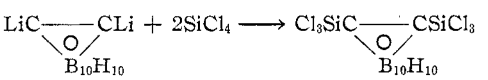
I, R = CH_3
II, R = C_6H_5

By applying the proper stoichiometry we were able to prepare the corresponding tetrachloro and hexachloro derivatives in surprisingly good yield.



(2)

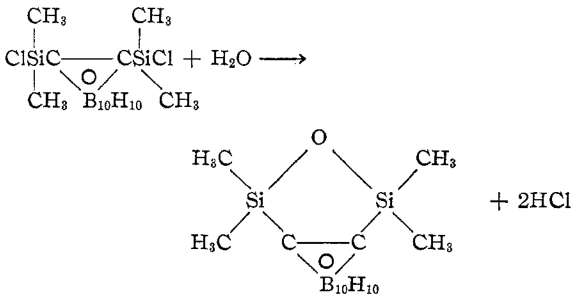
III



(3)

IV

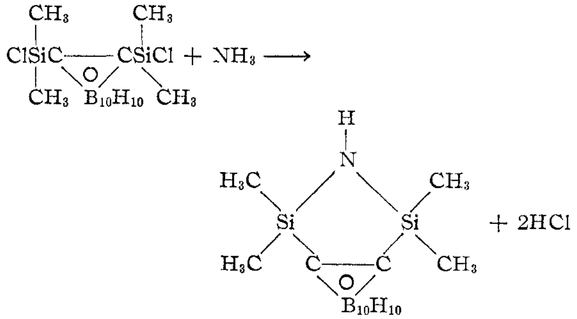
To determine whether 1,2-bis-(chlorodimethylsilyl)-carborane (I) would behave chemically as do the conventional organic derivatives, it was subjected to hydrolysis, expecting to form a macrocyclic siloxane, a linear silicone, or possibly the corresponding dihydroxy compound. To the contrary, under all of the many sets of conditions attempted to date, I was converted to the cyclic tetramethyldisilaoxane, V. In most instances it is achieved in high purity in essentially quantitative yield



(4)

V

The cyclic structure was first assigned on the basis of its elemental analysis, molecular weight, and infrared spectrum. This assignment was borne out subsequently by examination of its mass spectrum, which is in agreement in every detail. The same evidence has been gained for those novel cyclic structures discussed below. Compound V above has also been prepared by the reaction of dilithiocarborane with excess tetramethyldichlorodisiloxane.



(5)

VI

When 1,2-bis-(chlorodimethylsilyl)-carborane was treated with ammonia, a similar reaction occurred to

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[1] T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *Inorg. Chem.*, **2**, 1097 (1963).