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Carboranes. I. The Preparation and Chemistry of 1-Isopropenylcarborane and its Derivatives (a New Family of Stable Clovoboranes)

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The preparation of the first member of a new family of stable polycyclic boranes is reported. Treatment of isopropenylacetylene with derivatives of decaborane of the form $B_{10}H_{12}\cdot L_2$ (where L is any one of several Lewis bases) or with mixtures of decaborane and L give the new polycyclic borane. The general applicability of this reaction to other acetylenes is also reported. The cycloboranes which are formed contain a $=C_2B_{10}H_{10}$ unit and are members of the generic family, $C_2B_nH_{n+2}$. The nucleus exhibits a high degree of oxidative, hydrolytic, and thermal stability.

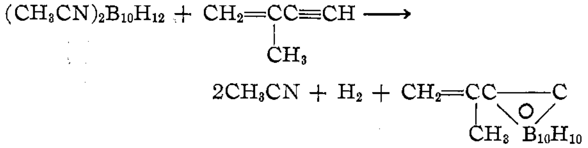
The interactions of the lower boron hydrides and their derivatives with unsaturated hydrocarbons have been extensively studied by many workers.[1] In this paper we report the formation of a unique cycloborane through the interaction of an olefinic acetylene such as isopropenylacetylene with a diligand derivative of decaborane, $B_{10}H_{12}\cdot L_2$, where L is a basic ligand such as acetonitrile. The broad applicability of this reaction to other acetylenic compounds with $B_{10}H_{14}$–Lewis base mixtures or $B_{10}H_{12}\cdot L_2$ is also reported.

Results and Discussion

The interaction of 6, 9-bis-(acetonitrile)-decaborane[2,3] with isopropenylacetylene resulted in the formation of a new borane with characteristically covalent properties. The product, a low melting solid, was soluble in both polar and nonpolar organic solvents and possessed a camphoraceous odor. Unlike conventional boron hydrides, the product was hydrolytically stable, nonreactive toward air, and thermally stable (under autogenous pressures) to at least 350°.

The cycloborane structure was assigned based upon the evidence which follows. The infrared spectrum of a KBr pellet (Fig. 1) of the purified product revealed a $>C{=}CH_2$ grouping with retention of the isopropenyl group, a B–H absorption displaced from 3.98 μ in 6,9-bis-(acetonitrile)-decaborane to 3.90 μ in the product, and the notable absence of a $-C{\equiv}CH$ grouping. Elemental analysis of the product revealed that nitrogen was absent and that the boron content was 57.9%. The "missing nitrogen" was found as free acetonitrile in the solvent. Careful monitoring of the reaction revealed that hydrogen was eliminated.

Mass spectral analyses of the product confirmed that evolution of one mole of hydrogen had occurred. The most intense peak in the polyisotopic spectrum occurred at m/e 184, with a parent peak at m/e 186, which is consistent with a compound of the empirical formula $^{12}C_5{}^1H_{16}{}^{11}B_{10}$. This evidence indicated a reaction occurring as presented in eq. 1.



$$(CH_3CN)_2B_{10}H_{12} + CH_2{=}\underset{CH_3}{C}C{\equiv}CH \longrightarrow 2CH_3CN + H_2 + CH_2{=}\underset{CH_3}{C}\underset{\diagdown O \diagup\; B_{10}H_{10}}{C\text{———}C} \quad (1)$$

The symbolism used for the product represents a polycyclic structure in which the nucleus of ten boron atoms is bridged by two carbon atoms and is not intended to imply a structure in which two carbons are attached to a common boron atom. The product is a derivative of a more general group of compounds $C_2B_nH_{n+2}$[4] and can be represented as $C_2B_{10}H_{11}R$, where R is the isopropenyl group. In keeping with the recommendation of the Committee on Nomenclature, the name "carborane" will be used for this specific C_2B_{10} nucleus and the product is properly identified as 1-isopropenylcarborane.

The reactions of 1-isopropenylcarborane indicated a far greater degree of chemical and thermal stability for the carborane nucleus than for the borane nucleus of its precursor or for decaborane. When it was dissolved in methanol and refluxed for 24 hr. to attempt an oxidative alcoholysis no gas was evolved and it was recovered essentially unchanged. When refluxed in water for 36 hr. no hydrolysis occurred so that it was found possible to purify 1-isopropenylcarborane by steam distillation. No degradation was noted when the product was treated with refluxing methanol (containing hydrochloric acid) for 24 hr., but treatment with refluxing methanolic caustic resulted in the evolution of exactly one mole of gas. The starting material was not recovered nor was the resultant borane isolated; it can be presumed that a new borane species was formed.

The remarkable resistance of the boron hydride moiety in 1-isopropenylcarborane toward oxidative attack was further evidenced when it was found that it could be recrystallized from hot 100% sulfuric acid (150°), an oxidizing acid.

Chemical proof of structure of the isopropenyl group in the product also served to demonstrate the stability of the carborane nucleus. Treatment with alkaline permanganate in acetone resulted in oxidation of the alkenyl group but with retention of the original nucleus.

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[1] D. T. Hurd, *J. Am. Chem. Soc.*, **70**, 2053 (1948); H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); R. Köster, *Angew. Chem.*, **69**, 684 (1957); B. C. Harrison, I. J. Solomon, R. D. Hites, and M. J. Klein, *J. Inorg. Nucl. Chem.*, **14**, 195 (1960).

[2] R. Schaeffer, *J. Am. Chem. Soc.*, **79**, 1006 (1957).

[3] J. van der Mass Reddy and W. N. Lipscomb, *ibid.*, **81**, 754 (1959).

[4] I. Shapiro, C. D. Good, and R. W. Williams, *ibid.*, **84**, 3837 (1962).

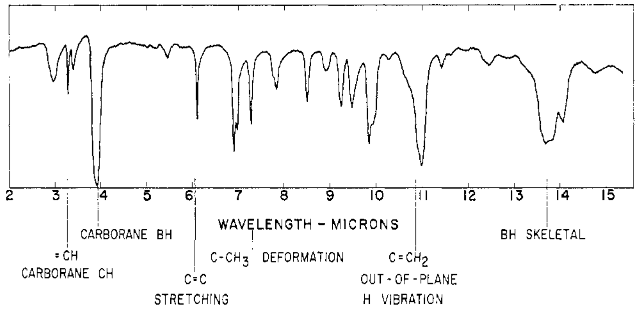
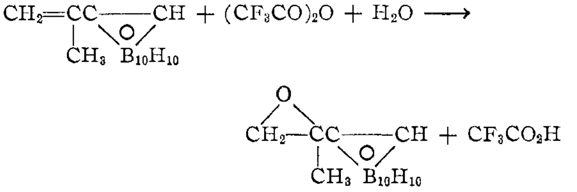


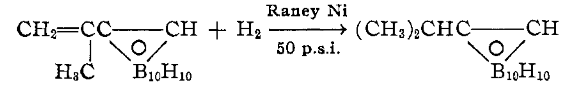
Fig. 1.—Infrared spectrum of 1-isopropenylcarborane.

Oxidation with trifluoroperacetic acid[5] resulted in the formation of the epoxide, which was identified by elemental analyses and infrared spectroscopy.



$$\mathrm{CH_2{=}\underset{CH_3}{C}C\underset{B_{10}H_{10}}{\diagdown O \diagup}CH + (CF_3CO)_2O + H_2O \longrightarrow CH_2\overset{O}{-}\underset{CH_3}{C}C\underset{B_{10}H_{10}}{\diagdown O \diagup}CH + CF_3CO_2H} \quad (2)$$

Raney nickel-catalyzed hydrogenation of 1-isopropenylcarborane proceeded readily and 1-isopropylcarborane, a mobile, colorless liquid, was formed. The infrared spectrum of the isopropyl compound showed retention of the carborane nucleus and reduction of the alkenyl group to the isopropyl group.



$$\mathrm{CH_2{=}\underset{H_3C}{C}C\underset{B_{10}H_{10}}{\diagdown O \diagup}CH + H_2 \xrightarrow[\text{50 p.s.i.}]{\text{Raney Ni}} (CH_3)_2CHC\underset{B_{10}H_{10}}{\diagdown O \diagup}CH} \quad (3)$$

These chemical reactions indicate a new nucleus which is radically different than the parent borane. If the structure is indeed a closed, polycyclic structure as proposed in the original equation, then its density would be expected to be high relative to other alkyldecaborane compounds. This proved to be the case.

Unlike decaborane or alkyldecaboranes, which can be titrated as monoprotic acids,[6] neither 1-isopropyl- nor 1-isopropenylcarborane could be titrated by the prescribed procedure as an acid with caustic in alcohol. The acidity of decaborane has been ascribed to the protonic nature of its bridge hydrogens,[7] and the lack of protonic acidity of these two carboranes is in keeping with a lack of bridge hydrogens.

The carborane portion of 1-isopropenylcarborane is not only resistant to chemical attack but it also appears to contribute to the over-all thermal stability of the molecule. When 1-isopropenylcarborane was heated in an isoteniscope (nitrogen atmosphere) no decomposition was noted up to 350°. Even at 400°, pressure changes which were noted could be attributed to polymerization and pyrolysis of the substituent group rather than degradation of the carborane nucleus. By contrast, decaborane and its derivatives exhibit thermal instability at significantly lower temperature.[8]

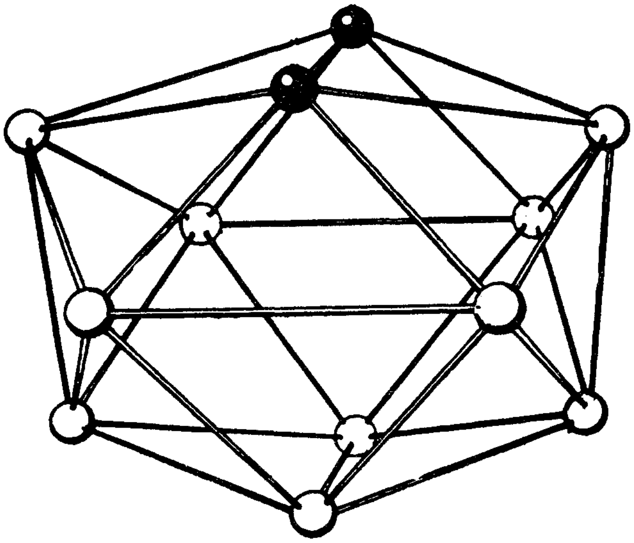


Fig. 2.—Icosahedral structure for carborane nucleus: ●, carbon atom; ○, boron atom (attatched hydrogen atom not shown).

The structure of this new borane nucleus has not been completely elucidated. One possibility is a structure in which an etheno bridge (—HC=CH—) connects the 6 and 9 boron atoms of the decaborane basket.[9] Another possibility is a polyhedron (Fig. 2) similar to the icosahedron suggested by Longuet-Higgins and Roberts[10] for the $B_{12}H_{12}^{-2}$ ion and considered by Hoffman and Lipscomb[11] for the several C_2B_{10} species.

There are several possible bonding variations in the icosahedral structure which arise from the nonidentity of carbon and boron, and these factors could make for either a regular or irregular icosahedron. In addition, the two carbons may bear an *ortho*, *meta*, or *para* relationship to each other.[11] Views on the structure of the carborane nucleus are also presented in a paper by Grafstein[12]; pending further data no definitive structure can be assigned but it is considered most probable that the structure is an irregular icosahedron in which two *ortho* carbons replace two of the boron atoms in the $B_{12}H_{12}^{-2}$ structure proposed by Longuet-Higgins.[10] The $B_{12}H_{12}^{-2}$ ion requires 26 bondng electrons, as would the structure for carborane. Such a structure would tend to evidence a high degree of delocalized bonding and consequently manifest pronounced electron-withdrawing effects.

Evidence indicates that there is electronic interaction between the isopropenyl double bond and the carborane nucleus. Thus, attempts to add bromine or iodine monobromide under electrophilic conditions were unsuccessful, thereby indicating decreased nucleophilicity of the isopropenyl group.

Treatment of the isopropenyl compound with sodium

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(5) W. D. Emmons, A. S. Pagano, and J. P. Freeman, *J. Am. Chem. Soc.*, **76**, 3472 (1954).

(6) G. A. Guter and G. W. Schaeffer, *ibid.*, **78**, 3546 (1956).

(7) R. W. Parry and L. J. Edwards, *ibid.*, **81**, 3554 (1959).

(8) I. Shapiro and R. W. Williams, *ibid.*, **81**, 4787 (1959); A. J. Owens, *J. Chem. Soc.*, 5438 (1961).

(9) This numbering system is the one accepted by the Boron Nomenclature Committee as described by G. Schaeffer, Abstracts of Papers, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April, 1958, p. 2L.

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

(11) R. Hoffman and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963).

(12) D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).

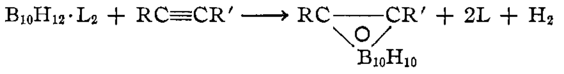
or lithium in liquid ammonia resulted in the addition of four equivalents of the alkali metal, whereas treatment of the isopropyl analog with sodium resulted in the addition of two equivalents of alkali metal. Therefore, two mole atoms of alkali metal added to the alkenyl group and is indicative of conjugated unsaturation as in arylated alkenes and conjugated alkenes.

A comparison of the ultraviolet absorption spectra of the isopropenyl and isopropyl compounds confirms that isopropenyl–carborane electronic interplay occurs in 1-isopropenylcarborane. Finally, the calculated molar refraction of 1-isopropenylcarborane differs by 0.29 cc. from the experimental value. This optical anomaly constitutes additional proof of electronic interaction between the nucleus and the alkenyl group.

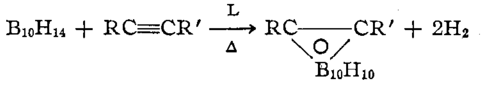
The generality of the carborane reaction was demonstrated by varying either the L component of $B_{10}H_{12}\cdot L_2$ or the acetylenic component.

The other $B_{10}H_{12}\cdot L_2$ compounds which were employed to produce greater than 50% yield of 1-isopropenylcarborane included those derived from N,N-dimethylformamide, N,N-dimethylacetamide, and N,N-dimethylaniline. Pre-formation of the bis-ligand derivative was not necessary. Instead, decaborane could be mixed with isopropenylacetylene, benzene, and various Lewis bases such as acetonitrile, N,N-dimethylacetamide, N,N-dimethylformamide, butyl methyl sulfide, tributylphosphine, and dimethyl cyanamide; yields were highest with the nitrile and sulfide. When triethylamine was used, a very low yield of the carborane (based on the decaborane charged) was obtained. It has since been demonstrated by Hawthorne[13] that triethylamine–decaborane interaction forms a compound of the type $[(C_2H_5)_3NH]_2{}^{+2}B_{10}H_{10}{}^{-2}$ as the major product rather than $[(C_2H_5)_3N]_2B_{10}H_{12}$, although the latter is also formed. In the absence of the Lewis base, no reaction occurred between decaborane and the acetylenic compound. It therefore appears that $B_{10}H_{12}L_2$ formation is a requirement for carborane formation.

The interaction of decaborane–acetonitrile mixtures, or 6,9-bis-(acetonitrile)-decaborane, with many terminal acetylenes, α,ω-diacetylenes, and internal acetylenes resulted in conversion of the acetylenic compound to the corresponding carborane. The initial equation, 1, may then be presented in a still broader form.


$$B_{10}H_{12}\cdot L_2 + RC{\equiv}CR' \longrightarrow \underset{B_{10}H_{10}}{RC{-}CR'} + 2L + H_2 \quad (4)$$

where R = H, alkyl, aryl, haloalkyl, carboalkoxy, or acetoxyalkyl and R′ = H, aryl, haloalkyl, carboalkoxy, or acetoxyalkyl, or more simply


$$B_{10}H_{14} + RC{\equiv}CR' \xrightarrow[\Delta]{L} \underset{B_{10}H_{10}}{RC{-}CR'} + 2H_2 \quad (5)$$

As typical examples of the formation of the carborane nucleus the preparations of carborane, 1-methylcarborane, 1-bromomethylcarborane, 1,2-diphenylcarborane, 1,2-bis-(bromomethyl)-carborane, 1,2-bis-(acetoxymethyl)-carborane, and 1,3-dicarboranylpropane are presented in Table I. A discussion of other syntheses will be presented in subsequent papers.

Experimental[14]

Reagents.—The decaborane used in this work was recrystallized from heptane prior to use. Reagent grade benzene dried over sodium was used, as well as reagent grade acetonitrile. The isopropenylacetylene was used as received from Air Reduction Company.

All data on gas evolution are corrected to STP. All yield figures are based on the boron hydride charged in the reaction. Melting points are uncorrected.

Instrumentation.—Infrared data were obtained on a Perkin-Elmer Model 21 infrared recording spectrophotometer; mass spectral analyses were conducted on a Bendix Model 12-100 time-of-flight mass spectrometer with Model 14 ion source; the ultraviolet absorption spectra were determined on a Beckman DK-2 ratio recording spectrophotometer.

Preparation of $B_{10}H_{12}\cdot L_2$.—**Bis-(acetonitrile)-decaborane** was prepared by the procedure of Schaeffer,[2] and the **bis-(dimethylacetamide)-decaborane** by the method of Pace.[15] In the latter case it was found advantageous to merely mix the reactants at room temperature in benzene for 24 hr. and then isolate the precipitated product.

6,9-Bis-(N,N-dimethylaniline)-decaborane.—N,N-Dimethylaniline, 1.0 mole, was added with stirring to a solution of 0.2 mole of decaborane in 215 ml. of toluene. The temperature of the deep orange solution was raised to 60° in 1 hr., at which time the flask was filled with a copious white precipitate. The mixture was maintained at 60° for 18 hr., during which time 0.22 mole of H_2 was evolved. The reaction mixture was cooled and filtered, and the solid product was washed and dried to give 65.7 g. (90.6% yield) of a product which melted at 120–123° with decomposition.

Anal. Calcd. for $C_{16}H_{34}B_{10}$: C, 52.99; H, 9.45; B, 29.84. Found: C, 52.81; H, 10.21; B, 29.76.

Preparation of 1-Isopropenylcarborane.—Benzene, 100 ml., 0.103 mole of bis-(acetonitrile)-decaborane, and 0.115 mole of isopropenylacetylene were added to a 500-ml., 3-neck flask equipped with a Dry Ice cooled condenser, an agitator, and a reflux condenser leading to a wet-test meter. The mixture was agitated for 3 hr., during which time 0.057 mole of gas (>90% hydrogen by gas chromatography) was evolved, most of the solid disappeared, and the solution turned orange. The mixture was cooled and 1.1 g. of unreacted borane was separated by filtration. The solvent was removed from the filtrate and collected. Infrared analysis revealed that the distillate was largely benzene containing acetonitrile. To the distillate was added 0.055 mole of decaborane and the mixture was heated at reflux for 24 hr., then cooled and filtered. A yellow solid was isolated which was washed with benzene and dried over paraffin for 2 to 3 days. The dried yellow-white solid was identified as being predominantly bis-(acetonitrile)-decaborane by infrared analysis [wt. 7 g. (equivalent to 0.0622 mole of CH_3CN), a 30% recovery of acetonitrile]. The sirup which remained after removal of solvent was heated further to 80° under a pressure of 10 mm., allowed to cool, and added slowly to vigorously agitated petroleum ether. The precipitated solid was removed by filtration, the solvent was removed from the filtrate at reduced pressure, and 14 g. of crude product was isolated [74% yield, m.p. 40–44.5°]. Several recrystallizations from methanol–water resulted in the recovery of 9.8 g. of white crystals, m.p. 46.7–47.7°; d^{25}_{4} 0.942; d^{51}_{4}

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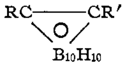
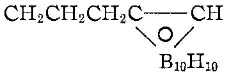
(13) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5519 (1959); W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, *ibid.*, **81**, 5833 (1959).

(14) We are grateful to Mr. Lawrence Adlum for spectral data, Mr. Fred Hoffman and Mr. Frank Billovits for elemental analyses, and Mr. Andrew Lum for physical constants.

(15) R. J. Pace, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 2196 (1961).

Table I

Representative Carboranes Synthesized from Acetylenes

 $\underset{B_{10}H_{10}}{RC\text{——}CR'}$	Carborane	1-Methylcarborane	1-Bromomethylcarborane[a]	1,2-Diphenylcarborane	1,2-(Acetoxymethyl)-carborane	1,3-(1,1'-Carboranyl)-propane	1,2-Bis-(bromomethyl)-carborane
R	H	CH_3	CH_2Br	C_6H_5	$CH_3CO_2CH_2$	H	CH_2Br
R'	H	H	H	C_6H_5	$CH_3CO_2CH_2$	 $CH_2CH_2CH_2\underset{B_{10}H_{10}}{C\text{——}CH}$	CH_2Br
Method of synthesis[b]	A	A	B	A	A	A	A
Melting point, °C.	285–287	214–215	47–49	148–149	42–43	346–348	68–69.5
Elemental analysis, %							
C (calcd.)	16.64	22.75	...	56.68	33.33	25.58	14.54
C (found)	16.82	22.4	...	57.11	33.22	26.05	14.93
H (calcd.)	8.38	8.91	...	6.80	6.99	8.59	4.27
H (found)	8.49	8.84	...	6.98	7.17	9.06	4.67
B (calcd.)	74.97	68.33	...	36.47	37.53	65.84	32.77
B (found)	74.68	67.2	...	36.79	37.18	64.03	32.15
Br (calcd.)	...	...	33.68	...	...	...	48.41
Br (found)	...	...	33.9	...	...	...	48.57

[a] Boiling point 85° (0.3 torr). [b] A, acetylenic plus bis-(acetonitrilo)-decaborane + aromatic solvent; B, acetylenic plus acetonitrile plus decaborane.

0.919; n^{50}D 1.5432. Vapor pressure measurements over a range of temperatures were made in an isoteniscope: 50°, 1.6 mm.; 100°, 8.0 mm.; 160°, 41.0 mm.; 200°, 130.0 mm.

Anal. Calcd. for $C_5H_{16}B_{10}$: C, 32.57; H, 8.75; B, 58.68; mol. wt., 184.4. Found: C, 31.90; H, 8.45; B, 58.40; mol. wt., 188 (cryoscopic in benzene). The ultraviolet absorption spectrum (methanol) shows a single absorption at 254.5 mμ; k 0.509, ϵ 27.8259; $R^{50°}_{\text{exptl}}$ 63.12 cc.; $R^{50°}_{\text{calcd}}$ 62.83 cc. The calculated value was obtained from the molar refraction of 1-isopropylcarborane and subtracting Eisenlohr's atomic refraction values for two hydrogen atoms and adding the atomic refraction value of a double bond; the optical anomaly value is 0.29 cc.

Variations in the above procedure in which the $B_{10}H_{12}\cdot L_2$ starting compound was changed from the acetonitrile ligand to dimethylacetamide, dimethylformamide, and N,N-dimethylaniline all gave the identical product in slightly lower yields. In addition, a series of reactions was studied in which the Lewis base was added to the decaborane–isopropenylacetylene–benzene (or toluene) mixture. The ligands employed successfully included acetonitrile, N,N-dimethylacetamide, N,N-dimethylformamide, butylmethyl sulfide, tributylphosphine, and dimethyl cyanamide. Triethylamine resulted in the formation of a $B_{10}H_{10}^{-2}$ derivative.[13] In the absence of Lewis base no carborane formation was observed.

Reactions of 1-Isopropenylcarborane. Reduction to 1-Isopropylcarborane.—A solution of 0.272 mole of 1-isopropenylcarborane in 100 ml. of hexane was placed in the bottle of a Parr low pressure hydrogenation apparatus and 1 g. of freshly prepared Raney nickel was added. The system was sealed, flushed with nitrogen, and finally placed under 50 p.s.i.g. hydrogen pressure with agitation. The temperature was raised to 50° and maintained at that temperature for 24 hr. The system was then allowed to cool, the bottle flushed with nitrogen, and the contents filtered. The solvent was pumped from the filtrate and a colorless oil remained. The oil was rectified and 43 g. (86% yield) of 1-isopropylcarborane, a mobile, colorless liquid, b.p. 100° (4 mm.), was collected; n^{25}D 1.5395; n^{50}D 1.5295; d^{25}_4 0.926; d^{50}_4 0.909; m.p. −4°.

Anal. Calcd. for $C_5H_{18}B_{10}$: C, 32.22; H, 9.73; B, 58.05. Found: C, 32.71; H, 9.66; B, 58.21. The infrared spectrum shows formation of a doublet at 7.16 and 7.26 μ (compare with Fig. 1) and disappearance of the 6.20 and 10.9 μ bands; $R^{50°}_{\text{exptl}}$ 63.30 cc. The ultraviolet absorption spectrum (methanol) exhibits a single absorption at 273 mμ, k 0.00473, ϵ 0.8816.

Oxidation to 1-(Epoxyisopropyl)-carborane.—A 500-ml. 3-neck flask fitted with a dropping funnel, reflux condenser, thermometer, and agitator was charged with 100 ml. of methylene chloride and 0.172 mole of the isopropenylcarborane. The mixture was stirred and cooled to 1°, 9 g. of 90% hydrogen peroxide was added dropwise over a period of 1 hr. with cooling, and then 25 g. of perfluoroacetic anhydride (Matheson Coleman and Bell) was added over a period of 3 hr. After 90 min. the temperature was maintained at 6°, and after 3 hr. at 10°. The mixture was allowed to warm overnight with continued stirring. After 18 hr., 20 ml. of water was added slowly, and the mixture was stirred and then transferred to a separatory funnel. The mixture separated into three phases; the middle methylene chloride layer was isolated, washed several times with water until a starch–iodate test for peroxide was negative, and then treated with sodium carbonate and dried with Drierite. The solvent was evaporated and 30 g. of a yellow oil isolated. This was distilled through a glass helix packed column and 0.116 mole (67.5% yield) of the epoxide, a colorless oil, was collected, b.p. 96–100° (0.3 mm.); n^{25}D 1.5483.

Anal. Calcd. for $C_5H_{16}B_{10}O$: C, 29.97; H, 8.05; B, 53.99. Found: C, 30.08; H, 8.25; B, 52.79. The infrared spectrum exhibited characteristic oxiran bands at 7.90 and 11.08 μ; the 6.20 and 10.98 μ bands (Fig. 1) were no longer present.

Attempted Alcoholysis.—A solution of 0.00815 mole of the isopropenylcarborane in 25 ml. of methanol was refluxed for 24 hr. Most of the solvent was then allowed to evaporate and infrared analysis of the concentrated solution showed it to consist of unreacted product and methanol.

The experiment was repeated and three drops of concentrated hydrochloric acid were added, and no gas evolution occurred. The addition of excess sodium hydroxide caused gas to evolve, but after 0.00817 mole of gas was collected, the evolution ceased.

Attempted Hydrolysis.—A mixture consisting of 1.0 g. of isopropenylcarborane and 25 ml. of water was refluxed for 36 hr. The mixture did not become homogeneous and there was no gas evolution; the product was recovered unchanged.

Attempted Oxidation with Alkaline Peroxide.—A solution of 8.5 g. of the isopropenylcarborane in 32 ml. of ethanol was mixed with a solution of 4 g. of sodium carbonate in 32 ml. of water and 24 ml. of 30% hydrogen peroxide. The mixture was refluxed for 3 hr. and cooled. The precipitate which formed was removed by filtration and dried, 8.2 g.; m.p. 43–44°; in admixture with the starting material, m.p. 43–44°; 96.5% recovery.

Reaction with Sodium in Liquid Ammonia.—To a mixture of 0.032 mole of 1-isopropenylcarborane and 100 ml. of sodium-dried liquid ammonia (under a blanket of argon) was added 0.126 g.-atom of sodium metal in small portions. At the first addition of sodium a yellow color appeared, which remained through subsequent additions until the total quantity of sodium was added.

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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Carboranes. II.[1] The Preparation of 1- and 1,2-Substituted Carboranes

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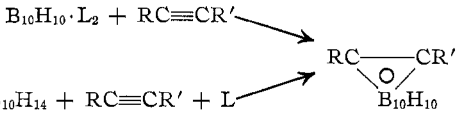
The broad applicability of the conversion of mono- and disubstituted acetylenes to carboranes by treatment with decaborane and Lewis bases is demonstrated. The resultant carboranes may then be treated as typically organic, covalent products and, by usual synthetic procedures, converted to other carboranes.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