acid and concentrated under reduced pressure to a volume of 12 ml. The crystalline hydroxy acid separated out in 92% yield; it melted with decomposition at a temperature which depended upon the rate of heating. Its infrared spectrum contained the expected absorptions at 2.95 (OH), 3.90 (BH), and 5.82, 7.18, and 7.98 μ (COOH). There were no significant absorptions at 5.55 (lactone C=O) or at 8.95 μ ($-CH_2OCH_2-$).

*Anal.* Calcd. for $C_4H_{14}B_{10}O_3$: C, 22.00; H, 6.46. Found: C, 21.71; H, 6.62.

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CONTRIBUTION FROM THE REACTION MOTORS DIVISION,
THIOKOL CHEMICAL CORPORATION, DENVILLE, NEW JERSEY

# Neocarboranes, a New Family of Stable Organoboranes Isomeric with the Carboranes

BY DANIEL GRAFSTEIN[1] AND JOSEPH DVORAK

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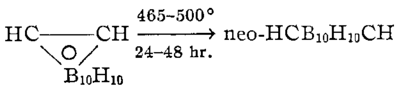
Heating of the recently described compound[2] carborane, $C_2B_{10}H_{12}$, at 465–500° for 24 hr. produced the first member of a new family of organoboranes. The name neocarborane has been assigned to this product, which is isomeric with the original carborane. The chemistry of neocarborane has been explored and is compared to that of carborane. In general, neocarborane derivatives are less polar and more stable than their carborane isomers. As in the carboranes, the $C_2B_{10}H_{10}$ unit is unusually inert and many standard organic processes can be effected on organofunctional substituents attached to the neocarborane carbon atoms. Carborane is assigned the distorted icosahedral structure, A, with the two carbon atoms sharing a short, depressed edge of an otherwise regular icosahedron. A regular icosahedral structure, C or D, is suggested for neocarborane. Electronic structures and possible reaction paths are indicated.

In the course of exploring the chemistry of the carborane[2a,b] system, an attempt was made to bring about the dimerization or polymerization of carborane, $C_2B_{10}H_{12}$, by thermal dehydrogenation. However, an unexpected thermal isomerization occurred and a new, even more stable family of organoboranes was discovered. The name neocarborane has been assigned to the first member of this family.

Upon heating carborane in an inert atmosphere in the temperature range of 465–500°, a slow isomerization took place and a volatile solid, m.p. 263–265°, sealed tube, was obtained. The product closely resembled carborane, m.p. 287–288°, in appearance, odor, and solubility characteristics. The melting points of mixtures of the isomers were not depressed but roughly followed a linear relationship. Except for the pronounced differences observed in the infrared spectrum, neocarborane could easily have been mistaken for carborane. The isomerization proceeded to completion without evolution of gaseous by-products. Gas chromatography gave distinctly different chromatograms. Mixtures of the two were cleanly separated by this technique, neocarborane appearing first, probably due to its higher vapor pressure.

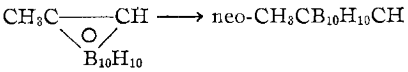


$$\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{HC\text{——}CH}} \xrightarrow[\text{24–48 hr.}]{465\text{–}500^\circ} \text{neo-}HCB_{10}H_{10}CH$$

The infrared spectrum of neocarborane (Fig. 1) when compared to carborane (Fig. 2) showed major changes in the 1250–900 cm.$^{-1}$ region. The prominent peak at 1212 cm.$^{-1}$ in carborane is entirely absent in neocarborane and the bands at 1149, 1034, 1015, and 985 cm.$^{-1}$ in carborane are replaced by bands at 1158, 1069, 1022, and 991 cm.$^{-1}$ in neocarborane. In addition, there is a pronounced intensity difference in the C–H absorption at 3060 cm.$^{-1}$ and a small shift in the characteristic carborane peak, 716 to 719 cm.$^{-1}$.

Attempts to accelerate the isomerization of carborane to neocarborane by going to higher temperatures resulted in the appearance of a competing polymerization reaction. At 514°, a nonvolatile, gray-white, insoluble, infusible glass was formed along with neocarborane. The infrared spectrum of the glass showed the retention of the typical $C_2B_{10}$ polyhedron peak (719 cm.$^{-1}$).

It was of interest to determine if substituted carboranes could be thermally isomerized. 1-Methylcarborane, m.p. 218–219°, was isomerized at 400° in an evacuated glass ampoule and at 472° in a stainless steel autoclave. C-Methylneocarborane[3] was isolated in 68.8% yield as a white wax which could be crystallized from hexane (m.p. 208–209.5°, sealed tube).



$$\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{CH_3C\text{——}CH}} \longrightarrow \text{neo-}CH_3CB_{10}H_{10}CH$$

The infrared spectrum of C-methylneocarborane differed considerably from 1-methylcarborane in the skeletal region. The differences were similar to those observed in the parent isomers. Again, each methyl isomer gave a distinct gas chromatogram and their mixtures were separated readily by this technique.

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(1) General Precision, Inc., Aerospace Group, Little Falls, N. J.

(2) (a) M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *Inorg. Chem.*, **2**, 1111 (1963); (b) D. Grafstein, *et al.*, *ibid.*, **2**, 1120 (1963).

(3) Pending the assignment of an unequivocal structure to neocarborane, C and C′ will be used to indicate substitution on the neocarboranyl carbon atoms.

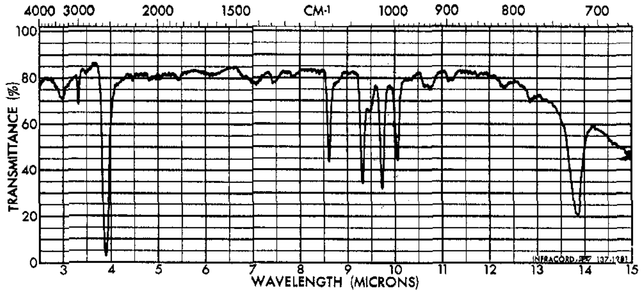


Fig. 1.—Infrared spectrum of neocarborane.

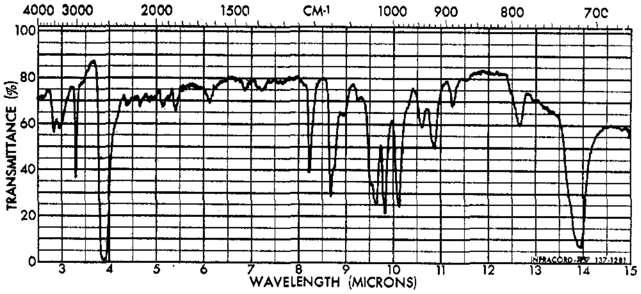


Fig. 2—Infrared spectrum of carborane.

Comparative mass spectral analysis proved the isomeric relationship with an ultimate $m/e$ of 160, confirming the empirical formula as $C_3B_{10}H_{14}$. The mass spectrum also showed the presence of a dimethyl- and trimethyl- (or methylethyl-) neocarborane trace impurity. Subsequently, the integrity of the $CH_3$–C bond in C-methylneocarborane was proven by synthesis from neocarborane.

Generally, the neocarboranes are less polar than their carborane isomers. Neocarborane is insoluble in nitromethane and liquid ammonia, whereas carborane is soluble. Both are insoluble in water but very soluble in the common organic solvents. In all cases studied, neocarborane and its many organofunctional derivatives are qualitatively more volatile and slightly less dense than their carborane analogs. With but few exceptions, the substituted neocarborane has the lower melting point.

The thermal isomerization of more complex organofunctional carboranes is generally unsatisfactory. Thus, at 400° 1,2-bis-(hydroxymethyl)-carborane and dimethyl 1,2-carboranedicarboxylate[2] were extensively degraded with accompanying borate formation. In the case of the lactone of 1-hydroxymethyl-2-carboranylcarboxylic acid at 400°, a poor yield of neocarborane was realized.

**Neocarborane Chemistry.**—The chemistry of neocarborane has many features in common as well as several surprising differences from that of its isomer.[2b] Both organoboranes are remarkably stable to mild oxidizing reagents and hot concentrated acids.[4] Like carborane, neocarborane undergoes facile stepwise metalation with butyllithium to give the synthetically useful C-lithium neocarborane and C,C′-dilithium neocarborane.

$$\text{neo-}HCB_{10}H_{10}CH + C_4H_9Li \longrightarrow \text{neo-}HCB_{10}H_{10}CLi + C_4H_{10}$$

$$\text{neo-}HCB_{10}H_{10}CH + 2C_4H_9Li \longrightarrow \text{neo-}LiCB_{10}H_{10}CLi + 2C_4H_{10}$$

Carbonation of C,C′-dilithium neocarborane followed by acid hydrolysis gave C,C′-neocarboranedicarboxylic acid, m.p. 202–204°. As in the case of every isomeric pair prepared to date, the infrared spectrum differed principally in the 1250–900 cm.$^{-1}$ region from 1,2-carboranedicarboxylic acid,[2b] m.p. 225°. Unlike its isomer, which could not be esterified directly with alcohols,[2b] the neocarboranedicarboxylic acid readily underwent acid-catalyzed esterification. The esterification of this diacid and its failure to form a cyclic anhydride can be rationalized on a steric basis.

$$\text{neo-}LiCB_{10}H_{10}CLi \xrightarrow[2,\ H^+]{1,\ CO_2} \text{neo-}HO_2CCB_{10}H_{10}CCO_2H$$

$$\text{neo-}HO_2CCB_{10}H_{10}CCO_2H \xrightarrow{CH_3OH\text{–}HCl} \text{neo-}CH_3O_2CCB_{10}H_{10}CCO_2CH_3$$

Paraformaldehyde reacted with C,C′-dilithium neocarborane in benzene to give C,C′-bis-(hydroxymethyl)-neocarborane, m.p. 194–196°. Its isomer, 1,2-bis-(hydroxymethyl)-carborane, does not melt but decomposes above 250°. Both diols can be oxidized by aqueous alkaline potassium permanganate to the unsubstituted polyhedra.[2b]

$$\text{neo-}LiCB_{10}H_{10}CLi + (CH_2O)_n \xrightarrow{C_6H_6} \text{neo-}HOCH_2CB_{10}H_{10}CCH_2OH$$

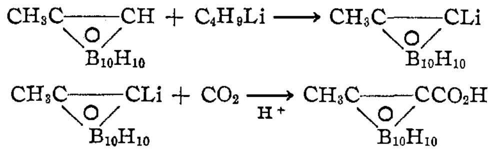
$$\text{neo-}HOCH_2CB_{10}H_{10}CCH_2OH \xrightarrow[OH^-]{KMnO_4} \text{neo-}HCB_{10}H_{10}CH$$

Methylation of C-lithium neocarborane with methyl iodide gave C-methylneocarborane, proving the retention of the $CH_3$–C bond in the isomerization reaction. As expected, C-methylneocarborane could be metalated with butyllithium. Subsequent carbonation and acidification gave C-methyl-C′-neocarboranylcarboxylic acid, m.p. 108–111°.

$$\text{neo-}CH_3CB_{10}H_{10}CH + C_4H_9Li \longrightarrow \text{neo-}CH_3CB_{10}H_{10}CLi$$

$$\text{neo-}CH_3CB_{10}H_{10}CLi + CO_2 \xrightarrow[H^+]{} \text{neo-}CH_3CB_{10}H_{10}CCO_2H$$

In order to compare acid strengths and thereby obtain a measure of comparative inductive forces, the corresponding 1-methyl-2-carboranylcarboxylic acid, m.p. 201–203°, was prepared in the same way from 1-methylcarborane. The acid was crystallized several times as white needles from carbon tetrachloride, while its "neo" isomer could not be crystallized from carbon tetrachloride but was crystallized several times from hexane as white needles.



$$\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{CH_3C\text{——}CH}} + C_4H_9Li \longrightarrow \underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{CH_3C\text{——}CLi}}$$

$$\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{CH_3C\text{——}CLi}} + CO_2 \xrightarrow[H^+]{} \underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{CH_3C\text{——}CCO_2H}}$$

Both acids were only slightly soluble in water. A potentiometric determination of acid strengths in 50% aqueous ethanol established that C-methyl-C′-neocarboranylcarboxylic acid, p$K_a$ 3.14, was a signifi-

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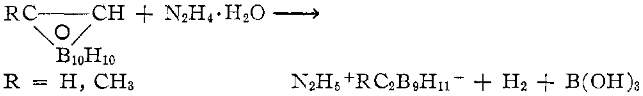
(4) Solutions and suspensions of these organoboranes and their derivatives in concentrated nitric acid are very shock sensitive.

cantly weaker acid than 1-methyl-2-carboranylcarboxylic acid, p$K_a$ 2.74.[5] NBS benzoic acid, p$K_a$ 5.34, was used as a relative reference acid. These results strongly suggest that the neocarborane polyhedron has the weaker electron-withdrawing character.

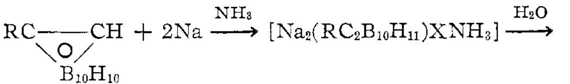
The neocarborane polyhedron is considerably more stable to attack by amines than is the carborane polyhedron. Thus, neocarborane did not react with piperidine in pentane or with *n*-propylamine in refluxing hexane, whereas carborane formed complex amine adducts under these conditions.[2b] Refluxing methanolic potassium hydroxide did not attack neocarborane, although this same reagent degrades carborane and its derivatives.[2b,5] That these differences are probably a matter of degree rather than kind is indicated by degradative studies with hydrazine hydrate. Refluxing hydrazine hydrate rapidly attacked carborane and 1-methylcarborane to give hydrazinium salts of dicarbaundecaborane and methyldicarbaundecaborane, respectively.[2b] With C-methylneocarborane, however, sluggish reaction occurred and most (~80%) of the starting organoborane sublimed from the reaction media. Repeated treatments of the recovered sublimate with the same reagent did consume C-methylneocarborane. Excess hydrogen (~5 moles) was evolved and a water-soluble, very impure organoborane similar to methyldicarbaundecaborane was formed. The new organoborane could be precipitated from its aqueous solution as a tetramethylammonium salt but its structure has not been established.



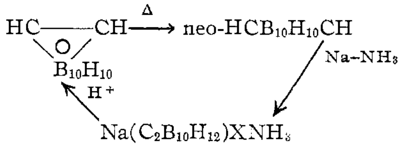
$$\underset{B_{10}H_{10}}{RC{-}CH} + N_2H_4\cdot H_2O \longrightarrow N_2H_5{}^+RC_2B_9H_{11}{}^- + H_2 + B(OH)_3$$

R = H, CH₃

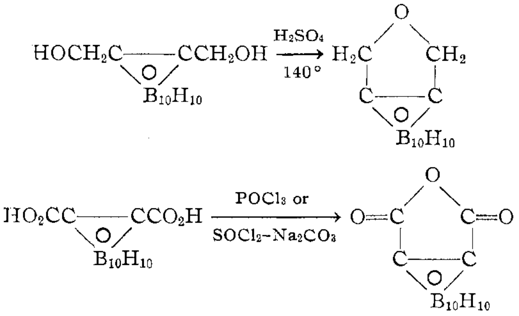
One of the more significant differences in the chemistry of carborane and neocarborane was observed in their reactions with the blue solutions of sodium in liquid ammonia. Carborane monoalkyl derivatives gave a precise and rapid 1:2 stoichiometry with sodium or lithium.[2a] The resultant adducts could be hydrolyzed to give water-soluble dicarbaundecaborane salts. No carboranes can be recovered from the hydrolyzed product. The alkali metal addition reaction does not appear to be stepwise as no evidence for an intermediate monosodium reaction was observed even in the presence of excess carborane. On the other hand, neocarborane reacts with the sodium–ammonia reagent in a stepwise manner. It instantly bleaches one equivalent of the blue solution and then takes up a second equivalent of sodium at a much slower rate. Aqueous acid hydrolysis of the 1:1 adduct gave a gas composed of hydrogen with small amounts of methane and ethane, water-soluble boranes, and carborane, thereby completing the cycle. Neither carborane nor neocarborane was isolated upon hydrolysis of the disodio adduct, the isolable degradation products being water-soluble.



$$\underset{B_{10}H_{10}}{RC{-}CH} + 2Na \xrightarrow{NH_3} [Na_2(RC_2B_{10}H_{11})XNH_3] \xrightarrow{H_2O} Na^+RC_2B_9H_{11}{}^-$$



1,2-Disubstituted carboranes are reported to form three-atomed exocycles with ease under quite mild conditions.[2b,6] For example, the following carboranyl exocycles can be prepared in near quantitative yields



On the other hand, all attempts to prepare similar three-atomed exocycles from disubstituted neocarboranes have been unsuccessful. No reactions were observed when the "neo" diacid was treated with refluxing thionyl chloride, refluxing acetic anhydride, or sulfuric acid at 175°. The diacid simply sublimed, without anhydride formation, at 220°. Phosphorus oxychloride converted it to intractable tars containing linear anhydride units (by infrared). Phosphorus pentachloride in ethyl ether gave a diacid chloride, b.p. 86° (0.5 mm.), in 70% yield. In turn, the neocarborane diacid chloride could be transformed into a diacid amide, m.p. 184–185.5°, but no cyclic imide resulted from pyrolysis. C,C′-Bis-(hydroxymethyl)-neocarborane did not react with concentrated sulfuric acid at 140°. At 175°, sulfonation did occur, but volative products were not observed.

Brief efforts to resolve the "neo" acids as brucine and cinchonine diastereoisomeric salts were unsuccessful. The results here are of a negative nature and are complicated by the difficulty in finding suitable solvents for fractional crystallization. An interesting outgrowth of this work was the observation that these salts could be thermally decarboxylated.

**Structures for the Isomers.**—Taken together, the extremes observed in the tendency toward exocycle formation and the differences in the reactivity of their carboxylic acid derivatives firmly suggest that steric factors play a dominant role in the chemistry of 1,2-disubstituted carboranes. The strong electron-withdrawing character of the carborane polyhedron[2b] should facilitate rather than hinder carbonyl addition reactions, particularly saponification. However, not only does 1,2-carboranedicarboxylic acid fail to undergo direct esterification with alcohols, but its dimethyl ester resists transesterification and undergoes simple sapon-

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(5) F. Hawthorne, private communication, also prepared 1-methyl-2-carboranylcarboxylic acid, p$K_a$ 2.87; benzoic acid, p$K_a$ 5.46.

(6) D. Grafstein, *et al.*, *Inorg. Chem.*, **2**, 1125 (1963).

ification only with considerable difficulty. A short separation between the carboranyl carbon atoms and a relatively acute external angle to their substituents is indicated.

Pending a definitive X-ray analysis of the isomers, carborane is assigned a distorted icosahedral structure, A (Fig. 3), isoelectronic with the regular icosahedral $B_{12}H_{12}^{-2}$ ion.[7–9] Its electronic structure is partially represented by the flat projection, B, where the numbered circles refer to the indicated boron atom of the decaborane basket and the straight lines represent bonding orbitals. The CH groups are mutually bonded by a normal two-electron single bond and each carbon atom participates in two three-centered bonds with its nearest boron neighbors. This electronic structure implies a short (≦1.54 Å.) carbon–carbon separation and an acute external angle to hydrogen, relative to the regular icosahedral values near 1.77 Å. and 121°, respectively.

Assigning a structure to the neocarborane isomer is more difficult, since there are no compelling reasons for eliminating any of the three regular icosahedral structures, C, D, or E. A distance of 1.77 Å., and certainly not much smaller than 1.70 Å., can be assigned[10] to the edges of a regular icosahedron. One can then calculate the distances between the shaded apices (the carbon atoms) in C, D, or E, and, using normal covalent radii, the distance available for bridging the carbon atoms by a three-atom exocycle. Thus in C, D, or E, the internal separations are estimated at 1.77, 2.86, and 3.37 Å., respectively. The unimpeded direct line distances separating the external carbon atoms in certain 1,2-derivatives of C or D are then approximately 3.39 and 5.48 Å., respectively. These distances exceed the maximal value near 2.54 Å. required for an unstrained C–O–C exocycle, and thus all three regular polyhedra would prohibit the formation of these particular exocyclic derivatives.

Since there has never been any laboratory evidence for the formation of more than one isomer in the thermal isomerization reaction, a unique mechanism for converting carborane to neocarborane is indicated. Accepting a distorted icosahedral structure, A, for carborane, it may be argued that the driving force for thermal isomerization is the conversion of a strained C–C bond in normal carborane by polyhedral expansion into a stable, unstrained regular structure, C, of neocarborane. A distinctly different electronic structure, F, can be written for C, in which the carbon atoms are totally boron-like and participate in three three-centered bonds with their near neighbors. In both electronic structures, B and F, carbon shares a full complement of eight electrons.

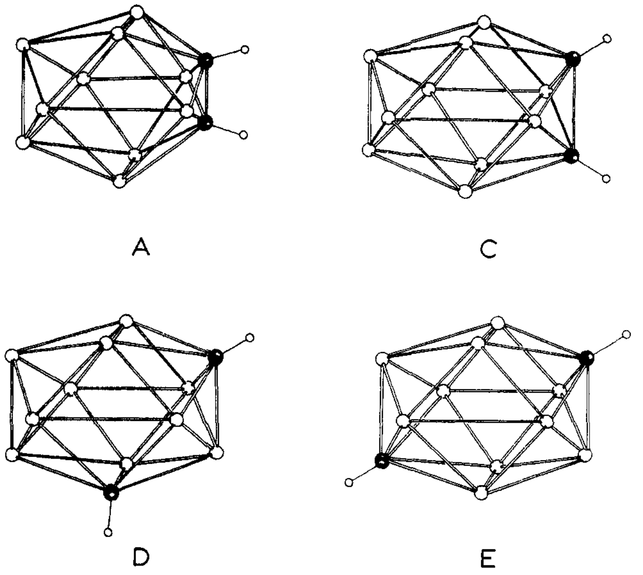
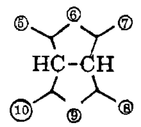
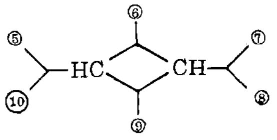


Figure 3.

However, a unique mechanism can also be suggested[11] to D, through a cuboctahedron intermediate. Thus, assuming that structure C is unstable, D might form irreversibly from A, going through C and a cuboctahedron as transition states. E could not be formed by this process, but it could be formed by cleavage of the carbon–carbon bond in A, followed by rotation of opposing pentagonal pyramids 72° to give D, or 144° to give E.[12] In view of the surprising reverse isomerization through Na, structure C is suggested for neocarborane, with D as the next most likely choice.



B



F

## Experimental[13]

The carborane used was prepared by the aqueous alkaline permanganate oxidation of 1,2-bis-(hydroxymethyl)-carborane, and 1-methylcarborane was prepared by hydrolysis of the Grignard reagent from 1-bromomethylcarborane.[2b] All reactions with *n*-butyllithium were conducted under argon in a three-necked, round-bottomed flask equipped with a mechanical stirrer, thermometer, and dropping funnel. The *n*-butyllithium employed was a commercial product, generally 1.5 *M* in heptane–pentane solution. All benzene and ethyl ether reaction solvents were sodium dried. Transformations involving neocarborane and C-methylneocarborane as reagents were always conducted with chromatographically pure samples prepared by thermal isomerization.

**Neocarborane.**—A 110-ml. stainless steel autoclave was

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

[8] A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 3228 (1960).

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

[10] J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Cryst.*, **13**, 436 (1950), report an average B–B distance of 1.77 Å. in the nearly icosahedral decaborane structure.

[11] W. N. Lipscomb and S. Britton, *J. Chem. Phys.*, **33**, 275 (1960); R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963).

[12] M. F. Hawthorne, private communication. Mr. John A. DuPont of the Rohm and Haas Corporation kindly obtained $B^{11}$ n.m.r. spectra of neocarborane and methylneocarborane. The highly symmetrical E would be expected to display one large doublet. Since this was not observed, he rejected E for neocarborane and chose D by "elimination."

[13] All melting points are uncorrected. Infrared spectra were obtained with a Perkin–Elmer Model 21 spectrometer.

charged at room temperature with 0.017 mole of carborane. The autoclave was sealed under argon (1 atm.) and was electrically heated for 24 hr. in the temperature range 465–500°. Internal temperatures were measured by means of an iron–constantan thermocouple. After cooling to room temperature, the autoclave was opened. No pressure build-up was noted. The crude product was scraped off the walls of the autoclave and then sublimed, 110° (0.1 mm.), to give 2.10 g. (84%) of chromatographically and spectrally pure neocarborane, m.p. 263.5–265° (sealed tube).

*Anal.* Calcd. for $C_2H_{12}B_{10}$: C, 16.64; H, 8.38; B, 74.97. Found: C, 16.85; H, 8.15; B, 74.12.

The mass spectra of carborane and neocarborane were obtained under similar instrumental conditions using a Model 12-100 Bendix time-of-flight instrument. The samples were introduced with the aid of a heat gun. The mass peaks observed were those of the doubly and singly ionized species. High recording sensitivities were necessary because of the low vapor pressure of the samples, particularly carborane, and because the inlet system was at room temperature. In both samples the parent ion was found at *m/e* 146, the most intense peak at *m/e* 143, and very small peaks at *m/e* 147 and 148 due to carbon-13 and heavy hydrogen. Gas chromatography was conducted on a Burrell Kromo-Tog Model No. K-2 with a 100-cm. column of 5% by weight polyester, prepared from adipic acid and 1,2-bis-(hydroxymethyl)-carborane, on Celite. Helium was used as the carrier gas and decane–acetone (10:1) was the solvent.

TABLE I

MASS SPECTRA OF NEOCARBORANE AND CARBORANE

| | Carborane | | Neocarborane | |
|---|---|---|---|---|
| *m/e* | Peak height | Relative intensity | Peak height | Relative intensity |
| 65 | 2.0 | 1.5 | 8.0 | 3.6 |
| 66 | 1.5 | 1.1 | 2.5 | 1.1 |
| 66.5 | 1.5 | 1.1 | 2.0 | 0.9 |
| 67 | 3.0 | 2.5 | 7.5 | 3.4 |
| 67.5 | 3.5 | 2.7 | 5.5 | 2.5 |
| 68 | 6.0 | 4.6 | 13.0 | 5.9 |
| 68.5 | 7.0 | 5.4 | 9.0 | 4.1 |
| 69 | 7.4 | 5.6 | 28.0 | 12.6 |
| 69.5 | 11.0 | 8.4 | 16.0 | 7.2 |
| 70 | 14.0 | 10.7 | 46.5 | 21.0 |
| 70.5 | 19.5 | 14.9 | 27.0 | 12.2 |
| 71 | 17.0 | 13.0 | 45.0 | 22.1 |
| 71.5 | 15.0 | 11.4 | 23.0 | 10.4 |
| 72 | 6.5 | 5.0 | 10.5 | 4.7 |
| 73 | 2.0 | 1.5 | 8.0 | 2.1 |
| 130 | 2.5 | 1.9 | 5.0 | 2.3 |
| 131 | 4.0 | 3.1 | 8.0 | 3.6 |
| 132 | 8.5 | 6.5 | 13.5 | 5.9 |
| 133 | 8.0 | 6.1 | 13.5 | 5.9 |
| 134 | 15.0 | 11.4 | 20.0 | 9.0 |
| 135 | 15.5 | 11.8 | 29.5 | 13.3 |
| 136 | 17.0 | 13.0 | 35.0 | 15.8 |
| 137 | 19.5 | 14.9 | 36.5 | 16.5 |
| 138 | 21.0 | 16.0 | 34.0 | 15.3 |
| 139 | 26.0 | 19.8 | 48.0 | 21.6 |
| 140 | 41.0 | 31.3 | 60.5 | 27.3 |
| 141 | 65.0 | 49.7 | 117.0 | 52.7 |
| 142 | 100.5 | 76.7 | 168.5 | 75.7 |
| 143 | 131.0 | 100.0 | 222.0 | 100.0 |
| 144 | 121.5 | 92.2 | 216.0 | 97.5 |
| 145 | 89.0 | 65.0 | 169.0 | 76.3 |
| 146 | 43.0 | 32.8 | 79.0 | 35.6 |
| 147 | 2.0 | 2.0 | 4.5 | 2.0 |
| 148 | 1.0 | 0.9 | 3.0 | 1.4 |

**C,C′-Neocarboranedicarboxylic Acid.**—A solution of 0.094 mole of neocarborane in 100 ml. of anhydrous ethyl ether was added dropwise to 0.187 mole of the *n*-butyllithium reagent in 100 ml. of anhydrous ethyl ether at 0–5°. After the addition was completed, the solution was stirred for 0.5 hr. and then excess gaseous carbon dioxide was rapidly bubbled into the reaction mixture. Hydrolysis was effected by cautious dropwise addition of concentrated hydrochloric acid to the reaction mixture. The organic layer was separated, washed with water, and dried over Drierite. The solvent was removed under vacuum and the solid residue was crystallized several times from ethylene dichloride to give 16.6 g. (77.7%) of C,C′-neocarboranedicarboxylic acid, m.p. 202–204°.

*Anal.* Calcd. for $C_4H_{12}B_{10}O_4$: C, 20.69; H, 5.17; B, 46.55; neut. equiv., 116. Found: C, 21.12; H, 5.36; B, 47.2; neut. equiv., 120.

**Dimethyl C,C′-Neocarboranedicarboxylate.**—Anhydrous hydrogen chloride was slowly bubbled through a refluxing solution of 0.0431 mole of C,C′-neocarboranedicarboxylic acid in 200 ml. of absolute methanol. The solution was concentrated to 75 ml. by distillation of the solvent. Addition of 125 ml. of water caused the formation of an oil suspension. The suspension was extracted with ethyl ether. The ether solution was dried over sodium sulfate and filtered, and the solvent was removed under vacuum to give a viscous oil. Vacuum distillation, b.p. 110° (0.7 mm.), gave 5.42 g. (48%) of dimethyl C,C′-neocarboranedicarboxylate, which solidified in the receiver, m.p. 52.5–54°.

*Anal.* Calcd. for $C_6H_{16}B_{10}O_4$: C, 27.69; H, 6.15; B, 41.6; sapon. equiv., 130.1. Found: C, 27.33; H, 6.32; B, 42.7; sapon. equiv., 129.6.

**C,C′-Bis-(hydroxymethyl)-neocarborane.**—A solution of 0.04 mole of neocarborane in 100 ml. of benzene was added to 0.08 mole of the *n*-butyllithium reagent in 100 ml. of benzene at 50°. Some 2.40 g. of paraformaldehyde (previously dried in a vacuum desiccator over phosphorus pentoxide) was added with vigorous stirring, and the temperature of the mixture was maintained at 70° for 2 hr. The mixture was hydrolyzed by pouring over cracked ice and hydrochloric acid. The benzene layer was separated, and the aqueous layer was extracted with ethyl ether. The combined organic solution was dried over sodium sulfate. Filtration and evaporation gave a crude product, m.p. 193–195°. Crystallization from toluene gave 2.00 g. (24%) of C,C′-bis-(hydroxymethyl)-neocarborane, m.p. 194–196°. The infrared spectrum was consistent with the assigned structure.

*Anal.* Calcd. for $C_4H_{16}B_{10}O_2$: B, 52.94. Found: B, 52.82.

**Permanganate Oxidation of C,C′-Bis-(hydroxymethyl)-neocarborane.**—Potassium permanganate (0.0136 mole) was added to a solution of 0.0055 mole of C,C′-bis-(hydroxymethyl)-neocarborane in 50 ml. of 20% aqueous potassium hydroxide. The mixture was stirred at room temperature for 12 hr. The brown-black precipitate was filtered, washed with water, and extracted several times with ethyl ether. The ether extracts were combined and dried over Drierite. Evaporation of the solvent gave a crude solid. Sublimation gave 0.13 g. (16%) of neocarborane. The product was identified by its melting point, 263–265°, and its infrared spectrum.

**C-Methyl-C′-neocarboranylcarboxylic Acid.**—*n*-Butyllithium (0.06 mole) was added to 0.06 mole of C-methylneocarborane in 150 ml. of anhydrous ethyl ether at 0–5°. The solution was stirred for 0.5 hr. and then excess gaseous carbon dioxide was bubbled through the reaction mixture. The mixture was hydrolyzed by the addition of 18% aqueous hydrochloric acid. The organic layer was separated, washed with water, and dried over sodium sulfate. Removal of the solvent under vacuum gave a crude solid which was crystallized from benzene and then recrystallized several times from hexane as white needles, m.p. 108–111°; yield 2.26 g. (18.5%).

*Anal.* Calcd. for $C_4H_{14}B_{10}O_2$: C, 23.74; H, 6.97; B, 53.48; neut. equiv., 202.3. Found: C, 23.68; H, 7.10; B, 53.19; neut. equiv. 213.

**1-Methyl-2-carboranylcarboxylic Acid.**—1-Methylcarborane (0.06 mole) was lithiated, carbonated, and hydrolyzed in exactly the same fashion as above. The organic solution was dried over Drierite. Filtration and evaporation of the solvents gave a crude solid product. Several recrystallizations from carbon tetrachloride gave 2.45 g. (20%) of white needles, m.p. 201–203°.

*Anal.* Calcd. for $C_4H_{14}B_{10}O_2$: C, 23.73; H, 6.97; B, 53.48; neut. equiv., 202.3. Found: C, 23.63; H, 6.93; B, 53.82; neut. equiv., 209.5.

**Methylation of Neocarborane.**—*n*-Butyllithium (0.05 mole) was slowly added to 0.05 mole of neocarborane in 100 ml. of anhydrous ethyl ether at 0–5° over a 30-min. period. After the addition was completed, 0.05 mole of methyl iodide in 20 ml. of ether was added. The reaction mixture was refluxed for 2 hr. and then hydrolyzed by pouring over a mixture of cracked ice and hydrochloric acid. The ether layer was separated, washed with aqueous sodium thiosulfate, and dried. After filtration, the solvent was removed under vacuum. Sublimation of the crude residue gave 3.06 g. (38.7%) of C-methylneocarborane, m.p. 208–210° (sealed tube). The infrared spectrum of the product was identical with that of the thermal isomerization product with slight, but discernible contamination by neocarborane.

**Hydrazine Hydrate Degradation of C-Methylneocarborane.**[14]—Methylneocarborane (0.010 mole) was added to 20 ml. of hydrazine hydrate and the mixture was refluxed for 3.5 hr. under a cold finger condenser. Solids that sublimed during this time were determined to be unreacted methylneocarborane (80% recovery). The gas, 220 ml. (corrected to N.T.P.), evolved during the reaction was found to be pure hydrogen by mass spectrum and represented 4.9 moles of hydrogen per mole of reacted methylneocarborane.

The solvent was removed by evaporation under reduced pressure, leaving a semisolid residue which has not been characterized further.

**Neocarborane and Sodium in Ammonia.**—Ammonia was condensed in a three-necked, round-bottom flask equipped with a Teflon stirring bar, Dry Ice condenser, thermometer, and gas inlet tube. The apparatus had previously been flamed out and continuously flushed with argon to prevent the return of moisture into the system. When 250 ml. of ammonia had been condensed, 0.0083 mole of spectrally and chromatographically pure neocarborane was added to the ammonia while the system was flushed with argon. Then sodium, cut in small pieces, was added, with almost instantaneous bleaching of the incipient blue color. The addition of sodium was stopped when the blue color persisted for 15 min. (0.0078 mole had been added). Evaporation of the ammonia left a gray-white hygroscopic solid from which the last trace of ammonia was removed under vacuum. The solid was then washed several times with sodium-dried benzene while an argon atmosphere was maintained over the mixture. Nothing was obtained from the benzene solution. When the solid was treated with 3 *N* aqueous hydrochloric acid, gas was evolved which contained over 50% hydrogen and lesser amounts of ammonia, methane, and ethane. A water-insoluble residue remained which was taken up in ethyl ether, and the ether solution was dried over calcium sulfate. A pink solid was obtained after the ether solution was removed at reduced pressure. Sublimation gave a white sublimate (0.20 g.) which was pure carborane (by its infrared spectrum) free of neocarborane. The residue from sublimation decomposed at 205°.

On treating the hydrochloric acid solution with tetramethylammonium hydroxide, 2.4 g. of a white solid precipitated which melted above 320° after being crystallized from methanol.

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[14] Reaction run by Mr. Harry F. Smith.

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CONTRIBUTION FROM THE CHEMISTRY RESEARCH DIVISION,
IIT RESEARCH INSTITUTE, TECHNOLOGY CENTER, CHICAGO 16, ILLINOIS

# The Reaction of Ethylene with Pentaborane-11

BY RICHARD G. MAGUIRE, IRVINE J. SOLOMON, AND MORTON J. KLEIN

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Ethylpentaborane-11 was found to be the major product in the reaction of ethylene with pentaborane-11. Also found were diborane, ethyldiboranes, diethylpentaborane-11, tetraborane, and dimethylenetetraborane. The amounts of these various products can be controlled by variations in the reaction conditions. A mechanism accounting for all the products is proposed. Decomposition of ethylpentaborane-11 resulted in a complex mixture of products. The mechanism postulated for this decomposition is supported by other studies.

As an interesting extension to the previously reported work on the reactions of ethylene with diborane,[1,2] tetraborane,[3] and pentaborane-9,[4] a study of the reaction of ethylene with pentaborane-11 was undertaken.

The major product of the reaction was identified as ethylpentaborane-11, $C_2H_5B_5H_{10}$. First, vapor density measurements showed a molecular weight of 94.5, compared with the calculated value of 93.6 for $C_2H_5B_5H_{10}$. Second, oxidative hydrolysis followed by titration of the boric acid gave 4.8 boron atoms and 9.7 active hydrogens per molecule, which indicated that the product was a pentaborane derivative. However, since the active hydrogen analysis was not accurate enough to distinguish between the derivatives of $B_5H_9$ and $B_5H_{11}$, infrared spectra were used for this purpose.

The infrared spectra of $B_5H_9$ and $B_5H_{11}$ are quite dif-

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