Anal. Calcd. for $C_7H_{18}B_{10}O_4$: C, 30.64; H, 6.61; B, 39.43; neut. equiv., 137.2. Found: C, 30.31; H, 7.29; B, 39.18; neut. equiv., 143.5.

Bis-(1-carboranylmethyl)-malonic Acid.—Saponification of diethyl bis-(1-carboranylmethyl)-malonate[2] (0.08 mole), m.p. 198–199°, was accomplished in benzene solution using 40 g. of 50% aqueous potassium hydroxide at room temperature. Then 12.7 g. of the dipotassium salt was isolated by filtration, dried by azeotropic distillation in benzene suspension, and acidified with hydrogen chloride. Bis-(1-carboranylmethyl)-malonic acid, 1.9 g., was isolated as a white hygroscopic solid, decomposing at 65–70°. Decarboxylation was observed in refluxing toluene.

Anal. Calcd.: neut. equiv., 416 and 208. Found: neut. equiv., 400 and 227.

Cyclic Ether from 1,2-Bis-(hydroxymethyl)-carborane.—A mixture of 0.05 mole of the diol and 55 ml. of concentrated sulfuric acid was heated at 135–140° for 5 hr. During this period 7.57 g. (81.2% yield) of the product sublimed from the reaction media at atmospheric pressure. The white solid, m.p. 259.5–260.5° (sealed tube), showed CH_2OCH_2 at 1170 cm.$^{-1}$, CH at 2870 cm.$^{-1}$, BH at 2550 cm.$^{-1}$, and another peak at 1070 cm.$^{-1}$ in its infrared spectrum. No hydroxyl peak was evident.

Hydrazinium Methyldicarbaundecaborane.—A mixture of 0.010 mole of 1-methylcarborane and 20 ml. of hydrazine hydrate was heated at reflux for 3.5 hr. During this period some 440 ml. (98%) of gas at STP, identified by mass spectroscopy as pure hydrogen, was liberated. Evaporation of the solvent then gave 2.22 g. of methyldicarbaundecaborane salt. The product was extracted with ethyl ether and the residue, which decomposes at 198°, was dissolved in water and precipitated as a tetramethylammonium salt for analytical purposes.

Anal. Calcd. for $C_7H_{26}B_9N$: C, 37.93; H, 11.82; B, 43.92; N, 6.35. Found: C, 36.31; H, 12.13; B, 43.97; N, 6.40.

Acknowledgment.—This work was supported by the U. S. Air Force, Edwards Air Force Base, under Contract AF33(616)-5639.

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

Carboranes. IV. Chemistry of Bis-(1-carboranylalkyl) Ethers

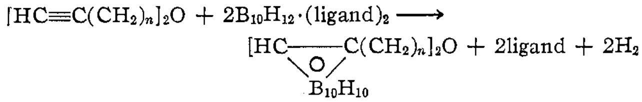
BY DANIEL GRAFSTEIN, JACK BOBINSKI, JOSEPH DVORAK, JOHN E. PAUSTIAN,
HARRY F. SMITH, SIDNEY KARLAN, CALVIN VOGEL, AND MARVIN M. FEIN

Received July 29, 1963

The carborane unit, $-\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{C\text{———}C}}-$, is exceptionally inert, and the chemical reactions of carboranes are limited principally to those of attached functional groups. The syntheses of two symmetrical dicarboranyl ethers are described. The lability of the 1-carboranyl hydrogen has been utilized to prepare several hydroxylic and carboxylic derivatives. The pyrolysis of the dicarboxylic acid, bis-(2-carboxy-1-carboranylmethyl) ether, gives rise to the lactone of 1-hydroxymethyl-2-carboranylcarboxylic acid.

In the initial paper of this series[1] the reaction of substituted acetylenes with 6,9-bis-(acetonitrile)-decaborane, $(CH_3CN)_2B_{10}H_{12}$, was described. The resulting carboranes, $B_{10}H_{10}C_2RR'$, were distinguished by unusual stability of the boron cage unit. In this paper are reported the results of an extension of this study to the synthesis, characterization, and reactions of dicarborane ethers and related difunctional derivatives.

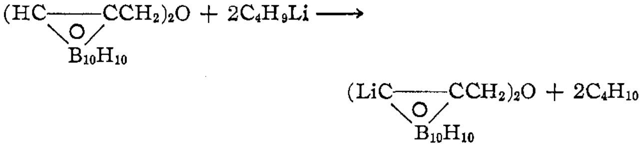
Propargyl and 3-butynyl ethers interacted with 6,9-bis-(acetonitrile)-decaborane to yield, respectively, bis-(1-carboranylmethyl) ether and β,β'-bis-(1-carboranyl)-diethyl ether, according to the equation



$$[HC{\equiv}C(CH_2)_n]_2O + 2B_{10}H_{12}\cdot(\text{ligand})_2 \longrightarrow [\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{HC\text{———}C}}(CH_2)_n]_2O + 2\text{ligand} + 2H_2$$

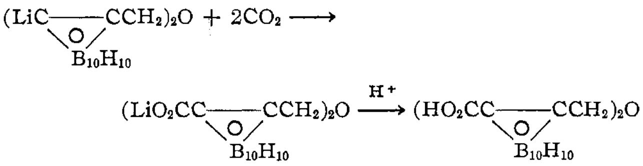
where $n = 1$ or 2. Yields were influenced by the nature of the ligand; the yield of the ether product, for example, was increased from 20% for the acetonitrile to 59% when 6,9-bis-(diethyl sulfide)-decaborane was used.

The dicarborane ethers showed the same stability characteristics of the borane unit as the parent carboranes. Hydrogen atoms attached to polyhedral carbon atoms of the new ethers were labile, like those of the parent carboranes, and their displacement by reaction with butyllithium formed the basis for the preparation of several interesting derivatives.



$$(\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{HC\text{———}C}}CH_2)_2O + 2C_4H_9Li \longrightarrow (\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{LiC\text{———}C}}CH_2)_2O + 2C_4H_{10}$$

Carbonation of the dilithio derivative in tetrahydrofuran gave a salt which upon acidification formed the diacid, bis-(2-carboxy-1-carboranylmethyl) ether, in high over-all yield.



$$(\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{LiC\text{———}C}}CH_2)_2O + 2CO_2 \longrightarrow (\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{LiO_2CC\text{———}C}}CH_2)_2O \xrightarrow{H^+} (\underset{B_{10}H_{10}}{\underset{\diagdown O \diagup}{HO_2CC\text{———}C}}CH_2)_2O$$

When only one equivalent of butyllithium was used, bis-(1-carboranylmethyl) ether was converted to the monolithium derivative, which upon carbonation and acidification gave the monobasic acid.

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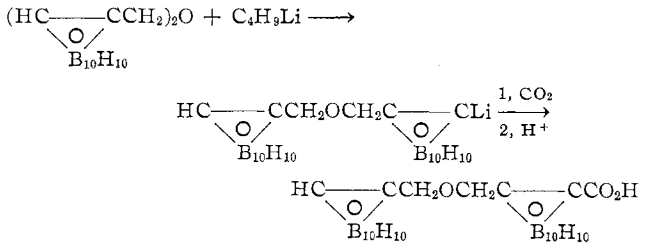
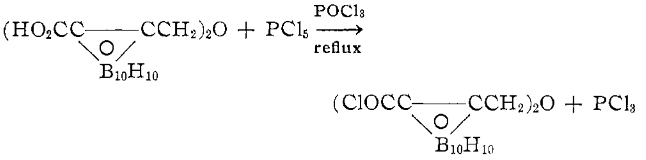
[1] M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *Inorg. Chem.*, **2**, 1111 (1963).



$$(\mathrm{HC}\underset{\substack{\diagdown\mathrm{O}\diagup\\ \mathrm{B_{10}H_{10}}}}{\text{——}}\mathrm{CCH_2})_2\mathrm{O} + \mathrm{C_4H_9Li} \longrightarrow \mathrm{HC}\underset{\substack{\diagdown\mathrm{O}\diagup\\ \mathrm{B_{10}H_{10}}}}{\text{——}}\mathrm{CCH_2OCH_2C}\underset{\substack{\diagdown\mathrm{O}\diagup\\ \mathrm{B_{10}H_{10}}}}{\text{——}}\mathrm{CLi} \xrightarrow[\text{2, H}^+]{\text{1, CO}_2} \mathrm{HC}\underset{\substack{\diagdown\mathrm{O}\diagup\\ \mathrm{B_{10}H_{10}}}}{\text{——}}\mathrm{CCH_2OCH_2C}\underset{\substack{\diagdown\mathrm{O}\diagup\\ \mathrm{B_{10}H_{10}}}}{\text{——}}\mathrm{CCO_2H}$$

The dicarborane ether differs in this respect from carborane itself, which, upon treatment with one equivalent of butyllithium and subsequent carbonation, was reported to yield a mixture of 1,2-carboranedicarboxylic acid and unreacted carborane.[2] The ether diacid and carboranedicarboxylic acid are similar in that both failed to undergo simple acid-catalyzed esterification. The ether diacid was degraded by prolonged refluxing in dilute acid. The ether diacid was decarboxylated by aqueous caustic to regenerate the parent compound, bis-(1-carboranylmethyl) ether; degradation to borates was also observed.

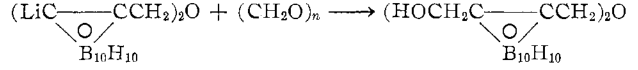
Failure to effect direct esterification of bis-(2-carboxy-1-carboranylmethyl) ether prompted an attempt to synthesize the corresponding acid chloride, bis-(2-chloroformyl-1-carboranylmethyl) ether. The ether diacid was unaffected by refluxing thionyl chloride or by treatment with chlorine in phosphorus oxychloride, but was chlorinated in 60–85% yields by refluxing in phosphorus oxychloride containing one equivalent of phosphorus pentachloride.



$$(\mathrm{HO_2CC}\underset{\substack{\diagdown\mathrm{O}\diagup\\ \mathrm{B_{10}H_{10}}}}{\text{——}}\mathrm{CCH_2})_2\mathrm{O} + \mathrm{PCl_5} \xrightarrow[\text{reflux}]{\mathrm{POCl_3}} (\mathrm{ClOCC}\underset{\substack{\diagdown\mathrm{O}\diagup\\ \mathrm{B_{10}H_{10}}}}{\text{——}}\mathrm{CCH_2})_2\mathrm{O} + \mathrm{PCl_3}$$

The acid chloride was also obtained by treatment of the 2,2′-dilithium derivative of the ether with phosgene or by the reaction of the dilithium salt of the diacid with excess oxalyl chloride. The acid chloride is relatively insensitive to hydrolysis by atmospheric moisture, but reacts exothermally with alcohols and readily forms condensation polymers with various polyols.[3]

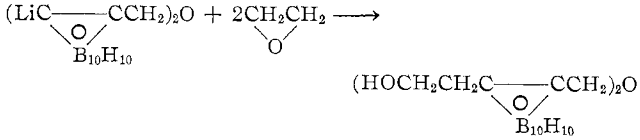
The bis-hydroxymethyl and bis-hydroxyethyl derivatives of bis-(1-carboranylmethyl) ether have been prepared. Treatment of bis-(2-lithio-1-carboranylmethyl) ether in benzene with paraformaldehyde gave bis-(2-hydroxymethyl-1-carboranylmethyl) ether in 50% yield; no reaction occurred when a similar synthesis was attempted with trioxane in ethyl ether.



$$(\mathrm{LiC}\underset{\substack{\diagdown\mathrm{O}\diagup\\ \mathrm{B_{10}H_{10}}}}{\text{——}}\mathrm{CCH_2})_2\mathrm{O} + (\mathrm{CH_2O})_n \xrightarrow{\mathrm{C_6H_6}} (\mathrm{HOCH_2C}\underset{\substack{\diagdown\mathrm{O}\diagup\\ \mathrm{B_{10}H_{10}}}}{\text{——}}\mathrm{CCH_2})_2\mathrm{O}$$

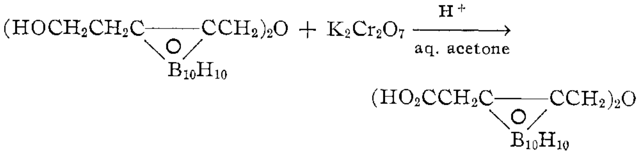
This diol could also be prepared by the lithium aluminum hydride reduction of the corresponding diacid. The hydroxyl functions reacted normally, readily forming diesters with aliphatic acids and polymers with succinic acid.[3]

The next higher ether diol homolog, bis-2-(β-hydroxyethyl)-1-carboranylmethyl ether, was synthesized by the reaction of ethylene oxide with the dilithium compound.



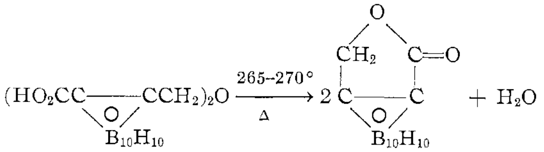
$$(\mathrm{LiC}\underset{\substack{\diagdown\mathrm{O}\diagup\\ \mathrm{B_{10}H_{10}}}}{\text{——}}\mathrm{CCH_2})_2\mathrm{O} + 2\underset{\diagdown\mathrm{O}\diagup}{\mathrm{CH_2CH_2}} \longrightarrow (\mathrm{HOCH_2CH_2C}\underset{\substack{\diagdown\mathrm{O}\diagup\\ \mathrm{B_{10}H_{10}}}}{\text{——}}\mathrm{CCH_2})_2\mathrm{O}$$

Chromic acid oxidation of the bis-(hydroxyethyl) compound proceeded smoothly in aqueous acetone and gave the next higher homologous ether diacid, in good yield.



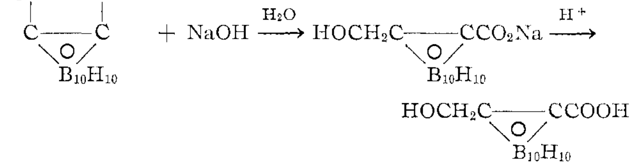
$$(\mathrm{HOCH_2CH_2C}\underset{\substack{\diagdown\mathrm{O}\diagup\\ \mathrm{B_{10}H_{10}}}}{\text{——}}\mathrm{CCH_2})_2\mathrm{O} + \mathrm{K_2Cr_2O_7} \xrightarrow[\text{aq. acetone}]{\mathrm{H}^+} (\mathrm{HO_2CCH_2C}\underset{\substack{\diagdown\mathrm{O}\diagup\\ \mathrm{B_{10}H_{10}}}}{\text{——}}\mathrm{CCH_2})_2\mathrm{O}$$

An unexpected reaction observed during the course of this study was the pyrolytic conversion of bis-(2-carboxy-1-carboranylmethyl) ether to the lactone of 1-hydroxymethyl-2-carboranylcarboxylic acid.



The evolution of water was observed, and crude lactone sublimed from the hot zone in 75% yield. The residue consisted of 14–17% bis-(1-carboranylmethyl) ether, indicating that decarboxylation occurred as a competing reaction. The formation of the lactone is another illustration of the relative ease with which the two polyhedral carbon atoms of carboranes can be incorporated into five- and seven-membered exocyclic systems.[2,3]

A suspension of the lactone in aqueous sodium hydroxide underwent slow hydrolysis at 18°. When the resulting solution was acidified and concentrated, crystals of 1-hydroxymethyl-2-carboranylcarboxylic acid were obtained in 93% yield.



This carborane hydroxy acid and its lactone represent the first mixed difunctional carboranes potentially capable of homopolymerization.

Experimental

Reagents.—The decaborane used in this work was recrystallized from heptane prior to use. Reagent grade, dried solvents and ligands were used. The dipropargyl ether was used as received from General Aniline and Film Corp., as was the dibutynyl ether from Dow Chemical.

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(2) D. Grafstein, *et al.*, *Inorg. Chem.*, **2**, 1120 (1963).

(3) J. Green, *et al.*, *J. Polymer Sci.*, to be published.

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

Bis-(1-carboranylmethyl) Ether.—A 500-ml. flask was charged with 0.816 mole of decaborane, 100 ml. of diethyl sulfide, 50 ml. of anhydrous toluene, and 50 ml. of anhydrous dioxane. This mixture was allowed to stand for 24 hr. while hydrogen was evolved and bis-(diethyl sulfide)-decaborane was formed. The reaction mixture was then heated to 60° and 0.408 mole of dipropargyl ether was added slowly to maintain controllable reflux. The addition required 7 hr., during which 33.2 l. of hydrogen was evolved. The reaction mixture was stirred overnight and then cooled to $-10°$. The copious precipitate of the product was separated by filtration and crystallized from dioxane. The first crop of crystals, which proved to be the monodioxanate, totaled 105 g.

Anal. Calcd. for product·dioxane, $C_{10}H_{34}B_{20}O_3$: C, 28.8; H, 8.2; B, 51.7. Found: C, 27.7; H, 8.2; B, 50.4.

Washing the solvated product with pentane gave 80 g. (59% yield) of the dicarboranyl product as white crystalline platelets, m.p. 342–344.5°.

Anal. Calcd. for $C_6H_{26}B_{20}O$: C, 21.79; H, 7.90; B, 65.43. Found: C, 21.01; H, 8.02; B, 65.26.

The infrared spectrum of the product (KBr pellet) exhibited the characteristic absorptions at 3.27 μ for the carborane CH and at 3.92 μ for the $-BH$ in addition to a major $-CH_2OCH_2-$ band at 8.85 μ.

β,β'-Bis-(1-carboranyl)-diethyl Ether.—Bis-(acetonitrile)-decaborane (0.2 mole) was mixed with a solution of 0.1 mole of 3-butynyl ether in 200 ml. of refluxing toluene for several hours. Insoluble products were removed by filtration and the solvent was distilled under vacuum. The residue was extracted with pentane and then with refluxing heptane. The hydrocarbon extract was evaporated and the product, 3.4 g. (10% yield), was crystallized from methanol, m.p. 117–118°. The infrared spectrum of the product was consistent with the assigned structure.

Anal. Calcd. for $C_8H_{30}B_{20}O$: C, 26.78; H, 8.45; B, 60.31; mol. wt., 358.7. Found: C, 26.45; H, 8.31; B, 59.61; mol. wt., 365 (cryoscopic in benzene).

Bis-(2-carboxy-1-carboranylmethyl) Ether.—To a solution of 0.138 mole of butyllithium in 50 ml. of dry tetrahydrofuran, under an argon atmosphere, was added a solution of 0.05 mole of bis-(1-carboranylmethyl) ether in 150 ml. of tetrahydrofuran. During the addition, which required 45 min., the reactants were maintained at 5–7°. The mixture of precipitated solid and solution was allowed to stand at 10–15° for 1.5 hr. and then poured over Dry Ice. The solvent was removed and the dry powdery residue suspended in benzene. The resultant slurry was extracted with water, and the aqueous solution was acidified with 12% hydrochloric acid at 1–5°. The solid which precipitated was separated by filtration, dissolved in ethyl ether, dried over Drierite, and filtered. Evaporation of the ether gave 18.5 g. (91% yield) of crude product. Crystallization from benzene gave 10.4 g. of first crop crystals as white needles, m.p. 232–233°. Recrystallization from a mixture of benzene and ethyl acetate gave pure crystalline plates, m.p. 235–235.5°: the product was identified by its infrared spectrum, which exhibited the usual $-BH$ and $-CO_2H$ bands as well as an ether band at 9.0 μ which is shifted from 8.85 μ in the parent ether.

Anal. Calcd. for $C_8H_{26}B_{20}O_5$: neut. equiv., 209. Found: neut. equiv., 212.

2-Carboxy-bis-(1-carboranylmethyl) Ether.—By a procedure similar to the above the use of equimolar quantities of butyllithium and bis-(1-carboranylmethyl) ether resulted in the formation of the monocarboxylic acid (50% yield), m.p. 73°.

Anal. Calcd.: neut. equiv., 374. Found: neut. equiv., 378. The infrared spectrum contained the absorptions expected for COOH, BH, and $-CH_2OCH_2-$ (8.95 μ).

Bis-(2-chloroformyl-1-carboranylmethyl) Ether.—The ether diacid (0.15 mole) was added to a suspension of 0.6 mole of phosphorus pentachloride in 500 ml. of phosphorus oxychloride. The mixture was heated at reflux for 2 hr. Distillation of the solvent, extraction of the residue with pentane, and crystallization from this solvent gave 55.5 g. (81% yield), m.p. 86–89°.

Anal. Calcd. for $C_8H_{24}B_{20}Cl_2O_3$: C, 21.09; H, 5.31; B, 47.48; Cl, 15.56. Found: C, 20.91; H, 5.41; B, 46.73; Cl, 13.87.

Bis-(2-hydroxymethyl-1-carboranylmethyl) Ether. From Bis-(1-carboranymethyl) Ether.—To 0.11 mole of butyllithium in 100 ml. of ethyl ether was added 0.05 mole of the dicarboranyl compound in 250 ml. of ethyl ether. The mixture was maintained at -5 to $+5°$ for a 0.5-hr. period with vigorous stirring and then allowed to warm to room temperature. The ether was removed by distillation as 300 ml. of benzene was slowly added. After the ether was removed, 3 g. of paraformaldehyde in 100 ml. of benzene was added and the reaction mixture was heated for 4 hr. at 70°. The reaction layer was then extracted with ether and the benzene–ether extracts were combined, washed with water, and dried. Removal of the solvents and crystallization from toluene gave 9.5 g. (50% yield) of the ether diol, which did not melt up to 350°. It exhibited infrared absorptions at 2.98 (OH), 3.90 (BH), 7.33 (CH_2), 8.95 (CH_2OCH_2), and 9.30 μ (COH).

Anal. Calcd. for $C_8H_{30}B_{20}O_3$: C, 24.59; H, 7.74; B, 55.38. Found: C, 25.56; H, 7.99; B, 54.45.

From Bis-(2-carboxy-1-carboranylmethyl) Ether.—To 0.0625 mole of lithium aluminum hydride in 125 ml. of ethyl ether was added a solution of 0.025 mole of the diacid in 150 ml. of ethyl ether over a 1-hr. period at 30°. After the addition was completed, the reaction mixture was refluxed for 1 hr. It was then cooled to 5° and cautiously hydrolyzed with 10% sulfuric acid until just acidic. The ether layer was separated, washed with water, and dried. Ether was removed and the residue was crystallized from toluene to give 1.50 g. (25% yield) of the ether diol.

Bis-(2-β-hydroxyethyl-1-carboranylmethyl) Ether.—Bis-(1-carboranylmethyl) ether (0.025 mole) was treated at 0° with 0.05 mole of butyllithium in 200 ml. of anhydrous ethyl ether. A nitrogen atmosphere was maintained over the resulting turbid solution while a chilled (0°) solution of 0.06 mole of ethylene oxide in 100 ml. of ethyl ether was added. Hydrolysis of the reaction product was effected with ice and hydrochloric acid to give 9 g. of product (86% yield), m.p. 126–128°.

Anal. Calcd. for $C_{10}H_{34}B_{20}O_3$: C, 28.6; H, 8.91; B, 51.6. Found: C, 29.49; H, 8.38; B, 51.2.

Bis(2-carboxymethyl-1-carboranylmethyl) Ether.—Bis-(2-hydroxyethyl-1-carboranylmethyl) ether (0.041 mole) in 160 ml. of acetone and 50 ml. of water was oxidized with 0.15 mole of potassium dichromate in 85 ml. of sulfuric acid. The reaction mixture was maintained below 20°. Work-up of the mixture gave 14 g. (73% yield) of the diacid as a white powder, m.p. 242–244°.

Anal. Calcd. for $C_{10}H_{30}B_{20}O_5$: C, 26.88; H, 6.76; B, 48.44; neut. equiv., 223. Found: C, 26.60; H, 6.74; B, 49.4; neut. equiv., 232.

Lactone of 1-Hydroxymethyl-2-carboranylcarboxylic Acid.—Bis-(2-carboxy-1-carboranylmethyl) ether (0.0048 mole) was heated to about 270° for 6 hr. The lactone was formed as a white, crystalline sublimate in 55% yield and recrystallized from an ether–pentane mixture, m.p. 253–254.5°.

Anal. Calcd. for $C_4H_{12}B_{10}O_2$: C, 23.98; H, 6.04; B, 54.02. Found: C, 24.15; H, 6.21; B, 53.54. Its infrared spectrum showed prominent absorptions at 3.90 (BH) and 5.55 μ (lactone C=O) and a characteristic lactone triplet at 9.30, 9.68, and 10.18 μ. The carbonyl band at 5.82 μ and the ether band at 8.95 μ in the original diacid were absent. The lactone is very soluble in benzene, carbon tetrachloride, tetrahydrofuran, dioxane, and ethyl ether. It is moderately soluble in pentane, hexane, and isopropyl ether and insoluble in water. The sublimation residue, 2.29 g. (14%), was shown by infrared analysis to be the decarboxylated product, bis-(1-carboranylmethyl) ether.

1-Hydroxymethyl-2-carboranylcarboxylic Acid.—The lactone (0.0024 mole) was suspended in 20 ml. of water containing 0.05 mole of sodium hydroxide and stirred for 92 hr. at 12–18°. The resulting solution was acidified with dilute hydrochloric 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.

Acknowledgment.—This work was supported by the U. S. Air Force, Edwards Air Force Base, under Contract AF33(616)-5639.

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

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

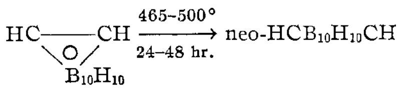
BY DANIEL GRAFSTEIN(1) AND JOSEPH DVORAK

Received July 8, 1963

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.

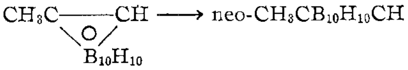


$$\underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{HC\text{——}CH} \xrightarrow[\text{24–48 hr.}]{465\text{–}500^\circ} \text{neo-}HCB_{10}H_{10}CH$$

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).



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

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.

(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.