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A New Series of Organoboranes. VI. The Synthesis and Reactions of Some Silyl Neocarboranes

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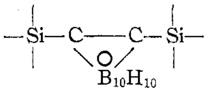
The preparation and some reactions of silyl neocarboranes are reported. These derivatives contrast the isomeric silyl carboranes since they do not tend to form exocyclic derivatives. Some differences in reactivity of chlorosilyl neocarboranes when compared with the similar carboranes are noted.

A principal goal of our research in the chemistry of silyl carboranes has been to prepare linear polymers, the backbond of which contains essentially



The preceding two papers[1,2] in this series have well illustrated the fact that there is an extreme tendency for very stable, cyclic molecules to be formed in reactions useful for the desired polymerizations and this tendency has thwarted our efforts to obtain such polymers. To overcome this problem we turned our attention to the isomeric neocarborane[3] system of compounds. This nucleus had been generally indicated to be stable at elevated temperature[1,3] and its geometry with the *meta* positioning of carbon atoms[4] should preclude the participation of these atoms in small, exocyclic rings, and, in fact, deliberate attempts to prepare such rings had failed.[3]

Although some derivative chemistry of neocarborane had been reported, no silyl derivatives had been prepared,[3] and we set about synthesizing and studying several such compounds of interest to us. When neocarborane (I) in ether was treated with two moles of butyllithium in ether, butane was evolved and dilithioneocarborane apparently formed as expected, although this intermediate did not precipitate from the solution as we had experienced with dilithiocarborane.[2] Consequently, we were not able to isolate and purify the dilithioneocarborane as we had become accustomed to doing in this laboratory[5] with dilithiocarborane. Addition of dichlorodimethylsilane to the dilithioneocarborane solution and subsequent isolation with much difficulty afforded a low yield of the desired C,C′-bis(chlorodimethylsilyl)neocarborane (II). We noted that most similar reactions reported[3] had likewise given poor yields. After some experimentation, it was found that when butyllithium as prepared in hexane was added to ethereal neocarborane, the dilithio salt precipitated so that it could be filtered and washed before redissolution in ether for reaction. Substantial improvement in yields was then obtained. In a similar manner, C,C′-bis(chlorodiphenylsilyl)neocarborane (III) was prepared. By allowing dilithioneocarborane to react with methyltrichlorosilane, the multifunctional C,C′-bis(methyldichlorosilyl)neocarborane (IV) was synthesized.

When bis(chlorodimethylsilyl)neocarborane (II) was treated with water no cyclization occurred as anticipated, and a practically quantitative yield of bis(hydroxydimethylsilyl)neocarborane (V) resulted. Reaction of the dichloro compound II with ammonia and with methanol gave the diamino (VI) and dimethoxy(VII) derivatives, respectively; we have, however, been unable to synthesize the carborane derivative analogous to VII. Bis(methyldichlorosilyl)neocarborane (IV) exhibited similar reactivity in that it could be quantitatively hydrolyzed to C,C′-bis(dihydroxymethylsilyl)neocarborane (VIII).

Bis(chlorodiphenylsilyl)neocarborane (III) was also readily hydrolyzed to bis(hydroxydiphenylsilyl)neocarborane (IX). This markedly contrasts the behavior of the analogous carborane derivative 1,2-bis(chlorodiphenylsilyl)carborane,[2] which has resisted all hydrolysis attempts. Treatment of bis(chloridiphenylsilyl)neocarborane (III) with methanol gave the expected methoxy derivative X. This difference in reactivity of analogous carborane and neocarborane derivatives presents another example of the operation of subtle forces which markedly affect the chemistry of carborane derivatives.[1] Whether these influences are primarily steric or electronic is not apparent as yet.

By turning to this silyl neocarborane system we have therefore been able to synthesize difunctional monomers which may be used to prepare polymers of the type desired. We found that these derivatives in general were very sluggish in their reactions; for example, bis(hydroxydimethylsilyl)neocarborane (V) resists dehydration to form a polysiloxane. Continued experimentation, however, afforded methods of effecting the desired polymerizations, and the formation of the polymers and the uncovering of interesting chemistry attendant to this research will be described in a subsequent paper.

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[1] S. Papetti, B. B. Schaeffer, H. J. Troscianiec, and T. L. Heying, *Inorg. Chem.*, **3**, 1444 (1964).

[2] S. Papetti and T. L. Heying, *ibid.*, **2**, 1105 (1963).

[3] D. Grafstein and S. Dvorak, *ibid.*, **2**, 1128 (1963).

[4] H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963).

[5] R. P. Alexander and H. Schroeder, *ibid.*, **2**, 1107 (1963).

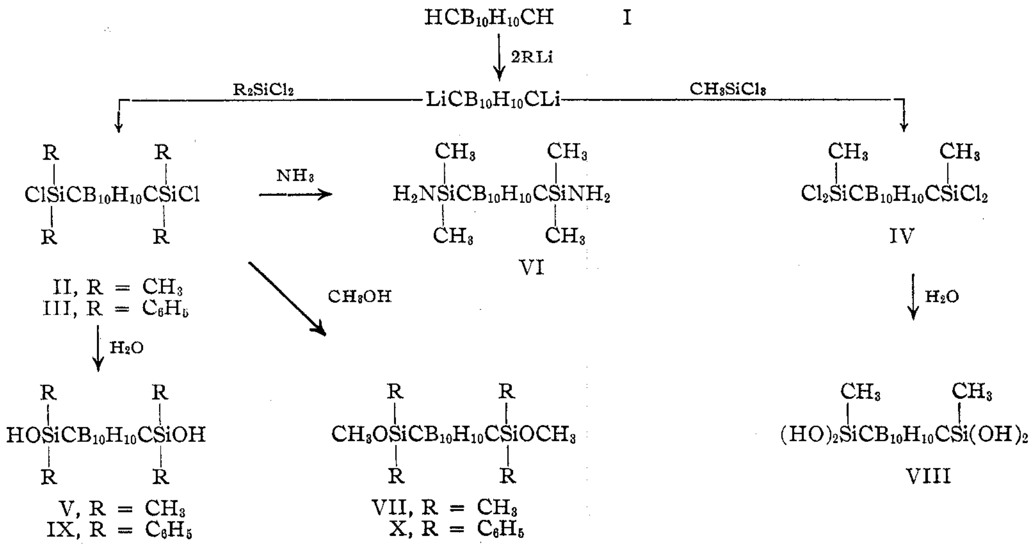

TABLE I

SILICON–NEOCARBORANE DERIVATIVES

			Elemental analysis[b]									
			Carbon		Hydrogen		Boron		Chlorine		Silicon	
Compd.	M.p.,[a] °C.	B.p., °C. (mm.)	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
II		102–104 (0.1)	21.84	22.10	6.86	6.88	32.79	32.69	21.49	21.40		
III	131–133		54.05	54.26	5.23	5.15	18.73	18.35	12.26	12.30	9.73	9.61
IV		103–105 (0.15)	12.97	12.72	4.35	4.37	29.22	28.98	38.29	38.50	18.79	18.95
V	98–99.5		24.63	24.35	8.27	8.25	36.97	36.57				
VI[c]	41.5–43.5		24.80	24.69	9.01	9.05	37.22	35.86			19.33	19.42
VII	36–37	108–110 (0.1)	29.96	29.71	8.50	8.93	33.74	33.78			17.52	17.90
VIII	136.5–138.5		15.93	16.77	6.67	6.80	36.55	36.48			18.79	18.95
IX	153–155		57.73	57.34	5.96	5.96	20.00	19.20			10.38	10.11
X	151–153		59.11	58.83	6.38	6.60	19.02	18.78			9.87	9.58

[a] Mel-Temp apparatus, uncorrected. [b] Corroborating infrared and mass spectral analyses also obtained. [c] Nitrogen: calcd., 9.64; found, 9.60.

Experimental

Neocarborane (I).—By slightly modifying the reported procedure,[3] neocarborane was prepared by heating carborane[6] at 470–480° for 6–18 hr., in a sealed, heavy-walled Pyrex combustion tube or a steel bomb, depending on the amount of neocarborane prepared. The product was recovered by dissolving it in ethyl ether, filtering, and evaporating the solution to dryness. The neocarborane was further purified either by recrystallization from low-boiling petroleum ether or by sublimation.

The conversion of carborane to neocarborane was verified by its infrared analysis and melting point (265°, sealed tube). The yield was usually greater than 90%.

C,C′-Bis(chlorodimethylsilyl)neocarborane (II).—A dilithioneocarborane solution was prepared from 144.3 g. (0.1 mole) of neocarborane in 1000 ml. of dry ether to which was added 2.2 moles of butyllithium[7] in hexane with ice cooling. The dilithioneocarborane precipitated and was filtered, washed twice with hexane, and redissolved in 1000 ml. of ether. This solution was slowly added to dichlorodimethylsilane (283.9 g., 2.2 moles) in 1000 ml. of ether and at ice temperature. The mixture was then stirred at room temperature for another 2 hr. and filtered. The filtrate was evaporated to dryness and the liquid residue was distilled under reduced pressure, using a 12-in. Vigreux column (oil bath at 130–150°). Bis(chlorodimethylsilyl)neocarborane was recovered in 84.2% yield.[8]

C,C′-Bis(chlorodiphenylsilyl)neocarborane (III).—The procedure was identical with that for II using 40.0 g. (0.277 mole) of neocarborane and 154.3 g. (0.6096 mole) of dichlorodiphenylsilane. The product was filtered and evaporated to dryness, and the residue was washed with 200 ml. of cold, low-boiling petroleum ether to remove the unreacted dichlorodiphenylsilane. The residue was crystallized from hexane. Bis(chlorodiphenylsilyl)neocarborane (III) was recovered in 65% yield.

C,C′-Bis(methyldichlorosilyl)neocarborane (IV).—A dilithioneocarborane solution was prepared from 30.3 g. (0.21 mole) of neocarborane and 0.462 mole of butyllithium in hexane and added to 69.0 g. (0.462 mole) of methyltrichlorosilane in a preparation identical with that for II. The crude product was distilled under reduced pressure using a 12-in. Vigreux column, and bis(methyldichlorosilyl)neocarborane was obtained in 68.1% yield.

C,C′-Bis(hydroxydimethylsilyl)neocarborane (V).—This compound is readily prepared by adding excess water to an acetone solution of bis(chlorodimethylsilyl)neocarborane (II) at room temperature. The resulting solution is concentrated under reduced pressure until most of the acetone is removed and the remainder is filtered. The residue is recrystallized from high-boiling petroleum ether, and bis(hydroxydimethylsilyl)neocarborane (V) is obtained in practically quantitative yield.

C,C′-Bis(aminodimethylsilyl)neocarborane (VI).—Bis(chlorodimethylsilyl)neocarborane (II) (11.3 g., 0.045 mole) was dissolved in 200 ml. of ether and cooled in an ice bath. Ammonia was passed through it for 45 min., during which time a precipitate formed. The mixture was filtered, the filtrate evaporated to dryness, and the residue sublimed under reduced pressure. Bis(aminodimethylsilyl)neocarborane was recovered in 77% yield.

C,C′-Bis(methoxydimethylsilyl)neocarborane (VII).—This compound is readily prepared by adding excess absolute methanol to bis(chlorodimethylsilyl)neocarborane (II) at room temperature, with stirring until solution is effected. After an additional hour of stirring the product is recovered either by concentrating

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(6) We thank Mr. R. W. Blundon for preparing a continuing supply of carborane for this work.

(7) Foote Mineral Co.

(8) Analysis and physical constants are listed in Table I.

and cooling the solution to precipitate the crystalline product or by evaporating the solution to dryness and distilling the residue under reduced pressure. In a typical experiment bis(methoxydimethylsilyl)neocarborane was recovered by the crystallization method in 93.5% yield.

C,C′-Bis(dihydroxymethylsilyl)neocarborane (VIII).—This compound is readily prepared by adding excess water to an acetone solution of bis(methyldichlorosilyl)neocarborane (IV) at room temperature. On evaporation in air, the product separates as crystals and can be recrystallized from xylene to give a practically quantitative yield.

C,C′-Bis(hydroxydiphenylsilyl)neocarborane (IX).—The preparation is identical with that for VIII using bis(chlorodiphenylsilyl)neocarborane. The crude product is crystallized from hexane, and bis(hydroxydiphenylsilyl)neocarborane is obtained in practically quantitative yield.

C,C′-Bis(methoxydiphenylsilyl)neocarborane (X).—This compound was prepared from 28.1 g. (0.0484 mole) of bis(chlorodiphenylsilyl)neocarborane (III) and 250 ml. of absolute methanol. Ethyl ether (150 ml.) was added to obtain a homogeneous solution and this solution was heated at reflux for 45 min. The product was evaporated to dryness and the residue recrystallized from ethanol. Bis(methoxydiphenylsilyl)neocarborane was recovered in 76% yield.

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Chemistry of Boranes. XVIII.[1] Oxidation of $B_{10}H_{10}^{-2}$ and Its Derivatives

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The chemical oxidation of $B_{10}H_{10}^{-2}$ and some of its substituted derivatives has produced a series of coupled ions and several neutral compounds. The reaction of these coupled ions and the neutral derivatives with hydroxide ion yields a variety of ionic species. The preparation and properties of several substituted derivatives of $B_{20}H_{18}^{-2}$ and $B_{20}H_{19}^{-3}$ are presented.

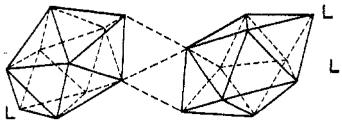
Results and Discussion

(A) $B_{20}H_{16}L_2$ Compounds.—Oxidative coupling of $B_{10}H_9L^-$ derivatives yielded several new $B_{20}H_{16}L_2$ compounds which may be considered as derivatives of the known $B_{20}H_{18}^{-2}$ ion.[2]

$$2B_{10}H_9L^- \longrightarrow B_{20}H_{16}L_2 + 2H^+ + 4e \tag{1}$$

The $B_{10}H_9L^-$ ions[3] which have yielded coupled structures are $B_{10}H_9S(CH_3)_2^-$, $B_{10}H_9IC_6H_5^-$, $B_{10}H_9O{=}\underbrace{C(CH_2)_3N}CH_3^-$, and $B_{10}H_9O_2S(CH_2)_4^-$. The ceric ion has proved most generally effective as the oxidant in these preparations. During the oxidation reaction, the neutral product appears as a water-insoluble solid which can be easily isolated and recrystallized from organic solvents.

Molecular weight and analytical data indicate a composition $B_{20}H_{16}L_2$. There are no bridge B–H–B stretching absorptions in the infared spectra of these compounds. The B_{10} polyhedra are believed to be structurally analogous to the $B_{20}H_{18}^{-2}$ ion.[4] The exact location of the ligands, L, has not been established, but it is reasonable to assume that they occupy the same position as in the parent ion and that no displacement or rearrangement occurs during the coupling reaction.[5] The location of the ligands on the B_{10} cage for the reagents used in this study had been previously determined.[3] The $S(CH_3)_2$ and IC_6H_5 groups occupy an apical position, while the $(CH_2)_4SO_2$ and $CH_3\underbrace{N(CH_2)_3C}{=}O$ ligands occupy an equatorial site. Structure **1** is proposed for the apically-substituted derivatives $B_{20}H_{16}[S(CH_3)_2]_2$ and $B_{20}H_{16}[IC_6H_5]_2$, and there is only one stereoisomer in this case. There are several possible stereoisomers for the equatorially-substituted compounds, $B_{20}H_{16}[O_2S(CH_2)_4]_2$ and $B_{20}H_{16}[O\underbrace{C(CH_2)_4N}CH_3]_2$, one of which is represented by structure 2.



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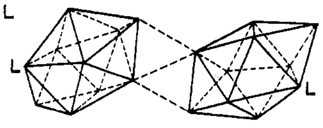

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(B) $B_{20}H_{16}(OH)L_2^-$ and $B_{20}H_{15}(OH)L_2^{-2}$ Derivatives.—Hydroxyl ion reacts with $B_{20}H_{16}L_2$ compounds to form ionic derivatives. This cleavage probably proceeds by the insertion of a hydroxyl group at an equatorial boron site and finally the formation of a direct two-center B–B bond.

$$B_{20}H_{16}L_2 + OH^- \longrightarrow B_{20}H_{16}(OH)L_2^- \tag{2}$$

$$B_{20}H_{16}(OH)L_2^- + OH^- \longrightarrow B_{20}H_{15}(OH)L_2^{-2} + H_2O \tag{3}$$

An acid–base equilibrium exists between these two substituted anions.

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(1) Paper XVII: N. E. Miller, B. L. Chamberland, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1064 (1964).

(2) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962).

(3) To be published.

(4) W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.*, **47**, 1791 (1961), proposed a centrosymmetric structure like **1** with B–H–B bonds between inter-apex–equatorial polyhedral boron atoms. However, R. L. Pilling, M. F. Hawthorne, and E. A. Pier, *J. Am. Chem. Soc.*, **86**, 3568 (1964), from a B^{11} n.m.r. study at 60 Mc. suggest two three-center B–B–B bonds for the linkage of the two polyhedra.

(5) Isomerizations of the type described by Kaczmarczyk, Dobrott, and Lipscomb (ref. 2) and by Lipscomb, *Inorg. Chem.*, **2**, 231 (1963), are considered to be quite unlikely in the oxidation of substituted polyhedral derivatives at room temperature. Polyhedral isomerizations in $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ derivatives are high-energy processes. Detailed studies of this type have been made in these laboratories and will be published.