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A New Series of Organoboranes. V. Some Chemistry of Cyclic Silyl Carboranes

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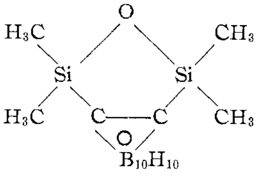
When the carbons of carborane participate in exocyclic rings the thermal rearrangement of the *ortho* carborane nucleus to the *meta* configuration is opposed. These molecules as a whole therefore resist degradation at elevated temperature. Chemically these cyclics are stable under acid conditions but the silicon–carborane carbon bond is attacked by bases. Additional types of cyclic silazanes are reported and reactions of some functional groups at the silicon atoms are described.

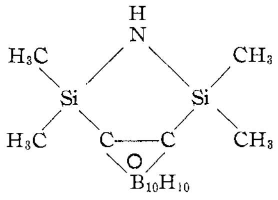
Results and Discussion

Considerable evidence of both a chemical and a physical nature has been amassed to establish the skeletal structure of 1,2-dicarbaclovododecaborane (12) (carborane) as an icosahedron of ten boron atoms and two atoms in which the carbon atoms are in nearest proximity or *ortho* to each other,[1–5] although other structures have been postulated.[4,6] A high degree of resistance to heat has been observed for this compound in that no change in the material develops until 465–500° (24 hr.) when an isomerization to neocarborane proceeds quantitatively.[7] The *meta* relationship of carbon atoms in this icosahedral molecule has been illustrated.[8] Substituted carboranes were also shown to undergo this isomerization.[7] During other work in this laboratory[8,9] we essentially confirmed these findings, although we observed that treatment of carborane at 475° for about 8 hr. was sufficient to effect this isomerization.

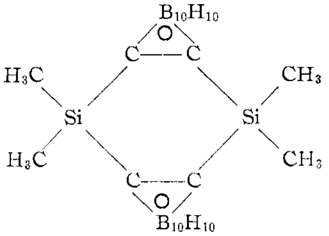
Numerous examples of the participation of the two carbon atoms of the carborane nucleus in exocyclic rings, especially where these are five-membered rings, have been reported.[3] Also examples of the participation of the carbon atoms from two carborane nuclei in six-membered rings have been established.[3,10] A cursory examination of several compounds showed that they too exhibited impressive resistance to heat. Two effects should come into opposition on heating such molecules; one is the tendency of the carborane nucleus to rearrange to the neocarborane structure and the second is the participation of the *ortho* carborane carbons in the exocyclic rings which should resist the former rearrangement. The geometry of the neocarborane molecule[8] should not permit these *meta* carbons to participate in a small exocyclic ring and indeed no such examples have been observed.

To examine more carefully the stability of such molecules at elevated temperature we chose to study first the known compounds I and II. We found that no change in the molecule occurred until signs of decomposition were observed at ∼495°. The first gaseous decomposition product in each case was predominantly methane with a minor amount of hydrogen. A rather gradual decomposition to give the same gaseous product in similar ratio persisted to ∼590°, whereupon a more severe decomposition set in as evidenced by a rapid rise in the rate of generation of hydrogen, but no other gaseous products were detected.


I


II

To determine whether replacement of the azane hydrogen atom of II by a methyl group would improve the stability, the N-methyl derivative III was synthesized from bis(chlorodimethylsilyl)carborane (V) and methylamine. In this instance the initial decomposition occurred. For comparison, the silane IV was similarly treated and in this instance decomposition began at ∼485°. We conclude therefore that these nuclei are essentially stable and work is in progress to incorporate them into suitable polymeric structures.


IV

To help establish the scope of the participation of the carborane carbon atoms in exocyclic rings the following reactions were studied. Bis(chlorodimethylsilyl)carborane (V) had reacted readily with ammonia to give

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(1) H. Schroeder, T. L. Heying, and H. R. Reiner, *Inorg. Chem.*, **2**, 1092 (1963).

(2) T. L. Heying, J. W. Ager, S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, **2**, 1097 (1963).

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

(4) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1111 (1963).

(5) J. A. Potenza and W. N. Lipscomb, *J. Am. Chem. Soc.*, **86**, 1874 (1964).

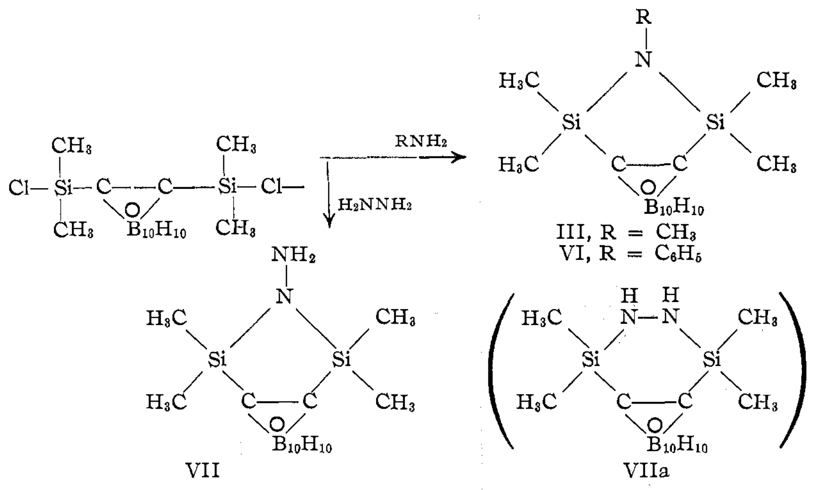
(6) L. I. Zakharkin, V. I. Stanko, V. A. Bratdshev, Y. A. Chapovskii, and Y. T. Dstruchkov, *Proc. Acad. Sci. USSR, Chem. Ser.*, 2069 (1963).

(7) D Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963).

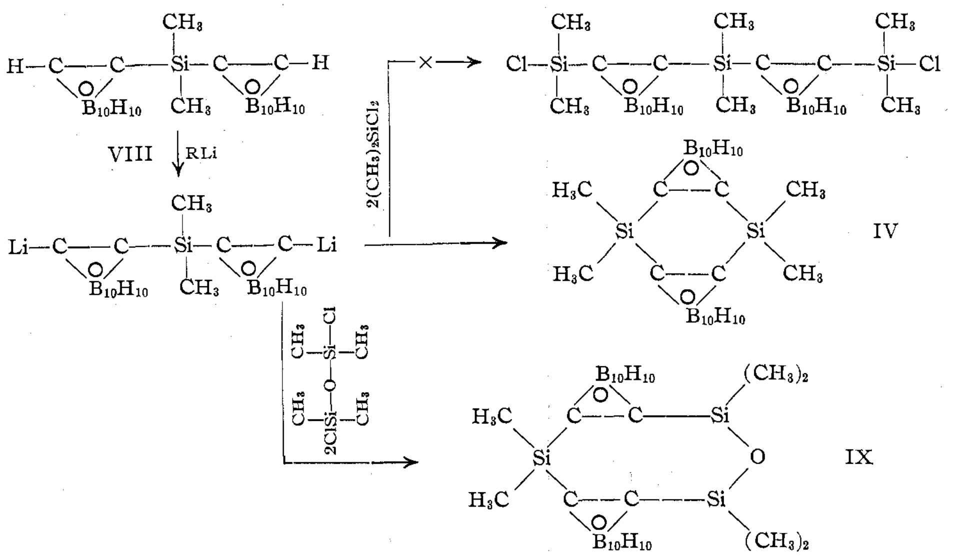
(8) H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963).

(9) S. Papetti and T. L. Heying, *ibid.*, **3**, 1448 (1964).

(10) R. P. Alexander and H. Schroeder, *ibid.*, **2**, 1107 (1963).



III, R = CH_3
VI, R = C_6H_5
VII
VIIa



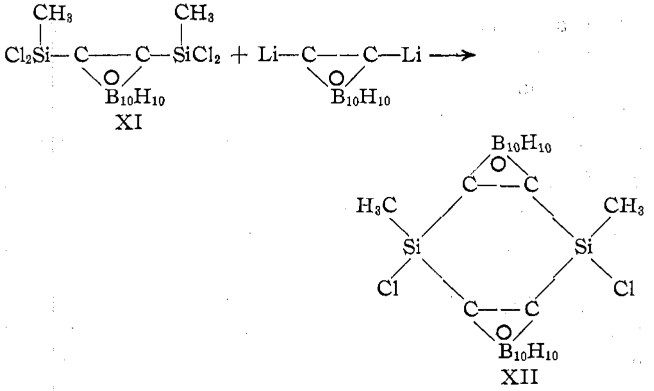
VIII
IV
IX

the cyclic silazanes II and III discussed above and aniline was found to react similarly to give the N-phenyl derivative VI. Hydrazine reacted readily to produce the compound we now write as the N-aminosilazane VII.

Although no examples of one carborane nucleus being involved in a six-membered exocyclic ring had been reported, we could not immediately rule out the possibility that the N-aminosilazane VII could have structure VIIa. Its mass spectrum showed major fragments of mass 17 and 271 which indicated the formation of ammonia by the expulsion of an $-NH_2$ group which combined with a hydrogen atom from a methyl group of the remaining (271) fragment. In order to favor the formation of a ring of type VIIa, the dichlorosilane V was allowed to react with *sym*-dimethylhydrazine and a complex mixture of noncyclic products resulted. We therefore conclude that structure VII is correct and that examples of one carborane nucleus participating in exocycles are still confined to five and seven[11] membered rings.

Dilithiocarborane has been used to synthesize a number of compounds with the ring system of compound IV above. We have now found that the dilithio derivative of dimethyldicarboran-1-ylsilane[3] (VIII) even when allowed to react with excess dichlorodimethylsilane forms only the cyclic IV and no uncyclized product. Similarly, when this dilithio derivative reacted with excess dichlorotetramethylsiloxane, the first example of two carborane nuclei in an eight-membered ring (IX) was realized.

Since compound IV was found to be quite thermally stable, we were anxious to have at hand a difunctional analog of IV, so the reaction of dilithiocarborane with bis(dichloromethylsilyl)carborane (XI) was conducted to give the dichloro compound XII. When the reac-



XI
XII

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[11] D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *Inorg. Chem.*, **2**, 1120 (1963).

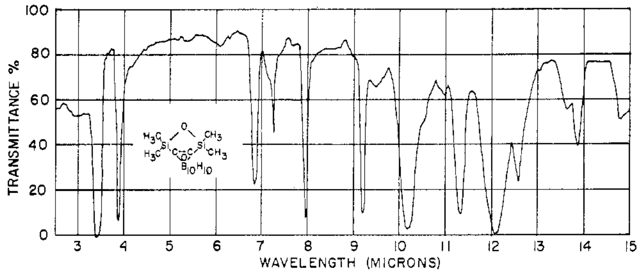
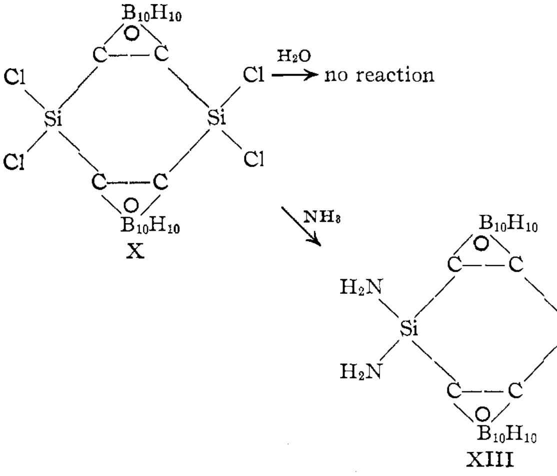
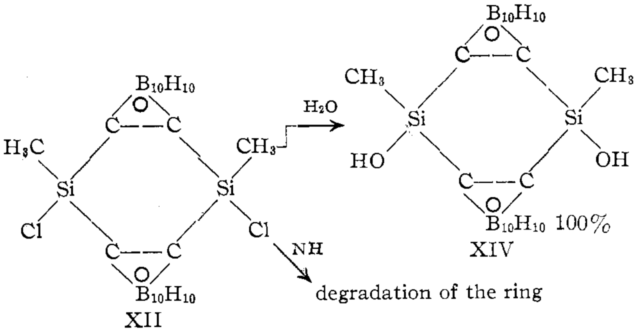
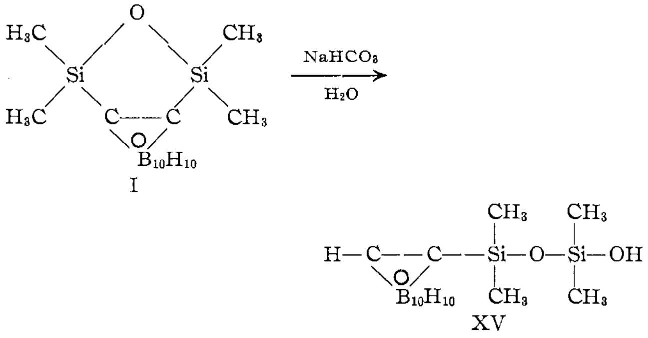


Fig. 1.—Infrared spectrum of 1,2-(1′,1′,3′,3′-tetramethyldisilaoxanyl-1′,3′)-carborane.







tions of XII and the analogous tetrachloro compound X with water and with ammonia were compared a marked effect of the slight difference in structure on reactivity became apparent. We can offer no reasonable explanation for this behavior but would note that we have observed other instances of a facile cleavage of the carbon–silicon bond. For example, treatment of the cyclic carboranylsiloxane I with either inorganic or organic bases generally converted it to carborane and a methyl silicone polymer. With sodium carbonate or sodium bicarbonate we were able to arrest the reaction and recover an oil (XV). The infrared spectrum of XV clearly shows absorptions at 3.0 (Si–OH) and 3.25 μ (carborane C–H); its mass spectrum also supported this formulation. Treatment of XV with absolute methanol generated one mole of water through the reaction $>\text{SiOH} + \text{HOCH}_3 \rightarrow >\text{SiOCH}_3 + \text{H}_2\text{O}$. Proton n.m.r. examination showed chemical shifts of 3.5 (carborane C–H) and 2.4 p.p.m. (–OH); the latter disappeared on deuterium exchange. Based on this evidence we conclude that the carboranyl carbon–silicon bond is subject to cleavage by the chemical action of bases and that the conversion of the cyclic siloxane I to structure XV is typical of such a cleavage.

This facile occurrence of this cleavage of the carborane carbon–silicon bond is reminiscent of a similar cleavage of benzyltrimethylsilanes which is facilitated by the presence of electron-withdrawing substituents on the benzene ring.[12] This emphasizes the electron-withdrawing power of the carborane nucleus, the effect of which has previously been observed in studies of the reactions of 1-substituted carboranes.[2,4,13] This effect is also apparent from the infrared spectra of the cyclic siloxane I (Fig. 1).[14]

Experimental

1,2-(Pentamethyldisilaazanyl-1′,3′)-carborane (III).—Methylamine was bubbled slowly through an ice-cooled solution of 7.3 g. of bis(chlorodimethylsilyl)carborane[3] in 75 ml. of ether. A solid which oiled separated during a 35-min. period, so the ether was evaporated. The residue was redissolved in 250 ml. of ether and the insoluble methylamine hydrochloride was removed by filtration. The filtrate was evaporated to dryness and the residue was recrystallized from 30–60° petroleum ether to give 6.2 g. (97%) of III, m.p.[15] 156–158°.

Anal. Calcd. for $C_7H_{25}B_{10}NSi_2$: C, 29.2; H, 7.7; B, 37.6; N, 4.87. Found: C, 29.26; H, 6.3; B, 37.42; N, 4.81.[16]

1,2-(1′,1′,3′,3′-Tetramethyl-2′-phenyldisilaazanyl-1′,3′)-carborane (VI).—Aniline (5.0 g., 0.0538 mole) was added over a 30-min. period to a solution of 5.5 g. (0.0167 mole) of bis(chlorodimethylsilyl)carborane in 50 ml. of dry benzene cooled with tap water. The reaction mixture was filtered, the filtrate evaporated to dryness, and the residue sublimed. 1,2-(1′,1′,3′,3′-Tetramethyl-2′-phenyldisilaazanyl-1′,3′)-carborane (m.p. 183–185°) was obtained in 74% yield.

Anal. Calcd. for $C_{12}H_{27}B_{10}NSi_2$: C, 41.23; H, 7.79; B, 30.97; N, 4.01. Found: C, 41.08; H, 7.79; B, 30.69; N, 3.95.

1,2-(1′,1′,3′,3′-Tetramethyl-2′-aminodisilaazanyl-1′,3′)-carborane (VII).—Bis(chlorodimethyl)carborane (1.0 g., 0.003 mole) was dissolved in 30 ml. of dry chloroform and 0.18 g.

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[12] C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 126 (1955).

[13] D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *Inorg. Chem.*, **2**, 1120 (1963).

[14] Dr. J. F. Brown, Jr., of the General Electric Research Laboratory has examined and correlated the position of the ν SiOSi bands in about 400 different siloxanes with the electron-withdrawing powers of various substituents. After considering the spectrum of our cyclic siloxane (I) in this regard he concludes that the carboranyl group must be one of the most strongly electron-withdrawing groups known.

[15] Melting points were taken with a Mel-Temp apparatus and are uncorrected.

[16] Analyses were by the Olin Microanalytical Section. Infrared and mass spectral examination was also performed on each sample to confirm structural characteristics, indicate molecular weight, etc.

(0.006 mole) of anhydrous hydrazine in 20 ml. of chloroform was added dropwise over a 0.5-hr. period at ice–water temperature. The mixture was filtered and the filtrate taken to dryness. The solid residue was sublimed. 1,2-(1′,1′,3′,3′-Tetramethyl-2′-aminodisilaazanyl-1′,3′)-carborane (m.p. 163–165°) was recovered in 78% yield.

Anal. Calcd. for $C_6H_{20}B_{10}N_2Si_2$: C, 24.47; H, 8.38; B, 37.53. Found: C, 24.86; H, 8.42; B, 38.05. Additional characterization is found in the Discussion.

Compound IX.—The dilithio derivative of dimethyl dicarboranylsilane[2] was prepared from 5.2285 g. (0.0015 mole) and the stoichiometric amount (0.0030 mole) of butyllithium in ethyl ether at ice–water temperature. This solution was added to dichlorotetramethyldisilane (6.75 g., 0.033 mole) dissolved in 50 ml. of ether at 0°. Then the mixture was refluxed overnight and filtered, and the filtrate was evaporated to dryness. The residue was crystallized from dioxane and sublimed. Compound IX (m.p. 207–208°) was recovered in 35% yield.

Anal. Calcd. for $C_{10}H_{38}B_{20}OSi_2$: C, 25.28; H, 8.06; B, 45.55; Si, 17.70. Found: C, 25.40; H, 8.00; B, 45.30; Si, 17.36.

Compound XII.—A dilithio carborane slurry in ether prepared from 10.2 g. (0.071 mole) of carborane was added to a cooled solution of 6.6 g. (0.0782 mole) of bis(dichloromethylsilyl)carborane[8] in ether. The mixture was refluxed overnight and filtered. The residue was extracted with several portions of benzene and these combined extracts were evaporated to dryness. The solid was recrystallized from benzene to give 6.4 g. of product. The ethereal filtrate from the original reaction was concentrated and the solid which formed was crystallized from 65–110° petroleum ether to give 2.0 g. of product. All mother liquors were combined and evaporated to dryness, and the residue was recrystallized from 65–110° petroleum ether to give an additional 7.3 g. All three materials were found to be identical and compound XII (m.p. 281–283°) was recovered in 51% yield.

Anal. Calcd. for $C_6H_{26}B_{20}Cl_2Si_2$: C, 16.32; H, 5.94; B, 49.0; Cl, 16.06; Si, 12.72. Found: C, 16.22; H, 5.96; B, 49.11; Cl, 16.51; Si,12.60.

Compound XIII.—Compound X[3] (1.1 g., 0.022 mole) was dissolved in 50 ml. of dry benzene and ammonia was slowly passed through the solution for 35 min. at room temperature. The mixture was filtered and the filtrate was evaporated to dryness. The residue was crystallized from dioxane. Compound XIII (m.p. 347–349°) was recovered in essentially quantitative yield.

Anal. Calcd. for $C_4H_{28}B_{10}N_4Si_2$: B, 53.47; N, 13.64; Si, 13.81. Found: B, 53.00; N, 12.88; Si, 13.83.

Compound XIV.—This compound is prepared by adding an excess of water to a benzene–acetone solution of compound XII at room temperature and adding more acetone as needed, to maintain solution. Then the solution is concentrated under vacuum. When the product crystallizes, the remaining solvent is removed by filtration and the product is dried under vacuum. Recrystallization is unnecessary and compound XIV is recovered in practically quantitative yield (m.p. 304°).

Anal. Calcd. for $C_6H_{24}B_{10}O_2Si_2$: C, 17.79; H, 6.97; B, 54.47; Si, 13.87. Found: C, 17.40; H, 6.98; B, 54.60; Si, 13.94.

1-(Hydroxydimethylsiloxydimethylsilyl)carborane (XV).—In a typical experiment, 10.0 g. of 1,2-(1′,1′,3′,3′-tetramethyldisilaazanyl-1′,3′)-carborane (I)[8] was dissolved in 175 ml. of ethyl ether and an aqueous solution of sodium bicarbonate was added dropwise while cooling in an ice–water bath. Then the mixture was stirred at room temperature for 1 hr. The ether layer was decanted, dried over $MgSO_4$ for several minutes, and filtered. The filtrate was taken to dryness and kept under vacuum (0.1 mm.) at room temperature overnight. One portion of the liquid product (~90%) was analyzed and the remainder was distilled under reduced pressure. The infrared and the elementary analyses of the crude and distilled products were practically identical.

Anal. Calcd. for $C_6H_{24}B_{10}O_2Si_2$: C, 24.63; H, 8.27; B, 36.97; Si, 19.20. Found (undistilled product): C, 24.41; H, 8.06; B, 36.80; Si, 19.20. Found (distilled product): C, 24.23; H, 8.20; B, 36.43; Si, 19.40.

A sample was dissolved in anhydrous methanol in such concentration that the resulting solution would contain 7.01% water generated from reaction of methanol with the one –Si–OH group. By Karl Fischer determination the solution was found to contain 6.1% water. Additional characterization appears in the Discussion.

Thermal Stability Procedure.—Samples are sealed under vacuum in suitably designed glass ampoules and heated at the desired temperature for 1 hr. In establishing the method it was determined that 1 hr. was more than sufficient for complete evolution of gaseous products at a given temperature. The ampoules are cooled and sealed to a calibrated vacuum apparatus, which is then evacuated. The ampoule is broken as provided for and the gaseous products of decomposition (if any) are measured. A sample of this gas is analyzed mass spectrometrically to identify and quantitatively determine the components. In all results described in this paper, methane and hydrogen were the only gaseous products.

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