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Perchlorocarborane and Perchloroneocarborane

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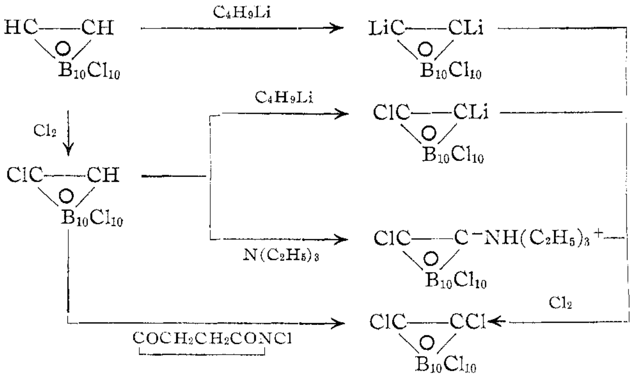
Direct chlorination of carborane and neocarborane results in undecachlorocarborane (o-$B_{10}Cl_{10}C_2HCl$)[1] and decachloroneocarborane (m-$B_{10}Cl_{10}C_2H_2$),[2] respectively, as the ultimate products. To achieve perchlorination, it became necessary to devise other methods to introduce the additional chlorine atoms. Since o-$B_{10}Cl_{10}C_2HCl$ and m-$B_{10}Cl_{10}C_2H_2$ are "carbon acids" of acidity comparable to nitroform, and since $KC(NO_2)_3$ reacts readily with chlorine to form $ClC(NO_2)_3$,[3] we suspected that metal and ammonium salts of polychlorocarboranes and polychloroneocarboranes would similarly react.

We now have found that such salts as indicated in the reaction scheme could be chlorinated as desired to give the perchlorinated compounds in almost quantitative yield. In addition we subsequently discovered that direct substitution of o-$B_{10}Cl_{10}C_2HCl$ could be effected with N-chlorosuccinimide, a reagent often used for the replacement of positive hydrogen with chlorine.

In a typical experiment, chlorine was passed into a well-stirred suspension of 25 g. (0.04 mole) of o-$(HN(C_2H_5)_3)(B_{10}Cl_{10}C_2Cl)$[1] in 800 ml. of refluxing carbon tetrachloride for 30 min. After filtration crude o-$B_{10}C_2Cl_{12}$ precipitated on cooling in an ice bath and was removed; additional product was recovered on concentrating the filtrate and again cooling. Purification of the combined portions by recrystallization from CCl_4 or hexane gave pure product [21.5 g., 93.5%, m.p. 448° [4] (sealed tube)].

Anal. Calcd. for $C_2B_{10}Cl_{12}$ (557.7): C, 4.31; B, 19.40; Cl, 76.20. Found (o-$B_{10}Cl_{10}C_2Cl_2$): C, 4.70; B, 19.38; Cl, 76.10; mol. wt., 564. Found (m-$B_{10}Cl_{10}C_2Cl_2$): C, 4.35; B, 19.79; Cl, 76.70; mol. wt., 566; m.p. 443° (sealed tube)].

Examination of the infrared spectra of the two compounds in the sodium chloride range (2.5–15 μ) revealed a striking similarity and simplicity as would be expected, having one very strong band between 9 and 10 μ which is ascribed to the boron–chlorine stretching frequency. Also as expected the ^{11}B n.m.r. spectrum of o-$B_{10}C_2Cl_{12}$ exhibits a low-field and a high-field singlet with a 2:8 ratio as do o-$B_{10}Cl_{10}C_2H_2$ and o-$B_{10}Cl_{10}C_2HCl$[1]; these absorptions arise from the presence of two sets of boron atoms in different environments as discussed in more detail recently.[2] On the other hand, we were surprised to find that the ^{11}B n.m.r. spectrum of m-$B_{10}C_2Cl_{12}$ also showed two singlets of the same ratio and of similar chemical shifts.



$$HCB_{10}Cl_{10}CH \xrightarrow{C_4H_9Li} LiCB_{10}Cl_{10}Li \xrightarrow{Cl_2} ClCB_{10}Cl_{10}CCl$$

Since the structure of neocarborane as proposed by one of us[2] should give rise to a three-singlet spectrum with a 2:6:2 ratio as was exhibited by m-$B_{10}Cl_{10}C_2H_2$, these results suggested the possibility that perchlorocarborane was the product obtained from both the carborane and neocarborane precursors. Despite the spectral similarities of the two perchlorinated products, certain physical differences such as crystalline form and solubility were apparent and prompted us to synthesize appropriate compounds suitable for a thorough elucidation of this phenomenon.

Accordingly, the C,C′-dimethyldecachloro- and C,C′-diethyldecachlorocarboranes and -neocarboranes were prepared from o-$B_{10}Cl_{10}C_2Li_2$ and m-$B_{10}Cl_{10}C_2Li_2$ and the respective alkyl iodides in ether or toluene solution by a method directly analogous to that for the preparation of bis(diphenylphosphino)carborane[5]; C-methyldecachlorocarborane and C-ethyldecachlorocarborane were similarly obtained.

Anal. Calcd. for $C_4H_6B_{10}Cl_{10}$ (516.9): C, 9.30; H, 1.17; B, 20.93; Cl, 68.60. Found (o-$B_{10}Cl_{10}C_2(CH_3)_2$): C, 9.64; H, 1.27; B, 21.15; Cl, 68.60. Found (m-$B_{10}Cl_{10}C_2(CH_3)_2$): C, 9.52; H, 1.20; B, 20.81; Cl, 67.70. Found (o-$B_{10}Cl_{10}C_2H(C_2H_5)$): C, 9.47; H, 2.05; B, 20.96; Cl, 67.60. Calcd. for $C_6H_{10}B_{10}Cl_{10}$ (544.9): C, 13.22; H, 1.85; B, 19.86; Cl, 65.07. Found (o-$B_{10}Cl_{10}C_2(C_2H_5)_2$): C, 13.29; H, 1.90; B, 18.75; Cl, 65.43. Found (m-$B_{10}Cl_{10}C_2(C_2H_5)_2$): C, 13.27; H, 1.83; B, 19.90; Cl, 65.00. Calcd. for $C_3H_4B_{10}Cl_{10}$ (502.8): C, 7.17; H, 0.80; B, 21.52; Cl, 70.51. Found (o-$B_{10}Cl_{10}C_2H(CH_3)$): C, 7.21; H, 0.90; B, 21.20; Cl, 70.00.

The ^{11}B n.m.r. spectrum of each of these six com-

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

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

[3] E. Schmidt, R. Schumacher, and H. Kuhlmann, *Ber.*, **54**, 1483 (1921).

[4] Melting points are uncorrected (Mel-Temp capillary tube apparatus).

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

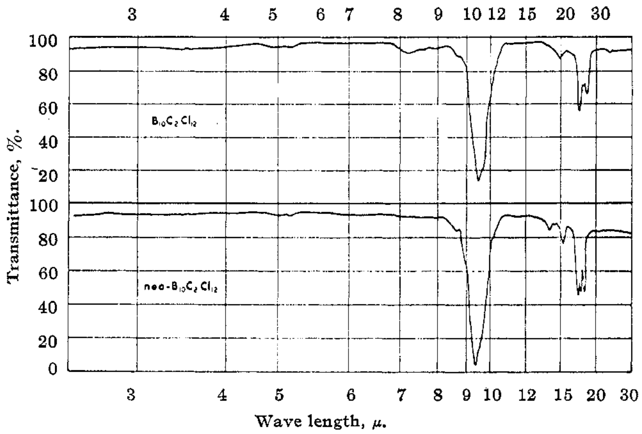

Fig. 1.—Infrared spectra of perchlorocarborane and perchloroneocarborane (KBr pellet).

TABLE I

^{11}B N.M.R. CHEMICAL SHIFTS OF DECACHLOROCARBORANE, DECACHLORONEOCARBORANE, AND DERIVATIVES IN P.P.M. FROM EXTERNAL METHYL BORATE

R_1	R_2	Low-field singlet	High-field singlet (A)	High-field singlet (B)	
H	H	16.8	28.0		
CH_3	H	16.1	27.4		
C_2H_5	H	17.5	27.3		R_1C——CR_2 \O/ $B_{10}Cl_{10}$
CH_3	CH_3	16.8	26.9		
C_2H_5	C_2H_5	17.8	26.3		
Cl	Cl	20.0	27.6		
H	H	21.8	27.3	31.4	
CH_3	CH_3	21.3	27.9	...	$R_1CB_{10}Cl_{10}CR_2$
C_2H_5	C_2H_5	21.5	27.0	...	
Cl	Cl	20.6	28.2	...	

pounds consists of two singlets (intensity ratio 2:8), the chemical shifts of which are presented in Table I. While the high-field chemical shifts are nearly identical in all compounds, the low-field shifts of m-$B_{10}Cl_{10}C_2(CH_3)_2$ and m-$B_{10}Cl_{10}C_2(C_2H_5)_2$ readily distinguish them from the corresponding carborane compounds. This strongly indicated that during the preparation and reaction of m-$B_{10}Cl_{10}C_2Li_2$ no reversion to the o-carborane structure occurs.

Additional evidence for differentiating the perchloro isomers was gained by examining their far-infrared spectra up to 30 μ (Fig. 1), which clearly differ in the position and relative intensity of characteristic triplet absorptions between 17 and 18.3 μ. Final evidence was obtained by differential scanning calorimetry, which showed that o-$B_{10}C_2Cl_{12}$ is transformed into m-$B_{10}C_2Cl_{12}$ at 380°. At this temperature a distinct exothermic reaction occurred and the sample recovered displayed the characteristic m-$B_{10}C_2Cl_{12}$ absorptions in the far-infrared.

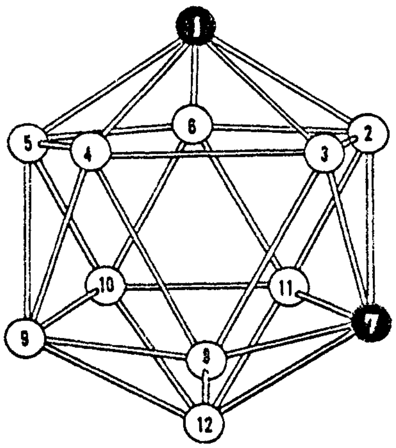

Fig. 2.—Neocarborane skeleton.

Although both ^{11}B n.m.r. shifts of the carborane derivatives are positioned as expected, in the neocarborane series the third peak (singlet B) shown by m-$B_{10}Cl_{10}C_2H_2$ at 31.4 p.p.m. is obviously absent in its dimethyl, diethyl, and dichloro derivatives. Apparently, substituents other than hydrogen at the carbon atoms of m-$B_{10}Cl_{10}C_2H_2$ effect the movement of the high-field singlet B to coincide with the high-field singlet A, the intensity of which is proportionately increased. Since two boron atoms (2, 3) (see Fig. 2) would be primarily influenced by any change occurring at the carbon atoms, we suspect that the high-field singlet B at 31.4 p.p.m. in m-$B_{10}Cl_{10}C_2H_2$, as well as the high-field doublet (centered at 32.6 p.p.m.) in neocarborane,[2] arise from these atoms.

These observations emphasize the fact that the interpretation of ^{11}B n.m.r. spectra of C,C′-substituted neocarboranes requires further exploration.

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Electronic and Magnetic Properties of $K_3Cu(NO_2)_5$

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To our knowledge, the literature does not contain electron spin resonance measurements on a pentacoordinated compound of copper. The number of well-substantiated examples of copper in this environment is small, and the only example where the five ligands are the same is $[Co(NH_3)_6]CuCl_5$.[1] Unfortunately, this compound is not very useful for e.s.r. work since it contains 32 molecules in the unit cell. Furthermore, it is not soluble in solvents convenient to study the substance in a glass. The structure of $NH_4Cu(NH_3)_5(ClO_4)_3$[2] has now been shown to be made up of

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(1) M. Mori, Y. Saito, and T. Watanabe, *Bull. Chem. Soc. Japan*, **34**, 295 (1961).

(2) M. Buskovska and M. A. Porai-Koshits, *Kristallografiya*, **5**, 140 (1960); **6**, 381 (1961).