allowed to go above 150°. Redistillation gives 89.1 g. of product distilling at 70° (0.3 mm.) (*i.e.*, $n^{25}_{\rm D}$ 1.5375) while the bath temperature is maintained below 170°.

By infrared, mass spectra, and $^{11}B$ n.m.r. analysis the product is identified as a mixture of two isomers of B-ethylcarborane. In addition, values of 62.7 and 62.8% boron (theory for $B_{10}C_4H_{17}$ is 62.8) were found.

**1-(*β*-Acetoxyethyl)-carborane (XVIII).**—A solution of 4.0 g. (0.0327 mole) of decaborane, 4.5 g. (0.0402 mole) of 3-butyn-1-yl acetate, and 1.5 g. (0.037 mole) of acetonitrile in 30 ml. of benzene was refluxed for 103 hr. The solvent was removed and 5.17 g. (71.7%) of liquid which solidifies to a white solid distilled at 108–118° (0.3 mm.). Mass spectrometric and infrared analysis showed it to be essentially pure 1-(*β*-acetoxyethyl)-carborane.

*Anal.* Calcd. for $B_{10}C_6H_{18}O_2$: C, 31.2; H, 7.9. Found: C, 31.7; H, 7.9.

**1-(*α*-Acetoxyethyl)-carborane (XIX).**—A solution of 4.0 g. (0.0327 mole) of decaborane, 4.5 g. (0.0402 mole) of 3-butyn-2-yl acetate, and 1.5 g. (0.0366 mole) of acetonitrile in 30 ml. benzene was refluxed for 95 hr. The benzene was removed and the residue was distilled at 85–95° (0.15–0.2 mm.) to recover 4.75 g. (65.7%) of a slightly yellow liquid, $n^{21}_{\rm D}$ 1.5291. Mass spectrometric and infrared examination indicated it to be essentially pure 1-(*α*-acetoxyethyl)-carborane.

*Anal.* Calcd. for $B_{10}C_6H_{18}O_2$: C, 31.2; H, 7.88. Found: C, 33.0; H, 7.81.

**1-(N,N-Dimethylaminomethyl)-carborane (XX).**—A solution of 6.1 g. of decaborane and 5.5 g. of N,N-diethylamino-2-propyne in 50 ml. of benzene was refluxed for 7.5 hr. After cooling, the mixture was filtered and the filtrate was extracted with dilute hydrochloric acid. The acid was neutralized and the amine which is released was recovered in ether. Isolation and recrystallization from pentane gives a waxy, white solid.

*Anal.* Calcd. for $B_{10}C_7H_{23}N$: C, 36.7; H, 10.1; B, 47.2; N, 6.1. Found: C, 37.1; H, 9.8; B, 45.8; N, 6.4.

**Other Compounds Reported.**—A number of compounds herein reported which are merely other examples of the fundamental reaction type were identified by a combination of infrared and detailed mass spectral analysis. The parent spectral peak (accounting for the normal isotopic distribution of boron) and the breakdown pattern were very characteristic and conclusively identified the compounds as well as indicating and often establishing minor impurities which would then have to be removed to obtain the pure product.

Compounds which were so identified are indicated in Tables I and II. They can be prepared from decaborane and the corresponding acetylenic compound by adapting one of the techniques above.

**Dimethyl Carborane-1,2-dicarboxylate (XXII).**—A mixture of 18.0 g. of bis-(acetonitrile)-decaborane, 15 g. of dimethyl acetylenedicarboxylate, and 50 ml. of toluene was refluxed for 22 hr. The toluene was removed under reduced pressure and the residue was treated with pentane to extract the product. Recrystallization from pentane gave 12.5 g. (53.6%) of dimethyl carborane-1,2-dicarboxylate.

*Anal.* Calcd. for $B_{10}C_6H_{16}O_4$: C, 27.7; H, 6.1; B, 41.7. Found: C, 28.0; H, 6.3; B, 41.6.

**Acknowledgments.**—This research was supported in large part by the United States Air Force under Contract AF 33(616)-5934 monitored by the Propulsion Laboratories, Air Force Flight Test Center, Edwards Air Force Base, California, and partly by the Office of Naval Research. The authors are grateful for the assistance of Dr. J. H. Norman, who interpreted the mass spectra, through which many of the compounds were initially identified, and who contributed many helpful suggestions. R. P. Alexander and J. A. Reid contributed experimental data.

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CONTRIBUTION FROM THE ORGANICS DIVISION,
OLIN MATHIESON CHEMICAL CORPORATION, NEW HAVEN, CONNECTICUT

# A New Series of Organoboranes. II. The Chlorination of 1,2-Dicarbaclovododecaborane(12)[1]

BY HANSJUERGEN SCHROEDER, THEODORE L. HEYING, AND JOSEPH R. REINER

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A detailed investigation of the chlorination of a new series of organoboranes derived from decaborane-14 resulted in the stepwise formation of a number of chlorocarboranes containing from two to eleven chlorine atoms per molecule. Some of their chemical characteristics are described; a detailed $B^{11}$ n.m.r. treatment of the parent carborane ($B_{10}H_{10}C_2H_2$), $B_{10}Cl_{10}C_2H_2$, and $B_{10}Cl_{10}C_2HCl$ as related to structural considerations is presented.

Semiorganic derivatives of higher boron hydrides have become of considerable interest because of their peculiar structure and the theoretical and chemical consequences which could be envisioned for them. Products derived from reactions of pentaborane-9 and acetylenes have been described in the literature,[2] but unfortunately, the parent compounds (carboranes) $B_nC_2H_{n+2}$ can be obtained only in very small amounts by means of complicated techniques.

These considerations prompted us to investigate another member of this series derived from decaborane-14 and which may be prepared in substantial quantities. A general method for synthesis of higher carborane derivatives of the formula $B_{10}H_{10}C_2R_2$, the parent compound of which is 1,2-dicarbaclovododecaborane(12) ($B_{10}H_{10}C_2H_2$),[3] has been reported in detail.[4]

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(1) Presented in part at the conference on Current Trends in Organometallic Chemistry, University of Cincinnati, June, 1963.

(2) R. E. Williams, C. D. Good, and I. Shapiro, 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961; T. P. Onak, R. E. Williams, and H. G. Weiss, *J. Am. Chem. Soc.*, **84**, 2830 (1962); I. Shapiro, C. D. Good, and R. E. Williams, *ibid.*, **84**, 3837 (1962).

(3) For brevity, in this series of publications the term carborane is used for 1,2-dicarbaclovododecaborane(12).

(4) Paper I of this series: T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963).

TABLE I

CHLORINATED DERIVATIVES OF CARBORANE

| | M.p., °C. | Molecular weight | | Carbon, % | | Hydrogen, % | | Boron, % | | Chlorine, % | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| $B_{10}H_8Cl_2C_2H_2$ | 232 | 213.2 | | 11.26 | 11.51 | 4.73 | 4.85 | 50.75 | 49.80 | 33.25 | 32.35 |
| $B_{10}H_8Cl_2C_2H_2$ | 250–251 | 213.2 | | 11.26 | 11.21 | 4.73 | 4.40 | 50.75 | 50.70 | 33.25 | 32.80 |
| $B_{10}H_7Cl_3C_2H_2$ | 241–243 | 247.7 | | 9.70 | 10.40 | 3.66 | 3.84 | 43.69 | 42.36 | 42.95 | 43.11 |
| $B_{10}H_6Cl_4C_2H_2$ | 250 | 282.1 | | 8.52 | 8.85 | 2.86 | 3.10 | 38.35 | 38.30 | 50.27 | 49.80 |
| $B_{10}H_6Cl_4C_2H_2$ | 351 | 282.1 | | 8.52 | 8.61 | 2.86 | 2.90 | 38.35 | 38.20 | 50.27 | 50.78 |
| $B_{10}H_4Cl_6C_2H_2$ | 306 | 351.0 | | 6.84 | 6.92 | 1.72 | 1.98 | 30.83 | 30.60 | 60.61 | 61.15 |
| $B_{10}H_2Cl_8C_2H_2$ | 272 | 419.9 | 408 | 5.72 | 5.85 | 0.96 | 1.54 | 25.77 | 25.80 | 67.55 | 68.33 |
| $B_{10}Cl_{10}C_2H_2$ | 259 | 488.8 | 483 | 4.91 | 4.98 | 0.41 | 0.90 | 22.14 | 22.30 | 72.54 | 72.48 |
| $B_{10}Cl_{10}C_2HCl$ | 279 | 523.3 | 525 | 4.59 | 4.55 | 0.19 | 0.50 | 20.68 | 20.50 | 74.54 | 74.42 |

This paper presents one phase of a comprehensive study of the chemistry of this unique moiety which has been conducted in recent years.

As part of the investigation dealing with the reactions of $B_{10}H_{10}C_2H_2$, we studied its chlorination, being interested both in obtaining information helpful to elucidate the structure of this new series of compounds and in utilizing the chlorinated compounds that would be formed as intermediates for further syntheses. $B_{10}H_{10}C_2H_2$ in inert solvents was found to react rapidly at elevated temperatures with gaseous chlorine. The reaction proceeded with the stepwise replacement of hydrogen atoms.

The use of $CCl_4$ as solvent proved to be fortuitous since it afforded a method of separating the several reaction products. While $B_{10}H_{10}C_2H_2$ is easily soluble, the chlorocarboranes formed are less soluble and several of them precipitated even from the refluxing solution depending upon the quantity of solvent used. This later made it possible to regulate the degree of substitution by adjusting the amount of solvent, the reaction time, and, to a lesser degree, the temperature and the use of ultraviolet light (see Experimental section).

The chlorination products isolated in experiments conducted for less than 3 hr. were compounds containing two, three, four, six, eight, and ten chlorine atoms per carborane unit. Their infrared spectra permitted conclusive determination of whether hydrogen atoms attached to boron and/or carbon had been exchanged. $B_{10}H_{10}C_2H_2$ shows typical C–H and B–H infrared stretching frequencies of 3.25 and 3.92 $\mu$, respectively. While the relative intensity of the 3.25 $\mu$ absorption remains unchanged in all compounds, the 3.92 $\mu$ absorption gradually declines as the chlorine content increases. The latter absorption is no longer observed in the spectrum of the decachloro compound, which consequently must be $B_{10}Cl_{10}C_2H_2$. However, when the reaction was allowed to proceed for approximately four more hours, one additional hydrogen could be replaced giving $B_{10}Cl_{10}C_2HCl$ as the final product in 80–90% yield. Complete chlorination to $B_{10}Cl_{10}C_2Cl_2$ has not been achieved by this procedure.

All chlorocarboranes characterized are listed in Table I. Their relatively sharp melting points suggest that they are singular compounds and not mixtures of isomers. In the cases of the dichloro- and tetrachlorocarboranes, distinct isomers were isolated. The highest melting and also least soluble member of this series is tetrachlorocarborane, m.p. 350°, while the lowest melting and most soluble derivative is dichlorocarborane, m.p. 230°. Besides the melting points, the most reliable method of differentiating the chlorocarboranes is infrared spectroscopy. All of these compounds show two strong characteristic bands in the region of 8–9 $\mu$, their exact position being essentially unaffected by the number of chlorine atoms present. In $B_{10}H_{10}C_2H_2$ they occur at 8.25 and 8.7 $\mu$ (Fig. 1). On the other hand, each derivative shows identifying absorptions at higher wave lengths. These differences (see Fig. 2) are especially important in establishing the separation of the octachloro, decachloro, and undecachloro compounds. Although cryoscopic determinations led to erratic results, excellent agreement between observed and theoretical molecular weights of these three compounds was achieved by the use of the differential vapor pressure method. Mass spectral analysis of $B_{10}H_6Cl_4C_2H_2$, $B_{10}H_2Cl_8C_2H_2$, and $B_{10}Cl_{10}C_2H_2$ also corresponded with the expected values; such analysis indicated the presence of $B_{10}H_5Cl_5C_2H_2$ and $B_{10}HCl_9C_2H_2$ as minor impurities. Attempts to isolate these derivatives in substantial quantities are in progress.

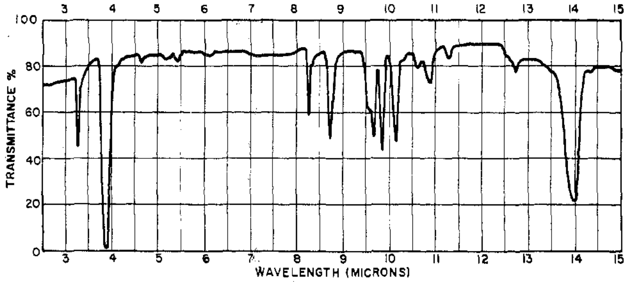

Fig. 1.—Infrared spectrum of $B_{10}H_{10}C_2H_2$ (Kel-F and Nujol mulls).

Some interesting chemical characteristics of these chlorocarboranes have been observed. For example, when $B_{10}Cl_{10}C_2H_2$ was treated with Swart's mixture ($SbF_3Cl_2$) at 240° to attempt halogen exchange and subsequently refluxed with water to remove the fluorinating agent, $B_{10}Cl_{10}C_2H_2$ was recovered quantitatively. In an attempt to induce $B_{10}H_2Cl_8C_2H_2$ to participate in a Friedel–Crafts reaction by refluxing it in benzene with $AlCl_3$, no reaction occurred. $B_{10}H_4Cl_6C_2H_2$ and $B_{10}H_6Cl_4C_2H_2$ (350°) in benzene solution did not react with ammonia or amines at room tempera-

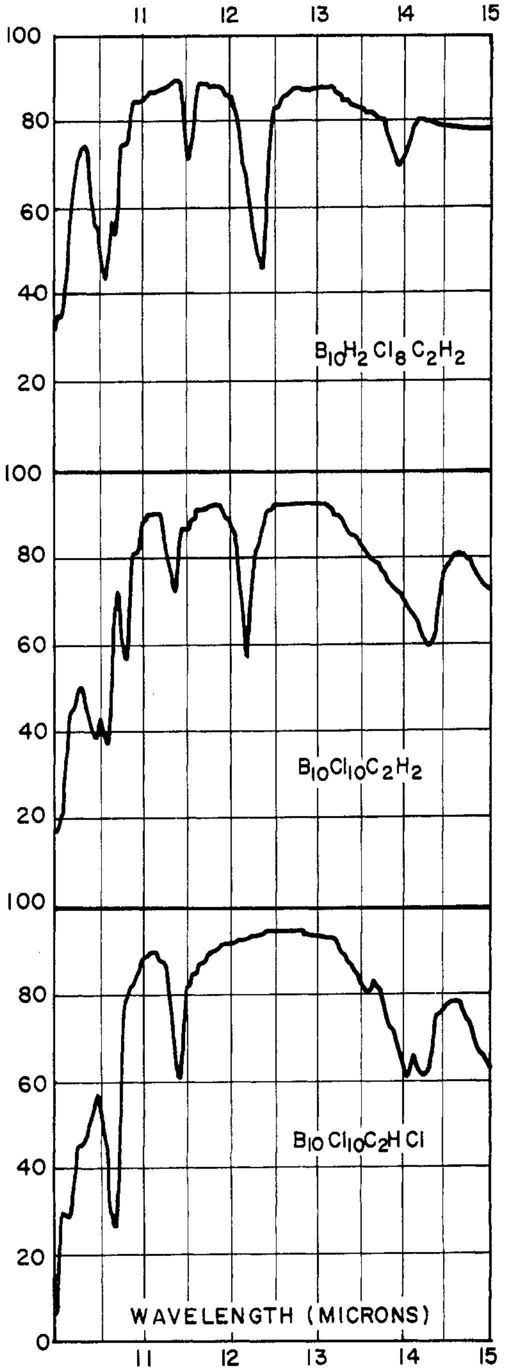

Fig. 2.—Infrared spectra of octachloro-, decachloro, and undecachlorocarborane between 10 and 15 $\mu$ (Nujol mull).

ture. These results indicate the unusual stability of the chlorine–boron bond in these carboranes. The chlorine atoms were removed by heating the chlorocarboranes at 100° in 50% aqueous potassium hydroxide in the presence of hydrogen peroxide. A brief description of the preparation of stable halogenated boron hydride anions such as $B_{12}Br_{12}^{-2}$ in polar solvents has been reported recently by Knoth, *et al.*[5]

Carboranes having 0 to 6 chlorine atoms cannot be titrated in ethanol or ethanol–water with sodium hydroxide. On the other hand, $B_{10}H_2Cl_8C_2H_2$ was titrated as a diprotoic acid in ethanol–water but not in ethanol alone. $B_{10}Cl_{10}C_2H_2$ and $B_{10}Cl_{10}C_2HCl$ titrate as diprotoic and monoprotoic acids, respectively, in either ethanol or ethanol–water. The strength of these "carbon acids" was further demonstrated by the formation of the appropriate mono- and bis-triethylammonium salts when they were treated with triethylamine in benzene or ethanol solution. It is of interest to note that only the bis-triethylammonium salts of $B_{10}H_2Cl_8C_2H_2$ and $B_{10}Cl_{10}C_2H_2$ could be isolated even when less than the stoichiometric amount of triethylamine was used, and that these salts slowly decompose on standing.

$$\begin{array}{rl}
B_{10}H_2Cl_8C_2H_2 \xrightarrow{N(C_2H_5)_3} & (HN(C_2H_5)_3)_2(B_{10}H_2Cl_8C_2) \\
B_{10}Cl_{10}C_2H_2 \xrightarrow{N(C_2H_5)_3} & (HN(C_2H_5)_3)_2(B_{10}Cl_{10}C_2) \\
B_{10}Cl_{10}C_2HCl \xrightarrow{N(C_2H_5)_3} & (HN(C_2H_5)_3)(B_{10}Cl_{10}C_2Cl) \\
 & \quad \big\downarrow {\scriptstyle (C_6H_5)_3PCH_3I} \\
 & ((C_6H_5)_3PCH_3)(B_{10}Cl_{10}C_2Cl)
\end{array}$$

In the case of reaction of undecachlorocarborane with triethylamine, two possible modes of salt formation exist to give products of the same empirical formula. One is indicated in the reaction shown, whereas the other would be the alternative structure $(B_{10}Cl_{10}CHCN(C_2H_5)_3Cl$. Proof of the former structure was established by the displacement of the triethylammonium ion by triphenylphosphonium ion by treatment of the salt in question with $(C_6H_5)_3PCH_3I$ in acetone.

**Structural Considerations.**—$B_{10}H_{10}C_2H_2$ is obtained by passing acetylene through a solution of $B_{10}H_{14}$ and diethyl sulfide in propyl ether, presumably *via* the intermediate $B_{10}H_{12}(S(C_2H_5)_2)_2$, a decaborane derivative having ligands at the 6,9 positions.[6] An obvious explanation of this reaction is that the $B_{10}H_{14}$ polyhedron is transformed into an icosahedron by insertion of the two carbon atoms into the boron hydride framework in positions related to the 6,9 borons as are the 1,3 borons of decaborane related to the 2,4 borons (see Fig. 3). Such icosahedral carborane structure[7] was specifically predicted by Hoffmann and Lipscomb.[8]

The hypothesis that the carbon atoms are in the nearest proximity to the 6,9 boron atoms has been supported by an examination of the $B^{11}$ nuclear magnetic resonance spectra of $B_{10}H_{10}C_2H_2$, $B_{10}Cl_{10}C_2H_2$, and $B_{10}Cl_{10}C_2HCl$ which are shown in Fig. 4. The $B^{11}$ spectrum of $B_{10}H_{10}C_2H_2$ exhibits two discernible doublets which were decoupled into singlets by selectively irradiating the boron-bonded hydrogens. By comparing the area of the resolved peak of the low-field doublet with the remainder of the spectrum (area ratio 1:9), it was determined that the low-field doublet represents two borons of the total ten, while the high-field doublet

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(5) W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, and E. L. Muetterties, *J. Am. Chem. Soc.*, **84**, 1056 (1962).

(6) D. E. Sand and A. Zalkin, Abstract of Papers, International Congress of Crystallography, 1960.

(7) Drs. D. J. Mangold and M. Hillman of these Laboratories first recognized the electronic relationship of carborane to the icosahedral borane predicted by H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc.* (London), **A230**, 110 (1955).

(8) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962); *Inorg. Chem.*, **2**, 231 (1963); R. Grimes, F. E. Wang, R. Lewin, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.*, **47**, 996 (1961).

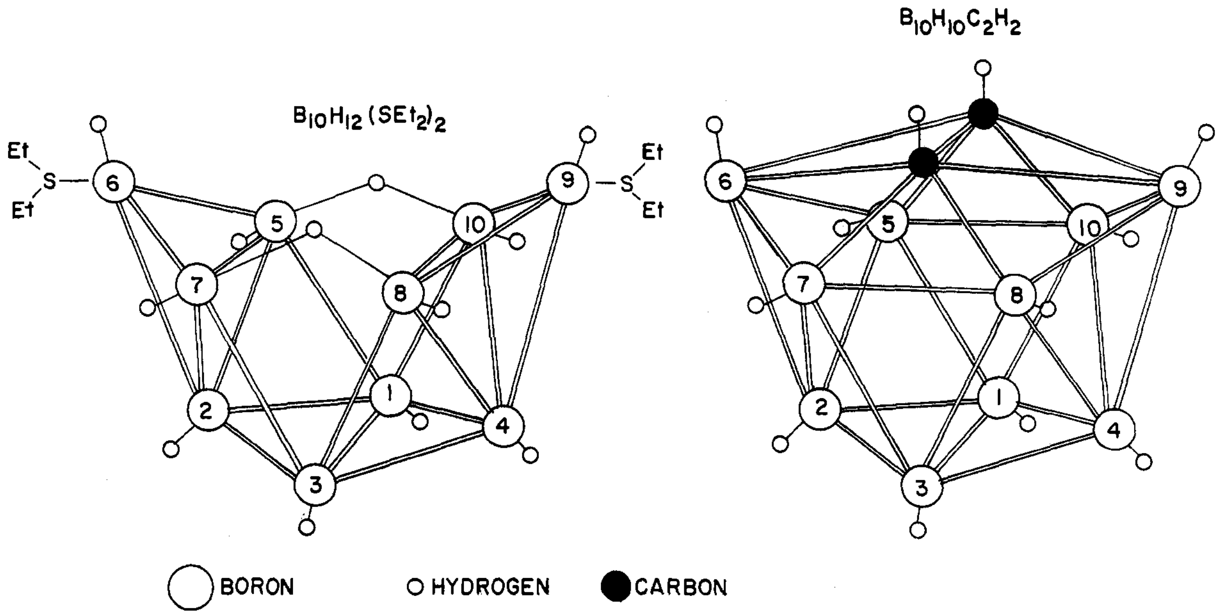

Fig. 3.—Basic structures of $B_{10}H_{12}(S(C_2H_5)_2)_2$ and $B_{10}H_{10}C_2H_2$.

arises from all other borons which, therefore, appear to be nearly equivalent. Since the splitting into doublets is the result of the coupling interaction between the boron atoms and the hydrogens attached to them, the $B^{11}$ spectrum of $B_{10}Cl_{10}C_2H_2$ in which each boron-bonded hydrogen is replaced by a noncoupling chlorine nucleus should consist only of a low-field and a high-field singlet.

The spectrum shows the required collapse of the doublets to singlets which remained unchanged upon attempted decoupling, and the observed ratio (by planimeter integration) of the area under the peaks is 2:8. Therefore the low-field peak originates from one pair of equivalent boron atoms, most probably from the 6,9 borons of the original decaborane basket.

The spectrum of $B_{10}Cl_{10}C_2HCl$ is essentially the same as that of $B_{10}Cl_{10}C_2H_2$, consisting of two singlets with a ratio of 2:8. Both singlets appear to have shifted slightly toward higher field.

Proton magnetic resonance studies of $B_{10}Cl_{10}C_2H_2$ and $B_{10}Cl_{10}C_2HCl$ also support the assumed structures, since only a singlet is present in both cases. It arises from the two carbon-bonded hydrogens in the decachloro compound and from the only hydrogen left in the undecachloro compound. As expected, they differ with regard to their chemical shift (5.70 $\tau$ in $B_{10}Cl_{10}C_2H_2$ and 3.96 $\tau$ in $B_{10}Cl_{10}C_2HCl$ with tetramethylsilane as standard). Upon substitution of chlorine for one of the hydrogens attached to carbon, the singlet arising from the remaining hydrogen shifts toward lower field. Further evidence for the assumed structure was that no other hydrogen was detected, which, in agreement with the infrared spectrum, rules out the possibility of addition of chlorine to the carborane nucleus without the concurrent replacement of hydrogen.

It should be mentioned that the $B^{11}$ spectra of $(HN(C_2H_5)_3)(B_{10}Cl_{10}C_2Cl)$ and $(CH_3P(C_6H_5)_3)(B_{10}Cl_{10}C_2Cl)$ are identical but different from that of $B_{10}Cl_{10}C_2HCl$, especially in the formation of a new singlet. This implies that the negative charge is not equally distributed over the carborane anion. A similar difference was observed in the spectra of $(HN(C_2H_5)_3)_2(B_{10}Cl_{10}C_2)$ and $B_{10}Cl_{10}C_2H_2$. An evaluation of these spectra and of those of the less chlorinated carboranes will be published when complete.

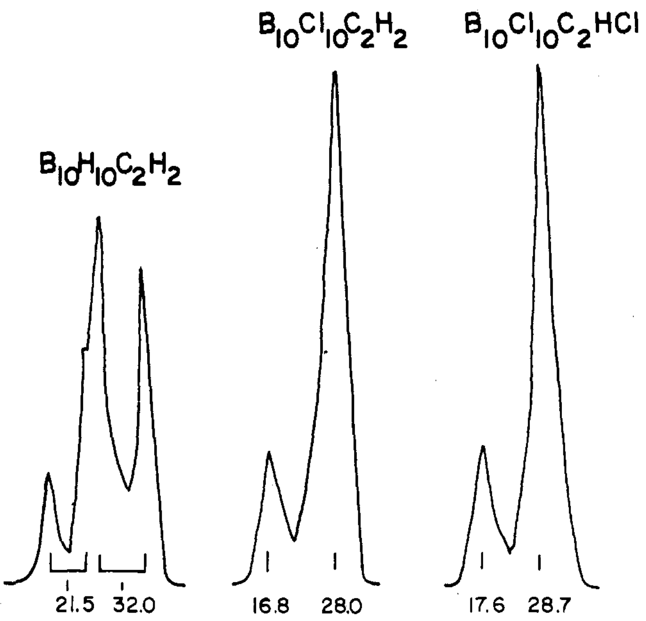

Fig. 4.—$B^{11}$ n.m.r. spectra of three carboranes in acetonitrile in displacement (in p.p.m.) from methyl borate.

## Experimental[9]

**Starting Materials.**—$B_{10}H_{10}C_2H_2$ was prepared in *n*-propyl ether (Eastman Kodak) as indicated in ref. 4 from resublimed $B_{10}H_{14}$, diethyl sulfide (Matheson Coleman and Bell), and acetylene which was purified by standard procedures.

**$B^{11}$ N.m.r. Spectra.**—A Varian high-resolution n.m.r. spectrometer was used at 19.3 Mc./sec. The spectra were obtained in acetonitrile and in acetone solution; the line positions were

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[9] Melting points are uncorrected (Mel-Temp capillary tube apparatus); analyses were by R. Rittner, R. Culmo, and D. E. Aylwin of the Olin Mathieson Microchemical Section.

determined with an accuracy of ±5 c.p.s. using trimethyl borate as an external standard.

**Infrared Spectra.**—The infrared spectra were obtained both as Kel-F and Nujol mulls on a Model 137B Perkin-Elmer Infracord spectrophotometer.

**Molecular Weights.**—These were obtained in benzene using a Mechrolab osmometer, Model 301.

**Dichlorocarborane.**—Gaseous chlorine was passed rapidly into a solution of $B_{10}H_{10}C_2H_2$ (2.88 g., 0.02 mole) in carbon tetrachloride (100 ml.) irradiated with ultraviolet. Shortly the evolution of hydrogen chloride was observed and the exothermic reaction raised the temperature to approximately 60°, whereupon the chlorination was abruptly stopped. After filtration, the solvent was removed to give a solid residue which was fractionally recrystallized from high-boiling (66–90°) and low-boiling (30–60°) petroleum ether to yield 0.8 g. (19%) of $B_{10}Cl_2H_8C_2H_2$ (m.p. 232°) and 1.4 g. (32%) of $B_{10}Cl_2H_8C_2H_2$, m.p. 250–252°.

**Tetrachlorocarborane (250°).**—The reaction was conducted as described for the preparation of dichlorocarborane, however when the temperature of the exothermic reaction began to subside, the chlorination was continued for an additional 5 min. The reaction mixture was evaporated to dryness, and the residue consisting of a mixture of $B_{10}H_8Cl_2C_2H_2$, $B_{10}H_7Cl_3C_2H_2$, and $B_{10}H_6Cl_4C_2H_2$ yielded on several recrystallizations from petroleum ether (66–90°)–*n*-heptane (1:1) the tetrachloro compound (m.p. 250°, 25% yield) as the least soluble component.

**Tetrachlorocarborane (351°) and Trichlorocarborane.**—A moderate stream of gaseous chlorine was passed through a *refluxing* solution of carborane (4 g.) in carbon tetrachloride (160 ml.) with ultraviolet irradiation. After approximately 15 min. a white solid began to separate and the reaction was discontinued. After cooling to 30° the solid was removed and recrystallized from chloroform (1 g. per 35 ml.) to give 4.1 g. (52%) of $B_{10}H_6Cl_4C_2H_2$, m.p. 351°.

The filtrate of the above reaction was evaporated and the remaining solid was recrystallized from petroleum ether (66–90°) to give 2 g. (13.8%) of $B_{10}H_7Cl_3C_2H_2$.

**Hexachlorocarborane.**—Carborane (8 g.) in $CCl_4$ (600 ml.) was treated as described for the preparation of tetrachlorocarborane (351°) using a greater flow of chlorine. A precipitate again formed but chlorination was continued until this solid began to redissolve. The reaction mixture was cooled to 0° to give 16.5 g. of crude $B_{10}H_4Cl_6C_2H_2$, m.p. 290–295°. Recrystallization from $CCl_4$ (1 g. per 70 ml.) gave pure hexachlorocarborane, m.p. 306°.

**Octachlorocarborane.**—The procedure as described for hexachlorocarborane was repeated; chlorination was continued until the aforementioned solid had completely redissolved to give a clear solution. After an additional period of chlorination (15–30 min.) the formation of a distinct haze was observed whereupon the hot solution was immediately filtered. Cooling of the filtrate precipitated 16 g. of practically pure $B_{10}H_2Cl_8C_2H_2$. Additional crude product was recovered by evaporating the solvent. Recrystallization from $CCl_4$ (1 g. per 40 ml.) gave a total of 19 g. (81.5%) of octachlorocarborane, m.p. 272°.

**Decachlorocarborane.**—Carborane (17 g.) in $CCl_4$ (1700 ml.) was chlorinated as described for the preparation of octachlorocarborane. After the haze became apparent, chlorination was continued for approximately 30 min. The hot reaction mixture was filtered, and from the filtrate 42 g. of product separated upon cooling to 5°. Evaporation of the filtrate gave another 13 g. of product. Repeated recrystallization of the combined yield from $CCl_4$ (1 g. from 15–20 ml.) gave fractions, the infrared spectra and melting points of which were carefully examined. From five such preparations the average yield of pure decachlorocarborane was 40 g. (69%) per run.

The elemental analysis of the boron-free solid which caused the haze approached the theoretical values expected for polyperchloroethylene. Although not definitely established, it is supposed that it originates from a portion of the carborane which was destroyed during the chlorination process.

**Undecachlorocarborane.**—Decachlorocarborane (23 g.) in refluxing $CCl_4$ (1000 ml.) was treated with a rapid stream of gaseous chlorine for 4 hr. in the presence of ultraviolet light. The hot reaction mixture was filtered, and when the filtrate was cooled to 0°, 20 g. of pure $B_{10}Cl_{10}C_2HCl$ precipitated. Evaporation of the filtrate gave additional product which was purified by recrystallization from $CCl_4$ (1 g. per 25 ml.).

**Bis-(triethylammonium)-decachlorocarborane.**—A solution of triethylamine (2.02 g., 0.02 mole) in ethanol (15 ml.) was added to a stirred solution of decachlorocarborane (4.89 g., 0.01 mole) in ethanol (40 ml.) at 25°. A first crop of crystalline reaction product (1.8 g.) separated within 20 min.; upon continued stirring for 1 hr., an additional 2.1 g. was obtained. The combined precipitate was washed with petroleum ether, dried *in vacuo* over phosphorus pentoxide, and proved to be the monoethanolate of $[HN(C_2H_5)_3]_2(B_{10}Cl_{10}C_2)$, m.p. 198–200°.

*Anal.* Calcd. for $C_{16}H_{32}B_{10}Cl_{10}N_2$ (691.2): C, 26.06; H, 5.20; B, 14.68; Cl, 48.10; N, 3.80. Found: C, 25.97; H, 5.47; B, 14.90; Cl, 47.50; N, 3.98.

Subsequently 0.5 g. of the unsolvated salt separated from the reaction mixture, m.p. 200–201°.

*Anal.* Calcd. for $C_{14}H_{32}B_{10}Cl_{10}N_2$ (691.2): C, 24.33; H, 4.67; B, 15.65; N, 4.05; Cl, 51.30. Found: C, 24.52; H, 5.34; B, 15.54; N, 4.15; Cl, 50.40.

Decomposition of both reaction products was noticed after 3–5 days.

**Bis-(triethylammonium)-octachlorocarborane** was prepared by essentially the same procedure from octachlorocarborane. The product separated as a flocculent precipitate in approximately 60% yield and proved to be pure $(HN(C_2H_5)_3)_2(B_{10}H_2Cl_8C_2)$, m.p. 185–187°. Decomposition became apparent within 2 days as indicated by the development of a pungent odor.

*Anal.* Calcd. for $C_{14}H_{34}B_{10}Cl_8N_2$ (622.3): C, 27.02; H, 5.51; B, 17.39; Cl, 45.58; N, 4.50. Found: C, 27.54; H, 5.75; B, 17.17; Cl, 45.00; N, 4.44.

**Triethylammoniumundecachlorocarborane** was prepared by essentially the same procedure from equimolar amounts of undecachlorocarborane and triethylamine but using benzene as solvent. The crude product separated in quantitative yield and was recrystallized from a mixture (10:1) of chloroform and acetonitrile; m.p. 166°.

*Anal.* Calcd. for $C_8H_{16}B_{10}Cl_{11}N$ (624.4): C, 15.39; H, 2.58; B, 17.32; Cl, 62.45; N, 2.24. Found: C, 15.50; H, 3.03; B, 17.14; Cl, 61.80; N, 2.39.

**Methyltriphenylphosphoniumundecachlorocarborane.**—A solution of triethylammoniumundecachlorocarborane (1.56 g., 0.0025 mole) and methyltriphenylphosphonium iodide (1.01 g., 0.0025 mole) in anhydrous acetone (45 ml.) was refluxed for 0.5 hr., then evaporated to dryness *in vacuo*. The residue was washed with water to give 1.5 g. of product, m.p. 145–155°. The pure compound was obtained by adding hot carbon tetrachloride to a hot chloroform solution of the crude product followed by cooling of the resulting mixture; m.p. 182°.

*Anal.* Calcd. for $C_{21}H_{18}B_{10}Cl_{11}P$ (799.6): C, 31.54; H, 2.27; B, 13.53; Cl, 48.78; P, 3.88. Found: C, 32.29; H, 2.47; B, 13.40; Cl, 48.00; P, 3.35.

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