1,12-Dilithio-*p*-carborane, prepared from *p*-carborane (10.0 g; 0.07 mol) and butyllithium (0.15 mol), was washed with petroleum ether (bp 30–60°) and then slurried with 75 ml of xylene. A solution of dimethyltin dichloride (16.74 g; 0.07623 mol) in 100 ml of xylene was added dropwise, at ambient temperature, to the *p*-$B_{10}H_{10}C_2Li_2$ suspension. The resulting slurry was heated at reflux for 6 hr and then cooled to ambient temperature. Filtration of the reaction mixture provided a precipitate which was washed successively with water, acetone, and ether to yield 14 g (69%) of product, mp 420–430°.

Dimethyltin *m*-Carborane–Dimethyltin *p*-Carborane Copolymer.—A slurry of dilithio-*m*- and -*p*-carborane in ether (100 ml) was prepared from 7.2 g (0.05 mol) of *m*-carborane, 7.2 g (0.05 mol) of *p*-carborane, and 0.22 mol of butyllithium. To this slurry was added, with ice cooling, a solution of dimethyltin dichloride (24.17 g; 0.11 mol) in ether (250 ml). The reaction mixture was then refluxed for 5 hr. After cooling to ambient temperature, the precipitate was collected by filtration and washed successively with water, acetone, and ether to provide 18 g (62%) of product, mp 370–375°, insoluble in common organic solvents.

Germanium Imino-*m*-carborane Polymer.—1,7-Bis(chlorodimethylgermanyl)-*m*-carborane (2.0 g) was dissolved in 50 ml of ethyl ether and cooled in an ice–water bath. Ammonia was passed through at a rapid rate for 30 min, during which time a precipitate formed. The mixture was filtered and the filtrate was evaporated to dryness. The residue so formed was recrystallized from high-boiling petroleum ether to give a polymeric material (molecular weight 1800). *Anal.* Calcd for $C_{30}H_{118}B_{50}Ge_{10}N_6$ (1830.2): C, 19.69; H, 6.50; B, 29.56; Ge, 39.66; N, 4.59. Found: C, 20.10; H, 6.83; B, 28.60; Ge, 40.02; N, 4.19.

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CONTRIBUTION FROM THE OLIN RESEARCH CENTER,
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Icosahedral Carboranes. XII. Direct Fluorination of *o*-, *m*-, and *p*-Carborane[1-3]

BY SANTAD KONGPRICHA AND HANSJUERGEN SCHROEDER

Received March 26, 1969

Reaction of the parent carboranes with excess elemental fluorine in liquid hydrogen fluoride resulted in *o*-, *m*-, and *p*-$B_{10}F_{10}C_2H_2$ in yields of 30, 60, and 85%, respectively. Replacement of carbon-bonded hydrogen did not occur; however, perfluoro-*m*-carborane was obtained by direct fluorination of *m*-$B_{10}H_{10}C_2F_2$. All three B-decafluorocarboranes will hydrolyze either on immersion in water or exposure to moist air contrasting the hydrolytic stability of all other B-polyhalocarborane species.

The preponderance of studies of the icosahedral carboranes concerns substitution at the two structural carbon atoms which is easily achieved *via* metathesis and insertion reactions involving the C,C′-dilithiocarboranes.[4] Replacement of hydrogen attached to the cage borons, on the other hand, is still limited to a few representatives[5] except for extensive studies of direct chlorination,[6-9] bromination,[9-11] and iodination[9,12,13] of *o*-, *m*-, and *p*-carborane. Some of these reaction products served in X-ray diffraction studies to elucidate the respective carborane structures.[14-16]

As a rule, only boron-attached hydrogens are replaced in such halogenation reactions.[7] In general, C,C′-dihalocarboranes can only be prepared by treatment of the respective dilithio salts with elemental halogen.[17-19]

Recently, we set out to prepare representatives of the heretofore unknown class of B-polyfluorocarboranes. Since halogen exchange in *o*-$B_{10}Cl_{10}C_2H_2$ by means of Swart's mixture[6] or fluoride salts such as AgF and KF had been unsuccessful, initial attempts concerned the action of chlorine monofluoride on *o*- or *m*-carborane suspensions in liquid HF. This pro-

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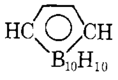
(1) Preceding communication: H. Schroeder, S. Papetti, R. P. Alexander, J. F. Sieckhaus, and T. L. Heying, *Inorg. Chem.*, **8**, 2444 (1969).

(2) Presented at the 4th International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1967.

(3) Nomenclature of the *closo* boron–carbon hydrides is discussed by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963), and appropriate rules approved by the Council of the American Chemical Society are presented in *Inorg. Chem.*, **7**, 1945 (1968). The terms *o*-, *m*-, and *p*-carborane are used to designate 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane. In accord with current practice, the following symbols are employed for representation of these isomers

$HCB_{10}H_{10}CH$,



(4) For a general review see: T. Onak, *Advan. Organometal. Chem.*, **3**, 263 (1965).

(5) Pertinent literature references on aryl-, alkyl-, alkoxy-, hydroxy-, and amino-B-substituted compounds are given by J. S. Roscoe, S. Kongpricha, and S. Papetti, *Inorg. Chem.*, in press.

(6) H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, **2**, 1092 (1963).

(7) L. I. Zakharkin and N. A. Ogorodnikova, *J. Organometal. Chem.* (Amsterdam), **12**, 13 (1968).

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

(9) J. F. Sieckhaus, N. S. Semenuk, T. A. Knowles, and H. Schroeder, *ibid.*, **8**, 2452 (1969); presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(10) H. D. Smith, T. A. Knowles, and H. A. Schroeder, *ibid.*, **4**, 107 (1965).

(11) L. I. Zakharkin and V. N. Kalinin, *Dokl. Akad. Nauk SSSR*, **169**, 590 (1966).

(12) L. I. Zakharkin and V. N. Kalinin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 575 (1966).

(13) V. I. Stanko and A. I. Klimova, *Zh. Obshch. Khim.*, **36**, 432 (1966).

(14) J. A. Potenza and W. N. Lipscomb, *J. Am. Chem. Soc.*, **86**, 1874 (1964); *Inorg. Chem.*, **3**, 1673 (1964).

(15) J. A. Potenza, W. N. Lipscomb, G. D. Vickers, and H. Schroeder, *J. Am. Chem. Soc.*, **88**, 628 (1966).

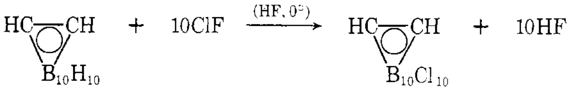
(16) J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **5**, 1471, 1478, 1483 (1966).

(17) H. Schroeder, J. R. Reiner, R. P. Alexander, and T. L. Heying, *ibid.*, **3**, 1464 (1964).

(18) L. I. Zakharkin and L. S. Podvisotskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 771 (1966).

(19) R. Maruca, H. Schroeder, and A. W. Laubengayer, *Inorg. Chem.*, **6**, 572 (1967).

cedure, however, led exclusively to the replacement of hydrogen by chlorine. When a considerable excess of ClF was passed through the reaction mixtures, the decachlorinated compounds were the final products obtained



$$HCB_{10}H_{10}CH + 10ClF \xrightarrow{(HF,\,0°)} HCB_{10}Cl_{10}CH + 10HF$$

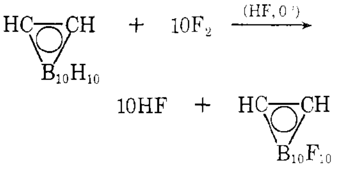
Such behavior of ClF is not surprising in view of (1) its known capability to chlorinate aromatic compounds[20] and (2) the knowledge that $B_{10}C_2$ skeletons are three-dimensional "superaromatic" polyhedra with extensive delocalization of electrons.

Subsequent experiments employed chlorine trifluoride as fluorinating agent in HF diluent. In contrast to the ClF reaction, both chlorine and fluorine substitutions of hydrogen were observed. The products obtained were mixtures of polychloromonofluorocarboranes as well as polychlorocarboranes as exemplified by

$$HCB_{10}H_{10}CH \xrightarrow[(HF,\,0°)]{ClF_3} HCB_{10}Cl_xH_{10-x}CH + HCB_{10}FCl_xH_{9-x}CH \quad (x = 1\text{–}6)$$

As with ClF, the findings with ClF_3 are understandable since it had been found previously to chlorofluorinate aromatic compounds.[21]

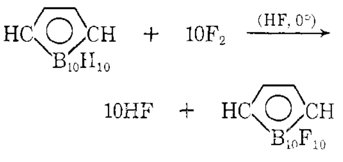
These results prompted us to treat the parent carboranes with elemental fluorine in inert solvents such as liquid HF, perfluorinated amines, or perfluoroethers. For our work in HF, we used a reactor made from Kel-F (see Figure 1) and stirred the suspension magnetically while passing in gaseous fluorine. Introduction of calculated amounts of fluorine such as 3 molar equiv did not result in strictly stepwise fluorination producing solely a trifluorinated product, but gave a mixture of polyfluorocarboranes containing one to ten fluorine atoms and unreacted parent carborane. Therefore, this procedure was next conducted with an excess of fluorine to arrive at the final products of fluorination which were found to be, with *o*-, *m*-, and *p*-carborane, the decafluorinated derivatives obtained in yields of 30, 60, and 85%, respectively.



(mp 258–261°, sealed tube)

$$HCB_{10}H_{10}CH + 10F_2 \xrightarrow{(HF,\,0°)}$$

$$10HF + HCB_{10}F_{10}CH \quad \text{(mp 240–242°, sealed tube)}$$



(mp 222–224°, sealed tube)

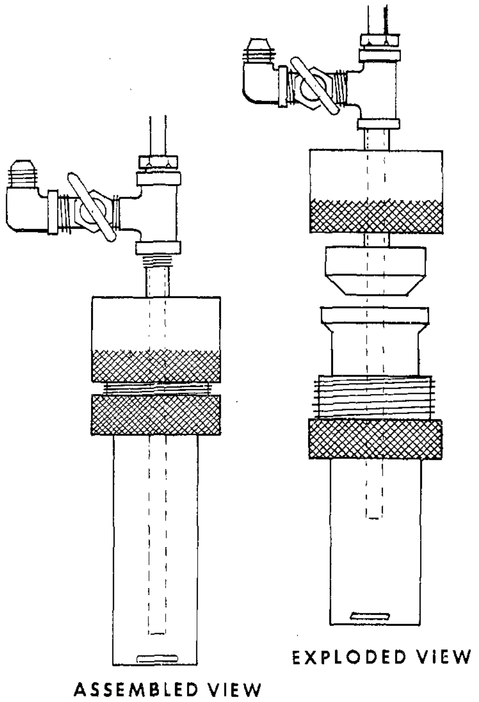


Figure 1.—Kel-F reactor.

These compounds were prepared in 10–20-g batches and purified by vacuum sublimation followed by recrystallization from CCl_4. It should be mentioned that even extension of treatment with fluorine over several days did not lead to replacement of carbon-bonded hydrogen. Perfluoro-*m*-carborane, however, could be obtained as illustrated by direct fluorination of *m*-$B_{10}H_{10}C_2F_2$, the latter compound resulting from the reaction of *m*-$B_{10}H_{10}C_2Li_2$ with perchloryl fluoride[22]

$$LiCB_{10}H_{10}CLi \xrightarrow[-2LiClO_3]{2ClO_3F} FCB_{10}H_{10}CF \xrightarrow[-10HF]{10F_2} FCB_{10}F_{10}CF$$

When comparing the infrared spectrum of the parent carborane with those of the carbon-fluorinated, boron-fluorinated, and perfluorinated derivatives (see Figure 2), the changes are as expected. In *m*-$B_{10}H_{10}C_2F_2$, the carbon–hydrogen stretching and deformation absorptions are absent as are the respective boron–hydrogen modes in *m*-$B_{10}F_{10}C_2H_2$. In the latter compound, the boron–fluorine stretching frequency between 7 and 8 μ has become most prominant. The ir spectrum of *m*-$B_{10}F_{10}C_2F_2$ is very simple showing only very strong and broad B–F stretching (concealing C–F stretching) and a moderate absorption resulting from the cage at 13.9 μ.

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[20] G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. 1, Interscience publishers, New York, N. Y., 1963, p 127.

[21] J. F. Ellis and W. K. R. Musgrave, *J. Chem. Soc.*, 3608 (1950); 1063 (1953).

[22] This compound was synthesized by M. M. Boudakian and C. O. Obenland. Utmost caution is recommended in this reaction, especially since a violent explosion occurred while attempting the preparation of the respective *o*-carborane derivative.

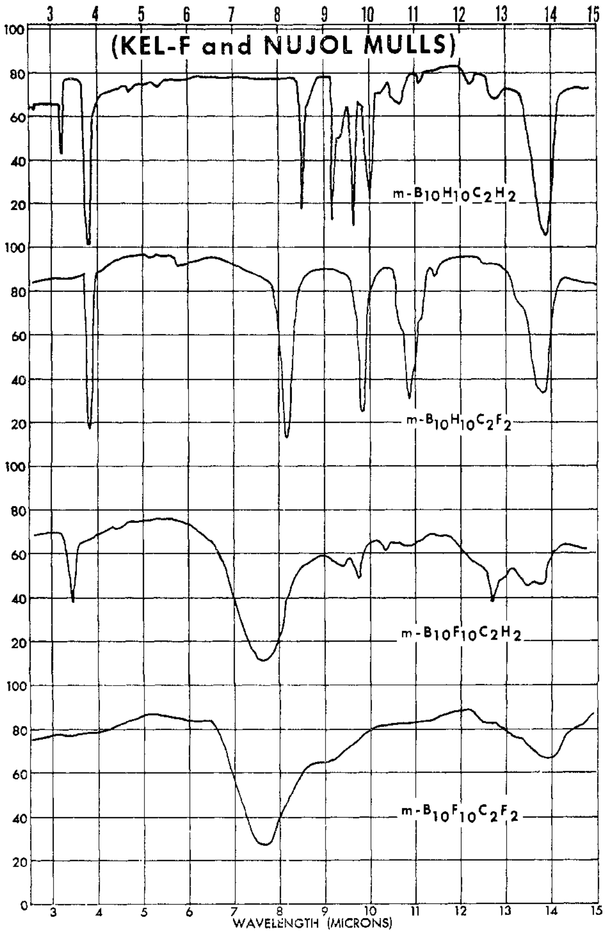

Figure 2.—Infrared spectra of *m*-carborane, 1,7-difluoro-*m*-carborane, B-decafluoro-*m*-carborane, and perfluoro-*m*-carborane.

Whereas other B-polyhalocarboranes such as *m*-$B_{10}Cl_{10}C_2H_2$ or *o*-$B_{10}H_7Br_3C_2H_2$ are completely recovered when refluxed in water or treated with NH_3 in hot benzene, *o*-$B_{10}F_{10}C_2H_2$ and *m*-$B_{10}F_{10}C_2H_2$ will hydrolyze easily. Even on exposure to moist air, the former will exchange all fluorine atoms for hydroxy groups within 2 days; the latter, within 1 week. The respective decahydroxy compounds assumed to be formed could be isolated only in the form of what appear to be polyhydrates; they will readily hydrolyze further to boric acid. In the case of *p*-$B_{10}F_{10}C_2H_2$, no sensitivity to atmospheric moisture was observed; however, upon treatment with water in acetonitrile solution again boric acid is produced as the final product. Further studies of nucleophilic displacement reactions in aprotic solvents with the objective of replacing fluorine without cage destruction are now in progress.

Experimental Section[23]

Decachloro-*o*-carborane (by ClF Chlorination).—*o*-Carborane (1.5 g, 0.0103 mol) was placed in a 150-ml Monel cylinder equipped with a pressure gauge and a Monel valve. Liquid HF (100 g, 5 mol) was then transferred into the cylinder *in vacuo* at Dry Ice temperature through an all-metal vacuum system. While the cylinder was still under vacuum at −78°, chlorine monofluoride was slowly allowed to fill it to atmospheric pressure. (*Caution!* Higher pressure of ClF results in a violent reaction.) The tightly closed cylinder was warmed during 1 hr to room temperature with constant agitation and then heated to 50° over another hour. The Monel cylinder was removed from the shaking device, attached to the vacuum system, and cooled to −78°. Gaseous products in the cylinder were analyzed by infrared spectrometry and found to be a mixture of BF_3, $CClF_3$, and CF_4. After the cylinder was evacuated to remove volatile products at −78°, more ClF was again allowed to fill it to atmospheric pressure. The closed cylinder was warmed to room temperature and then heated to 50° as described before.

This procedure was repeated until 25 g (0.463 mol) of ClF was consumed and some ClF was observed in the off-gases. After removal of HF solvent, the reaction product was extracted with CCl_4 and then recrystallized from hexane to give pure *o*-$B_{10}Cl_{10}C_2H_2$ (3.6 g, 64%); mp 273–275°; lit.[7] mp 274–276°. Elemental analysis and ir spectrum substantiated its identity.

Polychloro- and Polychloromonofluoro-*m*-carboranes.—Nitrogen-diluted ClF_3 was bubbled, at a rate of 0.5–0.75 g/hr, with stirring through a suspension of *m*-carborane (4 g., 0.0277 mole) in liquid HF (54 g) at 0°. The reaction vessel was a 130-ml Kel-F reactor (see Figure 1). After 8.4 g (0.091 mol) of ClF_3 was consumed, the reaction was discontinued and the HF solvent was removed to give 5.2 g of a brown, waxy solid. The product was extracted with acetone and dried *in vacuo* (0.15 mm) at 85°. Recrystallization from CCl_4 provided 1 g of a white solid, mp 140–180°.

Low-voltage mass spectrometry of the product, the elemental analysis of which corresponded to the formula $B_{10}H_6FCl_3C_2H_2$, showed molecular ions representing the following compounds: $B_{10}H_8Cl_2C_2H_2$, $B_{10}H_7Cl_3C_2H_2$, $B_{10}H_6Cl_4C_2H_2$, $B_{10}H_8ClFC_2H_2$, $B_{10}H_7Cl_2FC_2H_2$, $B_{10}H_6Cl_3FC_2H_2$. *Caution!* High concentration of ClF_3 in contact with carborane can cause sudden explosion of the mixture.

Decafluoro-*o*-carborane.—*o*-Carborane (3 g, 0.0208 mol) was placed in a 130-ml Kel-F reaction vessel containing a magnetic stirring bar and equipped with a Kel-F cap provided with openings for a Monel gas inlet, which reached about 1.5–2 in. above the flat bottom of the vessel, and an exit for gaseous products. Hydrogen fluoride (100 g, 5 mol) was condensed at Dry Ice temperature into the reaction vessel under vacuum through an all-metal (Monel and copper) system. At this point the *o*-carborane was observed to float on the surface of liquid HF.

The reaction vessel was then connected to a fluorination system which consisted of a 150-ml Monel cylinder containing predetermined amounts of fluorine and nitrogen at a weight ratio of 2:1 and a Kel-F oil bubbler which was connected to the exit tube of the reaction vessel. The reaction vessel was kept at 0 ± 2° by means of a constant-temperature bath having CCl_4 as a coolant.

The reaction was conducted by bubbling the F_2–N_2 mixture through the *o*-carborane suspension with constant stirring. During the first few hours of the reaction, the flow rate of F_2 should be low, approximately 0.8–1.3 g of F_2/hr, because the initial reaction is somewhat exothermic. Then it could be increased to about 2–3 g of F_2/hr. The reaction was continued until 16.6 g (0.437 mol) of F_2 was consumed. The HF solvent was then removed *in vacuo* from the reaction vessel and 3.4 g of crude product was obtained. It was purified by vacuum sublimation at 120° (0.15 mm) and recrystallized from a pentane–benzene mixture to give 2.0 g (30%) of product, mp 258–261°. *Anal.* Calcd for $C_2H_2B_{10}F_{10}$ (324.2): C, 7.41; H, 0.62; B, 33.37; F, 58.60. Found: C, 7.58; H, 0.83; B, 31.96; F, 55.75. Mass spectral analysis[24] showed molecular ions representing the

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[23] Melting points are uncorrected (Mel-Temp apparatus).

[24] The percentages quoted refer to relative abundance of the most intense molecular ion of the three species. Although they do not represent accurate concentrations, they are considered as good estimates since one would not expect the sensitivity of compounds in a homologous series of this type to differ greatly. Experience in our laboratories with other polyhalocarboranes has borne out this assumption.

following compounds: $H_2C_2B_{10}F_{10}$, 100%; $H_2C_2B_{10}F_9H$, 3%; $H_2C_2B_{10}F_8H_2$, 1%.

Decafluoro-*m*-carborane.—*m*-Carborane (10.3 g, 0.0715 mol) was placed in a 600-ml Teflon reaction vessel containing a Teflon-coated magnetic stirring bar. The reaction vessel was cooled to a Dry Ice temperature before liquid hydrogen fluoride (468 g, 23.4 mol) was transferred into the reaction vessel under the blanket of dry nitrogen. The reaction vessel was then closed tightly with a Teflon cap provided with openings for a Monel gas inlet, which reached about 1.5–2 in. above the flat bottom of the vessel, and an exit for gaseous products.

The reaction was conducted as described in the preparation of *o*-$B_{10}F_{10}C_2H_2$ except for consuming 83.5 g (2.2 mol) of fluorine and 22.0 g of crude product was obtained. Purification was achieved by vacuum sublimation at 120° (0.1 mm) followed by recrystallization from a mixture of chloroform and carbon tetrachloride to give 13.9 g (60%) of product, mp 240–242°. *Anal.* Calcd for $C_2H_2B_{10}F_{10}$ (324.2): C, 7.41; H, 0.62; B, 33.37; F, 58.60. Found: C, 7.45; H, 0.90; B, 33.25; F, 56.50.

Decafluoro-*p*-carborane.—*p*-Carborane (3.5 g, 0.0239 mol) in 100 g of liquid HF was treated, following the general procedure for the preparation of *o*-$B_{10}F_{10}C_2H_2$, with 38 g (1 mol) of F_2. The crude product (7.3 g) obtained was purified by vacuum sublimation at 130° (0.1 mm) and then recrystallized from CCl_4 to give 6.7 g (85%) of product, mp 222–224°. *Anal.* Calcd for $C_2H_2B_{10}F_{10}$ (324.2): C, 7.41; H, 0.62; B, 33.37; F, 58.60. Found: C, 7.90; H, 1.21; B, 34.92; F, 55.85.

1,7-Difluoro-*m*-carborane.[22]—A slow stream of perchloryl fluoride, diluted with an equal volume of nitrogen, was passed through a stirred slurry of 0.07 mol of 1,7-dilithio-*m*-carborane (prepared from 10 g of *m*-carborane) in ether (200 ml) at −15°. After evolution of heat from the exothermic reaction had ceased, the mixture was warmed to room temperature, flushed with nitrogen, and filtered. Evaporation of the filtrate gave 10.5 g of solid which was recrystallized from petroleum ether (bp 30–60°); mp (sealed tube) 230–231°. *Anal.* Calcd for $C_2H_{10}B_{10}F_2$: C, 13.35; H, 5.56; B, 59.94; F, 21.15. Found: C, 14.69; H, 5.70; B, 58.05; F, 19.90.

Perfluoro-*m*-carborane.—1,7-Difluoro-*m*-carborane (0.86 g, 0.048 mol) in HF suspension was treated with 6 g (0.16 mol) of elemental fluorine according to the general procedure described above. The crude product (1.67 g) obtained after removal of HF was purified by vacuum sublimation at 60° (0.1 mm) to give 0.8 g (41.6%) of moisture-sensitive *m*-$B_{10}C_2F_{12}$. *Anal.* Calcd for $C_2B_{10}F_{12}$ (360.1): C, 6.68; B, 30.00; F, 63.30. Found: C, 7.06; B, 29.59; F, 61.80.

Acknowledgment.—The authors wish to thank Dr. T. L. Heying for stimulating discussions and Mr. H. Hoberecht for obtaining and interpreting the mass spectra. They also appreciate the assistance of Dr. M. M. Boudakian and Mr. C. O. Obenland for providing a sample of 1,7-difluoro-*m*-carborane. This work was supported by the Office of Naval Research.

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Icosahedral Carboranes. XIII. Halogenation of *p*-Carborane[1-3]

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A method for the preparation and purification of substantial amounts of *p*-carborane is described. Chloro-, bromo-, and iodo-*p*-carboranes were obtained *via* direct halogenation. The various halogenated species were separated by either column or vapor-phase chromatography. In the chloro-*p*-carborane series, the mono-, nona-, and decachlorinated compounds are individual species; the others occur as mixtures of geometrical isomers. Separation of the latter was accomplished by high-resolution vpc using capillary column techniques. Interpretation of the chromatograms of these chlorinated derivatives proved consistent with the formation of all possible isomeric species in approximately those quantities which would be predicted on a statistical basis. None of these isomers was physically isolated, however. In contrast, partial fractionation of the dibromo- and diiodo-*p*-carborane isomer mixtures proved possible by common laboratory techniques.

The *ortho*[4] and *meta*[5] isomers of dicarba-*closo*-dodecaborane(12) have been known for some time and much of their chemistry has been elucidated.[6] Because of the difficulty involved in its preparation, however, the *para* isomer[7] (Figure 1) has remained a laboratory curiosity and little is known about its chemical properties. In this paper we wish to report a simplified method for the preparation of this third isomer and describe its behavior toward the halogens.

The hot-tube isomerization procedure developed for the production of *m*-carborane[8] is readily adaptable to the preparation of mixtures of the *meta* and *para* isomers. *o*-Carborane is vaporized at 200–250° and carried by means of nitrogen gas through a tube heated to 700°. This results in the conversion of approximately 90% of the *o*-carborane to a mixture of the *meta* (75%) and *para* (25%) isomers. It has now been found that these two species can be fractionated quite easily by column chromatography on basic alumina using petroleum ether as the eluent. *p*-Carborane of

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[1] Preceding communication: S. Kongpricha and H. Schroeder, *Inorg. Chem.*, **8**, 2449 (1969).

[2] Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[3] Nomenclature of the *closo* boron–carbon hydrides is discussed by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963), and appropriate rules approved by the Council of the American Chemical Society are presented in *Inorg. Chem.*, **7**, 1945 (1968). The terms *o*-, *m*-, and *p*-carborane are used to designate 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane, respectively.

[4] T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. J. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963).

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[6] For a general review see T. Onak, *Advan. Organometal. Chem.*, **3**, 263 (1965).

[7] S. Papetti and T. L. Heying, *J. Am. Chem. Soc.*, **86**, 2295 (1964).

[8] S. Papetti, C. Obenland, and T. L. Heying, *Ind. Eng. Chem., Prod. Res. Develop.*, **5**, 334 (1966).