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.

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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).

(5) D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).

(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).

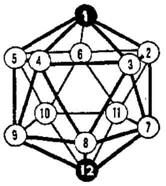

Figure 1.—p-Carborane skeleton.

99.5% purity is obtained by this method in quantities sufficient for experimental purposes.

Halogenation

In continuation of earlier studies on o- and m-carborane,[9–13] halogenation of p-carborane was performed by allowing it to react with the halogens in refluxing carbon tetrachloride either in the presence of ultraviolet radiation (chlorination) or aluminum trichloride (chlorination, bromination, and iodination). Photochemical chlorination proceeded with the formation of mixtures of the mono- through decachloro derivatives and eventually went to completion with 100% conversion to B-decachloro-p-carborane. The reaction was followed by vapor-phase chromatography and, in consecutive runs, was stopped at that point where the formation of each succeeding chlorinated species was maximized (approximately 45%). Each of these mixtures was then fractionated to obtain the major component in at least 98% purity (see Table I).

TABLE I

POLYHALO-p-CARBORANES

Compounds	Possible geometric isomers	Mp, °C	Mol wt	Mass spectrum m/e	% carbon		% hydrogen		% boron		% halogen	
					Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$C_2H_2B_{10}H_9Cl$	1	179–180	178.6	178	13.45	13.97	6.10	6.25	60.53	60.52	19.85	19.45
$C_2H_2B_{10}H_8Cl_2$	5	155–158	213.2	213	11.26	11.39	4.73	4.66	50.75	50.73	33.25	33.28
$C_2H_2B_{10}H_7Cl_3$	8	136–139	247.5	247	9.70	10.34	3.66	3.10	43.69	44.06	42.95	42.67
$C_2H_2B_{10}H_6Cl_4$	16	128–131	282.1	282	8.52	8.92	2.86	2.87	38.35	38.53	50.27	50.13
$C_2H_2B_{10}H_5Cl_5$	16	125–128	316.6	316	7.59	8.03	2.24	2.48	34.16	33.81	56.02	55.92
$C_2H_2B_{10}H_4Cl_6$	16	114–115	351.0	351	6.84	7.03	1.72	1.84	30.83	30.94	60.61	60.63
$C_2H_2B_{10}H_3Cl_7$	8	135–137	385.5	385	6.23	6.62	1.30	1.37	28.06	28.19	64.41	64.46
$C_2H_2B_{10}H_2Cl_8$	5	175–177	419.9	420	5.72	5.91	0.96	1.12	25.77	25.47	67.55	67.20
$C_2H_2B_{10}HCl_9$	1	216–218	454.4	454	5.29	5.99	0.66	0.62	23.80	23.60	70.25	70.30
$C_2H_2B_{10}Cl_{10}$	1	302–304	488.8	488	4.91	5.26	0.41	0.32	22.14	21.98	72.54	72.56
$C_2H_2B_{10}H_9Br$	1	150–151	223.1	223	10.76	10.55	4.93	5.10	48.49	48.51	35.81	35.30
$C_2H_2B_{10}H_8Br_2$	5	55–60	302.1	302	7.95	8.77	3.34	3.37	35.81	35.84	52.90	52.20
$C_2H_2B_{10}H_9I$	1	50–52	270.0	270	8.90	9.17	4.09	4.40	40.01	39.71	47.00	48.00
$C_2H_2B_{10}H_8I_2$	5	47–48	395.9	396	6.06	6.30	2.54	2.76	27.31	27.20	64.07	64.39

The mono- through pentachloro derivatives were isolated by column chromatography on basic alumina. By employing various petroleum ether–diethyl ether mixtures these species were eluted in order of increased chlorine substitution. Previous work with o- and m-carborane had shown that halogen substitution on the boron atoms enhances the acidity of the protons attached to the carbon atoms to such an extent that o-$C_2H_2B_{10}Cl_{10}$ and m-$C_2H_2B_{10}Cl_{10}$ can be titrated as "carbon acids."[9,14] The successive increases in acidity of the C–H protons with substitution of the first five chlorines on p-carborane[15] are significantly great to provide for effective separation of these species by the chromatographic method. With the hexa- through nonachloro derivatives, however, the changes of acidity are much smaller and fractionation by this method becomes much more tedious. Consequently, these latter species were obtained by preparative-scale vpc in quantities sufficient only for their characterization.

Electrophilic chlorination of p-carborane in the presence of $AlCl_3$ is a much slower reaction, proceeding only as far as the formation of a mixture of the mono-, di-, and trichloro species after 24 hr (photochemical chlorination goes to completion in 4–6 hr). Furthermore, p-carborane cannot be chlorinated by polychloromethanes in the presence of $AlCl_3$, a method recently demonstrated for both o- and m-carborane.[16,17]

Electrophilic halogenation of carboranes with bromine and iodine is rather sluggish also. Reaction of o-carborane with bromine in CCl_4 in the presence of $AlCl_3$ proceeds only as far as the tetrabromo derivative,[18] while the analogous reaction with m-carborane goes to the hexahalo species.[17] Iodination, on the other hand, produces the mono- through tetrasubstituted derivatives in each case.[18] With p-carborane only the mono and dibromo and iodo species could be isolated, but some evidence was obtained from vapor-

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

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

(11) L. I. Zakharkin, V. I. Stanko, and A. I. Klimova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 771 (1964); *Bull. Acad. Sci. USSR, Chem. Ser.*, 722 (1964).

(12) H. D. Smith, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **4**, 107 (1965).

(13) L. I. Zakharkin and V. N. Kalinin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 575, 586 (1966).

(14) H. Schroeder, J. R. Reiner, R. P. Alexander, and T. L. Heying, *Inorg. Chem.*, **3**, 1464 (1964).

(15) Infrared spectral data indicate that halogen attack occurs only at boron atoms. The C–H band at 3.3 μ remains unchanged in all compounds while the intensity of the B–H bands at 3.85 μ gradually decreases with increasing chlorine substitution.

(16) L. I. Zakharkin, O. Yu. Okhlobystin, G. K. Semin, and T. A. Babushkina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1913 (1965).

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

(18) V. I. Stanko, A. I. Klimova, and T. P. Klimova, *Zh. Obshch. Khim.*, **37**, 2236 (1967).

phase chromatograms for the formation of the trihalo derivatives. The brominated compounds were purified by column chromatography and the iodo-*p*-carboranes by recrystallization from hexane. All of the halogenated derivatives described above were characterized by elemental and mass spectral analyses (Table I).

Stereochemistry

p-Carborane differs significantly from its *ortho* and *meta* congeners in that all of the boron atoms are equivalent and, consequently, no preferential sites for electrophilic attack are provided. In contrast, a definite order of substitution on *o*- and *m*-carborane has been conclusively demonstrated[19,20] and it corresponds quite closely to the charge densities on the various boron atoms as calculated by Hoffmann and Lipscomb.[21] Those boron atoms furthest removed from the carbon atoms in these two species are most negative and, consequently, are attacked first in the electrophilic reactions. Since no such charge distribution exists in the *para* isomer, a large number of isomeric halogenated species was expected. Therefore, the derivatives containing two to eight halogens were studied by high-resolution vpc to determine both the number of isomeric species in each case and the orientation of substitution on the *p*-carborane cage.

Varying degrees of fractionation were attained depending upon the column and the instrument used, with essentially complete isomer separation accomplished through the use of capillary column techniques.

Figure 2 contains an incompletely resolved chromatogram of the mono- through nonachloro derivatives. It is a composite of the chromatograms of four different samples enriched in the various halogenated species and arranged in order of increasing chlorine substitution to demonstrate the similarity between those peaks corresponding to complementary structures (Cl_1–Cl_9; Cl_2–Cl_8; Cl_3–Cl_7; Cl_4–Cl_6). Each of these pairs of chlorinated species has the same possible isomeric configurations (Table I). Figure 3 contains the more completely resolved chromatograms of the mono- through through pentachloro derivatives, and their interpretation is consistent with the formation of all possible isomeric species in approximately those quantities which would be predicted on a statistical basis. This interpretation is based on the following considerations.

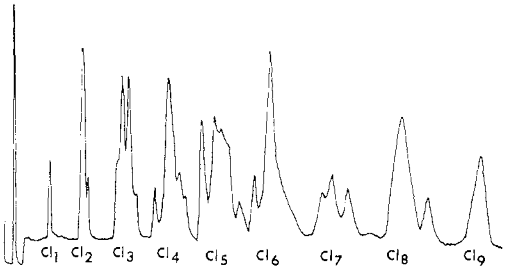

Figure 2.—Vapor-phase chromatographic separation of a polychloro-*p*-carborane isomer mixture. Column packing: 15% Qfl (fluorosilicone) on Chromosorb W (80–100 mesh); column dimensions: 1/8-in. o.d.; column temperature: 160–220°, 4°/min, hold at end of program.

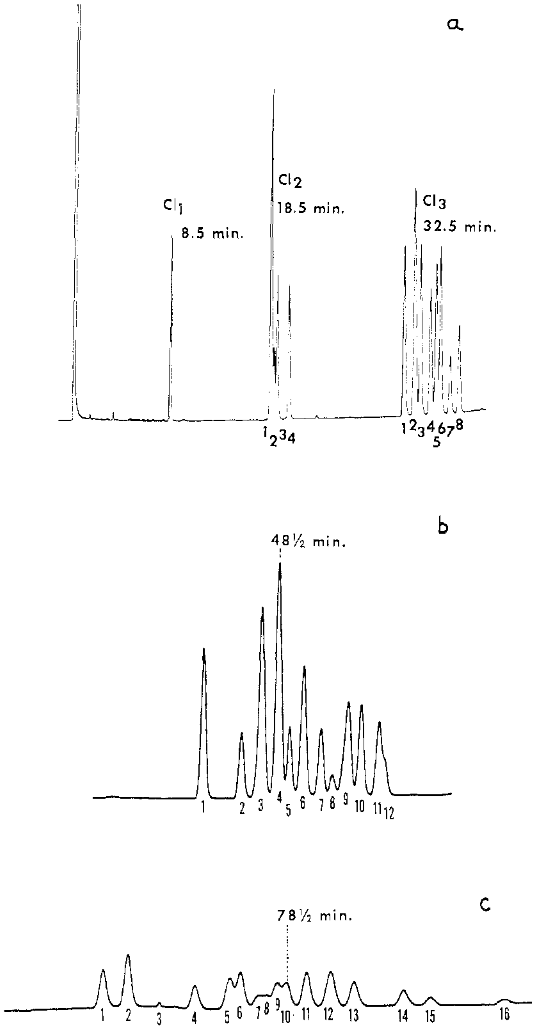

Figure 3.—(a) Separation of polychloro-*p*-carborane isomer mixtures; (b) separation of a tetrachloro-*p*-carborane isomer mixture; (c) separation of a pentachloro-*p*-carborane isomer mixture. Column packing: OS/38–Igepal–Apiezon–V930; column dimensions: 150 ft × 0.01 in.; column temperature: 170–200°, 2°/min, hold at end of program; instrument: Perkin-Elmer Model 226.

Examination of Figure 3 reveals that complete vpc fractionation was obtained for the trichloro and pentachloro derivatives, while only four of five dichloro (see Figure 4) and twelve of sixteen tetrachloro geometric isomers were resolved. Since all trichloro derivatives were observed, however, it was possible to determine what distribution of dichloro isomers gave rise to that per cent of trichloro species calculated by internal normalization of the peaks in Figure 3a. On a purely statistical basis, the distribution of dihalo isomers should be that given in Table II in the column

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

[20] H. Beall and W. N. Lipscomb, *Inorg. Chem.*, **6**, 874 (1967).

[21] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962).

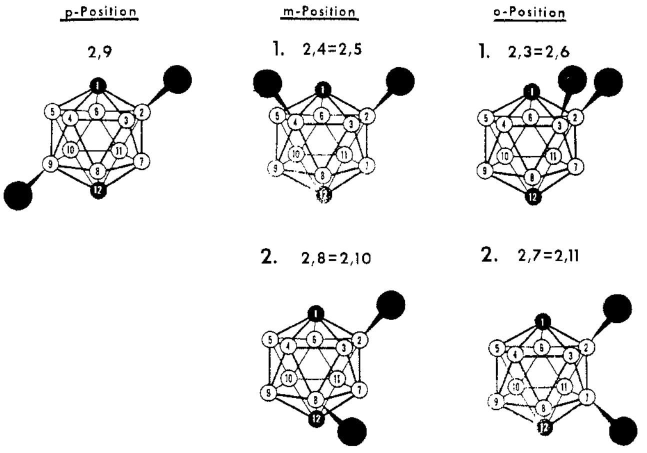

Figure 4.—B-Dichloro-*p*-carborane geometrical isomers.

for calculated per cent formation. Each of the disubstituted species with chlorines on *ortho* (adjacent) and *meta* (one removed) boron atoms can be formed from monochloro-*p*-carborane by addition of the second chlorine to two equivalent sites, while the *para* derivative can be formed in only one way. Hence the probability of formation of the *ortho* and *meta* species is $^2/_9$ or 0.222 and that of the *para* is $^1/_9$ or 0.111. If the first peak in the dichloro cluster in Figure 3a is assumed to be an equal mixture of either the two *ortho* or two *meta* derivatives, the over-all distribution is close to statistical (Table II).

TABLE II

DICHLORO-*p*-CARBORANE ISOMERS

Isomer	Type[a]	% formn Calcd	% formn Obsd[b]	Vpc peak no.	Obsd % formn/calcd % formn
I: 2,9	*para*	11.1	9.0	2	0.81
II: 2,8 (2,10)	*meta*	22.2	26.5	1	1.19
III: 2,4 (2,5)	*meta*	22.2	26.5	1	1.19
IV: 2,3 (2,6)	*ortho*	22.2	19.0	3 (or 4)	0.86
V: 2,7 (2,11)	*ortho*	22.2	19.0	3 (or 4)	0.86

[a] Indicates positions of halogens with respect to one another. [b] Determined by internal normalization of vpc peaks in Figure 3.

This reasonably good agreement prompted us to calculate the percentages of the various trichloro isomers which would arise from addition of the third chlorine (on a statistical basis) to such a mixture of disubstituted species. To begin with, the major peak in the dichloro cluster was assigned to the *meta* isomers on the premise that they would be eluted from the chromatographic column before the *ortho* derivatives because of their presumably lower dipole moments. This criterion has recently been used for assigning vpc peaks to a mixture of monobromo-*o*- and -*m*-carboranes.[22]

The origins of the eight trichloro species were then determined (Table III). The percentage of each of the dichloro isomers was substituted for the Roman numbers I–V in the expressions in Table III. The per cent distribution of trichloro species was then calculated by dividing the sum of the terms for each isomer by the sum of the terms of all isomers. The results are included in Table III and the agreement between calculated and observed isomer distributions is, in general, not too good. It must be noted, however, that there is significant deviation from a purely statistical distribution of isomers in the dichloro case and it may, in fact, indicate a very real substitution-orientating effect. It was therefore decided to calculate weighting coefficients based on the disparity between the observed and calculated distributions of dichloro isomers and apply them to the trichloro system. The coefficients were determined simply by dividing the observed per cent of the various dichloro isomers by that calculated on a statistical basis and these are given in Table II.

TABLE III

TRICHLORO-*p*-CARBORANE ISOMERS

Isomer	Origin[a]	% formn Calcd	% formn Obsd	Wtd calcd % formn	Vpc peak no.
2,3,9	4I (om) + 2II (op) + 2IV (mp)	15.9	13.3	13.9	5
2,4,9	4I (om) + 2III (op) + 2V (mp)	15.9	13.4	13.9	6
2,3,8	2II (oo) + 2IV (om) + 2V (om)	16.1	14.1	14.2	3
2,4,10	2II (mm) + III (mm)	9.9	15.1	14.7	1
2,4,8	2II (om) + 2III (om) + 2V (mm)	18.0	20.8	20.4	2
2,3,5	2III (om) + IV (mm)	9.0	11.1	10.2	4
2,3,4	III (oo) + 2IV (om)	8.1	7.5	7.4	8
2,3,7	IV (oo) + 2V (oo)	7.1	4.7	5.3	7

[a] Example: 4I (om): 4 is the number of different ways that the trichloro isomer (2, 3, 9) can be formed from the dichloro isomer I; (om) indicates that the third chlorine substitutes at a position ortho to one and meta to the other chlorine in dichloro isomer I.

The letters o, m, and p occurring after the Roman numbers I–V in Table III indicate the position that the third chlorine occupies relative to those present initially in the dichloro isomer. By substituting the weighting factors for *ortho*, *meta*, and *para* orientation where these letters appear and performing the calculations as before, a new distribution of isomers is obtained and the agreement between calculated and observed is substantially better. Similar calculations for the tetrachloro derivatives also conform quite closely to the observed distribution if peaks numbered 3, 4, and 9 in Figure 3b are assumed to have more than one component. Analysis of the distribution of pentachloro isomers produced a reasonably good correlation too. The hexa-, hepta-, and octachloro derivatives were not fractionated further than that depicted in Figure 2, but the fact that the shapes of the peaks of these species are almost identical with those of the tetra-, tri-, and disubstituted derivatives, respectively, suggests that the distribution of isomers in the p-$C_2H_2B_{10}Cl_nH_{10-n}$ and p-$C_2H_2B_{10}Cl_{10-n}H_n$ (where $n = 2$–4) species is quite similar.

The order of sequential substitution for the icosahedral borane anion $B_{12}H_{12}^{2-}$ has been calculated by

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(22) H. D. Kaesz, R. Bau, H. A. Beall, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **89**, 4218 (1967).

Hoffmann and Lipscomb[23] for the cases in which substituents act as either sources or sinks of electronic charge. Substituents which function as electron donors will presumably effect sequential attack at *ortho* sites while electron acceptors should cause substitution at the *meta* and *para* positions. While it is true that the distribution of isomeric polychloro-*p*-carboranes can best be interpreted by assuming a slight *meta*- (or *ortho*-) directing effect, such an effect does not result in the formation of certain isomers to the exclusion of all others. In this respect, sequential substitution on *p*-carborane apparently differs from that observed in the case of $B_{12}H_{10}I_2^{2-}$. Proton magnetic resonance data for this latter species suggest the presence of a 5:1 ratio of the *meta* and *para* isomers, agreeing with the prediction for the results of electrophilic halogenation of a monosubstituted $B_{12}H_{12}^{2-}$ derivative where the first substituent withdraws electrons inductively.[24]

In conclusion, it is possible to make two observations concerning the halogenation of *p*-carborane. First, all possible isomeric polyhalo derivatives are formed (the vapor-phase chromatograms of the dibromo and diiodo derivatives have not been completely resolved but their close similarity to that of the dichloro species suggests that all five isomers are formed). Second, an apparent substituent effect governs to a limited extent the order of sequential substitution on the *p*-carborane cage. In order to determine whether an *ortho* or a *meta* effect predominates, the assigned distribution of dichloro isomers (based only on dipole moments) must be confirmed by further experimental evidence. The reversal of peak assignments for the *o*- and *m*-dichloro isomers and subsequent recalculation of the distribution of trichloro and tetrachloro isomers produce the same numerical results and therefore provide us only with the information that either can be the predominant effect.

An obvious solution to this problem would be the isolation of a dihalo isomer, either *ortho* or *meta*, and determination of its structure and vpc retention time. This in turn will permit correct assignment of the peaks in the respective dihalo-*p*-carborane chromatogram. To date, a dichloro isomer has not been isolated but a pure diiodo isomer was obtained by fractional crystallization. The structure of this species is currently being determined by X-ray diffraction in Professor W. N. Lipscomb's laboratories, and, once the high-resolution vpc of diiodo-*p*-carborane is obtained, the problem should be resolved.

Experimental Section

***p*-Carborane.**—In the hot-tube isomerization apparatus described previously,[5] *o*-carborane (250 g) was vaporized at 200° and passed with nitrogen as carrier gas through a tube heated at 700°. A mixture of *m*- and *p*-carborane (225 g, 90%) was recovered, the latter isomer accounting for 25%. In the next step, a solution of 135 g of the isomerization product in 1000 ml of petroleum ether (bp 30–60°) was passed through a 1-m chromatographic column, 13 cm in diameter, containing 15 lb of basic aluminum oxide wetted with petroleum ether. Continued elution with petroleum ether gave 12 g of *p*-carborane (99% pure by vpc) besides various fractions of product mixture. Recycling of the *p*-carborane-enriched fractions produced another 8 g of pure *para* isomer. It is noteworthy to mention that the alumina can be reused with no loss of efficiency after washing with diethyl and petroleum ethers.

Photochemical Chlorination.—Gaseous chlorine was passed through a refluxing solution of *p*-carborane (3.0 g) in carbon tetrachloride (50 ml) with ultraviolet irradiation. The course of the reaction was followed by vpc and the per cent of various products determined from chromatograms after certain periods of time. Typical product ratios thus obtained are shown in Table IV; the numbers represent the per cent values of *p*-carborane and polychlorinated species. In this particular experiment complete conversion to *p*-$B_{10}Cl_{10}C_2H_2$ occurred after 6 hr; it was purified by recrystallization from CCl_4.

TABLE IV

Sample no.	Time, min	*p*-Carborane	Cl	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7
1	30	54	36	9	1	. . .	. . .	. . .	. . .
2	50	4	28	42	12	5	. . .	. . .	. . .
3	120	. . .	. . .	. . .	6	34	38	19	3

For isolation of the individual species, chlorination was stopped at consecutive intervals to give polychloro-*p*-carborane mixtures enriched in the desired chloro derivatives which were then fractionated by elution or vapor-phase chromatography. For example, 3.6 g of a polychloro-*p*-carborane mixture of composition similar to that of sample 2 in Table IV was dissolved in 24 ml of petroleum ether (bp 30–60°) and passed through a 250-ml column containing basic alumina. Elution with petroleum ether produced the separation shown in Table V. These samples were purified further by a second pass through the column. The tetra- and pentachloro derivatives were separated in similar fashion by elution with a petroleum ether–diethyl ether mixture. The hexa- through nonachloro species were obtained by preparative-scale vpc.

TABLE V

	%				
Wt, g	*p*-Carborane	Cl	Cl_2	Cl_3	Cl_4
0.6	3	93	3	. . .	. . .
0.8	. . .	. . .	99.5	. . .	. . .
0.6	. . .	. . .	1	98	1

Electrophilic Chlorination.—Gaseous chlorine was passed through a refluxing solution of *p*-carborane (2.0 g) and aluminum trichloride (0.2 g) in carbon tetrachloride (50 ml). After 24 hr the reaction had proceeded only as far as the formation of the trichloro (major component) and tetrachloro derivatives. The components were separated as described above.

Bromination.—In a typical example, a solution of *p*-carborane (2.02 g, 0.014 mol), Br_2 (2.21 g, 0.014 mol), and $AlCl_3$ (0.5 g) in 100 ml of CS_2 was refluxed, with stirring and under nitrogen, for 10 hr. After that time HBr evolution had ceased and the reflux condensate had become colorless. The dark reaction mixture was filtered and evaporated to dryness to give a brown solid which was decolorized with charcoal in petroleum ether. The resulting crude monobromo-*p*-carborane was purified by elution chromatography on basic alumina to produce the pure product (1.56 g, 50%), mp 150–151°.

Iodination.—A mixture of *p*-carborane (2.02 g, 0.014 mol), I_2 (7.12 g, 0.028 mol), anhydrous $AlCl_3$ (0.5 g), and CCl_4 (100 ml) was refluxed, under nitrogen, for 24 hr. The reaction mixture was then filtered and the solvent was removed *in vacuo*. The resulting dark viscous product was decolorized in ether solution with aqueous $Na_2S_2O_3$. Evaporation of the dried ether layer

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[23] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 520 (1962).

[24] W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964).

gave crude diiodo-*p*-carborane which was recrystallized twice from hexane. The colorless crystalline product (0.78 g, 14%) obtained proved to be pure diiodo compound and, in addition, a single isomer as shown by vpc.

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The Chemistry of μ-Mercaptodiborane

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Treatment of solid $[(C_2H_5)_4N][HS(BH_3)_2]$ with anhydrous hydrogen chloride at −78° produces hydrogen and the new compound μ-mercaptodiborane, $\mu\text{-HSB}_2\text{H}_5$. The bridge structure of μ-mercaptodiborane is confirmed by the ^{11}B nmr spectrum. Thermal decomposition of μ-mercaptodiborane in the gas phase at low pressure yields diborane, hydrogen sulfide, and involatile products. Liquid-phase decomposition results in the formation of diborane, hydrogen, and an involatile glassy solid. In the gas phase μ-mercaptodiborane undergoes boron isotope exchange with $^{10}B_2H_6$. Treatment of μ-mercaptodiborane with excess liquid deuterium chloride at −78° produces $\mu\text{-DSB}_2\text{H}_5$. The liquid-phase decomposition of $\mu\text{-DSB}_2\text{H}_5$ produces mainly HD, while gas-phase decomposition yields hydrogen sulfide containing deuterium and B_2H_6. The rate of decomposition of μ-mercaptodiborane in the gas phase is insensitive to the presence of diborane.

Introduction

In a recent communication[1] we reported the preparation and some of the properties of μ-mercaptodiborane. The only other reported compound of this type is the S-methyl derivative, $\mu\text{-CH}_3\text{SB}_2\text{H}_5$, prepared by Burg and Wagner[2] by passing diborane over $(CH_3SBH_2)_x$ or $(CH_3)_3N \cdot H_2BSCH_3$ at 90°. The μ-methylthiodiborane shows poor thermal stability at room temperature and quickly decomposes back to diborane and methylthioborane polymer. The sulfur-bridge structure postulated by the authors was later confirmed by ^{11}B nmr spectroscopy.[3]

The properties of μ-mercaptodiborane show some expected similarities to those of μ-methylthiodiborane, but the presence of a labile hydrogen in place of the methyl group gives rise to significant differences in chemical behavior. In this paper we describe the details of the preparation and characterization of μ-mercaptodiborane and report some of its basic chemical properties.

Experimental Section

General Information.—Conventional high-vacuum techniques were used throughout this investigation. Hydrogen sulfide, CP grade, was purchased from the Matheson Co. and was used without further purification. Tetraethylammonium borohydride was purchased from Alfa Inorganics, Inc., and was recrystallized from 2-propanol before use. The $^{10}B_2H_6$ was prepared by the reduction of $^{10}BF_3 \cdot O(C_2H_5)_2$ (96% ^{10}B; $^{10}BF_3$ obtained as $CaF_2 \cdot {}^{10}BF_3$ from Oak Ridge National Laboratories) with lithium aluminum hydride. All other compounds used in this work either were purchased commercially or were prepared by standard methods.

Nuclear magnetic resonance (nmr) spectra were obtained with a Varian HA-100 spectrometer equipped with standard accessories and a 32.1-MHz probe for ^{11}B studies. Boron-11 and proton chemical shifts are relative to diethyl ether–boron trifluoride and tetramethylsilane, respectively. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E double-focusing spectrometer. Infrared spectra were obtained with Perkin-Elmer 137 and 337 spectrophotometers.

Preparation of μ-Mercaptodiborane.—Typically, in a 500-ml reaction vessel 0.731 g (5.05 mmol) of tetraethylammonium borohydride was solvolyzed to $[(C_2H_5)_4N][HSBH_3]$ over a 24-hr period in 3 ml of liquid hydrogen sulfide at −78°.[4] After the hydrogen had been removed, 3.14 mmol of diborane was condensed into the vessel and the mixture was warmed to −78° and allowed to stand for 20 min. The resulting solution of $[(C_2H_5)_4N][HS(BH_3)_2]$[5] was cooled to −196°; the vessel was opened to the vacuum line and rewarmed to −78° so that the hydrogen sulfide would slowly sublime away over a 24-hr period. The solid residue was then treated with an excess of hydrogen chloride at −78° for 20 min; about 7.2 mmol of hydrogen was produced in this reaction. The μ-mercaptodiborane was isolated by fractionation through −78° into −126°; further purification was accomplished by distilling the product through −95° into −126°. This experiment produced 1.17 mmol (23% yield) of μ-mercaptodiborane.

For analysis the product was hydrolyzed in 1 *N* sulfuric acid to yield hydrogen of hydrolysis, hydrogen sulfide, and boric acid according to eq 1. Hydrogen was measured with a Toepler pump–gas buret assembly, hydrogen sulfide was isolated and determined by high-vacuum techniques, and boric acid was titrated as the D-mannitol complex with standard base.

$$\mu\text{-HSB}_2\text{H}_5 + 6\text{H}_2\text{O} \longrightarrow \text{H}_2\text{S} + 2\text{B(OH)}_3 + 5\text{H}_2 \qquad (1)$$

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(1) P. C. Keller, *Chem. Commun.*, 209 (1969).

(2) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **76**, 3307 (1954).

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(4) P. C. Keller, *ibid.*, **8**, 1965 (1969).

(5) The $[(C_2H_5)_4N][HS(BH_3)_2]$ can also be prepared from $[(C_2H_5)_4N]SH$ and B_2H_6 in liquid hydrogen sulfide: J. D. Cotton and T. C. Waddington, *J. Chem. Soc., A*, 789 (1966).