and two exotherms, a small one at 344° and a large one at 356°.

Although a substantial temperature difference exists between the two NH_4BrO_4 exotherms and no activity was observed in the sample after the first step in the decomposition, slow decomposition continues at the lower temperature when the sample is heated in a sealed tube, probably due to catalysis by the decomposition products. Thus a 70.4-mg sample, heated overnight at 170°, decomposed only partly but decomposed completely when heated at 260°. Another sample (1.80 mmol) decomposed completely in 3 days at 170°, leaving no solid residue. The major products were N_2 (0.58 mmol), O_2 (1.09 mmol), Br_2 (0.9 mmol), and H_2O (not measured), with small amounts of N_2O (0.1 mmol) and NO_2 (estimated 0.2 mmol). Thus the decomposition of NH_4BrO_4 more closely resembles that of NH_4BrO_3 (N_2, Br_2, O_2, H_2O) than that of NH_4ClO_4 (little N_2, nitrogen oxides major products).

However, firm conclusions about the stability or modes of decomposition of these salts must await the synthesis and purification of larger samples of both NH_4BrO_4 and NH_4BrO_3.

The powder diffraction spacings, presented in Table II, are correlated on the basis of an orthorhombic unit cell, with a = 9.20 Å, b = 6.04 Å, and c = 7.63 Å; the density, based on four molecules in the unit cell, is 2.54 g/cm^3 (by flotation, 2.5 g/cm^3). $KBrO_4$ is also orthorhombic,[6] as are NH_4ClO_4 and several metal perchlorates.

TABLE II

X-RAY POWDER DATA FOR NH_4BrO_4

d, Å			
Obsd	Calcd	Intens	*hkl*
5.85	5.87	50	101
5.24	...	4	...[a]
4.77	4.74	100	011
4.60	4.60	41	200
4.21	4.21	8	111
3.94	3.92	72	201
3.810	3.815	55	002
3.660	3.659	90	210
3.517	3.524	25	102
3.302	3.298	70	211
3.038	3.044	82	112
2.938	2.936	32	202
2.685	2.686	32	121
2.642	2.641	43	212
2.450	2.451	9	103
2.398	2.397	6	221
2.295	2.300	24	400
	2.293		122
2.209	2.222	37	401
	2.202		312
2.159	...	7	...[a]
2.106	2.105	5	222
2.088	2.088	3	213
1.905	1.905	28	004
	1.903		123
1.877	1.873	15	412
1.865	1.862	12	313

[a] Denotes impurity.

Acknowledgment.—Financial support for this research was provided by the Office of Naval Research, under Contract No. N00014-68-C-0279 with Dr. Richard L. Hanson as Scientific Officer. The authors wish to express their gratitude to Dr. Evan Appelman, Argonne National Laboratory, for providing them with a sample of perbromic acid, prepared in his laboratory, and for making available his data on perbromates in advance of publication.

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[6] S. Siegel, B. Tani, and E. Appelman, to be published.

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Icosahedral Carboranes. XIV. Preparation of Boron-Substituted Carboranes by Boron-Insertion Reaction[1,2]

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Received May 23, 1969

The syntheses of derivatives of *o*-carborane which bear aliphatic,[3-6] aromatic,[4] amino,[7] diethylamino,[6] hydroxy,[8] and ethoxy[6] substituents on the boron atom have been reported. A mixture of 8- and 9-ethyl-*o*-carboranes[3] was obtained from the reaction of 1- and 2-ethyldecaborane(14) with acetylene. The novel boron insertion reaction of Hawthorne, *et al.*,[4] afforded 3-ethyl-,[4] 3-phenyl-,[4] 3-diethylamino-,[6] and 3-ethoxy-*o*-carboranes.[6] The 3-aminocarborane[7] was produced by reduction of *o*- or *m*-carborane with sodium metal in liquid ammonia, followed by oxidation of the intermediate with potassium permanganate. This compound underwent Sandmeyer reaction to yield 3-halo-*o*-carborane.[9] The 9-hydroxy-*o*-carborane[8] was prepared from *o*-carborane by nitration with nitric acid and subsequent hydrolysis of the intermediate.

This paper describes an application of the Hawthorne

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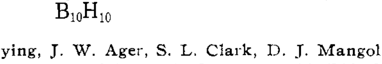
[1] Preceding communication: J. F. Sieckhaus, N. S. Semenuk, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **8**, 2452 (1969).

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



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

[4] M. F. Hawthorne and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 4392 (1965); **90**, 896 (1968).

[5] B. M. Mikhailov and T. V. Potapova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1629 (1967); *Chem. Abstr.*, **68**, 39680 (1968).

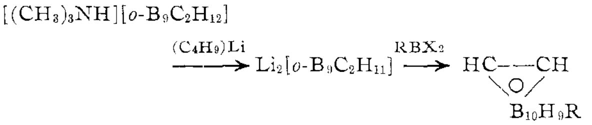
[6] T. V. Potapova and B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2367 (1967); *Chem. Abstr.*, **68**, 49671 (1968).

[7] L. I. Zakharkin and V. N. Kalinin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2585 (1967).

[8] L. I. Zakharkin, V. N. Kalinin, and L. S. Podvisotskaya, *ibid.*, 1713 (1965); *Chem. Abstr.*, **63**, 18135 (1965).

[9] (a) L. I. Zakharkin, V. N. Kalinin, B. A. Kvasov, and E. I. Fedin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2415 (1968); (b) L. I. Zakharkin and V. N. Kalinin, *ibid.*, 685 (1968).

reaction for the preparation of 3-fluoro-, 3-bromo-, and 3-diphenylamino-*o*-carboranes, and the extension of this reaction to the *m*-carborane system. The reactions involved in the syntheses of the *o*-carborane derivatives are



$$[(CH_3)_3NH][o\text{-}B_9C_2H_{12}] \xrightarrow{(C_4H_9)Li} Li_2[o\text{-}B_9C_2H_{11}] \xrightarrow{RBX_2} \underset{B_{10}H_9R}{HC\text{---}CH}$$

where R = F, Br, $N(C_6H_5)_2$.

$[(CH_3)_3NH][o\text{-}B_9C_2H_{12}]$, prepared according to the Hawthorne method,[10] was converted to the dilithio derivative, $Li_2[o\text{-}B_9C_2H_{11}]$, by treatment with butyllithium. This is advantageous over the treatment with sodium hydride[11] in that butyllithium is easier to handle than sodium hydride and that the resulting dilithio salt is more soluble in ethyl ether. The reaction of the dilithio intermediate with boron trifluoride etherate, boron tribromide, and diphenylaminodichloroborane[12] gave a good yield of 3-fluoro-*o*-carborane, a poor yield of 3-bromo-*o*-carborane, and a moderate yield of 3-diphenylamino-*o*-carborane, respectively.

It should be noted that the insertion reaction with boron trifluoride afforded a pure and hydrolytically stable 3-fluoro-*o*-carborane, while direct fluorination of *o*-carborane with elemental fluorine yielded predominantly decafluoro-*o*-carborane.[13] Even if a small amount of fluorine was treated with an excess of *o*-carborane, a mixture of B-fluorinated products was obtained which could be separated only by chromatography.

A preliminary investigation of the basicity of the nitrogen atom in 3-diphenylamino-*o*-carborane revealed that it did not form an adduct with HF, HCl, HBr, and HI. This is not surprising in view of the electron-withdrawing ability of the phenyl as well as *o*-carboranyl[14] substituents.

We also have been able to extend the Hawthorne reaction to the *m*-carborane system, using the trimethylammonium salt[10b,15] of $m\text{-}B_9C_2H_{12}^-$ as shown in

$$[(CH_3)_3NH][m\text{-}B_9C_2H_{12}] \xrightarrow{C_4H_9Li} Li_2[m\text{-}B_9C_2H_{11}] \xrightarrow{RBX_2} m\text{-}B_{10}C_2H_{11}R$$

where R = F, $N(C_6H_5)_2$.

When boron trifluoride etherate and diphenylaminodichloroborane were treated with $Li_2[m\text{-}B_9C_2H_{11}]$, 2-fluoro-*m*-carborane in a good yield and 2-diphenylamino-*m*-carborane in a poor yield, respectively, were obtained.

Pyrolysis of 3-fluoro-*o*-carborane in a sealed tube at 400° yielded two isomers of monofluorocarborane which were separated by liquid chromatography on a basic alumina column. One of the isomers was identical with the compound obtained from the insertion reaction of BF_3 to $Li_2[m\text{-}B_9C_2H_{11}]$ and was thus identified as 2-fluoro-*m*-carborane. The second isomer differed from the starting material and the first isomer in both an infrared absorption spectrum and a melting point.

The isomerization of 3-diphenylamino-*o*-carborane and the separation of the two isomeric products were accomplished in the same manner. The first isomer to be eluted from the column was identical with 2-diphenylamino-*m*-carborane prepared from the reaction between diphenylaminodichloroborane and $Li_2[m\text{-}B_9C_2H_{11}]$. The second isomer obtained was similar to the first only in an elemental analysis. It was entirely different from both the first isomer and the starting material in an infrared absorption spectrum as well as a melting point.

The structure determination of these pyrolysis products is in progress. However, it is interesting to mention here that when the molecular model of 3-R-*o*-carborane was statistically rearranged through the formation of cuboctahedral intermediates,[16,17] two major final products were obtained: 2-R-*m*-carborane and 4-R-*m*-carborane.

In an attempt to prepare a potassium salt of $p\text{-}B_9C_2H_{12}^-$, *p*-carborane was refluxed for several hours with an excess of potassium hydroxide in butanol. The starting material, however, was recovered.

Experimental Section[18]

Reagents.—Most of the reagents were purchased commercially and used as such with no further purification. Only few were prepared according to the methods described in the literature. In the preparation of diphenylaminodichloroborane,[12] it was found that this compound could be conveniently purified by vacuum sublimation (135° at 0.1 mm) instead of the reported high-vacuum fractional distillation.

Preparation of 3-Fluoro-*o*-carborane.—$[(CH_3)_3NH][o\text{-}B_9C_2H_{12}]$ (100 g, 0.52 mol) was placed in 1000 ml of anhydrous ethyl ether in a 5-l., three-necked flask with a Trubore stirrer, a dropping funnel with side arm to equalize the pressure, a reflux condenser, and a gas inlet and outlet. The system was flushed slowly with dry nitrogen while the operation was in progress. Five hundred milliliters of 2.1 *M* butyllithium in hexane solution was slowly added from the dropping funnel to this mixture with constant stirring at 28–30°. Some liberation of trimethylamine was observed during this period. When the addition was completed, the reaction mixture was heated to 55–58° for about 6–8 hr until trimethylamine was no longer detected. Then it was cooled to room temperature before 200 ml of ethyl ether was added to dissolve the resulting slurry of $Li_2[o\text{-}B_9C_2H_{11}]$. Boron trifluoride etherate (100 ml, 0.63 mol) was added slowly, with vigorous agitation, to the reaction mixture at ambient temperature. The agitation was continued for another 45 min after the addition was completed. The reaction mixture was then hydrolyzed with 200 ml of water to remove the excess of boron trifluoride. The ether–hexane layer was separated and then evaporated to dryness under vacuum. The resulting solid was purified by recrystallization from hexane to give 3-fluoro-*o*-carborane (58.5

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(15) L. I. Zakharkin and V. N. Kalinin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 462 (1967); *Chem. Abstr.*, **67**, 21953 (1967).

(16) R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963).

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

(18) Melting points are uncorrected (Mel-Temp apparatus). Infrared absorption spectra were recorded, using Nujol as well as Kel-F mulls of the materials.

g, 70% yield), mp 270–271° (sealed tube). *Anal.* Calcd for $C_2H_{11}B_{10}F$: C, 14.76; H, 6.83; B, 66.63; F, 11.68; mol wt 162.22. Found: C, 14.84; H, 6.67; B, 66.42; F, 11.63; mol wt 162 (by low-voltage mass spectrometry).

An infrared spectrum of the compound showed absorption bands (cm^{-1}) at 3050 (m), 2580 (vs), 1280 (vs), 1210 (w), 1135 (w), 1100 (m), 1025 (m), 1010 (w), 980 (m), 728 (m), 710 (m), and 678 (m).

Preparation of 3-Bromo-*o*-carborane.—$[(CH_3)_3NH][o\text{-}B_9C_2H_{12}]$ (10 g, 0.052 mol) was treated with butyllithium (50 ml of 2.1 *M* C_4H_9Li in hexane, 0.11 mol) to yield $Li_2[o\text{-}B_9C_2H_{11}]$ according to the procedure described above. This intermediate was treated with boron tribromide (15 g, 0.062 mol) in 50 ml of ethyl ether. Recrystallization of the crude solid product from hexane gave 3-bromo-*o*-carborane (3 g, 26% yield), mp 121–122°. *Anal.* Calcd for $C_2H_{11}B_{10}Br$: C, 10.77; H, 4.97; B, 48.45; Br, 35.81; mol wt 223.13. Found: C, 11.52; H, 5.06; B, 49.50; Br, 35.0; mol wt 223 (by low-voltage mass spectrometry).

The infrared absorption bands (cm^{-1}) of $o\text{-}B_{10}C_2H_{11}Br$ are 3050 (w), 2550 (s), 1200 (w), 1140 (m), 1020 (w), 995 (w, sh), 970 (vs), 945 (w), 910 (w), 840 (s), and 720 (s, b).

Preparation of 3-Diphenylamino-*o*-carborane.—The intermediate $Li_2[o\text{-}B_9C_2H_{11}]$ was prepared by treating $[(CH_3)_3NH][o\text{-}B_9C_2H_{12}]$ (132.3 g, 0.68 mol) with butyllithium (730 ml of 2.1 *M* C_4H_9Li in hexane, 1.53 mol) in 1200 ml of ethyl ether. Diphenylaminodichloroborane (17 g, 0.68 mol) in 300 ml of ethyl ether was then added to $Li_2[o\text{-}B_9C_2H_{11}]$ in the same manner as described above. The crude product was recrystallized twice from hexane to give 3-diphenylamino-*o*-carborane (128 g, 60% yield), mp 124–126°. *Anal.* Calcd for $C_{14}H_{21}H_{10}N$: C, 53.99; H, 6.80; B, 34.71; N, 4.50; mol wt 311.44. Found: C, 53.68; H, 7.08; B, 34.69; N, 4.31; mol wt 311 (by low-voltage mass spectrometry).

An infrared spectrum showed absorption bands (cm^{-1}) at 3030 (vw), 2550 (vs), 1580 (s), 1480 (vs), 1450 (m), 1430 (m), 1370 (w), 1330 (m, sh), 1300 (vs), 1250 (m), 1210 (w), 1175 (w), 1090 (w), 1065 (w), 1020 (m), 980 (m), 750 (s), 725 (w, b), 700 (vs), and 690 (m).

Preparation of 2-Fluoro-*m*-carborane.—$Li_2[m\text{-}B_9C_2H_{11}]$ was prepared by treating $[(CH_3)_3NH][m\text{-}B_9C_2H_{12}]$ (10 g, 0.052 mol) in 50 ml of ethyl ether with butyllithium (50 ml of 2.1 *M* C_4H_9Li in hexane, 0.11 mol) as described above. It was then treated with boron trifluoride etherate (15 ml. 0.094 mol) as described before. The product was purified by recrystallization from hexane to yield 2-fluoro-*m*-carborane (5.5 g, 65%), mp 259–260° (sealed tube). *Anal.* Calcd for $C_2H_{11}B_{10}F$: C, 14.76; H, 6.83; B, 66.63; F, 11.68; mol wt 162.22. Found: C, 14.66; H, 6.63; B, 66.59; F, 11.82; mol wt 162 (by low-voltage mass spectrometry).

Infrared absorption bands (cm^{-1}): 3080 (vw), 2590 (s), 1350 (m), 1310 (s), 1275 (s), 1150 (m), 1115 (m), 1060 (s), 1025 (m), 985 (m), 730 (s), 716 (m), and 690 (m).

Preparation of 2-Diphenylamino-*m*-carborane.—$Li_2[m\text{-}B_9C_2H_{11}]$ was obtained from the reaction between $[(CH_3)_3NH][m\text{-}B_9C_2H_{12}]$ (40 g, 0.21 mol) in 600 ml of ethyl ether and butyllithium (275 ml of 1.6 *M* C_4H_9Li in hexane, 0.44 mol). It was then treated with diphenylaminodichloroborane (52 g, 0.21 mol) according to the procedure described above. The crude product from the organic layer, however, was purified by fractional distillation under vacuum to obtain a fraction boiling at 136–146° (0.05 mm). The distillate solidified on cooling to room temperature and was further recrystallized from hexane to yield 3 g of 2-diphenylamino-*m*-carborane, mp 115–117°. *Anal.* Calcd for $C_{14}H_{21}B_{10}N$: C, 53.99; H, 6.80; B, 34.71; N, 4.50; mol wt 311.44. Found: C, 54.30; H, 6.77; B, 34.65; N, 4.37; mol wt 311 (by low-voltage mass spectrometry).

The infrared absorption bands of the compounds are (cm^{-1}) 3050 (vw), 2600 (s), 1590 (m), 1500 (s), 1430 (m), 1300 (s), 1250 (m), 1180 (vw), 1160 (vw), 1150 (w), 1115 (w), 1080 (vw), 1070 (m), 1060 (m), 1025 (m), 992 (w), 752 (m), 725 (w, b), 705 (s), and 690 (w).

Pyrolysis of 3-Fluoro-*o*-carborane.—$o\text{-}B_{10}C_2H_{11}F$ (3 g, 0.0185 mol), sealed in a 1-in. od heavy-walled Pyrex test tube under an atmosphere of nitrogen, was heated to 395–400° in a furnace for 18 hr. When the tube was opened, 2.7 g of white solid was obtained which, according to a vapor-phase chromatographic analysis, was a mixture of two components at a ratio of 2:1. Separation of the mixture on a basic aluminum oxide chromatographic column, using hexane as an eluting agent, yielded 1.7 g (60%) of the major component and 0.1 g of the second component.

The major component had an infrared spectrum and a melting point which were identical with those of 2-fluoro-*m*-carborane prepared by the insertion reaction as described above.

The second component, mp 263–265° (sealed tube), had a different infrared spectrum from either that of the starting material or that of 2-fluoro-*m*-carborane. Mass spectral and elemental analysis showed it to be $B_{10}C_2H_{11}F$.

Pyrolysis of 3-Diphenylamino-*o*-carborane.—The 3-diphenylamino-*o*-carborane (3 g, 0.0185 mol) was isomerized by the same procedure and under similar conditions as those described above. The pyrolysis product was dissolved in ethyl ether and then filtered to remove the insoluble materials. The filtrate was evaporated to dryness to yield 2.2 g of brown, sticky liquid. Analysis of the product by vapor-phase chromatography with a QF-1 (fluoroalkylsiloxane polymer) column showed one main component (95%) and two minor components. The major component, however, was separated into two isomers on the basic alumina chromatographic column, using hexane as an eluting agent. The first isomer (0.3 g) was identical in melting point and infrared spectrum with 2-diphenylamino-*m*-carborane prepared from the reaction between diphenylaminodichloroborane and $Li_2[m\text{-}B_9C_2H_{11}]$.

The second isomer (1.2 g), mp 68–70° (sealed tube), was similar to the starting material only in mass spectral and elemental analysis. However, it was quite different from both the starting material and the first isomer in an infrared absorption spectrum and a melting point.

Anal. Calcd for $C_{14}H_{21}B_{11}N$: C, 53.99; H, 6.80; B, 34.71; N, 4.50; mol wt 311.44. Found: C, 54.01; H, 6.70; B, 34.99; N, 4.48; mol wt 311 (by low-voltage mass spectrometry).

Acknowledgment.—The authors are grateful to T. L. Heying and H. A. Schroeder for helpful discussions and acknowledge the support of this work by the Office of Naval Research.

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Intensity as a Criterion in Assigning Electronic Transitions in Metal Complexes

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Received October 13, 1969

It is characteristic of transition metal complexes that their absorption spectra generally consist of bands of widely varying intensities with oscillator strengths (f) typically $\sim 5 \times 10^{-6}$–5×10^{-4} (ϵ_{max} $\sim$1–100) for the weakest to $f \approx 10^{-1}$ ($\epsilon_{max} \gtrsim 10{,}000$) for the strongest.[1] These limiting cases usually pose no problem when it comes to identification. The weak bands

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[1] T. M. Dunn, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 4.