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Halodicarbaundecaborate(11) Ions

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Ions of composition $B_9C_2H_{10}R_1R_2^-$ have been reported[2] as the product of alcoholic base on the $B_{10}C_2H_{10}R_1R_2$ carboranes. These ions are precursors to a variety of other compounds including carboranes[3] and organometallic analogs.[4] A route to monohalogenated derivatives of the $B_9C_2H_{10}R_1R_2^-$ ions has now been found.

Experimental

$B_9C_2H_{11}I^-$.—A solution of 5.9 g. of iodine (24 mmoles) in 25 ml. of absolute ethanol was slowly added to a stirred solution of 4.0 g. (24 mmoles) of $KB_9C_2H_{12}$ in 25 ml. of absolute ethanol. The color of the I_2 was rapidly discharged and KI precipitated during the addition. After filtration the ethanolic solution was diluted to 250 ml. with water and excess aqueous tetramethylammonium chloride was added. The solution was cooled to 0° and the tetramethylammonium salt of the monohalogenated ion was separated by filtration. Recrystallization of the crude tetramethylammonium salt from hot aqueous ethanol gave the product as plates in 75% yield. Iodinated derivatives of C-substituted anions were prepared in an identical manner. Replacement of I_2 by Br_2 gave an analogous monobrominated material. Relevant analytical data are presented in Table I. A representative ^{11}B n.m.r. spectrum is shown in Figure 1.

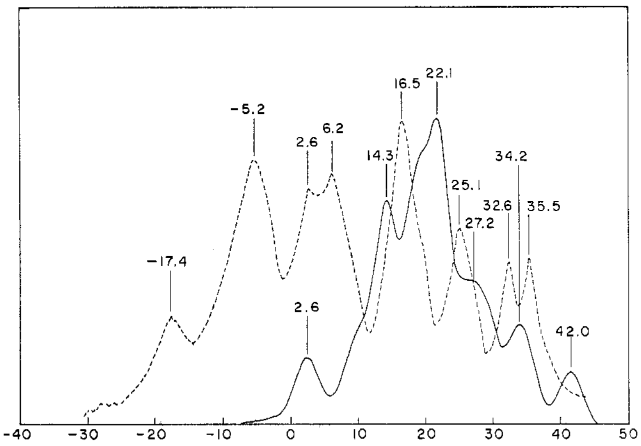

Figure 1.—^{11}B n.m.r. spectra of $(CH_3)_4NB_9C_2H_{11}I^-$ (- - - -) and $B_9C_2H_{12}I$ (———) at 19.3 Mc./sec.

$B_9C_2H_{12}I$.—A solution of $(CH_3)_4N^+B_9C_2H_{11}I^-$ in aqueous acetonitrile was passed through an acidic ion-exchange column and the resulting solution concentrated to dryness. The product was purified by sublimation at 40-50° under high vacuum. Like its unhalogenated analog,[2] the product was both extremely hygroscopic and thermally unstable.[3] The yield of purified product of m.p. 70–71° was about 10%.[5] *Anal.* Calcd. for $B_9C_2H_{12}I$: C, 9.23; H, 4.62; B, 37.4; I, 48.8; equiv. wt., 260. Found: C, 9.26; H, 5.11; B, 36.8; I, 48.8; equiv. wt., 262.

Results and Discussion

Addition of I_2 to an aqueous ethanol solution of $M^+B_9C_2H_{12}^-$ precipitated MI and left the H_3O^+ salt of $B_9C_2H_{11}I^-$ in solution. After the addition of 1 mole of I_2, the reaction was complete and any additional I_2 was not decolorized.

The structure shown in Figure 2 is favored for the product. Evidence in support thereof comes from the ^{11}B n.m.r. spectrum of $B_9C_2H_{12}I$ formed by protonation of $B_9C_2H_{11}I^-$. Electrophilic substitution is expected to occur at the open face of the $B_9C_2H_{12}^-$ ion. Since halogenated C,C′-dimethyl derivatives were obtained, attack at carbon is ruled out. Halogenation of the two types of boron atoms present in the open face would lead to products which may be differentiated on the basis of ^{11}B n.m.r. spectra. Halogenation of the boron atom which lies upon the plane of molecular symmetry would yield a product ion which contained only one doublet of relative intensity 1. Attack at the boron atoms which lie off the plane would make all

TABLE I

ANALYTICAL DATA FOR $(CH_3)_4N^+B_9H_9C_2R_1R_2X$

R_1	R_2	X	Yield, %	λ_{max}	ϵ	Equiv. wt. Calcd.	Equiv. wt. Found	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % B	Calcd, % X	Found, % C	Found, % H	Found, % N	Found, % B	Found, % X
H	H	I	75	229	3880	333	340	21.6	6.9	4.2	29.1	38.2	21.7	7.4	3.8	29.0	38.0
H	CH_3	I	78	231	4600	347	348	24.2	7.2	4.0	27.9	36.6	24.4	7.3	4.0	28.1	36.9
H	C_6H_5	I	83	226	6140	409	411	35.2	6.6	3.4	23.7	31.1	34.8	7.0	3.1	23.4	30.9
				255	6230												
CH_3	CH_3	I	76	231	550	361	371	26.6	7.5	3.9	26.9	35.2	26.5	7.5	4.0	26.8	35.3
CH_3	CH_3	Br	71	225	4100	314	314	30.6	8.6	4.5	30.9	25.5	30.6	8.8	4.7	30.7	25.7

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[1] Alfred P. Sloan Research Fellow.

[2] R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

[3] F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *ibid.*, **86**, 4222 (1964).

[4] M. F. Hawthorne, D. C. Young, and P. A. Wegner, *ibid.*, **87**, 1818 (1965); M. F. Hawthorne and T. D. Andrews, *ibid.*, **87**, 2496 (1965): M. F. Hawthorne and R. L. Pilling, *ibid.*, in press.

[5] The bulk of the material consisted of nonvolatile yellow solids.

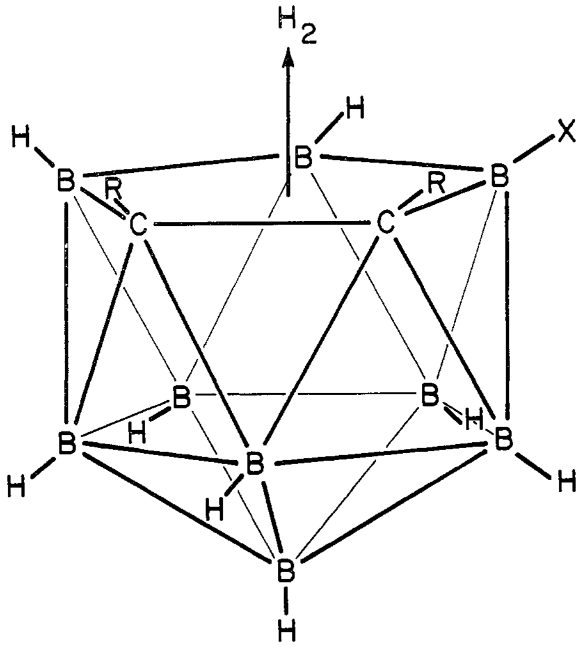

Figure 2.—A proposed structure for $B_9C_2H_{12}I$ where X = iodine.

nine boron atoms nonequivalent and lead to a spectrum which contained more than one doublet of relative intensity 1 (ideally, eight doublets would appear at high resolution). These arguments assume that the two extra protons present in $B_9C_2H_{12}I$ are only weakly coupled with their neighboring boron atoms in the open face. Since at least three doublets of relative intensity 1 are seen in the ^{11}B n.m.r. spectrum of $B_9C_2H_{12}I$, the latter structure is preferred. In addition, the ^1H n.m.r. signal which represents CH_3 protons in the C,C′-dimethyl derivative is rather broad and suggests that the two methyl groups are nonequivalent in the anion and this gives additional support to the proposed structure.

The iodination of $B_9C_2H_{12}^-$ is probably best viewed as an electrophilic substitution by I_2. In agreement with this concept, aryldiazonium ions (weak electrophiles) give intensely colored products in the presence of $B_9C_2H_{12}^-$ which are strongly reminiscent of the products of aryldiazonium ions on $B_{10}H_{10}^{-2}$.[2,6,7]

The bromine in $B_9C_2H_{11}Br^-$ was not particularly prone to nucleophilic displacement as shown by the recovery of unreacted $B_9C_2H_{11}Br^-(CH_3)_4N^+$ after 50 hr. reflux in acetone saturated with KI. Pyrolysis of the cesium salt of $B_9C_2H_{11}I^-$ produced CsI (85%) and the previously reported[3] $B_9C_2H_{11}$ (25%).

$B_9C_2H_{12}I$ is extremely hygroscopic and can only be handled in a water-free atmosphere. It decomposes at 70–71° with the evolution of H_2. The product obtained upon decomposition of the dry solid appears to be polymeric rather than the $B_9C_2H_{10}I$ which might be anticipated.

Acknowledgments.—The authors wish to thank the Alfred P. Sloan Foundation and the Army Research Office (Durham) for generous support of this work.

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Correspondence

Hydrogen Bonding in Manganese Dichloride Tetrahydrate

Sir:

In a recent paper on the crystal structure determination of $MnCl_2 \cdot 4H_2O$[1] a hydrogen-bonding scheme for this compound, based on a very accurate X-ray diffraction study, has been proposed. According to this study only four of the eight crystallographically different hydrogen atoms are involved in hydrogen bonds.[2] Although it is known that hydrogen atoms of water molecules do not always participate in hydrogen bonds (*e.g.*, the neutron diffraction study of $MgSO_4 \cdot 4H_2O$[3]), a closer inspection of the $MnCl_2 \cdot 4H_2O$ structure reveals that this is not the case here. Besides the four hydrogen bonds mentioned by Zalkin, Forrester, and Templeton (O(1)–H(11)···Cl(1), 3.17 Å.; O(2)–H(21)···Cl(2), 3.17 Å., O(2)–H(22)···O(1), 2.93 Å.; and O(4)–H(41)···Cl(1), 3.29 Å., where the distances are those between the water oxygen atoms and the acceptor atoms of the hydrogen bonds) four other hydrogen bonds can be shown to be possible. The oxygen atom O(1) has two more close neighbors, Cl(1) at 3.28 Å. and Cl(2) at 3.30 Å.; H(12) can form a bifurcated hydrogen bond to these chlorine atoms with a geometry similar to the one found for one of the hydrogen atoms in $BaCl_2 \cdot 2H_2O$ (according to a neutron diffraction investigation[4]). Atom O(3) has three close neighbors outside of the coordination polyhedron of the Mn^{2+} ion: Cl(2) at 3.20 and 3.32 Å. and O(3) at 3.13 Å. The latter distance cannot correspond to a hydrogen bond because the two O(3) atoms are related by a center of symmetry. The Cl(2)–O(3)–Cl(2) angle is 143°, which means that the O(3)–H···Cl(2) angles must be bent to 150°; a geometry similar to the one

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(1) A. Zalkin, J. D. Forrester, and D. H. Templeton, *Inorg. Chem.*, **3**, 529 (1964).

(2) In a private communication of April 13, 1965, Zalkin, Forrester, and Templeton state: "In our calculation of interatomic distances in $MnCl_2 \cdot 4H_2O$ we made an error in a data card which specified the symmetry. This error caused half of the atoms to be ignored in the search for neighbors, and we failed to find several of the hydrogen bonds which are correctly described by Baur."

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(4) V. M. Padmanabhan, W. R. Busing, and H. A. Levy, *ibid.*, **16**, A26 (1963).