fluoroalkanes have also been observed to undergo a similar reaction.[6]

The mechanism of the halogenation of decaborane by haloalkanes, however, remains unclear. There is one possibly related reaction among aliphatic compounds. Brewer[7] has found that cycloalkanes react with alkyl halides in the presence of aluminum chloride to give the corresponding cycloalkyl halide and alkane. This reaction is probably due to the concerted abstraction of a hydride ion from the cycloalkane and reaction with the alkyl halide–aluminum chloride complex. This reaction can account for the similar formation of chlorodecaborane, but analogous reactions involving hydride abstraction from decaborane are apparently unknown. The ethyl chloride that is formed as a by-product, however, is then available for alkylation to give the mono-, di-, and triethylchlorodecaborane and the hydrogen chloride also observed as products of the reaction.

By means of high resolution n.m.r., and using the samples prepared above, Williams[8] has recently shown that the chlorine atoms in the two isomers are in the same positions as the iodine atoms resulting from electrophilic iodination of decaborane, namely the 1 and 2 positions. This indicates either that the chlorination reaction is an electrophilic reaction or that the best candidates for hydride abstraction are in the same positions. The latter is consistent with the fact that except for negatively charged bridge hydrogen atoms, the most negatively charged hydrogen atoms should be bonded to the most electron-rich boron atoms.

The above mechanism is offered only as a possibility since firm evidence is still lacking.

(6) A. L. Henne and M. S. Newman, *J. Am. Chem. Soc.*, **60**, 1697 (1938); D. J. Burton, *Dissertation Abstr.*, **22**, 2190 (1962).

(7) C. P. Brewer and B. S. Greensfelder, *J. Am. Chem. Soc.*, **73**, 2257 (1951).

(8) R. E. Williams and E. Pier, *Inorg. Chem.*, **4**, 1357 (1965).

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Chlorodecaboranes Identified as 1-$ClB_{10}H_{13}$ and 2-$ClB_{10}H_{13}$ by 64.2-Mc. B^{11} Nuclear Magnetic Resonance Spectra

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A variety of halogen derivatives of B_2H_6, B_4H_{10}, B_5H_9, and $B_{10}H_{14}$ have been prepared and in a number of cases their structures have been deduced from (or at least correlated with) their n.m.r. spectra, *e.g.*, 2,4-$I_2B_{10}H_{12}$,[1,2] 2-$IB_{10}H_{13}$,[2] 1-$IB_{10}H_{13}$,[3] 1,2-$I_2B_{10}H_{12}$ (tentatively),[3] 2-$BrB_{10}H_{13}$,[2] 1-BrB_5H_8,[2] 1-IB_5H_8,[2] 2-ClB_5H_8,[4] 2-BrB_4H_9,[5] 1-BrB_2H_5,[6] 1-ClB_2H_5.[7]

Recent n.m.r. studies with experimental nuclear magnetic resonance equipment[8] capable of obtaining B^{11} n.m.r. spectra at 64.2 Mc. allow us to add 1-$ClB_{10}H_{13}$ and 2-$ClB_{10}H_{13}$ to the above list. The preparation of these species were published by Hillman and Mangold.[9]

Substitution of a single Cl for a single terminal hydrogen in a boron hydride collapses the substituted boron resonance and chemically shifts it to lower field in the cases previously encountered, *i.e.*, 1-ClB_2H_6, and 2-ClB_5H_8.[10] A rationale that this should be the case with all approximately sp^3 hybridized boron nuclei will be published elsewhere.[7] In contrast, Cl replacement of hydrogen in an sp^2 molecule or I replacement of hydrogen in either sp^3 or sp^2 hybridized species shifts the resonance to higher field.[7] In Figure 1 are displayed top to bottom the B^{11} 64.2-Mc. spectra[11] of a mixture of 1-$ClB_{10}H_{13}$ and 2-$ClB_{10}H_{13}$, $B_{10}H_{14}$, and 1-$ClB_{10}H_{13}$. The 2, 4, 5, 7, 8, and 10 positions of $B_{10}H_{14}$ had been assigned[1,2,12] previously; however, Schaeffer[13] and coworkers have unambiguously identified the lowest field doublet as representing the 1 and 3 positions; thus the B^{11} spectral assignment for $B_{10}H_{14}$ is now complete.

The spectrum of 1-$ClB_{10}H_{13}$ (m.p. 73°) is almost self-explanatory, since the spectrum is in such great detail at 64.2 Mc. Onak and Dunks[4] observed that Cl substitutions (in 2-ClB_5H_8) not only shifted boron to lower field but also that boron positioned diagonally across the base (nonadjacent) was chemically shifted to higher field. Substitution of Cl on the 2, 5, or 6 positions in $B_{10}H_{14}$ would create seven, ten, and seven "kinds" of boron, respectively, in a variety of ratios. Substitution in the 1 position, however, would create six kinds of boron in the specific ratio 1:1:2:2:2:2 representing positions 1 alone, 3 alone, 5 and 10, 6 and 9, 7 and 8, and 2 and 4. In the lowest spectrum of Figure 1, two doublets of ratio 2 are evidently overlapped into a triplet at 64.2 Mc. and substitution in the 1 position is required. The assignment in Figure 1 of the 5, 7; 6, 9; and 7, 8 doublets is tentative.

The "other" B^{11} spectrum shows the spectrum expected of 2-$ClB_{10}H_{13}$—collapse of a portion of the high-field doublet and the predicted[7] shift to lower field. However, the presence of an even greater amount

(1) R. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2726 (1957).

(2) R. Schaeffer, J. N. Shoolery, and R. Jones, *ibid.*, **80**, 2670 (1958).

(3) R. E. Williams and T. P. Onak, *ibid.*, **86**, 3159 (1964).

(4) T. P. Onak and G. B. Dunks, *Inorg. Chem.*, **3**, 1060 (1964).

(5) J. Dobson and R. Schaeffer, *ibid.*, **4**, 593 (1965).

(6) D. F. Gaines and R. Schaeffer, *J. Phys. Chem.*, **68**, 955 (1964).

(7) R. E. Williams, K. M. Harmon, and J. R. Spielman, submitted for publication.

(8) F. A. Nelson and H. E. Weaver, *Science*, **146**, 223 (1964).

(9) M. Hillman and D. J. Mangold, *Inorg. Chem.*, **4**, 1356 (1965).

(10) A referee points out that this generality does not hold when extensive or greatly differing species are compared; *e.g.*, the apex boron nuclei of $B_{10}Cl_{10}^{2-}$ and $B_{10}Br_{10}^{2-}$ are found at higher field than the apex boron nuclei in $B_{10}H_{10}^{2-}$ (W. H. Knoth, *et al.*, *ibid.*, **3**, 161 (1964).

(11) These spectra are obtained at the same sweep rate and the 24 positions were found to be superpositioned at 12.8 Mc., thus the spectra are comparable but no reference compound was utilized.

(12) R. E. Williams and I. Shapiro, *J. Chem. Phys.*, **29**, 677 (1958).

(13) R. Schaeffer, private communication.

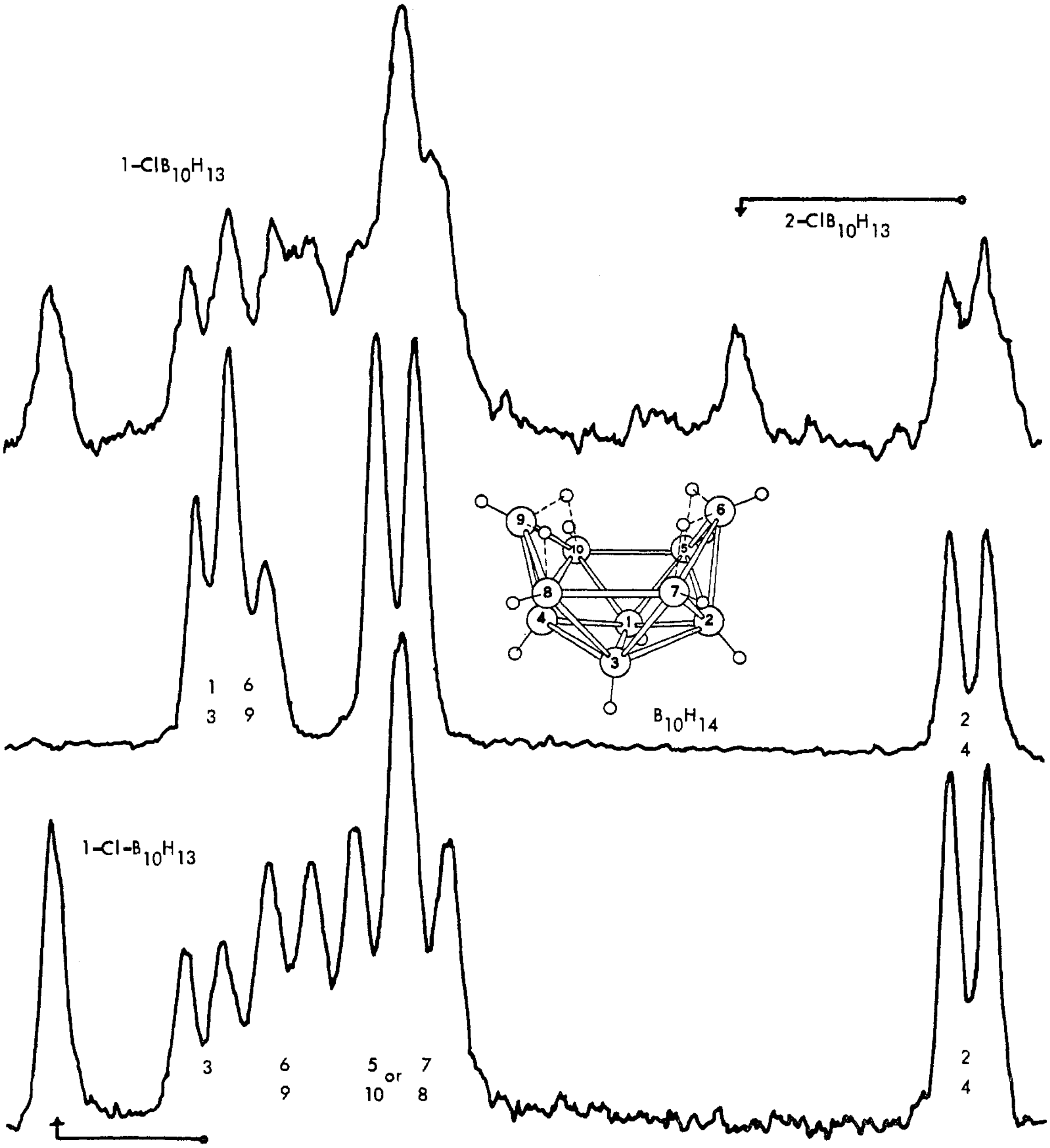

Figure 1.—B^{11} n.m.r. spectra (64.2 Mc.) of a $1\text{-}ClB_{10}H_{13}$ and $2\text{-}ClB_{10}H_{13}$ mixture, $B_{10}H_{14}$, and pure $1\text{-}ClB_{10}H_{13}$ in CS_2 solution.

of $1\text{-}ClB_{10}H_{13}$ is detected. Thus, the presumed $ClB_{10}H_{13}$ isomer (m.p. 59°) is in reality a mixture of two isomers.

It had been demonstrated that $2\text{-}IB_{10}H_{13}$ melts higher (116°,[2] 117° [14]) than $1\text{-}IB_{10}H_{13}$ (72°,[2] 98° [14]). $1\text{-}ClB_{10}H_{13}$ melts at 73°, pure $2\text{-}ClB_{10}H_{13}$ would be expected to have a higher melting point; however, mixtures rich in $1\text{-}ClB_{10}H_{13}$ may be expected to have lower melting points, thus accounting for the (59°) melting point of the $2\text{-}ClB_{10}H_{13}$-containing mixture.

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(14) M. Hillman, *J. Am. Chem. Soc.*, **82**, 1096 (1960).

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The Chemistry of Alane. V.[1] N,N,N′,N′-Tetramethylpropanediamine Alane[2]

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Davidson and Wartik[3] have reported the synthesis of a dimeric, 1:1 complex of N,N,N′,N′-tetramethyl-

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(1) Paper IV: A. R. Young, II, and R. Ehrlich, *J. Am. Chem. Soc.*, **86**, 5359 (1964).

(2) This research was supported by the Advanced Research Projects Agency under ARPA Order No. 24-60 and by the Air Force Flight Test Center, Air Force Systems Command, Edwards Air Force Base, Calif., under Contract AF33(616)-5935 (1960).

(3) J. M. Davidson and T. Wartik, *J. Am. Chem. Soc.*, **82**, 5506 (1960).