$$2S_2O_7^{2-} + 4NO_3^{-} = 4SO_4^{2-} + 4NO_2 + O_2 \qquad (9)$$

occurred at an appreciable rate even at the melting point of the eutectic. Because of this, the percentages of nitrogen oxides produced were not determined, although it was evident that when metals reacted nitrogen dioxide was evolved at an increased rate. With the less acidic dichromate ion, this reaction was not detectable in 0.8 *M* solutions until 400°. Examination of the gases produced below this temperature (Table I) showed an increasing proportion of nitrogen dioxide with a decreasing proportion of nitrous oxide and a striking decrease in the proportion of nitrogen from reactions with less strongly reducing metals.

The minimum temperatures at which detectable reaction took place (Table II) also indicated the importance of reaction 9, since the temperatures decreased as the acidity of the solutions increased. Although the precise temperatures of reaction depended to some extent on the surface and crystalline condition of the metal, since these factors were held constant valid comparisons could be made between the reactivity of different melt solutions.

The list of oxidation products formed by the metal in these reactions (Table II) shows that oxidation took place to the metal valency normally found with coordinated oxygen, V^{V}, Cr^{VI}, Fe^{III}, Co^{II}, etc. An exception was found with manganese in acidic solutions when Mn^{II} was formed. The reasons for the unexpected stability of this valency state are being further investigated.

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Notes

Contribution from the Research Laboratories,
Olin Mathieson Chemical Corporation,
New Haven, Connecticut, and
Brookhaven National Laboratory, Upton, New York

Chlorodecaborane[1]

By Manny Hillman[2] and D. J. Mangold[3]

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Two patents[4,5] indicate the preparation of a dichlorodecaborane, m.p. 115–122°, and a monochlorodecaborane, m.p. 40–55°. The preparation in both cases involves the unusual use of chloroform or 1,1-dichloroethane in the presence of aluminum chloride as the halogenating agent. Otherwise, nothing has been reported concerning chlorodecaboranes. Bromodecaborane and dibromodecaborane were also prepared by similar reactions using ethylene bromide or bromoform. Wunz[4] mentioned the possibility of preparing iododecaborane using iodoform, but does not give any results. Apparently, fluorodecaborane was neither suggested as a possibility nor prepared. The intent of the present work was to prepare fluorodecaborane and to try to elucidate some of the features of the reaction. This was not realized, for 1,1-difluoroethane reacted with aluminum chloride and decaborane to give a mixture of chlorodecaborane isomers.

Experimental

Preparation of Chlorodecaborane.—In four separate experiments a total of 50 ml. of 1,1-difluoroethane was slowly added to 100 g. of decaborane and 328 g. of aluminum chloride in 1 l. of carbon disulfide. The viscous mixture was stirred with difficulty. After 1 hr., the mixture began to reflux and became less viscous. Refluxing continued for about 2 hr., during which time some HCl was evolved. The reaction mixture was then filtered. Evaporation of the solvent gave 102.5 g. of a liquid. This was distilled, giving 54 g. of a liquid, b.p. 79–85° at 0.3–0.5 mm., and five additional arbitrary fractions of somewhat higher boiling points totaling 19 g. which, by mass spectrographic analysis of the parent peaks and associated isotopic distributions, were found to contain decreasing amounts of chlorodecaborane and increasing amounts of ethylchlorodecaborane, diethylchlorodecaborane, and in the last fraction some triethylchlorodecaborane.

The first and major fraction was cooled to 0° overnight and filtered while cool to give 21 g. of a colorless solid containing 94% chlorodecaborane, 5.7% ethylchlorodecaborane, and 0.3% diethylchlorodecaborane. The filtrate was redistilled. The first two fractions, 13 g., were cooled as above to yield 2.5 g. of additional solid. The filtrate and other distillation fractions were separately combined with an equal volume of pentane, seeded with the solid to give an additional 2 g. of solid. Other distillation fractions were treated by this last method to give another 1.5 g. of solid (total 27 g. containing 92–95% chlorodecaborane). Several crystallizations of the solid from pentane gave two apparently pure fractions, m.p. 73–74 and 58–60°. Infrared spectroscopic analysis of the higher melting isomer as a KBr pellet obtained bands at (cm.$^{-1}$) 702, 715, 736, 820, 850–860 (very strong—at least two bands), 875, 915, 923, 933, 986, 995, 1010, 1025, 1058, 1095, 1470, 1515, 1555, 1905, 1940, 2530, 2580, and several very weak bands. The lower melting isomer, however, appeared to be a mixture of the first isomer and a second isomer with additional bands at (cm.$^{-1}$) 800, 822, 890, 956, 1000, and 1050.

Discussion

That the reaction of a fluoroalkane with decaborane resulted in chlorodecaborane was originally somewhat surprising. However, by means of a mass spectrometric examination, it was found that 1,1-difluoroethane in carbon disulfide was essentially converted to 1,1-dichloroethane by aluminum chloride. Some other

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[1] This work was supported in part by the U. S. Air Force under Contract AF 33 (600)-33920 and by the Atomic Energy Commission.

[2] Brookhaven National Laboratory, Upton, N. Y.

[3] Olin Mathieson Chemical Corporation, New Haven, Conn.

[4] P. R. Wunz, U. S. Patent 3,046,086 (July 24, 1962).

[5] S. L. Clark and D. A. Fidler, U. S. Patent 3,010,783 (Nov. 28, 1961).

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).

Contribution from Space-General Corporation,
El Monte, California,
and Varian Associates, Palo Alto, California

Chlorodecaboranes Identified as $1\text{-ClB}_{10}\text{H}_{13}$ and $2\text{-ClB}_{10}\text{H}_{13}$ by 64.2-Mc. B^{11} Nuclear Magnetic Resonance Spectra

By Robert E. Williams and Eugene Pier

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A variety of halogen derivatives of B_2H_6, B_4H_{10}, B_5H_9, and $\text{B}_{10}\text{H}_{14}$ 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.*, $2,4\text{-I}_2\text{B}_{10}\text{H}_{12}$,[1,2] $2\text{-IB}_{10}\text{H}_{13}$,[2] $1\text{-IB}_{10}\text{H}_{13}$,[3] $1,2\text{-I}_2\text{B}_{10}\text{H}_{12}$ (tentatively),[3] $2\text{-BrB}_{10}\text{H}_{13}$,[2] $1\text{-BrB}_5\text{H}_8$,[2] $1\text{-IB}_5\text{H}_8$,[2] $2\text{-ClB}_5\text{H}_8$,[4] $2\text{-BrB}_4\text{H}_9$,[5] $1\text{-BrB}_2\text{H}_5$,[6] $1\text{-ClB}_2\text{H}_5$.[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 $1\text{-ClB}_{10}\text{H}_{13}$ and $2\text{-ClB}_{10}\text{H}_{13}$ 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.*, $1\text{-ClB}_2\text{H}_6$, and $2\text{-ClB}_5\text{H}_8$.[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 $1\text{-ClB}_{10}\text{H}_{13}$ and $2\text{-ClB}_{10}\text{H}_{13}$, $\text{B}_{10}\text{H}_{14}$, and $1\text{-ClB}_{10}\text{H}_{13}$. The 2, 4, 5, 7, 8, and 10 positions of $\text{B}_{10}\text{H}_{14}$ 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 $\text{B}_{10}\text{H}_{14}$ is now complete.

The spectrum of $1\text{-ClB}_{10}\text{H}_{13}$ (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 $2\text{-ClB}_5\text{H}_8$) 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 $\text{B}_{10}\text{H}_{14}$ 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 $2\text{-ClB}_{10}\text{H}_{13}$—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 $\text{B}_{10}\text{Cl}_{10}{}^{2-}$ and $\text{B}_{10}\text{Br}_{10}{}^{2-}$ are found at higher field than the apex boron nuclei in $\text{B}_{10}\text{H}_{10}{}^{2-}$ (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.