## ALUMINUM CARBIDE AS A ROUTE TO ORGANOBORON AND ORGANOALUMINUM COMPOUNDS

Sir:

Hilpert and Ditmar[1] have reported that, when hydrochloric acid solutions of certain group IV and group V elements are treated with aluminum carbide, methyl derivatives of these elements may form. Since trichloroborane is destroyed quickly upon contact with water, such a method cannot be used to prepare organoboranes. However, we now wish to report that the action of a gaseous mixture of hydrogen chloride and trichloroborane on aluminum carbide at elevated temperatures produces good yields of methylchloroboranes. Further, we wish to describe certain experiments which strongly support the view that the mechanism of this reaction involves the prior formation of methylaluminum dichloride and a subsequent alkyl–halogen exchange with trichloroborane.

Trichloroborane (1.803 mmoles), hydrogen chloride (11.19 mmoles), and aluminum carbide[2] (1.26 mmoles) were sealed in a cylindrical Pyrex reaction vessel of approximately 200 ml. capacity. The vessel was inserted, to approximately one half its length, into an air oven, and heating was initiated. At about $200°$ white crystals (probably aluminum chloride) were observed to condense in the cooler sections of the tube, the lower portion of which was eventually brought to $400°$ and maintained at that temperature for three hours. After it had been cooled to room temperature, the reaction vessel was opened to the vacuum system for removal of its volatile contents. These consisted of methane (1.231 mmoles), hydrogen chloride (0.213 mmole), and a mixture of methyldichloroborane and dimethylchloroborane (1.384 mmoles). No trichloroborane was recovered, and, based on the amount of this substance consumed, the yield of methylchloroboranes was 86.8%. The methylchloroboranes were identified by comparison of their infrared spectra with those of pure samples. In the experiment being described, the ratio of the monomethyl to the dimethyl compound in the gaseous products was 2.3 to 1.

That the product consisted largely of monomethylborane rather than more highly alkylated derivatives was not surprising, since a separate experiment showed that, at $400°$ in the presence of excess hydrogen chloride, approximately 70% of the methyl groups in trimethylborane were lost over a period of three hours. The only boranes detectable at the conclusion of this treatment were methyldichloroborane and small amounts of trichloroborane. Under the conditions employed, therefore, practically all of the trialkyl was converted to the monoalkyl compound according to the equation

$$B(CH_3)_3 + 2HCl \longrightarrow B(CH_3)Cl_2 + 2CH_4$$
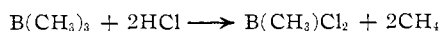
No methylaluminum compounds were observed among the products of the $HCl–BCl_3–Al_4C_3$ reaction, but it was suspected, nevertheless, that they might play an important role as intermediates. In an attempt to isolate any organoaluminum compounds that might be formed through the action of hydrogen chloride on aluminum carbide, a sealed-tube experiment involving these two reagents was carried out using procedures similar to those described above. Because the results were inconclusive, flow methods then were tried, and these involved passage of hydrogen chloride over a bed consisting of a large excess of aluminum carbide in a tube maintained at $300°$. Small amounts of a white solid volatile at room temperature were produced, and hydrolysis of this solid with D_2O yielded a gas non-condensable at $-196°$. Mass spec-
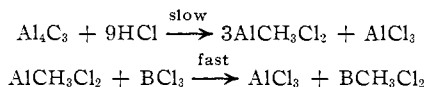
(1) S. Hilpert and M. Ditmar. *Ber.*, **46**, 3738 (1913).

(2) The aluminum carbide was obtained from Union Carbide Corporation

troscopic analysis of this gas showed it to consist almost exclusively of CH_3D. In subsequent experiments using larger quantities of reagents it was found possible to isolate a white solid with a melting point corresponding to the reported value[3] for $Al(CH_3)Cl_2$ $(72°)$. Gradual disproportionation of the mixed methyl chloride initially produced in these reactions occurred on storage, and chemical analysis of the volatile components in an aged sample yielded the composition $Al(CH_3)_{1.21}Cl_{1.85}$.

Having shown that methylaluminum chlorides can indeed be formed by the action of hydrogen chloride on aluminum carbide under appropriate conditions, we proceeded to prove (1) that aluminum alkyls can survive in the presence of hydrogen chloride over finite time intervals and (2) that aluminum and boron compounds can undergo instantaneous alkyl–halogen exchange. A mixture of trimethylaluminum and excess hydrogen chloride was allowed to warm to room temperature, and, after five minutes, 18% of the aluminum–methyl bonding was still present. (After 20 minutes, all but one per cent of the aluminum–methyl bonding had been destroyed.) Therefore, although the action of hydrogen chloride on trimethylaluminum at room temperature is rapid, it is not so to the extent that all aluminum–methyl bonding is destroyed immediately. A mixture of trimethylaluminum and trichloroborane, when warmed to room temperature from $-196°$, instantaneously deposited a white solid, and trimethylborane was recovered later in quantitative yield from the reaction mixture.

From the above results it appears that the path of the reaction being described involves the steps

$$Al_4C_3 + 9HCl \overset{slow}{\longrightarrow} 3AlCH_3Cl_2 + AlCl_3$$

$$AlCH_3Cl_2 + BCl_3 \overset{fast}{\longrightarrow} AlCl_3 + BCH_3Cl_2$$

Once in the form of methyldichloroborane, the methyl groups are relatively inert to the action of the excess hydrogen chloride present in the reaction mixture.

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PREPARATION OF XeF₄ (XENON TETRAFLUORIDE) BY ELECTRIC DISCHARGE[1]

Sir:

Thirty years ago Yost and Kaye[2] attempted to prepare fluorides of xenon by electric discharge without success. These authors stressed, however, that, "It does not follow that xenon fluoride is incapable of existing." Now that XeF_4 has been discovered by Claassen, *et al.*,[3,4] we have successfully prepared XeF_4 by electric discharge.

The apparatus was very similar to the one used in our discharge preparation of O_3F_2.[5] The diameter of the reaction vessel was 6.5 cm.; the electrodes (2 cm. in diameter) were 7.5 cm. apart. A gas mixture of 1 volume Xe + 2 volumes F_2 was fed at a rate of 136 cc. per hour at N.T.P. into the reaction vessel, cooled in a $195°K$. $(-78°)$ Dry Ice–Freon 12 bath, and quan-

(1) These results are part of the work supported by the Office of Naval Research, under Contract Nonr 3085(01).

(2) D. M. Yost and A. L. Kaye, *J. Am. Chem. Soc.*, **55**, 3890 (1933).

(3) H. H. Claassen, H. Selig and J. G. Malm, *ibid.*, **84**, 3593 (1962).

(4) C. L. Chernick, H. H. Claassen, *et al.*, *Science*, **138**, 136 (1962).

(5) A. D. Kirshenbaum and A. V. Grosse, *J. Am. Chem. Soc.*, **81**, 1277 (1959); see Fig. 1, p. 1278.

titatively converted to XeF_4. The discharge varied from 1100 volts and 31 milliamp. to 2800 volts and 12 milliamp. while the total pressure varied from 2 to 15 mm. In a typical run of 3.5 hours, 7.10 mmoles of Xe and 14.20 mmoles of F_2 were used and 1.465 g. (7.07 mmoles) of xenon fluoride was produced. The composition of the product, as determined from synthesis, is therefore XeF_4. The advantage of this method over Claassen's[3] thermal method is that it is continuous, quantitative and an excess of fluorine is not required.

The composition of our products was also confirmed by analysis. A 102.3 mg. sample of XeF_4 was hydrolyzed with dilute KOH solution,[3,4] liberating $64.9 \pm 1.0\%$ by weight of Xe (theoretical = 63.3 wt. %). The resulting solution contained, by titration with Th$(NO_3)_4$, $35.1 \pm 1.0\%$ by weight F^- (theoretical = 36.7 wt. %). In addition, a new analytical method for Xe was used. XeF_4 reacts quantitatively with excess Hg

$$XeF_4 + 4Hg \longrightarrow Xe \uparrow + 2Hg_2F_2 \text{ (or } 2HgF_2)$$
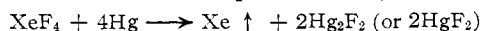
A sample of 136.4 mg. of our XeF_4 gave 87.3 (± 0.5) mg. of Xe or 64.0 (± 0.5) wt. %.

The product was vacuum sublimed into a glass tube and any trace of SiF_4 or O_2 pumped off; the clear colorless crystals formed were identical in appearance with those described previously.[3]

While these experiments were being completed, one of us (A. V. Grosse)—during a lecture trip in Germany— was shown the production of XeF_2 by the associates of Prof. Hoppe at the University of Münster. The XeF_2 was produced from a mixture of 1 volume of Xe + 1 volume of F_2, by the Ruhmkorff induction coil discharge in a quartz vessel, with quartz sealed electrodes, at $-78°$.

We wish to thank Mr. O. V. Carlson of Union Carbide Corporation for a gift of xenon and Dr. Balcar of the Air Reduction Company for a previous sample of xenon.

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THE STRUCTURE OF β-RHOMBOHEDRAL BORON[1]

Sir:

We have determined the structure for β-rhombohedral boron,[2,3] the phase obtained between 1500° and the melting point, where crystallization of a framework requiring a 105-atom unit becomes kinetically feasible.[3] B_{12} icosahedra are linked in a pattern which apparently is energetically superior to that achieved in the tetragonal[4] or, especially, the α-rhombohedral[5] polymorph.

Crystals (ca. 99.5% B) from the U. S. Borax Research Corporation give $a = 10.145 \pm 0.015$ Å., $\alpha = 65°$ $17' \pm 8'$ for the primitive rhombohedral unit. The 105-atom framework derives from the space group $D_{3d}^5-R\bar{3}m$, and carries (largely substitutional) impurities estimated as 0.11 Mg, 0.04 Al, 0.01 each of Si, Mn, Fe atoms. Three-dimensional intensity data from single crystals were counter-recorded using balanced filters with both Cu Kα and Mo Kα radiations. Structure determination through analysis of observed in-

(1) Supported by the National Science Foundation and the Advanced Research Projects Agency. We thank also the Cornell Computing Center, Mr. Richard C. Lesser, Director.
(2) D. E. Sands and J. L. Hoard, J. Am. Chem. Soc., 79, 5582 (1957).
(3) J. L. Hoard and A. E. Newkirk, ibid., 82, 70 (1960).
(4) J. L. Hoard, R. E. Hughes and D. E. Sands, ibid., 80, 4507 (1958); cf., J. L. Hoard, S. Geller and R. E. Hughes, ibid., 73, 1892 (1951).
(5) B. F. Decker and J. S. Kasper, Acta Cryst., 12, 503 (1959).

equalities and statistical relations connecting unitary structure factors, although demonstrably feasible, was short-circuited when one of us (R. E. H.) independently devised a model for the 84-atom subunit described below. The complete structure, free of interpretive ambiguity, then was obtained by Fourier synthesis in successive approximation. Presently R is 0.15 for all reflections of $(\sin \theta)/\lambda < 0.71$ and bond lengths are 1.65–1.87 Å., averaging 1.79 Å.

Excepting one atom at $^1/_2$, $^1/_2$, $^1/_2$, the structural unit is contained within a larger aggregate, itself recognizable in the crystal, of $13B_{12}$ icosahedra linked in a pattern retaining maximum symmetry. Take $r \cong 1.71$ Å. and $e \cong 1.80$ Å. as radius and edge of a regular B_{12} icosahedron, $l \cong 1.70$ Å. for a direct intericosahedral link. Consider a central B_{12} icosahedron radially linked to twelve others, with each secondary icosahedron derived from the central B_{12} through translation of $2r + l$ along the common fivefold axis and rotation of $2\pi/10$ about this axis. (This "eclipsed" configuration for linked B_{12} pairs is observed throughout.) Centers of the secondary icosahedra lie upon the surface of a sphere of diameter $4r + 2l \cong a = 10.145$ Å. Within this sphere are 84 atoms comprising the central B_{12} radially joined to 12 half-icosahedra or pentagonal pyramids; the 60 peripheral atoms occupy vertices of a truncated icosahedron (12 pentagonal, 20 hexagonal faces) in which the 30 edges connecting B_5 pentagons in pairs are also links connecting secondary B_{12} icosahedra in pairs nearly along (within 5° of) quasi-fivefold axes. Some compression of the central B_{12} with accompanying expansion of the attached icosahedra is observed: averaged edge lengths for the respective B_{12} types presently are 1.75 and 1.83 Å., intericosahedral links range from 1.65 to 1.75 Å. with, interestingly, the twelve radial links longest. When centered at a lattice point with symmetry $\bar{3}m$, the 84-atom subunit has six of its quasi-fivefold radii essentially along rhombohedral axes. Lattice translations generate an approximately cubic closest-packed assemblage of these subunits which are joined in an elegant three-dimensional framework through completion of B_{12} icosahedra centered at the midpoints of all rhombohedral edges. Thus, the 84-atom complex plays a role somewhat analogous to that of a B_{12} icosahedron in the simple α-rhombohedral structure.[5]

Each subunit has still six pentagonal pyramids with axes inclined alternatively $\pm 10°$ to the equatorial plane; these are capped, using just 20 atoms, to complete B_{12} icosahedra within partially condensed aggregates of symmetry $3m$. Three icosahedra, from three subunits, terminate in a single atom on the threefold axis. This atom has nine neighbors at the vertices of a polyhedron ($3m$) having three pentagonal and five triangular faces. Six of these nine atoms are shared between icosahedra and display eight-coördination; the remaining three retain six-coördination by forming each a bond with the 105th atom at the cell center ($\bar{3}m$). This last atom displays octahedral coördination in tying together the two sets of condensed icosahedra "centered" at $\pm (uuu)$ with $u = 0.385$. Bond distances of 1.72–1.86 Å., averaging 1.79 Å., characterize the internal crosslinking. (In the α structure, three center bonding provides the crosslinking.[5]) Over-all, the coördination number for 91 atoms is six, for 12 atoms, eight, for the final pair, nine. Two holes of modest size at $\pm (vvv)$, $v \cong 0.22$, carry no appreciable electron density. Preferential substitution by magnesium and aluminum (probably as Mg^{++}, Al^{+++}) in the octahedral or nine-coördinate positions seems probable, but is not proven.