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 spectroscopic 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

$$Al_4C_3 + 9HCl \xrightarrow{\text{slow}} 3AlCH_3Cl_2 + AlCl_3$$

$$AlCH_3Cl_2 + BCl_3 \xrightarrow{\text{fast}} AlCl_3 + BCH_3Cl_2$$

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.

The authors wish to express their gratitude to the Koppers Company, Inc., for their generous support of these investigations.

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(1) S. Hilpert and M. Ditmar, *Ber.*, **46**, 3738 (1913).

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

(3) A. Grosse and J. Mavity, *J. Org. Chem.*, **5**, 106 (1940).

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PREPARATION OF XeF_4 (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-

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(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.