Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

1,1,2,2-TETRAKIS(DIFLUOROBORYL)ETHANE

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(Received March 27th, 1968)

Although acetylene and excess diboron tetrachloride undergo ready 1,2 addition to give 1,1,2,2-tetrakis(dichloroboryl)ethane, $(Cl_2B)_2CHCH(BCl_2)_2$[1], the addition of diboron tetrafluoride to acetylene proceeds much less readily, and has not been reported to go beyond the 1 : 1 stage when $F_2B{-}CH{=}CH{-}BF_2$ is formed[2]. In attempts to prepare 1,1,2,2-tetrakis(difluoroboryl)ethane, mixtures of acetylene with excess diboron tetrafluoride were heated at 110° for several days, but gave no appreciable yield of any 1 : 2 addition product. The attempted fluorination of the 1,1,2,2-tetrakis(dichloroboryl)ethane, using either antimony trifluoride or lead(IV) fluoride, gave non-volatile residues and, mainly, boron trifluoride; it is likely that any partially fluorinated borylethane formed disproportionated into non-volatile chloro compounds and boron trifluoride at the elevated temperatures necessary to obtain any reaction.

Studies of the exchange between B_2X_4/BY_3 type compounds[3] have shown that no exchange occurs with X = Cl, Y = F but ready exchange occurs with X = F and Y = Cl, to give diboron tetrachloride and boron trifluoride. Exchange can also proceed between diboron tetrafluoride and diboron tetrachloride. These results suggested that diboron tetrafluoride might undergo exchange with the (dichloroboryl)ethane, and this possibility was therefore investigated. Rapid exchange was found to occur at room temperature, with formation of diboron tetrachloride and a new product. Degradation of the latter with alkaline peroxide yielded, qualitatively, boron (as borate), fluoride and glyoxal, but no chloride, suggesting that exchange was complete, and that the C–C bond was preserved. However, it proved unexpectedly difficult to obtain quantitative degradation of the new compound since the latter was remarkably resistant to the usual reagents. Ultimately, degradation was achieved by prolonged treatment with alkali and calcium nitrate, whereby the following reaction sequence was produced:

$$C_2H_2(BF_2)_4 \xrightarrow{OH^-} C_2H_2B_4(OH)_8 + 8\,F^- \quad (\text{as } CaF_2)$$
$$\xrightarrow{\text{heat}} C_2H_6 + 2\,B_2O_3 + 2\,H_2O$$

and this provided the only feasible method of analysis. Even so, somewhat low fluorine values cast doubt on the completeness of chlorine replacement; however, the frag-

mentation pattern of the mass spectrum gave no evidence for chlorine-containing ions, and a molecular weight determination and comparison of the infrared spectrum with that of 1,1,2,2-tetrakis(dichloroboryl)ethane confirmed the product as the corresponding difluoro compound.

1,1,2,2-Tetrakis(difluoroboryl)ethane showed even higher thermal stability than the dichloro compound; after heating at 110° for 7 days, 40% of the difluoro compound remained unchanged, the decomposition following the equation

$$n\ C_2H_2(BF_2)_4 \rightarrow 2n\ BF_3 + (CHBF)_{2n}$$

and yielding an involatile residue. Unlike the dichloro compound, reaction with trimethylamine occurred at ordinary temperatures, giving a crystalline solid, identified by its infrared spectrum as trimethylamine–boron trifluoride, and a viscous non-volatile residue; the reaction followed the stoichiometry represented by

$$n\ C_2H_2(BF_2)_4 + 2n\ Me_3N \rightarrow 2n\ Me_3N{\cdot}BF_3 + (BFCH)_{2n}$$

EXPERIMENTAL*

1,1,2,2-Tetrakis(dichloroboryl)ethane and diboron tetrafluoride were both prepared from diboron tetrachloride, by reaction with acetylene and antimony(III) fluoride respectively. In a typical reaction, 1,1,2,2-tetrakis(dichloroboryl)ethane (0.56) and diboron tetrafluoride (1.53) gave after 1 h at 20° diboron tetrachloride (0.64), boron trifluoride (0.20), unchanged diboron tetrafluoride (0.61) and a product (0.35) involatile at −45°. The latter after degradation with alkali and calcium nitrate gave on heating ethane (0.32), fluoride (2.66, as CaF_2), boron (1.38), giving a ratio B/F/CH = 1/1.94/0.45. Molecular weight by vapour density gave 225 ± 5 ($B_4F_8C_2H_2$ requires 222). Decomposition of $B_4F_8C_2H_2$ (0.18) gave, after 7 days at 110°, boron trifluoride (0.21), unchanged compound (0.08) and a solid residue of composition BFCH. Reaction of the compound (0.90) with trimethylamine (excess) gave, after 1 day at 30°, uptake of 2.0 trimethylamine, with formation of $Me_3N{\cdot}BF_3$ (sublimate, infrared spectrum) and a viscous non-volatile residue.

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* Units are mmole unless otherwise stated.