ture of ethanol and ethyl acetate to give 1.9 g. of prisms which soften at 269° and melt at 275–277° when heated at a rate of 5° per min. The compound was compared with a specimen of natural evodiamine from Professor T. Ohta[4] and had the same ultraviolet and infrared spectral properties.

Anal. Calcd. for $C_{19}H_{17}N_3O$: C, 75.22; H, 5.65. Found: C, 75.32, 75.25; H, 5.77, 5.85.

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Chlorination of Polyfluoroalkyl Borates[1a]

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Received February 5, 1960

In connection with recent studies on fluoro heterocycles an interest developed in the synthesis of perfluorinated *n*-alkyl borates. Orthoboric acid esters are generally prepared by reaction of the respective alcohol with either a boron halide, boron trioxide, or orthoboric acid. Perfluorinated alcohols were desired in this work, but primary perfluorinated alcohols are not isolable. However, work was started with alcohols of the type R_FCH_2OH which are commercially available. The orthoborates expected from these alcohols require final fluorination either by direct exchange of hydrogen for fluorine by silver difluoride or similar agents, or by halogenation with bromine or chlorine followed by replacement of bromine or chlorine by fluorine by means of an inorganic fluorinating agent such as silver fluoride.

Preliminary experiments showed that boron trifluoride etherate did not react with trifluoroethanol, pentafluoropropanol, and heptafluorobutanol even under reflux, whereas boron trichloride in petroleum ether solution reacted instantaneously at −20° to give the desired borates. Thus tris(trifluoroethyl)borate (I), tris(pentafluoropropyl)borate (II), and tris(heptafluorobutyl)borate (III) were obtained in a 60–70% yield.

While bromination was unsuccessful, compound I was chlorinated rapidly when exposed to ultraviolet light. Surprisingly, the absorption of chlorine never stopped and the volume of the reaction mixture started to decrease after a certain interval of time. The reaction mixture thus obtained was distilled under vacuum to give two compounds, bis(trifluoromonochloroethyl) chloroboronate (VII) and the higher boiling tris(trifluoromonochloroethyl)borate (IV).

This result proved that the chlorination first proceeds as desired with the substitution of three of the six available hydrogen atoms by chlorine. The resulting compound IV then chlorinates further, not by exchange of residual hydrogen for chlorine, but by splitting off an alkoxy group with the formation of VII.

$$\underset{\text{I, II, III}}{(R_FCH_2O)_3B} \xrightarrow{Cl_2,\ h\nu} \underset{\text{IV, V, VI}}{(R_FCHClO)_3B} \xrightarrow{Cl_2,\ h\nu} \underset{\text{VII, VIII, IX}}{(R_FCHClO)_2BCl}$$

I, IV, VII. $R_F = CF_3$
II, V, VIII. $R_F = C_2F_5$
III, VI, IX. $R_F = C_3F_7$

We assume that compound VII is also not stable to chlorine and is probably converted into trifluoromonochloroethyldichloroboronite (X) which in turn undergoes further reaction with chlorine to form boron trichloride.

Chlorination of II and III led to the corresponding compounds V, VI, VIII, and IX. Bis(heptafluoromonochlorobutyl)chloroboronate (IX) was obtained contaminated with heptafluoromonochlorobutyldichloroboronite (XI).

For proof of structure, IX was also prepared from VI and boron trichloride as another method of preparation of dialkyl chloroboronates.[2] When

$$2\ \underset{\text{VI}}{(CF_3CF_2CF_2CHClO)_3B} + BCl_3 \longrightarrow 3\ \underset{\text{IX}}{(CF_3CF_2CF_2CHClO)_2BC}$$

the preparation of XI, the monoalkoxy derivative, was attempted by using an excess of boron trichloride, surprisingly only the dialkoxy derivative, IX, was obtained.

Since bromination and chlorination had failed to produce a perhalogenated orthoborate, an attempt was made to prepare the desired perfluoroalkyl orthoborates by direct fluorination of the hydrogen atoms attached to the α-carbon atoms of the alkyl groups by means of silver difluoride. The only product obtained from III was a boron-free material, probably di-1,1-dihydroheptafluorobutyl ether.

EXPERIMENTAL[3]

Tris(heptafluorobutyl) borate (III). The solution of 23 g. of boron trichloride in 200 ml. of petroleum ether (b.p. 30–38°) was added dropwise to a stirred mixture of 100 g. of 1,1-dihydroheptafluorobutanol and 100 ml. of petroleum ether with ice-salt cooling during 40 min. To ensure complete reaction, the mixture was then kept for 20 min. at 20°. The separated solid, boric acid, was filtered off and the petroleum ether evaporated. Distillation of the residual product gave a forerun of heptafluorobutanol and then 66.5 g. of III (66%); b.p. 137° (200 mm.); n_D^{23} 1.2596. The use of pyridine as hydrogen chloride scavenger decreased the yield.

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(1)(a) This article is based on work performed under Project 116-B of The Ohio State University Research Foundation sponsored by The Olin Mathieson Chemical Corporation, New York, N. Y. (1)(b) Present address: Olin Mathieson Chemical Corporation, New Haven, Conn.

(2) W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 501 (1957).

(3) Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Despite the fact that considerable care was taken in the purification of the reaction products, some variance was observed between the analyses and the calculated values which is typical of compounds containing high percentages of fluorine.

Anal. Calcd. for $C_{12}H_6BF_{21}O_3$ (608.0): C, 23.70; H, 0.99; F, 65.63. Found: C, 24.29, 24.48; H, 1.18, 1.19; F, 64.50, 64.33.

Tris(pentafluoropropyl) borate (II). The procedure given for III was followed exactly except treating 58 g. of 1,1-dihydropentafluoropropanol suspended in 60 ml. of petroleum ether with 17 g. of boron trichloride in 150 ml. of petroleum ether; yield of II, 39 g. (66%); b.p. 110° (200 mm.); n_D^{23} 1.2940.

Anal. Calcd. for $C_9H_6BF_{15}O_3$ (458.0): C, 23.60; H, 1.32; B, 2.36; F, 62.63. Found: C, 23.63, 23.89; H, 1.98, 2.18; B, 2.06, 1.96; F, 63.53, 63.89.

Tris(trifluoroethyl) borate (I) was obtained in analogy to the procedure given for III in 60% yield; b.p. 77° (200 mm.); n_D^{23} 1.2975.

Anal. Calcd. for $C_6H_6BF_9O_3$ (307.9): C, 23.40; H, 1.96. Found: C, 23.32, 23.19; H, 2.34, 2.55.

The following procedure is typical of the experiments performed.

Chlorination of tris(1,1-dihydrotrifluoroethyl) borate (I). Gaseous chlorine was passed slowly into 13.1 g. of I exposed to an ultraviolet lamp. When after 25 hr. the contents of the flask began to diminish, the reaction mixture was distilled at 200 mm. and 12.0 g. of products was obtained. Repeated fractional distillation gave 3.5 g. of IV and 3.0 g. of VII.

The *chlorination of 16 g. of tris(1,1-dihydropentafluoropropyl) borate* (II) afforded 14 g. of reaction products. Repeated fractional distillation yielded 5.5 g. of V and 1.5 g. of VIII.

The *chlorination of 15 g. of tris(1,1-dihydroheptafluorobutyl) borate* (III) gave 6 g. of VI and 2 g. of a mixture of IX and XI. Separation by distillation yielded 0.5 g. of IX.

Tris(trifluoromonochloroethyl) borate (IV) boiled at 100° (200 mm.); n_D^{25} 1.3405.

Anal. Calcd. for $C_6H_3BCl_3F_9O_3$ (411.3): C, 17.50; H, 0.73; B, 2.62; Cl, 25.87. Found: C, 16.87, 16.62; H, 0.93, 1.09; B, 2.87, 3.06; Cl, 25.93, 26.12.

Tris(pentafluoromonochloropropyl) borate (V) boiled at 117° (200 mm.); n_D^{25} 1.3262.

Anal. Calcd. for $C_9H_3BCl_3F_{15}O_3$ (561.3): Cl, 18.95. Found: Cl, 17.95.

Tris(heptafluoromonochlorobutyl) borate (VI) boiled at 150° (200 mm.); n_D^{25} 1.3250.

Anal. Calcd. for $C_{12}H_3BCl_3F_{21}O_3$ (711.3): C, 20.11; H, 0.42; B, 1.52; Cl, 15.00; F, 56.00. Found: C, 19.87, 19.80; H, 0.82, 0.91; B, 1.75, 1.86; Cl, 14.68, 14.52; F, 55.35, 55.14.

Bis(trifluoromonochloroethyl) chloroboronate (VII) boiled at 77° (200 mm.); n_D^{25} 1.3490. It is extremely sensitive to moisture, and fumes heavily in the open air.

Anal. Calcd. for $C_4H_2BCl_3F_6O_2$ (313.3): C, 15.34; H, 0.64; B, 3.45; Cl, 34.00. Found: C, 15.42, 15.28; H, 0.77, 0.96; B, 4.27, 4.40; Cl, 34.24, 34.49.

Bis(pentafluoromonochloropropyl) chloroboronate (VIII) is extremely sensitive to moisture; n_D^{25} 1.3330.

Anal. Calcd. for $C_6H_2BCl_3F_{10}O_2$ (413.3): Cl, 25.80. Found: Cl, 25.47, 25.25.

Bis(heptafluoromonochlorobutyl) chloroboronate (IX) is extremely sensitive to moisture; n_D^{20} 1.3360.

Anal. Calcd. for $C_8H_2BCl_3F_{14}O_2$ (513.3): C, 18.70; H, 0.39; B, 2.10. Found: C, 17.92, 17.80; H, 0.45, 0.49; B, 2.09, 1.96.

Di-1,1-dihydroheptafluorobutyl ether (XII). A 10-g. sample of III was added to 25 g. of silver fluoride in a 50-ml. reaction flask immersed in an ice bath and provided with a reflux condenser. A vigorous reaction started immediately, then 5.5 g. of reaction product was distilled. It was added to 10 g. of silver fluoride and the reaction yielded 3.2 g. of products. This amount was added to 5 g. of silver fluoride, scarcely causing a reaction. Distillation at 200 mm. gave 2.3 g. of XII, b.p. 65° (200 mm.), n_D^{25} 1.2890.

Anal. Calcd. for $C_8H_4F_{14}O$ (382.1): C, 25.14; H, 1.05, F, 69.61. Found: C, 25.13, 25.22; H, 1.10, 1.30; F, 66.56, 66.41.

Acknowledgment. The author is very much indebted to the Olin Mathieson Chemical Corporation for their generous support of this work. Furthermore, he wishes to thank Dr. C. J. Grundmann for his interest in the work and for stimulating discussions.

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Acylation and Alkylation of Aminoboronic Acids[1]

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Received January 18, 1960

The syntheses of organoboron compounds which we have carried out[2-4] have been based on their possible utilization in the therapy of brain tumors by neutron capture irradiation. The study in C_3H mice with subcutaneous brain tumors has shown[5,6] that organoboron compounds with hydrophilic groups offer the most promise for this type of treatment.

On this basis it seemed desirable to prepare boron compounds with carboxylic acid functions. Many with the carboxyl group attached directly to the aromatic ring[2,5,6] had been prepared and tested. Their utility prompted the synthesis of organoboron compounds containing an aliphatic carboxylic acid group.

Acylation and alkylation of a compound such as *m*-aminobenzeneboronic acid would permit the introduction of such a group. However, the stability of the boronic acid moiety in simple aromatic compounds has been shown[2,7-11] in a variety of systems to vary and to be dependent upon substituents. It was considered possible, therefore, that acylation and alkylation of aminobenzeneboronic acids might occur with loss of the borono group, even though acylations of such amines have been effected[9,12] in certain instances without cleavage of the carbon-boron linkage.

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(1) This work was supported by grants from the National Cancer Institute C-3174 and from the Atomic Energy Commission AT(30-1)-1093.

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