[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Organoboron Halides. V. Perfluorovinylboron Compounds[1,2]

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RECEIVED MAY 20, 1960

The preparation and characterization of the perfluorovinylboron compounds $CF_2{:}CFBF_2$ (b.p., −14°), $CF_2{:}CFBCl_2$ (b.p., 48.0°), $(CF_2{:}CF)_2BCl$ (b.p., 100.5°) and $(CF_2{:}CF)_3B$ (b.p., 104.9°), are described. These compounds are the first reported examples of covalent boron compounds in which the organo-group is fully fluorinated.

This paper describes the preparation and certain properties of some perfluorovinylboron compounds. They are the first covalent organoboron compounds reported which contain no hydrogen atoms in the group bonded to boron. As such their existence and stability are of interest. Organoboron compounds having halogen atoms in the organo-groups show a marked propensity to decompose to form boron trihalides. Thus fluoromethyldifluoroborine (FCH_2BF_2) yields boron trifluoride,[4] and although β-haloethylborines have not yet been obtained in the pure state, there is clear evidence that they are unstable under certain conditions.[5] Furthermore, reaction between bisperfluoroethylmercury and boron trichloride yields small amounts of boron trifluoride,[6] suggesting the presence of an unstable perfluoroethylboron compound. In view of these results the thermal stability of the perfluorovinylboron compounds is good, although all the compounds are unstable over extended periods of time, even when kept at −78°.

A route for the preparation of these new substances was suggested by the recently demonstrated cleavage of perfluorovinyl groups from perfluorovinyltin compounds by protonic acids[7] and by the use of vinyltin compounds to prepare vinylboron halides.[8] Dimethyl-bis-(perfluorovinyl)-tin reacts with boron trichloride at moderate temperatures to afford either perfluorovinyldichloroborine or bis-(perfluorovinyl)-chloroborine as the principal product, depending on the ratio of reactants. Perfluorovinyldifluoroborine is best obtained by treating perfluorovinyldichloroborine with antimony trifluoride at −25°, while tris-(perfluorovinyl)-borine is satisfactorily prepared from bis-(perfluorovinyl)-chloroborine and dimethyl-bis-(perfluorovinyl)-tin.

Experimental

1. Preparation of Perfluorovinylboron Compounds. (a) **Perfluorovinyldichloroborine.**—A thoroughly dried 1-liter Pyrex bulb was attached to the vacuum line and evacuated. Dimethyl-bis-(perfluorovinyl)-tin[7] (4.49 g., 14.4 mmoles) and boron trichloride (713 cc.,[9] 31.8 mmoles) were condensed into the bulb, which was sealed off and allowed to warm to room temperature. White solid dimethyltin dichloride began to form immediately. The bulb was placed in an oven at 70° for 1 hr., after which it was attached to the vacuum line, opened and the volatile products crudely separated by fractional distillation through traps held at −65, −78 and −196°. Material collected at −78° proved to be perfluorovinyldichloroborine containing a little boron trichloride. Final purification was effected by refluxing at high vacuum against a vacuum-jacketed Vigreux column held at −78°, which the boron trichloride slowly passed. In this manner perfluorovinyldichloroborine (4.3 g., 93% yield) was obtained and characterized by its molecular weight (Found, 163. Calcd. for $C_2F_3BCl_2$, 162.8), by hydrolysis (a 46.2 cc. sample with water at 120° for 20 hr. yielded 46.3 cc. of trifluoroethylene, identified by its infrared spectrum) and by analysis[10] of its trimethylamine adduct.

Anal. Calcd. for $C_5H_9F_3Cl_2BN$: C, 27.0; H, 4.05; N, 6.31. Found: C, 27.2; H, 4.3; N, 6.1.

(b) **Bis-(perfluorovinyl)-chloroborine.**—An 8.44 g. (27.7 mmoles) sample of dimethyl-bis-(perfluorovinyl)-tin was treated with 605 cc. (27.0 mmoles) of boron trichloride as described above for the preparation of perfluorovinyldichloroborine. Fractionation of the products in the vacuum line through traps at 0, −65 and −196° afforded 4.80 g. (85% yield) of bis-(perfluorovinyl)-chloroborine, held at −65°. Bis-(perfluorovinyl)-chloroborine was characterized by hydrolysis (a 30.0 cc. sample afforded 55.0 cc. of trifluoroethylene, identified by its infrared spectrum, on treatment with water for 20 hr. at 120°) and by its molecular weight (Found, 208. Calcd. for C_4F_6BCl, 208.3).

(c) **Perfluorovinyldifluoroborine.**—Reaction between boron trifluoride and dimethyl-bis-(perfluorovinyl)-tin yielded a compound subsequently shown by its infrared spectrum to be perfluorovinyldifluoroborine, but in poor yield. Thus 11.5 mmoles of the tin compound with 25.7 mmoles of boron trifluoride gave only 4.1 mmoles (18% yield) of perfluorovinyldifluoroborine. To obtain the desired boron compound in a higher yield, a 250 cc. sample of perfluorovinyldichloroborine was distilled onto a large excess of antimony trifluoride, contained in a bulb fitted with a cold finger, and the mixture was allowed to stand at −23° for 12 hr. Volatile products were distilled through a trap at −96° to remove unreacted perfluorovinyldichloroborine. The latter was returned to the reaction vessel together with a fresh sample of perfluorovinyldichloroborine. This procedure was repeated until the total chlorocompound taken for reaction reached 948 cc. (42.3 mmoles). A total of 560 cc. (59% yield) of perfluorovinyldifluoroborine was recovered and characterized by molecular weight (Found: 129. Calcd. for C_2F_5B: 129.8) and by hydrolysis (a 26.8 cc. sample heated at 120° for 15 hr. yielded 26.4 cc. of trifluoroethylene, identified spectroscopically).

Although perfluorovinyldifluoroborine is considerably less volatile than boron trifluoride, the latter is very soluble in the perfluorovinyl compound. Therefore, to free perfluorovinyldifluoroborine from last traces of boron trifluoride, it was necessary to fractionate under high vacuum through a Vigreux column cooled at −125°.

(d) **Bis-(perfluorovinyl)-fluoroborine.**—In several attempts to prepare this compound bis-(perfluorovinyl)-chloroborine was treated with antimony trifluoride at −23°.

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(1) (a) Presented in part at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960. (b) Previous paper in this series, F. E. Brinckman and F. G. A. Stone, THIS JOURNAL, **82**, 6235 (1960).

(2) This research was supported by the United States Air Force under Contract No. AF 49(638)-518, monitored by the Air Force Office of Scientific Research of the Air Research and Development Command.

(3) Natvar Corporation Fellow at Harvard University, 1959–1960.

(4) J. Goubeau and K. H. Rohwedder, *Ann.*, **604**, 168 (1957).

(5) M. F. Hawthorne and J. A. Dupont, THIS JOURNAL, **80**, 5830 (1958).

(6) J. J. Lagowski and P. G. Thompson, *Proc. Chem. Soc.*, 301 (1959).

(7) H. D. Kaesz, S. L. Stafford and F. G. A. Stone, THIS JOURNAL, **82**, 6232 (1960).

(8) F. E. Brinckman and F. G. A. Stone, *ibid.*, **82**, 6218 (1960).

(9) Throughout this paper the abbreviation "cc." refers to gases at standard conditions.

(10) Microanalysis was performed by Dr. Carol K. Fitz, Needham Heights, Massachusetts.

The only volatile reaction products were boron trifluoride and perfluorovinyldifluoroborine.

(e) **Tris-(perfluorovinyl)-borine.**—Treatment of boron trichloride with excess of dimethyl-bis-(perfluorovinyl)-tin afforded a mixture of perfluorovinyl-chloroborines together with a new less volatile substance, the infrared spectrum of which showed new absorptions due to the CF_2:CF- group. This mixture of products, however, was difficult to separate, so a cleaner route to tris-(perfluorovinyl)-borine was sought. It was found that bis-(perfluorovinyl)-chloroborine would react with dimethyl-bis-(perfluorovinyl)-tin in 2:1 ratio at 50° with quantitative conversion of B–Cl bonds to B–CF:CF_2. In this manner, after distillation at reduced pressure (41–42.5° (45 mm.)), 3 ml. of tris-(perfluorovinyl)-borine were obtained, the compound being characterized by its molecular weight (Found, 250. Calcd. for C_6F_9B, 253.8) and by hydrolysis (a 12.5 cc. sample with water at 120° for 15 hr. gave 36.7 cc. of trifluoroethylene, identified spectroscopically).

2. **Vapor Pressures of the Perfluorovinylboron Compounds.**—Vapor tensions were measured using a tensimeter[11] and are given in Table I. The constants which may be derived from the data in Table I are summarized in Table III.

TABLE I

VAPOR TENSIONS OF SOME PERFLUOROVINYLBORON COMPOUNDS

t, °C.	$p_{mm.}$ (obsd.)	$p_{mm.}$ (calcd.)	t, °C.	$p_{mm.}$ (obsd.)	$p_{mm.}$ (calcd.)
(a)	CF_2:$CFBF_2$		(b)	CF_2:$CFBCl_2$	
−96.4	2.49	2.46	−35.6	12.1	12.2
−70.7	23.6	24.4	−30.7	16.6	16.7
−63.6	40.9	41.7	0	97.6	97.1
−54.8	77.4	77.1	4.9	125	124
−44.9	150	146	28.2	350	354
−35.6	252	252			
(c)	$(CF_2:CF)_2BCl$		(d)	$(CF_2:CF)_3B$	
7.6	17.5	17.1	24.1	21.5	21.7
15.0	25.1	25.3	31.6	32.6	32.7
24.3	39.6	40.4	40.6	51.9	52.1
33.5	61.6	62.1	49.6	81.8	80.9
40.4	84.5	84.5	56.5	111.8	111.4
49.2	124.0	123.0	62.4	144.7	144.9

3. **Infrared Spectra of the Perfluorovinylboron Compounds.**[12]—Spectra were recorded as gases in a 4 cm. cell, fitted with sodium chloride plates, using a Perkin–Elmer double-beam spectrometer having sodium chloride optics. Two different gas pressures were used in order to observe weak bands and to establish centers of the strong bands. Frequencies recorded in Table II were calibrated against polystyrene film.

4. **Hydrolysis Studies.**—Experiments were carried out to compare the ease of cleavage of perfluorovinyl groups from boron by water with the ease of cleavage of vinyl and ethyl groups. The procedure followed was to condense a measured volume of a particular organoboron compound onto distilled water (1 ml.) contained in a 150-cc. Pyrex bulb attached to the vacuum line and fitted with two break-off side arms. The bulb was sealed off, warmed to room temperature and allowed to stand for 2 hr. The contents were then frozen down and the bulb opened to the vacuum line through a tube-opener. Material passing a trap cooled to −78° was measured and identified by its infrared spectrum. Other substances were returned to the reaction vessel which was resealed and heated at 120° for 15 hr. The bulb was then opened as before and additional olefin formed measured, its purity being checked by its infrared spectrum. Boron compounds investigated in this manner are listed below. The two numbers in parentheses after each compound represent percentage organo-group cleavage (*i.e.*, trifluoroethylene, ethylene or ethane formed) after the two treatments described above: CF_2:$CFBF_2$ (5, 99); CF_2:$CFBCl_2$: (0, 100); $(CF_2:CF)_2BCl$ (0, 92); $(CF_2:CF)_3B$ (0, 98); CH_2:$CHBF_2$ (0, 97); $(CH_2:CH)BCl_2$ (0, 85); $(CH_2:CH)_2BCl$ (0, 30); and $C_2H_5BF_2$ (0, 0).

TABLE II

INFRARED SPECTRA OF PERFLUOROVINYLBORON COMPOUNDS (CM.$^{-1}$)[a]

(a) CF_2:$CFBF_2$ (p = 40, 10 mm.)	1728 (s); 1480, 1469 (w,d); 1410 (b,vs); 1328, 1319 (m,d); 1182 (s); 1042 (s); 684 (m); 704 (m)
(b) CF_2:$CFBCl_2$ (p = 40, 4 mm.)	1698 (s); 1667 (sh,w); 1351 (s); 1294 (s); 1286 (sh,w); 1158 (w); 1129 (m); 1022 (m); 981 (s); 864 (b,vs)
(c) $(CF_2:CF)_2BCl$ (p = 30, 5 mm.)	1681, 1673 (vs,d); 1360 (s); 1319 (m), 1303 (sh,w); 1255 (w); 1137 (m); 1110 (w); 982 (w); 958 (m); 931 (m); 904 (w); 857 (m); 835 (ms); 814 (m)
(d) $(CF_2:CF)_3B$ (p = 15, 3 mm.)	1678 (vs); 1363 (s); 1313 (s); 1301 (sh,w); 1209 (m); 1137 (m); 1112 (w); 877 (m); 856 (s), 836 (m)

[a] w, weak; m, medium; s, strong; d, doublet; v, very; b, broad; sh, shoulder.

Discussion

The perfluorovinylboron compounds (Table III) are colorless, air-sensitive substances. On contact with air they burn with a sooty flame, occasionally detonating under ill-defined conditions. With water at elevated temperatures all the perfluorovinylborines release more than 90% of their perfluorovinyl groups as trifluoroethylene. At ambient temperatures hydrolysis of perfluorovinyldifluoroborine affords small amounts of trifluoroethylene, but perfluorovinyldichloroborine and bis-(perfluorovinyl)-chloroborine react with water at low temperatures without release of trifluoroethylene, presumably forming perfluorovinylboronic acids. Tris-(perfluorovinyl)-borine does not detectably react with water at ambient temperatures over a period of hours. Since at elevated temperatures vinyldichloroborine and divinylchloroborine do not yield ethylene quantitatively on treatment with water, it appears that perfluorovinylboron compounds are more susceptible than vinylboron compounds to hydrolytic cleavage of their organo-groups.

TABLE III

PHYSICAL PROPERTIES OF SOME PERFLUOROVINYLBORON COMPOUNDS

Compound	M.p.,[a] (°C.)	Log $p_{(mm.)}$ = B − AT^{-1} B	A	B.p.[b] (°C.)	Trouton const.[b] (e.u.)	$\Delta H_{vap.}$ (kcal./mole)
CF_2:$CFBF_2$	− 96	8.247	1389	−14.0	24.6	6.39
CF_2:$CFBCl_2$	−108	8.008	1645	48.0	23.4	7.53
$(CF_2:CF)_2BCl$	− 57.5	7.861	1861	100.5	22.8	8.52
$(CF_2:CF)_3B$	−107	8.559	2147	104.9	26.0	9.83

[a] Stock magnetic plunger method. [b] By extrapolation of the vapor pressure equation.

In the gas phase at ambient temperatures perfluorovinyldifluoroborine decomposes to form boron trifluoride at a rate of about 5% in a week. A gas

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(11) A. B. Burg and H. I. Schlesinger, THIS JOURNAL, 59, 780 (1937).

(12) For a reproduction of some of these spectra see H. D. Kaesz and F. G. A. Stone, "Vinylmetallics," A.C.S. Monograph on Organometallic Compounds (Edited by H. Zeiss), Reinhold Publishing Corp., New York, N. Y., 1960.

phase sample of tris-(perfluorovinyl)-borine showed no detectable decomposition over a period of a week at room temperature but went entirely to perfluorovinyldifluoroborine and boron trifluoride on being heated to 100° for 5 hr. In the liquid phase perfluorovinyldifluoroborine and boron trifluoride are formed slowly, with about 5% decomposition in four days at room temperature. Perfluorovinyldichloroborine is able to withstand relatively short periods of heating (*e.g.*, 5 hr. at 100°) but on standing for a few days at room temperature it partially decomposes giving boron trifluoride. Formation of the latter substance is of special interest since it shows that B–F bonds can be formed from these compounds by a route not involving simple disproportionation. This latter mode of decomposition is, however, found with bis-(perfluorovinyl)-chloroborine, samples of which were observed to decompose completely into perfluorovinyldichloroborine and tris-(perfluorovinyl)-borine after one day at room temperature. In view of the high stability of vinyldifluoroborine toward disproportionation,[8] it is likely that the tendency of perfluorovinyldifluoroborine to give boron trifluoride does not involve disproportionation, but a fluorine shift type mechanism to electronically unsaturated boron atoms. Such a process, however, probably is inhibited by a contribution of the perfluorovinyl group's π-electrons to the boron atoms's pπ-orbital, with the result that perfluorovinylboron compounds might be thermally more stable than their as yet unknown perfluoroethyl analogs, in which the boron atom's pπ-orbitals would be relatively less satisfied.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Chemistry of the Metal Carbonyls. VI. The Nature of Cycloöctatriene–Iron Carbonyl Complexes[1,2]

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RECEIVED MAY 13, 1960

Reaction between iron pentacarbonyl and a mixture of cycloöctatrienes at about 140° yields a stable iron complex $C_8H_{10}\cdot Fe(CO)_3$ (I). Treatment of 1,3,5-cycloöctatriene with $Fe_3(CO)_{12}$ in refluxing benzene affords I and an isomeric $C_8H_{10}\cdot Fe(CO)_3$ (II), which may be converted into I by heating with $Fe(CO)_5$. Evidence is presented indicating that I is bicyclo[4.2.0]octa-2,4-diene-iron tricarbonyl and that II is most probably 1,3,5-cycloöctatriene-iron tricarbonyl.

Recent studies on the chemistry of metal carbonyls have led to the preparation of cyclooctatetraene–iron compounds[4] and of complexes of the diolefin 1,5-cycloöctadiene with iron,[5] chromium,[6] molybdenum[6-8] and tungsten.[6,7] Reactions between certain metal carbonyls and the cycloöctatrienes also have been investigated. However, because of the existence of both 1,3,5- and 1,3,6-cycloöctatriene, as well as the tautomeric equilibrium between 1,3,5-cycloöctatriene and bicyclo[4.2.0]octa-2,4-diene,[9] the cycloöctatriene system might be expected to form more than one type of metal complex. Indeed, Fischer, Palm and Fritz[10] have prepared both 1,3,5- and 1,3,6-cycloöctatriene complexes of the Group VI transition metals. In this work a complex of composition $C_8H_{10}\cdot Fe(CO)_3$ also was reported and formulated as 1,3,6-cycloöctatriene–iron tricarbonyl solely on the basis of a comparison of its infrared spectrum with the spectra of the cycloöctatriene–Group VI metal carbonyl complexes. In this Laboratory a complex $C_8H_{10}\cdot Fe(CO)_3$ (I) was isolated from the reaction between iron pentacarbonyl and a mixture of the cycloöctatrienes at 140°.[4b] On the basis of thermal degradation of the compound, yield data and the failure of the compound to absorb hydrogen over platinum catalyst, it was suggested that I was bicyclo[4.2.0]-octa-2,4-diene–iron tricarbonyl.

The exact correspondence of the infrared spectral bands reported by Fischer, *et al.*,[10] for their $C_8H_{10}\cdot Fe(CO)_3$ complex with those shown by our iron compound (I) indicates the identity of these two compounds. In an attempt to obtain further evidence for our formulation of the compound in question as bicyclo[4.2.0]octa-2,4-diene-iron tricarbonyl, the cycloöctatriene–iron carbonyl system was again investigated.

Experimental[11]

Infrared spectra were taken as liquid films of 0.015 mm. thickness, on a Perkin–Elmer Model 21 spectrophotometer equipped with sodium chloride optics. Ultraviolet spectra were recorded in spectroscopically pure cyclohexane on a Cary Model 11M recording spectrophotometer. Nuclear magnetic resonance spectra were recorded at 40 megacycles on a Varian Model 4300B high resolution spectrometer,

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[1] Previous paper in this series, H. D. Kaesz, R. B. King, T. A. Manuel, L. D. Nichols and F. G. A. Stone, THIS JOURNAL, **82**, 4749 (1960).

[2] We are indebted to the Clark Fund of Harvard University for financial support of this work.

[3] National Science Foundation Predoctoral Research Fellow, 1958–1960.

[4] (a) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959); (b) T. A. Manuel and F. G. A. Stone, THIS JOURNAL, **82**, 366 (1960); (c) M. D. Rausch and G. N. Schrauzer, *Chem. and Ind.* (*London*), 957 (1959); (d) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **32**, 880 (1959).

[5] T. A. Manuel and F. G. A. Stone, *Chem. and Ind.* (*London*), 231 (1960).

[6] E. O. Fischer and W. Fröhlich, *Ber.*, **92**, 2995 (1959).

[7] T. A. Manuel and F. G. A. Stone, *Chem. and Ind.* (*London*), 1349 (1959).

[8] M. A. Bennett and G. Wilkinson, *ibid.*, 1516 (1959).

[9] (a) A. C. Cope and W. J. Bailey, THIS JOURNAL, **70**, 2305 (1948); (b) A. C. Cope and F. A. Hochstein, *ibid.*, **72**, 2515 (1950); (c) A. C. Cope, A. C. Haven, F. L. Ramp and E. R. Trumbull, *ibid.*, **74**, 4867 (1952).

[10] E. O. Fischer, C. Palm and H. Fritz, *Ber.*, **92**, 2645 (1959).

[11] Microanalyses were performed by Dr. Carol K. Fitz, Needham Heights, Mass.