fluoride by an organic group with a compensatory increase in π-donation by the remaining fluorines could lead to magnetic unshielding of the fluorine nuclei with displacement of the resonance to lower applied field. It is significant that the F^{19} chemical shifts of the alkyldifluoroboranes, lying close together, appear at somewhat lower applied field than vinyldifluoroborane. This is in agreement with the idea of the presence of boron–carbon π-bonding in vinyldifluoroborane which would be expected to lead to the F^{19} resonances appearing in this compound at higher field than in ethyldifluoroborane.

TABLE VIII

F^{19} CHEMICAL SHIFTS[a] AND B^{11}–F^{19} COUPLING CONSTANTS IN ORGANODIFLUOROBORANES

Compound	δ(soln.)[b]	δ(i.d.)[c]	δ(liq.)[d]	$J_{(B^{11}-F^{19})}$[e]
CH_3BF_2	69.3	68.8	73.6	77
$C_2H_5BF_2$	74.9	74.6	78.4	81
$C_3H_7BF_2$	73.2	72.8	75.8	81
$C_2H_3BF_2$	88.9	88.6	92.7	67

[a] Parts per million relative to CCl_3F, increasing toward higher field. [b] Typical value, concentration *ca.* 15.5 mole %, in CCl_3F. [c] Extrapolated to zero concentration in CCl_3F. [d] Pure liquid, external reference CCl_3F in sealed capillary. [e] Cycles per second.

Concerning the suggestion put forward here that F^{19} chemical shifts in XBF_2 molecules may be related to the extent of F–B dative π-bonding, it has been found in studies reported elsewhere[27] that if X is one of a number of other atoms or groups, nominally less "electronegative" than fluorine, *e.g.*, Cl, Br, CF_2:CF, the F^{19} resonance appears at considerably lower field than in boron trifluoride. Moreover, the relative positions of the F^{19} resonances in a sequence of similar XBF_2 molecules are in agreement with present ideas concerning π-bonding between unlike atoms. Thus in $BrBF_2$ the F^{19} resonance appears at lower applied field than in $ClBF_2$. This is expected in terms of a chlorine atom's being able to partake in p_π–p_π bonding more effectively than a bromine atom but not so effectively as a fluorine atom. Moreover, in X_2BF compounds, where two fluorine atoms of boron trifluoride have been replaced, an even greater F^{19} shift to lower fields should occur because there should be greater π-bonding from fluorine to boron in X_2BF than in XBF_2. Results are in agreement with this expectation. In dimethylfluoroborane, for example, the F^{19} resonance lies about 20 p.p.m. on the CCl_3F scale.

Among the alkyldifluoroboranes it might be expected that apart from hyperconjugative contributions if any, effects on fluorine shielding would be rather similar and inductive in nature. In fact, the order of electron attracting power, by the nuclear magnetic resonance criterion, appears to be methyl > *n*-propyl > ethyl. It should be noted that this sequence has been observed in recent nuclear magnetic resonance studies of mercury alkyls[28] and triorganosilanes.[29]

Our results suggest, not surprisingly, that we cannot vary the substituent in the RBF_2 system without simultaneously inducing changes in the remainder of the molecule. It would be remarkable if this were not the case to some degree in any chemical system. The fluoroboranes, however, provide a particularly favorable situation for such interaction, having a relatively strong acceptor atom with a vacant orbital of suitable symmetry to overlap with the filled lone-pair orbitals of the adjacent atoms, with bond distances sufficiently short to permit significant overlap. This means in turn that simple substituent effects observed in other systems, *e.g.*, the alkylamines, may be wholly or partially obscured.

[27] T. D. Coyle and F. G. A. Stone, *J. Chem. Phys.*, **32**, 1892 (1960).

[28] R. E. Dessy, T. J. Flautt, H. H. Jaffé and G. F. Reynolds, *J. Chem. Phys.*, **30**, 1422 (1959).

[29] D. E. Webster, private communication.

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

Preparation and Study of Some Perfluoroalkyl Compounds of Tin and Lead[1,2]

BY H. D. KAESZ, J. R. PHILLIPS AND F. G. A. STONE

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Tetraalkyllead compounds react directly with perfluoroalkyl iodides, under the influence of ultraviolet light or on heating, to give compounds of the type $R_3PbC_nF_{2n+1}$. When similar reactions were carried out with tetraalkyltin compounds most of the perfluoroalkyl groups went to produce fluorocarbons, and only small amounts of the $R_3SnC_nF_{2n+1}$ compounds were detected. However, the tin–tin bond in hexaorganoditin compounds is cleaved readily by perfluoroalkyl iodides to give the desired $R_3SnC_nF_{2n+1}$ derivatives. The perfluoroalkyl group is quantitatively removed by base from the perfluoroalkyltin and -lead compounds, but treatment with electrophilic reagents leads to preferential cleavage of alkyl or aryl groups. Important features of the infrared spectra of the new compounds are described.

In this Laboratory we have for some time been interested in preparing organoboron compounds in which the organo-group bonded to boron is highly fluorinated. Therefore, a reaction between bis-(pentafluoroethyl)-mercury and boron trichloride at elevated temperatures was investigated, but the only product of significance was boron trifluoride.[3] It has long been the opinion of many workers in this field that a boron compound in which a highly fluorinated organo-group is attached

[1] 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.

[2] Presented at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, 1960. For a preliminary communication see H. D. Kaesz, J. R. Phillips and F. G. A. Stone, *Chem. Ind. (London)*, 1409 (1959).

[3] The same result was obtained in an independent study elsewhere. See J. J. Lagowski and P. G. Thompson, *Proc. Chem. Soc.*, 301 (1959).

to boron would tend to decompose with formation of substances having B–F bonds.[4] Production of boron trifluoride from the reaction between bis-(pentafluoroethyl)-mercury and boron trichloride supports the contention that the R_F–B group is unstable, at least at elevated temperatures. However, the discovery[5] that tetraorganotin compounds react even at room temperature with boron halides to give organohaloboranes suggested that perfluoroalkyltin or -lead compounds might react with boron halides at ambient temperatures to form perfluoroalkylboron compounds. Although the work with bis-(pentafluoroethyl)-mercury and boron trichloride suggested that this approach might not be too successful, it was felt that since perfluoroalkyllead and -tin compounds have themselves not been described in the literature the problem was worthy of study.[6]

Perfluoroalkyl compounds of several non-metals and metalloids have been prepared and well characterized by Emeléus[7a] and Haszeldine[7b] and their co-workers. Much less is known, however, about perfluoroalkyl derivatives of metals.[8] A reasonable route to perfluoroalkyl compounds of lead was suggested by the well-known tendency of both perfluoroalkyl iodides and tetraalkyllead compounds to undergo free radical reactions. Thus the synthesis of small quantities of the two compounds Me_3PbCF_3 and $Me_3PbC_2F_5$ was effected by heating or irradiating with ultraviolet light mixtures of tetramethyllead with trifluoroiodomethane or pentafluoroiodoethane, respectively. Reaction mixtures were subjected to vacuum-line fractionation for the removal of the considerable quantities of fluoroform or pentafluoroethane produced, and subsequent vapor phase chromatography freed the desired lead compounds from such other materials as unreacted tetramethyllead and methyl iodide.

When mixtures of tetraalkyltin compounds and trifluoroiodomethane or pentafluoroiodoethane are heated, or irradiated with ultraviolet light, most of the CF_3 or C_2F_5 groups abstract hydrogen from the alkyl groups forming fluoroform or pentafluoroethane. Only trace amounts of the desired $R_3SnC_nF_{2n+1}$ compounds were detected on chromatographing the reaction products. When tetramethyltin was used in the thermal reactions formation of trimethyltin fluoride was observed, suggesting that $R_3SnC_nF_{2n+1}$ compounds were indeed forming, but under the conditions necessary for breaking the Sn–C bonds in the tetraalkyltin compound, conditions more vigorous than those required to break Pb–C bonds, the desired compounds were decomposing.

$$R_3SnC_nF_{2n+1} \longrightarrow R_3SnF + (CF_2)_n$$

Moreover, since the tetraalkyltin compounds were not breaking down as readily as their lead analogs, there was an increased tendency for the C_nF_{2n+1} radicals to abstract hydrogen from the alkyl groups rather than to combine with tin. However, appreciable yields of perfluoroalkyltin compounds were obtained from reactions of the type

$$R_3Sn\text{–}SnR_3 + C_nF_{2n+1}I \xrightarrow[\text{or ultraviolet}]{\text{heat}} R_3SnI + R_3SnC_nF_{2n+1}$$

which parallels the familiar halogen cleavage of hexaorganoditin compounds,[9] with the perfluoroalkyl iodide playing the not unreasonable role[10] of pseudohalogen. In this manner, the compounds Me_3SnCF_3, $Me_3SnC_2F_5$, $(C_6H_5)_3SnC_2F_5$ and $Et_3SnC_2F_5$ were prepared. The compound $Me_3PbC_2F_5$ was made in a similar manner from hexamethyldilead. Yields in this reaction are somewhat better than in the reaction between tetramethyllead and pentafluoroiodoethane. With the exception of $(C_6H_5)_3SnC_2F_5$ (m.p. 127–128°), the new perfluoroalkyl compounds are all liquids (Table I), stable at ambient temperatures but tending to decompose on heating. Thus although $Me_3SnC_2F_5$ may be heated at 100° for 15 hr. without detectable decomposition, the compound decomposes appreciably above 180°. In the work with the hexaorganoditin compounds, and with hexamethyldilead, vapor phase chromatography was again used for separation of the desired compound. For separation of the tin compounds, chromatography columns packed with diisodecyl phthalate on crushed firebrick were satisfactory, while for separation of the lead compounds, columns of Carbowax 4000 (Union Carbide polyethylene glycol) on firebrick were used.

The effect of both acidic and basic reagents on the perfluoroalkyltin and -lead compounds was investigated. Such reagents cause one of two distinctly different types of cleavage reaction. Either the fluorinated or unfluorinated group is preferentially removed. Thus, for example, Me_3SnCF_3 evolves fluoroform quantitatively when treated with aqueous potassium hydroxide, but yields 80% of two moles of methane on warming with dry hydrogen chloride. Similarly, $Me_3SnC_2F_5$, $(C_6H_5)_3SnC_2F_5$ and the other C_2F_5 metal compounds in the presence of aqueous alkalies yield pentafluoroethane, while the action of the strong Lewis acid boron trichloride on $Me_3SnC_2F_5$ or $Me_3PbC_2F_5$ gave rise to a mixture of volatile products containing methyldichloroborane and unreacted boron trichloride. No perfluoroalkylboron compounds were detected. This behavior is in distinct contrast to that of perfluorovinylalkyltin compounds which with boron trifluoride

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(4) This idea has been expressed for example by A. B. Burg, Eighth Annual Technical Report to the Office of Naval Research, Contract No. N6onr-238-TO-I, November, 1954. In confirmation of this the new compound CF_2:$CFBCl_2$ very slowly forms BF_3, H. D. Kaesz, S. L. Stafford and F. G. A. Stone, THIS JOURNAL, **81**, 6336 (1959).

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

(6) As a result of our initial communication,[2] we became aware through a private communication from Dr. H. C. Clark that he and his co-workers have independently prepared and studied one of the compounds (Me_3SnCF_3) described in this paper; see H. C. Clark, *et al.*, THIS JOURNAL, **82**, 1888 (1960). Our own work in this area was first described in a series of status reports to the Air Force beginning in February, 1959.

(7) (a) H. J. Emeléus, *J. Chem. Soc.*, 2979 (1954); *Chem. Ind. (London)*, 1235 (1952). (b) R. N. Haszeldine, *Ann. Reports Chem. Soc.*, **51**, 279 (1954); *Angew. Chem.*, **66**, 693 (1954).

(8) For a recent review see J. J. Lagowski, *Quart. Rev.*, **13**, 233 (1959).

(9) G. E. Coates, "Organometallic Compounds," Methuen, London, 1956.

(10) It is pointed out in ref 8 that the effective electronegativity of a CF_3 group lies between that of fluorine and that of chlorine.

TABLE I

VAPOR PRESSURE CONSTANTS FOR SOME PERFLUOROALKYLTIN AND -LEAD COMPOUNDS

Compound	Log p(mm.) = $B - AT^{-1}$ B	A	B.p.[a] (°C.)	Trouton constant[a] (e.u.)	$\Delta H_{vap.}$[a] (kcal.·mole^{-1})
CF_3SnMe_3[b]	8.139	1961	100.0	24.0	8.98
$C_2F_5SnMe_3$	7.781	1863	107.0	22.4	8.52
$C_2F_5SnEt_3$	7.422	2046	177.4	20.8	9.36
$C_2F_5PbMe_3$	7.843	2040	138.0	22.7	9.34

[a] By extrapolation of the vapor pressure equation. [b] M.p. −50.9°.

or trichloride give $CF_2{:}CFBF_2$ and $CF_2{:}CFBCl_2$, respectively.[11]

A considerable amount of work has been done to establish relative orders of cleavage of various organo-groups from metals, leading to a correlation of the electronegativity of an organo-group with its position in the cleavage series.[12] Thus, for example, phenyl groups are cleaved more readily than alkyl groups from alkylphenylmetal compounds. This order of cleavage has been related to the greater electronegativity of phenyl groups compared with alkyl, in accord with theoretical considerations which predict that an sp^2-hybridized carbon atom will be more electronegative than an sp^3-hybridized carbon atom.[13] In this context the preferential cleavage of phenyl and alkyl groups by electrophilic reagents, from (perfluoroalkyl) tin and -lead compounds is surprising, since perfluoroalkyl groups are obviously very electronegative.[10] Since the position of the perfluoroalkyl group in the cleavage series does not apparently accord with its electronegativity, it seems worthwhile to reexamine the premise that group electronegativity can always be correlated with ease of cleavage. In attempting to predict which of several organo-groups will be cleaved first from a metal by an acid, and without making explicit assumptions as to the mechanism, it seems more plausible to consider which carbon atom bonded to the metal has the highest electron density around it. This carbon atom may not necessarily be part of the most electronegative group. In the perfluoroalkyltin and -lead compounds, because of the inductive factor, an unfluorinated carbon atom is probably more electron-rich than a fluorinated carbon atom, and, therefore, the unfluorinated group is preferentially cleaved by acids. However, on treatment of the perfluoroalkylmetal compounds with base, a nucleophilic attack on the metal, the perfluoroalkyl group is displaced easily, on account of the high polarity of the bond between the metal and the perfluoroalkyl group. It is interesting that in alkylperfluorovinylmetal chemistry perfluorovinyl groups are preferentially cleaved by acid.[11b] In these compounds cleavage of the highly fluorinated group before the alkyl group is understandable in terms of the effect of hybridization differences on electron density at a particular carbon atom. In the perfluorovinyltin compounds the fluoro-group is bonded to tin through a carbon atom which is sp^2-hybridized, not sp^3 as in the perfluoroalkyl derivatives. The presence of a filled p_π-orbital in the perfluorovinyl derivatives apparently is sufficient to attract the attacking electrophilic reagent.

The infrared spectra of the perfluoroalkyltin and -lead compounds exhibit bands in the C–F stretching region, but as expected the bands are more numerous in the perfluoroethyl than in the perfluoromethyl compounds. Thus Me_3SnCF_3, as a gas, has C–F stretching bands at 1066 and 1152 cm.$^{-1}$, while $Me_3PbC_2F_5$ has similar bands at 1070, 1085, 1198 and 1318 cm.$^{-1}$. Moreover, all of the C_2F_5– compounds have a single band at 927 ± 10 cm.$^{-1}$ due to a carbon–carbon skeletal mode. This band occurs at 917 cm.$^{-1}$ in C_2F_5I. Two broad, intense bands occur in the region near 750 cm.$^{-1}$ in the compounds $(CH_3)_3SnCF_3$ (782, 724 cm.$^{-1}$), $(CH_3)_3SnC_2F_5$ (781, 735 cm.$^{-1}$) and $(CH_3)_3PbC_2F_5$ (784, 733 cm.$^{-1}$). These result, respectively, from the symmetric and antisymmetric methyl rocking vibrations and are observed in all trimethyltin and -lead compounds. Aside from their intrinsic interest, the spectra provided a convenient guide in purifying the compounds and in following purification steps. The exceptional intensity of the C–F bands between 1050 and 1300 cm.$^{-1}$ makes possible the detection of perfluoroalkyl compounds in very low concentrations.

Experimental[14]

Infrared spectra were recorded using a Model 21 Perkin–Elmer double-beam spectrometer with sodium chloride optics. Much of the work described was carried out with the aid of a conventional-type high-vacuum system.

1. **Reaction between Tetraalkyllead Compounds and Perfluoroalkyl Iodides.**—To illustrate the procedure used, the reaction between lead tetramethyl and pentafluoroiodoethane is described. A 4 g. (15 mmoles) sample of tetramethyllead, together with 2–3 g. of 5% zinc amalgam[15] and 1 liter (45 mmoles) of pentafluoroiodoethane were sealed in a one-liter Pyrex bulb. The reaction vessel was heated for 8 hr. at 150°, during which time its interior surface became coated with a yellow powder. The bulb was cooled to −196°, attached to the vacuum line and opened with a tube-opener. Fractionation through traps held at −78, −112 and −196° gave 177 cc.[16] of pentafluoroethane at −196° and 634 cc. of pentafluoroiodoethane at −112°. Both compounds were identified by their infrared spectra. These amounts correspond to an 81% recovery of C_2F_5 groups. The contents of the −78° trap were removed from the vacuum line and chromatographed using a Perkin–Elmer Vapor Fractometer Model 154C containing a column packed with Carbowax 4000 on firebrick. The fractometer was modified to permit safe introduction and collection of toxic materials. Using a column temperature of 65° and a helium flow of 180 cc./min. four peaks were observed (approx. area ratio 2:1:1:4) at elution times of 2, 4, 5.5 and 8–10 minutes. The first peak was identified as resulting from unreacted tetramethyllead. The next two peaks corresponded to the elution of compounds having infrared spectra with no bands in the C–F region. The fourth and largest peak was from $Me_3PbC_2F_5$. Repeated chromatography yielded 2.0 g. (28% yield based on Me_4Pb taken for reaction) of lead compound.

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[11] (a) H. D. Kaesz, S. L. Stafford and F. G. A. Stone, THIS JOURNAL, **81**, 6336 (1959); (b) H. D. Kaesz, S. L. Stafford and F. G. A. Stone, *ibid.*, **82**, 6232 (1960); (c) S. L. Stafford and F. G. A. Stone, in press.

[12] H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955), and references cited therein.

[13] C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1952, p. 207.

[14] Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, New York.

[15] Amalgam or mercury was added in an attempt to remove iodine formed in the decomposition of the perfluoroalkyl iodides. However, comparable yields of product were obtained in some reactions where mercury or an amalgam was not added.

[16] Throughout this paper the abbreviation cc. refers to gases at standard conditions.

Anal. Calcd. for $C_5H_9F_5Pb$: C, 16.2; H, 2.4; F, 25.6; Pb, 55.8. Found: C, 16.3; H, 2.6; F, 25.7; Pb, 55.5.

2. **Reactions between Perfluoroalkyl Iodides and Tetraorganotin Compounds.**—In a representative experiment a mixture of tetramethyltin (5.5 g., 31 mmoles), trifluoroiodomethane (12.4 g., 63 mmoles) and 1 ml. mercury[15] was sealed in a Carius tube. The latter was irradiated with ultraviolet light for 8 hr., during which period the temperature of the Carius tube was near 100°. The reaction mixture turned dark amber, and white crystals were observed on the walls of the tube. Fractionation of the volatile products in the vacuum line, with identification by means of their infrared spectra, afforded 733 cc. (33 mmoles) of fluoroform at −196°, 302 cc. (13.5 mmoles) of trifluoroiodomethane at −150°, 63 cc. (3 mmoles) of methyl iodide at −96° and much liquid held at −78°. The infrared spectrum of this liquid, principally tetramethyltin, showed no bands in the C–F region where Me_3SnCF_3 absorbs strongly. The white crystals were recovered from the Carius tube and identified as trimethyltin fluoride.

Anal. Calcd. for C_3H_9FSn: C, 19.7; H, 5.0; F, 10.3. Found: C, 20.1; H, 5.3 and F, 9.3.

3. **Reactions between Perfluoroalkyl Iodides and Hexaorganoditin Compounds.**—To illustrate the procedure followed, the reaction between hexamethylditin and trifluoroiodomethane is described. A mixture of hexamethylditin (3.32 g., 10.1 mmoles) and trifluoroiodomethane (446 cc., 19.9 mmoles) was sealed in a Carius tube and irradiated with ultraviolet light from a sun lamp for 10 hr. The Carius tube then was cooled to −196°, and the volatile products taken into the vacuum system. Fractionation yielded 186 cc. of a mixture of fluoroform and hexafluoroethane, identified by their infrared spectra, at −196°, and 1.67 g. of liquid at −80°. Chromatography of this liquid yielded 1.10 g. (42% yield) of Me_3SnCF_3.

Anal. Calcd. for $C_4H_9F_3Sn$: C, 20.6; H, 3.9; F, 24.5; mol. wt., 233. Found: C, 20.3; H, 4.1; F, 24.3; mol. wt., 228.

It should be noted that the yield quoted is based on isolation of material with a purity better than 99%. Since the chromatography process resulted in some loss, higher yields of less pure material were actually obtained.

In the preparation of $(C_6H_5)_3SnC_2F_5$ and $Et_3SnC_2F_5$ a different procedure was used. In the case of $(C_6H_5)_3SnC_2F_5$ the desired compound is a solid, which has to be separated from unreacted hexaphenylditin, also a solid. A mixture of hexaphenylditin (20 g., 28.6 mmoles) and pentafluoroiodoethane (7.5 g., 30.5 mmoles) was heated to 220° for 15 hrs. in a steel bomb of 100 ml. capacity. After cooling to room temperature, volatile material was taken into the vacuum system and fractionated. No pentafluoroiodoethane was recovered, but 88.3 cc. (3.94 mmoles) of pentafluoroethane (identified by its infrared spectrum) was collected at −196°. A trace of material, the spectrum of which indicated the presence of phenyl groups, was retained at −96°. Solids were removed from the bomb, placed in a soxhlet, and extracted with 500 ml. of 30–60° petroleum ether for 5 hr. The petroleum ether solution then was titrated with a petroleum ether solution of iodine until the iodine color just persisted. This procedure quantitatively converted unreacted hexaphenylditin to triphenyltin iodide. Dry ammonia gas was then bubbled through the petroleum ether solution for 1 hr. During this time a white precipitate of the ammoniate of triphenyltin iodide[9] formed. The precipitate was removed by filtration and the petroleum ether solution concentrated. Crystals appeared, which were filtered to give 3.1 g. (22% yield based on hexaphenylditin taken for reaction) of $(C_6H_5)_3SnC_2F_5$ (m.p. 127–128°).

It proved impossible to separate effectively $Et_3SnC_2F_5$ from triethyltin iodide by distillation at reduced pressure. Gas chromatography could not be used for purification of $Et_3SnC_2F_5$ because of inordinately long elution times. For this reason Et_3SnI was removed as its ammoniate from $Et_3SnC_2F_5$, using petroleum ether as solvent. Filtration, followed by removal of petroleum ether at reduced pressure, yielded $Et_3SnC_2F_5$.

Analytical data for compounds prepared by cleavage of the M–M bonds in $R_3M{\cdot}MR_3$ are tabulated.

	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
$(C_6H_5)_3SnC_2F_5$	51.2	51.3	3.3	3.2
$Me_3SnC_2F_5$	21.4	21.2	3.2	3.1
$Et_3SnC_2F_5$	29.6	29.7	4.7	4.7
Me_3PbCF_3	17.0	16.4	3.2	3.1

4. **Vapor Pressures of Some Perfluoroalkyltin and -lead Compounds.**—Vapor tensions (using chromatographically pure samples except for $Et_3SnC_2F_5$, see above) were measured using a tensimeter of the type described by Burg and Schlesinger,[17] and are given in Table II. The constants which may be derived from the data in Table II are summarized in Table I.

TABLE II

VAPOR TENSIONS OF SOME PERFLUOROALKYL TIN AND LEAD COMPOUNDS

t, °C.	$p_{mm.}$ (obsd.)	$p_{mm.}$ (calcd.)	t, °C.	$p_{mm.}$ (obsd.)	$p_{mm.}$ (calcd.)
(a)	CF_3SnMe_3		(b)	$C_2F_5SnMe_3$	
3.1	10.9	11.0	22.7	30.5	30.6
14.5	21.0	21.0	28.3	40.1	40.0
25.5	37.3	37.4	34.4	53.0	53.0
28.9	44.5	44.4	38.3	63.0	63.2
30.1	47.0	47.0	42.6	76.0	76.0
45.7	97.6	97.5	47.0	92.0	91.8
49.5	115.0	115.1	56.4	134.5	134.6
(c)	$C_2F_5SnEt_3$		(d)	$C_2F_5PbMe_3$	
30.4	4.8	4.8	22.4	8.8	8.7
40.4	7.9	8.0	26.0	10.5	10.6
49.1	11.8	11.8	30.5	13.2	13.3
55.3	15.6	15.5	36.6	18.1	18.0
60.3	19.3	19.2	45.5	27.6	27.6
65.7	24.2	24.1	50.0	33.8	33.9
70.7	29.6	29.8	55.5	43.2	43.2

5. **Cleavage of Perfluoroalkyltin and -lead Compounds by Base and by Acid. (a) Base Hydrolysis.**—As an example of base hydrolysis an experiment with Me_3SnCF_3 is described. A 0.1583 g. (0.680 mmole) sample of Me_3SnCF_3 was distilled onto aqueous potassium hydroxide in a Pyrex tube which was then sealed off from the vacuum line. As soon as the reaction vessel warmed to near room temperature effervescence was observed. The tube was heated at 65° for 15 hr. and then attached to the vacuum line through a tube-opener. Fractionation gave 14.9 cc. (0.665 mmole) of spectroscopically pure fluoroform. This represents 97.9% recovery of CF_3 groups from Me_3SnCF_3. Under similar base hydrolytic conditions other perfluoroalkylmetal compounds mentioned in this paper all gave more than 90% of their perfluoroalkyl groups as fluorocarbons.

(b) **Protonic Acids.**—In a typical reaction of this type $(C_6H_5)_3SnC_2F_5$ (0.479 g., 1.021 mmoles) was treated with trifluoroacetic acid at 60° for 0.5 hr. On fractionation in the vacuum line no material passed a trap at −78°; therefore, no pentafluoroethane had formed in the reaction. Material retained at −78° was distilled to give 68.5 cc. (3.056 mmoles, equivalent to 99.7% of three phenyl groups) of benzene (purity checked by vapor phase chromatography, and identified by its infrared spectrum).

(c) **Reaction between Boron Trichloride and $Me_3SnC_2F_5$.**—A 0.387 g. (1.375 mmoles) sample of $Me_3SnC_2F_5$ was treated with 99 cc. of boron trichloride for 15 hr. at room temperature. A considerable quantity of white crystals formed. The gas recovered (99 cc.) had an infrared spectrum which showed the presence of boron trichloride and methyldichloroborane and the absence of boron trifluoride. No strong bands were observed in the C–F absorption region. In order to confirm the presence of methyldichloroborane, it was partially converted to methyldifluoroborane by combining the total gas recovered with an equal volume of trimethylamine and then heating the adducts with 81 cc. of boron trifluoride.[18] This treatment gave, after fractionation, 68 cc. of methyldifluoroborane (identified by comparing its infrared spectrum with that of an authentic sample of methyldifluoroborane).

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

(18) F. E. Brinckman and F. G. A. Stone, *Chem. Ind. (London)*, 254 (1959).

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

Synthesis and Cleavage of Perfluorovinyltin Compounds[1,2]

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The preparation and some properties of a series of tin compounds containing the $CF_2:CF-Sn$ group are described. Studies described here, in conjunction with those reported elsewhere, show that ease of cleavage of organic-groups from tin by protonic acids is in the sequence: perfluorovinyl $\simeq$ phenyl > vinyl > alkyl > perfluoroalkyl.

Previous work in this Laboratory has established that a variety of R_4Sn compounds, where R is alkyl, aryl, allyl or vinyl, react with boron halides to give organohaloboranes.[4] However, when the recently reported perfluoroalkyltin compounds, R_FSnR_3, were heated with boron trichloride, alkylchloroboranes rather than perfluoroalkylchloroboranes were formed.[5] Moreover, symmetrical perfluoroethyltin compounds, $(C_2F_5)_2SnR_2$ [R = CH_3, n-C_4H_9], do not react detectably with boron trichloride in the absence of a solvent even at elevated temperatures.[6] Protonic acids also cleaved alkyl rather than perfluoroalkyl groups from alkylperfluoroalkyltin compounds. The resistance of perfluoroalkyl groups bonded to tin to cleavage by acids led us to consider the probable effect of acids on perfluorovinyltin compounds. In contrast to perfluoroalkyltin compounds, the fluoro-organic group in these substances would be bonded to tin through an sp^2-hybridized carbon atom. The filled p_π-orbital of this carbon atom would attract acidic reagents and, therefore, the perfluorovinyl group should be removed easily from tin in electrophilic attack. Furthermore, if this supposition proved correct, perfluorovinyltin compounds should be useful reagents for making perfluorovinylboron compounds. Such boron compounds are of particular interest since an examination of their thermal stability would permit a test of the suggestion[5,7] that a boron compound having a highly fluorinated organic group bonded to boron would tend to decompose to boron trifluoride, a compound in which the boron p_π-orbital appears relatively well saturated.[8] These considerations led us to attempt the preparation of the hitherto unreported perfluorovinyltin compounds.

Since many organotin compounds can be made by treating tin halides with the appropriate Grignard reagent, it seemed probable that a Grignard reagent of a perfluorovinyl halide could be used to make the desired tin compounds. A diethyl ether solution of the Grignard reagent $CF_2:CFMgI$ has been reported previously,[9] but the iodide from which it is derived is rare. Bromotrifluoroethylene, however, is commercially available, and using tetrahydrofuran as solvent was found to react readily with magnesium. During the course of our work formation of $CF_2:CFMgBr$ with tetrahydrofuran as solvent was reported independently by Knunyants, *et al.*[10] The Russian workers have used perfluorovinylmagnesium bromide to prepare bis-(perfluorovinyl)-mercury[11a] and tetrakis-(perfluorovinyl)-silicon.[11b] In this Laboratory we have found that reactions like

$$Me_2SnCl_2 + 2CF_2{=}CFBr \xrightarrow{Mg/(CH_2)_4O} Me_2Sn(CF:CF_2)_2 + MgBr_2 + MgCl_2$$

proceed in good yield, and in this manner the compounds listed in Table I were prepared.

Experimental

1. **Starting Materials and Apparatus.**—We are indebted to Metal and Thermit Corporation for a gift of the alkyl- and phenyltin chlorides used in this work. Bromotrifluoroethylene was obtained from Columbia Organic Chemicals, and its purity was checked by gas chromatography before use.

Infrared spectra were recorded using a Model 21 Perkin-Elmer double-beam spectrometer with sodium chloride optics. Spectra of gases were recorded using 4 cm. cells. Conventional high-vacuum systems were used to evaluate reaction products.

2. **Preparation of Perfluorovinyltin Compounds.**—As an example of the procedure, the preparation of bis-(perfluorovinyl)-dimethyltin is described here.

A three-neck one-liter flask was fitted with a reflux condenser, Trubore stirrer and gas inlet tube. The exit of the condenser was connected to a manometer and through traps to a vacuum pump. The apparatus was flushed with nitrogen and freshly distilled tetrahydrofuran (500 ml.) and dimethyltin dichloride (34.2 g., 0.155 mole) added. The reaction flask then was cooled to 0° and magnesium (9.1 g., 0.37 g. atom) added. A weighing tube containing

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