Acknowledgment.—We are indebted to the Ethyl Corporation for supplying samples of tetramethyl- and tetraethyllead and to Metal and Thermit Corporation for a gift of hexaphenylditin.

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

Synthesis and Cleavage of Perfluorovinyltin Compounds[1,2]

BY H. D. KAESZ, S. L. STAFFORD[3] AND F. G. A. STONE

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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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(2) Presented at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960. For a preliminary communication, see H. D. Kaesz, S. L. Stafford and F. G. A. Stone, THIS JOURNAL, **81**, 6336 (1959).

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TABLE I

PERFLUOROVINYLTIN COMPOUNDS PREPARED BY THE GRIGNARD METHOD

Compound	Boiling range, °C.	Boiling range, mm.	Yield, %	Carbon, %[a] Calcd.	Carbon, %[a] Found	Hydrogen, %[a] Calcd.	Hydrogen, %[a] Found	Perfluorovinyl groups per tin atom[b] Calcd.	Perfluorovinyl groups per tin atom[b] Found
$(CF_2:CF)_4Sn$	52–54	19	31	..	..	..	..	4.0	3.84
$(CH_3)_2Sn(CF:CF_2)_2$	59–61	40	65	23.2	22.9	1.93	1.9	2.0	1.92
$(n\text{-}C_4H_9)_2Sn(CF:CF_2)_2$	60–63	0.4	72	36.5	36.4	4.56	4.5	2.0	2.0
$(n\text{-}C_4H_9)_3SnCF:CF_2$	81–82	0.4	63	45.3	45.5	7.3	7.2	1.0	0.97[c]
$(CH_2:CH)_2Sn(CF:CF_2)_2$	51–53	10	46	28.7	28.8	1.8	1.6	2.0	1.98
$(C_6H_5)_2Sn(CF:CF_2)_2$	75–80	0.02	67	44.2	43.7	2.3	2.1	..	..

[a] Microanalyses were performed by Dr. Carol Fitz, Needham Heights, Mass. [b] Determined by cleavage with trifluoroacetic acid to give a measured volume of trifloroethylene, identified by its infrared spectrum. [c] Normal butane is also a reaction product.

54.1 g. (0.336 mole) of bromotrifluoroethylene was attached to the gas inlet tube, and the apparatus then was evacuated until the pressure remaining was due only to tetrahydrofuran vapor. Bromotrifluoroethylene was introduced slowly. Evolution of heat, and accompanying pressure rise, indicated that initiation of Grignard formation had occurred. Rate of addition and cooling were adjusted so as to maintain the reaction flask near 40°, the temperature determined approximately from the vapor pressure of tetrahydrofuran, as shown on the manometer. When addition of bromotrifluoroethylene was completed, the ice-bath was replaced by a heating mantle and the reaction flask was heated at 45–50° for 15 hr. On cooling, all volatile material was removed into a distillation flask at −78° by pumping at 10^{-1} mm. Liquid obtained was then distilled at reduced pressure through a Vigreux column. Tetrahydrofuran was removed at 31° (208 mm.), after which $Me_2Sn(CF:CF_2)_2$ (31.4 g., 65% yield) was collected at 59–61° (40 mm.).

Analytical data for bis-(perfluorovinyl)-dimethyltin are given in Table I, along with similar data, and yields obtained, for other perfluorovinyltin compounds. The latter were all prepared by a technique similar to that described above. For the preparation of $(CF_2:CF)_4Sn$, tin tetrachloride was used. This halide forms a complex with tetrahydrofuran which is insoluble in excess of the ether. However, the adduct of tin tetrachloride and tetrahydrofuran, as a slurry in excess tetrahydrofuran, reacted with $CF_2:CFMgBr$ without difficulty.

3. Cleavage of Perfluorovinyltin Compounds with Hydrogen Chloride.—A study of the effect of acids on dialkyl-bis-(perfluorovinyl)-tin compounds established that perfluorovinyl groups were cleaved quantitatively with formation of R_2SnX_2 derivatives. For the purpose of placing the $CF_2:CF-$ group in the cleavage series, the effect of hydrogen chloride on the two symmetrical compounds $(CF_2:CF)_2Sn(CH:CH_2)_2$ and $(CF_2:CF)_2Sn(C_6H_5)_2$ was investigated. For cleavage studies of this type the purity of the starting materials is very important. Diphenyltin dichloride (Found: C, 41.9; H, 2.9. $C_{12}H_{10}Cl_2Sn$ requires C, 41.9; H, 2.9) was recrystallized twice before being converted to bis-(perfluorovinyl)-diphenyltin. Samples of bis-(perfluorovinyl)-divinyltin used in cleavage studies were purified by gas chromatography.[12] In this manner material studied had a minimum purity of 99%.

The procedure followed in the cleavage studies was different from that used previously in work of this type in that the course of the cleavage was followed by analyzing and measuring the volatile hydrocarbons formed, rather than isolating the organotin salts produced, or absorbing the olefins released in bromine. By use of high-vacuum techniques we were able to measure accurately the amount of cleaving reagent, determine how far cleavage had occurred at a given temperature, and examine the hydrocarbons produced very precisely by infrared spectroscopy and vapor phase chromatography.

In general, a weighed sample of the tin compound to be cleaved was introduced into a bulb of 170 cc. capacity attached to the vacuum line. A sample of hydrogen chloride of known volume, approximately equivalent to the tin compound, then was distilled into the bulb and allowed to react for a certain time. Unreacted hydrogen chloride together with the volatile cleavage products then was removed from the bulb. Treatment of the gases with solid sodium hydroxide removed hydrogen chloride, and after drying the remaining gas was measured, identified spectroscopically and analyzed by gas chromatography. The tin compound remaining in the bulb was treated with additional increments of hydrogen chloride, and the products evaluated in the same way. Results of some representative cleavage studies are given in Table II. Acid cleavage of the compound $(C_6H_5)_2Sn(CH:CH_2)_2$ has been studied previously in an investigation which placed the vinyl group in the cleavage series.[12a] The cleavage was repeated here by the new technique to determine whether the first increment of hydrogen chloride cleaved any vinyl groups at all.

TABLE II

CLEAVAGE OF ORGANOTIN COMPOUNDS BY HYDROGEN CHLORIDE

	1	2	3	4	5
	$(C_6H_5)_2Sn(CF:CF_2)_2$[a]				
Increments of HCl gas taken for reaction (cc.)[b]	144	144	144	144	144
Percentage HCl consumed	77	61	39	22	11
$CF_2:CFH$ formed (cc.)	56.2	53.4	41.4	22.7	12.9
$CF_2:CFH$ formed as percentage[c]	51	60	73	73	85
C_6H_6 formed (cc.)	54	35	15	8.3	2.3
C_6H_6 formed as percentage[c]	49	40	27	27	15
	$(CH_2:CH)_2Sn(CF:CF_2)_2$[d]				
Increments of HCl gas taken for reaction (cc.)[b]	113	113	113	113	...
Percentage HCl consumed	86	97	25	14	...
$CF_2:CFH$ formed (cc.)	94.6	104.3	23.8	4.7	...
$CF_2:CFH$ formed as percentage[c]	97	95	84	29	...
$CH_2:CH_2$ formed (cc.)	2.9	5.5	4.5	11.6	...
$CH_2:CH_2$ formed as percentage[c]	3	5	16	71	...
	$(CH_2:CH)_2Sn(C_6H_5)_2$[e]				
Increments of HCl gas taken for reaction (cc.)[b]	105	105	105	105	..
Percentage HCl consumed	92	96	66	27	..
C_6H_6 formed (cc.)	81.1	75.6	34.7	9.7	..
C_6H_6 formed as percentage[c]	84	75	50	34	..
$CH_2:CH_2$ formed (cc.)	15.5	25.2	34.6	18.7	..
$CH_2:CH_2$ formed as percentage[c]	16	25	50	66	...

[a] Quantity taken for reaction, 2.793 g. (6.42 mmoles) equivalent to 143.8 cc. at S.T.P; runs 1 through 4 were 24 hr. periods at 25°, for run 5 mixture was heated at 60° for 6 hr. [b] Abbreviation cc. refers to gas at standard conditions. [c] Percentage of total hydrocarbons produced. [d] Quantity taken for reaction, 1.682 g. (5.02 mmoles) equivalent to 112.4 cc. at S.T.P.; runs 1 through 3 were 6 hr. periods at 25°, for run 4 mixture was heated at 60° for 6 hr. [e] Quantity taken for reaction, 1.644 g. (5.03 mmoles) equivalent to 112.7 cc. at S.T.P.; runs 1 through 4 were heated at 60° for 6 hr.

4. Comparative Reactivities of Vinyl and Perfluorovinyl Groups.—Samples of $(CF_2:CF)_4Sn$ can be highly purified by vapor phase chromatography.[12] A column of paraffin on firebrick is satisfactory. At 62°, with a helium flow of 200 cc. per minute, retention times for $(CF_2:CF)_4Sn$

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[12] A Perkin-Elmer Model 154-C Vapor Fractometer, modified for the collection of air-sensitive materials, was used.

[12a] F. Seyferth, THIS JOURNAL, **79**, 2133 (1957).

and $CF_2:CFSnCl_3$ are 6 and 10 minutes, respectively, compared to tin tetrachloride which has a retention time of 21 minutes. Samples purified in this manner were used to compare the relative reactivities of vinyl and perfluorovinyl groups bonded to tin. The results are summarized in Table III.

TABLE III

DECOMPOSITION STUDIES ON $(CF_2:CF)_4Sn$ AND $(CH_2:CH)_4Sn$

Reagent	Conditions Time (hr.)	Temp. (°C.)	% Decomposition measured in terms of $CF_2:CFH$[a] from $(CF_2:CF)_4$-Sn	$CH_2:CH_2$[a] from $(CH_2:CH)_4$-Sn
Hydrogen chloride gas	60	100	96	82
Trifluoroacetic acid	15	100	..	74.8
	60	100	94	74.8[b]
Sodium hydroxide solution (20%)	60	100	96.5	6.5
Water	50	25	3	0
	60	100	66	7

[a] A high-vacuum system was used for these studies. Gases were manipulated quantitatively and identified by their infrared spectra, after having been purified by fractional condensation. [b] Only three vinyl groups cleaved even over a long period.

5. **Infrared Spectra.**—The infrared spectra of the new perfluorovinyltin compounds[13] in the region 3000–700 cm.$^{-1}$ show four very strong bands due to the $CF_2:CF-$ group. When the spectrum of a neat liquid film of a perfluorovinyltin compound is taken, absorptions due to the perfluorovinyl group are so intense that the band centers are off the intensity scale (Table IV, line 1). When spectra are taken in carbon disulfide or tetrachloroethylene, using dilute solutions, the broad off-scale bands are resolved (Table IV).

TABLE IV

INFRARED ABSORPTIONS OF THE PERFLUOROVINYL GROUP IN REPRESENTATIVE TIN COMPOUNDS[a]

Compound	C=C stretch (cm.$^{-1}$)	C–F stretch (cm.$^{-1}$)		
All $CF_2:CF-Sn$[b]	1770–1710	1340–1240	1190–1080	1030–980
$(CF_2:CF)_4Sn$	1725	1305, 1290	1160, 1147, 1136	1013
$(CF_2:CF)_2Sn(CH:CH_2)_2$	1722	1297, 1285	1160, 1140, 1125	1008
$(CF_2:CF)_2Sn(CH_3)_2$	1719	1284, 1272	1151, 1128, 1113	1005
$(CF_2:CF)_2Sn(C_6H_5)_2$	1719	1287, 1277	1155, 1131, 1117	1008
$(CF_2:CF)_2Sn(C_4H_9)_2$	1727	1290, 1278	1155, 1128, 1115	1005

[a] Measured both in CS_2 and C_2Cl_4 solutions. [b] As neat liquids, 0.015 mm. thick.

Discussion

The new perfluorovinyltin compounds are all clear, colorless liquids, having chemical properties markedly different from ordinary vinyltin compounds.[14] Thus, when exposed to air the perfluorovinyl derivatives slowly deposit white or pale yellow solids. In the case of bis-(perfluorovinyl)-dimethyltin, analytical data for the solid after increasing exposure times indicated that initial polymerization was followed by oxidation or hydrolysis of the polymer to varying degrees, ultimately resulting in dimethyltin oxide. However, in the presence of dry oxygen a different mode of instability was observed. Thus tetrakis-(perfluorovinyl)-tin sealed in a bulb under oxygen at 500 mm. pressure solidified in two days to a waxy white solid. On opening the reaction bulb to the vacuum line, the only volatile products, besides oxygen, were small quantities of carbonyl fluoride and trifluoroacetyl fluoride, representing less than 10% of the fluorine content of the perfluorovinyl groups originally present. The white wax-like solid remaining in the bulb must have been a polymer of $(CF_2:CF)_4Sn$, which was relatively stable to oxidation, but it was not investigated further. Tetravinyltin and related vinyltin compounds are not oxygen sensitive. Moreover, perfluorovinyltin compounds are much more easily cleaved than vinyltin compounds by base, and by warm water. Results of some comparative studies on the two compounds $(CF_2:CF)_4Sn$ and $(CH_2:CH)_4Sn$ are summarized in Table III.

In the complete absence of air, moisture, acid or base, perfluorovinyltin compounds appear to be as thermally stable as their vinyl analogs. A sample of tetrakis-(perfluorovinyl)-tin was heated in a small bulb at 150° for 6 hr. and was then recovered unchanged.

Previous workers[12a,15] have shown that cleavage of organo-groups from R_2SnR_2' compounds is in the order

$$C_6H_5 > CH_2:CH > CH_3 > C_2H_5 > n\text{-}C_3H_7 > n\text{-}C_4H_9$$

The results summarized in Table II establish that with hydrogen chloride the $CF_2{=}CF{-}$ group is equal to the phenyl in the cleavage series. As has been described elsewhere,[6] acid cleavage of the compound $(n\text{-}C_4H_9)_2Sn(C_2F_5)_2$ also has been studied in this Laboratory. Di-*n*-butyl-bis-(perfluoroethyl)-tin is essentially inert to hydrogen chloride at 60°. However, with trifluoroacetic acid at 80° $(n\text{-}C_4H_9)_2Sn(C_2F_5)_2$ affords small quantities of *n*-butane but no pentafluoroethane. These results permit extension of the cleavage series for tin to include the perfluoro- groups C_2F_3- and C_2F_5-

$$CF_2:CF \simeq C_6H_5 > CH_2:CH > \text{alkyl} > C_2F_5$$

A possible reason for the very different behaviors of the $CF_2:CF-Sn$ and C_2F_5-Sn groups toward protonic acids has been discussed previously.[2,5]

Although it is well known that for purposes of placing a group in the cleavage series only the results for cleavage of the first group from an R_2SnR_2' compound should be taken into account, the relative order of cleavage of subsequent groups brings forth some interesting facets of the nature of certain types of tin–carbon bond. The compound $(C_6H_5)_2Sn(CF:CF_2)_2$ when first treated with an equivalent amount of hydrogen chloride yields essentially equal amounts of benzene and trifluoroethylene. However, when a second equivalent of hydrogen chloride is added, although not statistically less favored, less benzene is produced. Succeeding increments of hydrogen chloride continue to cleave $CF_2:CF$ groups in preference to C_6H_5 groups, in spite of the unfavorable probability factor. There is thus some stabilizing effect which seems to be operating which causes phenyl groups to be less easily cleaved than perfluorovinyl in tin compounds *in which tin atoms are bonded to chlorine atoms.*

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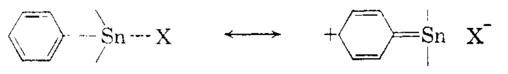
(13) For a reproduction of some of these spectra, as well as a review of the chemistry of vinylmetallic compounds, see H. D. Kaesz and F. G. A. Stone, "Vinylmetallics," A.C.S. Monograph on Organometallic Compounds, Edited by H. Zeiss, Reinhold Publishing Co., New York, N. Y., 1960, chapter 3.

(14) (a) A. D. Petrov and V. F. Mironov, *Izvest. Akad. Nauk S.S.S.R., Otdel khim. Nauk*, 1491 (1957). (b) D. Seyferth and F. G. A. Stone, THIS JOURNAL, **79**, 515 (1957). (c) S. D. Rosenberg, A. J. Gibbons and H. E. Ramsden, *ibid.*, **79**, 2137 (1957).

(15) See G. E. Coates, "Organometallic Compounds," Methuen, London, 1956, and references cited therein.

Perhaps an explanation for this behavior can be sought in the polar character of the tin–halogen bond in organotin halides, in which tin carries a positive charge.[15] The presence of the positive charge may contract the vacant *d*-orbitals of tin enough to permit conjugation with an organo-group, provided the organo-group has electrons in π-orbitals. Because greater electron delocalization would be involved, a phenyl group should conjugate with a tin atom more effectively than a perfluorovinyl group, so that the tin–phenyl bond in phenyltin halides would be strengthened over that in the neutral $(C_6H_5)_2SnR_2$ derivatives.



(three forms)

It is interesting to note in passing that resonance of this type in phenyltin halides has been postulated to account for their spectroscopic properties.[16] The situation with tin may be somewhat analogous to that in phosphorus chemistry. In neutral tetracoördinate phosphorus compounds *d*-orbital resonance does not appear to be important.[17a,b] However, if in a tetracoördinate phosphorus compound the phosphorus atom carries a positive charge, the idea that phosphorus *d*-orbitals are used in bonding accounts for certain properties.[17c] In neutral tetracoördinate tin compounds the tin *d*-orbitals may be too diffuse to be involved in bonding, at least in the ground state.

A subsequent paper will describe how perfluorovinyltin compounds can be used to prepare perfluorovinylboron halides such as $(CF_2{:}CF)_2BCl$ (b.p. extrap. 100.5°).

[16] V. S. Griffiths and G. A. W. Derwish, *J. Molec. Spectroscopy*, **3**, 165 (1959).

[17] (a) J. R. Van Wazer, This Journal, **78**, 5709 (1956). (b) H. D. Kaesz and F. G. A. Stone, *ibid.*, **82**, 6213 (1960). (c) W. von E. Doering and A. K. Hoffmann, *ibid.*, **77**, 521 (1955).

[Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts]

Organoboron Halides. IV. Exchange Reactions with Boron Trihalides[1,2]

By F. E. Brinckman[3] and F. G. A. Stone

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A mass spectrometric study has been made of a series of exchange reactions between boron trifluoride and organoboron halides, RBX_2 or R_2BX (X = Cl, Br). By using isotopically enriched boron trifluoride in these reactions, it was established that the mechanism does not involve rupture of boron–carbon bonds. Mass spectrometric evidence was obtained for the existence of species RB(F)X (X = Cl, Br).

Binary mixtures of boron trihalides equilibrate to form mixed boron halides such as BF_2Cl, $BBrCl_2$, *etc.*, establishing that halogen exchange between boron atoms readily occurs.[4] Organo-groups in unsymmetrical triorganoborines are also very labile, and compounds such as Me_2BEt have only a transitory existence even at low temperatures.[5] Disproportionation reactions also occur reversibly in organoboron halides.[6] However, these exchange reactions, involving both halogen and organo-group transfer from one boron atom to another, usually require the action of heat for their occurrence. Related to the disproportionation of organoboron halides, in the sense that exchange reactions occur, is the preparation of these compounds by heating mixtures of boron trihalides with triorganoboron compounds.[6,7]

The work described above prompted us to study reactions between organoboron halides and boron trihalides at temperatures below those which would normally bring about disproportionation of organoboron halides. Exchange processes would be expected to occur, but it was not possible to predict whether the reactions would be readily reversed or whether the exchange mechanism would involve halogen transfer only or whether organo-group transfer followed by halogen transfer would take place. Reactions such as

$$3EtBF_2 + 2BCl_3 = 3EtBCl_2 + 2BF_3$$

$$3Me_2BCl + BF_3 = 3Me_2BF + BCl_3$$

proved to be readily reversible, but the equilibria were not too labile to prevent isolation by fractional distillation of the compounds indicated in the equations. This is in contrast to the very labile equilibria involved in binary mixtures of boron trihalides. A mass spectrometric study of the reactions was made both to determine what kinds of atoms or groups were involved in the exchange and to obtain evidence for the existence of mixed species of the type RB(Cl)F.

Experimental

1. **Apparatus and Starting Materials.**—The organoboron halides used in this work were prepared from organotin compounds as previously described.[8] Boron trihalides were commercial samples purified by standard techniques. Boron trifluoride enriched in ^{10}B isotope was obtained by

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[1] Previous paper, T. D. Coyle and F. G. A. Stone, This Journal, **82**, 6223 (1960).

[2] The work described in this paper was made possible by the award of a Grant (G5106) from the National Science Foundation.

[3] Public Health Predoctoral Fellow of the National Cancer Institute.

[4] (a) L. P. Lindemann and M. K. Wilson, *J. Chem. Phys.*, **24**, 242 (1956); (b) R. E. Nightingale and B. Crawford, *ibid.*, **22**, 1468 (1954); T. H. S. Higgins, E. C. Leisegang, C. J. G. Raw and A. J. Rossouw, *ibid.*, **23**, 1544 (1955); (c) T. D. Coyle and F. G. A. Stone, *ibid.*, **32**, 1892 (1960); (d) L. H. Long and D. Dollimore, *J. Chem. Soc.*, 4457 (1954); (e) J. Goubeau, D. E. Richter and H. J. Becher, *Z. anorg. Chem.*, **278**, 12 (1955).

[5] T. D. Parsons, M. B. Silverman and D. M. Ritter, This Journal, **79**, 5091 (1957), and references cited therein.

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[7] V. W. Buls, O. L. Davis and R. I. Thomas, *ibid.*, **79**, 337 (1957).

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