yielded 8.8 g. of *o*-xylene. There was thus a 90.3% conversion of xylene, an 8.3% yield of benzoic acid, a 1.0% yield of thiophthalide, and a 45.1% yield of phthalic acid.

Run 18, Table II. The procedure followed that with the other xylenes and sulfur dioxide, except that a 1096-g. aliquot of the liquid phase of the reaction mixture was withdrawn at reaction temperature into ice (Aliquot B) and the remainder removed after cooling the autoclave to room temperature and releasing the hydrogen sulfide (Aliquot A). Using the same isolation procedure as that for *o*-xylene-sulfur reaction products, there was obtained from B, 15.5 g. of sulfur; 6.1 g. of a solid, red neutral by-product; 11.9 g. of benzoic acid; 18.1 g. of thiophthalide; and 200.0 g. of *o*-phthalic acid. From A was obtained 59.4 g. of sulfur, 63.6 g. of black neutral solids, 8.4 g. of benzoic acid, 13.2 g. of toluic acid, 72.7 g. of thiophthalide, and 156.1 g. of phthalic acid. The xylene conversion was 100%, with over-all yields of 4.1% benzoic and 2.5% toluic acids, 15.2% thiophthalide, and 53.5% phthalic acid. The molar ratio of phthalic acid to thiophthalide in B versus A is 10:1 versus 2:1 showing the effect of hydrogen sulfide on the equilibrium.

The extent to which phthalic acid can be favored using sulfur dioxide as the oxidant is illustrated by Experiment 20, Table II.

Oxidation of durene. The technique followed that with the xylene and sulfur dioxide. All liquid products were released while still hot into 8000 g. of ice. This mixture was filtered hot (80°) to give 103 g. of brown solids containing 77.7% free sulfur. The filtrate was neutralized to *p*H 7 with 109.5 g. of sodium hydroxide and evaporated to dryness, leaving 263 g. of yellow solids. These were taken up in hot water (400 cc.), carbon treated, acidified with hydrochloric acid to *p*H 1, chilled, and filtered. The washed and dried crystallized pyromellitic acid weighed 134 g., neutral equivalent 64.2 (theory = 63.5). Sublimation of a small sample gave pyromellitic anhydride, which after crystallization from acetone had a neutral equivalent of 54.5.

Reduction of m-toluic acid. The autoclave was charged with 1800 ml. of water, 340 g. of 95% *m*-toluic acid containing 0.55% benzoic acid, and 442 g. of hydrogen sulfide and heated with shaking to 340° for 1 hr. The pressure reached 293 atm. After cooling to room temperature, hydrogen sulfide was released and products were steam distilled to give 5.8 g. of an organic phase which, after washing with dilute caustic and drying, was analyzed by mass spectrography. It contained 76.7% xylene and 21.1% toluene as the major constituents. Filtration of the steam distillation residue gave 295.2 g. of dry solids containing 2.0 g. of elemental sulfur by analysis, 277.0 g. of *m*-toluic acid by isolation, and 0.41 g. of benzoic acid by analysis.

Identification of thiophthalide. In addition to the boiling point, this compound was identified from numerous experiments by first purifying by steam distillation followed by recrystallization from water to give a product with melting point 58.6–58.8°, saponification equivalent 146.4 (theory 150.19).

Anal. Calcd. for C_8H_6OS: C, 63.97; H, 4.03; S, 21.35. Found: C, 63.75, 63.85; H, 4.05, 4.23; S, 21.0; 21.4.

RICHMOND, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Vinyl Derivatives of the Metals. IX. Cleavage Reactions of Perfluorovinyltin Compounds[1,2]

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The preparation of seven new perfluorovinyltin compounds by a Barbier-type reaction of bromotrifluoroethylene, the respective organotin chloride and magnesium in tetrahydrofuran solution is described. Cleavage of the perfluorovinyl group in these compounds could be effected by their reaction with ethanol, acetic acid, hydrogen bromide, iodine, triphenyltin hydride, and alcoholic sodium ethoxide. The following new organotin compounds were prepared during the course of these cleavage studies: diethyl- and di-*n*-butyldiethoxytin, tri-*n*-butylethoxytin, di-*n*-butyltin diiodide, diethyl- and di-*n*-butyltin basic fluorides.

The recent development of the perfluorovinyl Grignard reagents, $CF_2{=}CFMgI$[3] and $CF_2{=}CFMgBr$,[4] has made possible studies in the field of perfluorovinyl-metal compounds. Such studies would be of particular interest, since the chemistry of organometallic compounds containing the vinyl group has been developed extensively in the last four years, thus permitting a comparison between the $M{-}CH{=}CH_2$ and the $M{-}CF{=}CF_2$ systems.

We report here a brief study of perfluorovinyl derivatives of tin. Our early work showed that perfluorovinyltin compounds can be prepared by the reaction of preformed $CF_2{=}CFMgBr$ in tetrahydrofuran (THF) with organotin chlorides. However, special precautions with regard to temperature and reagent concentration are required in the preparation of perfluorovinylmagnesium bromide in this solvent, and yields of $CF_2{=}CFMgBr$ at best were only 50–60%. Yields of products obtained in subsequent coupling reactions also were *ca.* 50–60%, and thus a low over-all yield, based on the expensive bromotrifluoroethylene, made this procedure fairly unattractive. However, it was found that such perfluorovinylations could be carried out readily using a Barbier-type procedure, in which a mixture of bromotrifluoroethylene in slight excess and the organotin chloride to be perfluorovinylated in tetrahydrofuran solution is added to a rapidly

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(1) Preliminary communication: D. Seyferth, K. A. Brändle, and G. Raab, *Angew Chem.*, **72**, 77 (1960).

(2) Part VIII of this series: D. Seyferth, *J. Am. Chem. Soc.*, **81**, 1844 (1959).

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TABLE I

PERFLUOROVINYLTIN COMPOUNDS

Compound	B.P., mm.	n_D^{25}	d_4^{25}	Carbon, %		Hydrogen, %		Fluorine, %		Tin, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$(C_2H_5)_3SnCF{=}CF_2$	66–67°/12	1.4392	1.401	33.49	33.66	5.27	5.49	19.87	19.54	41.38	41.10
$(C_2H_5)_2Sn(CF{=}CF_2)_2$	55–57°/12	1.4168	1.595	28.35	28.52	2.97	3.00	33.64	33.26		
$(C_4H_9)_3SnCF{=}CF_2$	73°/0.2	1.4512		45.32	44.98	7.34	7.36	15.36	15.04		
$(C_4H_9)_2Sn(CF{=}CF_2)_2$	53°/0.2	1.4283	1.404	36.49	36.60	4.59	4.66	28.86	29.46	30.05	29.3
$C_4H_9Sn(CF{=}CF_2)_3$	44–45°/1.3	1.4049	1.685	28.67	28.93	2.17	2.34	40.82	40.26		
$(C_6H_5)_3SnCF{=}CF_2$	M.p. 68°			55.73	55.94	3.51	3.56			27.54	27.50
$C_6H_5Sn(CF{=}CF_2)_3$	60°/0.65	1.4567	1.614	32.84	33.18	1.15	1.19	38.97	38.71		

stirred suspension of magnesium turnings in tetrahydrofuran at −10° to −15°. These reactions proceeded smoothly, and yields of perfluorovinyltin compounds ranging from *ca.* 50% to 80% were obtained. In general, the best yields resulted in the perfluorovinylation of triorganotin halides, the poorest in the complete perfluorovinylation of organotin trihalides. The compounds thus prepared are listed in Table I.

The electrophilic cleavage of vinyltin compounds has been examined in detail,[5] and it was found that protonic acids and the halogens cleave the carbon-tin bond in the $-\overset{|}{\underset{|}{Sn}}-CH{=}CH_2$ system quite readily, the vinyl group being intermediate between the phenyl group and the methyl group in the cleavage series. The rates of such cleavage reactions were found to increase with the acid strength of the cleavage reagent when protonic acids were used.[5a,c] It might be expected that the perfluorovinyl group would be cleaved more readily from a tin atom than the vinyl group itself, and this was found to be the case. Thus, the cleavage of tri-*n*-butylperfluorovinyltin with acetic acid proceeded much more readily than the cleavage of tri-*n*-propylvinyltin by the same reagent. Stronger acids, such as hydrogen bromide, caused ready fission of the $-\overset{|}{\underset{|}{Sn}}-CF{=}CF_2$ linkage. Cleavage of perfluorovinyl groups from tin with bromine and iodine was easily effected; cleavage with mercuric chloride in ether solution resulted in perfluorovinylmercuric chloride.

The ready cleavage of the perfluorovinyl group from a tin atom complicated the purification of perfluorovinyltin compounds. A convenient method of purifying tetraorganotin compounds contaminated with minor amounts of organotin halides uses treatment of the crude material with aqueous–alcoholic potassium fluoride solution to precipitate the organotin halides as the insoluble fluorides.[6] This method can be applied successfully to the purification of $R_3SnCF{=}CF_2$ compounds, but if two or more perfluorovinyl groups were present in the molecule, this procedure was not applicable. Treatment of pure di-*n*-butyldiperfluorovinyltin in ether solution with potassium fluoride solution caused partial cleavage, and ether-soluble di-*n*-butyltin oxide was formed. The action of potassium fluoride solution on crude diethyl- and di-*n*-butyldiperfluorovinyltin containing $R_2(CF_2{=}CF)SnCl$ impurities precipitated diethyl- and di-*n*-butyltin basic fluorides, members of a class of compounds not reported previously, and either partially or totally destroyed the $R_2Sn(CF{=}CF_2)_2$ compounds.

$$2\,R_2Sn(CF{=}CF_2)Cl + 2F^- + H_2O \longrightarrow \underset{\underset{F}{|}}{R_2Sn}-O-\underset{\underset{F}{|}}{SnR_2} + 2\,Cl^- + 2\,C_2F_3H$$

Ethanol alone, toward which vinyltin compounds are stable, caused cleavage of perfluorovinyl groups from tin in some cases. Thus, when an ethanolic solution of di-*n*-butyldiperfluorovinyltin was heated at reflux for twenty hours, di-*n*-butyldiethoxytin was produced in almost quantitative yield. The reactivity toward alcohol proved to be a function of the number of perfluorovinyl groups present in the molecule. Triethylperfluorovinyltin and triphenylperfluorovinyltin were not attacked by ethanol under comparable conditions. However, the reaction of alcoholic sodium ethoxide with tri-*n*-butylperfluorovinyltin gave tri-*n*-butylethoxytin in good yield.

The action of organolithium reagents on perfluorovinyltin compounds also resulted in a cleavage reaction giving the new perfluorovinyllithium reagent.[7] This reaction will be discussed in detail in a later publication. Triphenyltin hydride, which is known to add to the carbon-carbon double bond of triphenylvinyltin,[8] reacted with triphenylperfluorovinyltin to give hexaphenylditin instead of 1,1,2-trifluoro-1,2-bis(triphenylstannyl)ethane.

$$(C_6H_5)_3SnH + (C_6H_5)_3SnCF{=}CF_2 \longrightarrow (C_6H_5)_3SnSn(C_6H_5)_3 + C_2F_3H$$

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[5] (a) D. Seyferth, *J. Am. Chem. Soc.*, **79**, 2133 (1957); (b) S. D. Rosenberg and A. J. Gibbons, *J. Am. Chem. Soc.*, **79**, 2138 (1957); (c) A. Saitow, E. G. Rochow, and D. Seyferth, *J. Org. Chem.*, **23**, 116 (1958).

[6] E. Krause, *Ber.*, **51**, 1447 (1918).

[7] D. Seyferth, T. Wada, and G. Raab, *Tetrahedron Letters*, No. 22, 20 (1960).

[8] M. C. Henry and J. G. Noltes, *J. Am. Chem. Soc.*, **82**, 558 (1960).

TABLE II

REACTIONS OF PERFLUOROVINYL- AND VINYLTIN COMPOUNDS

Reagent	Reaction Observed Perfluorovinyltin Compound	 Vinyltin Compound
C_2H_5OH	$R_3SnCF{=}CF_2$, no reaction	$R_3SnCH{=}CH_2$, no reaction
C_2H_5OH	$R_2Sn(CF{=}CF_2)_2$, cleavage	$R_2Sn(CH{=}CH_2)_2$, no reaction
CH_3CO_2H	$R_3SnCF{=}CF_2$, cleavage	$R_3SnCH{=}CH_2$, cleavage
HBr	$R_3SnCF{=}CF_2$, cleavage	$R_3SnCH{=}CH_2$, cleavage
I_2, Br_2	$R_3SnCF{=}CF_2$, cleavage	$R_3SnCH{=}CH_2$, cleavage
$(C_6H_5)_3SnH$	$(C_6H_5)_3SnCF{=}CF_2$, cleavage	$(C_6H_5)_3SnCH{=}CH_2$, addition
C_2H_5ONa	$R_3SnCF{=}CF_2$, cleavage	$R_3SnCH{=}CH_2$, no reaction[a]

[a] M. A. Weiner, unpublished.

Table II summarizes the results of these selected reactions of perfluorovinyltin compounds and compares them with similar reactions of vinyltin compounds.

EXPERIMENTAL[9]

(1) *Preparation of perfluorovinyltin compounds.*[10] (a) *The Grignard procedure.* In a three-necked flask, equipped with a stirrer, dropping funnel, Dry Ice condenser and nitrogen inlet tube, was placed 10 g. (0.41 g.-atom) of magnesium turnings in 30 ml. of tetrahydrofuran. The magnesium was activated by adding 0.5 ml. of 1,2-dibromoethane. The flask was then cooled to −20°, and a solution of 40 g. (0.25 mole) of bromotrifluoroethylene in 60 ml. of tetrahydrofuran was added slowly with stirring. A deep brown solution resulted. This was filtered under nitrogen through glass wool to remove unused magnesium. Analysis of the Grignard solution (addition of excess of standard sulfuric acid and back titration with standard base) indicated a 53% yield of $CF_2{=}CFMgBr$ had been obtained. To the Grignard solution at −20° was added 18 g. (0.06 mole) of di-*n*-butyltin dichloride (Metal and Thermit Corp.) in 75 ml. of tetrahydrofuran. The mixture was allowed to come to room temperature while being stirred, then was heated at reflux for 16 hr. The dark brown reaction mixture was hydrolyzed with saturated ammonium chloride solution. The separated salts were washed with ether; the organic layer and the ether washings were combined and dried. After removal of solvents at reduced pressure, fractional distillation of the residue gave 13.1 g. of colorless liquid, b.p. 56–57°/0.6 mm., n_D^{25} 1.4290, and two smaller higher boiling fractions of n_D^{25} 1.4590 and n_D^{25} 1.4782 which contained chlorine. Redistillation of the first fraction resulted in pure di-*n*-butyldiperfluorovinyltin. The crude yield, based on di-*n*-butyltin dichloride, was 56%. On standing in a glass-stoppered vial, the pure product deposited small amounts of white solid.

(b) *The Barbier procedure.* In a similar apparatus was placed 18 g. (0.74 g.-atom) of magnesium turnings. These were just covered with dry tetrahydrofuran and activated by adding *ca.* 10 drops of 1,2-dibromoethane. After addition of 200 ml. of tetrahydrofuran, a small amount of bromotrifluoroethylene was injected. Upon initiation of Grignard reagent formation, as evidenced by a brown coloration, the flask was cooled to −15°; and a solution of 109 g. (0.68 mole) of bromotrifluoroethylene and 121 g. (0.5 mole) of triethyltin chloride (prepared by the Kocheshkov reaction from tetraethyltin) in 300 ml. of tetrahydrofuran was added slowly with vigorous stirring over a period of 4 hr. Subsequently the reaction mixture was stirred at −15° for 3 hr. After it had been allowed to stand at room temperature for a short while, the reaction mixture was cooled to 0° and hydrolyzed with saturated ammonium chloride solution. The organic layer was decanted, and the inorganic salts were washed with tetrahydrofuran. The combined organic layer and tetrahydrofuran washings were distilled rapidly at reduced pressure into a receiver cooled to −78°. Fractional distillation of this distillate gave 115 g. (80% based on triethyltin chloride) of triethylperfluorovinyltin, b.p. 66–67°/12 mm., as a colorless liquid.

This method served well in the preparation of tri-*n*-butylperfluorovinyltin, triphenylperfluorovinyltin, diethyldiperfluorovinyltin, di-*n*-butyldiperfluorovinyltin, *n*-butyltriperfluorovinyltin, and phenyltriperfluorovinyltin. Purification of the last two compounds required an added step in the procedure described above. For example, the reaction of 0.48 mole of bromotrifluoroethylene, 0.1 mole of phenyltin trichloride, and 0.5 g.-atom of magnesium in 500 ml. of tetrahydrofuran at −15°, followed by the steps outlined above, gave 37.2 g. of crude liquid product, distilling between 79° and 90° at 0.3 mm., which still contained chlorine. This material was diluted to 150 ml. with diethyl ether and treated with dry gaseous ammonia for 3 hr. The resulting white adduct formed between ammonia and the organotin chloride impurities present was filtered, and the filtrate was fractionally distilled to give 31.4 g. (71.5%) of chlorine-free phenyltriperfluorovinyltin, b.p. 60°/0.65 mm. A similar procedure is useful in the purification of other tin compounds containing two or three perfluorovinyl groups.

Triphenylperfluorovinyltin, a solid, was purified by recrystallization from methanol.

2) *Properties of perfluorovinyltin compounds.* All perfluorovinyltin compounds are easily characterized by their infrared spectra. These, when taken in chloroform solution, show an intense band due to the C=C stretching vibration at *ca.* 1705–1720 cm.$^{-1}$ and also four strong (and two weaker) absorptions due to the C—F links between 1300 and 990 cm.$^{-1}$ The observed frequencies are listed in Table III.

All liquid perfluorovinyltin compounds on standing slowly deposited white solid. The exact nature of this

TABLE III

INFRARED ABSORPTIONS DUE TO THE $CF_2{=}CF$ GROUP IN ORGANOTIN COMPOUNDS IN CHLOROFORM SOLUTION (cm.$^{-1}$)

Compound	$\nu_{C=C}$	Principal C—F Bands
$(C_2H_5)_3SnCF{=}CF_2$	1707	1280, 1266, 1098, 998
$(C_4H_9)_3SnCF{=}CF_2$	1707	1277, 1263, 1094, 994
$(C_6H_5)_3SnCF{=}CF_2$	1711	1287, 1275, 1110, 1002
$(C_4H_9)_2Sn(CF{=}CF_2)_2$	1712	1288, 1275, 1113, 1005
$C_4H_9Sn(CF{=}CF_2)_3$	1711	1295, 1283, 1122, 1007
$C_6H_5Sn(CF{=}CF_2)_3$	1715	1298, 1284, 1123, 1009

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[9] Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were determined using a Mel-Temp melting point apparatus. All reactions were carried out under an atmosphere of prepurified nitrogen.

[10] While the present study was under way, the synthesis of perfluorovinyltin compounds by the Grignard procedure was reported by H. D. Kaesz, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.*, **81**, 6336 (1959), and later in *J. Am. Chem. Soc.*, **82**, 6232 (1960).

decomposition is not yet understood. In the case of triethylperfluorovinyltin, the white solid formed contained 33.99% C, 5.56% H, 7.97% F, and 48.46% Sn; it could be sublimed in vacuum at 155°. Solid of somewhat similar composition (33.2% C, 5.3% H, 10.1% F) could be obtained in low yield simply by heating triethylperfluorovinyltin in dry air at 100–120° for 20 hr.

3) *Reactions of perfluorovinyltin compounds.* (a) *With ethanol.* A solution of 14 g. of di-*n*-butyldiperfluorovinyltin in 20 ml. of absolute ethanol was heated at reflux for 20 hr. in the absence of moisture. Distillation gave the extremely moisture-sensitive di-*n*-butyldiethoxytin, b.p. 95°/0.15 mm., as a colorless liquid in 95% yield.

Anal. Calcd. for $C_{12}H_{28}O_2Sn$: C, 44.61; H, 8.74. Found C, 44.60; H, 8.59.

A similar reaction of diethyldiperfluorovinyltin gave diethyldiethoxytin, b.p. 78°/0.1 mm., n_D^{25} 1.4828, d_4^{25} 1.370, in 76% yield. In view of the extremely ready hydrolysis of this compound, the values of the refractive index and density given may not be very exact.

Anal. Calcd. for $C_8H_{20}O_2Sn$: C, 35.99; H, 7.55. Found C, 35.68; H, 7.90.

(b) *With acetic acid.* Ten grams (0.027 mole) of tri-*n*-butylperfluorovinyltin and 1.8 g. (0.03 mole) of glacial acetic acid were heated on the steam bath for 1.5 hr. The mixture crystallized on cooling. Recrystallization from hexane gave pure tri-*n*-butyltin acetate, m.p. 86–87° in 90% yield (lit.[11] m.p. 84.5–85°).

(c) *With hydrogen bromide.* Two traps were connected in series. In the first was placed 10 g. (0.0253 mole) of di-*n*-butyldiperfluorovinyltin in 25 ml. of carbon tetrachloride, in the second 7.2 g. (0.045 mole) of bromine in 25 ml. of carbon tetrachloride. Both traps were cooled to 0°, and then gaseous hydrogen bromide was passed into the first trap until all of the bromine in the second trap had been consumed by reaction with the trifluoroethylene liberated in the cleavage reaction. The contents of the first trap were distilled to give 8.5 g. (85%) of di-*n*-butyltin dibromide, b.p. 90.5–92°/0.3 mm., m.p. 21.5–22°, n_D^{25} 1.5434 (lit.[12] m.p. 20°). The contents of the second trap were distilled to give 8.6 g. (71%) of 1,2-dibromo-1,1,2-trifluoroethane, b.p. 35°/90 mm., n_D^{25} 1.4098, d_4^{25} 2.165 (lit.[4] b.p. 76–76.5°, n_D^{18} 1.4125).

Anal. Calcd. for $C_2HF_3Br_2$: F, 23.57; Br, 66.08. Found: F, 23.28; Br, 66.06.

(d) *With iodine.* To a solution of 10 g. of di-*n*-butyldiperfluorovinyltin in 125 ml. of diethyl ether was added 12.84 g. (0.0506 mole) of iodine. The reaction commenced at room temperature as evidenced by gradual lightening of the color of the brown iodine solution. A 5-hr. reflux period resulted in a colorless solution. Distillation of the ether left a yellow oil and a small amount of white solid. Fractional distillation gave 9.0 g. (73%) of di-*n*-butyltin diiodide, b.p. 112°/0.6 mm., n_D^{25} 1.6020, d_4^{25} 1.996, as a colorless liquid which turned yellow rapidly on standing.

Anal. Calcd. for $C_8H_{18}I_2Sn$: C, 19.74; H, 3.73; I, 52.15. Found: C, 19.90; H, 3.75; I, 51.85.

(e) *With mercuric chloride.* In the distillation pot of a Soxhlet extractor was placed 7.0 g. (0.0189 mole) of tri-*n*-butylperfluorovinyltin in 100 ml. of diethyl ether. Mercuric chloride, 5.1 g. (0.0189 mole), was placed in the Soxhlet thimble. Circulation of ether for 15 hr. brought all the mercuric chloride into reaction. The resulting turbid ether solution was filtered, and *ca.* three-quarters of the ether was evaporated. Upon addition of pentane to the residue, 3.9 g. of white crystalline $CF_2{=}CFHgCl$ precipitated. After two recrystallizations from 90–100° ligroin, the compound still did not have a sharp melting point; when heated in a sealed capillary, it began to soften at 96° and was completely molten at 103–104°. Its infrared spectrum in chloroform solution showed strong bands at 1725, 1288, 1225, 1203, 1165, 1145, and 1014 cm.$^{-1}$

Anal. Calcd. for C_2F_3ClHg: Cl, 11.18; Hg, 63.27. Found: Cl, 11.18; Hg, 62.79.

Perfluorovinylmercuric chloride is soluble in ether and benzene and sublimes at room temperature in a high vacuum.

(f) *With triphenyltin hydride.* A mixture of 7 g. (0.0163 mole) of triphenylperfluorovinyltin and 6 g. (0.0166 mole) of triphenyltin hydride was heated in vacuum at 70° for 3 hr. During this time strong gas evolution and gradual solidification of the contents of the flask were apparent. Recrystallization of the solid product from benzene gave 9 g. (79%) of hexaphenylditin, m.p. 232–234°. Its identity was confirmed by a mixed melting point with an authentic sample.

(g) *With alcoholic sodium ethoxide.* Sodium, 2.6 g., was dissolved in 60 ml. of absolute ethanol, and 10 ml. of tri-*n*-butylperfluorovinyltin was added. The resulting turbid mixture was heated at reflux in the absence of moisture for 5 hr. Fractional distillation gave 12 g. of tri-*n*-butylethoxytin, b.p. 115°/0.1 mm., a moisture-sensitive liquid.

Anal. Calcd. for $C_{14}H_{32}OSn$: C, 50.18; H, 9.62; Sn, 35.42. Found: C, 49.98; H, 9.57; Sn, 34.89.

(h) *With aqueous-alcoholic potassium fluoride.* A solution of 11.3 g. of di-*n*-butyldiperfluorovinyltin in ether was shaken vigorously with an aqueous–alcoholic potassium fluoride solution. The ether layer was separated, dried, and distilled. Starting material was recovered in 51% yield (n_D^{25} 1.4300). The brown distillation residue was chromatographed on an alumina column. Evaporation of the eluate gave di-*n*-butyltin oxide.

Anal. Calcd. for $C_8H_{18}OSn$: C, 38.60; H, 7.12. Found: C, 39.07; H, 7.47; F, 0.0.

Treatment of crude, chlorine-containing diethyldiperfluorovinyltin with potassium fluoride solution in this manner resulted in precipitation of white solid. The latter was recrystallized from methanol. It sublimed readily at 170° and was soluble in 6*M* hydrochloric acid.

Anal. Calcd. for $C_8H_{20}OF_2Sn_2$: C, 23.57; H, 4.95; F, 9.32. Found: C, 23.72; H, 5.11; F, 9.13.

The infrared spectrum of this substance (in potassium bromide) confirmed the absence of $CF_2{=}CF$ groups.

Similar attempted purification of chlorine-containing di-*n*-butyldiperfluorovinyltin gave a white solid. This was dissolved in methanol; addition of water precipitated it again to give material of m.p. 140°.

Anal. Calcd. for $C_{16}H_{36}OF_2Sn_2$: C, 36.96; H, 6.98. Found: C, 37.41; H, 7.11.

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