N-*t*-Butyloxycarbonyl-γ-benzyl-L-glutamic Acid *p*-Nitrophenyl Ester.—γ-Benzyl-L-glutamic acid,[25] 2.37 g. (10 mmoles), and MgO, 0.80 g. (20 mmoles), were suspended in 40 ml. of 50% dioxane and stirred for 1 hr. at room temperature. Then 3.0 g. of *t*-butyloxycarbonyl azide[26,27] (21 mmoles) was added and the mixture was stirred at 45–50° for 6 hr. The mixture was then poured into 250 ml. of ice cold water and some insoluble material (MgO) was filtered off. The aqueous solution was then extracted with 150 ml. of ethyl acetate (three times) to remove excess *t*-butyloxycarbonyl azide. The ethyl acetate washings were then washed twice with 20 ml. of 7.5% sodium bicarbonate and once with 50 ml. of water. The combined aqueous extracts were cooled at 0°, and the pH was adjusted to 3 with 10% citric acid (approximately 40 ml.). The acidified solution was then saturated with sodium chloride and extracted twice with 150 ml. of ethyl acetate. The ethyl acetate was washed with saturated sodium chloride, and then dried over anhydrous sodium sulfate. The ethyl acetate was evaporated *in vacuo* (20–25° bath) to leave the N-*t*-butyloxycarbonyl-γ-benzyl-L-glutamic acid as an oil, homogeneous in paper chromatography, $R_{f\ \mathrm{BAW}} = 0.90$; $R_{f\ \mathrm{SBA}} = 0.58$ (chlorine detection). Wt., 1.54 g. (46%), 4.5 mmole. The oil was dissolved in 20 ml. of ethyl acetate, cooled to 0°, and then 0.63 g. of *p*-nitrophenol (4.5 mmoles) and 0.9 g. of dicyclohexylcarbodiimide (4.5 mmoles) were added. The mixture was stirred at 0° for 2 hr. It was then placed in the refrigerator (4°) overnight. The dicyclohexylurea was filtered off, [wt. 0.77 g. (75%)] and the ethyl acetate was evaporated *in vacuo* (20–25° bath). The *p*-nitrophenyl ester was crystallized from ethyl acetate–petroleum ether (20–30 ml.) to yield 0.53 g. (52%), m.p. 120–121°; $[\alpha]^{25}\mathrm{D}$ −32.7° (*c* 1, methanol).

Anal. Calcd. for $C_{23}H_{26}N_2O_8$ (458.3): C, 60.3; H, 5.68; N, 6.11. Found: C, 60.3; H, 5.90; N, 6.32.

N-*t*-Butyloxycarbonyl-γ-benzyl-L-glutamyl-L-histidyl-L-phenylalanyl-N^G-tosyl-L-arginyl-L-tryptophylglycine *t*-Butyl Ester (VII). N^{α}-carbobenzoxy - L - histidyl - L - phenylalanyl - N^G - tosyl-arginyl - L - tryptophylglycine *t*-butyl ester, 6.28 g. (6.0 mmoles), was dissolved in 150 ml. of methanol and catalytically hydrogenated with palladium from 2 g. of palladium chloride until no more carbon dioxide was detectable; $R_{f\ \mathrm{BAW}} = 0.60$. The palladium was filtered off and the methanol was evaporated *in vacuo* (20–25° bath). The residue was dissolved in 50 ml. of acetonitrile and 3 ml. of dimethylformamide. A 3.04-g. sample of *N*-butyloxycarbonyl-γ-benzylglutamic acid *p*-nitrophenyl ester (6.6 mmoles) was added and the mixture was stirred for 2 days at room temperature. During the course of the reaction, the mixture became gelatinous, and more acetonitrile (approximately 50 ml.) was added to insure good stirring and mixing. After the 2 days of stirring, the solvents were evaporated *in vacuo* (20–25° bath) and the residue treated with a large volume of ether. The resulting precipitate was filtered, washed well with ether, and then dried. Weight of crude VII was 6.8 g. (93%). The product was then crystallized from warm methanol to yield 5.7 g. (77%), m.p. 162–164°. $[\alpha]^{25}\mathrm{D}$ −22.5° (*c* 1, dimethylformamide).

Anal. Calcd. for $C_{62}H_{78}O_{13}N_{12}S_1$ (1231.4): C, 60.5; H, 6.38; N, 13.7. Found: C, 60.2; H, 6.43; N, 13.7.

γ-Benzyl-L-glutamyl-L-histidyl-L-phenylalanyl-N^G-tosyl-L-arginyl-L-tryptophylglycine (VIII).—The above protected hexapeptide, 0.62 g. (0.5 mmole), was dissolved in 2.0 ml. of trifluoroacetic acid in a nitrogen atmosphere. The solution was allowed to stand at room temperature for 15 min. and then added to 50 ml. of ether to precipitate the desired peptide. The precipitate was thoroughly washed with ether to remove excess trifluoroacetic acid, and then crystallized from the slow evaporation of a methanol solution to give 0.56 g. (86%), m.p. 165–168° (dec.); $[\alpha]^{25}\mathrm{D}$ +12.0° (*c* 1, dimethylformamide).

Anal. Calcd. for $C_{53}H_{62}O_{11}N_{12}S_1 \cdot (CF_3COOH)_2 \cdot CH_3OH$ (1335.3): C, 52.2; H, 5.13, N. 12.6. Found: C, 52.1, H, 5.53; N, 13.0.

L-Glutamyl-L-histidyl-L-phenylalanyl-L-arginyl-L-tryptophylglycine (IX).—The ditrifluoroacetate salt of VIII, 0.534 g., was dissolved in 100 ml. of liquid ammonia, and small pieces of sodium were added at the temperature of the boiling point of liquid ammonia (−33°) until the blue color persisted for 30 min.[11] The ammonia was then allowed to evaporate and the residue was dried completely in a vacuum desiccator over concentrated sulfuric acid. The residue was then desalted on an IRC-50 column, eluted with pyridine–acetic acid–water buffer (30:4:66), and then lyophylized to yield 0.300 g. (90%) of the crude free hexapeptide. A 50-mg. sample of this material was purified by zone electrophoresis on starch in 0.05 *M* sodium carbonate and run for 24 hr. at 200 volts to yield 37 mg. (74%) of a product that was homogeneous in paper chromatography in the BAW, SBA, and 1-butanol–pyridine–acetic acid–water (15:10:3:12) systems, and in paper electrophoresis in buffers of pH 3.6, 6.5, and 11.0. It appeared as a single spot, positive to ninhydrin, the Ehrlich, Pauly, and Sakaguchi reagents, and chlorine; $[\alpha]^{25}\mathrm{D}$ −17.3° (*c* 1, in acetic acid).

Anal. Calcd. for $C_{39}H_{50}N_{12}O_9 \cdot CH_3COOH \cdot H_2O$ (909.0): C, 54.2; H, 6.21; N, 18.5. Found: C, 54.3; H, 6.78; N, 18.7.

LAP Digest of the Hexapeptide.—The above hexapeptide, 0.8 mg., was dissolved in 0.5 ml. of tri(hydroxymethyl)aminomethane (TRIS)buffer, (pH 8.5, 0.01 *M* Mg^+) and 0.008 ml. of a LAP solution (1 mg. of Worthington LAP, lot no. 5917 in 0.2 ml. of water) was added and the solution was incubated at 37° for 24 hr. Amino acid analysis by the Spinco amino acid analyzer[13] gave the following molar ratios: $\mathrm{Glu}_{1.06}\mathrm{His}_{0.97}\mathrm{Phe}_{1.02}\mathrm{Arg}_{1.08}\mathrm{Try}_{0,97}\mathrm{Gly}_{0.95}$.

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Preparation and Reactions of Triphenyltinlithium

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The preparation, properties, and reactions of triphenyltinlithium with water, triphenyltin fluoride, tri-*n*-butyl phosphate, ethyl iodide, benzyl chloride, bromobenzene, chlorotriphenylsilane, chlorotrimethylsilane, and carbon dioxide are described.

The preparation of triphenyltinlithium has been described in the literature by several investigators. In 1950, G. Wittig[2a] reported its preparation from phenyllithium and diphenyltin, as well as from triphenyltin bromide and metallic lithium in liquid ammonia. Gilman and Rosenberg[2b] later reported the preparation of triphenyltinlithium from stannous chloride and phenyllithium. In this manner the intermediate preparation of diphenyltin was eliminated. Blake, Coates, and

$$C_6H_5Li + (C_6H_5)_2Sn \longrightarrow (C_6H_5)_3SnLi \qquad (1)$$

$$(C_6H_5)_3SnBr + 2Li \xrightarrow{NH_3} (C_6H_5)_3SnLi + LiBr \qquad (2)$$

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[2a] G. Wittig, *Angew. Chem.*, **62**, 231 (1950); (b) H. Gilman and S. D. Rosenberg, *J. Am. Chem. Soc.*, **74**, 531 (1952).

$$3C_6H_5Li + SnCl_2 \longrightarrow (C_6H_5)_3SnLi + 2LiCl \qquad (3)$$

Tate[3] recently reported on the preparation and reactions of tributyltin and triphenyltin derivatives of sodium and lithium. They prepared triphenyltinsodium by the reaction between sodium naphthalene and either hexaphenylditin, triphenyltin bromide, or tetraphenyltin in tetrahydrofuran (THF) or 1,2-dimethoxyethane as solvents. They prepared triphenyltinlithium, however, by the procedure of Gilman and Rosenberg[2b] (equation 3). Utilizing the organometallics so prepared, these investigators noted some differences in the reaction products and yields over those reported earlier in the literature[2b] for reactions between triphenyltinlithium and ethyl iodide or benzyl chloride. Since we have also observed differences in the reactions of triphenyltinlithium prepared by either equation 1 or 3 and by the method previously reported by us,[4] we now wish to report in more detail some properties and reactions of triphenyltinlithium.

It has been previously shown[4] that triphenyltinlithium can be prepared very easily from the reaction between triphenyltin chloride and metallic lithium in tetrahydrofuran or by the cleavage of hexaphenylditin with metallic lithium in tetrahydrofuran. It was suggested that the reactions occurring in the preparation of the organometallic are

$$(C_6H_5)_3SnCl + 2Li \xrightarrow{\text{THF}} (C_6H_5)_3SnLi + LiCl \qquad (4)$$

$$(C_6H_5)_3SnLi + (C_6H_5)_3SnCl \xrightarrow{\text{THF}} (C_6H_5)_3SnSn(C_6H_5)_3 + LiCl \qquad (5)$$

$$(C_6H_5)_3SnSn(C_6H_5)_3 + 2Li \xrightarrow{\text{THF}} 2(C_6H_5)_3SnLi \qquad (6)$$

Gilman[5] has previously suggested the same sequence of reactions for the direct preparation of triphenylsilyllithium from chlorotriphenylsilane and metallic lithium in tetrahydrofuran.

The triphenyltinlithium reagent prepared as described above (equations 4–6) is dark olive-green and is stable when subjected to refluxing in a tetrahydrofuran solution for at least twenty-four hours. No evidence of solvent cleavage was observed.

Carbonation of the triphenyltinlithium immediately after its preparation or after 24 hours of refluxing in tetrahydrofuran produced no benzoic acid. This observation indicates that triphenyltinlithium as prepared above does not exist as a complex[6] in equilibrium with diphenyltin and phenyllithium.

$$(C_6H_5)_3SnLi \rightleftarrows (C_6H_5)_2Sn + C_6H_5Li \qquad (7)$$

A sample of triphenyltinlithium in tetrahydrofuran solution when stored in a refrigerator (0°) over a period of one month showed no sign of decomposition as measured by titration.[7] The triphenyltinlithium reagent does give a positive Color Test I[8] which is conveniently used to follow the reactions. Conversely triphenyltinlithium prepared *via* equation 3 has been reported[9] to give a negative Color Test I.

When triphenyltinlithium was allowed to react with chlorotriphenylsilane, a mixture of products was obtained. The main products were triphenylsilyltriphenyltin, hexaphenyldisilane, and hexaphenylditin. Three other products in lesser quantities were also identified as triphenylsilanol, triphenylsiloxytriphenyltin, and tetraphenyltin. The presence of the first three compounds indicates that a metal–halogen interchange occurred.

$$(C_6H_5)_3SnLi + (C_6H_5)_3SiCl \longrightarrow (C_6H_5)_3SnCl + (C_6H_5)_3SiLi \qquad (8)$$

Various combinations of reactions between the organolithium intermediates with the metallic chlorides could account for the presence of the three major products. Separation of some of the products (triphenylsilyltriphenyltin and hexaphenyldisilane) by fractional crystallization was very difficult because of the similarity in solubilities. The desired product, triphenylsilyltriphenyltin, was finally separated from hexaphenyldisilane by repeated crystallizations from chloroform. Because of this separation difficulty, the exact yields of the products are unknown.

An attempt to prepare trimethylsilyltriphenyltin from triphenyltinlithium and chlorotrimethylsilane resulted again in a metal–halogen interchange yielding hexaphenylditin in 68.7% yield.

Several attempts to prepare triphenyltincarboxylic acid by carbonation of triphenyltinlithium have failed. Gilman and Rosenberg[9] and Blake, Coates, and Tate[3] also reported no triphenyltincarboxylic acid in carbonation reactions of triphenyltinlithium and triphenyltinsodium. Hexaphenylditin was isolated in our studies in an 85% yield.

The alkyl iodide, arylalkyl chloride, alkyl phosphate, aryl bromide, and triaryltin fluoride reacted in the normal metathetical manner to yield the desired products as shown in Table I.

TABLE I

REACTIONS OF TRIPHENYLTINLITHIUM

Reactants	Products	Yields, %
H_2O	$(C_6H_5)_3SnH$	69–74
$(C_6H_5)_3SnF$	$(C_6H_5)_3SnSn(C_6H_5)_3$	92
$(C_4H_9O)_3PO$	$(C_6H_5)_3SnC_4H_9$	70
C_2H_5I	$(C_6H_5)_3SnC_2H_5$	87
$C_6H_5CH_2Cl$	$(C_6H_5)_3SnCH_2C_6H_5$	78
C_6H_5Br	$(C_6H_5)_4Sn$	75
$(C_6H_5)_3SiCl$	$(C_6H_5)_3SiSn(C_6H_5)_3$, $(C_6H_5)_3SnSn(C_6H_5)_3$ $(C_6H_5)_3SiSi(C_6H_5)_3$, $(C_6H_5)_4Si$, $(C_6H_5)_3SiOSn(C_6H_5)_3$ $(C_6H_5)_3SiOH$	—
$(CH_3)_3SiCl$	$(C_6H_5)_3SnSn(C_6H_5)_3$	68.7
CO_2	$(C_6H_5)_3SnSn(C_6H_5)_3$	85

Essentially three different methods have been described in the literature for the preparation of organotin hydrides: (a) reduction of organotinsodium compounds[10] and organotinlithium compounds[11] with ammonium chloride or ammonium bromide in liquid am-

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(3) D. Blake, G. E. Coates, and J. M. Tate, *J. Chem. Soc.*, 618 (1961).

(4) C. Tamborski, F. E. Ford, W. L. Lehn, G. Moore, and E. J. Soloski, *J. Org. Chem.*, **27**, 619 (1962).

(5) D. Wittenberg and H. Gilman, *Quart. Rev.* (London), **13**, 116 (1959).

(6) J. D'Ans, H. Zimmer, E. Endrulat, and K. Lubke, *Naturwissenschaften*, **39**, 450 (1952).

(7) The per cent of triphenyltinlithium was determined utilizing the recently modified double titration method of H. Gilman and F. Cartledge (unpublished studies).

(8) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(9) H. Gilman and S. D. Rosenberg, *J. Org. Chem.*, **18**, 680 (1953).

(10) C. A. Kraus and W. N. Greer, *J. Am. Chem. Soc.*, **44**, 2629 (1922).

(11) G. Wittig, F. J. Meyer, and G. Lange, *Ann.*, **571**, 167 (1951).

monia, (b) reduction of organotin halide[12] with lithium aluminum hydride, (c) reduction of organotin halides with amalgamated aluminum.[13] Triphenyltinlithium as prepared in this study is readily hydrolyzed with either saturated aqueous ammonium chloride solution or dilute hydrochloric acid to yield triphenyltin hydride in 70–75% yields.[14] Previously reported attempts[2a,11,15] to hydrolyze triphenyltinlithium prepared by equations 1 or 3 to the expected triphenyltin hydride were unsuccessful.

Experimental

Preparation of Triphenyltinlithium from Hexaphenylditin.—To a rapidly stirred mixture of 35.0 g. (0.05 mole) of hexaphenylditin and 3.5 g. (0.5 g.-atom) of lithium clippings was added enough tetrahydrofuran to form a thick paste. After about 3 min. the mixture started turning yellow-green. A total of 250 ml. of tetrahydrofuran was added dropwise during 8 min. The dark olive-green mixture gave a positive Color Test I within 5 min. After being stirred for 3 hr. the greenish black mixture was filtered through glass wool and a derivative was formed by one of the reactions below.

Preparation of Triphenyltinlithium from Triphenyltin Chloride.—A solution of 38.5 g. (0.1 mole) of triphenyltin chloride in 110 ml. of tetrahydrofuran was added during 3 min. to a stirred suspension of 6.9 g. (1.0 g.-atom) of lithium clippings in 100 ml. of tetrahydrofuran. The reaction was exothermic and the dark olive-brown solution gave a positive Color Test I within 7 min. After being stirred for 1 hr. the mixture was filtered through glass wool and a derivative was formed by one of the reactions below.

Preparation of Triphenyltin Hydride from Hexaphenylditin.—A solution of triphenyltinlithium prepared as described above from 0.05 mole of hexaphenylditin was hydrolyzed by pouring into 1 *M* hydrochloric acid. The mixture was extracted with ether and the organic layer was dried over sodium sulfate. Evaporation of the solvents left a semisolid residue from which was filtered 3.3 g. (9.6%) of hexaphenylditin, m.p. 226–234° (mixture melting point). The filtrate was distilled to give 25.8 g. (74%) of triphenyltin hydride, b.p. 142–143° (0.1 mm.) (lit.,[11] b.p. 155–157° at 0.1 mm.), n^{25}_D 1.6345. The infrared spectrum of this material was identical with that of an authentic sample.

Preparation of Triphenyltin Hydride from Triphenyltin Chloride.—A solution of triphenyltinlithium prepared as described above from 0.05 mole of triphenyltin chloride was hydrolyzed by pouring into 1 *M* hydrochloric acid. The mixture was extracted with ether and the organic layer was dried over sodium sulfate. Evaporation of the solvents left a semisolid residue from which was filtered 1.9 g. (10.9%) of hexaphenylditin, m.p. 230–235° (mixture melting point). The filtrate was distilled to give 12.1 g. (69%) of triphenyltin hydride, b.p. 145–149° (0.1 mm.) (lit.,[11] b.p. 155–157° at 0.1 mm.), n^{25}_D 1.6342, d^{25}_4 1.3771 This product was identified by comparison of the infrared spectrum with that of an authentic sample and by derivatization with bromine to yield triphenyltin bromide.

Preparation of *n*-Butyltriphenyltin.—A solution of triphenyltinlithium, prepared as described above from 0.05 mole of triphenyltin chloride, was added to a stirred solution of 13.3 g. (0.05 mole) of redistilled tri-*n*-butyl phosphate in 30 ml. of tetrahydrofuran during 5 min. The black mixture gave a negative Color Test I and was stirred for 30 min. The mixture was hydrolyzed with water, ether was added, and the mixture was acidified with hydrochloric acid. The organic layer was combined with ether extracts of the aqueous layer and dried over sodium sulfate. Evaporation of solvents left a tarry solid which was crystallized from 2-propanol to give 14.3 g. (70.3%) of *n*-butyltriphenyltin, m.p. 60–62.5° (lit.,[16] m.p. 61–62°).

Anal. Calcd. for $C_{22}H_{24}Sn$: C, 64.90; H, 5.94; Sn, 29.16. Found: C, 64.50, 64.76; H, 5.82, 5.83; Sn, 29.4.

Preparation of Ethyltriphenyltin.—A solution of triphenyltinlithium, prepared as described above from 38.6 g. (0.1 mole) of triphenyltin chloride, was added to a solution of 15.6 g. (0.1 mole) of ethyl iodide dissolved in 100 ml. of tetrahydrofuran over a period of 10 min. A slight heat of reaction was observed and after 5 min. Color Test I was negative. The reaction was stirred for an additional 90 min. and then hydrolyzed with ammonium chloride. The organic layer was separated and dried over sodium sulfate. Evaporation of solvents left 35.1 g. (93.1%) of crude product. Recrystallization from 95% ethanol yielded 32.7 g. (86.4%) of pure ethyltriphenyltin, m.p. 62–63° (lit.,[3] m.p. 57°).

Anal. Calcd. for $C_{20}H_{20}Sn$: C, 63.37; H, 5.32; Sn, 31.31. Found: C, 63.12, 63.27; H, 5.28, 5.19; Sn, 31.46, 31.20.

Preparation of Triphenylbenzyltin.—To a solution of triphenyltinlithium prepared as described above from 21.5 g. (0.055 mole) of triphenyltin chloride was added a solution of 6.96 g. (0.055 mole) of benzyl chloride in 55 ml. of tetrahydrofuran. The reaction mixture changed from dark green to dark brown and Color Test I was negative after 15 min. The mixture was hydrolyzed with saturated ammonium chloride, and the organic layer was separated and dried over sodium sulfate. Evaporation of solvents left 20.7 g. (85.5%) of crude product. Recrystallization from 95% ethanol yielded 18.1 g. (77.4%) of pure triphenylbenzyltin, melting point and mixture melting point 89.5–90.5° (lit.,[2] m.p. 90–91°).

This compound was also made (72% yield) from triphenyltinlithium prepared from hexaphenylditin.

Preparation of Tetraphenyltin from Bromobenzene.—A solution of triphenyltinlithium, prepared from 38.5 g. (0.1 mole) of triphenyltin chloride was added to 15.7 g. (0.1 mole) of bromobenzene dissolved in 100 ml. of tetrahydrofuran over a period of 8 min. The reaction was exothermic and a white precipitate formed immediately. After 20 min. of stirring Color Test I was negative. The reaction mixture was hydrolyzed with ammonium chloride followed by the addition of 200 ml. of ether. A white precipitate formed at the interface and was filtered. The ether layer was dried over sodium sulfate. The material at the interface melted between 220–225°, and a mixture melting point with an authentic sample of tetraphenyltin was not depressed. The infrared spectrum of this material was identical with that of tetraphenyltin. The yield of tetraphenyltin was 32.0 g. (75%).

The dried ether layer was evaporated to give 12.6 g. of material. Repeated crystallizations of this material gave 4.7 g. (13%) of hexaphenylditin, m.p. 223–227°. This product was identified by a mixture melting point with an authentic sample and by comparison of the infrared spectra. No other products were isolated.

Preparation of Hexaphenylditin from Triphenyltin Fluoride.—To a stirred solution of 3.70 g. (0.01 mole) of triphenyltin fluoride suspended in 100 ml. of tetrahydrofuran was added 0.01 mole triphenyltinlithium during 1 min. This medium brown suspension gave a negative Color Test I within 2 hr. After hydrolyzing with saturated ammonium chloride ether was added and the solution phase separated. Distillation of the organic layer left a white crystalline material with a melting point of 214–220°. Recrystallization from benzene yielded 6.41 g. (91.6%) of pure hexaphenylditin, m.p. 232–234°, which was identified by a mixture melting point with an authentic sample. No other products were identified.

Preparation of Triphenylsilyltriphenyltin.—To a stirred solution of triphenyltinlithium prepared as described above from 0.11 mole of triphenyltin chloride was added a solution of 29.5 g. (0.1 mole) of chlorotriphenylsilane in 100 ml. of tetrahydrofuran during 1 min. The black suspension gave a faintly positive Color Test I throughout 4 hr. of stirring. After hydrolysis with saturated ammonium chloride solution and addition of ether the resulting gray precipitate was filtered and recrystallized from chloroform; 18.1 g. (29.7%) of crude triphenylsilyltriphenyltin was obtained, m.p. 298–309° (cor.). Further recrystallization from chloroform gave 11.8 g. (19.4%) of white prisms, m.p. 299–303° (cor.) [lit.,[2] m.p. 289–291° (uncor.)]. This product was identified by a mixture melting point with an authentic sample and by comparison of the infrared spectra. Also obtained from the gray precipitate was 20.4 g. of crude hexaphenyldisilane, m.p. 313–335° (cor.). Work-up of the filtrate gave 8.3 g. of crude hexaphenylditin, m.p. 200–230° (cor.), 1.8 g. of crude tetraphenyltin which melted at 225.5–227° (cor.) after recrystalli-

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(13) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luitjen, *Chem. Ind.* (London), 1290 (1958).

(14) Recently it has been shown that $[(C_6H_5)_3Sn]_2Mg$ can be hydrolyzed easily to yield triphenyltin hydride in 82% yield. C. Tamborski and E. J. Soloski, *J. Am. Chem. Soc.*, **83**, 3734 (1961).

(15) H. Gilman and S. D. Rosenberg, *J. Org. Chem.*, **18**, 1554 (1953).

(16) F. P. Kipping, *J. Chem. Soc.*, 2365 (1928).

zation from chloroform, 4.2 g. of crude triphenylsilanol which melted at 128–150° (cor.) after recrystallization from ligroin (b.p. 60–90°), and 5.9 g. of crude triphenylsiloxytriphenyltin which melted at 138–142° (cor.) after recrystallization from ligroin (b.p. 60–90°).

Attempted Preparation of Trimethylsilyltriphenyltin.—To a stirred solution of triphenyltinlithium, prepared as described above from 19.2 g (0.05 mole) of triphenyltin chloride, was added a solution of 8.2 g. (0.075 mole) of chlorotrimethylsilane in 50 ml. of tetrahydrofuran over a period of 4 min. The resulting black suspension gave a negative Color Test I and was stirred at room temperature for an additional 2 hr. After hydrolysis with 2 *M* hydrochloric acid and addition of ether the precipitate which formed was filtered. The ether layer was separated and dried over sodium sulfate. The precipitate which had formed at the interface was identified by infrared analysis and mixture melting point as hexaphenylditin. An additional small amount of hexaphenylditin was obtained from the ether layer. The total amount of hexaphenylditin obtained was 12.0 g. (68.7%), m.p. 233–236° (cor.). No attempt was made to isolate any other products resulting from the metal-halogen interchange.

Attempted Preparation of Triphenyltin Carboxylic Acid.—A solution of triphenyltinlithium prepared as described above from 0.05 mole of triphenyltin chloride was poured into a flask containing Dry Ice, forming a black mixture with a negative Color Test I. After the Dry Ice had disappeared, dry carbon dioxide was bubbled into the mixture intermittently for 20 hr. The mixture was hydrolyzed with cold 1 *M* hydrochloric acid and filtered to give 14.8 g. (85%) of hexaphenylditin, identified by a comparison of the infrared spectra and a mixture melting point with an authentic sample of hexaphenylditin. Work-up of the filtrate gave only a small amount of material which did not melt below 300°.

Secondary and Tertiary Perfluoroörganomercury Compounds

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Addition of mercuric fluoride to terminal fluoroölefins has been found to be a general method for the preparation of secondary and tertiary alkyl mercurials. Compounds we have prepared in this manner are bis(perfluoroisopropyl)mercury, bis(3H-1-trifluoromethylpentafluoropropyl)mercury, bis(3-chloro-1-trifluoromethylpentafluoropropyl)mercury, and bis(perfluoro-*t*-butyl)mercury. These organomercury compounds are unaffected by strong acids and bases at moderate temperatures. They are cleaved by halogens to secondary and tertiary perfluoroalkyl halides, which are useful for synthesis of other branched-chain fluorocarbon derivatives.

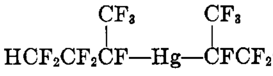
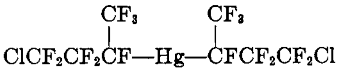
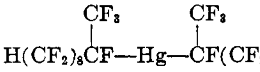
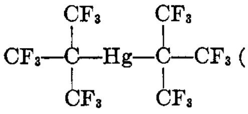
Several methods for preparing primary perfluoroalkyl mercurials have appeared in the literature. In one, fluoroalkyl iodides are heated with silver, copper, cadmium, zinc, or magnesium amalgam,[1] and in another mercuric fluoride is added to fluoroethylenes in arsenic trifluoride solution.[2] Branched fluoroalkyl mercurials are another matter, and until very recently no routes to such compounds were known. Because such branched mercurials should be starting materials for a great many secondary and tertiary fluoroalkyl derivatives, a largely unexplored area of chemistry, we have examined the addition of mercuric fluoride to terminally unsaturated fluoroölefins. This method has already been reported as a route to bis(perfluoroisopropyl)mercury,[3] a precursor of hexafluorothioacetone.

Preparation.—The synthesis described by Krespan, which utilizes arsenic trifluoride as a solvent, is not well suited for addition of mercuric fluoride to fluoroölefins containing more than two carbon atoms. However, the reaction proceeds readily with a large number of fluoroölefins when anhydrous hydrogen fluoride[4] is used as a solvent. Mercuric fluoride is soluble in hydrogen fluoride at 100° and autogenous pressure in an autoclave. Branched-chain mercurials synthesized by this method are given in Table I. The low yields for III and IV undoubtedly can be improved by more detailed examination of reaction conditions. The method can also be used to obtain the fluoroethyl mercurials, bis(pentafluoroethyl)mercury and bis(1-chloro-1,2,2,2-tetrafluoroethyl)mercury, described by Krespan.[2] In addition, we have made a new fluoroethyl derivative, bis(1,1-dichloro-2,2,2-trifluoroethyl)mercury, which was prepared in 69% yield from 1,1-dichloro-2,2-difluoroethylene.

TABLE I

FLUOROMERCURIALS FROM FLUOROÖLEFINS AND MERCURIC FLUORIDE

$$2R_1R_2C{=}CF_2 + HgF_2 \xrightarrow{HF} [R_1R_2CCF_3]_2Hg$$

Olefin	Product	Yield, %
$CF_3CF{=}CF_2$	$(CF_3)_2CF—Hg—CF(CF_3)_2$ (I)	60
$HCF_2CF_2CF{=}CF_2$	 $HCF_2CF_2\overset{CF_3}{\overset{\vert}{C}}F—Hg—\overset{CF_3}{\overset{\vert}{C}}FCF_2CF_2H$ (II)	73
$ClCF_2CF_2CF{=}CF_2$	 $ClCF_2CF_2\overset{CF_3}{\overset{\vert}{C}}F—Hg—\overset{CF_3}{\overset{\vert}{C}}FCF_2CF_2Cl$ (III)	*ca.* 5
$H(CF_2)_3CF{=}CF_2$	 $H(CF_2)_3\overset{CF_3}{\overset{\vert}{C}}F—Hg—\overset{CF_3}{\overset{\vert}{C}}F(CF_2)_3H$ (IV)	Low
$(CF_3)_2CF{=}CF_2$	 $CF_3—\underset{CF_3}{\overset{CF_3}{C}}—Hg—\underset{CF_3}{\overset{CF_3}{C}}—CF_3$ (V)	33

Usual conditions for these preparations are 100–150° and autogenous pressure. For bis(nonafluoro-*t*-butyl)-mercury (V), temperatures of 180–200° were necessary. Addition of mercuric fluoride to the internal double bonds in such compounds as octafluoro-2-butene and

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[1] (a) A. A. Banks, H. J. Emeleus, R. N. Haszeldine, and V. Kerrigan, *J. Chem. Soc.*, 2188 (1948); (b) H. J. Emeleus and R. N. Haszeldine, *ibid.*, 2948, 2953 (1949); (c) J. Banus, H. J. Emeleus, and R. N. Haszeldine, *ibid.*, 3041 (1950).

[2] C. G. Krespan, U. S. Patent 2,844,614 (July 29, 1958); *J. Org. Chem.*, **25**, 105 (1960).

[3] (a) E. G. Howard and W. J. Middleton, U. S. Patent 2,970,173 (January 31, 1961); (b) W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 2589 (1961); (c) W. T. Miller, Jr., M. B. Freedman, J. H. Fried, and H. F. Koch, *ibid.*, **83**, 4105 (1961).

[4] Use of hydrogen fluoride as a solvent was first suggested to us by Professor W. T. Miller, Jr.