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DECARBOXYLATION SYNTHESES OF SOME POLYFLUOROPHENYL -TIN AND -GERMANIUM COMPOUNDS *

G. B. Deacon and G. J. Farquharson

Chemistry Department, Monash University, Clayton, Victoria 3168
(Australia)

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Summary

The triphenyltin carboxylates, Ph_3SnO_2CR (R = C_6F_5, p-$MeOC_6F_4$, p-$EtOC_6F_4$, or o-HC_6F_4), p-$(Ph_3SnO_2C)_2C_6F_4.H_2O$, and o-$(Ph_3SnO_2C)_2C_6F_4.H_2O$ have been prepared by reaction of triphenyltin hydroxide with the appropriate polyfluorocarboxylic acids in methanol. Thermal decomposition of Ph_3SnO_2CR (R = C_6F_5, p-$MeOC_6F_4$, or p-$EtOC_6F_4$) in boiling pyridine gave the corresponding polyfluorophenyltriphenyltin compounds Ph_3SnR. For R = p-$MeOC_6F_4$, the yield was lowered owing to competing formation of tetraphenyltin. Similar decomposition of p-$(Ph_3SnO_2C)_2C_6F_4.H_2O$ gave p-$(Ph_3Sn)_2C_6F_4$ (major product) and Ph_3Sn-p-HC_6F_4, whilst o-$(Ph_3SnO_2C)_2C_6F_4$ gave triphenyltin fluoride, and Ph_3SnO_2C-o-HC_6F_4 failed to react. Di(phenylmercuric)tetrafluoroterephthalate and tetrafluorophthalate underwent decarboxylation in boiling pyridine giving p-$(PhHg)_2C_6F_4$ and o-$PhHgC_6F_4CO_2HgPh$ respectively, whilst p-$(Ph_3PbO_2C)_2C_6F_4$ gave p-$(Ph_3Pb)_2C_6F_4$, Ph_3Pb-p-HC_6F_4, and tetraphenyllead. Reaction of bromotriphenylgermane with silver pentafluorobenzoate in boiling pyridine gave pentafluorophenyltriphenylgermane, but analogous reactions with silver p-ethoxytetrafluorobenzoate and disilver tetrafluoroterephthalate gave, after work up, mixtures of polyfluorophenylgermanes, Ph_4Ge, and $(Ph_3Ge)_2O$.

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[*] Preliminary communication, Ref. [1].

Introduction

Thermal decarboxylation reactions have proved very useful for the synthesis of organomercurials, [2–7], particularly when the organic group contains electron withdrawing substituents [2]. Analogous preparations of organometallics of other elements are few by comparison [1]. Polyfluorophenyltriphenyllead compounds are formed on thermal decomposition of the corresponding triphenyllead carboxylates [8], and the method has recently been extended to bis(polyfluorophenyl)diphenyllead compounds [9]. Decarboxylation syntheses of polyfluoroaryltin compounds have not been reported, though several other organotin compounds have been obtained by this route [2, 10, 11], and no organogermanes have been obtained by decarboxylation. We now report preparations of polyfluorophenyl-tin and -germanium compounds by thermal decomposition of the appropriate polyfluorobenzoates, together with some related syntheses of mercurials and organolead compounds.

Results and Discussion

(a) Preparations of Triphenyltin Polyfluorocarboxylates

The organotin carboxylates, Ph_3SnO_2CR ($R = C_6F_5$, p-$MeOC_6F_4$, p-$EtOC_6F_4$, or o-HC_6F_4), p-$(Ph_3SnO_2C)_2C_6F_4.H_2O$, and o-$(Ph_3SnO_2C)_2C_6F_4.H_2O$ were prepared by reaction of triphenyltin hydroxide with the appropriate carboxylic acids in methanol.

$$Ph_3SnOH + RCO_2H \longrightarrow Ph_3SnO_2CR + H_2O \qquad (1)$$

Analytical data suggest that all complexes except triphenyltin pentafluorobenzoate should be formulated as hydrates (see Experimental). However, in the case of Ph_3SnO_2CR ($R = p$-$MeOC_6F_4$, p-$EtOC_6F_4$, or o-HC_6F_4), no supporting evidence for hydration could be obtained by infrared spectroscopy or PMR spectroscopy. Thermogravimetric analysis of triphenyltin p-methoxytetrafluorobenzoate was unhelpful, showing steady decomposition up to the melting-point (102°). Accordingly, it is likely that Ph_3SnO_2CR ($R = p$-$MeOC_6F_4$, p-$EtOC_6F_4$, or o-HC_6F_4) were obtained somewhat impure and not as hydrates. However, their identification is certain from mass spectrometry (molecular ions observed), and PMR, ^{19}F NMR, and infrared spectroscopy (see Experimental Section). Supporting evidence for the presence of water in p-$(Ph_3SnO_2C)_2C_6F_4.H_2O$ and o-$(Ph_3SnO_2C)_2C_6F_4.H_2O$ has been obtained. The PMR spectrum of the former in deuterochloroform showed a resonance indicative of water, and thermogravimetric analysis revealed an endothermic weight loss at 96°, though loss of water was evidently accompanied by partial decarboxylation. Microanalysis suggested that o-$(Ph_3SnO_2C)_2C_6F_4.H_2O$ underwent dehydration on being heated at 100° under vacuum.

The separations between the carboxylate stretching frequencies of solid Ph_3SnO_2CR (R = C_6F_5, p-$MeOC_6F_4$, or p-$EtOC_6F_4$) are comparable to those for the corresponding sodium carboxylates (Table 1), consistent [12] with bidentate or bridging bidentate carboxylate coordination. The carboxylate stretching frequencies are similar to those (Table 1) for the analogous triphenyllead carboxylates [8], which have associated structures with five coordinate lead and bridging bidentate carboxylate groups in the solid state, and it is probable that the tin compounds have similar structures. Numerous triorganotin carboxylates have been shown to have structures of this type [13] (see also Refs. given in [8]).

(b) Thermal Decomposition Reactions giving Polyfluorophenyltin Compounds

The products isolated from the thermal decomposition reactions are listed in Table 2.

The triphenyltin polyfluorocarboxylates, Ph_3SnO_2CR (R = C_6F_5, p-$MeOC_6F_4$, or p-$EtOC_6F_4$) and p-$(Ph_3SnO_2C)_2C_6F_4.H_2O$ underwent decarboxylation in

TABLE 1

CARBOXYLATE STRETCHING FREQUENCIES (cm^{-1})

Compound	$\nu(CO_2)$asym	$\nu(CO_2)$sym	Separation
$NaO_2CC_6F_5$ [a]	1610	1400	210
$Ph_3SnO_2CC_6F_5$	1607 and 1583	1395 and 1380	ca. 208
$Ph_3PbO_2CC_6F_5$ [a]	1581 and 1559	1399	171
NaO_2C-p-$MeOC_6F_4$ [a]	1596	1385	211
Ph_3SnO_2C-p-$MeOC_6F_4$	1577 and 1561	ca. 1380	ca. 189
Ph_3PbO_2C-p-$MeOC_6F_4$ [a]	1578 and 1559	1383	185
NaO_2C-p-$EtOC_6F_4$ [a]	1594	1383	211
Ph_3SnO_2C-p-$EtOC_6F_4$	1610 and 1578	1385	ca. 209
Ph_3PbO_2C-p-$EtOC_6F_4$ [a]	1579 and 1569	1380	194

[a] From Ref. [8].

TABLE 2

PRODUCTS FROM THERMAL DECOMPOSITION REACTIONS

Carboxylates	Reaction time (hr)	Products	Yield (%)
$Ph_3SnO_2CC_6F_5$	1	$Ph_3SnC_6F_5$	65
$Ph_3SnO_2C\text{-}\underline{p}\text{-}MeOC_6F_4$	1	$Ph_3Sn\text{-}\underline{p}\text{-}MeOC_6F_4$	14
		+ Ph_4Sn	4
		+ reactant carboxylate	ca. 15
$Ph_3SnO_2C\text{-}\underline{p}\text{-}MeOC_6F_4$	5	Ph_4Sn	[a]
$Ph_3SnO_2C\text{-}\underline{p}\text{-}EtOC_6F_4$	1	$Ph_3Sn\text{-}\underline{p}\text{-}EtOC_6F_4$	27
		+ reactant carboxylate	ca. 50
$Ph_3SnO_2C\text{-}\underline{p}\text{-}EtOC_6F_4$	5	$Ph_3Sn\text{-}\underline{p}\text{-}EtOC_6F_4$	47
		+ Ph_4Sn	trace
		+ reactant carboxylate	ca. 10
$Ph_3SnO_2C\text{-}\underline{o}\text{-}HC_6F_4$	4	reactant carboxylate	[a]
$\underline{p}\text{-}(Ph_3SnO_2C)_2C_6F_4.H_2O$	10	$\underline{p}\text{-}(Ph_3Sn)_2C_6F_4$	81
		+ $Ph_3Sn\text{-}\underline{p}\text{-}HC_6F_4$	15
$\underline{o}\text{-}(Ph_3SnO_2C)_2C_6F_4$	4	Ph_3SnF	[a]
$\underline{o}\text{-}(PhHgO_2C)_2C_6F_4$	2	$\underline{o}\text{-}PhHgC_6F_4CO_2HgPh$	85
$\underline{p}\text{-}(PhHgO_2C)_2C_6F_4$	2	$\underline{p}\text{-}(Ph\ Hg)_2C_6F_4$	68
$\underline{p}\text{-}(Ph_3PbO_2C)_2C_6F_4$	5	$\underline{p}\text{-}(Ph_3Pb)_2C_6F_4$	15
		+ $Ph_3Pb\text{-}\underline{p}\text{-}HC_6F_4$	12
		+ Ph_4Pb	68[b]
$[AgO_2CC_6F_5 + Ph_3GeBr]$	3	$Ph_3GeC_6F_5$	25
$[AgO_2C\text{-}\underline{p}\text{-}EtOC_6F_4 + Ph_3GeBr]$	6	$Ph_3Ge\text{-}\underline{p}\text{-}EtOC_6F_4$, $(Ph_3Ge)_2O$, Ph_4Ge	[c]
$[\underline{p}\text{-}(AgO_2C)_2C_6F_4 + 2\,Ph_3GeBr]$	7	$\underline{p}\text{-}(Ph_3Ge)_2C_6F_4$, $Ph_3Ge\text{-}\underline{p}\text{-}HC_6F_4$, $(Ph_3Ge)_2O$, Ph_4Ge	[c]

[a] Major organometallic product; yield not determined.

[b] Based on $\underline{p}\text{-}(Ph_3PbO_2C)_2C_6F_4 \longrightarrow Ph_4Pb + Ph_2Pb[\underline{p}\text{-}(O_2C)_2C_6F_4]$.

[c] Mixtures of products obtained; yields not determined.

boiling pyridine affording the corresponding polyfluorophenyltriphenyltin compounds.

$$Ph_3SnO_2CR \longrightarrow Ph_3SnR + CO_2 \qquad (2)$$

$$\underline{p}\text{-}(Ph_3SnO_2C)_2C_6F_4 \longrightarrow \underline{p}\text{-}(Ph_3Sn)_2C_6F_4 + 2CO_2 \qquad (3)$$

Identification of the compounds followed readily from analytical data, and infrared, mass, and ^{19}F NMR spectra (Experimental Section). Assignment of the major peaks in the infrared spectra followed straightforwardly from data for suitable reference compounds, e.g. diphenylthallium(III) halides [14] and bis(pentafluorophenyl)thallium(III) halides [15]. The mass spectra generally showed behaviour similar to that reported for pentafluorophenyltriphenyltin [16]. Assignments of the ^{19}F NMR spectra were based on published chemical shift data [17].

Thermal decomposition of Ph_3SnO_2CR (R = $\underline{p}$-$MeOC_6F_4$ or $\underline{p}$-$EtOC_6F_4$) gave tetraphenyltin in addition to the p-alkoxytetrafluorophenyltriphenyltin derivatives. The formation of tetraphenyltin can be attributed to the disproportionation reactions (4) or (5).

$$2Ph_3SnO_2CR \longrightarrow Ph_4Sn + Ph_2Sn(O_2CR)_2 \qquad (4)$$

$$2Ph_3SnR \longrightarrow Ph_4Sn + Ph_2SnR_2 \qquad (5)$$

Neither diphenyltin dicarboxylates nor bis(polyfluorophenyl)diphenyltin derivatives were isolated, but the former compounds would probably decompose further in pyridine or hydrolyse on work up (ready hydrolysis of diphenyltin benzoate has been observed [18]).

In addition to the high yield of $\underline{p}$-$(Ph_3Sn)_2C_6F_4$, a low yield of triphenyl-2,3,5,6-tetrafluorophenyltin was obtained from thermal decomposition of bis(triphenyltin) tetrafluoroterephthalate. The origin of this compound may be hydrolysis of the major product during thin layer chromatography.

$$\underline{p}\text{-}(Ph_3Sn)_2C_6F_4 + H_2O \longrightarrow Ph_3Sn\text{-}\underline{p}\text{-}HC_6F_4 + Ph_3SnOH \qquad (6)$$

Pyrolysis of bis(triphenyllead) tetrafluoroterephthalate, prepared by reaction of triphenyllead acetate with tetrafluoroterephthalic acid, was also examined. Both $\underline{p}$-$(Ph_3Pb)_2C_6F_4$ and Ph_3Pb-$\underline{p}$-HC_6F_4 were obtained, the proportion of the latter being greater than the proportion in the tin system. In addition, tetraphenyllead (major product) was isolated, whereas $\underline{p}$-$(Ph_3SnO_2C)_2C_6F_4$ did not give tetraphenyltin. Thermal decomposition of di(phenylmercuric) tetrafluoroterephthalate resulted in decarboxylation giving p-di(phenylmercuri)-tetrafluorobenzene in high yield.

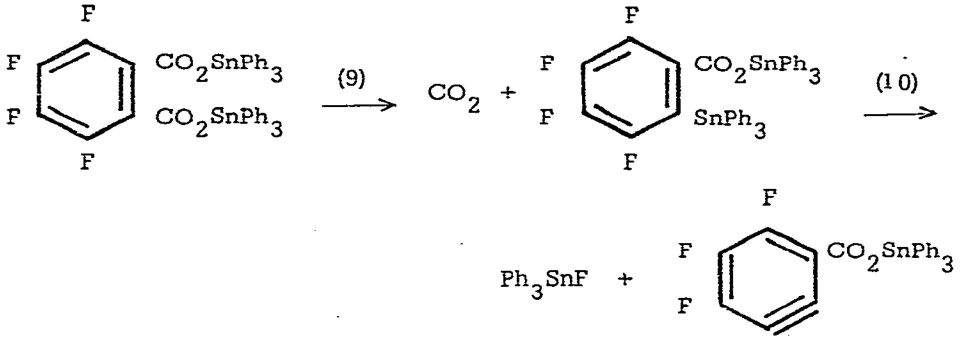
$$\underline{p}\text{-}(PhHgO_2C)_2C_6F_4 \longrightarrow 2CO_2 + \underline{p}\text{-}(PhHg)_2C_6F_4 \qquad (7)$$

Attempted recrystallization of this compound gave a less pure product possibly owing to disproportionation.

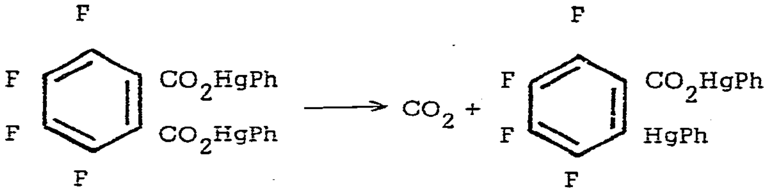
$$\underline{p}\text{-}(PhHg)_2C_6F_4 \longrightarrow Ph_2Hg + \left(\underline{p}\text{-}HgC_6F_4\right)_n \qquad (8)$$

A para-tetrafluorophenylenemercury polymer has previously been prepared by decarboxylation of mercuric tetrafluoroterephthalate [5].

Thermal decomposition of bis(triphenyltin) tetrafluorophthalate gave an insoluble high melting solid, identified as triphenyltin fluoride by infrared spectroscopy [19]. A possible reaction path comprises hemidecarboxylation (9) followed by elimination of the fluorine ortho to the bulky triphenyltin substituent (10).



Support for this path comes from the observation that di(phenylmercuric) tetrafluorophthalate gave phenylmercuric o-(phenylmercuri)tetrafluorobenzoate on thermal decomposition.



(11)

The product was identified by the ^{19}F NMR spectrum, which showed four equal intensity multiplets. The lowest field resonance was in a position appropriate for a fluorine ortho to a heavy metal [20], and showed satellites indicative of ^{199}Hg–F coupling. Decarboxylation reactions of mercuric salts of phthalic acids are characterized by preferential loss of one carbon dioxide [2]. Thus, hemidecarboxylation occurs in the Pesci reaction [21] between mercuric acetate and sodium phthalates, and mercuric tetrafluorophthalate loses one molecule of CO_2 at 220° giving $\left(\underline{o}\text{-}HgC_6F_4CO_2\right)_3$, which does not decompose into $\left(\underline{o}\text{-}HgC_6F_4\right)_3$ until 300° [22].

(c) Thermal Decomposition Reactions giving Polyfluorophenylgermanium Compounds

Reaction of silver pentafluorobenzoate with bromotriphenylgermane in refluxing pyridine gave pentafluorophenyltriphenylgermane (Table 2), presumably by formation and decarboxylation of triphenylgermanium pentafluorobenzoate.

$$Ph_3GeBr + AgO_2CC_6F_5 \rightarrow AgBr + [Ph_3GeO_2CC_6F_5] \rightarrow Ph_3GeC_6F_5 + CO_2$$

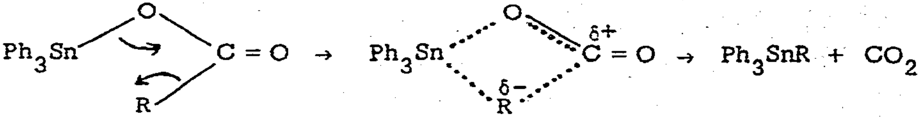
By contrast, reaction of bromotriphenylgermane with silver p-ethoxytetrafluorobenzoate and disilver tetrafluoroterephthalate gave other products (Table 2) in addition to Ph_3Ge-p-$EtOC_6F_4$ and p-$(Ph_3Ge)_2C_6F_4$. In each case, the polyfluorophenylgermane was obtained mixed with bis(triphenylgermanium) oxide after t.l.c. of the reaction product, and was identified by ^{19}F NMR spectroscopy. The germoxane, identified by the infrared spectrum [23], was probably formed by partial hydrolysis of the polyfluorophenylgermanes during chromatography.

e.g. $$Ph_3Ge\text{-}p\text{-}EtOC_6F_4 + H_2O \rightarrow p\text{-}HC_6F_4OEt + Ph_3GeOH \xrightarrow{-H_2O} (Ph_3Ge)_2O$$

The formation of tetraphenylgermane and triphenyl-2,3,5,6-tetrafluorophenylgermane (Table 2) can be explained in a similar manner to formation of the corresponding organotin compounds [reactions (4) and (6)].

(d) Preparative Utility of Decarboxylation for Polyfluorophenyl-tin and -germanium Compounds

The high yield of pentafluorophenyltriphenyltin obtained by decarboxylation (Table 2) and the comparative simplicity of the procedure should make the method competitive with the previously reported Grignard synthesis [24, 25]. The other polyfluorophenyltins are new compounds, and all except Ph_3Sn-p-$MeOC_6F_4$ were obtained in satisfactory yield. An attractive alternative route to Ph_3Sn-p-$MeOC_6F_4$ is not readily conceived. The Grignard or organolithium method would require prior synthesis of p-$MeOC_6F_4X$ (X = Br or I), which have to be purified by preparative g.l.c. [26]. Since decarboxylation of Ph_3SnO_2C-o-HC_6F_4 and o-$(Ph_3SnO_2C)_2C_6F_4$ could not be effected, it appears that two fluorines ortho to the carboxyl group are essential for carbon dioxide elimination to occur, thus imposing restrictions on the use of decarboxylation in formation of polyfluoroaryl-tin bonds. The substituent effects are consistent with electrophilic attack of tin on an organic group which develops considerable carbanionic character in the transition state.



Similar restrictions probably also apply to decarboxylation preparations of polyfluoroarylgermanes. In addition, the products are more susceptible to hydrolysis on work up than the corresponding organotin compounds. Although $Ph_3GeC_6F_5$ can be obtained conveniently by decarboxylation, the Grignard method [27] gives a higher yield. However, the present preparations are the first successful use of any elimination reaction in the formation of germanium-carbon bonds. Unsuccessful attempts to obtain perfluoroalkylgermanes by decarboxylation have been reported [28, 29].

Experimental

Microanalyses were by the Australian Microanalytical Service, Melbourne. Infrared spectra (4000-400 cm^{-1}) of compounds as Nujol and hexachlorobutadiene mulls were recorded with a Perkin-Elmer 180 spectrophotometer. Only bands of medium or greater intensity are listed.* Assignments (below) were based on reported data ($\nu(CO_2)$ [30], other vibrations [14, 15]). NMR spectra were obtained with a Bruker WH-90 or a Varian A56/60A instrument. Chemical shifts are given in p.p.m. downfield from tetramethylsilane (^1H) or upfield from $CFCl_3$ (^{19}F). Mass spectra were obtained with an AEI MS 30 double beam, double focussing instrument. Each listed m/e value is the most intense peak of a cluster with the correct isotope pattern for the assignment given. Only peaks above m/e 197 ($PhSn^+$) with intensities at least 15% of the main peak of the most prominent cluster (assigned 100% abundance) are given,* except that molecular-ions are given irrespective of intensity.

Pentafluorobenzoic acid, tetrafluorophthalic acid, and tetrafluoroterephthalic acid were from Bristol Organics, and bromotriphenylgermane was from ROC-RIC. Tetraphenyllead was from the Organisch Chemisch Institut, T.N.O., Utrecht, and tetraphenyltin was obtained from Fluka. Pyridine was refluxed over and distilled from potassium hydroxide under nitrogen and was stored over molecular sieves. Triphenyltin hydroxide [31], 2,3,4,5-tetrafluorobenzoic acid [32], bis(triphenylgermanium) oxide [33], silver

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* More complete details of the infrared and mass spectra are available on request to the authors.

pentafluorobenzoate [34], and the 4-alkoxy-2,3,5,6-tetrafluorobenzoic acids [8, 35] were prepared by reported methods. Silver 4-ethoxy-2,3,5,6-tetrafluorobenzoate and disilver tetrafluoroterephthalate were prepared by the method used previously for silver pentafluorobenzoate.

Silver 4-ethoxy-2,3,5,6-tetrafluorobenzoate (nc). M.p. 205° (dec.) (Found: C, 32.0; H, 1.9. $C_9H_5AgF_4O_3$ calcd.: C, 31.3; H, 1.5%). Infrared absorption: 2990m, 1703m (sh), 1653vs, ca. 1560vs (br) [$\nu_{as}(CO_2)$], 1505 and 1482vs, 1419 and 1390vs [$\nu_s(CO_2)$], 1277s, 1137 and 1120vs (br), 1028 and 990vs, 945s, 817s, 767 and 755vs, 723m, 506m (br) cm^{-1}.

Disilver tetrafluoroterephthalate (nc). M.p. > 300° (Found: C, 21.1. $C_8Ag_2F_4O_4$ calcd.: C, 21.3%). Infrared absorption: ca. 1565vs (br) [$\nu_{as}(CO_2)$], ca. 1475vs (br), ca. 1390vs (br) [$\nu_s(CO_2)$], 985vs (br), 766m, 741 and 722vs, 494s cm^{-1}.

(a) Preparation and thermal decomposition of triphenyltin polyfluorocarboxylates

Stoichiometric amounts of triphenyltin hydroxide and the appropriate acid each dissolved in hot methanol (ca. 75 ml) were mixed and the solution was boiled for 30 min. The carboxylate complexes were obtained quantitatively as white powders upon evaporation of the solvent *in vacuo*, and were used without purification. Thermal decomposition was effected by heating the carboxylate (ca. 1.0-2.0 gm) in pyridine (5 ml) under nitrogen. The solvent was removed *in vacuo* and the residue was dissolved in benzene and put on t.l.c. plates (1:1 mixture of Kieselgel HF_{254} and Kieselgel G : Merck). Reaction times and yields are listed in Table 2, detailed purification procedures being given with the individual compounds. All compounds were obtained as white crystals.

Triphenyltin pentafluorobenzoate (nc). M.p. 126-128° (Found: C, 52.9; H, 2.9. $C_{25}H_{15}F_5O_2Sn$ calcd.: C, 53.5; H, 2.7. $C_{25}H_{15}F_5O_2Sn.H_2O$ calcd.: C, 51.9; H, 3.0%). Infrared absorption: 3070 and 3055m [$\nu(CH)$], 1655s, 1607 and 1583vs (br) [$\nu_{as}(CO_2)$], 1566vs, 1533s, 1522vs, 1495vs (br), 1481s, 1471s, 1432vs [$\nu(CC)$], 1395 and 1380vs (br) [$\nu_s(CO_2)$], 1304m, 1123s, 1109s, 1078m, 995vs (br) [$\nu(CF)$], 934m, 829m, 765 and 760s, 750s, 727vs [$\gamma(CH)$], 695vs [$\phi(CC)$], 663m, 509m, 450 and 440s [X-sens. *y*] cm^{-1}. Mass spectrum: m/e 562 (2%, M^+), 485 (100, $Ph_2SnO_2CC_6F_5^+$), 441 (31, $Ph_2SnC_6F_5^+$), 293 (61, Ph_2SnF^+), 287 (19, $C_6F_5Sn^+$), 274 (19, Ph_2Sn^+), 197 (46, $PhSn^+$). PMR spectrum ($CDCl_3$): ca. 7.6 (m, Ph) p.p.m., unchanged after shaking the solution with D_2O. ^{19}F NMR spectrum ($CDCl_3$): 138.3 (m, 2F, F 2,6), 150.9 (m, 1F, F 4), 161.8 (m, 2F, F 3,5) p.p.m. *Thermal* decomposition: Elution of the benzene solubles with light petrol/acetone (9:1 v/v) gave one mobile band, which was extracted with acetone. Recrystallization from ethanol gave pentafluorophenyltriphenyltin, m.p. 84-85°, lit. [24] m.p. 86° (Found: C, 55.8; H, 3.0. $C_{24}H_{15}F_5Sn$ calcd.: C, 55.7; H, 2.9%). The infrared [24], mass [16], and ^{19}F NMR [20] spectra were in good agreement with reported data.

Triphenyltin 4-methoxy-2,3,5,6-tetrafluorobenzoate (nc). M.p. 102° (Found: C, 52.9; H, 3.6. $C_{26}H_{18}F_4O_3Sn$ calcd.: C, 54.5; H, 3.2. $C_{26}H_{18}F_4O_3Sn.H_2O$ calcd.: C, 52.3; H, 3.4%). Infrared absorption: 3070 and 3050m [ν(CH)], 1650s, 1597s (sh), 1577 and 1561vs [$\nu_{as}(CO_2)$], 1507s and 1485vs, 1432s [ν(CC)], ca. 1380vs (br) [$\nu_s(CO_2)$], 1337s (sh), 1283 and 1260s, 1195m, 1129 and 1120s [ν(CF)], 1078m, 1024m, 998vs and 977s [ν(CF)], 750s, 730vs [γ(CH)], 695vs [ϕ(CC)], 684m, 449s [X-sens. y] cm^{-1}. Mass spectrum: m/e 574 (2%, M^+), 497 (100, $Ph_2SnO_2CC_6F_4OMe^+$), 453 (52, $Ph_2SnC_6F_4OMe^+$), 293 (42, Ph_2SnF^+), 197 (35, $PhSn^+$). PMR spectrum ($CDCl_3$): 4.12 (s, 3H, OCH_3), ca. 7.7 (m, 15H, Ph) p.p.m., unchanged after shaking the solution with D_2O. ^{19}F NMR spectrum ($CDCl_3$): 139.7 (m, 2F, F 2,6), 158.5 (m, 2F, F 3,5) p.p.m. Thermal decomposition: (i) 1 hr reaction. Elution of the benzene solubles with light petrol/acetone (85:15 v/v) gave three bands, which were extracted with acetone. The fastest-moving band was tetraphenyltin, m.p. 222-224°, lit. [36a] m.p. 224-225° (infrared spectrum identical with that of an authentic sample). Recrystallization of the product from the second band from ethanol gave 4-methoxy-2,3,5,6-tetrafluorophenyltriphenyltin (nc), m.p. 89° (Found: C, 57.3; H, 3.7; F, 13.6. $C_{25}H_{18}F_4OSn$ calcd.: C, 56.8; H, 3.4; F, 14.4%). Infrared absorption: 3070 and 3050m [ν(CH)], 2945m, 1634s, 1495vs and 1484s, 1460vs (br), 1430vs [ν(CC)], 1368s, 1193m, 1100 and 1078vs [ν(CF)], 1025m, 997s, 970vs [ν(CF)], 936m, 731vs [γ(CH)], 700vs [ϕ(CC)], 448 vs [X-sens. y] cm^{-1}. Mass spectrum: m/e 453 (100%, $Ph_2SnC_6F_4OMe^+$), 351 (26, Ph_3Sn^+), 293 (44, Ph_2SnF^+), 274 (21, Ph_2Sn^+), 197 (49, $PhSn^+$). A molecular-ion cluster was not observed. PMR spectrum: ($CDCl_3$): 4.07 (s, 3H, OCH_3), ca. 7.5 (m, 15H, Ph) p.p.m. ^{19}F NMR spectrum ($CDCl_3$): 120.3 (m, 2F, F 2,6), 156.1 (m, 2F, F 3,5) p.p.m. The infrared spectrum of the material from the bottom band was similar to that of the reactant carboxylate. (ii) 5 hr reaction. Elution of the benzene solubles with light petrol/acetone (9:1 v/v) gave two bands, which were extracted with acetone. The faster-moving band was tetraphenyltin (infrared identification), while the infrared spectrum of the product from the second band was similar to that of the reactant carboxylate.

Triphenyltin 4-ethoxy-2,3,5,6-tetrafluorobenzoate (nc). M.p. 103-105° (Found: C, 54.0; H, 3.8. $C_{27}H_{20}F_4O_3Sn$ calcd.: C, 55.2; H, 3.4. $C_{27}H_{20}F_4O_3Sn.H_2O$ calcd.: C, 53.6; H, 3.7%). Infrared absorption: 3063 and 3045m [ν(CH)], 2992m, 1648vs, 1610vs (br) and 1578vs [$\nu_{as}(CO_2)$], 1562vs, 1504s, 1481vs, 1430vs [ν(CC)], 1385vs (br) [$\nu_s(CO_2)$], 1333s (sh), 1283m, 1260m, 1125vs (br) [ν(CF)], 1079m, 1020s and 992vs (br) [ν(CF)], 767 and 760m, 747s, 730vs [γ(CH)], 695vs [ϕ(CC)], 445 and 440s [X-sens. y] cm^{-1}. Mass spectrum: m/e 588 (3%, M^+), 511 (100, $Ph_2SnO_2CC_6F_4OEt^+$), 467 (56, $Ph_2SnC_6F_4OEt^+$), 351 (27, Ph_3Sn^+), 293 (83, Ph_2SnF^+), 197 (86, $PhSn^+$). PMR spectrum ($CDCl_3$): 1.40 (t, J 7 Hz, 3H, $OCH_2C\underline{\underline{H}}_3$), 4.37 (q, J 7 Hz, 2H, $OC\underline{\underline{H}}_2CH_3$), ca. 7.7 (m, 15H, Ph) p.p.m., unchanged after shaking the solution with D_2O. ^{19}F NMR spectrum ($CDCl_3$): 140.0 (m, 2F, F 2,6), 157.9 (m, 2F, F 3,5) p.p.m. Thermal decomposition: (i) 5 hr reaction. Elution of the benzene solubles with light petrol/acetone (85:15 v/v) gave three bands, which were extracted with acetone. The fastest-moving band was tetraphenyltin (infrared identification). Recrystallization from ethanol of the product from the second band gave 4-ethoxy-2,3,5,6-tetrafluorophenyltriphenyltin (nc), m.p. 63° (Found: C, 57.4; H, 3.8; F, 13.5. $C_{26}H_{20}F_4OSn$ calcd.: C, 57.5; H, 3.7; F, 14.0%). Infrared absorption: 3065 and 3050m [ν(CH)], 2990m, 1633m, 1491 and 1481s, 1460vs (br), 1428vs [ν(CC)], 1390s, 1369s and 1362vs, 1091vs and 1075s [ν(CF)], 1061m (sh), 997s, 957vs [ν(CF)], 726vs [γ(CH)], 695vs [ϕ(CC)], 446 and 438s [X-sens. y] cm^{-1}. Mass spectrum: m/e 544 (< 1%, M^+), 467 (100, $Ph_2SnC_6F_4OEt^+$), 361 (16, $PhSnC_6F_4O^+$), 293 (43, Ph_2SnF^+), 197 (50, $PhSn^+$). PMR spectrum ($CDCl_3$): 1.41 (t, J 7 Hz, 3H, $OCH_2C\underline{\underline{H}}_3$), 4.31 (q, J 7 Hz, 2H, $OC\underline{\underline{H}}_2CH_3$), ca. 7.5 (m, 15H, Ph). ^{19}F NMR spectrum ($CDCl_3$): 120.5 (m, 2F, F 2,6), 155.4 (m, 2F, F 3,5) p.p.m. The infrared spectrum of the product from the third band was similar to that of the reactant carboxylate. (ii) 1 hr reaction. Elution of the benzene solubles with acetone/light petrol (1:9 v/v) gave two bands, which were extracted with acetone. Recrystallization from ethanol of the product from the faster-moving band gave 4-ethoxy-2,3,5,6-tetrafluorophenyltriphenyltin, m.p. 63° (infrared identification). The infrared spectrum of the product from the second band was similar to that of the reactant carboxylate.

Triphenyltin 2,3,4,5-tetrafluorobenzoate (nc). M.p. 100-102° (Found: C, 54.0; H, 2.9. $C_{25}H_{16}F_4O_2Sn$ calcd.: C, 55.3; H, 3.0. $C_{25}H_{16}F_4O_2Sn.H_2O$ calcd.: C, 53.5; H, 3.2%). Infrared absorption: 3072m [ν(CH)], 1650vs (sh), 1635 and 1625vs, 1606vs (sh), 1578 [$\nu_{as}(CO_2)$] and 1561vs, 1525vs, 1480vs, 1431vs [ν(CC)], 1400 and 1378vs (br) [$\nu_s(CO_2)$], 1306 and 1296s, 1265vs, 1190m, 1099vs, 1076vs, 1036vs (br) [ν(CF)], 997s, 929vs [ν(CF)], 896s, 805m, 790vs, 778vs, 765s, 734vs (γ(CH)], 728s, 697vs [ϕ(CC)], 674m (sh), 661m, 554s and 543m (br), 452 and 441vs [X-sens. y], 430s cm^{-1}. Mass spectrum: m/e 544 (3%, M$^+$), 467 (100, $Ph_2SnO_2CC_6HF_4^+$), 423 (16, $Ph_2SnC_6HF_4^+$), 293 (39, Ph_2SnF^+), 197 (28, $PhSn^+$). PMR spectrum ($CDCl_3$): ca. 7.7 (m, Ph and $-C_6\underline{H}F_4$) p.p.m., unchanged after shaking the solution with D_2O. ^{19}F NMR spectrum [$(CD_3)_2SO$]: 137.4 (m, 1F, F2 or F5), 139.4 (m, 1F, F2 or F5), 152.3 (m, 1F, F3 or F4), 155.2 (m, 1F, F3 or F4) p.p.m. Thermal decomposition: Elution of the benzene soluble product with acetone/light petrol (2:3 v/v) gave a broad poorly resolved band which was extracted with acetone. The infrared spectrum of this product was similar to that of the reactant carboxylate.

Bis(triphenyltin) 2,3,5,6-tetrafluoroterephthalate hydrate (nc). M.p. 230-32° (Found: C, 55.2; F, 3.8. $C_{44}H_{30}F_4O_4Sn_2.H_2O$ calcd.: C, 55.4; H, 3.4. $C_{44}H_{30}F_4O_4Sn_2$ calcd.: C, 56.5; H, 3.2%). Infrared absorption: 3070m [ν(CH)], 1624vs (sh), 1600vs (br) [$\nu_{as}(CO_2)$], 1582vs (sh), 1570vs, 1500m, 1480s, 1450s, 1432vs [ν(CC)], 1377vs (br) [$\nu_s(CO_2)$], 1336m (sh), 1258m, 1081s, 1025m, 998s and 990vs [ν(CF)], 730vs [γ(CH)], 696vs [ϕ(CC)], 480m, 450vs [X-sens. y] cm^{-1}. Mass spectrum: m/e 466 (18%, $C_6F_4CO_2SnPh_2^+$), 351 (88, Ph_3Sn^+), 309 (31, $C_{12}H_{10}FOSn^+$), 293 (100, Ph_2SnF^+), 197 (60, $PhSn^+$). A molecular-ion cluster was not observed. PMR spectrum ($CDCl_3$): 3.45 (s, H_2O), ca. 7.7 (m, Ph) p.p.m. The resonance at 3.45 p.p.m. disappeared upon shaking the solution with D_2O. ^{19}F NMR spectrum ($CDCl_3$): 139.1 (s, $C_6\underline{F}_4$) p.p.m. Thermal decomposition: The residue after evaporation of the pyridine was dissolved in chloroform and put on t.l.c. plates. Elution with light petrol/acetone (4:1 v/v) gave two bands, which were extracted with acetone. The faster-moving band was triphenyl-2,3,5,6-tetrafluorophenyltin (nc), m.p. 90-93° (Found: C, 58.5; H, 3.6. $C_{24}H_{16}F_4Sn$ calcd.: C, 57.8; H, 3.2%). Mass spectrum: m/e 500 (≪1%, M$^+$), 423 (100, $C_6HF_4SnPh_2^+$), 346 (15, $C_6HF_4SnPh^+$), 293 (48, Ph_2SnF^+), 197 (29, $PhSn^+$). ^{19}F NMR spectrum ($CDCl_3$): 120.0 (m, 2F, F 2,6), 137.8 (m, 2F, F 3,5) p.p.m. Recrystallization from benzene-ethanol of the product from the second band gave 1,2,4,5-*tetrafluoro*-3,6-*bis(triphenylstannyl)benzene (nc)*, m.p. 236° (Found: C, 59.7; H, 3.6; F, 8.6. $C_{42}H_{30}F_4Sn_2$ calcd.: C, 59.5; H, 3.6; F, 9.0%). Infrared absorption: 3062m [ν(CH)], 1480s, 1432vs [ν(CC)], 1418vs, 1381s, 1206vs, 1075s, 1025m, 999s, 927vs [ν(CF)], 730vs [γ(CH)], 696vs [ϕ(CC)], 559s, 449 and 436s [X-sens. *y*], 406 m cm^{-1}. Mass spectrum: m/e 771 (21%, $Ph_5C_6F_4Sn_2^+$), 351 (100, Ph_3Sn^+), 197 (69, Ph Sn^+). A molecular-ion cluster was not observed. ^{19}F NMR spectrum ($CDCl_3$): 118.6 (s, with ^{117}SnF/^{119}SnF satellites *J* 21.4 Hz, $-C_6F_4-$) p.p.m.

Bis(triphenyltin) 3,4,5,6-*tetrafluorophthalate (nc)*. The carboxylate was isolated as a monohydrate after evaporation of the methanol (Found: C, 55.2; H, 3.3%). After drying (ca. 100°, $< 10^{-2}$ mm Hg), the complex had m.p. 158-160° (Found: C, 57.7; H, 3.0%). Infrared absorption (4000-200 cm^{-1}): 3056m [ν(CH)], 1680vs, 1651vs (br) and 1633s [$\nu_{as}(CO_2)$], 1520s, 1475vs, 1432vs [ν(CC)], 1390 and 1350vs [$\nu_s(CO_2)$], 1299vs, 1260vs, 1195m, 1127m, 1075vs [ν(CF)], 1026m, 998s, 951vs [ν(CF)], 930m, 832m, 810m, 780vs, 763vs, 732vs [γ(CH)], 699vs [ϕ(CC)], 665m, 652m, 560m and 543s, 447vs [X-sens. *y*], 420m, 333m, 294m (sh), 270vs, 238s, 220s cm^{-1}. Mass spectrum: m/e 351 (100%, Ph_3Sn^+), 309 (18, $C_{12}H_{10}FOSn^+$), 197 (30, $PhSn^+$). A molecular-ion cluster was not observed. ^{19}F NMR spectrum ($CDCl_3$): 137.7 (m, 2F, F 3,6), 151.9 (m, 2F, F 4,5) p.p.m. *Thermal decomposition:* The insoluble product was filtered off and identified as triphenyltin fluoride by the infrared spectrum [19].

(b) Preparation and thermal decomposition of mercuric and lead carboxylates

Bis(phenylmercuric) tetrafluoroterephthalate, bis(phenylmercuric) tetrafluorophthalate, and bis(triphenyllead) tetrafluoroterephthalate were prepared by reaction of stoichiometric amounts of phenylmercuric acetate or triphenyllead acetate with the appropriate acid in hot methanol. Thermal decomposition of the carboxylates was effected by heating in dry pyridine under nitrogen. Reaction times and yields are listed in Table 2, isolation and purification procedures being given with the individual compounds.

Bis(triphenyllead) 2,3,5,6-*tetrafluoroterephthalate (nc)*. M.p. 282-283° (dec.) (Found: C, 47.4; H, 2.8. $C_{44}H_{30}F_4O_4Pb_2$ calcd.: C, 47.5; H, 2.7%). Infrared absorption: 3055m [ν(CH)], ca. 1600 [$\nu_{as}(CO_2)$] and 1570vs, 1493m, 1474vs, 1435vs [ν(CC)], 1380vs (br) [$\nu_s(CO_2)$], 1255m, 1065m, 1019s, 997 and 985vs [ν(CF)], 735 and 726vs [γ(CH)], 692vs [ϕ(CC)], 474s, 440vs [X-sens. *y*] cm^{-1}. *Thermal decomposition:* After removal of the pyridine in vacuo, the product was recrystallized from a toluene-petrol mixture giving tetraphenyllead, m.p. 223-225°, lit. [36(b)] 227-228° (infrared spectrum identical with that of an authentic sample). The filtrate was evaporated and the recovered product was dissolved in chloroform and put on t.l.c. plates. Elution with acetone/light petrol (1:4 v/v) gave six bands. The fastest-moving band was tetraphenyllead (infrared identification). The second band gave triphenyl-2,3,5,6-tetrafluorophenyllead (nc), m.p. 97°. Infrared absorption: 3062s [ν(CH)], 1579m, 1470vs, 1430vs [ν(CC)], 1348vs, 1328m, 1213s, 1186s, 1165s, 1062m, 1017s, 999vs [ν(CF)], 896vs [ν(CF)], 854s, 723vs [γ(CH)], 705s and 694vs [φ(CC)], 661m, 440vs [X-sens. y] cm^{-1}. Mass spectrum: m/e 588 (< 1%, M^{+}), 511 (74, $Ph_2PbC_6HF_4^{+}$), 357 (45, $C_6HF_4Pb^{+}$), 285 (36, $PhPb^{+}$), 227 (43, PbF^{+}), 208 (100, Pb^{+}). ^{19}F NMR spectrum ($CDCl_3$): 119.2 (m, 2F, F 2,6), 137.8 (m, 2F, F 3,5) p.p.m. Recrystallization from light petrol of the product from the fourth band gave 1,2,4,5-tetrafluoro-3,6-bis(triphenylplumbyl)benzene (nc), m.p. 236°-238° (Found: C, 49.2; H, 2.9. $C_{42}H_{30}F_4Pb_2$ calcd.: C, 49.2; H, 2.9%). Infrared absorption: 3070s [ν(CH)], 3042m (sh), 1573m, 1477s, 1430vs [ν(CC)] and 1410s, 1376s, 1330m, 1300m, 1185vs, 1063m, 1019s, 995vs, 920vs [ν(CF)], 725vs [γ(CH)], 693vs [φ(CC)], 548s, 438vs [X-sens. y] cm^{-1}. Mass spectrum: m/e 1024 (< 1%, M^{+}), 947 (29, $C_6F_4Pb_2Ph_5^{+}$), 510 (23, $C_6F_4PbPh_2^{+}$), 439 (47, Ph_3Pb^{+}), 285 (78, $PhPb^{+}$), 227 (26, PbF^{+}), 208 (100, Pb^{+}). ^{19}F NMR spectrum ($CDCl_3$): 117.7 (s, $-C_6F_4-$) p.p.m. The products from the remaining bands were not obtained in sufficient yield for identification.

Bis(phenylmercuric) 2,3,5,6-tetrafluoroterephthalate (nc). M.p. > 300° (Found: C, 30.4; H, 1.5; F, 9.6. $C_{20}H_{10}F_4Hg_2O_4$ calcd.: C, 30.4; H, 1.3; F, 9.6%). Infrared absorption: 1660s (sh), 1657vs (sh), 1624 and 1610vs [$\nu_{as}(CO_2)$], 1575s, 1475vs, 1431s [ν(CC)], 1358vs (br) [$\nu_s(CO_2)$], 1317s (sh), 1272m, 1242vs, 1214m, 1080m, 1025s, 990vs [ν(CF)], 753 and 734vs [γ(CH)], 695vs [φ(CC)], 521vs, 445vs cm^{-1}. Thermal decomposition: The cooled reaction mixture was poured into light petrol (ca. 200 ml) and the precipitate was filtered off, washed with petrol, and dried in vacuo, giving 1,2,4,5-tetrafluoro-3,6-bis(phenylmercuri)benzene (nc), m.p. > 300° (Found: C, 30.1; H, 1.8. $C_{18}H_{10}F_4Hg_2$ calcd.: C, 30.7; H, 1.4%). Infrared absorption: 3065 and 3050m [ν(CH)], 1625m, 1426 and 1410vs [ν(CC)], 1371m, 1200vs, 1023m, 995m, 916vs [ν(CF)], 740m and 727vs [γ(CH)], 694vs [φ(CC)], 560m, 442m, 409m cm^{-1}. Attempted recrystallization of this product from a toluene-nitrobenzene mixture gave a less pure product (Found: C, 28.1; H, 1.5%).

Bis(phenylmercuric) 3,4,5,6-*tetrafluorophthalate (nc)*. M.p. > 230°, with slow decomposition. (Found: C, 30.0; H, 1.4%). Infrared absorption: 1644vs, 1610vs (br) [$\nu_{as}(CO_2)$], 1578vs, 1516s, 1481vs, 1436 and 1433s [ν(CC)], 1402vs (br) [$\nu_s(CO_2)$], 1356 and 1332vs, 1267s, 1120s, 1075vs [ν(CF)], 1026s, 1000s, 952vs [ν(CF)], 924s, 841s, 770 and 761vs, 726vs, 715m, 694vs, 620m, 551m, 530s, 455 and 448s, 419s cm^{-1}. *Thermal decomposition:* The cooled reaction mixture was poured into light petrol (ca. 200 ml). A small quantity of an unidentified insoluble product was filtered off, and the filtrate was evaporated giving *phenylmercuric* 2,3,4,5-*tetrafluoro*-6-*phenylmercuribenzoate (nc)*, m.p. > 300°. Infrared absorption: 3065 and 3055m [ν(CH)], 1620s (sh), 1610vs, 1558vs (br) [$\nu_{as}(CO_2)$], 1486 and 1479vs, 1455s, 1446s and 1431vs [ν(CC)], 1370 and 1355vs (br) [$\nu_s(CO_2)$], 1310m, 1270m, 1220m, 1090m, 1071m, 1049m, ca. 1030s [ν(CF)], 999m, 906m, 798m, 777m, 767m, 754s, 735 and 730vs [γ(CH)], 693s [ϕ(CC)], 645m, 451m [X-sens. *y*] cm^{-1}. ^{19}F NMR spectrum [$(CD_3)_2SO$]: 115.0 (m, with ^{199}HgF satellites J ca. 250 Hz, 1F, F 5), 131.3 (m, 1F, F 2), 150.2 (m, 1F, F3 or F4) and 155.4 (m, 1F, F3 or F4) p.p.m.

(c) Decarboxylation syntheses of organogermanium compounds

Bromotriphenylgermane and the stoichiometric amount of the appropriate silver salt were refluxed in dry pyridine under nitrogen for ca. 3 hr. The cooled solution was filtered from silver bromide. Addition of dichloromethane to the filtrate usually resulted in precipitation of additional silver bromide, which was filtered off. The filtrate was concentrated and then put on t.l.c. plates. Detailed product analysis is given with the individual compounds. *Pentafluorophenyltriphenylgermane*. Elution with light petrol/acetone (9:1 v/v) gave one mobile band, which was extracted with acetone. Recrystallization from light petrol gave the required *compound*, m.p. 116-117°, lit. [27] m.p. 114-116° (Found: C, 62.1; H, 3.5. $C_{24}H_{15}F_5Ge$ calcd.: C, 61.2; H, 3.2%). The infrared [27] and ^{19}F NMR [20] spectra were in good agreement with reported data, except the absorption noted [27] at 1560 cm^{-1} in the infrared spectrum was not observed. Mass spectrum: m/e 472 (11%, M^+), 395 (100, $C_6F_5GePh_2^+$), 318 (50, $C_6F_5GePh^+$), 305 (55, Ph_3Ge^+), 247 (100, Ph_2GeF^+), 228 (28, Ph_2Ge^+).
4-*Ethoxy*-2,3,5,6-*tetrafluorophenyltriphenylgermane (nc)*. Elution with light petrol/acetone (9:1 v/v) gave three prominent bands, which were extracted with acetone. The fastest moving band was tetraphenylgermane, m.p. 225°,

lit. [36(c)] m.p. 233-4° (infrared identification [37]). The second band was a mixture of bis(triphenylgermanium) oxide (infrared identical with that of the authentic compound) and the required compound. PMR spectrum ($CDCl_3$): 1.41 (t, J 7 Hz, 3H, $OCH_2C\underline{H}_3$), 4.32 (q, J 7 Hz, 2H, $OC\underline{H}_2CH_3$), ca. 7.4 (m, >> 15H, Ph of both the required compound and the germoxane) p.p.m. ^{19}F NMR spectrum ($CDCl_3$): 124.5 (m, 2F, F 2,6), 156.3 (m, 2F, F 3,5) p.p.m. The third band was the germoxane (infrared identification).

1,2,4,5-Tetrafluoro-3,6-bis(triphenylgermyl)benzene (nc). Elution with acetone/light petrol (1:4 v/v) gave three prominent bands, which were extracted with acetone. The fastest-moving band was tetraphenylgermane (infrared identification). The second band was a mixture of the required compound, triphenyl-2,3,5,6-tetrafluorophenylgermane (nc), and the germoxane. ^{19}F NMR spectrum ($CDCl_3$): 122.6 (s, $C_6\underline{F}_4(GePh_3)_2$), 123.6 (m, F 2,6 of Ph_3Ge-p-$HC_6\underline{F}_4$), 138.4 (m, F 3,5 of Ph_3Ge-p-$HC_6\underline{F}_4$) p.p.m., the last two resonances having equal intensities. The third band was the germoxane (infrared identification).

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