922. *Polyfluoroaryl Organometallic Compounds. Part I.*[1] *Pentafluorophenyl Derivatives of Tin.*

By R. D. Chambers and T. Chivers.

Pentafluorophenyl compounds of the series $(Me)_{4-x}Sn(C_6F_5)_x$, $Ph_{4-x}Sn(C_6F_5)_x$, where $x = 1$—4, and $(C_6F_5)_{4-x}Sn(p\text{-tolyl})_x$, where $x = 1$ and 2, have been prepared. These compounds undergo ready nucleophilic cleavage of pentafluorophenyl and an unusual halide- or cyanide-ion-catalysed hydrolysis; a mechanism is suggested for the process. Electrophilic cleavage by hydrogen chloride and boron halides has been studied as a route to some pentafluorophenyltin halides and pentafluorophenylboron dihalides, respectively. Cleavage of methylpentafluorophenylmercury with stannic chloride and bromide provides an excellent route to pentafluorophenyltin trihalides.

A NUMBER of fluoroalkyl derivatives of metals and non-metals have been prepared, and some of them have shown unusual properties.[2] Recent preparations of polyfluoroaryl Grignard reagents [3-5] have provided a route to polyfluoroaryl derivatives, and considerable

[1] Preliminary communication, Chambers and Chivers, *Proc. Chem. Soc.*, 1963, 208.
[2] Clark, " Advances in Fluorine Chemistry," Butterworths, London, 1963, Vol. III, p. 19; Banks and Haszeldine, *Adv. Inorg. and Radiochemistry*, 1961, **3**, 338.
[3] Nield, Stephens, and Tatlow, *J.*, 1959, 166.
[4] Wall, Donadio, and Pummer, *J. Amer. Chem. Soc.*, 1960, **82**, 4846.
[5] Brooke, Chambers, Heyes, and Musgrave, *Proc. Chem. Soc.*, 1963, 94.

differences between phenyl and polyfluorophenyl derivatives have been found.   Wall and his co-workers [4] have prepared pentafluorophenyl derivatives of silicon and phosphorus, mercurials have been investigated in this laboratory,[6] and derivatives of tin,[1,7] boron,[1,8] and thallium [9] have been reported.

We have prepared three series of tin compounds, $(Me)_{4-x}Sn(C_6F_5)_x$, $(C_6H_5)_{4-x}Sn(C_6F_5)_x$, where $x = 1—4$ and $(C_6F_5)_{4-x}Sn(p\text{-tolyl})_x$ where $x = 1$ or 2, by using pentafluorophenyl-magnesium bromide [3] and the appropriate organotin halide in diethyl ether.   Tetrakis-pentafluorophenyltin melts at $221°$, near tetraphenyltin which melts at $227°$ but, like other aryltin compounds, a reduction in the symmetry of the molecule is accompanied by a considerable change in melting point, *e.g.*, trispentafluorophenylphenyltin melts at $95°$.

Unlike trifluoromethyl,[10] pentafluorophenyl attached to tin is not inherently thermally unstable, *e.g.*, trimethylpentafluorophenyltin was conveniently purified by gas chromato-graphy at $200—250°$, although rapid decomposition did occur at $350°$.   The phenyl-pentafluorophenyl compounds were more stable at this temperature but decomposed quickly at $400°$; tetrakis(pentafluorophenyl)tin was unchanged after 2 hours at $400°$ but charred after a prolonged time at this temperature.

Nucleophilic Cleavage.—Pentafluorophenyltin compounds are water-repellent but dis-solve readily in aqueous ethanol and can be recovered from solution unchanged.   However, these compounds are very susceptible to nucleophilic cleavage, *e.g.*, alcoholic bases caused rapid hydrolysis, giving pentafluorobenzene and, after acidification, the corresponding tin hydroxide or oxide, *e.g.*:

$$Me_3SnC_6F_5 \xrightarrow[\text{EtOH}]{\text{NaOH}^-} Me_3SnOH + C_6F_5H$$
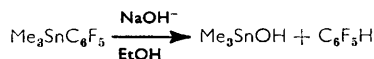
Even potassium fluoride in anhydrous ethanol, under reflux, cleaved pentafluorophenyltri-methyltin, giving trimethyltin fluoride and pentafluorobenzene.   These reactions illustrate the ease of nucleophilic displacement of pentafluorophenyl from tin, but what is surprising, however, is that hydrolysis may be catalysed by halide or cyanide ions.   We observed this reaction because, in the normal purification of organotin compounds, unchanged tin halides may be removed by treating an ethereal solution of the tetraorganotin compound with aqueous-alcoholic potassium fluoride;[11]   when this procedure was employed with, for example, trimethylpentafluorophenyltin, cleavage of pentafluorophenyl occurred.   The same result was later observed by adding only a small crystal of potassium fluoride to an aqueous-alcoholic solution of trimethylpentafluorophenyltin;   an immediate precipitation of trimethyltin hydroxide occurred, and the other product was pentafluorobenzene.   All the pentafluorophenyltin compounds that we have prepared are susceptible to halide-ion catalysed hydrolysis in this way, *e.g.*, dimethylbispentafluorophenyltin gave dimethyltin oxide and tetrakispentafluorophenyltin after a short period under reflux, gave an oxide of ill-defined composition, but containing pentafluorophenyl groups.   Cleavage occurred immediately with compounds of the methyl series, but the phenyl series required reflux conditions for a few minutes.

This hydrolytic instability induced by halide ions may be a more general property of fluorocarbon–tin compounds;   since this work began, Seyferth and his co-workers [12] have reported that trifluorovinyltin compounds containing two or more trifluorovinyl groups are converted into oxides or basic fluorides by aqueous-alcoholic potassium fluoride, and

⁶ Chambers, Coates, Livingstone, and Musgrave, *J.*, 1962, 4367.
⁷ Holmes, Peacock, and Tatlow, *Proc. Chem. Soc.*, 1963, 108.
⁸ Massey, Park, and Stone, *Proc. Chem. Soc.*, 1963, 212.
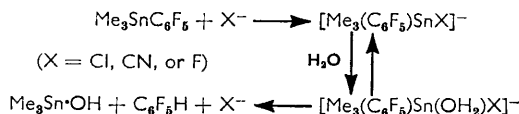⁹ Deacon and Nyholm, *Chem. and Ind.*, 1963, 1803.
¹⁰ Clark and Willis, *J. Amer. Chem. Soc.*, 1960, **82**, 1888.
¹¹ Coates, " Organometallic Compounds," Methuen, London, 1960, p. 178.
¹² Seyferth, Raab, and Brandle, *J. Org. Chem.*, 1961, **26**, 2934.

we find [13] that trimethyltrifluoromethyltin containing halide impurities is slowly hydrolysed, whereas samples purified by gas chromatography are stable.

Hydrolysis catalysed by halide ions must involve initial co-ordination of the halide to tin. It is probable that a five-covalent species is formed, which enables co-ordination of water followed by elimination of pentafluorobenzene to take place, *e.g.*:

$$Me_3SnC_6F_5 + X^- \longrightarrow [Me_3(C_6F_5)SnX]^-$$

$$(X = Cl, CN, or F) \qquad H_2O \downarrow\uparrow$$

$$Me_3Sn\cdot OH + C_6F_5H + X^- \longleftarrow [Me_3(C_6F_5)Sn(OH_2)X]^-$$

Direct displacement of pentafluorophenyl as a carbanion by fluoride ion is unlikely, since the product would be trimethyltin fluoride, which is not hydrolysed to the hydroxide. That presence of a fluorocarbon group enables the central atom to increase its covalency has been illustrated previously, since stable complex anions containing trifluoromethyl have been reported for boron and germanium, *e.g.*, $K[CF_3BF_3]$[14] and $K_2[CF_3GeF_5]$[15] have been characterised. Pentafluorophenyl enhances the acceptor properties of mercury, since bispentafluorophenylmercury forms some stable, neutral co-ordination complexes,[6] but attempts to isolate similar complexes with tetrakispentafluorophenyltin or other tetra-organo-derivatives of tin have been unsuccessful.

Electrophilic Cleavage.—There has been considerable interest in the electrophilic cleavage of organic groups from metals, and the idea, which persisted for some time, that the ease of cleavage of a group depends on its electronegativity (more electronegative groups being most easily cleaved), has recently been discounted,[16] since substituent effects on the rates of cleavage of aryl–tin bonds by acid can be quantitatively explained in terms of ease of electrophilic attack at the tin-bonded carbon atom. Also, cleavage of trimethyltrifluoro-methyltin by acid and by halogens removes the less electronegative methyl exclusively.[10,17] The order of cleavage of pentafluorophenyl could not be predicted with certainty, since the balance between retarding inductive electron-withdrawal and assisting mesomeric electron-release by aromatic fluorine varies with the reaction system (cf. chlorination and nitration of fluorobenzene [18]).

We have studied the electrophilic cleavage of pentafluorophenyltin derivatives with a view to the preparation of pentafluorophenyltin halides and pentafluorophenylboron dihalides. Particular regard has been paid to a comparison of the reactivity of the various derivatives and to whether cleavage of specific groups could be achieved. Cleavage reactions have been carried out with hydrogen chloride (see Table 1) and boron trihalides, and the overall order of ease of electrophilic cleavage of groups from tin is *p*-tolyl > C_6H_5 > C_6F_5 > Me, which is consistent with the results of cleavage from mercury.[6] Cleavage in this series is determined by the ease of electrophilic substitution at the various groups, but overall reactivity is governed by the number of pentafluorophenyl groups in the molecule. An increase in the number of pentafluorophenyls leads to a decrease in reactivity in both the methyl and the phenyl series. Tetra-aryl derivatives are usually considerably less easily cleaved electrophilically than trialkyl-aryl derivatives, and this has been attributed to inductive electron-withdrawal by phenyl,[19] *e.g.*, tetraphenyltin is unaffected by hydrogen chloride in the conditions that we used (Table 1). The considerable reactivity of pentafluorophenyltriphenyltin, which is comparable with that of trimethylpentafluoro-phenyltin, is then surprising; this indicates that mesomeric electron-release from phenyl (*i.e.*, $d\pi — p\pi$ interaction with tin) occurs in the cleavage of pentafluorophenyltriphenyltin.

[13] Chambers, unpublished observation.
[14] Chambers, Clark, and Willis, *J. Amer. Chem. Soc.*, 1960, **82**, 5298.
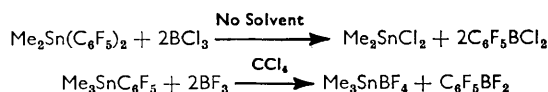[15] Clark and Willis, *J. Amer. Chem. Soc.*, 1962, **84**, 898.
[16] Eaborn and Pande, *J.*, 1961, 3715.
[17] Chambers, Clark, and Willis, *Canad. J. Chem.*, 1961, **39**, 131.
[18] de la Mare and Ridd, " Aromatic Substitution," Butterworths, London, 1959, p. 240.
[19] Eaborn and Waters, *J.*, 1961, 542; Bott, Eaborn, and Waters, *J.*, 1963, 681.

Electrophilic cleavage of methylpentafluorophenyltin compounds with boron trichloride and trifluoride gave the corresponding pentafluorophenylboron dihalides and the reactions of these compounds will be discussed elsewhere.[20]

$$Me_2Sn(C_6F_5)_2 + 2BCl_3 \xrightarrow{\text{No Solvent}} Me_2SnCl_2 + 2C_6F_5BCl_2$$

$$Me_3SnC_6F_5 + 2BF_3 \xrightarrow{\text{CCl}_4} Me_3SnBF_4 + C_6F_5BF_2$$

Preparation of Pentafluorophenyltin Halides.—It was possible to replace one phenyl exclusively by chlorine (see Table 1) in pentafluorophenyltriphenyltin and in bis(penta-

TABLE 1.

Cleavage with one molecular equivalent of hydrogen chloride.

Compound	Conditions	Composition (%) of volatile products		Conversion (%)
$Me_3SnC_6F_5$	20°/24 hr.	100	C_6F_5H	100
$Me_2Sn(C_6F_5)_2$	110°/15 min.	100	C_6F_5H	93
$MeSn(C_6F_5)_3$	210°/20 hr.	100	C_6F_5H	30
$Ph_3SnC_6F_5$	20°/15 min.	100	C_6H_6	51 ⎫
	20°/3 days	100	C_6H_6	95 ⎭
$Ph_2Sn(C_6F_5)_2$	20°/12 hr.	100	C_6H_6	50 ⎫
	20°/5 days	100	C_6H_6	100 ⎭
$PhSn(C_6F_5)_3$	130°/16 hr.	25	C_6H_6: 75 C_6F_5H	63
p-TolylSn$(C_6F_5)_3$	100°/17 hr.	99	$C_6H_5CH_3$ ⎫	87
		1	C_6F_5H ⎭	
$(p$-Tolyl$)_2Sn(C_6F_5)_2$ *	95°/7 hr.	85	$C_6H_5CH_3$ ⎫	80
		15	C_6F_5H ⎭	
$Sn(C_6F_5)_4$	240°/16 hr.		C_6F_5H	10
$SnPh_4$	110°/6 hr.	No reaction		

* Two molecular proportions of hydrogen chloride used.

fluorophenyl)diphenyltin by using hydrogen chloride; in both cases, benzene, but no pentafluorobenzene, was obtained. This is a convenient method for the preparation of the corresponding chlorides, *e.g.*, $Ph_3SnC_6F_5 + HCl \longrightarrow Ph_2(C_6F_5)SnCl + C_6H_6$, but the chlorides so prepared could not be distilled without disproportionation. Reaction with two molecular proportions of hydrogen chloride was more difficult, and cleavage of pentafluorophenyl as well as phenyl occurred, and this difficulty also arose in the reaction of tris(pentafluorophenyl)phenyltin with one molecular proportion of hydrogen chloride. However, specific cleavage of p-tolyl from tris(pentafluorophenyl)-p-tolyltin occurred, giving trispentafluorophenyltin chloride, $(C_6F_5)_3Sn(p$-tolyl$) + HCl \longrightarrow (C_6F_5)_3SnCl + C_6H_5Me$.

Pentafluorophenyltin trichloride and bispentafluorophenyltin dichloride could not be prepared by preferential cleavage of groups with hydrogen chloride, but the trichloride was prepared by reaction of stannic chloride with methylpentafluorophenylmercury. The latter compound has already been shown to be extremely susceptible to electrophilic cleavage,[6] and reaction with stannic chloride occurred immediately at room temperature: $MeHgC_6F_5 + SnCl_4 \longrightarrow MeHgCl + C_6F_5SnCl_3$. Separation of the products was particularly easy, because methylmercury(II) chloride is insoluble in light petroleum and extraction with this solvent gave the required trihalide; cleavage with stannic bromide occurs in an analogous manner. Preparation of the dihalides by this route was not possible, since reaction of pentafluorophenyltin trichloride with methylpentafluorophenylmercury was very slow, and the trihalide caused disproportion of the mercurial into dimethylmercury and bispentafluorophenylmercury. However, preparation of the dichloride from dimethylbispentafluorophenyltin and stannic chloride has been reported.[7]

Hydrolysis of trispentafluorophenyltin chloride required very mild conditions, since cleavage of pentafluorophenyl occurred with strong alkali, but this cleavage was avoided

[20] Chambers and Chivers, forthcoming publication.

Chambers and Chivers:

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TABLE 2.

Infrared spectra in cm.$^{-1}$ * (KBr discs).

Me$_3$SnC$_6$F$_5$ †	Me$_2$Sn(C$_6$F$_5$)$_2$ †	MeSn(C$_6$F$_5$)$_3$	Ph$_3$SnC$_6$F$_5$	Ph$_2$Sn(C$_6$F$_5$)$_2$
3000m	2923m	2955w	3040w	3052m
2920m	2864w	2925m		3025w
		2851w		
1639s	1644s	1637s	1636m	1633s
*1511*vs	*1513*vs	*1506*vs	*1512*s	*1505*vs
*1466*vs	*1459*vs	*1465*vs	*1466*vs	*1462*vs
1449vs			1448s	1444vs
1408w	1412m		1428s	1425s
1370s	1370vs	1369s	1371m	1369s
1274s	1282s	1276s	1268w	1266m
1199m	1208m			1190w
1128w	1136m	1139m		1153m
		1121m		1130w
1071vs	1075vs	1086vs	1080s	1076vs
1054vs	1068vs	1072vs	1074s	1064vs
1017m	1010s	1021m	1021m	1019m
1007m		1013m	998m	994m
957vs	961vs	963vs	962s	959vs
781vs	786vs	796 } 783 } m	786w	787m
729m	723m	744 } 721 } w	730vs	727vs
			697vs	691s
602w	609m	611m	606w	605m
	582w	582w		
533vs	546m	542m		
514s	528m			

PhSn(C$_6$F$_5$)$_3$	(C$_6$F$_5$)$_4$Sn	(C$_6$F$_5$)$_3$SnCl	(C$_6$F$_5$)$_3$Sn(*p*-Tolyl)	C$_6$F$_5$SnCl$_3$ †
			2950w	
			2915m	
			2855w	
1638s	1639m	1639s	1639s	1639s
*1508*vs	*1512*s	*1509*vs	*1512*vs	*1513*vs
*1468*vs	*1471*vs	*1472*vs	*1475*vs	*1481*vs
1448s	1452s		1447vs	1464vs
1428m				
1369s	1373s	1376s	1370s	1387m
1274m	1280s	1282m	1278m	1289w
1190w				
1136w	1138m			
			1079 } 1065 } s	
1082vs	1088vs	1090vs		1091vs
	1076s	1073vs		1078vs
1006m	1019m	1024w		1017w
			1014 } 1004 } w	1006w
997m		1012w		
961vs	965vs	965vs	961s	970vs
796m	805m	805m	799s	805w
	746 } 722 } w	745 } 720 } w	743 } 718 } w	719 w
724m				
690m				
	616 } 611 } w			
607m	583w	608m	608m	610w
		584w	578w	

* Italic figures indicate a characteristic doublet.   † Liquid film.
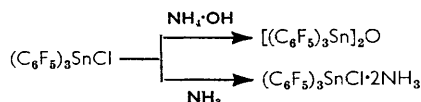
TABLE 3.

^{19}F Chemical shifts (from CCl$_3$F) for pentafluorophenyltin compounds.*

	Ortho (p.p.m.)	Para (p.p.m.)	Meta (p.p.m.)		Ortho (p.p.m.)	Para (p.p.m.)	Meta (p.p.m.)
Me$_3$SnC$_6$F$_5$ † ...	122·2	153·9	161·4	(C$_6$F$_5$)$_3$SnPh ‡...	121·0	148·8	159·0
Me$_2$Sn(C$_6$F$_5$)$_2$ † ...	122·1	151·4	160·2	(C$_6$F$_5$)$_4$Sn ‡ ...	121·4	148·8	159·4
MeSn(C$_6$F$_5$)$_3$ ‡...	122·1	148·9	159·0	C$_6$F$_5$SnCl$_3$ † ...	121·6	143·1	156·7
Ph$_3$SnC$_6$F$_5$ ‡ ...	118·5	151·7	160·0	(C$_6$F$_5$)$_3$SnCl † ...	122·5	145·7	157·8
Ph$_2$Sn(C$_6$F$_5$)$_2$ ‡...	119·7	150·2	159·5				

* CCl$_3$F as internal standard.   † No solvent.   ‡ Acetone as solvent.

by using aqueous ammonia, and trispentafluorophenyltin oxide was eventually isolated. Reaction of the chloride with ammonia in dry ether gave a complex containing two molecular proportions of ammonia:

$$(C_6F_5)_3SnCl \xrightarrow{\quad NH_4 \cdot OH \quad} [(C_6F_5)_3Sn]_2O$$
$$(C_6F_5)_3SnCl \xrightarrow[\quad NH_3 \quad]{} (C_6F_5)_3SnCl \cdot 2NH_3$$

Pentafluorophenyltin trichloride fumed in moist air and deposited a white solid.

Infrared Spectra.—Absorption bands are recorded in Table 2. There are several well-defined regions, which are common to each series of compounds, and these must therefore be associated with pentafluorophenyl, namely, at approximately 1640, 1510 and 1460 (doublet), 1370, 1270, 1080, 1070, 1020, 1010, 960, and 600 cm.$^{-1}$. A doublet in the region 1500 and a band at 1640 cm.$^{-1}$ appear to be the most useful diagnostic features for pentafluorophenyl compounds, since they are contained in the spectra of pentafluorophenyl derivatives of boron, tin, mercury,[6] and phosphorus.[4] Absorption in the region 1300—1000 cm.$^{-1}$ can be attributed to C–F stretch. The spectra of a number of methyltin compounds have been analysed,[21] and from these we can assign some bands in the methyl series, in the regions 780, 730 (Sn–CH$_3$ rock), 540 (asym. Sn–C stretch), and 520 cm.$^{-1}$ (sym. Sn–C stretch).

Nuclear Magnetic Resonance Spectra.—^{19}F Chemical shifts for pentafluorophenyltin compounds are recorded in Table 3. The, now well-established, shift to low field of *ortho*-fluorine resonance [22] is illustrated, but the *para* shifts are probably most significant. Taft and his co-workers [23] have shown recently that for *para*-substituted monofluorobenzenes there is theoretical justification for relating ^{19}F shielding with the π-charge density at the fluorine atom. Similarly, it has been shown that the *para*-^{19}F chemical shift in C$_6$F$_5$X is sensitive to resonance interaction of the group X with the ring.[24] We have been interested in the variation of *para*-^{19}F chemical shift in pentafluorophenyl while other groups attached to tin were varied, since this may have reflected π-interaction of pentafluorophenyl with tin. Interaction of phenyl with tin has already been suggested to account for the unusual reactivity of pentafluorophenyltriphenyltin (see above). For tetraorgano-compounds there is a slight trend to low field with increase in the number of pentafluorophenyl groups, which parallels a decrease in ease of electrophilic cleavage, but the differences are too small to be significant. The constancy of the *para* shifts in fact indicates that there is little or no $d\pi$–$p\pi$ interaction of tin with pentafluorophenyl in these compounds, but the relatively large *para* shift to low field, which is observed for the chlorides (while the *ortho* and *meta* values show relatively less variation), indicates that interaction is significant in these cases.

EXPERIMENTAL

Bromopentafluorobenzene was obtained from the Imperial Smelting Corporation, and by bromination of pentafluorobenzene [3] which was prepared in this laboratory by chlorofluorination of benzene and dehalogenation of the product.[25] Infrared spectra were recorded with a Grubb–Parsons model G.S. 2A spectrometer and ultraviolet spectra (Table 4) were recorded with an Optica, model CF4DR, ratio-recording instrument.

Trimethylpentafluorophenyltin.—Trimethyltin bromide (14 g., 57·5 mmoles) in ether (25 ml.) was added to a slight excess of pentafluorophenylmagnesium bromide [3] (62·5 mmoles) in ether (120 ml.), and the mixture was heated under reflux for 48 hr. Hydrolysis was effected by (10%) aqueous ammonium chloride to prevent the formation of an emulsion (halide-ion-catalysed cleavage only occurs when alcohol is added as a co-solvent). The ether layer was separated

[21] Kriegsmann and Kessler, *Z. anorg. Chem.*, 1962, **318**, 266.
[22] Bourn, Gillies, and Randall, *Proc. Chem. Soc.*, 1963, 200, and references therein; Emsley, forthcoming publication.
[23] Taft, Prosser, Goodman, and Davis, *J. Chem. Phys.*, 1963, **38**, 380.
[24] Emsley, unpublished observations.
[25] Johncock, Mobbs, and Musgrave, *Ind. Eng. Chem. Process Design and Development*, 1962, **1**, 267.

and dried (MgSO$_4$), and the ether removed under a vacuum. Distillation of the liquid residue at 34—36°/10⁻² mm. gave *trimethylpentafluorophenyltin* (11·5 g., 60%) (Found: F, 28·2; Sn, 35·6. C$_9$H$_9$F$_5$Sn requires F, 28·7; Sn, 35·9%).

Dimethylbispentafluorophenyltin.—Dimethyltin dibromide (8·8 g.; 28·5 mmoles) in ether

TABLE 4.

Ultraviolet spectra.

Compound	In cyclohexane		In methanol	
	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε
Me$_3$SnC$_6$F$_5$	263	600	262·5	1270
Me$_2$Sn(C$_6$F$_5$)$_2$	265	1540	261·5	1140
MeSn(C$_6$F$_5$)$_3$	266·5	2880	263	1990
Ph$_3$SnC$_6$F$_5$	253	1120	254	2030
	259·5	1590	260	2390
	265	1520	264, 269,* 253 *	2340, 1980, 2020
Ph$_2$Sn(C$_6$F$_5$)$_2$	260	2130	259	2630
	264·5	2300	264, 268 *	2740, 2400
PhSn(C$_6$F$_5$)$_3$	265	3050	263	3100
(C$_6$F$_5$)$_4$Sn.........................	267	3890	265	3090
(C$_6$F$_5$)$_3$SnCl.........................	270	—	262	—

* Inflexion.

(25 ml.) and pentafluorophenylmagnesium bromide (62·5 mmoles) in ether (120 ml.) were heated under reflux for 2 days and then worked up as described above, giving *dimethylbispentafluoro-phenyltin* (8·0 g., 58%), after distillation at 74—76°/10⁻² mm. (Found: F, 39·9; Sn, 24·3. C$_{14}$H$_6$F$_{10}$Sn requires F, 39·3; Sn, 24·6%).

Methyltrispentafluorophenyltin.—Methyltin tribromide (7·2 g.; 19·2 mmoles) in ether (30 ml.) and pentafluorophenylmagnesium bromide (62·5 mmoles) in ether (120 ml.) after 3 days under reflux gave *methyltrispentafluorophenyltin* (8·4 g., 69%), m. p. 72—73°, after sublimation at 60—65°/10⁻³ mm., followed by recrystallisation from propan-1-ol, (Found: F, 45·1; Sn, 18·8. C$_{19}$H$_3$F$_{15}$Sn requires F, 44·9; Sn, 18·7%).

Pentafluorophenyltriphenyltin.—Triphenyltin bromide (11·5 g., 26·8 mmoles) in ether (30 ml.) and pentafluorophenylmagnesium bromide (29·5 mmoles) in ether (100 ml.), after 3 days under reflux, gave *pentafluorophenyltriphenyltin* (9·4 g., 68%), m. p. 86°, after recrystallisation from ethanol (charcoal) (Found: C, 55·7; F, 18·5. C$_{24}$H$_{15}$F$_5$Sn requires C, 55·7; F, 18·4%).

Bis(pentafluorophenyl)diphenyltin.—Diphenyltin dibromide (12·4 g., 28·7 mmoles) in ether (30 ml.) and pentafluorophenylmagnesium bromide (62·5 mmoles) in ether (120 ml.) after 48 hr. under reflux, gave *bis(pentafluorophenyl)diphenyltin* (9·5 g., 54%), m. p. 85°, after re-crystallisation from ethanol (charcoal) (Found: C, 47·8; F, 30·6. C$_{24}$H$_{10}$F$_{10}$Sn requires C, 47·5; F, 31·3%).

Tris(pentafluorophenyl)phenyltin.—Phenyltin tribromide (12·5 g., 28·7 mmoles) in ether (30 ml.) and pentafluorophenylmagnesium bromide (94 mmoles) in ether (180 ml.), after 3 days under reflux, gave *tris(pentafluorophenyl)phenyltin* (17·0 g., 85%), m. p. 95—96°, after sublim-ation at 80—90°/10⁻³ mm. and recrystallisation from ethanol (Found: C, 41·1; F, 41·1. C$_{24}$H$_5$F$_{15}$Sn requires C, 41·3; F, 40·9%).

Tetrakispentafluorophenyltin.—Tin(IV) bromide (5 g., 11·4 mmoles) in ether (25 ml.) and pentafluorophenylmagnesium bromide (48·8 mmoles) in ether (100 ml.) after 3 days under reflux gave *tetrakispentafluorophenyltin* (4·6 g., 51%), m. p. 221°, after sublimation at 160°/10⁻³ mm. and recrystallisation from cyclohexane (Found: F, 47·9; Sn, 14·9. C$_{24}$F$_{20}$Sn requires F, 48·3; Sn, 15·1%).

p-*Tolyltrispentafluorophenyltin.*—*p*-Tolyltin trichloride (10 g., 31·6 mmoles) in ether (50 ml.) and pentafluorophenylmagnesium bromide (122 mmoles) in ether (200 ml.) after 19 hr. under reflux, gave a brown solid from which p-*tolyltrispentafluorophenyltin* (18 g., 80%) was obtained as white crystals by sublimation at 140°/0·01 mm., m. p. 107° after recrystallisation twice from propanol (Found: F, 40·2; Sn, 16·6. C$_{25}$H$_7$F$_{15}$Sn requires F, 40·1; Sn, 16·7%).

Di-p-tolylbispentafluorophenyltin.—Di-*p*-tolyltin dichloride (7·4 g., 20 mmoles) in ether (40 ml.) and pentafluorophenylmagnesium bromide (50 mmoles) in ether (150 ml.) after 11 hr. under reflux gave a dark brown viscous liquid (8·1 g.). A portion of this was distilled at 160—164°/0·001 mm., to give a colourless liquid, which deposited crystals, m. p. 57—59°, in several weeks.

The rest of the product was eluted in light petroleum (b. p. 40—60°) through an alumina column. Removal of the solvent gave a pale yellow liquid which deposited crystals of *di*-p-*tolylbispenta-fluorophenyltin*, m. p. 73—75° (from propan-2-ol) (Found: C, 48·8; F, 30·3. $C_{26}H_{14}F_{10}Sn$ requires C, 49·2; F, 29·9%).

Cleavage Reactions.—(*a*) *With alkali.* Trimethylpentafluorophenyltin (0·250 g., 0·76 mmoles) was shaken with 2 ml. of 50% aqueous-alcoholic potassium hydroxide (4N). A white precipitate appeared, and the mixture was acidified with hydrochloric acid; the volatile product and solvent were removed by distillation, leaving a white solid; this was trimethyltin hydroxide (0·120 g., 0·66 mmoles), m. p. 117° (sublimes) (lit.,[26] 118°). The infrared spectrum was identical with that of an authentic specimen. Pentafluorobenzene was shown by gas chromatography to be present in the distillate.

(*b*) *With aqueous-alcoholic potassium fluoride.* (i) Trimethylpentafluorophenyltin (0·35 g., 1·1 mmoles), which had been purified by gas chromatography, was shaken with 90% ethanol–water (2 ml.). There was no reaction (in a separate experiment the starting material was recovered). A very small crystal of potassium fluoride was added, and a white precipitate then appeared immediately. Solvent was removed by distillation and shown by gas chromatography to contain pentafluorobenzene. The residue was sublimed in a vacuum to give trimethyltin hydroxide (0·19 g., 1·1 mmoles), m. p. 117°. In further experiments potassium chloride or potassium cyanide was used instead of potassium fluoride; trimethyltin hydroxide and penta-fluorobenzene were obtained in each case.

(ii) Dimethylbispentafluorophenyltin, when treated with aqueous-alcoholic potassium fluoride, as described above, gave dimethyltin oxide (correct infrared spectrum).

(iii) Bis(pentafluorophenyl)diphenyltin was treated as described above, except that the mixture was heated under reflux for 30 min. Diphenyltin oxide was obtained (correct infrared spectrum).

(iv) Tetrakispentafluorophenyltin was treated as above, except that the mixture was refluxed for 5 min. Removal of solvent gave a high-melting (>400°) oxide (Found: Sn, 31·8; C, 27·0%. This corresponds to $(C_6H_5)_{1.4}SnO_{1.3}$).

(*c*) *With potassium fluoride in anhydrous ethanol.* Trimethylpentafluorophenyltin (1·25 g., 3·8 mmoles) and potassium fluoride (0·22 g., 3·8 mmoles) in anhydrous ethanol (10 ml.) was heated under reflux for 8 hr. Solid material was filtered off, washed with water, dried, and identified as trimethyltin fluoride (0·22 g., 1·2 mmoles) by its infrared spectrum.

(*d*) *With hydrogen chloride.* Trimethylpentafluorophenyltin (1·72 g., 5·2 mmoles) was weighed into a small tube, and hydrogen chloride (0·19 g., 5·2 mmoles) was condensed into the tube from a vacuum system. The tube was sealed under a vacuum, allowed to warm to room temperature, and kept for one day. Volatile material was distilled off under a vacuum, and identified as pentafluorobenzene (0·87 g., 5·2 mmoles) by its infrared spectrum and by gas chromatography. The residue in the tube was trimethyltin chloride, m. p. 35° (lit.,[27] 37°), which was converted into a complex with ammonia, $Me_3SnCl\cdot NH_3$ whose infrared spectrum was identical with that of an authentic specimen.

The other cleavage reactions quoted in Table 1 were carried out similarly; the volatile products were estimated and identified by gas chromatography and by their infrared spectra.

Trispentafluorophenyltin Chloride.—p-Tolyltrispentafluorophenyltin (5·52 g., 7·8 mmoles) and hydrogen chloride (0·26 g., 7·3 mmoles) was heated in a Carius tube at 100° for 17 hr. Volatile material collected from the tube by vacuum transfer was toluene (0·59 g., 6·5 mmoles) containing a trace (~1%) of pentafluorobenzene. The residue (5·16 g.) in the Carius tube was recrystallised twice from light petroleum (b. p. 40—60°) to give white crystals, m. p. 108—109° of *trispenta-fluorophenyltin chloride* (3·8 g., 75%) (Found: C, 33·0; Sn, 18·0. $C_{18}ClF_{15}Sn$ requires C, 33·0; Sn, 18·1%).

Dry ammonia was bubbled into a solution of trispentafluorophenyltin chloride (0·33 g.) in light petroleum (10 ml.). A white precipitate of *trispentafluorophenyltin chloride* 2-*ammonia* was formed, which was filtered off (0·2 g.; m. p. 155—170°) (Found: C, 31·4. $C_{18}H_6ClF_{15}N_2Sn$ requires C, 31·4%).

Hydrolysis of Trispentafluorophenyltin Chloride.—Trispentafluorophenyltin chloride (0·46 g., 0·71 mmoles) in ether (5 ml.) was added to 2N-ammonia (2 ml.). A white precipitate, which

[26] Kraus and Bullard, *J. Amer. Chem. Soc.*, 1929, **51**, 3605.
[27] Kraus and Cullis, *J. Amer. Chem. Soc.*, 1923, **45**, 2628.

dissolved on shaking, was formed. The ethereal layer was separated and dried ($MgSO_4$) and the solvent was removed by vacuum transfer, to give a white solid, *trispentafluorophenyltin oxide* (0·43 g., 0·34 mmoles) (Found: C, 33·5; Sn, 19·3. $C_{36}H_{30}OSn_2$ requires C, 34·4; Sn, 18·9%).

Pentafluorophenyltin Trichloride.—Tin(IV) chloride (0·64 g., 2·5 mmoles) was condensed into a Carius tube containing methylpentafluorophenylmercury (0·94 g., 2·5 mmoles). The tube was sealed under a vacuum and allowed to reach 20°; after 5 min. at this temperature a white solid appeared. After 20 hr., the contents of the tube were extracted with light petroleum (b. p. 40—60°; 4 ml.). A white solid was filtered off and shown by its infrared spectrum to be methylmercury(II) chloride (0·62 g., 2·5 mmoles). Solvent was removed by vacuum transfer, and the liquid residue was distilled at 54—56°/0·02 mm., to give pentafluorophenyltin trichloride (0·9 g., 2·3 mmoles) (Found: F, 23·9; Cl, 27·3. $C_6Cl_3F_5Sn$ requires F, 24·2; Cl, 27·2%).

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