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SOME NEW POLYHALOARYL DERIVATIVES OF TIN

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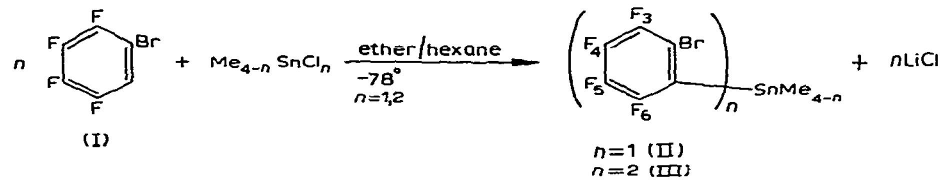
SUMMARY

Some new polyhaloaryltin compounds, 2-$BrC_6F_4SnMe_3$, (2-$BrC_6F_4)_2SnMe_2$, 1,2-$C_6F_4(SnMe_3)_2$, 1,4-$C_6F_4(SnMe_3)_2$ and 4-$HC_6F_4SnMe_3$ have been synthesised from the appropriate polyhaloaryl–lithium reagent and dimethyl- or trimethyltin chloride. ^1H and ^{19}F NMR data for these compounds are reported. There is no evidence for intramolecular Sn–Br interaction in 2-$BrC_6F_4SnMe_3$ from the ^1H NMR spectrum at −60°.

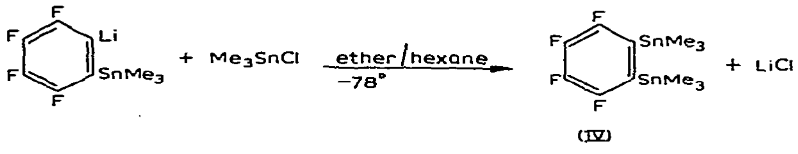
In connection with our interest in the possibility of intramolecular tin–*ortho*-halogen interactions in halogen substituted aryltin derivatives[1], we have prepared some new polyhaloaryl derivatives of tin. We report here the synthesis and ^1H and ^{19}F NMR spectra of (2-bromo-3,4,5,6-tetrafluorophenyl)trimethyltin (II), bis(2-bromo-3,4,5,6-tetrafluorophenyl)dimethyltin (III), (2,3,5,6-tetrafluoro-1,4-phenylene)bis(trimethyltin) (IV), (3,4,5,6-tetrafluoro-1,2-phenylene)bis(trimethyltin) (V) and (2,3,5,6-tetrafluorophenyl)trimethyltin (VI).

2-Bromotetrafluorophenyllithium (I) has been reported recently[2] and used in the preparation of 2-bromotetrafluorophenyl derivatives of mercury[3–5], silicon[5], germanium[3], tin[4] and sulphur[4,5]. We have used this reagent to prepare (II) and (III) by reaction with the appropriate methyltin chloride in diethyl ether at −78°. Treatment of (II) with n-butyllithium and then trimethyltin chloride in ether at −78° gave (IV).



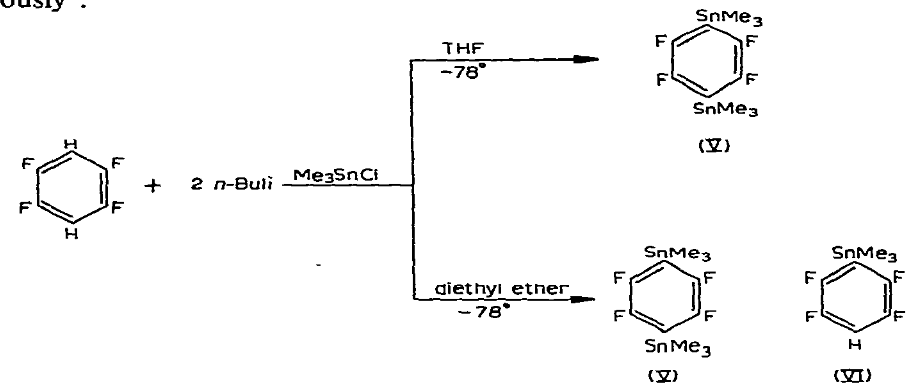
(I)

n=1 (II)
n=2 (III)



(IV)

(V) was obtained in 40% yield by treatment of 2,3,5,6-tetrafluorobenzene with 2 equivalents of n-butyllithium in tetrahydrofuran at −78° followed by addition of trimethyltin chloride. With diethyl ether as solvent, the major product (65%) was (VI), with minor amounts (10%) of (V). The superiority of tetrahydrofuran as a solvent for metalation of polyfluorobenzenes by n-butyllithium has been demonstrated previously[6].



In an attempt to prepare (IV) by insertion of tetrafluorobenzene into the metal–metal bond of hexamethylditin, a solution of pentafluorophenyllithium in diethyl ether was warmed to 25° in the presence of hexamethylditin. The only fluorocarbon product which was isolated was identified by its NMR spectrum as 2-hydrononafluorobiphenyl, which arises from interaction of tetrafluorobenzyne with unreacted pentafluorophenyllithium (via nonafluoro-2-biphenylyllithium)[7].

TABLE 1

^{1}H NMR DATA FOR POLYHALOARYLTIN COMPOUNDS

Compound[a]	$\delta(\tau)$	$J(\mathrm{H{-}F})$[b]	$J(^{119}\mathrm{Sn{-}Me})$[b]
$2\text{-}BrC_6F_4SnMe_3$	9.47	1.4 (doublet)	57.8
$(2\text{-}BrC_6F_4)_2SnMe_2$	9.06	1.15 (triplet)	63.8
$1,2\text{-}C_6F_4(SnMe_3)_2$	9.60	0.6 (doublet)	55.6
$1,4\text{-}C_6F_4(SnMe_3)_2$	9.55	0.35 (quintet)	57.6
$4\text{-}HC_6F_4SnMe_3$	9.50	0.6 (triplet)	58.0

[a] 20–30% solution in CCl_4; Me_4Si was used as internal reference. [b] Hz.

The ^{1}H NMR data for compounds (II)–(VI) are recorded in Table 1. Coupling between MeSn protons and *ortho*-fluorine atoms is observed for all the compounds, and has been observed previously for (pentafluorophenyl)tin compounds[8,9]. The resulting fine structure provides confirmatory structural information for these derivatives. The ^{1}H NMR spectrum of $1,4\text{-}C_6F_4(Me_3Sn)_2$ appears as a quintet, $J(CH_3\text{-}F) \sim 0.35$ Hz, the outer lines of which are difficult to resolve. Because of the high symmetry of this compound, it must be analysed as an $X_9AA'A''A'''X'_9$ system. A "virtual" coupling effect of the isochronous *ortho* and *meta* fluorines would be expected to give a five-line pattern, to a first approximation, with a splitting equal to the mean of $J(CH_3\text{-}F_o)$ and $J(CH_3\text{-}F_m)$. The observed splitting is indeed about half

TABLE 2

CHEMICAL SHIFTS AND COUPLING CONSTANTS IN $(2\text{-BrC}_6F_4)_nSnMe_{4-n}$

	$n=1$	$n=2$
Chemical shifts (ppm)		
F_3	126.1	125.5
F_4	152.8	150.6
F_5	155.7	154.3
F_6	118.6	118.9
Coupling constants (Hz)		
F_3–F_4	19.3	20.15
F_3–F_5	3.3	3.85
F_3–F_6	12.8	12.0
F_4–F_5	18.9	18.7
F_4–F_6	3.5	4.25
F_5–F_6	26.2	25.15

that observed in cases of lower symmetry*.

The $J(^{119}Sn\text{–}Me)$ coupling constants are high for tetraorganotin compounds, [*cf.* Me_4Sn, $J(^{119}Sn\text{–}Me)=54.0$ Hz][10], which indicates the highly electronegative nature of the polyhaloaryl groups. A triplet of triplets is observed for the aromatic proton in (VI) at τ 3.15, $J(H\text{–}F_o)=9.2$ Hz; $J(H\text{–}F_m)=7.2$ Hz.

The ^{19}F NMR spectra of (II) and (III) are to a first approximation those of an AMPX system. The observed coupling constants and chemical shifts are shown in Table 2 and they are in good agreement with those found for similar derivatives of germanium and mercury[3]. The two low field absorptions are assigned to the *ortho*-fluorines F_3 and F_6 by comparison with values obtained for pentafluorophenyl derivatives. The absorption at 119 ppm shows broadening due to coupling with MeSn protons and is accordingly assigned to F_6. It follows that the eight line multiplet at 126 ppm corresponds to F_3. Assignment of the other two absorptions to F_4 and F_5 follows from analysis of the coupling constants. The ^{19}F NMR spectrum of (IV) is that of an AA'XX' spectrum with absorptions at 115.1 ppm and 155.9 ppm. The low field absorption is broadened to give the appearance of a doublet owing to coupling with MeSn protons. This absorption is therefore assigned to the *ortho*-fluorines. The absorption at 155.9 ppm is typical of an AA'XX' spectrum[11], but only 8 lines are discernible, possibly due to overlap of two pairs of lines. The ^{19}F NMR spectrum of (V) shows a broad singlet at 123.3 ppm, $J(Sn\text{–}F)=22.2$ Hz (peak width at half-height $=2.2$ Hz, due to coupling with Me_3Sn protons).

We have investigated the possibility of intramolecular tin–*ortho*-bromine interaction in (II) by studying the low temperature NMR behaviour of a chloroform solution.

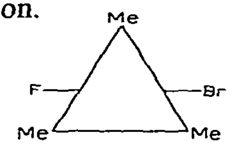


Fig. 1. Schematic representation of $2\text{-BrC}_6F_4SnMe_3$ looking down $Sn\text{–}C_{Ar}$ bond.

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* The author is grateful to a referee for this suggestion.

If coordination of *ortho*-bromine to tin occurs, rotation of the Me_3Sn group about the Sn–C_{aryl} bond would now be restricted, thus giving rise to magnetic inequivalence of the methyl groups. However, the ^1H spectrum of (II) in chloroform solution at −60° is identical with the spectrum of the same sample at room temperature, which indicates that intramolecular coordination, if it occurs at all, is very weak. Mössbauer studies of some polyhaloaryltin compounds also provide no evidence for intramolecular tin–*ortho*-halogen coordination in these compounds[12].

EXPERIMENTAL

The reactions involving lithium reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. 1,2-Dibromo-3,4,5,6-tetrafluorobenzene and 1,2,3,4-tetrafluorobenzene were obtained commercially from Imperial Smelting Corporation, Ltd., England. ^1H NMR spectra were obtained using a Varian A60 instrument at 60.0 MHz by Miss P. Watson, and ^{19}F NMR spectra were obtained using a Varian HA100 instrument at 94.1 MHz by Mr. R. Burton. IR spectra were recorded on a Perkin–Elmer 457 instrument using KBr optics. Microanalyses were performed by Mr. P. Borda of this Department. Tetrahydrofuran was freshly distilled from lithium aluminium hydride. n-Butyllithium in hexane solution was purchased from Alfa Inorganics; diethyl ether was anhydrous grade. Hexamethylditin was prepared according to the literature[13].

Preparation of (2-bromo-3,4,5,6-tetrafluorophenyl)trimethyltin

(2-Bromo-3,4,5,6-tetrafluorophenyl)lithium was prepared by addition of n-butyllithium (0.03 mole, 14 ml of a hexane solution) to 1,2-dibromo-3,4,5,6-tetrafluorobenzene (9.24 g, 0.03 mole) in diethyl ether (50 ml) at −78°. The reaction mixture was stirred for 20 min at −78° before addition of trimethyltin chloride (5.9 g, 0.0296 mole). The reaction mixture was allowed to come to room temperature during 4 h, and then stirring was continued for 12 h. Lithium salts were filtered off, and solvent was removed under vacuum to give a yellow liquid (7.99 g) which on distillation gave colourless (2-bromo-3,4,5,6-tetrafluorophenyl)trimethyltin (5.03 g, 0.0128 mole) b.p. 73–74°/0.03 mm (lit[4]: b.p. ~83°/0.05 mm). (Found: C, 27.9; H, 2.6; F, 19.2. $C_9H_9BrF_4Sn$ calcd.: C, 27.6; H, 2.3; F, 19.4%.)

Preparation of bis(2-bromo-3,4,5,6-tetrafluorophenyl)dimethyltin

(2-Bromo-3,4,5,6-tetrafluorophenyl)lithium was prepared by addition of n-butyllithium (0.019 mole, 8.5 ml of a hexane solution) to 1,2-dibromo-3,4,5,6-tetrafluorobenzene (5.71 g, 0.019 mole) in diethyl ether (50 ml) at −78°. The reaction mixture was stirred for 20 min at −78° before dropwise addition of dimethyltin dichloride (1.98 g, 0.009 mole) in ether (50 ml). The reaction mixture was stirred at −78° for 2 h and then at its ambient temperature overnight. Lithium salts were filtered off and solvents were removed at 20 mm to give a pale yellow liquid (3.88 g). Distillation gave two fractions: (a) b.p. 136–142°/0.1 mm, 1.0 g; (b) b.p. 142–143°/0.1 mm, 1.5 g. After 2 days at room temperature fraction (b) gave white crystals of bis-(2-bromo-3,4,5,6-tetrafluorophenyl)dimethyltin, m.p. 56–58°. (Found: C, 27.6; H, 1.1; F, 24.85. $C_{14}H_6Br_2F_8Sn$ calcd.: C, 27.8; H, 1.0; F, 25.1%.)

Preparation of (3,4,5,6-tetrafluoro-1,2-phenylene)bis(trimethyltin)

n-Butyllithium (5.35 mmoles, 2.4 ml of a hexane solution) was added dropwise to (2-bromo-3,4,5,6-tetrafluorophenyl)trimethyltin (2.1 g, 5.35 mmoles) in diethyl ether (30 ml) at −78°. The reaction mixture was stirred at −78° for 45 min, and then trimethyltin chloride (1.05 g, 5.29 mmoles) in ether (30 ml) was added dropwise. The reaction mixture was allowed to come to room temperature during 4 h, and then it was stirred for 12 h. Lithium salts were filtered off and solvents were removed at 20 mm to give a white solid (1.62 g) which on sublimation (60°/0.01 mm) gave (3,4,5,6-tetrafluoro-1,2-phenylene)bis(trimethyltin) m.p. 73–77°. Two recrystallisations from n-propanol gave white needles m.p. 82–83°. (Found: C, 30.2; H, 3.8; F, 16.2. $C_{12}H_{18}F_4Sn_2$ calcd.: C, 30.3; H, 3.8; F, 16.0%.)

Preparation of (2,3,5,6-tetrafluoro-1,4-phenylene)bis(trimethyltin) in tetrahydrofuran

n-Butyllithium (0.02 mole, 8.5 ml of a hexane solution) was added dropwise to 2,3,5,6-tetrafluorobenzene (1.50 g, 0.01 mole) in dry tetrahydrofuran (70 ml) at −78°. The reaction mixture was stirred at −78° for 40 min before dropwise addition of trimethyltin chloride (3.90 g, 0.02 mole) in tetrahydrofuran (30 ml). The reaction mixture was stirred at −78° for 2 h and then at its ambient temperature for 20 h. Hydrolysis was effected by 0.1 *N* HCl (100 ml); the organic layer was separated, dried, and solvent was removed at 20 mm to give a white solid (2.76 g) which on sublimation (80°/0.01 mm) gave (2,3,5,6-tetrafluoro-1,4-phenylene)bis(trimethyltin) (1.84 g, 0.0039 mole) m.p. 101–103°. Recrystallisation from n-propanol raised the m.p. to 107–108°. (Found: C, 30.8; H, 4.1; F, 15.8. $C_{12}H_8F_4Sn_2$ calcd.: C, 30.3; H, 3.8, F, 16.0%.)

Preparation of (2,3,5,6-tetrafluoro-1,4-phenylene)bis(trimethyltin) in diethyl ether

n-Butyllithium (0.04 mole, 17 ml of a hexane solution) was added dropwise to 2,3,5,6-tetrafluorobenzene (3.01 g, 0.02 mole) in diethyl ether (50 ml) at −78°. The reaction mixture was stirred at −78° for 30 min before dropwise addition of trimethyltin chloride (8.08 g, 0.04 mole) in ether (50 ml). The reaction mixture was stirred at −78° for $1\frac{1}{2}$ h, and then at its ambient temperature overnight. Hydrolysis was effected by addition of 0.1 *N* HCl (100 ml). The ether layer was separated, dried, and solvents were removed at 20 mm to give a colourless liquid (8.8 g). Distillation gave 3 fractions: (a) n-butyltrimethyltin (2.8 g) b.p. 32–36°/4 mm, identified by its IR spectrum; (b) (2,3,5,6-tetrafluorophenyl)trimethyltin (4.01 g, 0.013 mole) b.p. 60°/3 mm; (Found: C, 35.3; H, 3.3; F, 23.9. $C_9H_{10}F_4Sn$ calcd.: C, 34.55; H, 3.2; F, 24.3%.) (c) (2,3,5,6-tetrafluoro-1,4-phenylene)bis(trimethyltin) (1.0 g, 0.0021 mole) b.p. 109–110°/0.001 mm which crystallised in the receiver m.p. 100–103°, and was characterised by comparison of its IR spectrum with that of an authentic specimen.

Reaction of tetrafluorobenzyne with hexamethylditin

A solution of pentafluorophenyllithium in diethyl ether (100 ml) at −78° was prepared from pentafluorobenzene (4.2 g, 0.025 mole) and n-butyllithium (0.025 mole, 10.6 ml of a hexane solution.) Hexamethylditin (8.8 g, 0.027 mole) in ether (30 ml) was added, and the reaction mixture was immediately warmed to 25°. After 3 h, the reaction mixture was hydrolysed by addition of *N* HCl (100 ml). The ether layer was separated, dried ($MgSO_4$) and solvents were removed at 20 mm to give a pale yellow liquid (10.0 g). Distillation gave: (a) hexamethylditin (2.9 g) b.p. 25–26°/0.4 mm; (b) 2-

hydrononafluorobiphenyl (1.5 g) b.p. 54°/0.2 mm which was identified by its NMR spectrum, which had peaks at 137.2, 138.5, 140.5, 152.5, 154.5, 161.6 ppm with relative areas 1/1/2/2/1/2 (*cf.* ref. 7). An IR spectrum of the residue in the distillation pot showed no evidence for the formation of (3,4,5,6-tetrafluoro-1,2-phenylene)bis(trimethyltin) which is the expected product from the insertion of tetrafluorobenzyne into the Sn–Sn bond of hexamethylditin.

Infrared spectra (cm^{-1})

2-$BrC_6F_4SnMe_3$ (liquid film): 2985 w, 2915 w, 1610 m, 1595 w, 1490 s, 1425 s, 1354 s, 1310 m, 1292 s, 1252 m, 1190 w, 1108 w, 1094 s, 1080 w, 1031 m, 1018 s, 824 s, 780 s, 730 m.

(2-$BrC_6F_4)_2SnMe_2$ (Nujol mull): 1616 w, 1602 w, 1497 s, 1438 s, 1320 w, 1300 w, 1260 w, 1118 w, 1102 m, 1090 w, 1038 w, 1022 s, 831 s, 773 m, 543 w, 530 w.

1,2-$C_6F_4(SnMe_3)_2$ (Nujol mull): 1610 m, 1599 m, 1400 s, 1280 s, 1235 m, 1199 w, 1087 s, 1007 vs, 782 s, 725 m, 533 s, 520 m.

1,4-$C_6F_4(SnMe_3)_2$ (Nujol mull): 1431 vs, 1406 s, 1211 m, 1203 s, 1197 s, 926 s, 783 s, 731 m, 560 w, 540 s, 521 m.

4-$HC_6F_4SnMe_3$ (liquid film): 3105 vw, 3000 w, 2970 w, 2935 m, 2885 w, 2870 w, 1016 w, 1600 w, 1470 vs, 1356 m, 1224 s, 1200 m, 1171 s, 903 vs, 851 m, 787 m, 735 m, 710 m, 541 m, 520 w.

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REFERENCES

1 T. Chivers and B. David, *J. Organometal. Chem.*, 13 (1968) 177.
2 S. C. Cohen, D. E. Fenton, A. J. Tomlinson and A. G. Massey, *J. Organometal. Chem.*, 6 (1966) 301.
3 S. C. Cohen and A. G. Massey, *J. Organometal. Chem.*, 12 (1968) 341.
S. C. Cohen and A. G. Massey, *Chem. Commun.*, (1966) 457.
4 R. D. Chambers, J. A. Cunningham and D. A. Pyke, *Tetrahedron*, 24 (1968) 2783.
R. D. Chambers and J. A. Cunningham, *Chem. Commun.*, (1966) 469.
5 C. Tamborski and E. J. Soloski, *J. Organometal. Chem.*, 10 (1967) 385.
6 R. J. Harper, E. J. Soloski and C. Tamborski, *J. Org. Chem.*, 29 (1964) 2385.
7 D. E. Fenton and A. G. Massey, *Tetrahedron*, 21 (1965) 3009.
8 A. G. Massey, E. W. Randall and D. Shaw, *Chem. Ind. (London)*, (1963) 1244.
9 J. Burdon, *Tetrahedron*, 21 (1965) 1101.
10 R. V. Parish and R. H. Platt, *Chem. Commun.*, (1968) 1118.
11 J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Vol. I, Pergamon Press, 1966, p. 396.
12 T. Chivers and J. R. Sams, *Chem. Commun.*, (1969) 249.
13 C. A. Kraus and W. V. Sessions, *J. Amer. Chem. Soc.*, 47 (1925) 2361.