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NOTE

ALKYLTIN TETRAFLUOROBORATES

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Alkyltin tetrafluoroborates have been prepared in the past in two ways: (*i*) cleavage of a tin–carbon bond in tetraalkyltin compounds with boron trifluoride[1] (1) and (*ii*) by the silver salt method[2,3], using CH_3CN or liquid SO_2 as a solvent (2). Recently, reactions of aminostannanes with $BF_3 \cdot OEt_2$ and Et_3OBF_4, yielding organotin tetrafluoroborates according to (3) and (4), have been reported[4]:

$$Me_4Sn + 2\,BF_3 \rightarrow Me_3SnBF_4 + MeBF_2 \quad (1)$$

$$Me_3SnX + AgBF_4 \xrightarrow[\text{liq. } SO_2]{CH_3CN \text{ or}} Me_3SnBF_4 + AgX \quad (2)$$

$$2\ \text{n-}Bu_3SnNEt_2 \xrightarrow{BF_3 \cdot OEt_2} 2\ \text{n-}Bu_3SnBF_4 + (F_2BNEt_2)_2 \quad (3)$$

$$\text{n-}Bu_3SnNEt_2 + 2\,Et_3OBF_4 \xrightarrow{CH_2Cl_2} \text{n-}Bu_3SnBF_4 + (Et_4N)BF_4 + 2\,Et_2O \quad (4)$$

The reaction products in (3) are trialkyltin fluorides and tris(dialkylamino)boranes[5], when stoichiometric amounts of the reactants are used; however, with excess boron trifluoride–etherate a further reaction (5) takes place:

$$3\,R_3SnNR'_2 + BF_3 \rightarrow 3\,R_3SnF + B(NR'_2)_3 \xrightarrow{BF_3 \cdot OEt_2} R_3SnBF_4 + (F_2BNR'_2)_2 \quad (5)$$

In consequence, reaction (6) provides a simple and quantitative route to alkyltin tetrafluoroborates, starting from easily available organotin fluorides[6–8] as "hard bases" and allowing these compounds to react with the "hard acid" BF_3. Silyl fluorides behave differently[9], but similar acid–base type reactions[10,11] are known [eqns. (7) and (8)]:

$$R_{4-n}SnF_n + n\,BF_3 \cdot OEt_2 \rightarrow R_{4-n}Sn(BF_4)_n + n\,Et_2O \quad (6)$$

$$Me_3SnCF_3 + BF_3 \rightarrow Me_3Sn(CF_3BF_3) \quad (7)$$

$$Me_3SnF + PF_5 \rightarrow Me_3SnPF_6 \quad (8)$$

Alkyltin fluorides dissolve completely in refluxing boron trifluoride–etherate

TABLE 1

PHYSICAL DATA FOR ALKYLTIN FLUORIDES AND TETRAFLUOROBORATES

Compound		M.p. (°C) (uncorr.) [B.p. (°C/mm)]	NMR data[a]			
			$\delta[CH_3(-C-Sn)]$	$\Delta\delta$[b]	$J(^{117}Sn-CH_3)$	$J(^{119}Sn-CH_3)$
(I) Me_3SnF	Colourl. needles	>300 (subl.)[c]	−0.45		66.1	69.0
(II) Me_2SnF_2	Colourl., micro-cryst. powder	>360	−0.75		80.2	84.1
(III) Et_3SnF	Colourl. needles	300 (subl.)[c]	−1.30	−0.17	91.5	95.8
(IV) Et_2SnF_2	Colourl. crystals	285–290 (subl.)[c]	−1.50	+0.17	132.5	138.0
(V) Bu_3SnF	Colourl. needles	250 (subl. ~200)	−1.03	[d]	[d]	[d]
(VI) Bu_2SnF_2	Colourl. crystals	155–158[c]	−0.95	[d]	96.0	99.0
(VII) Me_3SnBF_4[e]	Colourl. crystals	85–90[c] [120–125/0.001]	−0.53		66.0	69.0
(VIII) Et_3SnBF_4	Colourl. crystals	220–225 (subl.) [160–170/0.001]	−1.33	−0.13	93.5	97.5
(IX) $Et_2Sn(BF_4)_2$	Colourl. crystals	175–180 (dec.)	−1.35	+0.28	153.0	160.0
(X) Bu_3SnBF_4	Colourl. crystals	~245 (subl.)[c] [170–180/0.001]	−0.96	[d]	93.0	96.5
(XI) $Bu_2Sn(BF_4)_2$	Colourl. crystals	170–175 (subl.)	−0.96	[d]	96.0	100.5

[a] Spectra recorded on a Varian HA-100 NMR spectrometer with saturated solutions of (I)–(XI) in CH_3OH with TMS as internal reference, chemical shifts downfield from TMS in ppm, coupling constants in Hz. [b] $\Delta\delta = \delta[CH_3(-C-Sn)] - \delta[-CH_2(-Sn)]$. [c] Reported: (I), m.p. 375° (dec.) (ref. 8); (III), m.p. 295°, 302° (ref. 8); (IV), m.p. 287–290° (ref. 8); (VI), 157–160° (ref. 7); (VII), m.p. 89° (ref. 1); (X), m.p. 240–260° (ref. 4). [d] Signals not resolved. [e] ^{11}B-NME: +1.4 ppm, in CH_2Cl_2 sol. with $BF_3 \cdot OEt_2$ as ext. ref.

(only Me_2SnF_2 being insoluble) and after removing excess $BF_3 \cdot OEt_2$ *in vacuo* the corresponding alkyltin tetrafluoroborates are obtained in yields of 80–95% either by recrystallization from ether/pentane or by rapid, short-path vacuum distillation.

The identification of alkyltin fluorides (I)–(VI) and tetrafluoroborates (VII)–(XI) is facilitated by the characteristic IR spectra *e.g.* alkyltin tetrafluoroborates exhibit in their IR spectrum the typical pattern of B–F stretching modes in the 9–11 μ region. Proton-chemical shifts vary only over a small range, and the variations may be due to factors such as changes in electronegativity, diamagnetic anisotropy, and solvent effects.

Alkyltin fluorides and tetrafluoroborates have been intensively investigated by spectroscopic[3,12] and X-ray methods[13] and tentative structural assignments for both types of compound have been made. Critical reconsideration of earlier experiments[14] indicate that final conclusions concerning the molecular geometry of these compounds cannot yet be reached.

EXPERIMENTAL

Organotin fluorides have been prepared from the corresponding tin halides by reaction with KHF_2 in aqueous ethanol, following standard methods[6–8]. Boron trifluoride–etherate was purified by refluxing with copper powder for several hours and distillation *in vacuo*. Satisfactory analytical and physical data were obtained for all compounds listed in Table 1. Since all preparations were carried out identically, a standard procedure is given below.

Trimethyltin tetrafluoroborate

5 g (27 mmole) Me_3SnF were refluxed in 30 ml of BF_3–etherate for 30 min, during which the fluoride completely dissolved. Evaporation of the solvent yielded a colourless, crystalline solid, purified by rapid short-path vacuum distillation. The compound Me_3SnBF_4 shows a measurable vapor pressure of BF_3 because of dissociation, and so in this case the yield was lowered to 5.4 g (80%) of Me_3SnBF_4, col. crystals, m.p. 85–90° (lit. 89°), b.p. 120–125°/0.001 mm.

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