

NOTE

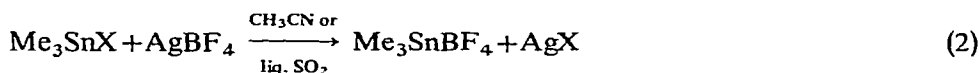
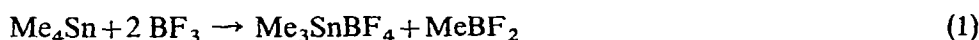
ALKYLTIN TETRAFLUOROBORATES

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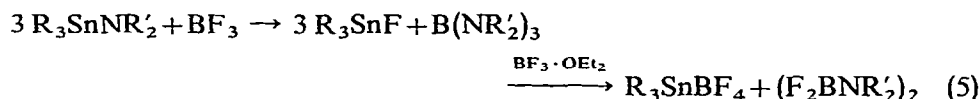
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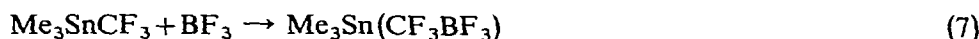
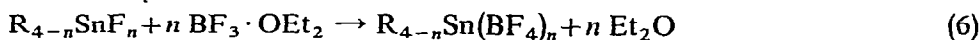
Alkyltin tetrafluoroborates have been prepared in the past in two ways: (i) cleavage of a tin-carbon bond in tetraalkyltin compounds with boron trifluoride<sup>1</sup> (1) and (ii) by the silver salt method<sup>2,3</sup>, using CH<sub>3</sub>CN or liquid SO<sub>2</sub> as a solvent (2). Recently, reactions of aminostannanes with BF<sub>3</sub>·OEt<sub>2</sub> and Et<sub>3</sub>OBF<sub>4</sub>, yielding organotin tetrafluoroborates according to (3) and (4), have been reported<sup>4</sup>:



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



In consequence, reaction (6) provides a simple and quantitative route to alkyltin tetrafluoroborates, starting from easily available organotin fluorides<sup>6-8</sup> as "hard bases" and allowing these compounds to react with the "hard acid" BF<sub>3</sub>. Silyl fluorides behave differently<sup>9</sup>, but similar acid-base type reactions<sup>10,11</sup> are known [eqns. (7) and (8)]:



Alkyltin fluorides dissolve completely in refluxing boron trifluoride-etherate

TABLE I  
PHYSICAL DATA FOR ALKYL TIN FLUORIDES AND TETRAFLUOROBORATES

Compound	M.p. (°C) (uncorr.) [B.p. (°C/mm)]	NMR data <sup>a</sup>		
		$\delta$ [CH <sub>3</sub> (-C-Sn)]	$\Delta\delta^b$	$J(^{117}\text{Sn-CH}_3)$ $J(^{119}\text{Sn-CH}_3)$
(I) Me <sub>3</sub> SnF	Colour, needles	-0.45		66.1
(II) Me <sub>2</sub> SnF <sub>2</sub>	Colour, micro-cryst. powder	-0.75		84.1
(III) Et <sub>3</sub> SnF	Colour, needles	-1.30	-0.17	91.5
(IV) Et <sub>2</sub> SnF <sub>2</sub>	Colour, crystals	-1.50	+0.17	132.5
(V) Bu <sub>3</sub> SnF	Colour, needles	-1.03	<sup>d</sup>	<sup>d</sup>
(VI) Bu <sub>2</sub> SnF <sub>2</sub>	Colour, crystals	-0.95	<sup>d</sup>	96.0
(VII) Me <sub>3</sub> SnBF <sub>4</sub> <sup>e</sup>	Colour, crystals	-0.53		66.0
(VIII) Et <sub>3</sub> SnBF <sub>4</sub>	Colour, crystals	-1.33	-0.13	93.5
(IX) Et <sub>2</sub> Sn(BF <sub>4</sub> ) <sub>2</sub>	Colour, crystals	-1.35	+0.28	153.0
(X) Bu <sub>3</sub> SnBF <sub>4</sub>	Colour, crystals	-0.96	<sup>d</sup>	93.0
(XI) Bu <sub>2</sub> Sn(BF <sub>4</sub> ) <sub>2</sub>	Colour, crystals	-0.96	<sup>d</sup>	96.0

<sup>a</sup> Spectra recorded on a Varian HA-100 NMR spectrometer with saturated solutions of (I)-(XI) in CH<sub>3</sub>OH with TMS as internal reference, chemical shifts downfield from TMS in ppm, coupling constants in Hz. <sup>b</sup>  $\Delta\delta = \delta[\text{CH}_3(-\text{C-Sn})] - \delta[-\text{CH}_2(-\text{Sn})]$ . <sup>c</sup> Reported: (I), m.p. 375° (dec.); (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). <sup>d</sup> Signals not resolved. <sup>e</sup> <sup>11</sup>B-NMR: +1.4 ppm, in CH<sub>2</sub>Cl<sub>2</sub> sol. with BF<sub>3</sub>·OEt<sub>2</sub> as ext. ref.

(only  $\text{Me}_2\text{SnF}_2$  being insoluble) and after removing excess  $\text{BF}_3 \cdot \text{OEt}_2$  *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  $\mu$  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<sup>3,12</sup> and X-ray methods<sup>13</sup> and tentative structural assignments for both types of compound have been made. Critical reconsideration of earlier experiments<sup>14</sup> 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  $\text{KHF}_2$  in aqueous ethanol, following standard methods<sup>6–8</sup>. 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)  $\text{Me}_3\text{SnF}$  were refluxed in 30 ml of  $\text{BF}_3$ –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  $\text{Me}_3\text{SnBF}_4$  shows a measurable vapor pressure of  $\text{BF}_3$  because of dissociation, and so in this case the yield was lowered to 5.4 g (80%) of  $\text{Me}_3\text{SnBF}_4$ , col. crystals, m.p. 85–90° (lit. 89°), b.p. 120–125°/0.001 mm.

#### ACKNOWLEDGEMENT

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