# SOME REACTIONS AND SPECTROSCOPIC STUDIES ON THE ORGANOTIN THIOLATES Bu<sub>3</sub>SnSR AND Bu<sub>2</sub>Sn(SR)<sub>2</sub>

CHARLES I. BALCOMBE, ELWOOD C. MACMULLIN and MICHAEL E. PEACH Department of Chemistry, Acadia University, Wolfville, Nova Scotia, Canada BOP 1XO

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Abstract—The properties of the organotin compounds  $Bu_2Sn(SR)_2$  and  $Bu_3SnSR$  (R = Me, Ph or  $C_6F_5$ ) were studied. Fracture of the Sn–S bond with various metallic and non-metallic halides is a predominant feature of the reactions: the tin atom did not act as an acceptor or the sulfur as a donor. Details are presented of the vibrational, mass and Mössbauer spectra.

### INTRODUCTION

ORGANOTIN compounds of the type  $R_{+x}Sn(SR')_x$  (x = 1, 2) should show donor and acceptor properties, with the tin atom acting as an electron acceptor and the sulfur as an electron donor. The reactions of the compounds  $R_2Sn(SR')_2$  (R' = Me, R = Et, Me; R = Bu, R' = Me, Ph,  $C_6F_5$ ) and Bu<sub>3</sub>SnSR (R = Me, Ph,  $C_6F_5$ ) with methyl iodide, various metal halides and carbonyls, and some donor solvents are reported, together with details of the vibrational, mass and Mössbauer spectra.

One of the objectives of this paper was to study the compounds  $R_3 Sn SR'$  and  $R_2 Sn(SR')_2$  as potential ligands. Compounds containing two or more thiolate groups should theoretically be able to act as bidentate sulfur ligands. Few examples of this are found in organotin chemistry. The compound Me<sub>2</sub>Sn(SMe)<sub>2</sub>Cr(CO)<sub>4</sub>, prepared from Me<sub>2</sub>Sn(SMe)<sub>2</sub> and Cr(CO)<sub>6</sub>[1] may have this type of structure,



containing presumably an Sn-Cr bond. It is also possible to form sulfur bridges when metal halides react with metal thiolates, and such compounds have been formed from  $\pi$ Cp<sub>2</sub>M(SMe)<sub>2</sub> and M'Hal<sub>2</sub>[2].

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$$\pi Cp_2 M \bigvee_{Me}^{Me} M' Hal_2$$

$$M = Mo; M' = Fe; Hal = Cl$$

$$M = Mo, W; M' = Co; Hal = Cl, Br, SCN$$

No examples of the latter reaction are known in

organotin chemistry, where preferential fracture of the Sn-S bond occurs.

## RESULTS AND DISCUSSION

Reactions with methyl iodide Methyl iodide fractured the Sn-S bond in  $R_2$ Sn(SMe)<sub>2</sub>

(R = Me, Et, Bu) and  $Bu_3SnSMe$ .

$$R_2$$
Sn(SMe)<sub>2</sub> + 4MeI  $\rightarrow$   $R_2$ SnI<sub>2</sub> + Me<sub>3</sub>S<sup>+</sup>I<sup>-</sup>.

No reaction was observed between MeI and  $Bu_2Sn(SR)_2$ or  $Bu_3SnSR$  ( $R = Ph, C_6F_5$ ). This may be attributed either to the lack of coordinating ability of the sulfur atom in XSPh or  $XSC_6F_5$  or lack of sulfur nucleophilicity in these compounds. The coordinating ability of  $(C_6F_5)_2S$  is virtually zero [3], while that of  $Ph_2S$  is very much less than that of Me<sub>2</sub>S, as measured by their protonation in liquid hydrogen chloride [4]. The reaction was totally inhibited when studied in a methanol solution of sodium fluoride. The mechanism of the reaction probably involves a 5-coordinate intermediate,



rather than an ionic mechanism.

$$Bu_2Sn(SMe)_2 + MeI \implies Bu_2Sn(SMe)_2 + I$$

### Reactions with metal halides

When Me<sub>3</sub>SnSMe reacts with various metal and metalloid halides fracture of the Sn-S bond occurs [5, 6]. The compound  $Ge(SC_6Cl_5)_4$  has been prepared from  $GeCl_4$  and  $Bu_2Sn(SC_6Cl_5)_2$ [7].

The Sn-S bond in Bu<sub>2</sub>Sn(SPh)<sub>2</sub> and Bu<sub>2</sub>Sn(SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> was fractured by a variety of reagents in methanol solution and the following compounds have been formed: Ni(SPh)<sub>2</sub> (from NiCl<sub>2</sub>), CdCl(SPh). H<sub>2</sub>O (from CdCl<sub>2</sub>, 2, 5H<sub>2</sub>O), HgCl(SPh), 2H<sub>2</sub>O (from HgCl<sub>2</sub>, 3H<sub>2</sub>O), Pb(SPh)<sub>2</sub> (from Pb(OAc)<sub>2</sub>), Ag(SPh) (from AgNO<sub>3</sub>), Ni(SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (from NiCl<sub>2</sub>) and Hg(SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (from HgCl<sub>2</sub>.3H<sub>2</sub>O) respectively. Some reactions occurred between Bu<sub>2</sub>Sn(SPh)<sub>2</sub> and TiCl<sub>4</sub>, ZrCl<sub>4</sub>, FeCl<sub>3</sub> and BeCl<sub>2</sub> when mixed in an inert solvent such as benzene, but the reaction did not go to completion or very unstable products were isolated. Certain transition metal ions, such as Co(III), Fe(III), Cu(II) and Au(III) gave poorly characterized products.

### Reactions with metal carbonyls

The reactions of Me<sub>3</sub>Sn(SR) (R = Me, Et) with M(CO)<sub>6</sub> (M = Cr.)Mo) and  $C_{5}H_{5}Mn(CO)_{3}$ vielded Me<sub>3</sub>Sn(SR)M(CO)<sub>5</sub> and Me<sub>3</sub>SnSMeMn(CO)<sub>5</sub>C<sub>5</sub>H<sub>5</sub> respectively. In the reactions of  $C_5H_5V(CO)_4$ ,  $Mo(CO)_6$ , and Ni(CO)<sub>4</sub> with Me<sub>3</sub>SnSMe the transient formation of a species with an M-SMe-Sn group in solution was observed, but this could not be isolated. The reaction of Fe<sub>2</sub>(CO)<sub>9</sub> and Me<sub>3</sub>SnSMe yielded Fe(CO)<sub>5</sub>, CO, [(CO)<sub>3</sub>FeSMe]<sub>2</sub>, and [(CO)<sub>4</sub>FeSn(SMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>[8]. Similarly  $Me_2Sn(SMe)_2$ reacted with  $Cr(CO)_{6}$ to form Me<sub>2</sub>Sn(SMe)<sub>2</sub>Cr(CO)<sub>4</sub>[1]. Trimeric alkylthiotricarbonyl clusters of manganese and rhenium have been prepared using organotin thiolates. This reaction may

 $Mn(CO)_5Br + Me_2Sn(SMe)_2$ 

 $\rightarrow 1/3(Mn(CO)_3SMe)_3 + Me_2Sn(SMe)Br + 2CO$ 

proceed via the formation of an intermediate such as  $R_2Sn(SR')_2M(CO)_3X[9]$ .

The reactions of the carbonyls  $Cr(CO)_6$ ,  $Mo(CO)_6$ ,  $Fe(CO)_5$  and  $Ni(CO)_4$  and 2,2,1-bicycloheptadiene molybdenum carbonyl were studied with the various organotin compounds  $Bu_2Sn(SR)_2$  and  $Bu_3SnSR$ . The reactions were studied in an oxygen free nitrogen atmosphere in THF solution and could be induced by u.v. irradiation. Separation of the reactants and products was in all cases impossible. The products were also heat sensitive. The i.r. spectra of all the crude products showed carbonyl frequencies that were shifted from those in the parent carbonyl and in the impure chromium compound were similar to those observed in  $Me_2Sn(SMe)_2Cr(CO)_4$ [1]. There was no indication of the formation of any carbonyl bridges. The compounds  $Bu_3SnSC_6F_5$  and  $Bu_2Sn(SC_6F_5)_2$ did not react with chromium carbonyl. The formation of compounds such as  $Bu_3SnCo(CO)_4$ [10] was not observed as all the products contained varying amounts of sulfur, but the presence of such compounds in a mixture cannot be excluded.

### Reactions with donor solvents

The tin atom in various organotin compounds, such as Ph<sub>2</sub>SnCl<sub>2</sub>, acts as an acceptor forming adducts with a range of donors, for example DMSO[11]. The Mössbauer spectra of Bu<sub>3</sub>SnSPh and related compounds in pyridine solution have been interpreted in terms of a weak 5-coordinated compound[12]. No coordination compounds were isolated when Bu<sub>2</sub>Sn(SR)<sub>2</sub> or Bu<sub>3</sub>SnSR  $(R = Me, Ph, C_6F_5)$  were dissolved in various donor pyridine, solvents such as dimethylformamide, triethylamine, hexamethylphosphoramide, and benzonitrile or ether or ethanol solutions of 2,2'-dipyridyl, Ph<sub>3</sub>PO, Bu<sub>3</sub>PO, Ph<sub>3</sub>AsO and 1, 10-phenanthroline, but partial hydrolysis was observed. The solvent may have absorbed atmospheric water. The hydrolysis was quantitative when a stoichiometric amount of water was added. The hydrolysis can be considered to be the reverse of the method of preparation from the oxide and the thiol[13].

#### Summary

These results suggest that in the compounds examined, fracture of the Sn-S bond is a primary reaction. The coordinating ability of the sulfur and the acceptor properties of the tin are virtually minimal.

### Spectroscopic studies

The i.r. and both the proton and fluorine NMR spectra of the compounds  $Bu_3SnSR$  and  $Bu_2Sn(SR)_2$  (R = Me, Ph, C<sub>6</sub>F<sub>3</sub>) have been reported [13]. The Raman, mass and Mössbauer spectra have been recorded and the i.r. spectra reexamined.

### Vibrational spectra

The observed frequencies in the vibrational spectra have been correlated with those of the alkyl and aryl groups present. Specific Sn-C, Sn-S and C-S frequencies

Compound	δ(SnSC) Raman	$\nu_{s(Sn-S)}$		$\nu_{as(Sn-S)}$		$\nu_{s(Sn-C)}$		$\nu_{\rm as(Sn-C)}$		ν(S-C)	
		I.R.	Raman	I.R.	Raman	I.R.	Raman	I.R.	Raman	1.R.	Raman
Bu <sub>3</sub> SnSMe	184 sh	342 vs	336 vs	393 w	388 w	459 w		516 m	507 s	696 s	700 m
Bu <sub>2</sub> Sn(SMe) <sub>2</sub>	191 m	349 vs	336 vs	395 w	390 w	460 w	452 vw	519 m	508 m	698 s	657 m
Bu <sub>2</sub> SnSPh	192 sh	341 m	338 s	393 w	388 w	459 w	453 w	516 m	506 m	695 vs	700 m
Bu <sub>2</sub> Sn(SPh) <sub>2</sub>	191 s	347 s	343 s				456 w	503 sh	509 m	692 vs	700 s
Bu <sub>3</sub> SnSC <sub>4</sub> F <sub>5</sub>	_	320 m	326 m	386 w	384 w	459 w	445 m	520 m	512 s	520 m	512 s
$Bu_2Sn(SC_6F_5)_2$	_	337 s	326 s	391 m	390 sh	460 w	_	521 m	508 m	521 m	508 m

Table 1. Features of the vibrational spectra (cm<sup>-1</sup>)

are shown in Table 1. These values are within the ranges previously observed. Tin-carbon frequencies, both symmetric and asymmetric, are observed between 500 and  $550 \text{ cm}^{-1}$  in methyl tin compounds [14], while in butyl tin compounds they are somewhat lower [15]. The tin-sulfur frequencies in both thiolates and sulfides,  $R_3 Sn SR'$  and  $(R_3 \text{Sn})_2 \text{S}$  occur around 350 cm<sup>-1</sup>[14] and the bending mode SnSC around 190–200 cm<sup>-1</sup>[14]. The position of the S-C stretching frequency depends on the group attached to the carbon. In C<sub>6</sub>F<sub>5</sub>S derivatives this frequency is observed at 500-520  $\text{cm}^{-1}$ , being relatively weak in the i.r. and strong in the Raman spectra, whereas the C-S for S-CH<sub>2</sub>R occurs between 650 and 700 cm<sup>-1</sup>, being nearer  $700 \text{ cm}^{-1}$  when R = H[16]. In systems examined containing the PhS group, such as PhSMe[17], the Ph-S stretching frequency occurs at 689-701 cm<sup>-1</sup> and the Me-S at 722 cm<sup>-1</sup>.

### Mass spectra

Relatively few studies have been made of the mass spectra of organotin compounds [18, 19]. The only organotinthiolates that have been examined are  $Me_2Sn(SMe)_2[14]$ , and some compounds derived from dicyano ethylene-1,2-dithiol[20]. The general features of organotin mass spectra, including the preferred formation of even electron tin containing species, elimination of alkenes or other neutral molecules [19, 21], are observed.

The main features of the spectra are tabulated in Table

2. The molecular ion is either absent or is of relatively weak intensity. The most abundant tin containing ions in all the spectra are the even electron ions  $Bu_2SnSR^+$ , except in the spectrum of  $Bu_2Sn(SMe)_2$  where the  $BuSn(SMe)_2^+$  ion is the most abundant. Metastable peaks indicate the conversion of one even electron containing ion to another.

$$Bu_2SnSPh^+ \rightarrow SnSPh^+ + Bu_2$$

Rearrangement and recombination must be observed in the formation of ions such as  $SnH^+$ ,  $SnSH^+$  and reactions postulated such as,

$$BuSn^+ \rightarrow SnH^+ + C_4H_8$$

although only confirmed by metastable peaks in the spectrum of  $Bu_2Sn(SMe)_2$ . The formation of Sn-F bonds, in the ions  $SnF^+$  and  $Bu_2SnF^+$ ,

$$Bu_2Sn(SC_6F_5)^+ \rightarrow Bu_2SnF^+ + C_6F_4S$$

is analogous to that observed in other compounds containing the  $SC_6F_5$  group, for example ions with As-F bonds are observed in the mass spectrum of As( $SC_6F_5$ )<sub>3</sub>[22]. The ion  $SnF^+$  is also formed in fragmentation of organotin compounds containing a  $CF_3$  or  $C_2F_5$ 

Table 2. Relative abundances of ions in mass spectra\*

Compound						
Ion	$Bu_2Sn(SC_6F_5)_2$	$Bu_2Sn(SPh)_2$	$Bu_2Sn(SMe)_2$	Bu <sub>3</sub> SnSC <sub>6</sub> F <sub>5</sub>	Bu <sub>3</sub> SnSPh	Bu₃SnSMe
Bu <sub>3</sub> SnSR <sup>+</sup>			_	0.3(490)	10.7(400)	0.2(338)
Bu <sub>2</sub> SnSR <sup>+</sup>	50.0(433)	27.8(343)	15-1(281)	10.9(433)	<u>100</u> (343)	<u>100</u> (281)
BuSnSR <sup>+</sup>	1.7(376)	0.5(286)	8.0(244)	0.2(376)	0.6(286)	6.1(224)
SnSR <sup>+</sup>	27.3(319)	50.0(229)	84-6(167)	4.8(319)	61.7(229)	26-8(167)
$Bu_2Sn(SR)_2^+$	1.6(632)	2.4(452)	1.8(328)	_		_
$BuSn(SR)_2^+$	2.6(575)	17.7(395)	<u>100(271)</u>			5.1(271)
$Sn(SR)_2^+$	-	0.9(338)	10.6(214)	_		-
R SBu <sup>±</sup>	1.1(256)	10.4(166)	0.6(104)	0.3(256)	0.2(166)	-
<i>R</i> SSnS <sup>+</sup>	0.4(351)	1.0(261)	5.5(199)	—		
$(RS)_{2}^{+}$	1.9(398)	1.3(218)	0.6(94)	40.8(398)	0.6(218)	-
R SH <sup>†</sup>	100(200)	100(110)	8.0(48)	30.2(200)	13.8(110)	3.1(48)
$RS^+$	32(199)	25.6(109)	9.9(47)	100(199)	4.1(109)	4.1(47)
$Bu_3Sn^+(291)$			_	1.5	4.0	3.5
$Bu_2Sn^{+}(234)$	0.4	1.0	1.0	1.8		4.4
BuSn <sup>+</sup> (177)	10.0	1.0	5.0	10.6	11.1	13.4
SnH <sup>+</sup> (121)	3.8	1.5	7.5	4.3	5.5	9.3
$Bu_2SnF^+(253)$	15.0	_		5.3		
SnF <sup>+</sup> (139)	31.8			4.3		
SnSH <sup>+</sup> (153)	3.1	7.9	6.3	0.6	11.9	4.3
<sup>116</sup> Sn <sup>‡</sup> (116)	7.8	0.6	1.5	0.5	1.0	1.1
$Bu_2^+(114)$	_			0.1		
Bu⁺(57)	52.7	6.2	22.8	8.0	5.1	7.2
S <sup>†</sup> (32)		0.6	3.5	0.3		0.5
$S_2^{+}(64)$		1.0		1.1	0.2	
$S_8^{+}(256)$	1.1	0.1	1.0	0.3	0.2	-
Sample						
Temp(°C)	79	24	30	45	30	24

\*Based on <sup>120</sup>Sn, except where stated. Ratio m/e indicated in brackets.

group, as in  $[C_2F_5C(O)OSnMe_2]_2O[21]$ . Rearrangements involving the formation of thiols are a feature of all the spectra and the RSH<sup>+</sup> ions are the most abundant ions in the spectra of Bu<sub>2</sub>Sn(SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and Bu<sub>2</sub>Sn(SPh)<sub>2</sub>. Rearrangement and the formation of sulfides and disulfides occur in the spectra of Bu<sub>2</sub>Sn(SPh)<sub>2</sub> and Bu<sub>3</sub>SnSC<sub>6</sub>F<sub>5</sub> where the ions BuSPh<sup>+</sup> and (C<sub>6</sub>F<sub>5</sub>S)<sub>2</sub><sup>+</sup> are observed.

### Mössbauer spectra

The data from the Mössbauer spectra are shown in Table 3. Relatively little data has been published on the Mössbauer spectra of organotin thiolates of the type  $R_3SnSR'$  and  $R_2Sn(SR')_2$  and the results obtained here are comparable with those recorded previously [12, 23, 24].

The isomer shifts of the compounds are relatively insensitive to the nature of the mercapto group attached to the tin. The sulfur atom is effectively shielding the tin nucleus from any  $\sigma$ -interactions with the alkyl or aryl constituent of the mercapto group. Normally the value of  $\delta$  decreases as the electron withdrawing power of the ligand substituent increases, but in the compounds studied the value of  $\delta$  increased as the group R' became more electronegative. This also supports the argument that the sulfur effectively shields the tin from  $\sigma$ -interactions beyond the sulfur.

The values of the isomer shift  $\delta$  are within the range normally observed for organotin compounds of this type[12, 23] and the polarity of the Sn-S bond can be assumed to be about the same as that of the Sn-C bond.

The values of the quadrupole splitting parameters,  $\Delta$ , of the methyl thio and butyl thio derivatives are consistent with a tetrahedral structure in the solid state. Previous results on solid Bu<sub>3</sub>SnSPh indicated a tetrahedral structure, but a five coordinate structure was postulated when it was frozen in pyridine solution [12]. Similarly the spectra of the dithiolates, Bu<sub>2</sub>Sn(SR)<sub>2</sub> (R = Me, Ph) have been interpreted in terms of a tetrahedral structure [24]. The values of  $\Delta$  for the pentafluorophenylthio derivatives are somewhat larger, suggesting a higher coordination number in the solid state. It is noteworthy that the pentafluorophenylthio group is the most bulky thio group studied and deviations from a regular tetrahedral structure can be expected. These derivatives are the only ones that are solids at room temperature.

Table 3. Mössbauer parameters\*

Compound	δ	Δ	Гı	$\Gamma_2$
Bu <sub>3</sub> SnSMe	1.39	1.71	0.94	0.88
$Bu_2Sn(SMe)_2$	1.43	2.02	1.06	1.12
Lit. 24	1.48	2.11		
Bu₃SnSPh	1.42	2.00	0.90	0.88
Lit. 12	1.42	2.03	0.88	0.82
Bu <sub>2</sub> Sn(SPh) <sub>2</sub>	1.46	1.91	0.85	0.85
Lit. 24	1.50	1.96		
Bu₃SnSC <sub>6</sub> F₅	1.45	2.32	0.88	0.83
$Bu_2Sn(SC_6F_5)_2$	1.49	2.51	0.98	0.76

\*Recorded at  $8.2 \pm 2^{\circ}$ K, literature values recorded at  $78^{\circ}$ K.

### EXPERIMENTAL

Most reagents were available commercially. Microanalyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, W. Germany.

Organotin (IV) thiolates were prepared from the corresponding thiol and organotin oxide or chloride by literature methods [13]. All experiments were performed with 10-20 mmole of reactants.

I.R. spectra were recorded as liquid films or mulls with Nujol or hexachlorobutadiene on a Perkin-Elmer 457. Laser Raman spectra were recorded as liquids on a Spex double monochromator model 1401 with a Carson argon ion laser, frequency of excitation 4880 Å. The 70 eV mass spectra were obtained with a DuPont/CEC Model 21-110B mass spectrometer with direct introduction. Mössbauer spectra were obtained with a constant acceleration type spectrometer (Austin Science Associates drive) with a Nuclear Chicago 400 word analyser as counter. The  $\gamma$ radiation source was 5 mC <sup>119</sup>Sn as barium stannate. A flyback was employed to give a single 400 point spectrum. Samples were cooled to  $8\cdot2\pm2^{\circ}K$ .

Reactions with methyl iodide are summarized in Table 4. No reaction occurred when these reactions were studied in 0.1, 1 or 10% solutions of NaF in methanol.

The reactions with metal salts were studied in MeOH solution. In a typical reaction 20·0 mmole each of the metal salt and the tin compound were dissolved in 10·0 ml of MeOH. After 24 hr one product was filtered off, and the other recovered on removal of the solvent. The products were identified by m.ps and i.r. spectra or, when unknown compounds were isolated, these were characterized by chemical analysis. Ni(SPh)<sub>2</sub>, m.p. (d) 180°, lit. d. 180° [28]. CdCl(SPh). H<sub>2</sub>O, m.p. 300°, white; Found: C, 26·2; H, 1·9; S, 11·9; Calcd. for C<sub>6</sub>H<sub>7</sub>OCdClS: C, 26·2; H, 2·6; S, 11·7; HgCl(SPh). 2H<sub>2</sub>O, white, m.p. (d) >200°; Found: C, 19·1; H, 1·4; S, 8·1. Calcd. for C<sub>6</sub>H<sub>9</sub>O<sub>2</sub>ClHgS: C, 18·9; H, 2·4; S, 8·3. Pb(SPh)<sub>2</sub>, yellow, m.p. (d) 198°; Found: S, 14·8; Calcd. for C<sub>12</sub>H<sub>10</sub>PbS: S, 15·1. AgSPh, yellow-white, m.p. > 300°; Found: S, 14·8. Calcd. for C<sub>6</sub>H<sub>3</sub>AgS: S, 15·0. Hg(SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, m.p. 187–8°, lit. 187–8°[29]. Ni(SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, m.p. >300°, lit. 340°[29].

The reactions with metal carbonyls were studied in dry THF. The calculated amount of organotin thiolate was added to the magnetically stirred carbonyl solution and irradiated with long wavelength u.v. in a dry oxygen free nitrogen atmosphere for about 6 hr. Unreacted carbonyl precipitated as the solvent was removed. Further unreacted carbonyl was precipitated on addition of 100 ml pentane and allowing to stand overnight. This procedure was repeated. Chemical analysis of the products showed them to be impure, except in the cases of  $Bu_3SnSC_6F_5$  and  $Bu_2Sn(SC_6F_5)_2$  where the pure organotin thiolate was recovered.

No reaction, or a very slow reaction resulting in hydrolysis, occurred between  $Bu_2Sn(SR)_2$  or  $Bu_3SnSR$  (R = Me, Ph,  $C_6F_3$ ) and the donor solvents Py, DMF, DMSO, PhCN, HMPA, and Et<sub>3</sub>N or EtOH or Et<sub>2</sub>O solutions of 2,2'-dipyridyl, Ph<sub>3</sub>PO, Bu<sub>3</sub>PO, Ph<sub>3</sub>AsO, or 1,10-phenanthroline. When a stoichiometric amount of water was added to solutions of  $Bu_2Sn(SR)_2$  (R = Me, Ph,  $C_6F_3$ ) in MeOH the hydrated oxide  $Bu_2SnO \cdot H_2O$  was recovered after 72 hr in varying yields; 80 per cent (R = Me), 65 per cent (R = Ph), 68 per cent ( $R = C_6F_5$ ). Similar hydrolysis of  $Bu_2Sn(SMe)_2$  occurred on adding water to its solutions in PhCN, DMF, DMSO and Et<sub>3</sub>N.

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Organotin (IV) derivative	Solvent	Products*					
Me <sub>2</sub> Sn(SMe) <sub>2</sub>	Neat	Me <sub>2</sub> SnI <sub>2</sub>	(60%)	(CH <sub>3</sub> ) <sub>3</sub> SI	(67%)		
	MeOH (stirred)		(70%)		(71%)		
	MeOH (renux)		(81%)		(80%)		
		E. G. I	(12%)		(70%)		
$Et_2Sn(SMe)_2$	Neat	$Et_2SnI_2$	(69%)	$(CH_3)_3SI$	(58%)		
	MeOH (reflux)		(62%)		(65%)		
	MeOH (reflux)		(75%)		(72%)		
	CCl₄		(71%)		(66%)		
$Bu_2Sn(SMe)_2$	Neat	$Bu_2SnI_2$	(40%)	(CH <sub>3</sub> ) <sub>3</sub> SI	(39%)		
	MeOH (stirred)		(42%)		(38%)		
	CCl		(69%)		(69%)		
Bu <sub>3</sub> Sn(SMe) <sub>2</sub>	Neat	Bu <sub>3</sub> SnI	(44%)	(CH <sub>3</sub> ) <sub>3</sub> SI	(49%)		
	MeOH (stirred)	2.	(51%)		(52%)		
	CCL		(44%)		(50%)		
$Bu_{-}Sn(SR)_{4n}$	Neat	No reaction			(		
where $n = 2.3$	MeOH (stirred)	No reaction					
$R = Ph, Ph_F$	CCl <sub>4</sub>	No reaction					

### Table 4. Reactions with methyl iodide

\* $Me_2SnI_2$  m.p. 44–5°C lit.<sup>25</sup> 44°C;  $Et_2SnI_2$  m.p. 44–6°C lit.<sup>11</sup> 45°C;  $Bu_2SnI_2$  b.p. 92°C/0·3 mm lit.<sup>26</sup> 145°C/6 mm;  $Bu_3SnI$  b.p. 11°C/0·3 mm lit.<sup>25</sup> 168°C/8 mm; (CH<sub>3</sub>)<sub>3</sub>SI m.p. d 234°C lit.[27] d 235°C.

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