Inorganica Chimica Acta, 49 (1981) 31–36

(Hydroxyalkyl)- and (4-Hydroxyphenyl)-organostannyl Sulfides: Synthesis and Characterization by Infrared, ^{1}H NMR and Mössbauer Spectroscopy

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Received September 27, 1980

(Hydroxyalkyl)- and (4-hydroxyphenyl)-tri- and -diorganostannyl sulfides R_3SnSX and $R_2Sn(SX)_2$ (R = Me, Ph; X = CH_2CH_2OH, $CH_2CHOHCH_2OH$, 4-C_6H_4OH), and $R_2Sn(SCH_2CH_2O)$ have been prepared from R_3SnOH or $[(R_2Sn)O]_n$ and HSX in $CHCl_3$ or – in some cases – diethylether. $R_2Sn(SCH_2CH_2OH)_2$ decomposes to $R_2Sn(SCH_2CH_2O)$ and $HSCH_2CH_2OH$; $Me_3SnSCH_2CH_2OH$ gives $Me_2Sn(SCH_2CH_2O)$, Me_4Sn and $HSCH_2CH_2O$. According to spectroscopic data the ligands in R_3SnSX and $R_2Sn(SX)_2$ are bonded to tetracoordinate Sn through S, the molecules being H-bonded in the solid state. For

TABLE I. Organotin Derivatives of 2-Mercaptoethanol, 3-Mercaptopropandiol-1,1 and 4-Mercaptophenol. Analytical Data.

Compound	Procedure	Yield	% C found (calcd.)	% H found (calcd.)	% Sn found (calcd.)
$Ph_3SnSCH_2CH_2OH$	I	85	56.28 (56.24)	4.71 (4.72)	27.8 (27.79)
$Me_3SnSCH_2CH_2OH$	II	94	24.90 (24.93)	5.82 (5.86)	49.0 (49.27)
$Ph_3SnSCH_2CHOHCH_2OH$	I	77	54.95 (55.17)	4.77 (4.85)	26.2 (25.96)
$Me_3SnSCH_2CHOHCH_2OH$	II	88	26.78 (26.60)	5.91 (5.95)	43.6 (43.81)
$Ph_3Sn(4\text{-}SC_6H_4OH)$	I	73	60.22 (60.66)	4.20 (4.24)	25.1 (24.98)
$Me_3Sn(4\text{-}SC_6H_4OH)$	II	68	37.95 (37.41)	4.82 (4.88)	39.8 (41.07)
$Ph_2Sn(SCH_2CH_2OH)_2$	II	90	44.52 (44.99)	4.70 (4.72)	27.5 (27.79)
$Me_2Sn(SCH_2CH_2OH)_2$	II	93	23.60 (23.78)	5.27 (5.32)	39.4 (39.17)
$Ph_2Sn(SCH_2CHOHCH_2OH)_2$	II	85	44.49 (44.38)	4.85 (4.97)	24.2 (24.36)
$Me_2Sn(SCH_2CHOHCH_2OH)_2$	II	89	26.27 (26.47)	5.41 (5.55)	32.9 (32.69)
$Ph_2Sn(4\text{-}SC_6H_4OH)_2$	II	58	54.94 (55.09)	3.81 (3.85)	22.7 (22.68)
$Me_2Sn(4\text{-}SC_6H_4OH)_2$	II	68	42.32 (42.13)	4.13 (4.04)	29.7 (29.74)
$Ph_2Sn(SCH_2CH_2O)$	III	18	48.02 (48.18)	4.06 (4.04)	33.8 (34.01)
$Me_2Sn(SCH_2CH_2O)$	III	67	21.43 (21.36)	4.41 (4.48)	52.6 (52.78)

TABLE II. IR Data[a] (cm^{-1}) and NMR Sn–C–H Coupling Constants (Hz) of Organotin Derivatives of Mercaptoethanol, 3-Mercaptopropandiol-1,2 and 4-Mercaptophenol.

Compound	ν(OH)	ν(CO)	ν_{as} (SnC)	ν_{sy} (SnC)	ν(SnS)	$J(^{117}Sn-C-H)$	$J(^{119}Sn-C-H)$
$Ph_3SnSCH_2CH_2OH$	3440 b	1050 s	–	–	340 m	–	–
$Ph_3SnSCH_2CHOHCH_2OH$	3400 b	1070 s	–	–	355 m	–	–
$Ph_3Sn(4\text{-}SC_6H_4OH)$	3270 b	1220 s	–	–	375 m	–	–
$Me_3SnSCH_2CH_2OH$	3400 b	1050 s	540 s	515 m	345 m	54	57
$Me_3SnSCH_2CHOHCH_2OH$	3400 b	1070 s	545 s	520 m	347 m	55	58
$Me_3Sn(4\text{-}SC_6H_4OH)$	3260 b	1220 s	540 s	513 m	370 w	53	56
$Ph_2Sn(SCH_2CH_2OH)_2$	3350 b	1060 s	–	–	365 m	–	–
$Ph_2Sn(SCH_2CHOHCH_2OH)_2$	3400 b	1070 s	–	–	360 m	–	–
$Ph_2Sn(4\text{-}SC_6H_4OH)_2$	3270 b	1220 s	–	–	380 m	–	–
$Me_2Sn(SCH_2CH_2OH)_2$	3350 b	1060 s	555 m	520 m	355 m	64	67
$Me_2Sn(SCH_2CHOHCH_2OH)_2$	3400 b	1070 s	565 m	530 m	365 m	65	68
$Me_2Sn(4\text{-}SC_6H_4OH)_2$	3350 b	1220 s	545 s	RA530 s	375 m	63	66
$Ph_2Sn(SCH_2CH_2O)$	n.o.	1050 s	–	–	355 m	–	–
$Me_2Sn(SCH_2CH_2O)$	n.o.	1050 s	b	b	335 m	c	c

[a] s = strong; m = medium; w = weak; b = broad; RA = Raman; n.o. = not observed. [b] Accurate values could not be obtained due to peak overlapping. [c] N.o. due to low solubility.

$Me_2Sn(SCH_2CH_2O)$ a polymeric chain structure with pentacoordinate Sn (R's and S in the equatorial plane) is suggested by vibrational spectroscopy and Mössbauer data (point charge model treatment of ΔE and lattice dynamics parameters).

Introduction

Organotin derivatives of mercaptanes and thiophenols RSH, where R is an unsubstituted organoligand, have been extensively studied, but reactions of organotin compounds with bifunctional mercaptocompounds, *e.g.* mercaptoalkanols or mercaptophenols, have found less interest. Examples of organotin derivatives of the latter type of ligands are: $Bu^n_3SnSCH_2CHOHCH_2OH$, $PhMe_2SnSCH_2CHOHCH_2OH$ and $Bu^n_2Sn(SCH_2CHOHCH_2OH)_2$ [1], $Bu^n_2Sn(SCH_2CH_2OH)_2$ [2, 3], $R_2Sn(SCH_2CH_2O)$ (R = Et [4], Bu$^{n\prime}$, Oct^n [5]) or $R_3SnOCH_2CH_2OSnR_3$ (R = Et, Bu^n [4]). Possible applications are mentioned in some patents [1, 2, 6]. The synthesis of such compounds has been achieved by reacting mercaptoalkanols with organotin methoxides [1] or with organostannoxanes during azeotropic distillation [1, 2]. Dibutyltin ethoxide reacted with 3-mercaptopropandiol-1,2 to give $Bu^n_2Sn(SCH_2CHOHCH_2OH)_2$, however with 2-mercaptoethanol only the chelate $Bu^n_2Sn(SCH_2CH_2O)$ was produced [3]. $Et_2Sn(SCH_2CH_2O)$ has been prepared by reaction of $(Et_3Sn)_2O$ with ethylenethiocarbonate, $(SCH_2CH_2O)CO$ [4]. We report here a simple method of synthesizing organotin derivatives of mercaptoalkanols and 4-mercaptophenol, and results on behaviour and structural features of some new compounds prepared in this way.

Results and Discussion

Synthesis and Reactivity; Configuration of Compounds R_3SnSR' and $R_2Sn(SR')_2$

The compounds of Table I were prepared as pure substances, and in most cases in good yields by reaction of 2-mercaptoethanol, 3-mercaptopropandiol-1,2 or 4-mercaptophenol with the appropriate triorganotin hydroxide (molar ratio 1:1) or diorganostannoxane (molar ratio 2:1) using $CHCl_3$ or – in some cases – diethylether as reaction medium.

Triorganotin hydroxides reacted at room temperature. When molar ratios other than 1:1 were applied, also only 1:1 products resulted, which however always contained unreacted educt. This means, neither a Sn–C bond has been broken by acidolysis (under formation of a R_2Sn-compound), nor a bistriphenyltin derivative of the type $R_3Sn-SCH_2CH_2O-SnR_3$ has been formed. The reaction mixtures of diorganostannoxanes and mercaptanes had to be warmed slightly, and it was important, that the stannoxanes were used immediately after their preparation. Products of the reactions of diorganostannoxanes with HSR′ (R′ = CH_2CH_2OH, $CH_2CHOHCH_2OH$, $4\text{-}C_6H_4OH$) always were of the type $R_2Sn(SR')_2$ independently from the molar ratio of the educts. The ligands were bound to Sn through

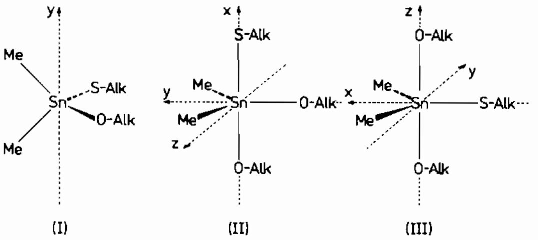

Fig. 1. Regular tetrahedral(I) and trigonal bipyramidal (II, III) structures of tin environments assumed in the point-charge estimate of ΔE. The directions of the principal components of the diagonalized E F G tensor are shown for (II) and (III), while y only is reported for (I) (Z and X lye in the Sn S O plane; Z forms an angle of 9.1° right hand side to the perpendicular to the Sn C C plane, when p.q.s.'s values of Table III are employed).

S (see below). The tri- and diorganotin derivatives of 4-mercaptophenol, $Ph_3SnSCH_2CH_2OH$, and $Me_2Sn(SCH_2CH_2O)$ are colourless solids, the other compounds prepared are viscous liquids.

$Ph_2Sn(SCH_2CH_2OH)_2$ and $Me_2Sn(SCH_2CH_2OH)_2$ are transformed to $R_2Sn(SCH_2CH_2O)$ according to eqn. 1 on warming to about 30 and 50 °C, respectively, for some days:

$$R_2Sn(SCH_2CH_2OH)_2 \rightarrow R_2Sn(SCH_2CH_2O) + HSCH_2CH_2OH \quad (1)$$

This reaction slowly proceeds already at room temperature. $Me_3SnSCH_2CH_2OH$ tends to decompose. Even after only two days standing at 35 °C the oily compound becomes less viscous and white crystals of $Me_2Sn(SCH_2CH_2O)$ appear. In the liquid Me_4Sn and $HSCH_2CH_2OH$ could be identified by NMR spectroscopy beside unreacted $Me_3SnSCH_2CH_2OH$. Therefore it can be concluded, that $Me_3SnSCH_2CH_2OH$ first redistributes [7] according to eqn.. 2:

$$2Me_3SnSCH_2CH_2OH \rightarrow Me_4Sn + Me_2Sn(SCH_2CH_2OH)_2 \quad (2)$$

Then $Me_2Sn(SCH_2CH_2OH)_2$ decomposes according to eqn. 1 rendering the other products observed. The overall reaction can be formulated according to eqn. 3:

$$2Me_3SnSCH_2CH_2OH \rightarrow Me_2Sn(SCH_2CH_2O) + Me_4Sn + HSCH_2CH_2OH \quad (3)$$

$Ph_3SnSCH_2CH_2OH$ (M.p. 91 °C) does not decompose at comparable temperatures. This is in accordance with the well known fact, that aryltin compounds are more stable than the corresponding alkyltin compounds.

In the vibrational spectra of all mercaptoalkanol derivatives listed in Table I no ν(SH) frequency (appearing in the mercapto educt at about 2545 cm^{-1}) can be observed, but an intensive ν(SnS) frequency, which is Raman active, between 335 and 365 cm^{-1} [8] (see Table II). Accordingly the *H*S signal at about 1–2 ppm is missing in the ^1H NMR spectrum. The spectra of all triorganotin derivatives and of the diorganotin compounds of the type $R_2Sn(SR')_2$ show a broad intensive ν(OH) frequency between 3350 and 3440 cm^{-1}. In the ^1H NMR spectra the *H*O-signal appears nearly unshifted – compared to the mercaptoalkanol – between 2 and 5 ppm. From these observations it can be concluded, that in all compounds the ligand is bound to Sn through S and not through O and that the OH group of the ligand forms H–bonds in the solid state at room temperature, which are broken in solution phase. Appreciable bonding interactions between OH and Sn cannot be assumed, since δ_{oop}(OH) at 650 cm^{-1} and ν(CO) at 1050–1070 cm^{-1} are, in comparison to the appropriate mercaptoalkanol, practically unchanged.

The spectral data of the organotin derivatives of 4-mercaptophenol indicate an analogous bonding situation. ν(OH) appears at 3270–3350 cm^{-1}, ν(CO) at 1220 cm^{-1}, corresponding to band positions in 4-mercaptophenol. The ν(SnS) frequency at 370–380 cm^{-1} is about 20 cm^{-1} higher than in the mercaptoalkanol derivatives. This can be ascribed to stronger Sn–S bonding, correlating with the observed higher stabilities of the mercaptophenol derivatives. ν_{as}(SnC) and ν_{sy}(SnC) are observed in the infrared and in the Raman spectra of all trimethyltin derivatives at 540–545 and 513–520 cm^{-1}, respectively [8]. Therefore the existence of a planar Me_3Sn group can be excluded. The dimethyltin compounds do not contain a linear Me_2Sn group since they also do not obey the exclusion rule [ν_{as}(SnC): 545–565 cm^{-1}; ν_{sy}(SnC): 520–530 cm^{-1}] [8, 9]. The coupling constants [$J(^{117}Sn-CH_3)$, $J(^{119}Sn-CH_3)$; see Table II] correspond to values of organotin compounds (in $CHCl_3$ solution) in which Sn has coordination number 4 [8].

Considering all data and observations a simple molecular structure can be proposed for the compounds at room temperature, in which according to the formulas $R_3Sn-S-R'-OH$ and $R_2Sn(S-R'-OH)_2$ (R = Me, Ph; R' = CH_2CH_2, $CH_2CHOHCH_2$, 4-C_6H_4) the central atom Sn (in the solid state and in solution) is tetracoordinated and bonds the ligands through S.

The Structure of $R_2Sn(SCH_2CH_2O)$ Compounds

The structure of our $R_3Sn(SCH_2CH_2O)$ derivatives did not appear so straightforward (*vide infra*);

TABLE III. Structural Data for $Me_2Sn(SCH_2CH_2O)$ from Mössbauer Spectroscopy.

A) Mössbauer parameters[a], and point-charge values of ΔE

δ[b] (mm s^{-1})	ΔE_{exp}[c] (mm s^{-1})	Structure[d]	ΔE_{calcd}[e] (mm s^{-1})
1.232 ± 0.002	2.724 ± 0.003	(I)	−2.305
		(II)	+2.143
		(III)	−2.514

B) Lattice dynamics parameters in the temperature range 77.3–126.3 K

dlnA/dT[f] ($\times 10^2$, K^{-2})	$\langle X^2 \rangle$[g] ($\times 10^{18}$, cm^2)	θ_D[h] (K)	$M\theta_D^2$[i] ($\times 10^{-6}$, a.m.u. × K^2)
−1.622(0.990)	0.86–1.40	76.4	1.31
	(0.82–1.47)	(75.8 ± 0.4)	(1.29)

[a] Experimental parameters are average values from temperature dependent measurements (eight data points) with standard error. Sample thickness, 1.21 mg $^{119}Sn/cm^2$. Full width at half height of the resonant peaks, average (Lorentzian fits), is 1.069 mm s^{-1}. [b] Isomer shift [10] with respect to R.T. $CaSnO_3$. [c] Nuclear quadrupole splitting [10]. [d] See Fig. 1. [e] P.q.s.'s values employed in the calculations are: $([Alk] - [hal])^{tet} = -1.37$ mm s^{-1} [10]; $([S\text{-}Alk] - [hal])^{tet} = -0.50$[11]; $([O\text{-}Alk] - [hal])^{tet} = -0.27$ (see text); $\{Alk\}^{tbe} = -1.13$ [12]; $\{S\text{-}Alk\}^{tba} = -0.595$; $\{S\text{-}Alk\}^{tbe} = -0.60$; $\{O\text{-}Alk\}^{tba} = -0.13$; $\{O\text{-}Alk\}^{tbe} = +0.02$ (see text for the latter four values). [f] Least squares slope of the experimental function lnA(T) (eight A(T) data points), A being the total (Lorentzian) area under the resonant doublets, mm s^{-1}, at given T. Correlation coefficient is in parenthesis. [g] Mean square displacements of the Mössbauer atoms at the limiting temperatures here investigated. [h] Debye-Mössbauer Temperature. [i] Parameter of intermolecular force constant. [g–i] Values in the first line are obtained from dlnA/dT, while data in parentheses, with standard error for θ_D, are calculated from 'absolute' recoil free fractions [13, 14].

then, in addition to infrared work, Mössbauer spectroscopy has also been employed (including a temperature dependent investigation) in order to get a better characterization of $Me_2Sn(SCH_2CH_2O)$, and the results obtained are reported in Table III. In fact, $Me_2Sn(SCH_2CH_2O)$ is nearly insoluble in common organic solvents; it dissolves in hot pyridine, probably owing to further coordination of tin to the solvent, but the original compound is recovered unchanged upon cooling. This would suggest a polymeric structure in the solid state. Instead, Alk_2Sn^{IV}thioglycoxides (Alk = Et, Bu^n, Oct^n) are readily soluble and form dimers in organic solvents; a trigonal bipyramidal type structure [such as II, Fig. 1], involving bridging oxygen atoms, has been proposed both in the liquid state and in solution [5]. On the other hand, Me_2Ge^{IV}thioglycoxide has been demonstrated to be monomeric [15].

The infrared spectra of our $R_2Sn(SCH_2CH_2O)$ compounds are characterized by two new intense absorption bands at 565 and 455 cm^{-1} [besides $\nu(SnS)$, (see Table II)] which are likely to originate from Sn–O bonds and are missing in the other products. By a careful inspection of infrared data insofar reported for compounds with Sn–O bonds [8, 9], it appears that these two bands of $R_2Sn(SCH_2CH_2O)$ correspond to absorptions detected for $Bu^n_2Sn(OR)_2$, which have been attributed to $\nu_{as}(SnC_2) + \nu_{as}(SnO_2)$ (R = Me: 616 w, 603 sh; R = Pr^n: 603 mw, 581 sh) and to $\nu_{sy}(SnO_2)$ modes (471 mw; 485 w) [16]. Compounds $Alk_2Sn(OAlk)_2$ are dimeric in the liquid and polymeric in the solid state, due to bridging three-coordinated oxygen atoms [5]; the latter could occur also for the oxygen of our $R_2Sn(SCH_2CH_2O)$ compounds, in view of the analogy of vibrational absorptions attributable to Sn–O modes.

The Mössbauer parameter isomer shift of $Me_2Sn(SCH_2CH_2O)$ (Table III) is in the range typical of dialkyltin(IV) derivatives [10]; the magnitude of the nuclear quadrupole splitting, ΔE_{exp} (Table III), is consistent with that of five-coordinated dialkyltin(IV) complexes where a ligand atom is consistently less electronegative than the other two (*e.g.*, Et_2SnI-oxinate and Me_2Sn–SNO complexes [10, 17]). More precise and detailed structural information is obtained from Mössbauer spectroscopy by the rationalization of ΔE_{exp} according to the point-charge model formalism [10, 12] and by the determination of lattice dynamics parameters [13, 14], and these studies are commented in the following.

Point-charge model calculations of ΔE have been carried out for structures (I)–(III), Fig. 1, which reflect the possible (ideal) configurations of tin environments in $R_2Sn(SCH_2CH_2O)$ discussed above. Equatorial methyl radicals have been assumed in (II) and (III), in line with the numerous structural reports on R_2SnX_3 compounds. Six-coordination of tin has been not considered, since it would imply the occurrence of bridging, three coordinated sulfur (which

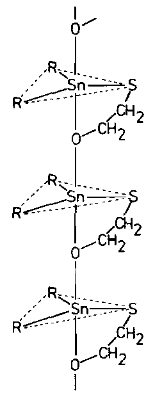

Fig. 2. The proposed structure of $R_2Sn(SCH_2CH_2O)$ in the solid state. The chain would be bent at oxygen atoms, while the environment of tin would be sensibly distorted owing to the formation of a five-membered ring upon chelation.

certainly does not occur, for example, in dialkyltin(IV) dithiolates [11]). Partial quadrupole splittings, p.q.s., employed in the calculations have been taken from the literature or estimated in this work [footnote (e) of Table III]. The latter have been obtained by published procedures [10, 12] as follows. The p.q.s. $([\text{O-Alk}]-[\text{hal}])^{tet}$ has been estimated from ΔE_{av} = 2.20 mm s^{-1} of Bu_3^nSnOR (R = Et, Pr^n, Bu^t), which seem to be monomeric, tetrahedral type, species [5]. The value for $\{\text{S-Alk}\}^{tba}$ (in fact, $\{\text{S-aryl}\}^{tba}$) has been extracted from ΔE's of R_2Sn^{IV}- and $RClSn^{IV}$–SNO complexes (R = Alk, Ph) [17, 18]; the related procedures are to be published. The p.q.s.'s $\{\text{O-Alk}\}^{tba}$ and $\{\text{O-Alk}\}^{tbe}$ concern bridging, three coordinated oxygen; the tba value has been calculated from ΔE_{av} = 2.86 mm s^{-1} of Alk_3SnOMe (Alk = Et, Pr^n, Bu^n), which are trigonal bipyramidal polymers with axially bridging OMe groups [5]. P.q.s.'s $\{L\}^{tbe}$ have been evaluated from $\{L\}^{tba}$ according to literature [12]. It is worth observing that our $\{\text{O-Alk}\}^{tba}$ value is identical to tabulated $\{OH\}^{tba}$, the latter being extracted from ΔE of Me_3SnOH [12], a trigonal bipyramidal polymer with OH bridges [19a].

It clearly appears from Table III that ΔE_{exp} of $Me_2Sn(SCH_2CH_2O)$ agrees well with ΔE_{calcd} for structure (III), while differs from ΔE_{calcd} for (I) and (II) more than the limiting value 0.4 mm s^{-1} [20]. Then, the actual configuration of the environment of tin in our solid compound would be of type (III) (obviously distorted), in consonance with the five-coordination detected for $Alk_2Sn(SCH_2CH_2O)$ (Alk = Bu^n, Oct^n) [5], but with the difference that the sulfur atom is equatorial.

The lattice dynamics parameters give an estimate of the extent of intermolecular coupling then allowing to state whether the compound under study is monomeric or polymeric [13, 14]. In the case of $Me_2Sn(SCH_2CH_2O)$, the magnitudes of dlnA/dT, of $\langle x^2 \rangle$ (T) data points, of θ_D and $M\theta_D^2$ [see Table III and footnotes (f)–(i)] are all in agreement with values and trends detected for a number of monodimensional polymers [13, 14, 21, 22].

In conclusion, a polymeric structure of the type reported in Fig. 2 is strongly suggested to occur for $Me_2Sn(SCH_2CH_2O)$ by vibrational spectroscopy, point-charge model treatment of ΔE and lattice dynamics parameters. The same could be assumed also for the homologous Ph_2Sn^{IV} derivative. It is interesting to point out that this structure practically corresponds to those of trigonal bipyramidal polymers R_3SnOR' [5, 23] and R_3SnOH [19]: the oxygen atoms bridge organotin (IV) moieties in all compounds, while in $Me_2Sn(SCH_2CH_2O)$ the less electronegative sulfur donor atom takes the place of an equatorial carbon of the R_3Sn^{IV} derivatives. An analogous situation has been assumed in R_2Sn^{IV}-penicillaminates, where bridging is realized through axially coordinated carboxyl (monodentate) and amino groups, while the ω-sulfur atom occupies an equatorial position upon coordination [24].

Experimental and Treatment of Data

Vibrational spectra were recorded with a Perkin-Elmer 457 Grating IR spectrophotometer and with a Coderg Laser-Raman-spectrometer PHO. ^1H NMR spectra were obtained with a Perkin Elmer R 32 (90 MHz, solvent $CDCl_3$). The Mössbauer spectra have been determined by the apparatus and techniques previously described [13, 14], using a Ca $^{119}SnO_3$ source (10mCi; R.C., Amersham) at room temperature, with constant acceleration and triangular waveform; a set-up cryostat-temperature controller-insert from A.E.R.E. Harwell (MVTIN 200, CTC 200) has been used. Suitable computer programs have been employed in fitting experimental spectra with Lorentzian lineshapes, in point-charge model calculations of ΔE and in the estimates of lattice dynamics parameters.

The organotin educts have been prepared and purified by usual methods. Mercaptoalkanols and 4-mercaptophenol have been obtained from Fluka, and have been purified by distillation or recrystallization.

The compounds listed in Table I have been prepared according to the following procedures:

Procedure I

A solution of $5 \cdot 10^{-3}$ mol of the mercapto-compound in 15 ml $CHCl_3$ was added to a suspension of $5 \cdot 10^{-3}$ mol Ph_3SnOH in 25 ml $CHCl_3$, and then it was stirred at room temperature (under mild refluxing during the reaction of 4-mercaptophenol) until the solution was clear or nearly clear. After drying with Na_2SO_4, petroleum ether was added and the mixture was put into a refrigerator for crystallization overnight. In the case of the reactions with mercaptoethanol and 4-mercaptophenol colourless crystals formed, which, after filtration, have been washed with petroleum ether ($Ph_3SnSC_6H_4OH$ with petroleum ether and diethyl ether, M.p. 119 °C) and dried *in vacuo*. In the case of 3-mercaptopropanol-1,2 a colourless highly viscous oil was separated, which has been washed several times with petroleum ether and diethyl ether (1:1) and then dried *in vacuo* at 10 °C.

Procedure II

$5 \cdot 10^{-3}$ mol diorganostannoxane (freshly prepared!) or Me_3SnOH and 10^{-2} mol (in the case of reactions with Me_3SnOH:$5 \cdot 10^{-3}$ mol) mercapto-compound in 25 ml $CHCl_3$ have been reacted at room temperature or (in the case of stannoxanes and mercaptoalkanols) under slight warming until the solution was clear. If necessary small amounts undissolved are filtered off. Water formed during the reaction was removed with Na_2SO_4, and then the dry solution was brought to a volume of about 10 ml in a rotary evaporator at 10 °C. Petroleum ether was added in small portions to the solution and put into the freezer of a refrigerator overnight. The products were isolated according to procedure I.

Procedure III

Freshly (!) prepared R_2SnO (R = Me, Ph) was reacted with mercaptoethanol in a molar ratio 1:2 according to procedure II. The oil, which had separated from the dried solution after addition of petroleum ether, solidified whilst standing for several days at 30–50 °C. The crystals were filtered, washed with $CHCl_3$ and methanol, and dried *in vacuo*.

Acknowledgement

We thank Deutsche Forschungsgemeinschaft and Consiglio Nazionale delle Ricerche for financial assistance.

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