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A ^{119}Sn NMR AND MÖSSBAUER STUDY OF SOME DI- AND TRI-ALKYLTIN(IV) ALKOXIDES*

PETER J. SMITH and R. F. M. WHITE
Chemistry Department, City of London Polytechnic, Sir John Cass School of Science and Technology, Jewry Street, London, EC3N 2EY (Great Britain)
LES SMITH
Christopher Ingold Laboratories, University College, 20, Gordon Street, London, WC1H 0AJ (Great Britain)

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SUMMARY

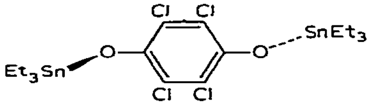
^{119}Sn chemical shifts and ^{119m}Sn Mössbauer parameters of a series of tributyltin alkoxides and cyclic and acyclic dibutyltin alkoxides have been recorded, in order to study the self-association of these molecules in the solid and in the liquid states.

The results show that the degree of association is markedly dependent upon the size and number of alkoxide groups attached to the tin atom. Dilution and temperature effects on the ^{119}Sn chemical shifts are also described.

INTRODUCTION

There is very little structural information available on the organotin(IV) alkoxides[1] due to their hydrolytic instability and the consequent difficulties involved in handling them.

The only X-ray structure determination on a compound of this type is that by Wheatley, who showed that, in the solid state, tetrachloro-1,4-bis(triethylstannoxy)-benzene (I) consists of discrete molecules with *trans*-triethylstannoxy groups and near-tetrahedral tin-atom geometries[2].



(I)

On the other hand, molecular weight and IR spectral studies on cyclic[3] and acyclic[4] dialkyltin alkoxides showed that, in certain cases, these are associated into dimers in the pure liquids and in solution. Similar results were found for the dialkyltin methoxide halides[5,6].

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* This term is also used to include phenoxides.

RESULTS AND DISCUSSION

Acyclic dialkyltin alkoxides, $R_2Sn(OR')_2$ and trialkyltin alkoxides, R_3SnOR'

The ^{119}Sn chemical shifts for a series of di- and tri-n-butyltin alkoxides, as the neat liquids at room temperature, are shown in Table 1. Since the first application of tin–119 NMR spectroscopy to structural organotin(IV) chemistry[9], it has been found that coordinative association usually results in a shift of the ^{119}Sn signal to high-field[10]. This is clearly illustrated in Table 1, where the ^{119}Sn chemical shifts of the dimeric dialkoxides are well upfield from those of the monomeric dialkoxides. Tributyltin methoxide[7] and tributyltin trimethylsiloxide[8] are known to be monomeric in benzene. The similarity of their chemical shifts (Table 1) to those found for the other monoalkoxides indicates that these are also unassociated.

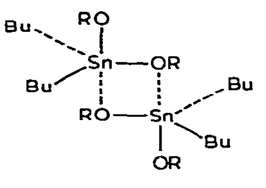
TABLE 1

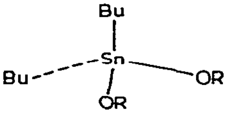
^{119}Sn CHEMICAL SHIFTS[a] OF DIBUTYLTIN AND TRIBUTYLTIN ALKOXIDES

R	$(C_4H_9)_2Sn(OR)_2$	$(C_4H_9)_3SnOR$
CH_3	$+165\pm2$[b,c]	-83 ± 7[d]
CH_2CH_3	$+161\pm2$	-86 ± 5
$CH_2CH_2CH_3$	$+159\pm5$[b]	-87 ± 2
$CH(CH_3)_2$	$+90\pm5$	-76 ± 2
$CH_2CH_2CH_2CH_3$	$+161\pm5$[b,c]	-91 ± 5
$CH_2CH(CH_3)_2$	$+150\pm2$	-82 ± 5
$CH(CH_3)(C_2H_5)$	$+34\pm2$	-80 ± 2
$C(CH_3)_3$	$+34\pm5$[e]	-60 ± 2
C_6H_5	$+138\pm2$[f] $+120\pm2$[g]	-105 ± 7
$Si(C_6H_5)_3$	$+36\pm2$[f,h] $+45\pm2$[g]	-89 ± 2
$Si(CH_3)_3$	[i]	-71 ± 2[d]

[a] ppm rel. to tetramethyltin. [b] IR spectrum indicates[4] dimer. [c] Molecular weight approaches dimer with increasing concentration in C_6H_6[3,7]. [d] Monomeric in C_6H_6[7,8] (cryoscopy). [e] IR spectrum indicates monomer[4]. [f] Sat. soln. in CCl_4 or C_6H_6. [g] Neat liq. at m.p. [h] Monomeric in C_6H_6 (vapour pressure osmometry). [i] Unstable compound; decomposes to distannoxane, $[Bu_2Sn(OSiMe_3)]_2O$.

It has been suggested on the basis of molecular weight and IR measurements, however, that dibutyltin dimethoxide[3,4], dipropoxide[4] and dibutoxide[4] are associated into dimers in the pure liquid state [(IIa), R = Me, n-Pr and n-Bu], whilst the di-tert-butoxide is monomeric[4] [(IIb), R = t-Bu]. The ^{119}Sn chemical shifts are clearly able to differentiate between these two situations: the former three dialkoxides, together with dibutyltin diethoxide, show the highest field shifts (+159 to +165 ppm), whilst


(IIa)


(IIb)

dibutyltin di-tert-butoxide and di-sec-butoxide (in which the bulky R groups prevent association) show the lowest field shifts (+34 ppm). The compound dibutyltin bis-(triphenylsiloxide),$Bu_2Sn(OSiPh_3)_2$, which we have found to be monomeric in benzene (0.004 *M* and 0.007 *M*), shows a similar low-field signal. The intermediate chemical shift values found for dibutyltin di-isopropoxide and di-isobutoxide thus indicate that they are incompletely associated in the pure liquids.

Replacement of the two oxygen atoms in these dialkoxides by sulphur, a poorer bridging atom, would also be expected to discourage intermolecular association. In line with this, we find that dibutyltin dithioethoxide, $Bu_2Sn(SEt)_2$, shows a low-field chemical shift (-123 ± 2 ppm) in boiling benzene, in which it is known to be monomeric[11]. The same chemical shift is shown by a neat liquid sample at room temperature.

The degree of dissociation (α) of the dialkoxides, as measured by their ^{119}Sn chemical shifts, would be expected to increase with increasing dilution and/or temperature. That this is indeed the case can be seen by inspection of Fig. 1. The most dramatic change is observed with dibutyltin di-isopropoxide, where dilution of the sample to ca. 20 mole% with carbon tetrachloride or an increase in temperature of the pure liquid to 60° causes the chemical shift to fall by 60 ppm, from +90 ppm to the monomer value; dibutyltin di-isobutoxide, which is also incompletely associated, shows a pronounced downfield shift at higher dilutions. The fully associated molecules, dibutyltin dimethoxide, diethoxide and dipropoxide, and the fully dissociated molecule dibutyltin di-tert-butoxide, were found to show little or no decrease in chemical shift within the range studied (down to ca. 15 mole%; at higher dilutions accurate measurement of the shift was not possible).

We have estimated ΔH values for the reaction dimer $\rightleftharpoons$ monomer for two alkoxides, dibutyltin di-isopropoxide and dibutyltin di-n-butoxide, which were found

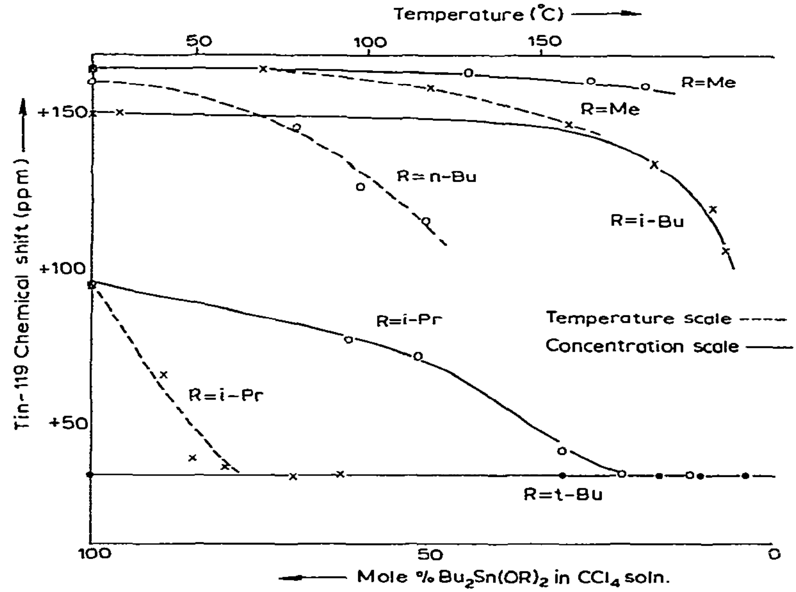


Fig. 1. Effect of dilution and temperature on ^{119}Sn chemical shifts of $Bu_2Sn(OR)_2$ compounds.

to show appreciable variations in chemical shift with temperature (the effective temperature range was sometimes limited by thermal decomposition of the sample).

The degree of dissociation may be written in terms of the observed chemical shifts, δ^*_{obs}, and that of the dimer, δ^*_{D}

$$\alpha = 1 - \frac{\delta^*_{\text{obs}}}{\delta^*_{\text{D}}}$$

where δ^*_{obs} and δ^*_{D} are expressed relative to the monomer. The equilibrium constant, K, for the dimer $\rightleftarrows$ 2 (monomer) reaction [see (II)] is given by

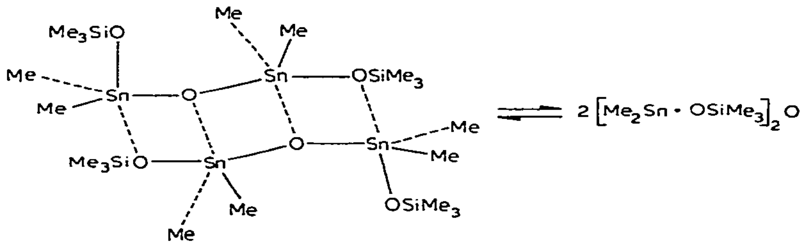
$$K = \frac{4\,\alpha^2 \cdot n}{(1-\alpha)v} \text{ mol} \cdot \text{l}^{-1}$$

where n=number of moles of dimer

Using the Van t'Hoff equation $\mathrm{d}/\mathrm{d}T \ln K = \Delta H/R \cdot T^2$, ΔH values could be obtained from the equilibrium constants determined at various temperatures. This treatment gave

$$\Delta H\,[(\text{II}), \text{R}=\text{i-Pr}] = 24 \pm 4 \text{ kcal} \cdot \text{mol}^{-1}$$
$$\Delta H\,[(\text{II}), \text{R}=\text{n-Bu}] = 14 \pm 3 \text{ kcal} \cdot \text{mol}^{-1}$$

These values compare with the lower ΔH of 9±1 kcal·mol^{-1} found[12] for the dedimerisation of tetramethyl-1,3-bis(trimethylsiloxy)distannoxane (III). The intermolecular Sn–O coordinate linkages in this distannoxane are known by X-ray crystallography[13] to be considerably longer (2.8 Å) than the intramolecular Sn–O bonds (2.3 Å), indicating that the intermolecular bonds may indeed be rather weak.



(III)

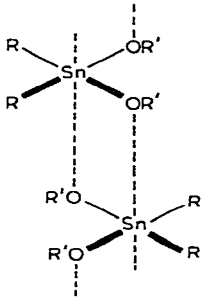
TABLE 2

MÖSSBAUER PARAMETERS OF $R_2Sn(OR')_2$ COMPOUNDS

$R_2Sn(OR')_2$	δ^a (mm·sec^{-1})	ΔE_q (mm·sec^{-1})
$Me_2Sn(OMe)_2$	0.99	2.31[b]
$Et_2Sn(OMe)_2$	1.08	2.38[c]
$Bu_2Sn(OMe)_2$	1.10	2.32
$Bu_2Sn(OEt)_2$	1.30	2.00[d]

[a] Relative to SnO_2 at 77°K. [b] Ref. 14. [c] Ref. 15. [d] Ref. 16.

In order to gain an insight into the structure of these organotin alkoxides in the solid state, their ^{119m}Sn Mössbauer spectra will now be discussed. Table 2 shows Mössbauer parameters which have been reported in the literature for three dialkyltin dimethoxides and for dibutyltin diethoxide. The quadrupole splitting values are all low ($\Delta E_q < 2.4$ mm·sec^{-1}) but are unlikely to be indicative of unassociated tetrahedral R_2SnX_2 species [*cf.* $Bu_2Sn(OSiPh_3)_2$, $\Delta E_q = 2.40$ mm·sec^{-1}] in view of the preceding discussion. However, a dimeric structure in the solid, where the tin atoms are pentacoordinate and occupying a trigonal bipyramidal *cis*-R_2SnX_3 geometry (IIa) is also unlikely, since appreciably larger splittings (2.8–3.3 mm·sec^{-1}) are usually found[17] in this case. A polymeric structure in which the tin atoms are now six-coordinate and occupying an octahedral *cis*-R_2SnX_4 configuration (IV) in the solid state is consistent with the observed low ΔE_q values.



(IV)

Mössbauer data for nine trialkyltin alkoxides are shown in Table 3. Although the observed low-field ^{119}Sn chemical shifts are indicative of unassociated species in the pure liquids, the trialkyltin methoxides and phenoxides show markedly higher quadrupole splitting values ($\Delta E_q = 2.85$–3.09 mm·sec^{-1}) than would be expected if they were tetrahedral R_3SnX monomers in the solid state, as in tetrachloro-1,4-bis(triethylstannoxy)benzene[2].

Within experimental error, the Mössbauer parameters for tributyltin hydroxide, Bu_3SnOH ($\delta = 1.37$, $\Delta E_q = 2.99$ mm·sec^{-1})[20] and tributyltin methoxide (Table

TABLE 3

MÖSSBAUER PARAMETERS FOR R_3SnOR' COMPOUNDS

R_3SnOR'	*δ (mm·sec^{-1})*	*ΔE_q (mm·sec^{-1})*
Et_3SnOMe	1.41	2.86[a]
Et_3SnOPh	1.49	3.09[b]
Pr_3SnOMe	1.40	2.81[c]
Bu_3SnOMe	1.38	2.92
Bu_3SnOEt	1.29	2.11
Bu_3SnO-n-Pr	1.36	2.57
Bu_3SnO-t-Bu	1.29	1.91
$Bu_3SnOCPh_3$	1.32	1.92
Bu_3SnOPh	1.42	2.85

[a] Ref. 18. [b] Ref. 19. [c] Ref. 15.

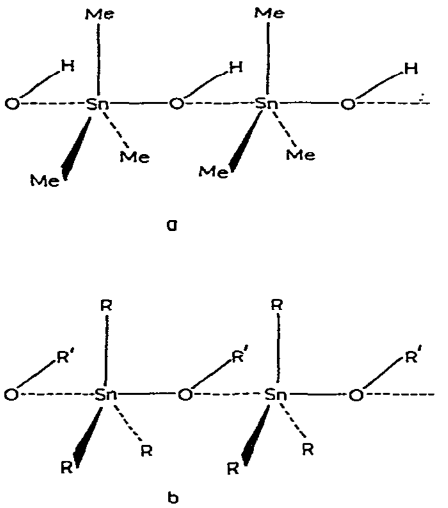


Fig. 2. (a) Structure of Me_3SnOH; (b) proposed structure for R_3SnOMe and R_3SnOPh compounds.

3) are identical; the tri-n-alkyltin hydroxides are self-associated in the solid state into linear chain polymers containing pentacoordinate trigonal bipyramidal R_3SnX_2 tin atoms[20,21]. Fig. 2a shows the structure[21] of trimethyltin hydroxide ($\Delta E_q = 2.89$ mm·sec^{-1}) The similarity of the ΔE_q values of the trialkyltin hydroxides to those of the trialkyltin methoxides and phenoxides suggests that the latter are similarly associated in the solid state at 77°K (Fig. 2b, R' = Me, Ph or H). The compact methyl and planar phenyl groups, like hydrogen, are easily able to occupy the spaces between planar R_3Sn moieties, whereas larger organic substituents, R', disrupt this O–Sn coordination.

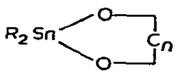
Relative basicities of the oxygen atoms in tributyltin methoxide and phenoxide have been estimated by IR measurements in methanol and pyrrole solutions[22], and IR studies on the trialkyl*lead* methoxides suggest that these are also linear polymers in the solid state[23].

An attempt to observe whether the ^{119}Sn chemical shift of tributyltin methoxide (pure liquid) moves upfield with decrease in temperature, corresponding to intermolecular association, was unsuccessful due to a very rapid increase in viscosity of the sample on cooling.

Similar studies on the simple organotin trialkoxides, $BuSn(OR)_3$, are now in progress and will be reported at a later date.

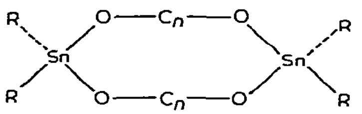
Cyclic dialkyltin alkoxides

These cyclic diorganotin alkoxides, which may be formally represented as

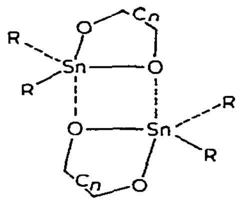


are known from molecular weight studies[3,24,25] to self-associate in many organic solvents at room temperature. These measurements have, in general, indicated dimeric species in dilute solutions (when $n=1$–3), although there is also some evidence for higher molecular weight oligomers.

Two structures have been suggested[3,25] for the dimer in solution: the large ring (Va) in which the tin atoms are four coordinate and tetrahedral, or the oxygen-bridged dimer (Vb), in which the two tin atoms are occupying a trigonal bipyramidal *cis*-R_2SnX_3 geometry. An associated structure (Vb), which is very similar to that proposed for the acyclic dimeric dialkoxides in the pure liquids (IIa), would be expected to show a ^{119}Sn chemical shift to high field (ca. +160 ppm), whereas a lower field shift (ca. +30 ppm) should result from the four-coordinate species (Va).

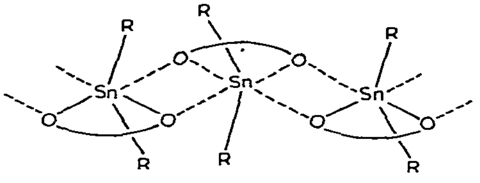


(Va)



(Vb)

Table 4 shows tin–119 NMR results for a series of cyclic dibutyltin alkoxides derived from 1,2-, 1,3- and 1,4-diols, and also for two cyclic derivatives of 2-mercaptoethanol. The chemical shifts of the cyclic dialkoxides are all situated well upfield from tetramethyltin (+154 to +228 ppm). An associated structure such as the dimer (Vb), or a polymeric species (VI), is thus present in solution. The three alkoxides derived from 1,3-diols show the highest field shifts (+213 to +233 ppm) and may exist as oligomeric species in solution, such as (VI), containing six-coordinate tin atoms, whereas the other alkoxides are pentacoordinate dimers (Vb), *cf.* $Bu_2Sn(OCOMe)_2$, which probably has a similar distorted *trans*-octahedral structure, (VI), in the pure liquid, with two bidentate carboxylate groups, and shows[26] $\delta(^{119}Sn)=+195$ ppm.



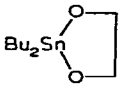
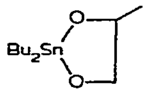
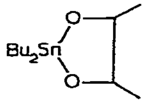
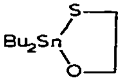
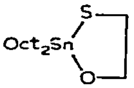
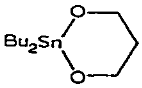
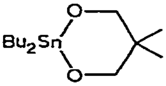
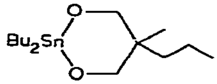
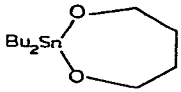
(VI)

In addition, the degree of association (as measured by the ^{119}Sn chemical shift) is found to show little variation in going from a saturated solution to a molten sample, or on progressive dilutions within the range where measurements are possible.

The chemical shifts of the two cyclic dialkyltin thioglycoxides—molecular weight measurements show that compounds of this class also dimerise in organic solvents[27,28]—are still situated upfield from tetramethyltin. This is presumably due to replacement of the non-bridging axial oxygen atoms by sulphur in structure (Vb), leaving the Sn–O ring and the pentacoordinate dimer intact.

TABLE 4

^{119}Sn CHEMICAL SHIFTS OF CYCLIC DIALKYLTIN ALKOXIDES

Tin alkoxide	$\delta(^{119}Sn)^a$
	$+189\pm5^b$
	$+164\pm5^b$
	$+155\pm5^b$
	$+32\pm2^b$ $+24\pm5^c$
	30 ± 5^b
	$+228\pm10^b$ $+288\pm2^d$
	$+213\pm5^{e,f}$
	$+233\pm5^{f,g}$
	$+161\pm2^h$ $+154\pm5^g$

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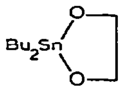
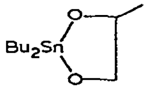
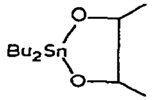
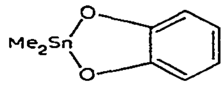
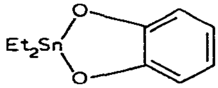
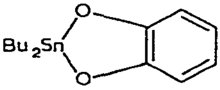
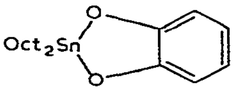
[a] Relative to tetramethyltin. [b] Sat.soln. in $CDCl_3$. [c] Neat liq. at 128°. [d] Neat liq. at 96°. [e] Neat liq. at 120°. [f] Small amount of diol impurity present in sample. [g] Sat.soln. in CCl_4. [h] Neat liq. at 25°.

Solid state (Mössbauer) data for the three cyclic dibutyltin 1,2-glycoxides and for four dialkyltin catechoxides (the latter compounds being too insoluble for NMR measurements) are shown in Table 5. The quadrupole splitting values of the three dibutyltin 1,2-glycoxides ($\Delta E_q = 2.72$–2.85 mm·sec^{-1}), which are larger than those found for the acyclic dialkoxides, lie within the range found for trigonal bipyramidal *cis*-R_2SnX_3 compounds[17] and are thus consistent with the pentacoordinate dimer (Vb) in the solid state.

TABLE 5

MÖSSBAUER PARAMETERS FOR CYCLIC DIALKYLTIN ALKOXIDES

Tin alkoxide	δ (*mm·sec*$^{-1}$)	ΔE_q (*mm·sec*$^{-1}$)
	1.10	2.80
	1.13	2.72
	1.25	2.85
	1.32 1.14	3.35 3.24[a]
	1.50	3.60
	1.52 1.29	3.62 3.40[a]
	1.36	3.41

[a] Ref. 29.

The four dialkyltin catechoxides show the largest splittings so far observed for any organotin alkoxide ($\Delta E_q = 3.35$–3.60 mm·sec^{-1}) and their high melting points and insolubilities suggest a polymeric structure. The linear polymer (VI), in which the tin atoms are six-coordinate and occupying a distorted *trans*-octahedral R_2SnX_4 geometry, would account for the large splittings (similar ΔE_q values have been found for other organotin compounds with this distorted octahedral configuration[30]).

CONCLUSIONS

From these studies the main results may now be summarised for the alkoxides, $R_nSn(OR')_{4-n}$, where $n=2$ and 3. The degree of association increases with (a) decreasing n, and (b) decreasing bulkiness of the group R′ for a fixed R and n. In addition, the monoalkoxides with small R′ groups only appear to associate at 77°K, whereas both the cyclic and acyclic dialkoxides associate into dimers or oligomers in the solid and in solution.

EXPERIMENTAL

Tin–119 chemical shifts were obtained by the heteronuclear double magnetic resonance technique[31]. Proton spectra were recorded in the field sweep mode throughout. The spectrometer used was a JEOL C–60–H instrument operating at a proton frequency of 60 MHz containing an extra coil within the probe. The ^{119}Sn frequency (22.37 MHz) was provided by a Schlumberger frequency synthesiser Model FS 30.

Mössbauer spectra were recorded with both $^{119m}SnO_2$ source and absorber cooled to 77°K, using a constant velocity cam-driven spectrometer. The values of δ and ΔE_q are considered accurate to ± 0.08 mm·sec^{-1}.

Molecular weights were determined by vapour pressure osmometry, using a Hitachi–Perkin–Elmer Model 115 apparatus. The solvent, benzene, was dried over molecular sieves.

Tributyltin alkoxides

Tributyltin methoxide, ethoxide, n-propoxide, phenoxide and triphenylmethoxide were prepared[32] by reacting bis(tributyltin)oxide with the appropriate dialkyl carbonate or the alcohol, the boiling points being in good agreement with reported values[32].

Tributyltin isopropoxide, n-butoxide[33] and t-butoxide[34] were synthesised from tributyltin chloride and the sodium alkoxide; tributyltin triphenylsiloxide (b.p. 190°/0.2 mmHg; lit.[35] 228–236°/4 mmHg) was prepared by transalkoxylation of tributyltin isopropoxide with triphenylsilanol in dry benzene, and tributyltin trimethylsiloxide[8] by reacting tributyltin chloride with lithium trimethylsiloxide[36] in dry ether.

Tributyltin isobutoxide and sec-butoxide were unexpectedly obtained when the products from the reaction of dibutyltin dichloride with the sodium alkoxides were distilled *in vacuo*. Similar thermal disproportionation of some dialkyltin dialkoxides under reduced pressure (in the presence of dibutyltin oxide) has been observed previously[37]. Other boiling points and analytical data are shown in Table 6.

TABLE 6

ANALYTICAL DATA FOR Bu_3SnOR COMPOUNDS

R	*Analysis found (calcd.) (%)*		*B.p. (°C/mmHg)*
	C	*H*	
i-Pr	51.90	9.76	84–86/0.1
	(51.57)	(9.73)	
n-Bu	53.30	10.16	118–120/0.9
	(52.89)	(9.92)	(137–138/1.4)[a]
i-Bu	53.10	9.73	122–126/0.9
	(52.89)	(9.92)	(110/0.1)[b]
s-Bu	52.80	9.80	116–118/0.9
	(52.89)	(9.92)	(102/0.35)[c]
t-Bu	53.47	10.07	90/0.3
	(52.89)	(9.92)	(96–97/1.2)[d]

[a] Ref. 33.. [b] Ref. 32. [c] Ref. 38. [d] Ref. 34.

Dibutyltin dialkoxides

Dibutyltin dimethoxide[39], diethoxide[40], di-n-propoxide[40], di-isopropoxide[41], di-n-butoxide[40] and di-tert-butoxide[42] were all prepared from dibutyltin dichloride and the sodium alkoxide; boiling points were in good agreement with literature values[39–42].

Dibutyltin diphenoxide[43] was obtained by transalkoxylation of dibutyltin dimethoxide with phenol in benzene, and dibutyltin bis(triphenylsiloxide) by co-dehydrating dibutyltin oxide and triphenylsilanol in benzene (m.p. 70°; lit.[44] 71°).

Dibutyltin di-isobutoxide, b.p. 100–104°/0.2 mmHg, was prepared by alcoholysis in benzene at room temperature of a sample of dibutyltin bis(diethylamide)*. (Found: C, 50.50; H, 9.65. $C_{16}H_{36}SnO_2$ calcd.: C, 50.66; H, 9.49%.)

Dibutyltin di-sec-butoxide*, b.p. 92–94°/0.07 mmHg, was prepared by the same method. (Found: C, 50.40; H, 9.70. $C_{16}H_{36}SnO_2$ calcd.: C, 50.66; H, 9.49%.) Attempts to prepare the latter two compounds from dibutyltin dichloride and the sodium alkoxides led only to the recovery of the monoalkoxides, as mentioned earlier.

Cyclic alkoxides

The dibutyltin alkoxides derived from ethylene glycol (m.p. 225–228°; lit.[25] 223–226.5°), 1,2-propanediol (m.p. 185–188°; lit.[3] 185°) and 2,3-butanediol (m.p. 121–124°; lit.[3] 120°) were prepared by refluxing equimolar amounts of dibutyltin oxide and diol in benzene (1 h) using a Dean and Stark separator, and were recrystallised from the same solvent.

The catechoxides of dimethyltin (m.p. >360°, subl. 290°/0.1 mmHg; lit.[45] >360°), diethyltin (m.p. >330°, subl. 210°/0.1 mmHg), dibutyltin (m.p. 269–271°, subl. 210°/0.2 mmHg; lit.[45] 272°) and dioctyltin (m.p. 162–164°) were prepared similarly in toluene and purified by vacuum sublimation, or, in the case of the dioctyltin compound, by recrystallisation from toluene. ($Et_2\overline{SnOC_6H_4O}$-2, found: C, 42.47; H, 5.02. $C_{10}H_{14}SnO_2$ calcd.: C, 42.10; H, 4.91%.) ($Oct_2\overline{SnOC_6H_4O}$-2, found: C, 58.05; H, 8.25. $C_{22}H_{38}SnO_2$ calcd.: C, 58.28; H, 8.39%.)

The dibutyltin alkoxides derived from 1,3-propanediol (b.p. 182–186°/0.3 mmHg; lit.[24] 184–185°/0.3 mmHg), 2,2-dimethyl-1,3-propanediol (b.p. 188–190°/0.3 mmHg), 2-methyl-2-n-propyl-1,3-propanediol (b.p. 200°/0.03 mmHg) and 1,4-butanediol (b.p. 162–164°/0.2 mmHg; lit.[24] 175–178°/0.4 mmHg) were prepared by refluxing equimolar quantities of dibutyltin diethoxide and diol in dry benzene[24] (15 min). Satisfactory analyses for the two new substituted 1,3-propanediol derivatives could not be obtained owing to their contamination by hydrolysis products.

Thio-alkoxides

Dibutyltin dithioethoxide (b.p. 150–152°/0.5 mmHg; lit.[11] 97–100°/0.4 mmHg) was prepared by co-dehydrating dibutyltin oxide and ethanethiol in benzene[11].

Dibutyltin 2-thioglycoxide (m.p. 89–90°; lit.[46] 89–90°) and dioctyltin 2-thioglycoxide (m.p. 73–75°) were prepared by Wada's method[28]. ($Oct_2\overline{SnOCH_2CH_2S}$, found: C, 51.40; H, 9.02; S, 7.60. $C_{18}H_{38}SSnO$ calcd.: C, 51.31; H, 9.03; S, 7.43%.)

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