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Steric effects on the formation of isolable products in the reactions of dibutyltin oxides with carboxylic acids

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Abstract

Reaction of dibutyltin oxides, $^{x}Bu_2SnO$ [x = n (normal), i (iso), s (secondary) and t (tertiary)] with carboxylic acids [RCOOH; R = CH_3 (Me), CH_3CH_2 (Et), $(CH_3)_2CH$ (^{i}Pr) and $(CH_3)_3C$ (^{t}Bu)] in 1:1 and 1:2 stoichiometry were investigated. The products formed in these reactions were characterized by elemental analyses, IR and NMR (^{1}H, ^{13}C and ^{119}Sn) data. Reactions in 1:2 stoichiometry afforded dibutyltin dicarboxylates which have six-coordinate tin atom. Steric effects of the butyl group and the R group of the carboxylate ligand play an important role in 1:1 reactions. Dicarboxylatotetraorganostannoxanes were formed with $^{n}Bu_2SnO$ while hydroxo complexes, $[^{t}Bu_2Sn(\mu\text{-}OH)(OOCR)]_2$ were the sole products with $^{t}Bu_2SnO$. The stereochemistry of all these complexes is discussed on the basis of NMR data.

Introduction

Organotin carboxylates find a wide range of applications in industry as homogeneous catalysts for polyurethane and RTV silicon polymerization, for transesterification reactions and as agrochemicals [1–6]. The diorganotin(IV) compounds can be readily obtained by the reactions of the corresponding oxide with protic ligands. Hydrolysis of these compounds proceeds in a stepwise manner and three different types of products are identified [2]. The formation of isolable hydrolysis products depends on the reaction conditions, the nature of the ligand, the steric and electronic properties of the R group on tin. Tetraorganodistannoxanes of the types **IV** and **V** (Scheme 1) have been studied quite extensively in recent years. The X-ray structural analyses of several such molecules revealed the predominance of "ladder" or "staircase" structures based on a planar four-membered Sn_2O_2 ring. Tetraorganodistannoxanes are the partial hydrolysis products of R_2SnX_2 and are believed to form via an intermediate of the type **III**. In order to rationalize the steric demand of the R groups both on tin and on the ligand moiety on the formation of isolable products, we have carried out reactions of dibutyltin oxides,

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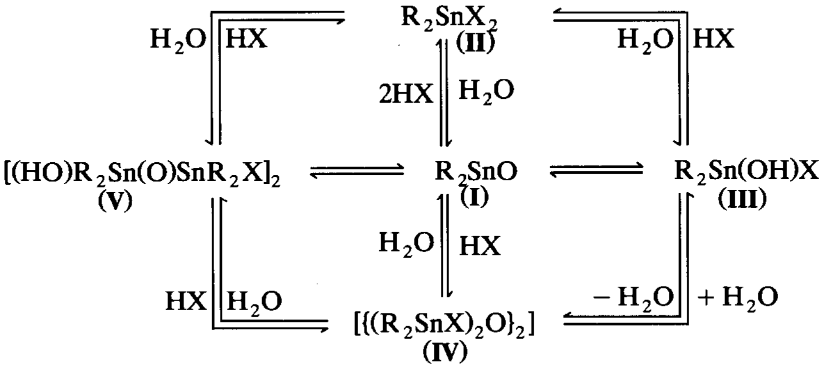


Scheme 1.

${}^{x}Bu_2SnO$ (x = n, i, s, t) with carboxylic acids [RCOOH, R = CH_3, CH_3CH_2, $(CH_3)_2CH$, $(CH_3)_3C$] in 1:1 and 1:2 stoichiometry. The results of this work are reported here.

Results and discussion

Dibutyltin(IV) dicarboxylates, [${}^{x}Bu_2Sn(OOCR)_2$]

Reactions of dibutyltin oxides with carboxylic acids in 1:2 stoichiometry in refluxing benzene readily gave dibutyltin dicarboxylates. They are colourless liquids or crystalline solids and are volatile under reduced pressure. Characterization data for these complexes are given in Tables 1 and 2. A few such complexes have been reported earlier [7–9]. The IR spectra of these complexes displayed a medium to strong intensity band in the region 1580–1610 cm^{-1} suggesting the chelating nature of the carboxylate group [10].

The ${}^{1}H$ NMR spectra of free carboxylic acids exhibited a broad resonance at $\delta \sim 11$ ppm, attributable to the hydroxyl proton, which was absent in the spectra of these complexes indicating deprotonation of the carboxylic acids by a dibutyltin(IV) species. The ${}^{1}H$ NMR spectra showed the expected integration and peak multiplicities. The di-t-butyltin(IV) compounds displayed a singlet at $\delta \sim 1.3$ ppm for ${}^{t}Bu_2Sn$ protons with ${}^{3}J({}^{119}Sn-{}^{1}H) \sim 118$ Hz. The magnitude of ${}^{3}J({}^{119}Sn-{}^{1}H)$ for ${}^{t}Bu_2Sn^{IV}$ complexes is in the range reported for similar other di-t-butyltin derivatives [9–11] and is seemingly unaffected by the coordination number of tin.

The ${}^{13}C\{{}^{1}H\}$ NMR spectra displayed a single set of resonances for the carboxylate moiety and the butyl groups attached to tin. The butyltin C-1 carbon resonance deshielded with a progressive decrease in the ${}^{1}J({}^{119}Sn-{}^{13}C)$ coupling constant as the ramification of the butyl group increased in the following order: ${}^{n}Bu < {}^{i}Bu < {}^{s}Bu < {}^{t}Bu$. A small variation in the magnitude of ${}^{1}J({}^{119}Sn-{}^{13}C)$ has been observed with the changes in the steric demands of the R group on the carboxylate moiety. The C–Sn–C angle for ${}^{n}Bu_2Sn^{IV}$ compounds can be estimated as $\sim 134°$ using the equation ${}^{1}J({}^{119}Sn-{}^{13}C) = (9.99 \pm 0.73)\theta - (746 \pm 100)$ [12]. X-Ray analyses of a number of $R_2Sn(OOCR')_2$ have shown that the C–Sn–C angle varies between 130 and 152° with the carboxylate group acting in an anisobidentate fashion [13–19].

Table 1

Analysis, IR and ^{1}H NMR data for $[{}^{x}Bu_2Sn(OOCR)_2]$

Carboxylic acid/ complex [a]	Analysis Sn % Found (calc.)	ν(CO) (cm^{-1})	^{1}H NMR data	
			Bu–Sn protons	Ligand protons
MeCOOH	–	1709	–	2.02 (s, Me); 11.32 (s, OH)
EtCOOH	–	1720	–	1.14 (t, 7 Hz, Me); 2.37 (q, 7 Hz, CH_2–); 10.89 (s, br, OH)
$^{i}PrCOOH$	–	1720	–	1.15 (d, 7 Hz, Me); 2.50 (m, CH); 11.64 (s, OH)
$^{t}BuCOOH$	–	1715	–	1.24 (s, Me); 11.02 (s, OH)
$[{}^{n}Bu_2Sn(OOCMe)_2]$	33.8 (33.8)	1605	0.86 (t); 1.35 (br); 1.60 (br)	2.04 (s)
$[{}^{n}Bu_2Sn(OOCEt)_2]$	31.2 (31.3)	1605	0.86 (t); 1.33 (br); 1.61 (br)	1.12 (t, 7 Hz, Me); 2.34 (q, 7 Hz, CH_2–)
$[{}^{n}Bu_2Sn(OOC{}^{i}Pr)_2]$	29.1 (29.2)	1610	0.86 (t); 1.35 (br); 1.62 (br)	1.16 (d, 7 Hz, Me); 2.59 (m, CH)
$[{}^{n}Bu_2Sn(OOC{}^{t}Bu)_2]$	27.1 (27.3)	1595	0.60; 0.70; 1.30 (br)	0.95 (s, Me)
$[{}^{i}Bu_2Sn(OOCMe)_2]$	33.7 (33.8)	1580	0.90 (d, Me); 1.50 (d, CH_2); 2.00 (m, CH)	1.95 (s, Me)
$[{}^{i}Bu_2Sn(OOCEt)_2]$	31.1 (31.3)	1580	1.00 (d, Me); 1.65 (d, CH_2); 2.12 (m, CH)	1.18 (t, 7 Hz, Me); 2.38 (q, 7 Hz, CH_2)
$[{}^{i}Bu_2Sn(OOC{}^{i}Pr)_2]$	29.2 (29.2)	1600	1.00 (d, Me); 1.61 (d, CH_2); 2.10 (m, CH)	1.20 (d, 7 Hz, Me); 2.65 (m, CH)
$[{}^{i}Bu_2Sn(OOC{}^{t}Bu)_2]$	27.1 (27.3)	1595	0.90 (d, Me); 1.55 (d, CH_2); 2.05 (m, CH)	1.22 (s, Me)
$[{}^{s}Bu_2Sn(OOCMe)_2]$ [a]	34.4 (33.8)	1603	0.81 (t, 7 Hz, Me); 1.14 (d, 7 Hz, Me); $^{3}J(^{119}Sn-^{1}H)$ = 132 Hz); 1.50 (m, CH_2) CH merged in the base of methyl signal of OAc	1.86 (s, Me)
$[{}^{s}Bu_2Sn(OOCEt)_2]$	31.3 (31.3)	1603	0.85 (t, 7 Hz, Me); 1.18 (d, 7 Hz, Me) 1.54 (q, CH_2); 1.92 (m, CH)	0.99 (t, 7 Hz, Me); 2.22 (q, 7 Hz, CH_2)
$[{}^{s}Bu_2Sn(OOC{}^{i}Pr)_2]$	29.3 (29.2)	1600	0.81 (t, 7 Hz, Me); 1.15 (d, 7 Hz, Me); 1.50 (q, CH_2); 1.90 (m, CH)	1.00 (d, 7 Hz, Me); 2.90 (m, CH)
$[{}^{s}Bu_2Sn(OOC{}^{t}Bu)_2$	27.7 (27.3)	1600	0.82 (t, 7 Hz, Me); 1.14 (d, 7 Hz, Me); 1.40 (q, CH_2); 1.70 (m, CH)	1.04 (s, Me)
$[{}^{t}Bu_2Sn(OOCMe)_2]$ [b]	33.9 (33.8)	1610	1.32 (s, Me); $^{3}J(^{119}Sn-$ $^{1}H)$ = 118 Hz	2.05 (s, Me)
$[{}^{t}Bu_2Sn(OOCEt)_2]$	31.5 (31.3)	1610	1.31 (s, Me); $^{3}J(^{119}Sn-$ $^{1}H)$ = 119 Hz	1.13 (t, 7 Hz, Me); 2.35 (q, 7 Hz, CH_2)
$[{}^{t}Bu_2Sn(OOC{}^{i}Pr)_2]$	29.4 (29.2)	1607	1.30 (s, Me); $^{3}J(^{119}Sn-$ $^{1}H)$ = 119 Hz	1.16 (d, 7 Hz, Me); 2.61 (m, CH)
$[{}^{t}Bu_2Sn(OOC{}^{t}Bu)_2]$ [c]	27.2 (27.3)	1602	1.30 (s, Me); $^{3}J(^{119}Sn-$ $^{1}H)$ = 116 Hz	1.22 (s, Me)

[a] Distilled *in vacuo* 85–115°C/0.1–1.5 mmHg. [b] Sublimed *in vacuo* (1.5 mmHg), m.p. 85–88°C. [c] m.p. 53–54°C.

Table 2

^{13}C{^{1}H} and ^{119}Sn{^{1}H} NMR data for [$Bu_2Sn(OOCR)_2$] in $CDCl_3$

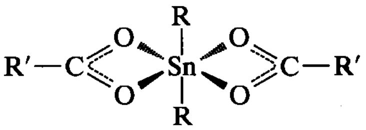
Carboxylic acid/ complex	δ ^{119}Sn (ppm)	δ ^{13}C{^{1}H} NMR data			
		Bu–Sn carbons [a]		Ligand carbons	
		C-1	C-2 to C-4	Carbonyl	alkyl group
MeCOOH	–	–	–	177.8	20.4
CH_3CH_2COOH	–	–	–	180.7	8.6 (CH_3); 27.3 (CH_2)
$Me_2CHCOOH$	–	–	–	183.8	18.5 (CH_3); 33.8 (CH)
Me_3C-COOH	–	–	–	185.5	26.7 (CH_3); 38.3 (–C)
[$^nBu_2Sn(OOCMe)_2$]	–149	24.6(584)	26.3 (34; C-2) 25.9 (95; C-3) 13.2 (C-4)	181.0	20.2 (CH_3)
[$^nBu_2Sn(OOCEt)_2$]	–149	24.4(590)	26.2 (C-2) 25.8 (C-3) 13.0 (C-4)	184.1	9.3 (CH_3); 27.0 (CH_2)
[$^nBu_2Sn(OOC^iPr)_2$]	–153	24.6(588)	26.4 (37; C-2) 26.0 (89; C-3) 13.3 (C-4)	187.3	19.2 (CH_3); 33.7 (CH)
[$^nBu_2Sn(OOC^tBu)_2$]	–161	24.4(606)	26.6 (C-2) 26.0 (C-3) 13.4 (C-4)	189.2	27.4 (CH_3); 38.5 (–C)
[$^iBu_2Sn(OOCMe)_2$] [b]	–150	35.8(574)	25.2 (77, C-2) 25.4 (30, C-3)	180.8	20.1 (CH_3)
[$^iBu_2Sn(OOCEt)_2$]	–149	35.9(575)	25.4 (76; C-2) 25.6 (31, C-3)	184.2	9.4 (CH_3); 27.3 (CH_2)
[$^iBu_2Sn(OOC^iPr)_2$]	–152	35.8(582)	25.3 (77; C-2) 25.6 (33; C-3)	186.9	19.0 (CH_3); 33.6 (CH)
[$^iBu_2Sn(OOC^tBu)_2$]	–158	35.8(590)	25.5 (C-2) 25.8 (C-3)	188.9	27.4 (CH_3); 38.4 (–C)
[$^sBu_2Sn(OOCMe)_2$]	–188	40.5(539)	26.7 (CH_2) 15.9 (CH_3) 13.5 (CH_3 of Et)	180.8	15.9 (CH_3) [c]
[$^sBu_2Sn(OOCEt)_2$]	–189	40.4(558)	26.8 (CH_2) 16.0 (CH_3) 13.6 (CH_3 of Et)	183.8	9.1 (CH_3); 26.8 (CH_2) [d]
[$^sBu_2Sn(OOC^iPr)_2$]	–192	40.7(555)	27.1 (CH_2) 16.3 (CH_3) 13.9 (CH_3 of Et)	186.8	18.9 (CH_3); 33.5 (CH)
[$^sBu_2Sn(OOC^tBu)_2$]	–199	40.8(580)	27.3 (CH_2) 16.6 (CH_3) 14.1 (CH_3 of Et)	188.9	27.3 (CH_3); 38.3 (–C) [e]
[$^tBu_2Sn(OOCMe)_2$]	–211	44.7	29.3 (66; CH_3)	180.3	19.9 (CH_3)
[$^tBu_2Sn(OOCEt)_2$]	–215	44.5(536)	29.2 (66; CH_3)	183.4	9.5 (CH_3); 26.9 (CH_2)
[$^tBu_2Sn(OOC^iPr)_2$]	–221	44.7(515)	29.3 (66; CH_3)	186.3	19.1 (CH_3); 33.5 (CH)
[$^tBu_2Sn(OOC^tBu)_2$]	–232	44.9	29.6 (CH_3)	188.6	27.5 (CH_3); 38.5 (–C)

[a] Values in parenthesis are $^nJ(^{119}Sn-^{13}C)$. [b] Assignment of C-2 and C-3 carbons for iso-butyltin compounds is based on their intensity. [c] ^{s}Bu–Sn methyl and ligand methyl carbons signals overlapped. [d] ^{s}Bu–Sn methylene and ligand methylene carbons signals overlapped. [e] ^{s}Bu–Sn methylene and ligand methyl carbons signals overlapped.

The carbonyl carbon signal is deshielded on complexation, whereas the resonances attributable to the R group showed little change in their position on coordination with tin.

The ^{119}Sn NMR spectra of [^{x}Bu$_2$Sn(OOCR)$_2$] displayed a single resonance in the region δ -149 to -232 ppm. The observed ^{119}Sn chemical shifts are consistent with those reported for diorganotin dicarboxylates [20–22]. The changes in the steric requirements of the butyl or R group are reflected in the ^{119}Sn NMR data. For the same series of dibutyltin dicarboxylates, the ^{119}Sn NMR chemical shift moved to a higher field in the following order of the R group variation which is the order of the Taft σ^* value variation of the R group: Me $\approx$ Et $<$ ^{i}Pr $<$ ^{t}Bu. This trend is consistent with the order reported earlier for similar compounds [23]. For a given carboxylic acid, shielding of the ^{119}Sn signal is much larger with the butyl group variation and is in the following order of butyl group: ^{n}Bu $\approx$ ^{i}Bu $<$ ^{s}Bu $<$ ^{t}Bu.

For simple diorganotin dicarboxylates three different structures, namely monomeric with chelating carboxylate groups (VI), dimeric with two carboxylates bridging (VII) and polymeric with carboxylate bridges (VIII), have been suggested on the basis of spectroscopic data [2,9,20,24–28]. However, recent X-ray structural analysis of a number of such molecules has revealed a monomeric structure with skew trapezoidal planar geometry (IX) for the hexa-coordinate tin atom [13–19]. The spectroscopic data for dibutyltin dicarboxylates reported here can be best interpreted in terms of the compounds containing an asymmetrical chelating carboxylate group.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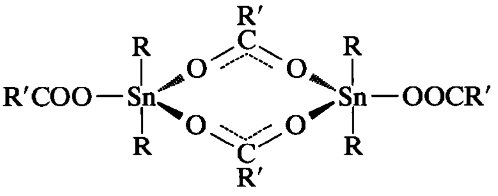
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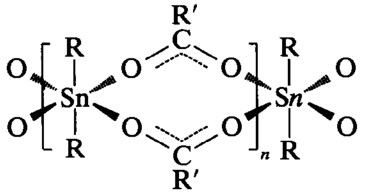
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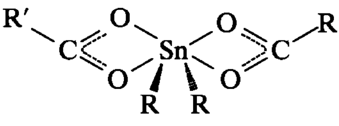
(IX)

Dicarboxylato tetraorganodistannoxanes

Reactions of dibutyltin oxides with carboxylic acid in 1 : 1 stoichiometry showed pronounced dependence on the steric demands of the butyl group in the formation of isolable products. All these reactions were monitored by NMR spectroscopy (^{1}H, ^{13}C or ^{119}Sn). Treatment of di-n-butyltin oxide with carboxylic acid in 1 : 1 stoichiometry afforded complexes of the type [{^{n}Bu$_2$Sn(OOCR)}$_2$O]$_2$ (see below). Similar reactions of di-i-butyltin oxide gave a mixture of tetraorganodistannoxane and [^{i}Bu$_2$Sn(OOCR)$_2$]; formation of the latter increased in the increasing order of steric demands of R group, i.e. Me $<$ Et $<$ ^{i}Pr $<$ ^{t}Bu. The di-s-butyltin oxide in these reactions invariably gave [^{s}Bu$_2$Sn(OOCR)$_2$] leaving behind 50% unreacted

Table 3

Melting point, analysis, IR and ^1H NMR data for tetraorganodistannoxanes and dibutyltin (hydroxy) carboxylates

Complex	Recrystallization solvent (m.p., °C)	% Analyses found (calc.)			$\nu(CO)$ (cm^{-1})	^1H NMR data (δ)
		C	H	Sn		
$[\{^nBu_2Sn(OOCMe)\}_2O]_2$	Benzene/hexane (48–49)	39.4 (40.0)	7.2 (7.1)	39.5 (39.6)	1640	0.90 (br); 1.40 (br) [Bu]; 1.90 (s, OAc)
$[\{^nBu_2Sn(OOCEt)\}_2O]_2$	Benzene/hexane (41–42)	–	–	38.0 (37.8)	1640	0.95 (br), 1.40 (br) [Bu]; 1.05 (t, 7 Hz, Me); 2.15 (q, CH_2)
$[\{^nBu_2Sn(OOC^iPr)\}_2O]_2$	Benzene/hexane (110)	44.2 (43.9)	8.3 (7.7)	36.1 (36.2)	1620	0.91 (t); 1.37 (br); 1.61 (br) [Bu]; 1.14 (d, 6.5 Hz, Me); 2.40 (br, CH)
$[\{^nBu_2Sn(OOC^tBu)\}_2O]_2$	Diethyl ether (120)	45.5 (45.7)	8.2 (8.0)	34.3 (34.7)	1605	
$[^sBu_2Sn(\mu\text{-}OH)(OOCMe)]_2$	CH_2Cl_2/hexane (160)	38.5 (38.9)	7.5 (7.2)	39.6 (38.4)	1602 (benzene) 1595 (Nujol)	0.99 (t, 7 Hz, Me), 1.33 (d, 7 Hz, Me); 1.72 (q, CH_2); 1.95 (s, OAc)
$[^tBu_2Sn(\mu\text{-}OH)(OOCMe)]_2$	$CHCl_3$/acetone (111–112)	38.6 (38.9)	7.3 (7.2)	38.9 (38.4)	1596	1.35 (s, ^tBu, $^3J(^{119}Sn-^1H)$ = 116 Hz); 1.95 (s, OAc)
$[^tBu_2Sn(\mu\text{-}OH)(OOCEt)]_2$	$CHCl_3$/acetone (104–105)	40.1 (40.9)	7.5 (7.5)	37.9 (36.7)	1577	1.33 (s, ^tBu, $^3J(^{119}Sn-^1H)$ = 110 Hz); 1.05 (t, 7 Hz, Me); 2.20 (q, 7 Hz, CH_2)
$[^tBu_2Sn(\mu\text{-}OH)(OOC^iPr)]_2$	Benzene/hexane (107–108)	41.9 (42.8)	7.7 (7.8)	36.1 (35.2)	1584	1.35 (s, ^tBu, $^3J(^{119}Sn-^1H)$ = 110 Hz); 1.10 (d, 7 Hz, Me); 2.43 (m, CH)
$[^tBu_2Sn(\mu\text{-}OH)(OOC^tBu)]_2$	$CHCl_3$/acetone (118–119)	44.3 (44.5)	8.1 (8.0)	34.8 (33.8)	1585	1.35 (s, ^tBu, $^3J(^{119}Sn-^1H)$ = 110 Hz); 1.15 (s, OOC^tBu)

Table 4

$^{13}C\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR data for tetrabutyldistannoxanes and dibutyltin(hydroxy) carboxylates

Complex	δ ^{119}Sn (ppm)	$^{13}C\{^1H\}$ NMR data		
		Bu–Sn carbons	Carbonyl	Ligand R carbons
$[\{^nBu_2Sn(OOCMe)\}_2O]_2$	−204, −219	26.6, 27.0, 27.3, 28.4 (C-1 to C-3); 13.3 (C-4)	177.6	22.1
$[\{^nBu_2Sn(OOCEt)\}_2O]_2$	−202, −217	26.7, 27.5, 28.1, 29.3 (C-1 to C-3); 13.5 (C-4)	180.5	9.9 (Me); 27.2 (CH_2)
$[\{^nBu_2Sn(OOC^iPr)\}_2O]_2$	−209, −215	26.8, 26.9, 27.1, 27.3, 27.6 (C-1 to C-3); 13.5 (C-4)	183.7	19.7 (Me); 35.6 (CH)
$[\{^nBu_2Sn(OOC^tBu)\}_2O]_2$	−194, −210	26.7, 26.8, 27.3 (C-1 to C-3); 13.4 (C-4)	185.4	27.7 (Me); 39.3 (C–)
$[(^iBu_2SnCl)_2O]_2$	−94, −142	45.0, 44.4 (C-1) 26.1, 26.0 (C-2); 25.8, 25.6 (C-3)	–	–
$[^sBu_2(\mu\text{-}OH)(OOCMe)]$	−214, −242	39.1 (C-1); 27.0 (CH_2), 16.3 (Me), 13.9 (Me of C_2H_5)	180.4	22.3
$[^tBu_2Sn(\mu\text{-}OH)(OOCMe)]_2$	−267	40.2 (C-1, $^1J(^{119}Sn-^{13}C)$ = 604 Hz); 29.8 (Me)	179.9	23.4
$[^tBu_2Sn(\mu\text{-}OH)(OOCEt)]_2$	−267	40.3 (C-1); 30.0 (Me)	182.7	10.2 (Me); 19.6 (CH_2)
$[^tBu_2Sn(\mu\text{-}OH)(OOC^iPr)]_2$	−268	40.1 (C-1); 29.9 (Me)	185.1	19.7 (Me); 36.7 (CH)
$[^tBu_2Sn(\mu\text{-}OH)(OOC^tBu)]_2$	−268	40.3 (C-1); 29.9 (Me)	186.6	27.9

$^sBu_2SnO$ as revealed by ^{119}Sn NMR spectroscopy. Di-t-butyltin oxide, however, behaved differently and gave $[^tBu_2Sn(\mu\text{-}OH)(OOCR)]_2$ as an isolable product (see below).

The compounds obtained in the 1:1 reaction of di-n-butyltin oxide with carboxylic acids have been characterized as dicarboxylatotetraorganodistannoxane; $[\{^nBu_2Sn(OOCR)\}_2O]_2$, compounds where R = Me [25,29–31] or ^{t}Bu [32] have been reported earlier. The ^{119}Sn NMR spectra of these compounds showed two well separated resonances characteristic of disubstituted tetraorganodistannoxanes [31,32]. The low and high field resonances have been attributed to the exocyclic and endocyclic tin atoms, respectively. Two sets of ^{n}Bu–Sn resonances are expected in the ^{13}C NMR; due to overlapping of C-1 to C-3 resonances, fewer number of signals are observed for these carbons. Ligand carbon resonances appeared as singlets in all cases. The carbonyl carbon signal showed little change in its position on complexation. Single crystal X-ray analyses of $[\{R_2Sn(OOC^tBu)\}_2O]_2$ (R = Me or Et) [32] have revealed that both the compounds adopt the dicarboxylatotetraorganodistannoxane structure with a planar Sn_2O_2 ring.

Nature of Sn_2O_2 ring in $[(R_2SnX)_2O]_2$

X-Ray structural analyses of a number of disubstituted tetraorganodistannoxanes have shown that the four-membered Sn_2O_2 ring is invariably planar irrespective of the nature of the R group on tin and the anionic ligand (X) [16,32–45]. The Sn_2O_2 ring of these compounds has the following salient features:

(a) Two of the ring Sn–O bonds are longer than the other two by ~ 0.1 Å, but in extreme cases this difference may be as small as 0.01 Å (*e.g.* $[Ph_2Sn(Cl)OSnPh_2(OH)]_2$ [38]) or as large as 0.6 Å (*e.g.* $[\{Me_2Sn(OSiMe_3)\}_2O]_2$ [33]). The Sn–O distances for a bond between the ring oxygen and exocyclic tin are even smaller than the Sn–O distances of the Sn_2O_2 ring. All these Sn–O distances are shorter than the Sn–O single bond length usually observed.

(b) The Sn–Sn distance (~ 3.3 Å) in the four-membered planar Sn_2O_2 ring is smaller than the sum of the van der Waals radius of two tin atoms (4.34 Å).

These features are in juxtaposition with those of the recently reported dimers, $[\{(Me_3Si)_2CH_2\}Sn(\mu\text{-}O)]_2$ [46] and $[Si(C_6H_2Me_3\text{-}2,4,6)_2(\mu\text{-}O)]_2$ [47]; for the latter, Si–Si bonding has been suggested. Recently *ab initio* calculations for a number of three and four membered ring electron-sufficient compounds containing first and second row elements have been performed and structures have been explained using the concept of σ-bridged π-bonding [48]. In disubstituted tetraorganodistannoxanes, significant electron delocalization from oxygen lone pairs to tin empty orbitals may result in more effective σ-bridged π-bonding and consequently lead to a planar Sn_2O_2 ring.

Dibutyl(hydroxy)carboxylates, $[^xBu_2Sn(\mu\text{-}OH)(OOCR)]_2$

The reactions of di-tert-butyltin oxide with all four carboxylic acids in 1:1 stoichiometry afforded hydroxo-bridged dinuclear complexes. Alkaline hydrolysis of $[^tBu_2Sn(OAc)_2]$ and $[^sBu_2Sn(OAc)_2]$ also gave hydroxo-bridged complexes.

The IR spectra of these complexes exhibited a strong band in the region 1577–1602 cm^{-1}, a region where absorption for chelated carboxylate group appears. The X-ray analysis of $[^tBu_2Sn(\mu\text{-}OH)(OAc)]_2$ [49] has, however, shown that the carboxylate group is bonded to tin in a monodentate fashion. The hydroxyl absorption, which seems to merge with the CH stretchings possibly forms strong intramolecular hydrogen bonds with the carbonyl oxygen. Hydroxyhalides, $[^tBu_2Sn(OH)X]$ have intermolecular hydrogen bonding and OH stretchings for these complexes shift to lower wave numbers with decreasing mass of the halides, and when X = F, OH stretchings appear at 3060 cm^{-1}. The complex $[^tBu_2Sn(OH)(OAc)]$ displayed an OH band at 3370 cm^{-1}.

The ^1H NMR spectra exhibited expected peak multiplicities and integration. Except for integration and the magnitude of $^3J(^{119}Sn\text{–}^1H)$, the proton NMR spectral features were similar to those of the corresponding $[^tBu_2Sn(OOCR)_2]$. The Sn–OH proton signal is possibly merged with the butyltin resonance. In triorganotin hydroxides, the Sn–OH signal appears at δ ~ 1.0 ppm [50].

A single set of resonances was observed for the butyl group on tin and the ligand in the ^{13}C NMR spectra. The carbonyl carbon in the complexes is deshielded from its position in the free acids; however, it is shielded from the corresponding bis complexes.

The ^{119}Sn NMR spectra of $[^tBu_2Sn(\mu\text{-}OH)(OOCR)]_2$ displayed only one resonance at δ −267 ppm, and is considerably shielded from the corresponding bis complexes. Unlike $[^tBu_2Sn(OOCR)_2]$, the R group has little influence on the ^{119}Sn NMR chemical shifts suggesting that all the complexes have similar structures. The complex $[^sBu_2Sn(\mu\text{-}OH)(OAc)]$ however showed two resonances at δ −214 and −242 ppm. The latter signal can be assigned to a dimeric species with a structure similar to $[^tBu_2Sn(\mu\text{-}OH)OAc]$. The former resonance may be attributed to a monomeric species formed by bridge cleavage in solution, and possibly has a chelating acetate group.

Conclusion

Steric demands of the ligand as well as the organic groups attached to the R_2Sn^{IV} moiety play an important role in the formation of various isolable products. Reactions of diorganotin oxides with protic ligands initially give a hydroxo species which are stable when steric demands of R group on tin are severe. With less bulky R groups, the hydroxo species loses a water molecule resulting in an isolable tetraorganodistannoxane. The σ-bridged π-bonding in disubstituted tetraorganodistannoxanes seems to be responsible for a planar Sn_2O_2 ring.

Experimental

IR spectra were recorded as a Nujol mull, neat liquid or in benzene solution on Perkin–Elmer 7738 and Matason FT-IR spectrometers. The ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Varian FT-80A spectrometer in $CDCl_3$ solution operating at 79.542, 20.0 and 29.603 MHz, respectively. Chemical shifts are reported in ppm from an internal chloroform peak (δ 7.26 ppm for ^1H and δ 77.0 ppm for ^{13}C) and from external 33% Me_4Sn in C_6D_6 for ^{119}Sn. Tin was determined as SnO_2, and microanalyses for C and H were performed by the Analytical Division of this research centre.

$^nBu_2SnO$ (Fluka) and RCOOH (R = Me, Et, ^iPr, ^tBu) were obtained from commercial sources. $^tBu_2SnCl_2$ was prepared by the reaction of ^tBuMgCl with $SnCl_4$ as described previously [51]. $^sBu_2SnBr_2$ was prepared by the reaction of $^sBu_4Sn$ (b.p. 100°C/0.9 mm) with bromine in carbon tetrachloride [52]. The dibromide thus obtained was treated with 2 equiv. of sodium hydroxide solution (0.1 *N*) to give $^sBu_2SnO$. The latter was converted to $[^sBu_2Sn(OAc)_2]$ and distilled fractionally under a vacuum, and on hydrolysis with 2 equiv. of NaOH solution gave analytically pure $^sBu_2SnO$. $^iBu_2SnO$ was prepared by the following method.

Preparation of $^iBu_2SnO$

A mixture of tetra-i-butyltin (b.p. 95–100°C/0.8 mmHg) (27.4 g, 78.9 mmol), prepared by the conventional Grignard method, and tin tetrachloride (20.6 g, 79.0 mmol, 9.3 ml) was heated at 150°C in an oil bath for 10 h under a nitrogen atmosphere. The turbid liquid was distilled under a vacuum (85–97°C/0.4 mmHg). The ^{119}Sn NMR spectrum of the product indicated the formation of a mixture of chlorides $^iBu_{4-n}SnCl_n$ ($n = 1$–3), their relative ratio varied from one preparation to another (^{119}Sn in $CDCl_3$ δ 145.3 ($^iBu_3SnCl$), 119.7 ($^iBu_2SnCl_2$) and −5.7 ppm ($^iBuSnCl_3$), a typical relative ratio from integration being 1:8:2.

To an ethanolic solution of the above mixture (26.1 g, 85.9 mmol), an aqueous solution of NaOH (0.5 *N*, 173 ml = 3.44 g NaOH, 86.0 mmol) was added slowly with vigorous stirring. The whole was digested on a water bath for 1 h to give a pale yellow precipitate. This was filtered, washed with water (4 × 50 ml), ethanol (2 × 10 ml) and diethyl ether (15 ml) and finally dried in a vacuum. The solid was dissolved in acetone and filtered; the filtrate on slow evaporation gave white crystals of $[({}^{i}Bu_2SnCl)_2O]_2$, which were recrystallized two to three times from acetone (yield 10 g, 42%), m.p. 205–206°C. Anal. Found: C, 34.9; H, 6.8; Cl, 13.5. $[({}^{i}Bu_2SnCl)_2O]_2$ calc.: C, 34.9; H, 6.5; Cl, 12.8%.

To a hot ethanolic solution of $[({}^{i}Bu_2SnCl)_2O]_2$ (6.9 g, 12.5 mmol), a solution of sodium hydroxide (0.5 *N*, 60 ml = 1.2 g NaOH, 30 mmol) was added with stirring to give a white precipitate. The whole was digested on a water bath for 1 h. The precipitate was filtered, washed with water, ethanol and diethyl ether and dried *in vacuo* (yield 6.0 g, 96%). Anal. Found: Sn 48.0%. ${}^{i}Bu_2SnO$ calc.: 47.7%.

Synthesis of $[{}^{x}Bu_2Sn(OOCR)_2]$

All these compounds were prepared by the reaction of dibutyl oxide with carboxylic acid in 1:2 stoichiometry in refluxing benzene; a typical method is given below.

To a benzene suspension of ${}^{s}Bu_2SnO$ (5.753 g, 23.13 mmol), a solution of acetic acid (2.778 g, 46.3 mmol) was added and the whole was refluxed on a Dean and Stark apparatus. Water formed during the reaction was removed azeotropically. The solvent was stripped off *in vacuo* and the residue was distilled (110–115°C, 0.2 mmHg) as a colourless liquid (5.173 g, 64%).

Preparation of dicarboxylatotetraorganodistannoxane

To a benzene suspension of ${}^{n}Bu_2SnO$ (2.36 g, 9.49 mmol) was added a solution of propionic acid (0.70 g, 9.46 mmol). The mixture was refluxed for 4 h and the water formed during the reaction was removed azeotropically with a Dean and Stark apparatus. The resulting clear solution was evaporated *in vacuo*, leaving a white solid which was recrystallized from benzene/hexane in 60% yield.

Similar reactions of ${}^{i}Bu_2SnO$ and ${}^{s}Bu_2SnO$ with carboxylic acid were carried out in 1:1 stoichiometry in refluxing benzene and the products left after solvent removal were characterized by ${}^{119}Sn$ NMR spectroscopy.

Preparation of dibutyltin(hydroxy)carboxylate

(a) To a benzene suspension of ${}^{t}Bu_2SnO$ (0.711 g, 2.86 mmol) was added a benzene solution of trimethylacetic acid (0.292 g, 2.86 mmol) and the whole was stirred at room temperature for 6 h to give a clear solution. The solvent was evaporated *in vacuo* to give a white solid which was recrystallized from a chloroform/acetone mixture in 60% yield.

(b) To an acetone solution (20 ml) of $[{}^{s}Bu_2Sn(OAc)_2]$ (3.852 g, 10.98 mmol), an aqueous solution of sodium hydroxide (0.49 *N*, 22.4 ml = 0.439 g NaOH, 10.98 mmol) was added dropwise with vigorous stirring during which a thick white precipitate formed. This was stirred at room temperature for 30 min and then filtered, washed with acetone (5 ml) and dried *in vacuo* (2.8 g, 82%). Hydrolysis of $[{}^{t}Bu_2Sn(OOCR)_2]$ compounds was carried out similarly.

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