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TELOMERIZATION OF POLY(DIALKYLTIN OXIDE) AND ALKANE- OR ALKENE-1,2-DIOLS: THE IDENTIFICATION OF CYCLIC DERIVATIVES OF OLIGOMERIC DIBUTYLTIN OXIDE

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Summary

1,1-Dibutyl-1,3,2-dioxastannolan and 1,1-dibutyl-4,5-diphenyl-1,3,2-dioxastannolen undergo a telomerization reaction with dibutyltin oxide to give a series of oligomers which have been isolated and characterised.

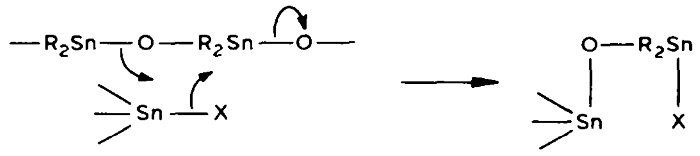
Introduction

Dialkylsiloxanes, R_2SiO, exist as linear polymers or cyclic oligomers [1], whereas the corresponding dialkyltin oxides, R_2SnO are coordinatively crosslinked, and usually exist as intractable, insoluble solids which do not melt before they decompose [2]; it is only when such association is sterically inhibited that oligomers such as $(Bu^t_2SnO)_3$ are recognised to be formed [3]. Some years ago, however, we showed that a telomerization reaction would occur between dialkyltin oxides and dialkyltin dichlorides or alkyltin trichlorides, to give dialkyltin oligomers with halogen end groups [4].

$$Bu_2SnCl_2 + 2n Bu_2SnO \rightarrow Bu_2Sn[(OSnBu_2)_nCl]_2 \qquad (1)$$

$$BuSnCl_3 + 3n Bu_2SnO \rightarrow BuSn[(OSnBu_2)_nCl]_3 \qquad (2)$$

The basic reaction here may be regarded as a metathesis between an Sn–O and Sn–X bond, which inserts an R_2SnO unit between Sn and X.



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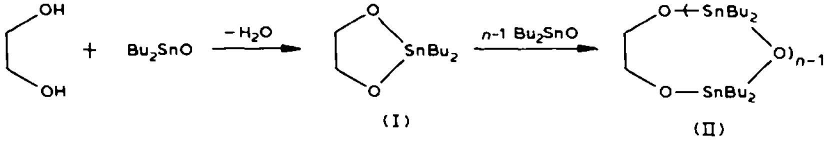
Results and discussion

We now report that a similar reaction occurs between dibutyltin oxide and 1,3,2-dioxastannolans (I) (eq. 4) or 1,3,2-dioxastannolens (III) [5] (eq. 5) to give a series of tractable cyclic oligomers (II and IV).



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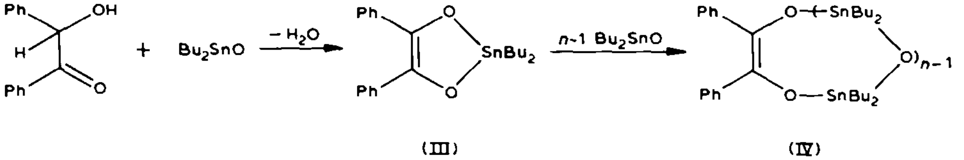

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The dioxastannolan (I) or dioxastannolen (III) was heated under reflux in benzene or toluene, under nitrogen with the appropriate amount of dibutyltin oxide (Method A). After about an hour, the solution became homogeneous. The oligomers (II) usually separated when the solutions were cooled, and the more soluble oligomers (IV) were recovered when the solutions were concentrated. The products were collected and "recrystallised" from benzene, toluene, or hexane. Alternatively the compounds I and III can be formed, and caused to react further in situ, by using a Dean and Stark trap to remove water from a mixture of the diol or acyloin and dibutyltin oxide (Method B). Both methods gave the oligomers in about 90% yield,

TABLE 1

DIALKYLSTANNOXAN OLIGOMERS (II) BASED ON ETHANE-1,2-DIOL

Preparative method	Product n	Yield (%)	m.p. (°C)	Analysis (Found (calcd.) (%))		
				C	H	M
B	1	90	224–225			
B	2	87	187–188 [a]	40.1 (39.9)	7.4 (7.4)	1077 (1084)
A	2	92	ca. 187			
B	3	93	187 (d)	39.5 (39.5)	7.1 (7.4)	1479 (1590)
A	3	91	187 (d) [b]			
B	4	93	192 (d)	39.3 (39.4)	6.8 (7.2)	2057 (2040)
A	10	90	> 300 (d)	38.7 (38.9)	7.1 (7.3)	4516 (5178)

[a] From hexane; the compound reverted to the dioxastannolan (n = 1), m.p. 223°C, when an attempt was made to recrystallise it from dichloromethane. [b] Also obtained in 92% yield when the telomer, n = 2, was heated with the appropriate amount of dibutyltin oxide.

TABLE 2

^{1}H NMR AND ^{119m}Sn MÖSSBAUER SPECTRA OF OLIGOMERS (II)

n	NMR spectrum $\tau(CH_2O)$ [a]	Mössbauer spectrum	
		δ (mm s^{-1})	ΔE_q (mm s^{-1})
1	6.32 [b]	1.10	2.80
2	6.27 [c]	0.88 1.36	2.42 2.77
3	6.37	0.93 1.39	2.30 2.63
4	6.32	1.03	2.26
10	6.43	1.02	2.18

[a] $CDCl_3$ solvent. [b] $J(^{119}Sn-H)$ 32 Hz. [c] $J(^{119}Sn-H)$ 30 Hz.

usually as amorphous solids, but a mixture of oligomers IV, which could usually be separated, was frequently obtained from reaction 5.

Details are given in the Tables.

The compositions were confirmed by integrated ^{1}H NMR spectroscopy and by elemental analysis, although of course this would not differentiate between a single compound and a mixture of close oligomers.

The derivatives II of ethane-1,2-diol all showed bands in the infrared spectrum at 690, 720, and 730 cm^{-1} which are probably associated with the Sn–O bonds. In solution they showed molecular weights close to the values required for dimeric molecules, suggesting a coordinatively associated structure V which is analogous to that which has been proposed for the dioxastannolane (I), and which has been

TABLE 3

DIALKYLSTANNOXAN OLIGOMERS (IV) BASED ON 1,2-DIPHENYLETHENE-1,2-DIOL

Preparative method	Product n	Yield (%)	m.p. (°C)	Analysis (Found (calcd.) (%))		
				C	H	M
A	1	81	89–90	60.0 (59.6)	6.1 (6.3)	463 (443)
A	2	61 [a]	oil			
A	3	36 [b]	98–100	48.9 (48.5)	6.4 (6.8)	907 (941)
A	4	34 [c]	ca. 140	45.9 (46.4)	6.9 (7.0)	
A	5	53 [d]	ca. 120	44.1 (45.4)	6.8 (6.4)	
A	7	95	ca. 150	42.0 (41.6)	7.0 (7.4)	
A	10	81	decomp			

[a] Also $n = 1$, 25%. [b] Also $n = 5$, 53%. [c] Also $n = 5$, 48%. [d] From the reaction between the reactants in the ratio 1/3.

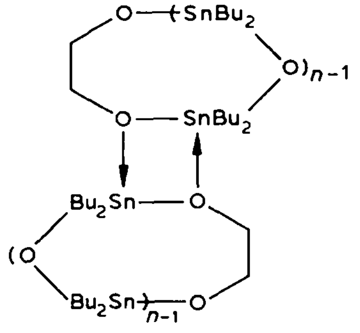
TABLE 4

^{119}Sn NMR AND ^{119m}Sn MÖSSBAUER SPECTRA OF OLIGOMERS (IV)

n	NMR spectrum [a] $\delta(^{119}\mathrm{Sn})$	Mössbauer spectrum [b]	
		δ (mm s^{-1})	ΔE_q (mm s^{-1})
1	ca. −216	1.46	3.55
2	ca. −215	1.23	2.92
3	−198.4 [c] −275.0	0.95 1.16	2.17 2.62
4		1.35	2.44
5	−193.5 [d] −244.6	0.99 1.37	2.36 2.57
7	[e]	1.03	2.11
10	[e]	1.06 1.69	2.64 2.35

[a] In $CHCl_3$ relative to Me_4Sn. [b] At 77 K, relative to SnO_2. [c] Relative areas 2.0/1.0. [d] Relative areas 5.1/1.0. [e] Insufficiently soluble.

established crystallographically for the derivative of methyl 4,6-di-*o*-benzylidene-α-D-glucopyranoside [6].



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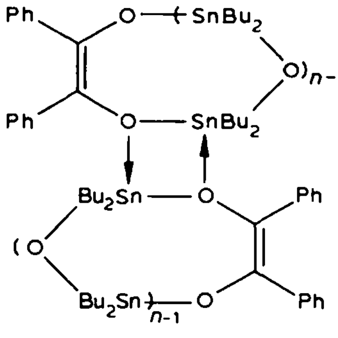

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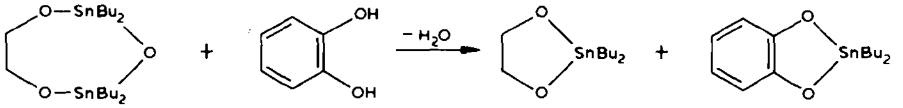
The Mössbauer spectra (see Table 2) are compatible with this structure. When $n = 1$, 2, or 3, the doublet with δ 1.1–1.4, and ΔE_q 2.6–2.8 mm s^{-1} may be ascribed to the trigonal bipyramidal bridging atoms in the environment R_2SnX_3. When $n = 1$ or 3, the appearance of a second doublet of equal or double the intensity, respectively, results from the presence of non-bridging tin atoms. The value of the quadrupole coupling of 2.3–2.4 mm s^{-1} is in the region appropriate for tetrahedral R_2SnX_2. When $n = 4$ or 10, this latter doublet dominates the spectrum, and the former doublet cannot be distinguished.

An excess of dibutyltin oxide can similarly be dissolved in a hot solution of propane-1,2-diol or of pinacol, and it seems very likely that these and other 1,2-diols will form families of dialkylstannoxane oligomers of the type described here. The reaction between catechol and dibutyltin oxide, however, appeared to be restricted to the formation of the familiar monostannoxane derivative, which could not be caused to react with further dialkyltin oxide. This same derivative (VII) was formed when the distannoxane compound (VI) was treated with catechol, as shown in eq. 6 and 7: it appears that these oligomers may provide a soluble, reactive, source of dibutyltin oxide which may be useful in synthesis.



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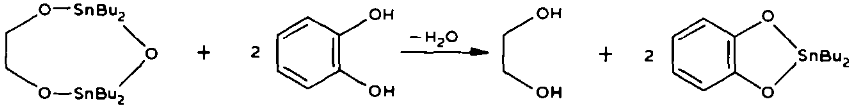
(VI) (VII)



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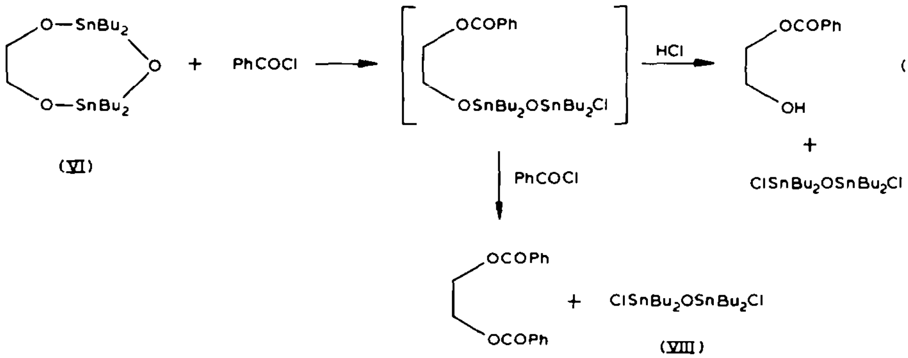
Benzoyl chloride reacted with the distannoxane VI to give, first, glycol monobenzoate, and then glycol dibenzoate and the dichlorodistannoxane VIII.



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(VI) (VIII)

The alkoxy–tin bond in VI is thus more reactive than the stannyloxy–tin bond, in conformity with the relative reactivity of RO–SnR_3 and R_3SnO–SnR_3 which is usually observed.

The unsaturated distannoxanes IV showed infrared bands at ca. 670 and 725 cm^{-1}, as well as a band at 1650–1660 cm^{-1} associated with the carbon–carbon double bond. They had less tendency to dimerize than the saturated analogues II. In dilute solution, IV ($n = 3$), was monomeric like its progenitor III. In more concentrated solution, however, the stannoxanes IV ($n = 3$ and $n = 5$) showed the presence of two ^{119}Sn NMR signals, of the appropriate intensities, suggesting that these compounds were associated into dimers (IX). A signal of intensity 1 at high field can be ascribed to the 5-coordinate tin at the position of association, and a signal of intensity $n - 1$ at lower field can be ascribed to the unassociated tin atoms. Similarly the Mössbauer spectra could sometimes be resolved into two overlapping doublets, the less intense one, ascribed to the bridging tin atoms, showing the larger quadrupole splitting. The unsaturated oligomers IV showed a similar hydrolytic stability to that of the saturated oligomers II, but like the parent enediolate III, they are more sensitive to oxygen, and if a solution is exposed to air, benzil and not benzoin is formed, as dibutyltin oxide is deposited.

Experimental

Molecular weights were determined on solutions in chloroform, using a Mechrolab Vapour Pressure Osmometer, Model 302, calibrated with benzil. ^{119}Sn NMR spectra were recorded on chloroform solutions against an external reference of tetramethyltin in hexadeuterioacetone, using a Varian XL 200 spectrometer. Mössbauer spectra were measured by the University of London Intercollegiate Research Service at Birkbeck College, and are quoted at 85 K with respect to SnO_2. We are grateful to Drs. B.W. Fitzsimmonds and I. Sayer for carrying out these measurements.

Telomerization reactions

The following reactions illustrate the two general methods.

Method A. 2,2-Dibutyl-1,3,2-dioxastannolan (0.50 g, 1.7 mmol) in toluene (30 cm^3) was heated under reflux with dibutyltin oxide (0.85 g, 3.4 mmol). After 10 min, the oxide had dissolved. The toluene was removed under reduced pressure leaving a viscous oil which was recovered from hexane (40 cm^3), giving the telomer II ($n = 3$), m.p. ca. 187°C.

Method B. Benzoin (2.5 g, 12 mmol) and dibutyltin oxide (6.0 g, 24 mmol) were refluxed under nitrogen in benzene (100 cm^3) under a Dean and Stark trap. After 90 min, a turbid solution was formed, from which dibutyltin oxide (0.1 g) was recovered by filtration. The benzene was distilled off under reduced pressure leaving a red oil which was treated with pentane yielding the dioxastannolen (III) as a white powder (2.0 g, 25%), m.p. and mixed m.p. 88–90°C. The pentane was removed from the filtrate leaving the oligomer IV ($n = 2$). Physical characteristics are given in Tables 3 and 4.

Reaction of oligomer II ($n = 2$) with benzoyl chloride

(1) The reaction between benzoyl chloride (1.48 g, 10.5 mmol) and the oligomer II ($n = 2$) (5.70 g, 10.5 mmol) in carbon tetrachloride was exothermic. The mixture was heated under reflux for 30 min, then treated with HCl gas (10.5 mmol) yielding 2-hydroxyethyl benzoate, m.p. 39–40°C (from ether, 0.60 g, 34%) and 1,1,3,3-tetrabutyl-1,3-dichlorodistannoxan, m.p. 110–111°C (38%).

(2) A similar reaction between the oligomer (1.55 g, 2.4 mmol) and benzoyl chloride (0.66 g., 4.7 mmol) gave ethylene dibenzoate, m.p. 70–71°C (0.56 g, 88%), and the tetrabutyldichlorodistannoxan, m.p. 106–109°C.

Acknowledgements

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