

tertiary allylic proton; 2.2 (4 H), a multiplet, allylic protons and protons adjacent to a carbonyl bond; a complex envelope from 1.1 to 1.8 (7 H), ring and side-chain protons; and two superimposed doublets at 0.95 (9 H), three sets of methyl group protons. Vapor phase chromatography of this liquid on a 5 ft \times 0.25 in. UCON Polar column showed only one peak with a retention time of 31 min. This peak was collected and evaporatively distilled (bath temperature 90°, 0.05 mm).

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.52; H, 9.92.

The yield of *cis*-2-isoamyl-3-methyl-4-keto-2,3,4,5,6,7-hexahydrobenzofuran (**4b**, 5.47 g) was 79%.

4,6-Dichloro-3-bromomethylphenyl Acetate (10b).—*N*-Bromosuccinimide (17.8 g, 0.1 mol), which had been freshly recrystallized from water and dried in a vacuum desiccator over phosphorus pentoxide, was refluxed in a solution of 21.8 g (0.1 mol) of 4,6-dichloro-3-methylphenyl acetate¹⁴ in 200 ml of carbon tetrachloride, with the addition of 200 mg of benzoyl peroxide. Refluxing was continued for 4 hr and the mixture was allowed to stand overnight. The succinimide was removed by filtration and washed several times with carbon tetrachloride. The solvent was evaporated under vacuum at 35° and the resulting yellow oil was taken up in 100 ml of petroleum ether. After standing in the freezer overnight, the product crystallized, giving 18.4 g (mp 38–46°) of yellow oily crystals. Concentration of the mother liquor gave an additional 6.0 g of product. Recrystallization, with decolorization with activated charcoal, from petroleum ether gave 22.0 g (mp 51–53°, 74% yield). An analytical sample (mp 52.2–53°) was prepared by four recrystallizations from petroleum ether. The ir and nmr spectra were in agreement with those for the structure.

Anal. Calcd for $C_9H_7BrCl_2O_2$: C, 36.27; H, 2.37. Found: C, 36.28; H, 2.52.

4,6-Dichloro-3-methoxymethylphenol (10c).—The bromomethyl compound **10b** (19.6 g) was treated dropwise at room temperature with a solution of 4.8 g of sodium in 75 ml of dry methanol and was stirred overnight. Water (50 ml) was added carefully, and the mixture was refluxed for 2 hr. Conventional work-up gave an oil, which was distilled through a 4-in. Vigreux column. The main fraction was 10.6 g (74% yield) of a colorless liquid, bp 113–116° (0.6 mm), which crystallized, mp 61–64°. An analytical sample was prepared by three recrystallizations from petroleum ether and sublimation (bath temperature 60°, 0.5 mm). The pure sample of **10c** had mp 68–69.5°. The ir spectrum ($CHCl_3$) had bands at 3400 cm^{-1} , hydroxyl; 1080, 1170, and 1200, ether and phenol C–O stretching. The nmr spectrum (CCl_4) showed singlets at 3.43 ppm (3 H), methoxy

protons; 4.42 (2 H), benzylic methylene protons; 6.59 (1 H), broad, phenolic protons; 7.02 (1 H) and 7.19 (1 H), aromatic protons.

Anal. Calcd for $C_9H_9Cl_2O_2$: C, 46.40; H, 3.89. Found: C, 46.51; H, 3.79.

3-(4,6-Dichloro-3-methoxymethylphenyl)-6-methyl-2-heptanone (10d) was prepared in the usual way from 9.0 g of the phenol, 8.9 g of 3-bromo-6-methyl-2-heptanone, 2.0 g of potassium carbonate, and a few milligrams of potassium iodide in 25 ml of dry acetone. Vapor phase chromatography of the resulting liquid on a 25% QF-1 column showed peaks at 1.7 and 8.3 min. The second peak, **10d**, about 90% of the mixture, was collected and evaporatively distilled (bath temperature 90°, 0.5). The ir spectrum (liquid film) had bands at 1720 cm^{-1} , carbonyl stretching; 1250, 1195, 1168, 1105, and 1080, ether stretching bands; and a doublet at 1360 and 1380, *gem*-dimethyl group. The nmr spectrum (CCl_4) had a doublet at 0.92 ppm (6 H), *gem*-dimethyl group; a complex envelope from 1.1 to 1.9 (5 H), aliphatic methylene and methine protons; a singlet at 2.23 (3 H), methyl ketone protons; a singlet at 3.40 (3 H), methoxyl protons; a singlet at 4.37 superimposed upon a multiplet at 4.50 (3 H, total), benzylic ether and ketone ether protons; a singlet at 6.95 (1 H), aromatic proton; and a singlet at 7.32 (1 H), aromatic proton.

Anal. Calcd for $C_{15}H_{22}Cl_2O_3$: C, 57.66; H, 6.65. Found: C, 57.59; H, 6.51.

Attempted Cyclization of 3-(4,6-Dichloro-3-methoxymethylphenoxy)-6-methyl-2-heptanone (10d).—3-(4,6-Dichloro-3-methoxymethylphenoxy)-6-methyl-2-heptanone (2.0 g, 0.006 mol), was cooled in an ice bath to 0°. Ice-cold sulfuric acid (5 ml) was added and the mixture was stirred for 12 min. The dark red mass was mixed thoroughly with 50 g of ice. The brown oily precipitate was extracted into five 25-ml portions of ethyl ether. The combined ether extracts were washed with water, 10% sodium hydroxide, and again with water and dried. The nmr and ir spectra of the viscous liquid residue were identical with those of the starting material. The experiment was repeated, replacing the sulfuric acid with polyphosphoric acid, at 0° for 2 hr, and at room temperature for 18 hr. When these mixtures were worked up as above, only starting material could be detected by nmr or ir spectra.

Registry No.—**1a**, 24099-57-8; **1b**, 24099-58-9; **2b**, 24099-59-0; **4b**, 24099-60-3; **6b**, 24099-61-4; **7b**, 24099-62-5; **8a**, 18113-13-8; **8b**, 24099-64-7; **9a**, 24099-65-8; **9b**, 24099-66-9; **10b**, 24099-67-0; **10c**, 24099-68-1; **10d**, 24099-69-2.

(14) S. E. Cremer and D. S. Tarbell, *J. Org. Chem.*, **26**, 3653 (1961).

Reaction of Hexaalkyl- and α,α' -Dichlorotetraalkyldistannoxanes with Cyclic Carbonates

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Hexaalkyldistannoxanes react with equimolar amounts of ethylene or propylene carbonate at 80–180° to give bis(trialkyltin) alkylene glycolates and/or 2-dialkylstanna-1,3-dioxolanes. However, α,α' -dichlorotetraalkyldistannoxane gives rise to 2-dialkylstanna-1,3-dioxolane exclusively. Formation of the stannadioxolanes was confirmed through a new cyclization reaction of bis(tributyltin) ethylene glycolates, $R_3SnOC_2H_4OSnR_3$, and their cyclizing tendencies were as follows: $ClEt_2Sn, Me_3Sn > Et_3Sn > n-Bu_3Sn$. Reactions of hexaethyl- and hexabutyl-distannoxanes with ethylene monothiolcarbonate at higher temperature afford bis(trialkyltin) monothioethylene glycolates, together with small amounts of 2-dialkylstanna-1-oxa-3-thialanes.

Davies and coworkers have reported the reaction of hexabutyl-distannoxane with ethylene carbonate to afford bis(tributyltin) ethylene glycolate in a good yield.¹ In the course of our study on the reaction of distannoxane with cyclic carbonate, we obtained a cyclic organo-

tin alkoxide, instead of the ethylene glycolate, for instance, 2-diethylstanna-1,3-dioxolane from hexaethyl-distannoxane and ethylene carbonate. We investigated the similar reactions of four kinds of the distannoxanes with ethylene or propylene carbonate and ethylene thiolcarbonate at various temperature, which provided a new type of cyclization reaction of sterically less hindered bis(trialkyltin) alkylene glycolate

(1) A. G. Davies, P. R. Palan, and S. C. Vasishtha, *Chem. Ind. (London)*, 229 (1967).

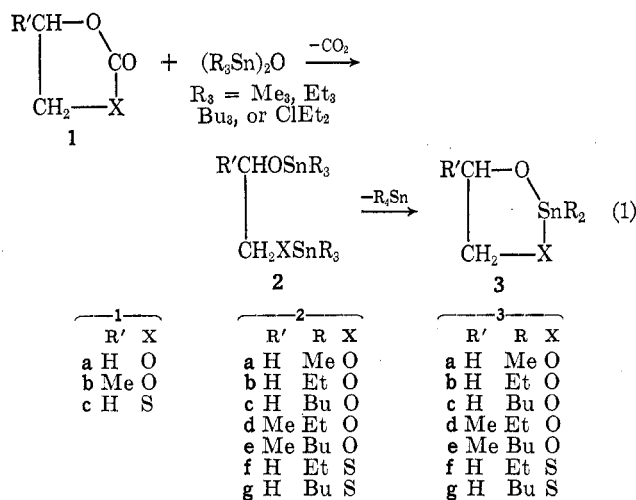
to 2-dialkylstanna-1,3-dioxolane.² The analogous reaction between ethylene thiolcarbonate and the above-mentioned distannoxanes was investigated.

Results and Discussions

A mixture of equimolar amounts of hexaethylidistannoxane and ethylene carbonate was heated under nitrogen at 100° to give 12% of bis(triethyltin) ethylene glycolate and an 85% yield of 2-diethylstanna-1,3-dioxolane, together with a quantitative yield of tetraethyltin. Results concerning the reactions of some hexaalkyldistannoxanes with ethylene or propylene carbonate are summarized in Table I.

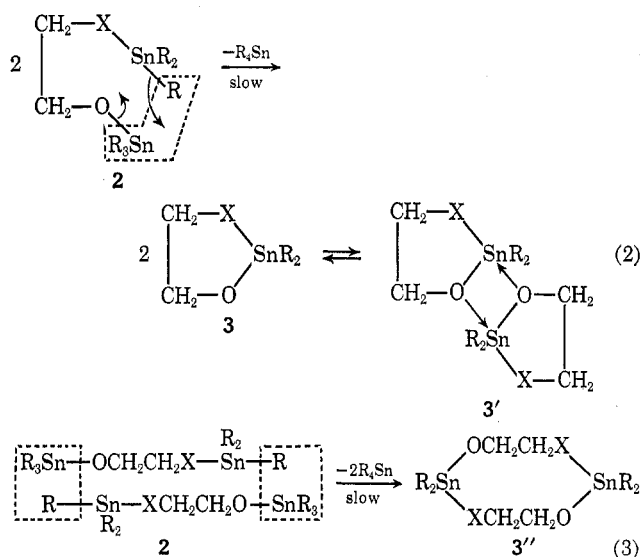
It seems of interest that the reaction of ethylene carbonate with hexabutyldistannoxane at 100° gave a fairly good yield of linear dialkoxide, while, in the case of the reaction with hexamethyldistannoxane, cyclic dialkoxide was a only product. These results would suggest that the cyclization reaction of a linear dialkoxide to a cyclic product is sterically hindered by the bulky alkyltin group. However, at higher reaction temperature, such as 180°, the reaction between hexabutyldistannoxane and ethylene carbonate could give the cyclic dialkoxide **3c** in fairly good yield.

However, when bis(triethyltin) ethylene glycolate (**2b**) was heated at 100° for 3 hr, 2-diethylstanna-1,3-dioxolane (**3b**) and tetraethyltin were quantitatively obtained, supporting the reaction path $1 \rightarrow 2 \rightarrow 3$ as shown in eq 1.



Even when di-*t*-butyl peroxide or diphenylpicrylhydrazyl was added in the reaction of hexaethylidistannoxane with ethylene carbonate at 100°, the yields of cyclic and linear dialkoxide were not affected, indicating a coordination mechanism (eq 2 or 3) as has been suggested for redistribution reactions of trialkyltin hydroxide⁸ and methoxide,⁹ rather than a free-radical

mechanism. Equilibrium phenomena among **3**, **3'**, and **3''** were documented by Pommier and Valade⁷ and the dimer form **3'** or **3''** was suggested to be stable.¹⁰ By our experiment, the rate of the cyclization reaction of bis(triethyltin) ethylene glycolate at 137° in mixed xylene was followed by the first-order kinetics, and therefore, an intramolecular process (2) seems to be more preferable than intermolecular path (3).



Hexaethylidistannoxane was found to react with ethylene monothiolcarbonate (**1c**) at 150° for 2 hr, to yield 59% of bis(triethyltin) monothioethylene glycolate (**2f**) and 12% of 2-diethylstanna-1,3-thioxolane (**3f**). The necessity of higher reaction temperature is indicative of the lower reactivity of the monothiolcarbonate than the carbonate, which would be affected by the electronegativity of heteroatom X in cyclic compounds. In spite of the higher reaction temperature, the low yield of cyclic thio compound **3f** and relatively high yield of **2f** could result from a smaller cyclization rate of the linear thio compound **2f** to **3f**, owing to the stable tin-sulfur bond.¹¹

A mixture of hexabutyldistannoxane and monothiolcarbonate was heated at 150° for 2 hr, affording solely a linear product **2g**, probably because of steric hindrance on the cyclization reaction.

α,α' -Dichlorotetraethylidistannoxane makes a stable dimer¹² and was less reactive than hexaethylidistannoxane, which exists as monomer in solution. In the reaction with ethylene carbonate, the former required 2 days of heating at 80° to react quantitatively, while the latter reacted completely in only 2 hr. The dimeric distannoxane was less reactive than the monomeric one in the ring-opening reactions of cyclic esters.¹³

Reaction of α,α' -dichlorotetraethylidistannoxane with ethylene carbonate at 80° afforded cyclic dialkoxide **3b** in 88% yield and no linear dialkoxide **5** was isolated, suggesting the facile cyclization reaction of **5**

(2) Stannadioxolanes were also prepared by another methods from dibutyltin dichloride,³ dibutyltin oxide,^{4,5} and dibutyltin methoxide.^{6,7}

(3) H. E. Remsen and C. K. Banks, U. S. Patent 2,789,994 (1957); *Chem. Abstr.*, **51**, 14786 (1957).

(4) J. Bornstein, B. R. La Liberte, T. M. Andrews, and J. C. Monterroso, *J. Org. Chem.*, **24**, 886 (1959).

(5) W. J. Conside, *J. Organometal. Chem.*, **5**, 263 (1966).

(6) R. C. Mehrota and V. D. Gupta, *ibid.*, **4**, 145 (1965).

(7) J. Pommier and J. Valade, *ibid.*, **12**, 433 (1968).

(8) C. A. Krauss and R. H. Bullard, *J. Amer. Chem. Soc.*, **51**, 3605 (1929).

(9) E. Amberger and M. Kula, *Chem. Ber.*, **96**, 2562 (1963).

(10) Cyclic butyltin compound **3** in eq 1 and eq 4 was shown conventionally as monomer, but the stable form seems to be dimer⁷ in equilibrium among **3**, **3'**, or **3''**.

(11) K. Itoh, Y. Kato, and Y. Ishii, *J. Org. Chem.*, **34**, 459 (1969).

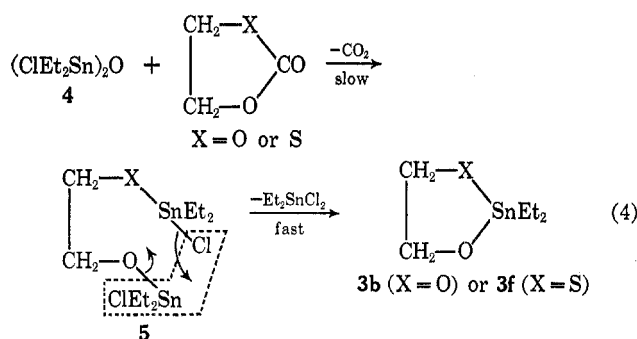
(12) R. Okawara and M. Wada, *J. Organometal. Chem.*, **1**, 84 (1963).

(13) S. Sakai, Y. Kiyohara, M. Kokura, K. Itoh, and Y. Ishii, unpublished work.

TABLE I
 REACTIONS OF DISTANNOXANES WITH CYCLIC CARBONATES

Reactants		Reaction		Dialkoxides formed, %	
Carbonates	Distannoxanes	Temp, °C	Time, hr	2	3
Ethylene carbonate	(Me ₃ Sn) ₂ O	100	0.166	0 (2a)	64 (3a)
Ethylene carbonate	(Et ₃ Sn) ₂ O	80	2	60-70 (2b)	5-10 (3b)
Ethylene carbonate	(Et ₃ Sn) ₂ O ^a	80	2	64 (2b)	9 (3b)
Ethylene carbonate	(Et ₃ Sn) ₂ O	100	2	12 (2b)	85 (3b)
Ethylene carbonate	(Et ₃ Sn) ₂ O ^b	100	2	18 (2b)	80 (3b)
Ethylene carbonate	(Bu ₃ Sn) ₂ O	100	6	88 (2c)	3 ^c (3c)
Ethylene carbonate	(Bu ₃ Sn) ₂ O	120	6	86 (2c)	5 ^c (3c)
Ethylene carbonate	(Bu ₃ Sn) ₂ O	180	6	0	90 (3c)
Propylene carbonate	(Et ₃ Sn) ₂ O	100	2	0	78 (3d)
Propylene carbonate	(Bu ₃ Sn) ₂ O	120	6	75 (2e)	3 ^c (3e)
Ethylene monothiolcarbonate	(Et ₃ Sn) ₂ O	150	2	59 (2f)	12 (3f)
Ethylene monothiolcarbonate	(Bu ₃ Sn) ₂ O	150	2	60 (2g)	1 (3g)
Ethylene carbonate	(ClEt ₂ Sn) ₂ O	80	48	0	88 (3b)
Ethylene monothiolcarbonate	(ClEt ₂ Sn) ₂ O	150	3	0	85 (3f)

^a Dibenzoyl peroxide (0.3 wt %) was added. ^b Diphenylpicrylhydrazyl (0.3 wt %) was added. ^c Cyclic dialkoxide 3 was formed during high-temperature distillation up to 240°.



to **3b** and the larger mobility of the chlorine atom in comparison with the ethyl group. Analogous phenomena were also observed in the reaction of dichlorotetraethylstannoxane with ethylene monothiolcarbonate to give the cyclic thio compound **3f**.

In the mass spectral inspections, all cyclic dialkoxides **3a-e**, seem to show parent mass numbers of the dimer,^{14,15} while 2-diethylstanna-1-oxa-3-thialane has that of monomer. Both stannadioxolane and stannaoxathialane would exist mainly as dimers in equilibrium, $3 \rightleftharpoons 3'$ or $3''$,¹⁶ but the association of two molecules of stannaoxathialane would be weaker than that of the cyclic dialkoxide; so the former might show the parent mass number of monomer in mass spectral measurements.

Experimental Section

Boiling points and melting points have not been corrected. Infrared spectra were recorded on a JASCO Model IR-S spectrometer. Nmr spectra were measured on a Japan Electron Optics Laboratory Model JNM-MH 60, using tetramethylsilane (TMS, τ 10) as an internal standard. Mass spectral data (75 eV, calcd for ¹¹⁸Sn) were obtained with a Japan Electron Optics Type JMS-OISG mass spectrometer. Microanalyses were done

(14) Maximum mass number observed was dimer of cyclic dialkoxide-alkyl group, as has been reported on the other organotin compounds by DeLidder, and Dijkstra.¹⁵

(15) J. J. DeLidder, and G. Dijkstra, *Recl. Trav. Chim. Pays-Bas*, **86**, 737 (1967).

(16) M. Wada, T. Okada, and R. Okawara (read at Symposium on Organometallic Compounds in Osaka, Oct 1969) suggested that the stannaoxathialane would be dimeric in solution from the ir and nmr data in carbon tetrachloride and chloroform solutions.

by the Analytical Center of Kyoto University, and the content of tin atom in the products was analyzed by Gilman's method.¹⁷

Materials.—Ethylene thiolcarbonate (Aldrich Chemical Corp.), ethylene, and propylene carbonate were redistilled *in vacuo*. Hexaethyl-, hexabutyl-,¹⁸ and hexamethyldistannoxane¹⁹ were prepared by literature methods. Bis(triethyltin) ethylene glycolate was obtained by Lorberth and Kula's method.²⁰

Reaction of Hexaethylstannoxane with Ethylene Carbonate (General Procedure).—Hexaethylstannoxane (15.9 mmol) and ethylene carbonate (16.0 mmol) were added to a 30-ml distilling flask which was heated at 80° for 2 hr under nitrogen; the reaction mixture was distilled, giving a 12% yield (based on the distannoxane used) of the linear dialkoxide **2b**, bp 112-114° (0.1 mm), and an 85% yield of the cyclic dialkoxide **3b** as distillation residue, mp 280° (recrystallized from CHCl₃). Tetraethyltin was condensed in a cold trap.

2b: ir (CCl₄) 1055, 1010 (C-O) and 880 cm⁻¹; nmr (CCl₄) τ 6.67 (s, 4) and \sim 9.2 (broad, 30); ir and nmr spectra coincided well with those of an authentic sample prepared from N,N-diethyltriethylstannylamine and ethylene glycol.¹⁸

3b: ir (KBr) 1120, 1068 (C-O), 965, 950, 895, and 680 cm⁻¹; nmr (CHCl₃) τ 6.48 (s, 4, CH₂O) and \sim 8.8 (broad, 10, Et-Sn); mass spectrum (*m/e*) 443 (calcd for (3b)₂-Et, 443). *Anal.* Calcd for C₆H₁₄O₂Sn: C, 30.43; H, 5.96; S, 50.11. Found: C, 30.39; H, 5.95; Sn, 49.76.

Reaction of Hexamethyldistannoxane with Ethylene Carbonate.—Hexamethyldistannoxane reacted with ethylene carbonate at 100° for 10 min analogously giving a 64% yield of **3a**: mp <270°; ir (KBr) 1230, 1120, 1185, 1070 (C-O), 900, and 780 cm⁻¹; nmr measurement could not be done owing to its poor solubility; mass spectrum (*m/e*) 403 (calcd for (3a)₂-Me, 403). *Anal.* Calcd for C₄H₁₀O₂Sn: C, 23.01; H, 4.83; Sn, 56.84. Found: C, 22.75; H, 5.05; Sn, 56.65.

Reaction of Hexabutylstannoxane with Ethylene Carbonate.—Hexabutylstannoxane reacted with ethylene carbonate at 180° for 6 hr, and the reaction mixture was recrystallized from carbon tetrachloride giving a 90% yield of **3c**: mp 222-223° (lit.⁷ 215-220°, lit.⁵ 223-227°); ir (KBr) 1120, 1060, 895, and 710 cm⁻¹; nmr (CHCl₃) τ 6.51 (s, 4, CH₂O) and 8.60-9.20 (m, 18, Bu-Sn). Ir and nmr spectra were quite similar when compared with those of the authentic material.⁷ Tetraethyltin (86% yield) was condensed in a cold trap.

The reaction of hexabutylstannoxane with ethylene carbonate at 100° gave an 88% yield of **2c**: bp 175-180° (0.2 mm); ir (CCl₄) 1110, 1070, 1040, and 870 cm⁻¹; nmr (CCl₄) τ 6.57 (s, 4, CH₂) 8.85-9.37 (m, 54, Bu-Sn). **2c** had the same ir and nmr spectra of authentic sample prepared from ethylene glycol and N,N-diethyltributylstannylamine.¹⁹ A small amount of **3c**,

(17) H. Gilman and W. B. King, *J. Amer. Chem. Soc.*, **51**, 1213 (1929).

(18) G. S. Sasin, *J. Org. Chem.*, **18**, 1142 (1953).

(19) T. Harada, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)*, **35**, 146 (1940).

(20) J. Lorberth and M. R. Kula, *Chem. Ber.*, **97**, 3444 (1964).

formed during high-temperature distillation up to 200°, was found in distillation residue.

Reaction of Hexaethylidistannoxane with Propylene Carbonate.

—A mixture of equimolar amounts of two reagents was heated at 100° for 2 hr, and the reaction mixture was distilled, giving a 78% yield of **3d**: mp 255–257°; ir (KBr) 1140, 1050, 950, 930, 850, and 680 cm⁻¹; nmr (CHCl₃) τ 8.98 (d, 3, J = 6.0 Hz, CH₂CHO), \sim 8.8 (broad, 10, Et-Sn), and 6.45 (M, ABCX₃ pattern, 3, OCH-CH₂);²¹ mass spectrum (m/e) 473 (calcd for (3d)₂-Et, 473). Anal. Calcd for C₇H₁₆O₃Sn: C, 33.51; H, 6.43; Sn, 47.31. Found: C, 33.70; H, 6.41; Sn, 47.20.

Reaction of Hexabutylidistannoxane with Propylene Carbonate.

—A mixture of equimolar amounts of two reagents was heated at 120° for 6 hr. The distillation products were 75% **2e**: bp 155–160° (0.02 mm); ir (CCl₄) 1150, 1070, 1050, 960, 875, and 860 cm⁻¹; nmr (CCl₄) τ 6.64 (m, 3, CH₂CHO), and 8.5–9.1 (broad, Bu-Sn and CH₃-CHO). Spectra were the same as those of an authentic sample prepared by another method.²⁰ From the distillation residue, a 3% yield of **3e** was obtained, which was identified by the comparison with the ir and nmr spectra of an authentic sample prepared by Remsen and Bank's method:⁸ mp 181–183°; ir (KBr) 1140, 1050, 930, 855, and 680 cm⁻¹.

Anal. Calcd for C₁₁H₂₄O₃Sn: C, 43.04; H, 7.88; Sn, 38.66. Found: C, 43.03; H, 8.03; Sn, 38.61.

Reaction of Hexaethylidistannoxane with Ethylene Monothiolcarbonate.—A mixture of equimolar amounts of the two reagents was heated at 150° for 2 hr and distilled to give a 59% yield of **2f**, bp 146–149° (0.3 mm), and 12% yield of **3f**, mp 205–207°.

2f: ir (CCl₄) 1180, 1050, 1010, 950, and 650 cm⁻¹; nmr (CCl₄) τ 6.39 (t, 2, J = 5.8 Hz, CH₂O), 7.51 (t, 2, J = 5.8 Hz, CH₂S), 8.9 (broad, 30, Et-Sn).

3f: ir (CHCl₃) 1280, 1220, 1175, 1165, 1055, 1010, 960, and 670 cm⁻¹; nmr (CHCl₃) τ 6.36 (t, 2, J = 5.4 Hz, CH₂O), 7.21 (t, 2, J = 5.4 Hz, CH₂S), and \sim 8.7 (broad, 10, Et-Sn); mass spectrum (m/e) 254 (calcd for **3f**, 254). Anal. Calcd for C₆H₁₄OSSn: C, 28.49; H, 5.58; Sn, 46.93. Found: C, 28.79; H, 5.79; Sn, 46.65.

Reaction of Hexabutylidistannoxane with Ethylene Monothiolcarbonate.—The two reagents reacted at 150° for 2 hr, giving trace amounts (<1%) of **3g** [bp 165–168° (0.5 mm); mp 89–90°; ir and nmr spectra (CHCl₃) were the same as those of the sample prepared from dibutyltin dimethoxide and mercaptoethanol], and 60% yield of **2g** [bp 180–185° (0.2 mm); ir (CCl₄) 1070, 1050, 1015, 950, and 870 cm⁻¹; nmr (CCl₄) τ 6.45 (t, 2, J = 6.0 Hz, CH₂O), 7.53 (t, 2, J = 6.0 Hz, CH₂S), and 8.6–9.1 (broad, 54, Bu-Sn); spectra identical with those of an authentic sample prepared from mercaptoethanol and N,N-diethyltributylstannylamine²⁰].

(21) Ambiguous ABCX₃ pattern analogous to that of propylene carbonate was observed, but poor solubility of the product prevented analysis.

Reaction of α,α' -Dichlorotetraethylidistannoxane with Ethylene Carbonate.—A mixture of equimolar amounts of the two reagents was heated at 80° for 2 days in dry toluene, and the reaction mixture was recrystallized from a mixture of hexane and chloroform, giving an 81% yield of dibutyltin dichloride, mp 83–84° (lit.²² 83–84), and an 88% yield of **3b**, mp >270°; ir and nmr spectra were the same as mentioned above.

Reaction of α,α' -Dichlorotetraethylidistannoxane with Ethylene Monothiolcarbonate.—A mixture of equimolar amounts of the two reagents was heated at 150° for 3 hr, and the reaction mixture was recrystallized from carbon tetrachloride, giving an 85% yield of **3f**, mp 206–208°. Dibutyltin dichloride was isolated from the mother liquor.

Thermal Decomposition of Bis(tributyltin) Ethylene Glycolate.—The ethylene glycolate was heated in a sealed glass tube at 100° for 3 hr, and the reaction mixture was recrystallized from carbon tetrachloride giving a 93% yield of **3b**; ir and nmr spectra were the same as those mentioned above. Tetraethyltin was isolated in 90% yield by distillation of the filtrate.

Kinetic Measurement on the Rate of Cyclization Reaction.—The solutions of bis(tributyltin) ethylene glycolate at the initial concentrations of 1.090 and 1.985 M in dry xylene were heated at 137.0 \pm 0.5° in glass tube, and the tetraethyltin formed was analyzed by vapor phase chromatography with a column of Apiezon L. Table II shows the results.

TABLE II

THE RATE OF FORMATION OF TETRAETHYL TIN IN THE THERMAL DECOMPOSITION OF **2b** AT 137.0°

Initial concn, M	Tetraethyltin formed (mol/l.)				
	4.0 ^a	8.0	12.0	16.0	20.0
1.090	0.042	0.081	0.120	0.150	0.190
1.985	0.130	0.227	0.290	0.320	0.390

^a Reaction time in hours.

The plots of the data in Table II by the first-order rate law showed straight lines, and the rate constants of the cyclization reaction of **2b** were estimated to be 1.2×10^{-6} and 1.3×10^{-6} sec⁻¹ for the initial concentrations of 1.090 and 1.985 mol/l., respectively.

Registry No.—**1a**, 96-49-1; **1b**, 108-32-7; **1c**, 3326-89-4; **2f**, 24471-68-9; **3a**, 24471-69-0; **3b**, 24471-70-3; **3d**, 24471-71-4; **3f**, 24471-72-5; (Me₃Sn)₂O 1692-18-8; (Et₃Sn)₂O, 1112-63-6; (Bu₃Sn)₂O, 56-35-9; (ClEt₃Sn)₂O, 17973-82-9.

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A Novel Synthesis of Cyclic Thioncarbonates and Spiro Orthocarbonates from Bis(tributyltin) Alkylene Glycolates and Carbon Disulfide

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Cyclic thioncarbonates and symmetrical spiro orthocarbonates were readily prepared in excellent yields from carbon disulfide and bis(tributyltin) alkylene glycolates having a C₂-C₃ glycol unit, together with bis(tributyltin) sulfide. Unsymmetrical spiro orthocarbonates were obtained by the reaction of alkylene thioncarbonates with other types of bis(tributyltin) alkylene glycolates. On the other hand, bis(tributyltin) alkylene glycolate having a bulky or longer glycol unit above C₅ reacted with carbon disulfide to form the insertion product to the tin-oxygen bond, but did not give any cyclic compound.

Hitherto, thioncarbonates were obtained by thiocarbonylation reactions of diols using thiocarbonylimidazole,¹ thiophosgene,² or carbon disulfide, butyllithium, and methyl iodide.³ Orthocarbonates have

been so far prepared from sodium alkoxide and chloropierin⁴ or thiocarbonyl perchloride (Cl₃CSCl).⁵

In this report, a novel synthetic method of cyclic thioncarbonates and spiro orthocarbonates by the

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