

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<sup>-1</sup>; nmr (CHCl<sub>3</sub>)  $\tau$  8.98 (d, 3,  $J$  = 6.0 Hz, CH<sub>2</sub>CHO),  $\sim$ 8.8 (broad, 10, Et-Sn), and 6.45 (M, ABCX<sub>3</sub> pattern, 3, OCH-CH<sub>2</sub>);<sup>21</sup> mass spectrum ( $m/e$ ) 473 (calcd for (3d)<sub>2</sub>-Et, 473). Anal. Calcd for C<sub>7</sub>H<sub>16</sub>O<sub>3</sub>Sn: 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 (CCl<sub>4</sub>) 1150, 1070, 1050, 960, 875, and 860 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\tau$  6.64 (m, 3, CH<sub>2</sub>CHO), and 8.5–9.1 (broad, Bu-Sn and CH<sub>3</sub>-CHO). Spectra were the same as those of an authentic sample prepared by another method.<sup>20</sup> 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:<sup>8</sup> mp 181–183°; ir (KBr) 1140, 1050, 930, 855, and 680 cm<sup>-1</sup>.

Anal. Calcd for C<sub>11</sub>H<sub>24</sub>O<sub>3</sub>Sn: 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 (CCl<sub>4</sub>) 1180, 1050, 1010, 950, and 650 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\tau$  6.39 (t, 2,  $J$  = 5.8 Hz, CH<sub>2</sub>O), 7.51 (t, 2,  $J$  = 5.8 Hz, CH<sub>2</sub>S), 8.9 (broad, 30, Et-Sn).

**3f**: ir (CHCl<sub>3</sub>) 1280, 1220, 1175, 1165, 1055, 1010, 960, and 670 cm<sup>-1</sup>; nmr (CHCl<sub>3</sub>)  $\tau$  6.36 (t, 2,  $J$  = 5.4 Hz, CH<sub>2</sub>O), 7.21 (t, 2,  $J$  = 5.4 Hz, CH<sub>2</sub>S), and  $\sim$ 8.7 (broad, 10, Et-Sn); mass spectrum ( $m/e$ ) 254 (calcd for **3f**, 254). Anal. Calcd for C<sub>6</sub>H<sub>14</sub>OSSn: 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 (CHCl<sub>3</sub>) 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 (CCl<sub>4</sub>) 1070, 1050, 1015, 950, and 870 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\tau$  6.45 (t, 2,  $J$  = 6.0 Hz, CH<sub>2</sub>O), 7.53 (t, 2,  $J$  = 6.0 Hz, CH<sub>2</sub>S), and 8.6–9.1 (broad, 54, Bu-Sn); spectra identical with those of an authentic sample prepared from mercaptoethanol and N,N-diethyltributylstannylamine<sup>20</sup>].

(21) Ambiguous ABCX<sub>3</sub> pattern analogous to that of propylene carbonate was observed, but poor solubility of the product prevented analysis.

**Reaction of  $\alpha,\alpha'$ -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.<sup>22</sup> 83–84), and an 88% yield of **3b**, mp >270°; ir and nmr spectra were the same as mentioned above.

**Reaction of  $\alpha,\alpha'$ -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 <sup>a</sup>	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

<sup>a</sup> 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  $1.2 \times 10^{-6}$  and  $1.3 \times 10^{-6}$  sec<sup>-1</sup> 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; (Me<sub>3</sub>Sn)<sub>2</sub>O 1692-18-8; (Et<sub>3</sub>Sn)<sub>2</sub>O, 1112-63-6; (Bu<sub>3</sub>Sn)<sub>2</sub>O, 56-35-9; (ClEt<sub>3</sub>Sn)<sub>2</sub>O, 17973-82-9.

(22) A. C. Smith and E. G. Rochow, *J. Amer. Chem. Soc.*, **75**, 4103 (1953).

## 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 C<sub>2</sub>-C<sub>3</sub> 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 C<sub>5</sub> 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,<sup>1</sup> thiophosgene,<sup>2</sup> or carbon disulfide, butyllithium, and methyl iodide.<sup>3</sup> Orthocarbonates have

been so far prepared from sodium alkoxide and chloropierin<sup>4</sup> or thiocarbonyl perchloride (Cl<sub>3</sub>CSCl).<sup>5</sup>

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

(1) H. A. Staab and G. Walthers, *Ann.*, **657**, 98 (1962).

(2) F. N. Jones and S. Andreades, *J. Org. Chem.*, **34**, 3011 (1969).

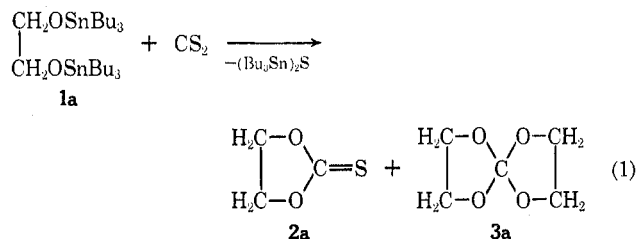
(3) E. J. Corey and R. A. Winter, *J. Amer. Chem. Soc.*, **85**, 2677 (1963).

(4) J. D. Roberts and R. E. McMashon, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 200.

(5) H. Tieckelman and H. W. Post, *J. Org. Chem.*, **13**, 265 (1948).

reaction of bis(tributyltin) alkylene glycolates with carbon disulfide is disclosed.

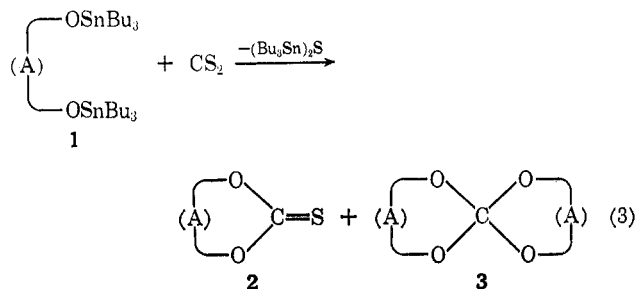
For a standard example, bis(tributyltin) ethylene glycolate (**1a**) reacted with excess amounts of carbon disulfide in dry nitrogen at room temperature, giving a 69% yield of ethylene thioncarbonate (**2a**), 26% yield of bis(ethylene) orthocarbonate (**3a**), and bis(tributyltin) sulfide. The cyclic thioncarbonate **2a** showed a  $\nu_{C=S}$  band at  $1155\text{ cm}^{-1}$  in the ir spectrum and a sharp singlet at  $\tau$  5.23 in the nmr spectrum, whereas **3a** had a strong  $\nu_{C-O}$  band at  $1050\text{ cm}^{-1}$ , a sharp singlet at  $\tau$  5.95, and the molecular peak at 132 ( $m/e$ ) in the mass spectrum.



As has already been well established,<sup>6-9</sup> trialkyltin alkoxide can add across the A=B type unsaturated bond of acceptor molecules: tributyltin methoxide reacted exothermically with carbon disulfide at room temperature to give relatively stable methyl tributyltin xanthate as shown in eq 2.



It is interesting that monotributyltin alkoxide gave the xanthate, while bis(tributyltin) dialkoxide **1a** afforded the thion- and the orthocarbonates, **2a** and **3a**, in the reaction with carbon disulfide under the same reaction conditions. Now, we have established an excellent thiocarbonylation reaction of glycols and a new preparative method of some new spiro orthocarbonates by the reaction of bis(tributyltin)alkylene glycolate with carbon disulfide, since bis(tributyltin)alkyleneglycolates, especially the ethylene glycolate, are easily prepared from glycols.<sup>10</sup> The results of the reaction of various glycolates, **1**, with carbon disulfide at room temperature are summarized in Table I.



(6) A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.*, 5238 (1965); *C*, 299 (1966).

(7) A. G. Davies and W. R. Symes, *ibid.*, *C*, 1009 (1967).

(8) A. J. Bloodworth, A. G. Davies, and S. C. Vasishtha, *ibid.*, 1309 (1967).

(9) A. G. Davies and P. G. Harrison, *ibid.*, 1313 (1967).

(10) Bis(tributyltin) ethylene or propylene glycolate solution prepared by heating ethylene or propylene carbonate with bis(tributyltin) oxide in toluene can be used as a starting material. Other preparation methods of bis(trialkyltin) alkylene glycolates from glycols were also reported.<sup>11-16</sup>

(11) J. Loberth and M. Kula, *Chem. Ber.*, **97**, 3444 (1964).

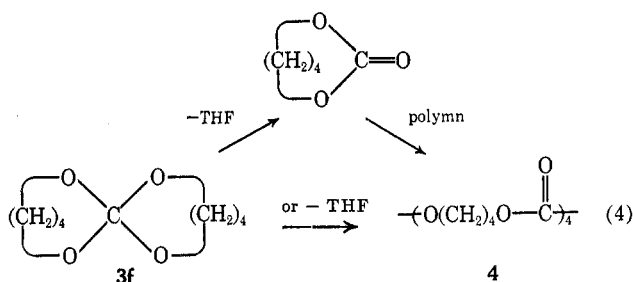
TABLE I  
SYMMETRICAL SPIRO ORTHOCARBONATES AND CYCLIC  
THIONCARBONATES PREPARED FROM BIS(TRIBUTYLTIN) ALKYLENE  
GLYCOLATES AND CARBON DISULFIDE WITHOUT SOLVENT

No.	A in bis(tributyltin) glycolate used	Product yield, %	
		2	3
1	(CH <sub>2</sub> ) <sub>2</sub> ( <b>1a</b> )	69 ( <b>2a</b> )	26 ( <b>3a</b> )
2	CH <sub>2</sub> CH(CH <sub>3</sub> ) ( <b>1b</b> )	6 (66) <sup>a</sup> ( <b>2b</b> )	75 (25) <sup>a</sup> ( <b>3b</b> )
3	CH(CH <sub>3</sub> )CH(CH <sub>3</sub> ) ( <b>1c</b> )	56 ( <b>2c</b> )	32 ( <b>3c</b> )
4	C(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> ( <b>1d</b> )	0	0
5	(CH <sub>2</sub> ) <sub>3</sub> ( <b>1e</b> )	0	65 ( <b>3e</b> )
6	(CH <sub>2</sub> ) <sub>4</sub> ( <b>1f</b> )	0	29 <sup>b</sup> ( <b>3f</b> )
7	(CH <sub>2</sub> ) <sub>5</sub> ( <b>1g</b> )	0	0
8	(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> ( <b>1h</b> )	0	0

<sup>a</sup> Numbers in parentheses showed the yields in the reaction in toluene. <sup>b</sup> Poly(1,4-butylene carbonate) was also formed in 45% yield.

The results in Table I indicate that reaction 3 is generally applicable to sterically unhindered 1,2-glycol and  $\alpha,\omega$ -glycol derivatives having less than five carbon atoms. The 1,2-glycolates, except 2,3-dimethyl-2,3-butylene glycolate (**1d**), gave high yields of thioncarbonate and spiro orthocarbonate. Because reaction 3 consists of very fast two-step reactions as will be discussed later, the ratios of the yield of thioncarbonates to that of spiro orthocarbonates may be affected by the solvent used and other reaction conditions; e.g., the yield of propylene thioncarbonate (**2b**) was improved by adding toluene to the reaction of bis(tributyltin) 1,2-propylene glycolate (**1b**) with carbon disulfide.

Contrary to the reaction of the 1,2-glycolates, the reactions of the 1,3- and 1,4-glycolate gave only spiro orthocarbonates. The reaction of 1,4-butylene glycolate (**1f**) with carbon disulfide gave a low yield (29%) of spiro orthocarbonate and 45% yield of poly(1,4-butylene carbonate), which will be formed by the decomposition of **3f** to tetrahydrofuran and 1,4-butylene carbonate and the subsequent polymerization of the latter, or by the direct polymerization of **3f**, as indicated in eq 4, because a small amount of tetrahydrofuran was detected in the reaction mixture by ir and vpc measurements.



The reaction mixture of bis(tributyltin) pentamethylene glycolate (**1g**) and carbon disulfide showed a strong  $\nu_{C=S}$  band at about  $1200\text{ cm}^{-1}$ , but **1g** was recovered

(12) R. C. Mehrotra and V. D. Gupta, *J. Organometal. Chem.*, **4**, 145 (1965).

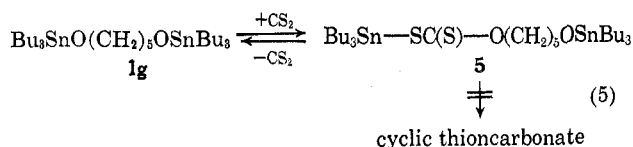
(13) R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

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

(15) D. L. Ailleston and A. G. Davies, *J. Chem. Soc.*, 2050 (1962).

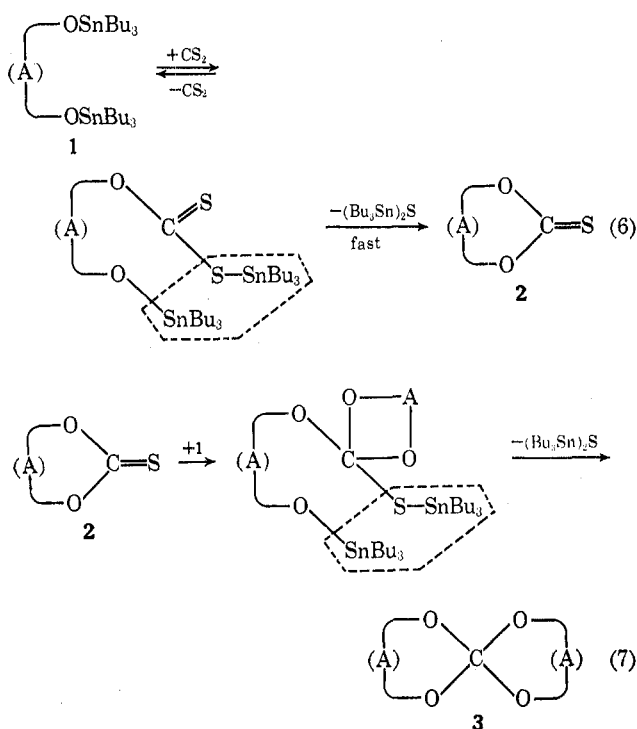
(16) A. G. Davies, P. R. Palan, and S. C. Vasishtha, *Chem. Ind. (London)*, 229 (1967).

by distillation, suggesting the reversible insertion reaction of carbon disulfide to the tin-oxygen bond (eq 5).



The same phenomena were observed in the reactions of tributyltin derivatives of pinacol and of diethylene glycol.

The above reaction (3) would be explained by addition-elimination mechanisms shown by eq 6 and 7. The formation of stable Sn-S-Sn bond might be a driving force in the reaction as in other desulfurization reactions,<sup>17-19</sup> and cyclization assisted by coordination would be an important factor, because 2 was formed only when carbon chain length in A was from two to four. The desulfurization reaction to give linear product did not occur at room temperature in the case of more than five-carbon chain length or bulky glycol unit in A.



This two-step mechanism in the formation of spiro orthocarbonates was confirmed by the fact that the reaction of ethylene or propylene thioncarbonate with another bis(tributyltin)alkylene glycolate in chloroform solution at room temperature afforded unsymmetrical spiro orthocarbonates in good yield, where thioncarbonate acted as a new type of acceptor molecule for the addition of organotin alkoxide, as was shown by eq 8. The results are listed in Table II.

(17) K. Itoh, I. K. Lee, I. Matsuda, S. Sakai, and Y. Ishii, *Tetrahedron Lett.*, 2640 (1967).

(18) K. Itoh, Y. Fukumoto, and Y. Ishii, *ibid.*, 3199 (1968).

(19) A. J. Bloodworth, A. G. Davies, and S. C. Vasishtha, *J. Chem. Soc., C*, 2640 (1968).

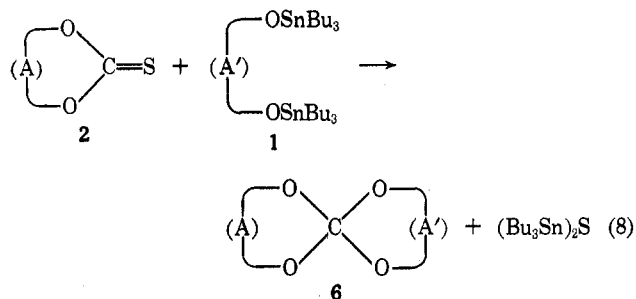


TABLE II

UNSYMMETRICAL SPIRO ORTHOCARBONATES  
PREPARED BY THE REACTION OF CYCLIC THIONCARBONATE WITH  
BIS(TRIBUTYLTIN) ALKYLENE GLYCOLATE IN CHLOROFORM

No.	A in cyclic thioncarbonate	A in $\text{Bu}_3\text{SnO}(\text{A})\text{OSnBu}_3$	Product yield, %
11	$(\text{CH}_2)_2$	$\text{CH}_2\text{CH}(\text{CH}_3)$	61 (6a)
12	$(\text{CH}_2)_2$	$(\text{CH}_2)_3$	82 (6b)
13	$(\text{CH}_2)_2$	$(\text{CH}_2)_4$	76 (6c)
14	$\text{CH}_2\text{CH}(\text{CH}_3)$	$(\text{CH}_2)_3$	86 (6d)
15	$\text{CH}_2\text{CH}(\text{CH}_3)$	$(\text{CH}_2)_4$	55 (6e)

### Experimental Section

**General.**—Melting points and boiling points are uncorrected. Elementary analyses were performed by the Analysis Center of Kyoto University. Ir and nmr (TMS as internal standard) were recorded on JASCO Model IR-S spectrometer, and on Japan Electron Optics Model JMN-MH60 spectrometer, respectively. Mass spectra were obtained by Japan Electron Optics Type JMS-OISG mass spectrometer. Vapor phase chromatography was carried out by a Yanagimoto Type GCG-5DH chromatograph with a column of Apiezon.

**Materials.**—All glycols and solvents were dried with sodium or calcium hydride and distilled before use. Tributyltin chloride, bis(tributyltin) oxide, and ethylene and propylene carbonates were commercially available and were distilled *in vacuo*.

**Bis(tributyltin) Alkylene Glycolates (1).** **Method A.**<sup>18</sup>—A mixture of ethylene carbonate (0.10 mol) and hexabutylstannoxane (0.12 mol) in 60 ml of toluene was allowed to reflux for 5–15 hr under nitrogen. After evaporation of toluene and excess amounts of distannoxane, vacuum distillation gave a 92.5% yield of bis(tributyltin) ethylene glycolate (1a), bp 185–188° (0.3 mm), and a 5.5% yield of 2-dibutylstanna-1,3-dioxolane, mp 223–224° (lit.<sup>20</sup> 223–227°).<sup>21</sup> Bis(tributyltin) 1,2-propylene glycolate was also prepared by this method, yield 92%, bp 180–182° (0.1 mm).

**Method B.**—This is a modification of Kula<sup>14</sup> and Davies' methods.<sup>5,22</sup> Disodium alkylene glycolate was obtained by refluxing a mixture of the glycol and 2 equiv of sodium metal in toluene for 2–5 hr, followed by the reaction with 2 equiv of tributyltin chloride at the refluxing temperature. After dilution with dry toluene, sodium chloride was separated by centrifuge, and the solution was fractionally distilled. Yields and boiling points of bis(tributyltin) 1,3-propylene, 1,4-butylene, 2,3-butylene, 2,3-dimethyl-2,3-butylene, 1,5-pentamethylene, and diethylene glycolates were 49, 46, 57, 35, 50, and 55%, and 195° (0.1 mm), 212° (0.1 mm), 195–204° (0.1 mm), 199° (0.1 mm), 223° (0.1 mm), and 217–218° (0.1 mm), respectively.

**Reaction of Bis(tributyltin) Ethylene Glycolate (1a) with  $\text{CS}_2$ .**—Bis(tributyltin) ethylene glycolate (86 mmol) and  $\text{CS}_2$  (170 mmol) were allowed to react in nitrogen at room temperature for 0.5–2 hr and distilled, giving 26% of bis(ethylene) orthocarbonate (3a) and 68.5% of ethylene thioncarbonate (2a).

(20) J. Pommier and J. Valade, *J. Organometal. Chem.*, **12**, 433 (1968).

(21) The stannadioxolane was formed during distillation.

(22) Distillation of the reaction product of trimethyltin chloride with sodium methoxide gave a mixture of trimethyltin methoxide and trimethyltin chloride,<sup>15</sup> while pure bis(tributyltin) alkylene glycolates were obtained by the distillation of the reaction mixture of tributyltin chloride with disodium alkylene glycolate, because the boiling points of 1a–1h were much higher than that of tributyltin chloride.

**3a:** needle crystals, bp (subln) 60–70° (0.5 mm), mp (CCl<sub>4</sub>) 143.0–143.5°; ir (CCl<sub>4</sub>) 1356, 1245, 1200, 1060 (strong), 1019, and 945 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>)  $\tau$  5.95 (s, 4, CH<sub>2</sub>O); mass spectrum (30 eV) *m/e* (relative intensity) 132 (92, molecular ion peak), 102 (100), 88 (86), 72 (89) 44 (91), and 30 (38). *Anal.* Calcd for C<sub>5</sub>H<sub>8</sub>O<sub>4</sub>: C, 45.46; H, 6.10. Found: C, 45.46; H, 6.09.

**2a:** plate crystal; bp 99° (0.3 mm); mp (CHCl<sub>3</sub>-CCl<sub>4</sub>) 1:10 51–52°; ir (CHCl<sub>3</sub>) 2985, 1375, 1155, 1015, and 955 cm<sup>-1</sup>; nmr (CHCl<sub>3</sub>)  $\tau$  5.23 (s, 4, CH<sub>2</sub>O); mass spectrum (30 eV) *m/e* (relative intensity) 104 (100, molecular ion peak), 60 (85), and 44 (45). *Anal.* Calcd for C<sub>3</sub>H<sub>4</sub>O<sub>2</sub>S: C, 34.61; H, 3.87; S, 30.79. Found: C, 34.89; H, 3.91; S, 30.69.

**Reaction of Bis(tributyltin) 1,2-Propylene Glycolate (1b) with CS<sub>2</sub>.**—The glycolate 1b (184 mmol) and CS<sub>2</sub> (920 mmol) were allowed to react in the same manner as mentioned above and distilled, giving 75% of bis(1,2-propylene) orthocarbonate (**3b**): bp 73° (2 mm); ir (CHCl<sub>3</sub>) 1225, 1195, 1051, and 1030 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\tau$  8.71 (d, 3, *J* = 6.6 Hz, CH<sub>3</sub>-C), 5.5–6.7 (ABCX<sub>3</sub> pattern, 3, OCH<sub>2</sub>CHO); molecular ion peak on mass spectrum (30 eV) *m/e* 160. *Anal.* Calcd for C<sub>7</sub>H<sub>12</sub>O<sub>4</sub>: C, 52.49; H, 7.55. Found: C, 52.51; H, 7.56. High-vacuum distillation of the residue gave 6% of 1,2-propylene thioncarbonate (**2b**): bp 78° (0.1 mm); ir (CHCl<sub>3</sub>) 1485, 1355, 1295, 1175, and 988 cm<sup>-1</sup>; nmr (CHCl<sub>3</sub>)  $\tau$  8.43 (d, 3, *J* = 6.0 Hz, CH<sub>3</sub>-C), 4.9–5.85 (ABCX<sub>3</sub> pattern, 3, OCH<sub>2</sub>CHO); molecular ion peak on mass spectrum (30 eV) *m/e* 118. *Anal.* Calcd for C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>S: C, 40.66; H, 5.12. Found: C, 41.01; H, 5.27.

**Reaction in Toluene.**—A mixture of 0.2 mol of propylene carbonate, 0.25 mol of hexabutylstannoxane, and 100 ml of dry toluene was refluxed for 10 hr with stirring; then an additional 100 ml of toluene and 1.05 mol of CS<sub>2</sub> were added and the mixture was stirred for 1 hr, and 66% of **2b** and 25% of **3b** were obtained by distillation.

**Reaction of Bis(tributyltin) 2,3-Butylene Glycolate (1c) with CS<sub>2</sub>.**—The glycolate 1c (41 mmol) and 200 mmol of CS<sub>2</sub> were allowed to react without solvent in the same manner, as mentioned above, giving 32% of bis(2,3-butylene) orthocarbonate (**3c**): bp 86° (3.5 mm); ir (CCl<sub>4</sub>) 1380, 1200, 1080, and 1060 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)<sup>23</sup>  $\tau$  8.86 (d, 12  $\times$  70%, *J* = 6.1 Hz, *cis*-CH<sub>3</sub>CH), 8.76 (d, 12  $\times$  30%, *J* = 6.1 Hz, *trans*-CH<sub>3</sub>CH), 6.05–6.35 (m, 4  $\times$  30%, *trans*-CH<sub>3</sub>CH), and 5.62–5.87 (m, 4  $\times$  70%, *cis*-CH<sub>3</sub>CH); molecular ion peak on mass spectrum (30 eV) *m/e* 188; the sample was not analytically pure.<sup>24</sup>

Further distillation of the residue gave 56% of **2c**: bp 115° (3 mm); ir (CCl<sub>4</sub>) 1460, 1320, 1280, 1185, 1135, 1060, and 913 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\tau$  8.56 (d, 6  $\times$  70%, *J* = 6.3 Hz, *cis*-CH<sub>3</sub>CH), 8.46 (d, 6  $\times$  30%, *J* = 6.3 Hz, *trans*-CH<sub>3</sub>CH), *ca.* 5.35 (m, 2  $\times$  30%, *trans*-CH<sub>3</sub>CH), and 4.75–5.00 (m, 2  $\times$  70%, *cis*-CH<sub>3</sub>CH); molecular ion peak on mass spectrum (30 eV) *m/e* 132. *Anal.* Calcd for C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>S: C, 45.43; H, 6.10. Found: C, 45.70; H, 6.39.

**Reaction of Bis(tributyltin) 1,3-Propylene Glycolate (1e) with CS<sub>2</sub>.**—The glycolate 1e (49 mmol) was allowed to react with CS<sub>2</sub> (200 mmol), giving only one product, bis(1,3-propylene) orthocarbonate (**3e**): 65%; bp (subln) 90° (0.06 mm); mp (*n*-hexane) 132–133°; ir (CHCl<sub>3</sub>) 1145, 1120, 1100, and 915 cm<sup>-1</sup>; nmr (CHCl<sub>3</sub>)  $\tau$  5.97 (t, 8, *J* = 5.4 Hz, CH<sub>2</sub>O) and 8.24 (q, 4, *J* = 5.4 Hz, CH<sub>2</sub>CH<sub>2</sub>O); parent peak on mass spectrum (35 eV) *m/e* 160. *Anal.* Calcd for C<sub>7</sub>H<sub>12</sub>O<sub>4</sub>: C, 52.49; H, 7.55. Found: C, 52.58; H, 7.44.

**Reaction of Bis(tributyltin) 1,4-Butylene Glycolate (1f) with CS<sub>2</sub>.**—Carbon disulfide (198 mmol) and 1f (46 mmol) were mixed, and distillation, at first, gave a trace of tetrahydrofuran in a cold trap, which was detected by the comparisons of the ir and vpc with the authentic sample; thereafter bis(1,4-butylene) orthocarbonate (**3f**) was isolated by vacuum distillation.

**3f:** yield 29%; bp (subln) 110° (0.1 mm); mp (*n*-hexane) 109–110°; ir (CCl<sub>4</sub>) 1145, 1105, 1055, and 970 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\tau$  6.38 (m, 8, OCH<sub>2</sub>CH<sub>2</sub>) and 8.40 (m, 8, OCH<sub>2</sub>CH<sub>2</sub>); molecular ion peak on mass spectrum (35 eV) *m/e* 188. *Anal.* Calcd for C<sub>8</sub>H<sub>16</sub>O<sub>4</sub>: C, 57.43; H, 8.59. Found: C, 57.23; H, 8.60.

The distillation residue was diluted with *n*-hexane to precipitate the polymer, which was separated by filtration and showed a strong  $\nu_{C-O}$  band at 1750 cm<sup>-1</sup> in the ir spectrum;  $\tau$  5.83 (broad, 4, CH<sub>2</sub>-O) and 8.24 (broad, 4, CH<sub>2</sub>CH<sub>2</sub>O) in the nmr spectrum; on the hydrolysis, 1,4-glycol and CO<sub>2</sub> were formed, suggesting the polycarbonate structure of **4**. The polymer yield was about 45%.

Evaporating *n*-hexane from the filtrate, bis(tributyltin) sulfide was obtained in 93% yield, which was identified by the comparison of the ir spectrum with that of an authentic sample.

**Reaction of Bis(tributyltin) 1,5-Pentamethylene Glycolate (1g) with CS<sub>2</sub>.**—The glycolate 1g reacted with excess CS<sub>2</sub> at room temperature in nitrogen, and the ir spectrum of the reaction mixture showed a band  $\nu_{C-S}$  at 1200 cm<sup>-1</sup>, suggesting the formation of the xanthate structure **5**. Thereafter the reaction mixture was refluxed for 90 min, and its ir spectrum had no band assigned to cyclic or linear thioncarbonate. Vacuum distillation of the product afforded 1g in good yield.

**Reaction of Bis(tributyltin)  $\alpha,\omega$ -Diethylene Glycolate (1h) with CS<sub>2</sub>.**—The glycolate 1h was mixed with excess amounts of CS<sub>2</sub> at room temperature in nitrogen and showed a  $\nu_{C-S}$  band at 1190 cm<sup>-1</sup> in the ir spectrum and downfield shifts from  $\tau$  6.21 (t, 4, *J* = 5.0 Hz, SnOCH<sub>2</sub>) and 6.57 (t, 4, *J* = 5.0, CH<sub>2</sub>OCH<sub>2</sub>) to 5.43 (broad, 4, SnSC(S)OCH<sub>2</sub>) and 6.19 (broad, 4, CH<sub>2</sub>OCH<sub>2</sub>) in the nmr spectrum, suggesting the insertion reaction of CS<sub>2</sub> into the Sn-O bond. Then the reaction mixture was refluxed for 1 hr and distilled; compound 1h was recovered quantitatively.

**Reaction of Bis(tributyltin) 2,3-Dimethyl-2,3-butylene Glycolate (1d) with CS<sub>2</sub>.**—The glycolate 1d was refluxed in excess amounts of CS<sub>2</sub> for 1 hr and distilled, giving the starting material 1d only.

**Preparation of Unsymmetrical Spiro Orthocarbonates.**—Bis(tributyltin) alkylene glycolate and an equimolar amount (20 mmol) of ethylene or propylene thioncarbonate (dissolved in dry chloroform) were mixed at room temperature in dry nitrogen and distilled to afford unsymmetrical spiro orthocarbonate.

**Ethylene 1,2-propylene orthocarbonate (6a)** was obtained in 61% yield from **2a** and **1b**: bp 87° (7 mm); ir (CCl<sub>4</sub>) 2986, 2906, 1230, 1197, 1053, 1023, and 945 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\tau$  6.00 (s, 4, OCH<sub>2</sub>), 8.74 (d, 3, *J* = 6.1 Hz, CH<sub>3</sub>CH), and 5.36–6.65 (m, 3, CH<sub>2</sub>CHO). *Anal.* Calcd for C<sub>6</sub>H<sub>10</sub>O<sub>4</sub>: C, 49.31; H, 6.90. Found: C, 49.30; H, 6.80.

**Ethylene 1,3-propylene orthocarbonate (6b)** was prepared in 82% yield from **2a** and **1e**: bp 68° (1.0 mm); ir (CHCl<sub>3</sub>) 1155, 1080, 1028, 948, and 927 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\tau$  6.04 (s, 4, OCH<sub>2</sub>), 6.02 (t, 4, *J* = 6.0 Hz, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), and 8.32 (quintet, 2, *J* = 6.0 Hz, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O). *Anal.* Calcd for C<sub>6</sub>H<sub>10</sub>O<sub>4</sub>: C, 49.31; H, 6.90. Found: C, 49.01; H, 7.00.

**Ethylene 1,4-butylene orthocarbonate (6c)** was prepared in 76% yield from **2a** and **1f**: bp 76–77° (2.5 mm); ir (CCl<sub>4</sub>) 2964, 2904, 1190, 1080, 994, and 945 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\tau$  6.04 (s, 4, OCH<sub>2</sub>), 6.27 (broad, 4, OCH<sub>2</sub>CH<sub>2</sub>), and 8.34 (broad, 4, OCH<sub>2</sub>CH<sub>2</sub>). *Anal.* Calcd for C<sub>7</sub>H<sub>12</sub>O<sub>4</sub>: C, 52.49; H, 7.55. Found: C, 52.60; H, 7.71.

**1,2-Propylene 1,3-propylene orthocarbonate (6d)** was obtained in 86% yield from **2b** and **1e**: bp 70° (5 mm); ir (CCl<sub>4</sub>) 2964, 2884, 1210 1160, 1075, 1042, and 930 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\tau$  8.72 (d, 3, *J* = 6.1 Hz, CH<sub>3</sub>CH) 8.34 (quintet, 2, *J* = 6.1 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 5.98 (t, 4, *J* = 6.1 Hz, OCH<sub>2</sub>CH<sub>2</sub>), and 5.48–6.59 (ABCX<sub>3</sub> pattern, 3, OCH<sub>2</sub>CHO). *Anal.* Calcd for C<sub>7</sub>H<sub>12</sub>O<sub>4</sub>: C, 52.48; H, 7.55. Found: C, 52.46; H, 7.69.

**1,2-Propylene 1,4-butylene orthocarbonate (6e)** was prepared in 55% yield from **2b** and **1f**: bp 83° (2.7 mm); ir (CCl<sub>4</sub>) 2965, 1185, 1075, and 1005 cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\tau$  8.75 (d, 3, *J* = 6.2 Hz, CH<sub>3</sub>C), 8.35 (broad, 4, OCH<sub>2</sub>CH<sub>2</sub>C), 6.30 (broad, 4, OCH<sub>2</sub>CH<sub>2</sub>C), and 5.67–6.67 (ABCX<sub>3</sub> pattern, 3, OCH<sub>2</sub>CHO). *Anal.* Calcd for C<sub>8</sub>H<sub>14</sub>O<sub>4</sub>: C, 55.16; H, 8.10. Found: C, 55.46; H, 8.31.

**Registry No.**—Carbon disulfide, 75-15-0; **1c**, 24471-92-9; **1d**, 24471-93-0; **1e**, 24471-90-7; **1f**, 24471-91-8; **1g**, 24471-94-1; **1h**, 24471-95-2; **2a**, 20628-59-5; **2b**, 13303-26-9; **2c**, 24471-98-5; **3a**, 24471-99-6; **3b**, 24472-00-2; **3c**, 24472-01-3; **3e**, 24472-02-4; **3f**, 24472-03-5; **6a**, 24472-04-6; **6b**, 24472-05-7; **6c**, 24472-06-8; **6d**, 24472-07-9; **6e**, 24472-08-0.

(23) The mixed 2,3-butylene glycol (*erythro:threo* = 7:3) was used in the preparation of **1e**, from which a mixture of *cis*- and *trans*-2,3-butylene thioncarbonate (**2e**) or spiro orthocarbonate **3e** was formed, giving a complex nmr spectrum.

(24) A weak band of carbonate at 1820 cm<sup>-1</sup> was observed, as a spiro orthocarbonate having a tertiary alkoxyl group was found to be decomposed to cyclic carbonate and epoxide.