Reaction of Dialkyltin Dialkoxides with Carbon Disulfide at Higher Temperature. Preparation of Orthocarbonates[1]

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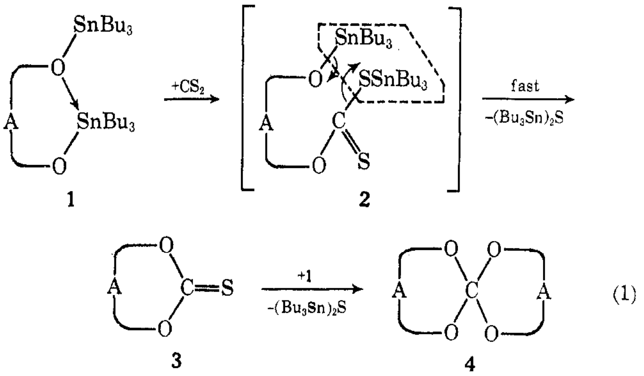
Received April 13, 1970

Five- and six-membered cyclic dibutyltin dialkoxides, except 4,4,5,5-tetramethyl-2-dibutylstanna-1,3-dioxolane, reacted with carbon disulfide at about 100–110° to give quantitatively five- and six-membered spiro orthocarbonates, respectively, along with dibutyltin sulfide. Seven-membered cyclic dibutyltin dialkoxide reacted with carbon disulfide at room temperature to form the inserted product of carbon disulfide to the tin–oxygen bond, which was converted at 50° to the corresponding spiro orthocarbonate and its decomposition products. Acyclic dibutyltin and dioctyltin dialkoxides derived from primary C_1–C_6 alcohols reacted with carbon disulfide giving good yields of tetraalkyl orthocarbonates, while the dialkoxides from secondary and tertiary alcohols gave dialkyl carbonates and olefin, respectively.

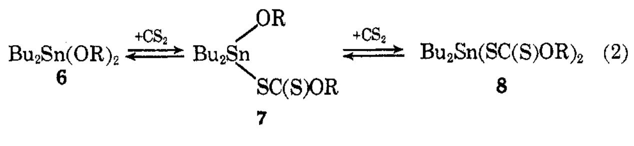
In our previous paper[2] a novel synthesis of spiro orthocarbonate and cyclic thioncarbonate from the reaction of bis(tributyltin) alkylene glycolate (**1**) with carbon disulfide at room temperature was reported (eq 1).



(1)

The formation of thioncarbonates and orthocarbonates from the reaction of carbon disulfide with the linear dialkoxides **1**, where the addition products **2** could not be detected even spectrometrically, exhibits a striking contrast to the reversible addition reaction of carbon disulfide with tributyltin monoalkoxide to give *O*-alkyl *S*-tributyltin dithiocarbonate.[3] This difference could be ascribed to the cyclization tendency assisted by coordination of a sulfur atom to a tributyltin group in the intermediate adduct **2**.

In 1967 Davies and Harrison found that the reaction of dibutyltin dimethoxide (**6**, R = Me) with carbon disulfide took place very fast at room temperature, affording *S*-dibutyl(methoxy)tin *O*-methyl dithiocarbonate (**7**, R = Me) and *S*-dibutyltin bis(*O*-methyl dithiocarbonate) (**8**, R = Me) (eq 2).[4]



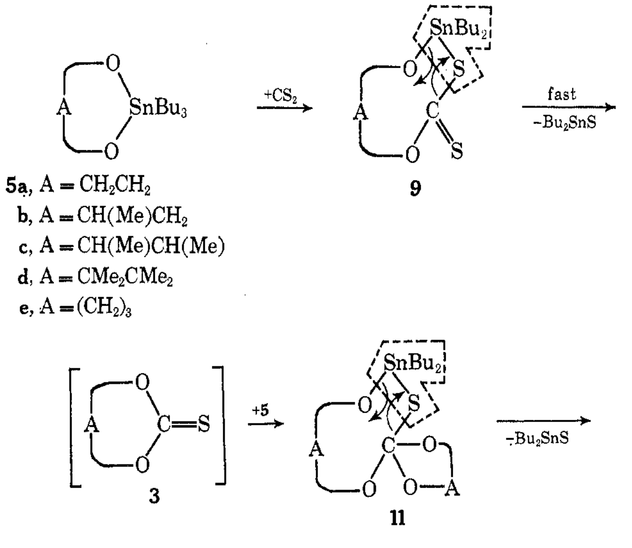
$$\underset{\mathbf{6}}{Bu_2Sn(OR)_2} \overset{+CS_2}{\rightleftharpoons} \underset{\mathbf{7}}{Bu_2Sn\begin{smallmatrix} OR \\ SC(S)OR \end{smallmatrix}} \overset{+CS_2}{\rightleftharpoons} \underset{\mathbf{8}}{Bu_2Sn(SC(S)OR)_2} \quad (2)$$

We confirmed their results in the reaction of carbon disulfide with dialkyltin dialkoxides at room temperature. However, when the reactions were carried out in a glass autoclave at higher reaction temperatures than the boiling point of carbon disulfide, orthocarbonates or their decomposition products were obtained in excellent yields.

Hitherto, orthocarbonates have been prepared from sodium alkoxides and chloropicrin or thiocarbonylperchloride (Cl_3CSCl) through troublesome reaction steps.[5,6] In this publication the reactions of carbon disulfide with both cyclic and acyclic dialkoxides having an O–Sn–O bond were studied extensively for the purpose of establishing a novel preparative method for orthocarbonates from the dialkyltin dialkoxides which were easily obtained from dialkyltin dichloride or oxide.

Results and Discussion

Reaction of Cyclic Dibutyltin Dialkoxides.—Cyclic dibutyltin dialkoxide (**5**) and carbon disulfide reacted at 100–110° in ethylene dichloride in a glass autoclave to give spiro orthocarbonate and dibutyltin sulfide in good yields (eq 3). The reaction conditions and the yields of the products are summarized in Table I.



5a, A = CH_2CH_2
b, A = $CH(Me)CH_2$
c, A = $CH(Me)CH(Me)$
d, A = CMe_2CMe_2
e, A = $(CH_2)_3$

4a, A = CH_2CH_2
b, A = $CH(Me)CH_2$
c, A = $CH(Me)CH(Me)$ (3)
d, A = CMe_2CMe_2
e, A = $(CH_2)_3$

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[1] Taken in part from our preliminary report in *Chem. Commun.*, 235 (1970).

[2] S. Sakai, Y. Kiyohara, K. Itoh, and Y. Ishii, *J. Org. Chem.*, **35**, 2347 (1970).

[3] A. J. Bloodworth, A. G. Davies, and S. C. Vasistha, *J. Chem. Soc. C*, 1309 (1967).

[4] A. G. Davies and P. G. Harrison, *ibid.*, 1313 (1967).

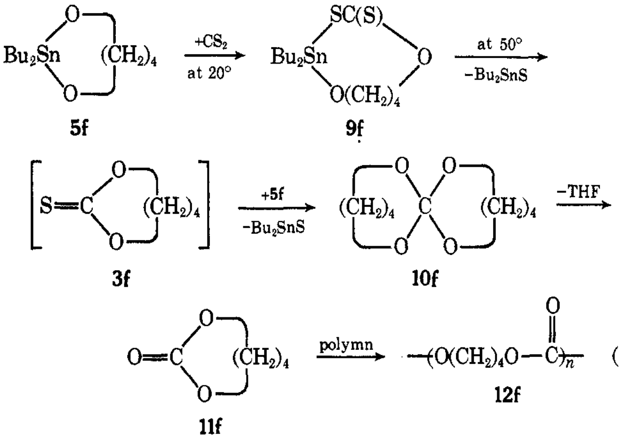
[5] J. D. Roberts and R. E. McMashon, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 457.

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

Five- and six-membered[7] cyclic dialkoxides, **5a–e**, can be readily prepared by several methods[8–14] and are relatively stable against moisture in the air, so the reaction of **5a**, **5b**, **5c**, and **5e** with carbon disulfide at higher reaction temperature will be a convenient synthetic method for five- and six-membered spiro orthocarbonates. The spiro orthocarbonates **4a** and **4e** are stable and volatile solids, but **4b** and **4c** are relatively unstable liquids which were partially decomposed to the carbonates even when they were stored in sealed glass tubes at room temperature for 2 months. Cyclic dialkoxide **5d** reacted only slightly with carbon disulfide at 125° for 20 hr and was recovered from the reaction mixture in a 92% yield along with small amounts of a low boiling product which showed a strong $\nu_{C=O}$ band at 1790 cm^{-1} and the same retention time as that of the authentic sample of 2,3-dimethyl-2,3-butylene carbonate in the vapor phase chromatography. The carbonate would be presumably formed by the decomposition of the orthocarbonate **4d** as was reported in our previous papers.[1,15] Remarkable contrast between **5c** and **5d** in their reactivities could be attributed to a steric effect of methyl groups on the formation of spiro orthocarbonates, which was also observed in the case of the linear dialkoxide **1**.[1]

The reaction scheme (eq 3) would be a reasonable one, similar to eq 1 in the case of the linear dialkoxide, but in the reaction of the cyclic dialkoxide **5**, thioncarbonate **3** could not be detected even by ir and nmr spectroscopies, probably due to the higher reaction temperature employed which would accelerate further reaction of thioncarbonate with **5** to form spiro orthocarbonate. Moreover, in the case of **5a–e**, the inserted products **9** could not be detected in the reaction mixture at any temperature.

Contrary to the reaction of five- and six-membered cyclic dialkoxides, a seven-membered cyclic dialkoxide, 1,3-dioxa-2-dibutylstannacycloheptane (**5f**), reacted very rapidly at room temperature, and the reaction mixture showed the ir absorption bands at 1050 and 1175 cm^{-1} which would be assigned to dithiocarbonate structure in the inserted product **9f** in eq 4. Subsequent heating of **9f** at 50° for 2 hr gave a 37% yield of bis(1,4-butylene) orthocarbonate (**10f**), a 62% yield of poly(1,4-butylene carbonate), mp 141–153°, and trace amounts of tetrahydrofuran. The reaction course from the spiro compound **10f** to the polymer **12f** was confirmed by the redistillation of **10f** in the presence of dibutyltin sulfide to give **12f**.

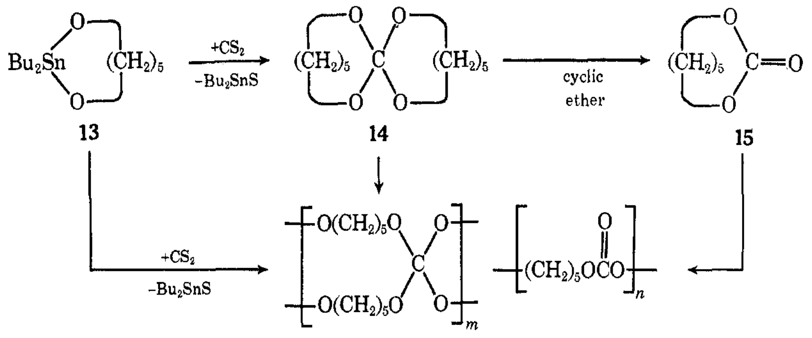


(4)

The seven-membered spiro orthocarbonate **10f** is relatively unstable due to its ring strain in the two seven-membered rings and is decomposed to tetrahydrofuran and 1,4-butylene carbonate (**11f**), the latter polymerizing easily to give the polycarbonate **12f**.

As mentioned above, a remarkable contrast exists between the reactivity of the seven-membered cyclic dialkoxide **5f** and of the five- and six-membered cyclic dialkoxides **5a–e**. Pommier and Valade[7b] reported that the liquid seven-membered cyclic dialkoxide is monomeric, while the solid five- and six-membered cyclic dialkoxides are dimeric even in dilute solution. Therefore, the association degree of cyclic dialkoxides would be conceivable to be a dominating factor in their reactivities; monomeric dialkoxide can react more readily than dimeric one.

The attempt to prepare the eight-membered spiro orthocarbonate **14**, or the cyclic carbonate **15**, in eq 5 was unsuccessful. The reaction of the eight-membered cyclic dialkoxide **13** gave dibutyltin sulfide and an insoluble polymer of a net structure **16** having orthocarbonate and carbonate segments which would be formed



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[7] (a) Five- and six-membered cyclic dialkoxides exist mainly as dimeric forms in solution, but, in this paper, they are conventionally depicted as monomeric forms. Dimer–monomer equilibrium was discussed by Pommier and Valade.[7b] (b) J. Pommier and J. Valade, *J. Organometal. Chem.*, **12**, 433 (1968).

[8] S. Sakai, Y. Fujimura, and Y. Ishii, *J. Org. Chem.*, **35**, 2344 (1970).

[9] H. E. Remsden and C. K. Banks, U. S. Patent 2,789,994 (1957); *Chem. Abstr.*, **51**, 14786 (1957).

[10] J. Bornstein, B. R. La Liberter, T. M. Andrews, and J. C. Montermoso, *J. Org. Chem.*, **24**, 886 (1959).

[11] W. J. Considine, *J. Organometal. Chem.*, **5**, 263 (1966).

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

[13] R. K. Ingham and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

[14] Cyclic dialkoxide must be completely dried to avoid the hydrolysis of the orthocarbonate formed: *e.g.*, powdered dialkoxide was heated at 150° *in vacuo* (1 mm). Some spiro orthocarbonates are volatile solids or liquids at room temperature; so care should be taken, especially in the drying procedure.

[15] S. Sakai, Y. Asai, Y. Kiyohara, K. Itoh, and Y. Ishii, *Organometal. Chem. Syn.*, **1**, 45 (1970).

TABLE I
REACTION PRODUCTS FROM CYCLIC DIBUTYLTIN DIALKOXIDES AND CARBON DISULFIDE IN ETHYLENE DICHLORIDE

A in cyclic dialkoxide	Reaction condition Temp, °C	Time, hr	Yields of spiro orthocarbonate, %
CH_2CH_2 (**5a**)	105	10	82 (**4a**)
$CH_2CH(CH_3)$ (**5b**)	105	10	87 (**4b**)
$CH(CH_3)CH(CH_3)$ (**5c**)	110	10	90 (**4c**)
$C(CH_3)_2C(CH_3)_2$ (**5d**)	125	20	0[a]
$(CH_2)_3$ (**5e**)	105	10	92 (**4e**)
$(CH_2)_4$ (**5f**)	50	2[c]	37 (**4f**)[b]
$(CH_2)_5$ (**13**)	105	3	0[d]

[a] Trace amounts of 2,3-dimethyl-2,3-butylene carbonate were formed. [b] The polycarbonate **12f** was formed in 62% yield. [c] Without solvent. [d] The polymer **16** was obtained.

TABLE II
REACTION PRODUCTS FROM $R'_2Sn(OR)_2$ AND CARBON DISULFIDE

Dialkoxide used		Reaction condition		
R'	R	Temp, °C	Time, hr	Products and yields, %
Bu	CH_3 (**6a**)	100	10	$C(OCH_3)_4$ (**18a**), 95
Bu	C_2H_5 (**6b**)	96	5	$C(OC_2H_5)_4$ (**18b**), 80
Bu	*n*-C_3H_7 (**6c**)	120	20	C(O-*n*-$C_3H_7)_4$ (**18c**), 86
Bu	*i*-C_3H_7 (**6d**)	120	20	O=C(O-*i*-$C_3H_7)_2$ (**19d**), 90
Bu	*tert*-C_4H_7 (**6e**)	120	20	$CH_2=C(CH_3)_2$, *ca.* 80
Bu	*n*-C_4H_7 (**6f**)	120	20	C(O-*n*-$C_4H_9)_4$ (**18f**), 85
Bu	*n*-C_8H_{17} (**6g**)	120	20	C(O-*n*-$C_8H_{17})_4$ (**18g**), *a*
Oct	*n*-C_6H_{13} (**6h**)	120	20	C(O-*n*-$C_6H_{13})_4$ (**18h**), 49[b]
Oct	*n*-C_8H_{17} (**6i**)	120	20	O=C(O-*n*-$C_8H_{17})_2$ (**19g**), 80[a]

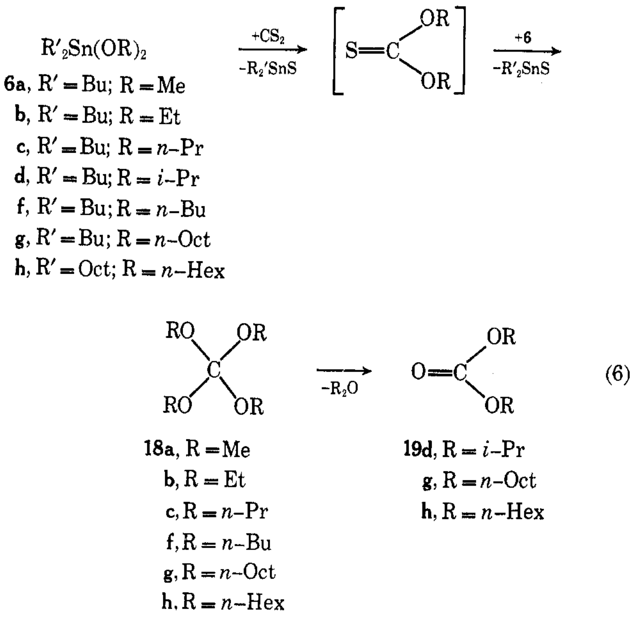
[a] The orthocarbonate, **18g**, was formed but decomposed on the distillation to give the carbonate **19g**. [b] The decomposition product from **18h**, *i.e.*, **19h**, was also obtained in 20% yield.

directly from **13** or indirectly *via* the intermediates **14** and **15**.

Reactions of Acyclic Dialkyltin Dialkoxides.—Dibutyltin diethoxide (**6b**) reacted with excess amounts of carbon disulfide at room temperature giving the insertion products **7** and **8** (R = Et in eq 2), as was reported by Davies and Harrison.[4] However, at higher reaction temperature we obtained tetraethyl orthocarbonate and dibutyltin sulfide in quantitative yields. Tetraalkyl orthocarbonates, **18a**, **18b**, **18c**, **18f**, and **18g**, were formed in good yields in the reaction of carbon disulfide with dibutyltin di(primary)alkoxides, **6a**, **6b**, **6c**, **6f**, and **6g**, respectively, at 110–120° for 5–20 hr. These results are tabulated in Table II.

In the reaction of dibutyltin dialkoxide from *n*-hexyl or *n*-octyl alcohol with carbon disulfide at 120°, the formation of the orthocarbonate was confirmed by a strong ν_{CO} band at 1120 cm^{-1} and a nmr peak at about τ 6.4 of methylene oxy group in the spectra of the reaction mixture. However, on distillation the mixture of dibutyltin sulfide and the orthocarbonate or its decomposition products was obtained. Column chromatographic separation was unsuccessful because the orthocarbonate was hydrolyzed in the column to afford the carbonate.

Dioctyltin dihexoxide (**6h**) reacted also with carbon disulfide at 120° for 20 hr to form tetrahexyl orthocarbonate from which the orthocarbonate **18h** (49% yield) and its decomposition product, dihexyl carbonate **19h** (20% yield), were obtained on the distillation. Dioctyltin dioctoxide (**6i**) was allowed to react with carbon disulfide under the same reaction condition and tetraoctyl orthocarbonate (**18g**) was formed, but dioctyl carbonate **19g** was only obtained as a decomposed product in 80% yield by distillation (eq 6).



6a, R' = Bu; R = Me
b, R' = Bu; R = Et
c, R' = Bu; R = *n*–Pr
d, R' = Bu; R = *i*–Pr
f, R' = Bu; R = *n*–Bu
g, R' = Bu; R = *n*–Oct
h, R' = Oct; R = *n*–Hex

(6)

18a, R = Me
b, R = Et
c, R = *n*–Pr
f, R = *n*–Bu
g, R = *n*–Oct
h, R = *n*–Hex

19d, R = *i*–Pr
g, R = *n*–Oct
h, R = *n*–Hex

In contrast to the reaction of a dibutyltin primary dialkoxide, such as di-*n*-propoxide **6c**, the reaction of dibutyltin diisopropoxide with carbon disulfide under the same reaction condition (at 120° for 20 hr) afforded diisopropyl carbonate in a 90% yield (based on eq 6), probably because the secondary orthocarbonate is so thermally unstable that it is decomposed. Dibutyltin di-*tert*-butoxide did not react completely at 100° for 20 hr, and a mixture of the starting dialkoxide and isobutene was obtained. In the reaction with carbon disulfide at 120° for 20 hr, tetra-*n*-butyl orthocarbonate (**18f**) was formed from dibutyltin di-*n*-butoxide (**6f**), while isobutene was obtained in about 80% yield from dibutyltin di-*tert*-butoxide (**6e**) (eq 7).

$$\begin{tikzcd}
\underset{\textbf{6e}}{Bu_2Sn(tert\text{-}OBu)_2} \arrow[r, "+CS_2", "-Bu_2SnS"'] & \underset{\textbf{17e}}{[S{=}C(tert\text{-}OBu)_2]} \arrow[r, "+\textbf{6e}", "-Bu_2SnS"'] \arrow[d, "-COS"] & \underset{\textbf{18e}}{[C(tert\text{-}OBu)_4]} \arrow[d, "tert\text{-}OBu_2"] \\
& CH_2{=}CMe_2 & {[O{=}C(tert\text{-}OBu_2)_2]} \arrow[l, "-CO_2, H_2O"]
\end{tikzcd} \qquad (7)$$

The evolution of a gas containing isobutene and carbonyl sulfide was observed, and isobutene was formed from the decomposition of the thioncarbonate **17e**. However, small amounts of carbon dioxide were found in the reaction mixture; so the formation of isobutene *via* the orthocarbonate **18e** was undeniable.

Experimental Section

General.—Melting and boiling points were uncorrected. Microanalyses were performed by the Analysis Centre of Kyoto University. Ir and nmr (TMS as an internal standard) were recorded on a JASCO Model IR-S spectrometer and on a Japan Electron Optics Laboratory Co., Model JMN-MH60 spectrometer, respectively. Vapor phase chromatography was carried out on a Yanagimoto Manufacturing Co., Ltd., Type GCG-5DH chromatograph using an Apiezon column.

Materials.—All alcohols, glycols, and toluene were dried with sodium metal or calcium hydride and distilled before use. Carbon disulfide and 1,2-dichloroethane were dried over phosphorus pentoxide and distilled. Dibutyltin and dioctyltin chloride were purified, but dibutyltin oxide of industrial grade was used without any purification.

Cyclic dialkoxides were prepared from the glycols and dialkyltin dichloride,[9] dimethoxide,[11,12] or oxide,[10] and were strictly dried.[14] Their melting points were as follows: **5a**, 224–226°; **5b**, 183–185°; **5c**, 119–121°; and **5e** 86–88°. Boiling points of **5d**, **5f**, and **13** were 188–189° (0.1 mm), 177–178° (0.6 mm), and 165–175° (0.5 mm), respectively. Dibutyltin dimethoxide, diethoxide, di-*n*- or -isopropoxide, and di-*n*- or -*tert*-butoxide were prepared from dibutyltin dichloride and sodium alkoxides in excess amounts of the corresponding alcohols by the common method.[13] Their boiling points were as follows: **6a**, 131–132° (0.3 mm); **6b**, 115–120° (0.2 mm); **6c**, 119–121° (0.25 mm); **6d**, 81–85° (0.15 mm); **6e**, 152–154° (27 mm); **6f**, 125–127° (0.1 mm); and **6g**, 173–175° (0.4 mm), respectively. Dioctyltin dihexoxide (**6h**) and octaoxide (**6i**) were prepared by a trans-alcoholysis reaction of dioctyltin dimethoxide with equimolar amounts of the corresponding alcohol by heating to 150° *in vacuo* and were used as starting materials in the reactions with carbon disulfide without further purification, because these dialkoxides were decomposed on the distillations.[16]

Reaction of the Cyclic Dialkoxide 5a with CS_2.—Powder of **5a** (8.7 g, 30 mmol), ethylene dichloride (40 ml), and excess amounts of CS_2 (5 ml) were introduced into a glass autoclave equipped with a mechanical stirrer and gauge, and the mixture was heated for 10 hr in a oil bath kept at 100–110°. The reaction was heterogeneous in the initial stage but became a clear solution after several hours. Nitrogen atmosphere was not applied in the autoclave, because dimeric dialkoxide is relatively stable against moisture. The reaction pressure was about 1.5–3.0 kg/cm^2. After evaporation of excess amounts of CS_2 and the solvent, a large quantity of *n*-hexane was added to the reaction mixture to precipitate bis(ethylene) orthocarbonate (**4a**): yield 82%; mp (toluene) 143–144° (lit.[2] 143.0–143.5°); the ir and nmr spectra coincided well with those of an authentic sample prepared in a previous paper.[2] Dibutyltin sulfide was obtained in a 94% yield by the distillation of the filtrate.

Reaction of the Cyclic Dialkoxide 5b with CS_2.—The cyclic dialkoxide **5b** was allowed to react with CS_2 at 105° for 10 hr analogously, and the distillation gave an 87% yield of bis(1,2-propylene) orthocarbonate (**4b**): bp 71–73° (2 mm) [lit.[2] 73° (2 mm)]; the ir and nmr spectra were the same as those reported in the previous paper.[2] The orthocarbonate **4b** was stored in a sealed glass tube, but it showed a strong carbonyl band which was assigned to the carbonyl group of 1,2-propylene carbonate by comparison of the retention time and the ir and nmr spectra of the decomposed product with those of an authentic sample.

Reaction of the Cyclic Dialkoxide 5c with CS_2.—The cyclic dialkoxide **5c** was allowed to react with CS_2 at 110° for 10 hr as was mentioned above, and distillation of the reaction mixture gave the spiro orthocarbonate **4c** in a 90% yield. The ir and nmr spectra of the product were the same as those reported in our previous paper.[2]

Reaction of the Cyclic Dialkoxide 5d with CS_2.—The cyclic dialkoxide **5d** (20 mmol) and CS_2 (5 ml) were allowed to react at 110° for 10 hr in ethylene dichloride (40 ml) in an autoclave, but no reaction occurred. Further heating of the mixture at 125° for 20 hr and vacuum distillation gave small amounts of low boiling product in a cold trap which showed a strong $\nu_{C=O}$ band at 1790 cm^{-1} and the same retention time as that of the authentic 2,3-dimethyl-2,3-butylene carbonate. The unreacted dialkoxide **5d** was recovered in a 92% yield on distillation of the residue.

Reaction of the Cyclic Dialkoxide 5e with CS_2.—The cyclic dialkoxide **5e** was allowed to react with CS_2 at 105° for 10 hr in ethylene dichloride, and the reaction mixture was refrigerated and filtrated to give a 92% yield of crude bis(1,3-propylene) orthocarbonate (**4e**) which was sublimated and recrystallized, mp (CCl_4–*n*-hexane) 132–133° (lit.[2] 132–133°). The distillation of the filtrate gave a 95% yield of dibutyltin sulfide.

Reaction of the Cyclic Dialkoxide 5f with CS_2.—The cyclic dialkoxide **5f** (20 mmol) was added to 5 ml of CS_2 under nitrogen at room temperature. The reaction mixture showed strong ir bands at 1175 and 1050 cm^{-1}, suggesting the formation of the inserted product **9f**. Subsequent heating of the mixture at 50° for 2 hr and distillation gave a 37% yield of bis(1,4-butylene) orthocarbonate (**10f**): bp (with sublimination) 80° (0.1 mm); mp (toluene) 109–110° (lit.[2] 109–110°); ir and nmr spectra coincided well with those of the authentic sample.[2] The tetrahydrofuran formed was detected by ir spectroscopic and gas chromatographic measurements of the condensed product in a cold trap of the distillation.

Large amounts of *n*-hexane were added to the distillation residue to precipitate the polymer formed, **12f**, mp about 141–153°, which showed a strong carbonyl band at 1750 cm^{-1} in the ir spectrum ($CHCl_3$) and two broad resonance peaks at τ 5.83 (OCH_2CH_2) and 8.24 (OCH_2CH_2) in the nmr spectrum ($CHCl_3$), and gave 1,4-butylene glycol by basic hydrolysis suggesting the polycarbonate structure **12f**. The redistillation of the orthocarbonate **10f** in the presence of dibutyltin sulfide afforded the polycarbonate **12f**.

Reaction of the Cyclic Dialkoxide 13 with CS_2.—The mixture of cyclic dialkoxide **13** (20 mmol), CS_2 (5 ml), and ethylene dichloride (40 ml) was heated at 105° for 3 hr in a glass autoclave, giving a solid polymer (80% yield) and dibutyltin sulfide which was isolated by distillation after the separation of the polymer by filtration. The polymer was insoluble in dimethylformamide, phenol, or formic acid, showed a very strong ν_{C-O} band at 1120 cm^{-1} and a weak $\nu_{C=O}$ band at 1745 cm^{-1} in the ir spectrum, and gave carbon dioxide and pentamethylene glycol on the acid hydrolysis in 20% sulfuric acid at 100°.

Reaction of Dibutyltin Dimethoxide (6a) with CS_2.—The methoxide **6a** (20 mmol, 5.9 g) and CS_2 (1.2 ml) were mixed at room temperature and gave a solid inserted product as reported by Davies and Harrison,[4] which was heated at 100° for 5–10 hr in a sealed glass tube. The liquid reaction mixture was distilled giving a 95% yield of tetramethyl orthocarbonate (**18a**): bp 62–63°; ir ($CHCl_3$) 1125 cm^{-1} (strong ν_{C-O}); nmr (CCl_4) τ 6.78 (s, 12, CH_3O).

Anal. Calcd for $C_5H_{12}O_4$: C, 44.11; H, 8.88. Found: C, 43.95; H, 8.68.

Further distillation of the residue gave dibutyltin sulfide (97%).

Reaction of Dibutyltin Diethoxide (6b) with CS_2.—The diethoxide **6b** (6.44 g, 20 mmol) and CS_2 (1.2 ml, 20 mmol) were allowed to react at 96° for 5 hr in a glass tube giving tetraethyl orthocarbonate (**18b**) in 80% yield on distillation: bp 47–52° (24 mm) (lit.[5] 158–161°); ir ($CHCl_3$) 1195, 1120 (strong ν_{C-O}), and 1035 cm^{-1}; nmr ($CHCl_3$) τ 6.39 (q, 8, J = 6.9 Hz, OCH_2) and 8.77 (t, 12, J = 6.9 Hz, CH_2CH_3).

Reaction of Dibutyltin Di-*n*-propoxide (6c) with CS_2.—The dialkoxide **6c** (20 mmol) and CS_2 were allowed to react at 120° for 20 hr as in the case of **6b**, and the reaction mixture was distilled giving an 86% yield of tetra-*n*-propyl orthocarbonate (**18c**): bp 56.5–57.5° (0.5 mm); ir ($CHCl_3$) 1119 (ν_{C-O}); nmr ($CHCl_3$) τ 6.45 (t, 8, J = 7.1 Hz, OCH_2), 8.35 (sextet, 8, J = 7, 1 Hz, CCH_2), and 9.07 (t, 12, J = 7.1 Hz, CCH_3).

Anal. Calcd for $C_{13}H_{28}O_4$: C, 62.87; H, 11.36. Found: C, 63.03; H, 11.22.

Reaction of Dibutyltin Diisopropoxide (6d) with CS_2.—The dialkoxide **6d** (20 mmol) and equimolar amounts of CS_2 were allowed to react at 120° for 20 hr as in the case of **6c**, and the reaction mixture was distilled giving diisopropyl carbonate (**19d**) in a 90% yield (calculated assuming the reaction occurred as in eq 6): bp 67–69° (0.5 mm); ir ($CHCl_3$) 1735 ($\nu_{C=O}$), 1268, and 1098 cm^{-1}; nmr (CCl_4) τ 8.75 (d, 12, J = 6.2 Hz, CH_3C) and 5.27 (seven, 2, J = 6.2 Hz, OCH).

Reaction of Dibutyltin Di-*tert*-butoxide (6e) with CS_2.—The dialkoxide **6e** (20 mmol) and equimolar amounts of CS_2 were sealed in a glass tube and heated at 120° for 20 hr giving an ~80% yield of isobutene (based on **6e** used) which was identified by comparison of the nmr spectrum and the retention time in the gas chromatogram with those of a commercially available sample. The mixture condensed in a cold trap on distillation showed a strong ir band at 2050 cm^{-1} (COS) and a weak band at 2450 cm^{-1} (CO_2) in its ir spectrum.

On the other hand, the reaction at 110° for 20 hr gave an ~40% yield of isobutene and an ~45% yield of the unreacted dialkoxide **6e** which was isolated by distillation.

Reaction of Dibutyltin Di-*n*-butoxide (6f) with CS_2.—The dialkoxide **6f** (20 mmol) and equimolar amounts of CS_2 were allowed to react, as in the case of **6c**, giving an 85% yield of

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[16] The dialkoxides of dioctyltin were decomposed at about 160° on distillations.

tetra-*n*-butyl orthocarbonate (**18f**): bp 85–89° (0.4 mm); ir ($CHCl_3$) 1175, 1120 (ν_{C-O}), 1050, and 970 cm^{-1}; nmr ($CHCl_3$) τ 6.44 (t, 8, J = 6.2 Hz, OCH_2), 8.1–8.8 (m, 16, CCH_2CH_2C), and 9.07 (t, 12, J = 6.1 Hz, CCH_3).

Reaction of Dibutyltin Di-*n*-octoxide (6g) with CS_2.—The dialkoxide **6g** (20 mmol) and equimolar amounts of CS_2 were heated at 120° for 20 hr, and the reaction mixture showed a strong ν_{C-O} band at 1115 cm^{-1} and a very weak $\nu_{C=O}$ band at 1750 cm^{-1} in the ir spectrum, suggesting the formation of tetra-*n*-octyl orthocarbonate. However, the pure orthocarbonate could not be obtained on distillation or column chromatography of the mixture, because it was decomposed to dioctyl carbonate in these procedures.

Reaction of Dioctyltin Di-*n*-hexoxide (6h) with CS_2.—Crude dialkoxide **6h** (10 mmol),[16] prepared *in situ* from dioctyltin dimethoxide and dried 1-hexanol by heating the mixture in a distillation flask to 120° *in vacuo* (20 mm), was allowed to react with CS_2 (0.6 ml) at 120° for 20 hr under argon to give a 49% yield of tetra-*n*-hexyl orthocarbonate (**18h**) and a 20% yield of di-*n*-hexyl carbonate (**19h**) (yields based on the crude **6h** used).

18h: bp 119–121° (0.04 mm); ir ($CHCl_3$) 1118 cm^{-1} (ν_{C-O}); nmr ($CHCl_3$) τ 6.51 (t, 8, J = 6.0 Hz, OCH_2), 8.3–8.9 (m, 32, $C(CH_2)_4C$), and 9.13 (t, 12, J = 5.8 Hz, CCH_3).

Anal. Calcd for $C_{25}H_{52}O_4$: C, 72.06; H, 12.58. Found: C, 72.25; H, 12.74.

19h: bp 61–63° (0.03 mm); ir ($CHCl_3$) 1742 ($\nu_{C=O}$) and 1260 cm^{-1}; nmr (CCl_4) τ 5.87 (t, 4, J = 6.0 Hz, OCH_2), 8.1–8.9 (m, 16, $C(CH_2)_4C$), and 9.11 (t, 6, J = 5.7 Hz, CCH_3).

Anal. Calcd for $C_{13}H_{26}O_3$: C, 67.79; H, 11.38. Found: C, 67.80; H, 11.19.

Reaction of Dioctyltin Di-*n*-octoxide (6i) with CS_2.—Crude dialkoxide **6i** (10 mmol),[16] prepared from dioctyltin dimethoxide and dried 1-octanol as was discussed above, reacted with CS_2 (0.6 ml) at 120° for 20 hr. The reaction mixture showed a strong ether band of tetraalkyl orthocarbonate at 1115 cm^{-1}, but, on distillation (the oil bath temperature used was increased to 220°), di-*n*-octyl carbonate (**19i**) was obtained in a 80% yield suggesting the decomposition of **18g** to **19g**: bp 120° (0.04 mm); ir ($CHCl_3$) 1740 ($\nu_{C=O}$) and 1265 cm^{-1}; nmr ($CHCl_3$) τ 5.85 (t, 4, J = 6.2 Hz, OCH_2), and 8.1–9.3 (m, 30, CC_7H_{15}).

Anal. Calcd for $C_{17}H_{35}O_4$: C, 71.28; H, 11.96. Found: C, 71.46; H, 11.89.

Registry No.—**5a**, 3590-59-8; **5b**, 3590-60-1; **5c**, 3590-63-4; **5d**, 3590-67-8; **5e**, 3744-99-8; **5f**, 3590-62-3; **6a**, 1067-55-6; **6b**, 1067-41-0; **6c**, 3349-35-7; **6d**, 14538-83-1; **6e**, 3349-40-4; **6f**, 3349-36-8; **6g**, 3349-38-0; **13**, 3590-65-6; **18a**, 1850-14-2; **18b**, 78-09-1; **18c**, 597-72-8; **18f**, 25335-30-2; **18h**, 28131-23-9; **19d**, 6482-34-4; **19h**, 7523-15-1; **19i**, 1680-31-5; carbon disulfide, 75-15-0.

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[16] The dialkoxides of dioctyltin were decomposed at ~160° on distillation.

The Reactions of Amines, Alcohols, and Pivalic Acid with Di-*tert*-butyl Dithiol Tricarbonate and Di-*tert*-butyl Tricarbonate[1,2]

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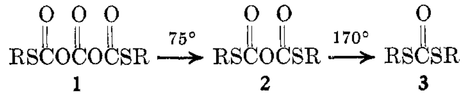
Received August 11, 1970

Nucleophilic attack by amines on di-*tert*-butyl dithiol tricarbonate and di-*tert*-butyl tricarbonate is shown to take place at the central carbonyl group. Primary aromatic amines give rise to symmetrical ureas, secondary amines produce the corresponding carbonic carbamic anhydrides, and tertiary amines catalyze the decomposition of the tricarbonates to their corresponding dicarbonates. Ethyl and isopropyl alcohols react to produce the corresponding mixed dicarbonates. Pivalic acid reacts to produce RSCOOCOOCOR (R = *tert*-Bu), almost certainly by attack at the central carbonyl group of the tricarbonate.

The present paper describes the action of primary and secondary amines, of alcohols, and of pivalic acid on the tricarbonates whose preparation and properties were reported previously. The present work will be described most clearly by reference to some of our earlier observations.

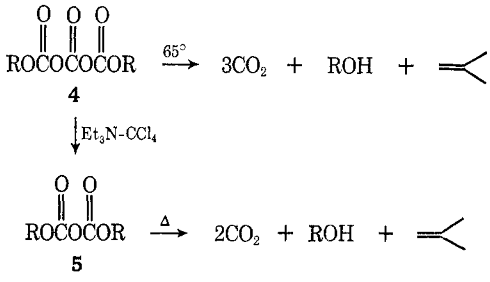
The thermal decomposition of di-*tert*-butyl dithiol tricarbonate (**1**) has been shown to give di-*tert*-butyl dithiol dicarbonate (**2**), which may be further decomposed to the corresponding monocarbonate **3**[3–5] (eq 1).



$$\underset{\mathbf{1}}{\mathrm{RS\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}SR}} \xrightarrow{75^\circ} \underset{\mathbf{2}}{\mathrm{RS\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}SR}} \xrightarrow{170^\circ} \underset{\mathbf{3}}{\mathrm{RS\overset{O}{\overset{\|}{C}}SR}} \qquad (1)$$

R = *tert*-Bu

In contrast to this behavior, di-*tert*-butyl tricarbonate (**4**), when thermally decomposed, fragments into three molecules of carbon dioxide, one molecule of *tert*-butyl alcohol, and one molecule of isobutene[4,5] (eq 2). By refluxing in carbon tetrachloride with a trace of triethylamine, the decomposition is arrested at the di-*tert*-butyl dicarbonate[6,7] **5** stage. Under all of the conditions tried, **5** could not be converted into the known monocar-



(2)

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[1] Aided by Grant GP-7874 from the National Science Foundation.

[2] The nomenclature of the di- and tricarbonates described in this and the preceding papers of this series is a vexing problem. The dicarbonates, ROCOOCOR, have been known for some time (ref 6 and 7 below) and are usually called "pyrocarbonates;" they have received considerable attention as mild acylating agents for compounds of biochemical importance [*e.g.*, N. J. Leonard, J. J. McDonald, and M. E. Reichmann, *Proc. Nat. Acad. Sci. U. S.*, **67**, 93 (1970), and references therein]. R. Sayre [*J. Amer. Chem. Soc.*, **74**, 3647 (1952)] has named EtOCOSCSOEt "diethyl thionothiodiformate" and gives other less descriptive names. In our work, we have preferred the "dicarbonate" and "tricarbonate" scheme to emphasize the similarities between the two types, derived formally from HOCOOCOOH and HOCOOCOOCOOH, as well as from the corresponding sulfur carbonic acids, HSCOOCOSH and HSCOOCOOCOSH. The di- and triphosphates, as in adenosine triphosphate and adenosine diphosphate, are reasonable analogs to our usage.

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