

Sodium [2-(2-Acetamidoethylthiomethyl)phenyl]methanesulfinate (6).—Sodium (460 mg, 20 mg-atoms) dissolved in MeOH (20 ml) was added dropwise to a mixture of **5** (4.00 g, 20.0 mmol) and **1** (2.38 g, 20.0 mmol) in MeOH (50 ml) with stirring at ca. 25°. After addition was complete (ca. 10 min), dry Et₂O (ca. 500 ml) was added to the reaction mixture until no more precipitate appeared. Solvent was decanted, and the white precipitate was redissolved in MeOH (10 ml) and reprecipitated with dry Et₂O. Decantation and drying at 0.1 mm for 24 hr at 25° gave 5.00 g (73%) of white **6**, mp 110–112° dec. Tlc showed one spot (1:1 MeOH:Me₂CO); ir 3400, 1650, 1530, 1010, 960, and 750 cm⁻¹. Additional tlc spots appeared a few minutes after dissolution of **6** in H₂O or (more slowly) MeOH.

Anal. Calcd for C₁₂H₁₂NNaO₃S₂: C, 42.22; H, 4.69; N, 4.10; S, 28.15. Found: C, 42.33; H, 4.65; N, 3.74; S, 27.95.

Disodium 2,2'-(Trithiodimethyl)bis(phenylmethanesulfinate) (8).—A solution of commercial Na₂S·9H₂O (1.5 mmol) in MeOH (5 ml) was added slowly to the dioxide **5** (0.60 g, 3.00 mmol) in MeOH (25 ml) at 0–5° with good stirring during 30 min. After the addition was complete (the pH then was 7), the reaction mixture showed only one spot for **8** by tlc (1:1 MeOH:Me₂CO) and none for **5**. Addition of Et₂O (600 ml) at 0° gave a white precipitate. Most of the solvent was decanted, after which drying at 0.1 mm gave 0.60 g (84%) of white **8**, mp 192–194° dec. This **8** was dissolved in a little MeOH, and a small amount of dry Et₂O was added until a cloudy precipitate began to appear. A colorless, clear solution then resulted upon removal of the small amount of precipitate by centrifugation as quickly as possible. Dry Et₂O again was added to this solution until appearance of a white precipitate was complete. Decantation and drying at 0.1 mm for 24 hr at ca. 25° gave 0.50 g (70%) of **8**, mp 192–194 dec. Tlc showed one spot (1:1 MeOH:Me₂CO); ir 3400 (H₂O), 1640 (H₂O), 1010 and 970 (very strong, SO₂⁻), and 760 cm⁻¹. Additional tlc spots appeared a few minutes after dissolution of **8** in H₂O or (more slowly) MeOH.

Anal. Calcd for C₁₆H₁₆Na₂O₄S₅·3H₂O (dried at 25°): C, 36.09; H, 4.13; S, 30.07. Found: C, 36.28, 36.36; H, 4.24, 4.40; S, 29.60, 29.45.

Drying to constant weight (100° overnight) gave hygroscopic, anhydrous **8**.

Anal. Calcd for C₁₆H₁₆O₄S₅N₂: C, 40.17; H, 3.34; S, 33.47. Found: C, 39.42; H, 3.81; S, 31.66.

When the analyst kindly exposed anhydrous **8** for ca. 2 days to ambient air and then redried, the weight loss was 10.64% (calcd for **8**·3H₂O, 10.13%).

Disodium 4,4'-(Trithiobis(threo-2,3-diacetoxybutanesulfinate) (10).—A solution of Na₂S·9H₂O (3.6 mmol) in MeOH (20 ml) was added dropwise to the *trans*-diacetate dioxide **9** (2.00 g, 7.46 mmol)¹³ in MeOH (50 ml) at 0–5° with good stirring. After addition was complete (the pH then was ca. 7), the reaction mixture showed one spot for **10** by tlc (1:1 MeOH:Me₂CO). Addition of Et₂O (500 ml) at 0° gave a white precipitate. As with **8**, the **10** was redissolved in a little MeOH and a little dry Et₂O was added until a precipitate began to appear. Centrifugation as quickly as possible again removed a little solid and left a clear solution. Dry Et₂O was added to this solution until appearance of a white precipitate was complete. Decantation and drying at 0.1 mm for 24 hr at 25° gave 2.0 g (90%) of **10**, mp 178–180° dec. Tlc showed one spot (1:1 MeOH:Me₂CO); ir 3440 (H₂O), 1730, 1620 (H₂O), 1380, 1220, 1030 (broad), 950 cm⁻¹.

Anal. Calcd for C₁₈H₂₄Na₂O₁₂S₅·H₂O: C, 30.37; H, 4.11; S, 25.31; H₂O, 2.84. Found: C, 29.80; H, 4.19; S, 26.19; H₂O, 3.15.

Drying to constant weight (100° overnight, then 120°) of a sample moderately dried for the foregoing analysis removed only 1.02% H₂O.

Anal. Calcd for C₁₈H₂₄O₁₂S₅Na₂: C, 31.27; H, 3.90; S, 26.05. Found: C, 29.85, 29.75; H, 4.04, 4.24; S, 26.40, 26.36.

Registry No.—**3**, 36540-20-2; **6**, 36540-21-3; **8**, 36540-22-4; **10**, 36540-23-5.

(13) We are indebted to Dr. Y. H. Kim for the preparation of **9**, as reported by L. Field and Y. H. Kim in ref 9.

Preparation of Orthocarbonates from Thallous Alkoxides and Carbon Disulfide

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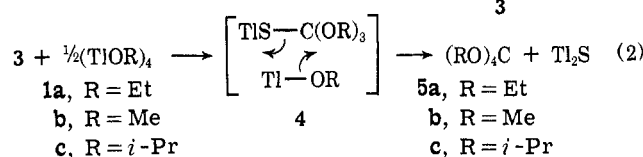
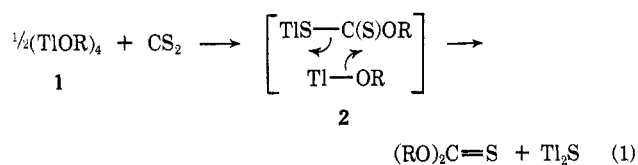
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During our studies on new types of orthocarbonate syntheses from organometallic alkoxides and carbon disulfide,^{2,3} Lee reported that dimethylthallium alkoxide reacted with carbon dioxide, carbon disulfide, and sulfur dioxide to form insertion products across the thallium(III)-oxygen bond.⁴ Although insertion reactions of heterocumulenes are well known for R₃SnOR⁵ and other organometallic alkoxides, the syntheses of orthocarbonates could be realized only in the case of the reactions of bis(trialkyltin) glycolates² and dialkyltin dialkoxides³ with carbon disulfide.

In this note, we report the reaction of thallium(I)-oxygen compounds with carbon disulfide and dioxide, and show a new type of utilization of thallous alkoxides for orthocarbonate syntheses.

Thallous ethoxide reacted with an equimolar amount of carbon disulfide in dry methylene dichloride to afford tetraethyl orthocarbonate in 97% yield. The orthocarbonate formed was identified by comparison with the melting point and ir and nmr spectra of an authentic sample.³ Tetramethyl orthocarbonate was also obtained in good yield by the reaction of thallous methoxide with carbon disulfide.

Furthermore, when thallous ethoxide was treated with an excess of carbon disulfide, the ir spectrum of the reaction mixture indicated the presence of a small amount of diethyl thioncarbonate. Consequently, the reaction scheme may be formulated by eq 1 and 2, as in the reactions of dialkyltin dialkoxides with carbon disulfide.²



The adducts of carbon disulfide with trialkyltin alkoxides⁶ [R₃SnSC(S)OR'], dimethylthallialkoxide, and thallous phenoxide^{4,6} were found to be stable at room temperature, while the adducts of thallous alkoxides are unstable and decomposed to give thioncarbonates, **3**, or orthocarbonates, **5**. These results are in-

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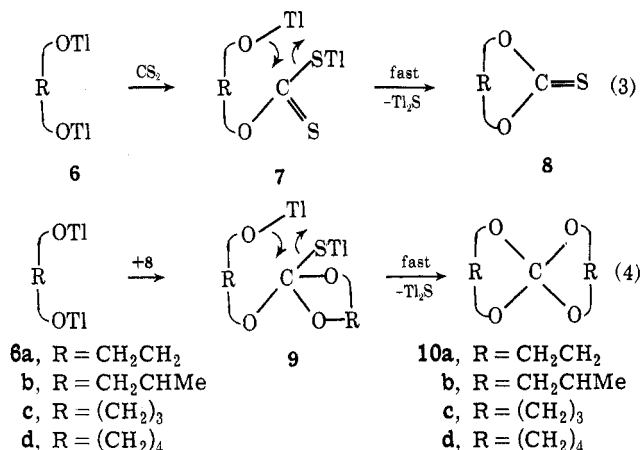
teresting but difficult to explain at present. However, both the stability of the adduct and the reactivity of alkoxide might be affected by the acidity of the metal atom toward a sulfur atom and by the nucleophilicity of the alkoxy group. Bonati and coworkers showed that the mean degrees of association of organotin(IV), dimethylthallic, and thallos dithiophosphinates were about 1.0, 1.5, and 2.0, respectively,⁷ suggesting that intermolecular coordination to the sulfur atom is in the order thallium(I) > dimethylthallium(III) > trialkyltin(IV). Furthermore, thallos-oxygen compounds, such as thallos hydroxide and ethoxide, are strong bases, while organotin-oxygen compounds are weak bases.^{8,9} Therefore, the nucleophilic attack of the alkoxy group at the electron-deficient carbon atom in the coordination transition state such as 2 or 4 will be facilitated by the larger basicity of thallos alkoxide. Moreover, an association of thallos alkoxide to form cubic tetramer^{10,11} would probably assist sterically reactions 1 and 2.

Thallos isopropoxide was prepared by the alcoholysis reaction of thallos methoxide with isopropyl alcohol, and reacted with carbon disulfide in benzene at room temperature to afford tetraisopropyl orthocarbonate in a moderate yield. This new compound is more liable to hydrolysis to give diisopropyl carbonate than primary orthocarbonates.¹² The high reactivity of thallos isopropoxide gave a new route to prepare an acyclic secondary orthocarbonate, which is not obtainable by other methods, although bis(2,3-butylene) spiroorthocarbonate, a cyclic secondary orthocarbonate, was afforded by the reaction of bis(trialkyltin) 2,3-butylene glycolate with carbon disulfide.²

Preparation of spiroorthocarbonates from dithallos glycolates were also examined. Pure dithallos alkylene glycolates are difficult to prepare by the alcoholysis reactions of thallos ethoxide with glycols, because mono- and dithallos glycolates are insoluble in organic solvents and sensitive to moisture and carbon dioxide in the atmosphere. However, the crude glycolates reacted with equimolar amounts of carbon disulfide in benzene at room temperature for 2 hr, affording moderate yields of bis(alkylene) spiroorthocarbonates, 10.

When an excess amount of carbon disulfide was used in the reaction, ethylene thioncarbonate (8, R = CH₂-CH₂) and bis(ethylene) orthocarbonate (10a) were formed (eq 3 and 4), as in the reactions of bis(tributyltin) alkylene glycolates.²

Dithallos ethylene glycolate also reacted with carbon dioxide to give a solid which showed strong ir absorption bands at 1681, 1610, 1309, and 1073 cm⁻¹, assigned to the adduct resulting from addition of carbon dioxide across the thallium-oxygen bond. The adduct is stable in the solid state for 3 hr at 90° or in refluxing dichloroethane for several hours. These results show that the reactions of carbon disulfide with



thallos alkoxide are only successful for preparations of orthocarbonates.

Experimental Section

General.—Melting points and boiling points were uncorrected. Analyses were performed by the Analysis Center of Kyoto University or by Toa-gosei Chemical Co., Ltd. Ir and nmr spectra were recorded on a JASCO Model IR-S spectrometer and on a Japan Electron Optics Model HL-60 spectrometer (TMS as an internal standard), respectively.

All operations were carried out under a dry nitrogen atmosphere.

Materials.—Carbon disulfide, alcohols, and solvents used were strictly dried by common methods. Thallos ethoxide, methoxide, and isopropoxide were prepared by the methods of Kahlbaum,¹³ Sidgwick,¹⁰ and Dahl,¹¹ respectively.

Dithallos glycolates were prepared and isolated by the deForcrand procedure.¹⁴ Elemental analyses indicated that the formed dithallos glycolates were impure. Their analyses were very difficult because they are sensitive to moisture and carbon dioxide in air. Typical cases of isolations and analytical data of the glycolates follow.

To the solution of thallos ethoxide (20 mmol) in benzene (30 ml), was slowly added the glycol (10 mmol), with stirring for 2 hr at 50–60°. The reaction mixture was filtered, and the white residue was washed with dry benzene. The crude glycolate 6 was dried on silica gel, obtained in nearly quantitative yield, and was insoluble in ordinary organic solvents, thereby preventing further purifications. The melting points of the glycolates were in the range of 200–209° dec. Analytical data follow. 6a: Calcd for C₂H₄O₂Tl₂: C, 5.16; H, 0.86. Found: C, 6.03; H, 1.07. 6c: Calcd for C₃H₆O₂Tl₂: C, 7.46; H, 1.25. Found: C, 7.79; H, 1.22. 6d: Calcd for C₄H₈O₂Tl₂: C, 9.67; H, 1.62. Found: C, 8.71; H, 1.67.

Reaction of Thallos Ethoxide with CS₂.—Thallos ethoxide (1a) (4.95 g, 19.8 g mmol) was allowed to react with CS₂ (0.42 g, 5.5 mmol) in dry dichloromethane (30 ml) with stirring for 4 hr at room temperature. A black precipitate, Tl₂S, formed soon after the addition of CS₂, was filtered off and washed with CS₂. Thallium sulfide was obtained in 97% yield. The filtrate was evaporated *in vacuo*, giving crude tetraethyl orthocarbonate in 94% yield (0.90 g). Distillation of the crude orthocarbonate gave the pure orthocarbonate in 69% yield. Its ir and nmr spectra coincided well with those of an authentic sample, bp 48–51° (18 mm) [lit.³ bp 47–52° (24 mm)].

When an excess amount of CS₂ (1.42 g, 18.7 mmol) was treated with thallos ethoxide (4.77 g, 9.1 mmol) in the same manner, the ir spectrum of the filtrate from the reaction mixture showed strong ν_{C=O} bands of tetraethyl orthocarbonate (5a) at 1195 and 1120 cm⁻¹, and weak bands of diethyl thioncarbonate (3, R = Et) at 1312, 1291, and 1232 cm⁻¹.

Reaction of Thallos Methoxide with CS₂.—Thallos methoxide (1b) (9.42 g, 40 mmol) was allowed to react with CS₂ (0.84 g, 11 mmol) as in the case of thallos ethoxide. The crude product showed a strong ν_{C=O} band at 1125 cm⁻¹ in the ir spectrum (CHCl₃), and distillation gave a 72% yield of tetramethyl orthocarbonate (5b), bp 61–64° (lit.³ bp 62–63°).

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Reaction of Thallous Isopropoxide with CS₂.—Thallous isopropoxide (1c) (10.5 g, 40 mmol) was allowed to react with CS₂ (0.80 g, 10.5 mmol) as in the case of thallous ethoxide. Distillation of the filtrate from the reaction mixture afforded tetraisopropyl orthocarbonate (5c) in 55% yield (1.35 g, 5.5 mmol): bp 47–51° (3.5 mm); ir (CHCl₃) 1471, 1384, 1188, 1155, 1080 (strong), and 961 cm⁻¹; nmr (CHCl₃) τ 8.85 (d, 24, *J* = 6.0 Hz, CH₃C) and 5.94 (heptet, 4, *J* = 6.0 Hz, CHO).

Anal. Calcd for C₁₃H₂₈O₄: C, 62.87; H, 11.37. Found: C, 62.51; H, 10.98.

The orthocarbonate 5c was rapidly hydrolyzed by moisture in air to give diisopropyl carbonate, and the $\nu_{C=O}$ band of the carbonate at 1738 cm⁻¹ emerged during the ir measurement.

When the crude thallous isopropoxide, prepared by the alcoholysis of thallous ethoxide with isopropyl alcohol, and containing about 20 mol % of thallous ethoxide, was submitted to reaction with CS₂, a small amount of diisopropyl dithiocarbonate was formed along with the ethyl and isopropyl orthocarbonates. The dithiocarbonate in the reaction mixture was detected by its characteristic peaks at τ 4.23 (heptet, *J* = 6.0 Hz) in the nmr spectrum.

Reaction of Dithallous Ethylene Glycolate with CS₂. A.—Dithallous ethylene glycolate (6a) (1.32 g, 2.81 mmol) was dispersed in dry benzene (30 ml), and CS₂ (0.083 g, 1.1 mmol) was introduced slowly into the dispersion, which was stirred for 2 hr at room temperature. The thallous sulfide formed was filtered off, and benzene in the filtrate was evaporated to separate the crude crystals of the spiroorthocarbonate 10a in 60% yield (0.070 g, 0.50 mmol). This compound showed a strong $\nu_{C=O}$ band at 1058 cm⁻¹ in the ir spectrum (benzene) and a peak at τ 6.40 (s, 8, CH₂) in the nmr spectrum (benzene), which were the same values as for an authentic sample,² mp (CCl₄) 140.5–141.0° (lit.² mp 143–144°).

B.—Dithallous ethylene glycolate (6a) (0.49 g, 1.04 mmol) was allowed to react with an excess of CS₂ (3.05 g, 40 mmol) for 2.5 hr at room temperature with stirring. The ir spectrum in carbon disulfide of the crude product displayed absorption bands at 1360, 1250, 1210, 1140, 1058, 1018, and 958 cm⁻¹ (but a ν_{OH} band at ~3600 cm⁻¹ was not observed), and the nmr peaks at τ 5.45 (s) and 6.13 (s) coincided with those of a mixture of 40 mol % of ethylene thioncarbonate and 60 mol % of bis(ethylene) orthocarbonate (10a).

Reactions of CS₂ with Dithallous 1,2- or 1,3-Propylene and 1,4-Butylene Glycolates.—The dithallous glycolates 6b, 6c, and 6d were allowed to react with CS₂ as in procedure A described above, giving the crude orthocarbonates 10b (about 50% yield), 10c (73% yield), and 10d (35% yield), respectively. The products, purified by distillations or by recrystallizations, were identified by comparisons of boiling point, melting point, ir, and nmr spectra with those of authentic samples.

Registry No.—5a, 78-09-1; 5c, 36597-49-6; 6a, 36597-50-9; 6c, 36601-78-2; 6d, 36601-79-3; 10a, 24471-99-6; carbon disulfide, 75-15-0.

Observations Related to the Alkylation of Thallium Enolates of β -Keto Sulfoxides, β -Diketones, and β -Keto Esters. An Alternative Viewpoint

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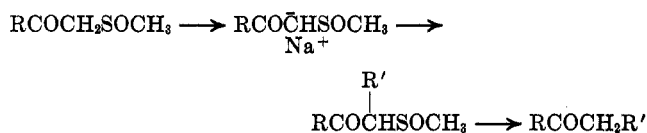
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The alkylation^{1,2} of β -keto sulfoxides³ (as their sodium enolates), followed by reductive fission of the sulfoxide

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function,^{1,4} represents a useful alternative to the acetoacetic ester route for the synthesis of ketones. Mono- and dialkylated derivatives are formed in good yields,

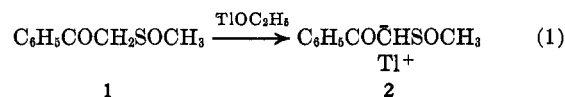


but attempts to extend this method to secondary halides have as yet been unpromising, resulting in "extremely poor yields of alkylation product."²

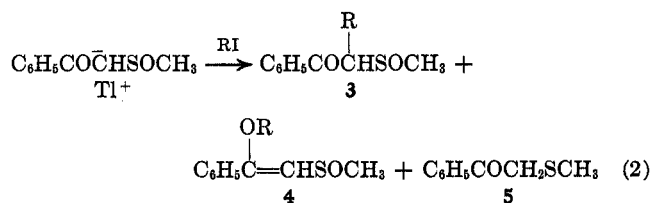
In the light of prior results, we investigated the use of thallium enolates for this purpose, since Tl derivatives of 1,3-dicarbonyl compounds (β -diketones or β -keto esters) are reported to possess a variety of attractive synthetic features.^{5–7} Thallium enolates (i) are easily formed in virtually quantitative yield, (ii) are crystalline, stable, nonhygroscopic solids, and (iii) react with alkyl iodides to give *exclusively*, in essentially quantitative yield, *the product of C-alkylation*—even for secondary substrates (isopropyl iodide). In addition, the heterogeneous thallium cation–ambident anion combination reportedly avoids *all* the traditionally encountered obstacles associated with β -dicarbonyl anion alkylations (O-alkylation, dialkylation, Claisen-type condensations, β -keto cleavage, oxidative coupling, etc.).⁵

For exploratory synthetic purposes we considered that Tl β -dicarbonyl enolates might serve as reasonable models for Tl β -keto sulfoxides since in each parent substrate the active methylene is flanked by two atoms each of which is "doubly" bonded to oxygen. Moreover, Tl enolates are highly insoluble, and, among the several factors responsible for promoting predominant C- rather than O-alkylation of ambident anions, heterogeneity⁸ plays a significant role.⁹

Reaction of keto sulfoxide 1 with thallous ethoxide¹⁰ led to quantitative precipitation of salt 2 (eq 1). The



results of heterogeneous alkylation experiments employing 2 with methyl, ethyl, or isopropyl iodide are summarized in eq 2 (see Experimental Section for



Alkylating agent	Isolated product yield, %		
	3	4	5
CH ₃ I	81		
C ₂ H ₅ I	38	17	28
<i>i</i> -C ₃ H ₇ I		42	36

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