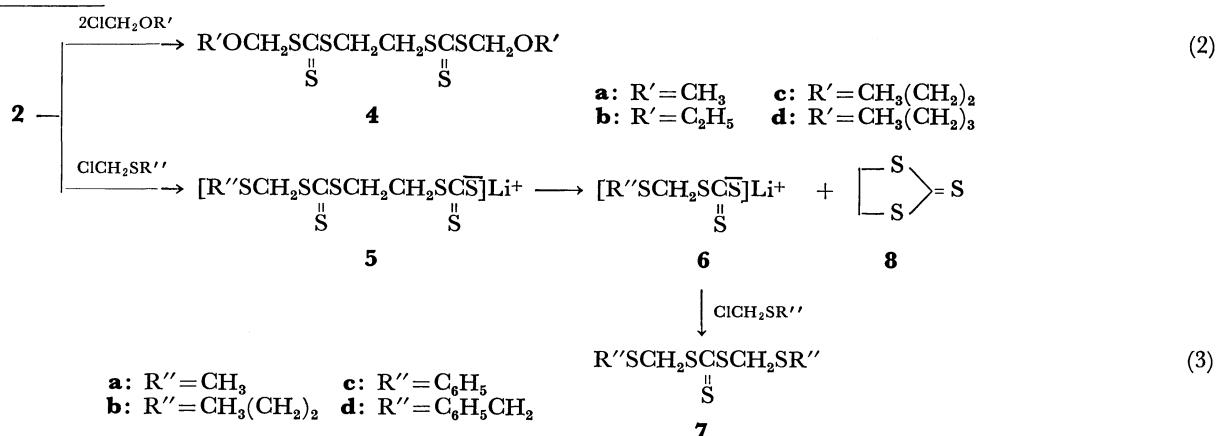


a) All **3** products gave satisfactory elemental analyses and exhibited spectral properties in accordance with the assigned structures. The ¹H-NMR spectra (δ values, in CDCl₃) are as follows: **3a**: 3.47(s, 4H), 3.52(s, 6H), 3.97(s, 4H). **3b**: 1.21(t, 6H), 3.50(s, 4H), 3.97(s, 4H), 4.00(q, 4H). **3c**: 0.89(t, 6H), 1.2—1.9(m, 4H), 3.50(s, 4H), 3.90(t, 4H), 3.97(s, 4H). **3f**: 0.82(t, 6H), 1.0—1.7(m, 8H), 3.40(s, 4H), 3.81(t, 4H), 3.86(s, 4H). **3g**: 3.39(s, 4H), 3.91(s, 4H), 4.86(s, 4H), 6.7—7.1(m, 10H). Although a relatively small amount of **8** was observed in all runs, we were unable to find any bis(alkoxycarbonylmethyl) trithiocarbonate, which is supposed to arise simultaneously, within the limits of our detection.

dence leads us to favor the above mechanism. The products obtained by the reaction of **2** with several chloromethyl ethers and sulfides are listed in Tables 2 and 3, along with their physical data.



Among the products described in this report, **3** and **4** are difficult to synthesize by the other routes; moreover, the former may have great synthetic potential resulting from the presence of the two alkoxy carbonyl groups at both molecular ends.

Experimental

Reaction Summarized in Tables 1, 2, and 3. In each experiment, 2.0 g (6.6 mmol) of 2,2'-[1,2-ethanedithiolylbis-(thio)]bis-1,3-dithiolane (**1**) was used; the mole ratio of electrophilic reagents to **1** and the eluents used for column

chromatography are noted in the tables. All the reactions were carried out in the manner described in the preceding report.¹⁾

References

- 1) S. Tanimoto, T. Oida, K. Hatanaka, and T. Sugimoto, *Tetrahedron Lett.*, **1981**, 655.
- 2) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Company, New York (1962), p. 10.
- 3) H. J. Renner, G. Schneider, and J. Weissflog, Ger. (East) Patent 15431; *Chem. Abstr.*, **54**, 2650 (1960).

TABLE 2. REACTION OF THE 1,2-ETHANEDIYLBIS(TRITHIOCARBONIC ACID) DIANION WITH SEVERAL CHLOROMETHYL ETHERS

Chloromethyl ether used R'	Moles per mol 1	Eluent used for chromatography	Products ^{a)} (yield/%)	Bp θ_b /°C(Torr)
CH ₃	2.7	CH ₂ Cl ₂ /C ₆ H ₁₄ , (1:1)	4a (48), 8 (33) CH ₃ OCH ₂ SCSCH ₂ OCH ₃ S (11)	124—129 (3) — ^{b)}
C ₂ H ₅	2.5	C ₂ H ₅ OC ₂ H ₅ /C ₆ H ₁₄ , (1:1)	4b (72), 8 (16)	137—143 (3)
CH ₃ (CH ₂) ₂	2.5	C ₂ H ₅ OC ₂ H ₅ /C ₆ H ₁₄ , (1:1)	4c (73), 8 (20)	152—158 (3)
CH ₃ (CH ₂) ₃	2.5	C ₂ H ₅ OC ₂ H ₅ /C ₆ H ₁₄ , (1:1)	4d (77), 8 (18)	162—167 (2.5)

a) The ¹H-NMR spectra of **4** (δ values, in CDCl₃) are as follows. **4a**: 3.43(s, 6H), 4.02(s, 4H), 5.53(s, 4H). **4b**: 1.20(t, 6H), 3.60(q, 4H), 4.00(s, 4H), 5.56(s, 4H). **4c**: 0.90(t, 6H), 1.2—1.9(m, 4H), 3.49(t, 4H), 3.97(s, 4H), 5.53(s, 4H). **4d**: 0.89(t, 6H), 1.1—1.8(m, 8H), 3.53(t, 4H), 3.99(s, 4H), 5.53(s, 4H). b) Mp or bp could not be determined because of the limited amounts.

¹H-NMR (in CDCl₃): δ 3.39(s, 6H), 5.52(s, 4H).

TABLE 3. REACTION OF THE 1,2-ETHANEDIYLBIS(TRITHIOCARBONIC ACID) DIANION WITH SEVERAL CHLOROMETHYL SULFIDES

Chloromethyl sulfide used R''	Moles per mol 1	Eluent used for chromatography	Products ^{a)} (yield/%)	Bp θ_b /°C(Torr)
CH ₃	3.0	CH ₂ Cl ₂ /C ₆ H ₁₄ , (1:1)	7a (71), 8 (78)	154—158 (3), Lit. ³⁾ mp 41 °C
CH ₃ (CH ₂) ₂	2.7	C ₂ H ₅ OC ₂ H ₅ /C ₆ H ₁₄ , (1:1)	7b (79), 8 (80)	174—179 (2.5)
C ₆ H ₅	2.3	C ₂ H ₅ OC ₂ H ₅ /C ₆ H ₁₄ , (1:2)	7c (48), 8 (76)	195—198 (2.5—3)
C ₆ H ₅ CH ₂	2.0	C ₂ H ₅ OC ₂ H ₅ /C ₆ H ₁₄ , (1:2)	7d (74), 8 (87)	223—227 (3)

a) The ¹H-NMR spectra of **7** (δ values, in CDCl₃) are as follows. **7a**: 2.17(s, 6H), 4.45(s, 4H). **7b**: 0.98(t, 6H), 1.2—2.0(m, 4H), 2.61(t, 4H), 4.46(s, 4H). **7c**: 4.70(s, 4H), 7.0—7.7(m, 10H). **7d**: 3.76(s, 4H), 4.27(s, 4H), 7.0—7.5(m, 10H).