The Reactions of the 1,2-Ethanediylbis(trithiocarbonic acid) Dianion with Several Electrophilic Reagents

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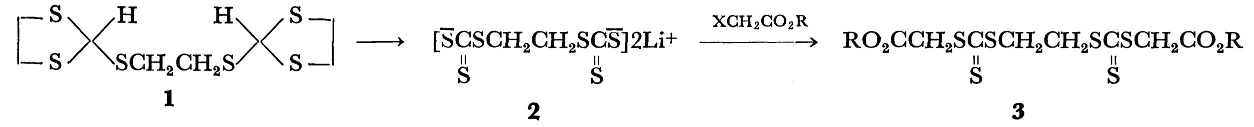
(Received June 17, 1981)

Synopsis. It has been found that the reaction of the 1,2-ethanediylbis(trithiocarbonic acid) dianion with haloacetic esters, chloromethyl ethers, and chloromethyl sulfides in tetrahydrofuran proceeds smoothly to afford 1,2-ethanediylbis(alkoxycarbonylmethyl trithiocarbonates), 1,2-ethanediylbis(alkoxymethyl trithiocarbonates) and bis(alkylthiomethyl) trithiocarbonates plus ethylene trithiocarbonate respectively.

We have recently reported[1] that 2,2′-[1,2-ethanediylbis(thio)]bis-1,3-dithiolane (**1**) is easily metalated with butyllithium in tetrahydrofuran to generate the 1,2-ethanediylbis(trithiocarbonic acid) dianion (**2**), with the elimination of 2 moles of ethylene; the dianion is then condensed with a variety of alkyl bromides and iodides to give 1,2-ethanediylbis(alkyl trithiocarbonates) and/or dialkyl trithiocarbonates plus ethylene trithiocarbonate (**8**). However, to the best of our knowledge, there has not been any other information concerning the synthetic utility of this anion. In this paper we would like to report the results of the reactions of **2** with several electrophilic reagents, such as haloacetic esters, chloromethyl ethers, and chloromethyl sulfides. The reaction of **2** with alkyl chlorides, studied under like conditions, did not show the formation of any products, suggesting a selectivity of **2** toward alkyl halides. Such selectivity was not observed in the reaction with haloacetic esters as the trapping agent. Bromoacetic esters undergo a condensation reaction with **2** similar to that observed with methyl iodide to afford 1,2-ethanediylbis(alkoxycarbonylmethyl trithiocarbonates) (**3**), along with a small amount of **8**. The reaction utilizing the chloro analogs, chloroacetic esters, had the same result, but the yields were somewhat lower. The results obtained by the reaction of **2** with several haloacetic esters are listed in Table 1, along with the physical data of the products.


(1)

a: X=Cl, R=CH_3, **b**: X=Cl, R=C_2H_5, **c**: X=Br, R=CH_3, **d**: X=Br, R=C_2H_5,
e: X=Br, R=$CH_3(CH_2)_2$, **f**: X=Br, R=$CH_3(CH_2)_3$, **g**: X=Br, R=$C_6H_5CH_2$

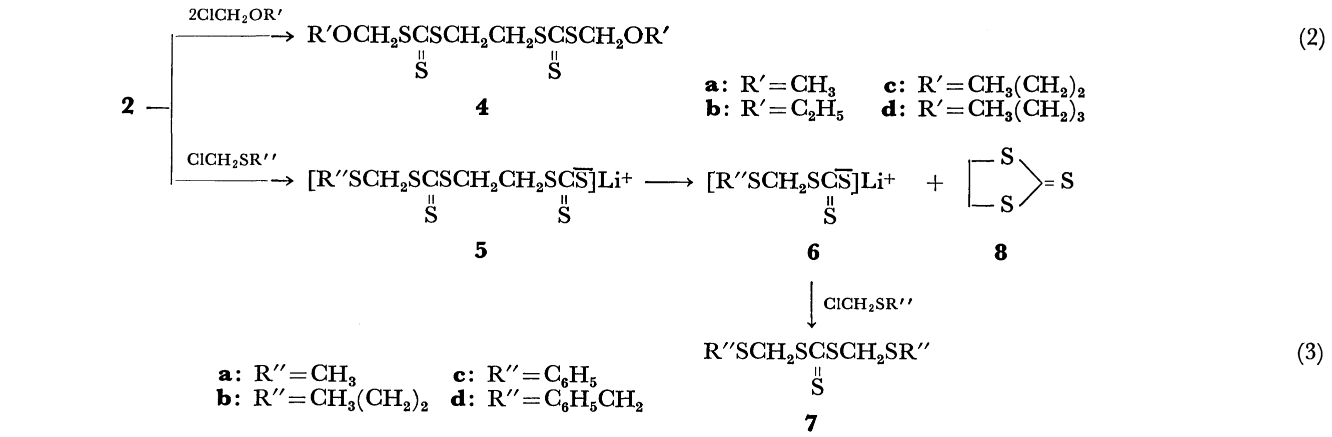
Price and Oae[2] have pointed out that, in a certain nucleophilic substitution reaction, chloromethyl ethyl sulfide reacts about several thousand times as fast as butyl chloride; furthermore, chloromethyl ethyl ether was found to react far faster than the sulfur analog. Thus, we have investigated the reactions of **2** with chloromethyl ethers and sulfides. When some chloromethyl ethers were employed, 1,2-ethanediylbis(alkoxymethyl trithiocarbonates) (**4**) were obtained, suggesting that the ethers attack directly both of the nucleophilic ends of **2** (Eq. 2). On the other hand, when some chloromethyl sulfides were used, the products consist of an approximately equal mixture of bis(alkylthiomethyl) trithiocarbonates (**7**) and **8**, indicating that the reaction assuredly occurred acoording to Eq. 3. Thus, an obvious difference in behavior between chloromethyl ethers and sulfides was noted. In addition, it was found that the fragmentation of **2** by the intramolecular attack of its own nucleophilic end does not occur under the given conditions; that is, even if a solution of **2** in tetrahydrofuran had been stored at −5—−10 °C for 5 h or more prior to the addition of haloacetic esters or chloromethyl ethers, substantially the same result was obtained. This evi-

Table 1. Reaction of the 1,2-ethanediylbis(trithiocarbonic acid) dianion with several haloacetic esters

Haloacetic ester used			Eluent used for chromatography	Products[a)] (yield/%)	Mp θ_m/°C (recryst. from C_6H_{14})
X	R	Moles per mol **1**			
Cl	CH_3	2.8	CH_2Cl_2/C_6H_{14}, (1:1)	**3a**(27), **8**(19)	63—65
Cl	C_2H_5	2.7	CH_2Cl_2/C_6H_{14}, (1:1)	**3b**(44), **8**(20)	55.5—57.5
Br	CH_3	2.7	CH_2Cl_2/C_6H_{14}, (1:1)	**3a**(75), **8**(15)	64—65
Br	C_2H_5	2.7	CH_2Cl_2/C_6H_{14}, (1:1)	**3b**(55), **8**(15)	56—57.5
Br	$CH_3(CH_2)_2$	2.7	CH_2Cl_2/C_6H_{14}, (1:2)	**3e**(73), **8**(<11)	46—47.5
Br	$CH_3(CH_2)_3$	2.7	CH_2Cl_2/C_6H_{14}, (1:2)	**3f**(85), **8**(4)	45—47
Br	$C_6H_5CH_2$	2.5	CH_2Cl_2/C_6H_{14}, (2:1)	**3g**(54), **8**(<6)	66.5—68

a) All **3** products gave satisfactory elemental analyses and exhibited spectral properties in accordance with the assigned structures. The ^{1}H-NMR spectra (δ values, in $CDCl_3$) 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). **3e**: 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 alkoxycarbonyl 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-ethanediylbis(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 preceeding 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		Eluent used for chromatography	Products[a)] (yield/%)	Bp θ_b/°C(Torr)
R′	Moles per mol **1**			
CH_3	2.7	CH_2Cl_2/C_6H_{14}, (1:1)	**4a**(48), **8**(33)	124—129(3)
			$CH_3OCH_2SC(=S)SCH_2OCH_3$ (11)	—[b)]
C_2H_5	2.5	$C_2H_5OC_2H_5/C_6H_{14}$, (1:1)	**4b**(72), **8**(16)	137—143(3)
$CH_3(CH_2)_2$	2.5	$C_2H_5OC_2H_5/C_6H_{14}$, (1:1)	**4c**(73), **8**(20)	152—158(3)
$CH_3(CH_2)_3$	2.5	$C_2H_5OC_2H_5/C_6H_{14}$, (1:1)	**4d**(77), **8**(18)	162—167(2.5)

a) The ^{1}H-NMR spectra of **4** (δ values, in $CDCl_3$) 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. ^{1}H-NMR (in $CDCl_3$): 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		Eluent used for chromatography	Products[a)] (yield/%)	Bp θ_b/°C(Torr)
R″	Moles per mol **1**			
CH_3	3.0	CH_2Cl_2/C_6H_{14}, (1:1)	**7a**(71), **8**(78)	154—158(3), Lit,[3)] mp 41 °C
$CH_3(CH_2)_2$	2.7	$C_2H_5OC_2H_5/C_6H_{14}$, (1:1)	**7b**(79), **8**(80)	174—179(2.5)
C_6H_5	2.3	$C_2H_5OC_2H_5/C_6H_{14}$, (1:2)	**7c**(48), **8**(76)	195—198(2.5—3)
$C_6H_5CH_2$	2.0	$C_2H_5OC_2H_5/C_6H_{14}$, (1:2)	**7d**(74), **8**(87)	223—227(3)

a) The ^{1}H-NMR spectra of **7** (δ values, in $CDCl_3$) 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).