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GENERATION OF 1,2-ETHANEBIS(TRITHIOCARBONIC ACID) DIANION FROM 2,2'-[1,2-ETHANEDIYLBIS(THIO)]-BIS-1,3-DITHIOLANE AND ITS REACTION WITH ALKYL HALIDES

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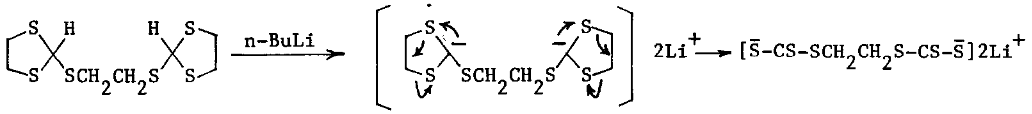
Summary: Generation of 1,2-ethanbis(trithiocarbonic acid) dianion from 2,2'-[1,2-ethanediylbis(thio)]bis-1,3-dithiolane and its reaction with alkyl halides were investigated.

The recent development has made many diverse type of dianions available by simple deprotonation reactions.[1] In this note, we wish to report our findings concerning reactions of a dianion from 2,2'-[1,2-ethanediylbis(thio)]bis-1,3-dithiolane. The dianion formation is readily accomplished at -5— -10°C by the addition of slightly over 2 equivalents of butyllithium (n-BuLi) in hexane to 2,2'-[1,2-ethanediylbis(thio)]bis-1,3-dithiolane in tetrahydrofuran under nitrogen. Although a little precipitation occurred after addition of the n-BuLi, stirring was possible and the addition of hexamethylphosphoric triamide (HMPA), which serves to solubilize the precipitation, was not necessary. In all instances, no substantial improvement in yields of final products was obtained when HMPA was used. Although the initially formed dianion (1) in this case is probably that resulting from loss of two methine hydrogens, 1 is considered to be unstable under the reaction conditions.[2] The dianion 1 therefore undergoes ring opening leading to 1,2-ethanebis(trithiocarbonic acid) dianion 2 with elimination of two moles of ethylene. Reasonable scheme for the formation of 2 from 1 is outlined below and is based on analogy to known reaction.[3] The dianion 2 thus formed was subsequently alkylated by alkyl halides as highly electrophilic as methyl iodide, ethyl iodide, methyl and benzyl bromides to produce predominantly the corresponding 1,2-ethanebis(alkyl trithiocarbonates) 3.



1

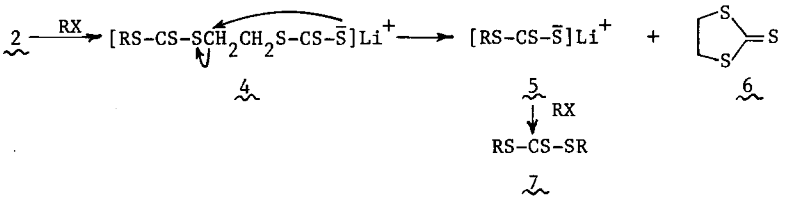
2

$\xrightarrow{RX}$ RS-CS-SCH$_2$CH$_2$S-CS-SR

3

a R=CH_3, X=I
b R=C_2H_5, X=I
c R=CH_3, X=Br
d R=$C_6H_5CH_2$, X=Br
e R=n-C_3H_7, X=I
f R=n-C_4H_9, X=I

In reactions with less electrophilic alkyl halides such as ethyl, n-propyl and n-butyl bromides, the alkylation proceeded only at one of the nucleophilic ends in 2 to give a monoanion 4, which underwent fragmentation to afford 5 and 6. The former could be then attacked by the alkyl halides to give the corresponding dialkyl trithiocarbonates 7.

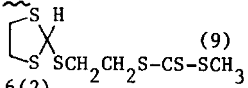
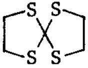


a R=C_2H_5, X=Br
b R=n-C_3H_7, X=Br
c R=n-C_4H_9, X=Br
d R=$-(CH_2)_2-$, X=Br
e R=$-(CH_2)_3-$, X=Br
f R=$-CH_2\underset{|}{C}HCH_3$, X=Br
g R=$-CH_2\underset{|}{C}HCH_2CH_3$, X=Br
h R=$-CH_2CH_2\underset{|}{C}HCH_3$, X=Br
i R=n-C_3H_7, X=I
j R=n-C_4H_9, X=I

In cases where some alkylene dibromides were employed, cyclic alkylene trithiocarbonates were obtained, but the yields were less than those in the cases using ethyl, n-propyl and n-butyl bromides. Furthermore, in the reaction with n-propyl or n-butyl iodide both the conversion to 3 and that to 7 competitively took place. Even when a solution of 2 in tetrahydrofuran, which had been stored for 3 hr or more, was submitted to the alkylation with ethyl iodide, none of diethyl trithiocarbonate 7a was obtained. This suggests that the fragmentation of 2 by intramolecular attack of its own nucleophilic end does not substantially occur.

The general procedure is as follows: To a stirred solution of 2,2'-[1,2-ethanediylbis(thio)]bis-1,3-dithiolane (4.0g, 13.2 mmol) in tetrahydrofuran (220 ml) was added at -5—-10°C a 1.56 molar solution (20 ml, 31.2 mmol) of n-BuLi in hexane under nitrogen, followed by stirring at the same temperature for 30 min. A white precipitate appears during the addition. To this cooled mixture was added dropwise a chilled solution of an alkyl halide (52.8 mmol) (26.4 mmol was used as regards alkylene dibromide) in tetrahydrofuran (10 ml). After the addition, the resulting solution was stirred at -5— -10°C for 1 hr and further at room temperature for 24 hr. Water (100 ml) and saturated aqueous solution (100 ml) of ammonium chloride were added, and most of the tetrahydrofuran was removed from the mixture at reduced pressure. The mixture was then extracted with ether (3×200 ml). The combined

Table 1. Products Formed in Reactions of 1,2-Ethanebis(trithiocarbonic acid) Dianion with Alkyl Bromides

RBr	Eluent used for column chromatography	Product(%yield[a])	m.p.(°C) (recryst. from) or b.p.(°C/torr)
CH_3Br	$C_2H_5OC_2H_5/C_6H_{14}$(1:6)	3c[4](88)  (9) 6(2)	56.5-59(CH_3OH) 41-44(C_6H_{14}) 37-38(C_2H_5OH), lit.[5] 37°C
$C_6H_5CH_2Br$	$C_2H_5OC_2H_5/C_6H_{14}$(1:20)	3d(65) 6(8)	62-64(C_2H_5OH) —
C_2H_5Br	$C_2H_5OC_2H_5/C_6H_{14}$(1:1)	7a(80) 6(66)	81-84/3, lit.[6] 90.5°C/2.6torr —
n-C_3H_7Br	$C_2H_5OC_2H_5/C_6H_{14}$(1:1)	7b(76) 6(59)	107-112/2, lit.[7] 98°C/0.75torr —
n-C_4H_9Br	$C_2H_5OC_2H_5/C_6H_{14}$(1:1)	7c(74) 6(58)	131-137/2, lit.[7] 106-108°C/0.4torr —
$Br(CH_2)_2Br$	$C_2H_5OC_2H_5/C_6H_{14}$(1:1)	(7d[b]+6)(52)  (31)	— 136-139(C_6H_{14}), lit.[8] 142-143°C
$Br(CH_2)_3Br$	$C_2H_5OC_2H_5/C_6H_{14}$(1:2)	7e(41) 6(51)	76-78(C_2H_5OH), lit.[7] 78°C —
$BrCH_2\underset{Br}{C}HCH_3$	$C_2H_5OC_2H_5/C_6H_{14}$(1:2)	7f(19) 6(23)	108-112/1.5, lit.[9] 124-126°C/3torr —
$BrCH_2\underset{Br}{C}HCH_2CH_3$	$C_2H_5OC_2H_5/C_6H_{14}$(1:2)	7g(47) 6(33)	103-107/2 —
$BrCH_2CH_2\underset{Br}{C}HCH_3$	$CHCl_3/C_6H_{14}$(1:2)	7h(52) 6(76)	46.5-48.5(C_2H_5OH), lit.[10] 50.5°C —

[a] Yield of isolated product based on 2,2'-[1,2-ethanediylbis(thio)]bis-1,3-dithiolane.
[b] 7d is identical to 6.

extracts were dried ($MgSO_4$), filtered, and concentrated in vacuo to give a yellow coloured residue. The products were isolated by column chromatography using silica gel and eluents as described in individual cases.

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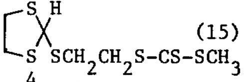
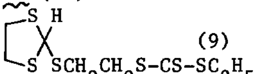
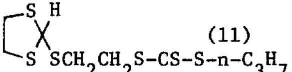
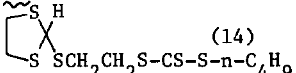
Table 2. Products Formed in Reactions of 1,2-Ethanebis(trithiocarbonic acid) Dianion with Alkyl Iodides

RI	Eluent used for column chromatography	Product(%yield[a])	m.p.(°C) (recryst. from) or b.p.(°C/torr)
CH_3I	$C_2H_5OC_2H_5/C_6H_{14}$(1:10)	3a[b](85)	—
		 (15)	—
C_2H_5I	$C_2H_5OC_2H_5/C_6H_{14}$(1:6)	3b[4](82)	35-36.5(C_2H_5OH)
		 (9)	—[c]
		6(7)	—
n-C_3H_7I	$C_2H_5OC_2H_5/C_6H_{14}$(1:20)	3e(41)	32-33(C_2H_5OH)
		7i[b](38)	—
		 (11)	—[c]
		6(36)	—
n-C_4H_9I	$C_2H_5OC_2H_5/C_6H_{14}$(1:20)	3f(38)	33-34.5(C_2H_5OH)
		7j[b](22)	—
		 (14)	—[c]
		6(28)	—

[a] Yield of isolated product based on 2,2'-[1,2-ethanediylbis(thio)]bis-1,3-dithiolane.
[b] 3a, 7i and 7j are identical to 3c, 7b and 7c, respectively.
[c] The melting point could not be determined because of the limited amounts.

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2. It is also confirmed that I is unstable and decomposes similarly even at -78°C.
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