

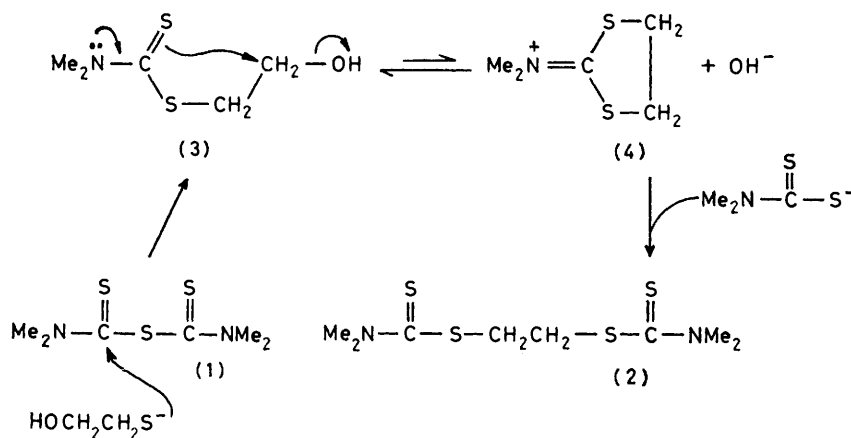
## Mechanism of the Formation of Ethylene Bis(dimethyldithiocarbamate) from Tetramethylthiuram Monosulphide and Sodium 2-Hydroxyethanethiolate

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It is shown that the ethylene bis(dimethyldithiocarbamate) which is produced as a minor product in the reaction of tetramethylthiuram monosulphide with sodium 2-hydroxyethanethiolate probably arises through addition of dimethyldithiocarbamate ion to the 2-dimethyliminio-1,3-dithiolan ion.

In a previous communication<sup>1</sup> it was reported that from the reaction between tetramethylthiuram monosulphide (1) and the sodium salt of 2-mercaptoethanol, a minor product [ethylene bis(dimethyldithiocarbamate)] (2) was obtained in addition to the expected one [2-hydroxyethyl dimethyldithiocarbamate] (3). The mechanism of

confirmed that this reaction also occurs under the experimental conditions (overnight reaction at room temperature in aqueous ethanol) used in my previous communication,<sup>1</sup> albeit in much lower yield (5%) than reported by Nakai and Okawara.<sup>4</sup> Furthermore, compound (3) itself has now been shown to react with dimethyl-



SCHEME

formation of compound (1) was not established. However, upon reflection, it seemed possible that it might arise from compound (3) according to the Scheme.

### RESULTS AND DISCUSSION

Here it is envisaged that the C-O bond in compound (3) is more labile than in a simple alcohol because of anchimeric assistance by the dimethyldithiocarbamate group. The resulting 2-dimethyliminio-1,3-dithiolan ion (4) then reacts with dimethyldithiocarbamate ion (present in the reaction mixture) to give compound (2). Neighbouring-group participation in similar compounds has previously been reported. For example, ion (4) is a major product of the equimolar reaction of 1,2-dichloroethane with sodium dimethyldithiocarbamate,<sup>2</sup> and 2-phenoxyethyl dimethyldithiocarbamates have been found to possess an unusually labile alkyl-oxygen bond.<sup>3</sup>

It has previously been shown that, under some conditions, ion (4) reacts quantitatively with dimethyldithiocarbamate to give compound (2).<sup>2,4</sup> It is now

dithiocarbamate at room temperature in aqueous ethanol to give a low yield (0.15%) of compound (2). Thus the Scheme appears justified as the explanation for the formation of compound (2) in the reaction between compound (1) and sodium 2-hydroxyethanethiolate.

During this work the <sup>13</sup>C n.m.r. spectra of compound (3), ion (4), and the corresponding ethyl analogues were recorded; the data are shown in the Table. Restricted rotation about the N-CS bond was noted in the two dithiocarbamate esters. The largest change in chemical shift upon conversion into the 2-dialkyliminio-1,3-dithiolan ions is the downfield movement of the resonance of the CH<sub>3</sub>-N and -CH<sub>2</sub>-N groups as the charge on the nitrogen atom changes from a partial to a full positive charge. On the other hand, it is interesting that the resonance of the ester thiocarbonyl carbon undergoes no significant change upon conversion into the ion.

### EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Mass spectra were determined with an A.E.I. MS9 spectro-

meter, and  $^{13}\text{C}$  n.m.r. spectra with a JEOL FX 60 spectrometer.

*2-Hydroxyethyl Dimethyldithiocarbamate (3) and 2-Hydroxyethyl Diethyldithiocarbamate.*—These compounds were prepared by the method of Nachmias<sup>5</sup> from pure starting materials and the resulting pale yellow liquids were not distilled. Their identity and purity were established by  $^{13}\text{C}$  n.m.r. and mass spectrometry.

*2-Dimethyliminio-1,3-dithiolan Perchlorate.*—This compound was prepared according to the method of Nakai and Okawara,<sup>4</sup> m.p. 181–183 °C (lit.,<sup>4</sup> 179–180 °C). It was

$^{13}\text{C}$ N.m.r. chemical shifts ( $\delta$ /p.p.m. from $\text{SiMe}_4$ )			
Compound	Solvent	C Atom	Chemical Shift
$\text{Me}_2\text{N}-\overset{\text{S}}{\parallel}{\text{C}}-\text{S}-\text{CH}_2\text{CH}_2\text{OH}$	$\text{CDCl}_3$	$\text{CH}_3$	41.65, 45.55
		$\text{C}=\text{S}$	196.903
		$\text{S}-\text{CH}_3$	39.51
		$\text{CH}_2-\text{O}$	61.23
$\text{Et}_2\text{N}-\overset{\text{S}}{\parallel}{\text{C}}-\text{S}-\text{CH}_2\text{CH}_2\text{OH}$	$\text{CDCl}_3$	$\text{CH}_3$	11.523, 12.426
		$\text{CH}_2-\text{N}$	46.943, 49.784
		$\text{C}=\text{S}$	195.410
		$\text{S}-\text{CH}_3$	39.065
$\left[ \text{Me}_2\text{N}^+=\overset{\text{S}-\text{CH}_2}{\text{C}} \begin{array}{c} \text{S}-\text{CH}_2 \\   \\ \text{S}-\text{CH}_2 \end{array} \right] \left[ \text{ClO}_4 \right]^-$	$(\text{CD}_3)_2\text{SO}$	$\text{CH}_2-\text{O}$	61.563
		$\text{CH}_3$	49.996
		$\text{N}=\text{C}$	196.903
		$\text{S}-\text{CH}_2$	43.016
$\left[ \text{Et}_2\text{N}^+=\overset{\text{S}-\text{CH}_2}{\text{C}} \begin{array}{c} \text{S}-\text{CH}_2 \\   \\ \text{S}-\text{CH}_2 \end{array} \right] \left[ \text{ClO}_4 \right]^-$	$(\text{CD}_3)_2\text{SO}$	$\text{CH}_3$	12.986
		$\text{CH}_2-\text{N}$	56.165
		$\text{N}=\text{C}$	196.416
		$\text{S}-\text{CH}_2$	42.529

also prepared as follows: compound (3) (1.65 g, 0.01 mol) and a concentrated aqueous solution of  $\text{HClO}_4$  (ca. 0.01 mol) were mixed. Heat was evolved and the mixture crystallised. The solid was recrystallised from acetone (1.4 g, 57%), m.p. 181–183 °C.

*2-Diethyliminio-1,3-dithiolan Perchlorate.*—This compound

was prepared according to the method of Nakai and Okawara,<sup>4</sup> m.p. 89–90 °C (lit.,<sup>4</sup> 89–90 °C).

*Ethylene Bis(dimethyldithiocarbamate) (2).*—This compound was prepared according to the method of Nakai and Okawara<sup>4</sup> from 2-dimethyliminio-1,3-dithiolan perchlorate and sodium dimethyldithiocarbamate. Using their conditions a yield of 90% was easily obtained. However, when the reactants (0.01 mol of each) were left overnight at room temperature in a mixture of ethanol (75 ml) and water (25 ml) (see ref. 1) only 0.14 g (5%) of compound (2) was produced.

Compound (2) was also prepared as follows: compound (3) (13.9 g, 0.085 mol) and sodium dimethyldithiocarbamate (0.085 mol) were dissolved in a mixture of ethanol (75 ml) and water (25 ml) and left at room temperature overnight. The volume was reduced by evaporation under reduced pressure, and water and chloroform were then added to the mixture. The chloroform layer was dried ( $\text{MgSO}_4$ ) and evaporated under reduced pressure. Upon standing, some crystalline material appeared which was isolated by centrifugation and recrystallised from chloroform-ethanol (1 : 6), yield 0.03 g, m.p. 187–190 °C (lit.,<sup>6</sup> 189 °C);  $m/e$  268 ( $M^+$ ), 180, 148, 120, and 88 (base).

It was also confirmed that compound (2) arises from the reaction of compound (1) and sodium 2-hydroxyethanethiolate, as previously reported.<sup>1</sup> However, the yield of this material is very variable; typically 20–30 mg of compound (2) is obtained from 0.01 mol of starting materials, but sometimes none is isolable.

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