

### 173. The Methyl Thioethers derived from 2 : 2'-Dichlorodiethyl Sulphide and its Analogues. Part II. Pyrolysis Experiments.

By R. J. CHARNOCK and (the late) R. C. G. MOGGRIDGE.

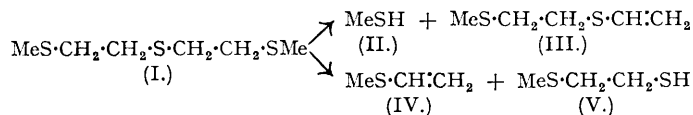
The following compounds have been isolated from the products of pyrolysis of 2 : 2'-dimethylthiodiethyl sulphide (I) : methylthiol (II), methyl vinyl sulphide (IV), 2-methylthioethylthiol (V), dithian, and the compound (VI). (VI) is thought to arise by the spontaneous combination of 2-methylthioethyl vinyl sulphide (III) and (V). 1 : 2-Dimethylthioethane (VII) was also isolated as a secondary reaction product, probably formed by the combination of (II) and (IV).

These results confirm the conclusion from Part I that the isolation of small amounts of (VI) from the products of reaction of sodium thiomethoxide on mustard gas mixtures must not be taken as proof that these mixtures contain 1 : 2-di-(2-chloroethylthio)ethane (VIII).

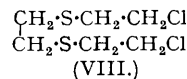
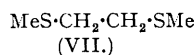
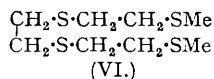
In Part I of this series (Meade and Moggridge, preceding paper) the presence of low-boiling material obtained on distillation of this family of thioethers was noted. It seemed likely that this material resulted from decomposition; and, in view of the possible use of these compounds for distillation analysis, it was decided that the nature of this decomposition ought to be studied in greater detail.

2 : 2'-Dimethylthiodiethyl sulphide (I; cf. Part I) was therefore subjected to pyrolysis, being heated to boiling at atmospheric pressure for 2½ hours. The following compounds were isolated from the complex mixture of products: methylthiol (II), methyl vinyl sulphide (IV), 2-methylthioethylthiol (V), dithian, unchanged (I), and, in low yield, 1 : 2-di-(2-methylthioethylthio)ethane (VI). The structure of (IV) was confirmed by reaction with phenylthiol to give 1-phenylthio-2-methylthioethane, and oxidation of this to the corresponding disulphone.

Rothstein (*J.*, 1940, 1550 *et seq.*) has predicted on theoretical grounds that a compound of the type  $\text{CHAR}\cdot\text{CH}_2\cdot\text{SR}'$  (where A is a group capable of forming a stable anion) will be liable to decompose to give  $\text{R}\cdot\text{CH}=\text{CH}\cdot\text{SR}' + \text{HA}$ . If this is applied to the compound (I) the following decomposition routes would be expected :



It is seen that these routes provide a ready explanation for the formation of (II), (IV), and (V). The fact that (III) was not isolated should not, it is considered, be taken as evidence against the decomposition routes; the complexity of the mixture obtained after pyrolysis made the isolation of the constituents difficult, and it is not at all improbable that (III) was present though never isolated. The presence of dithian shows that some more complex decomposition mechanisms were also involved. The formation of (VI) is discussed below.



1 : 2-Dimethylthioethane (VII) was also isolated from the pyrolysis experiments as a result of a curious secondary reaction. Methyl vinyl sulphide (IV) was first obtained from the pyrolysis mixture as a crude fraction, b. p. 40—80°, at atmospheric pressure. When this fraction was redistilled immediately the compound (IV) was obtained pure, and no sign of high-boiling material was noted. When, however, the crude fraction was kept for some hours before it was redistilled, it was found to contain appreciable quantities of higher-boiling (60°/5 mm.) compound (VII), identified by oxidation to its disulphone (cf. Otto, *J. pr. Chem.*, 1887, 36, 445).

It is thought that the explanation of this phenomenon is that the crude material, b. p. 40—80°, contained appreciable quantities of dissolved methylthiol; and that this compound, if not immediately removed by distillation, reacted with (IV) to give (VII).

The suspected occurrence of this reaction suggested that the other thiols and vinyl compounds present in the pyrolysis mixture might also combine spontaneously. Thus (II) and (III), (IV) and (V) could recombine to give (I); while (III) and (V) would give (VI). The spontaneous occurrence of several of these thiol-vinyl additions [of (II) to (IV), (IV) to (V), and (III) to (V)] has since been demonstrated (cf. Part III, following paper). The occurrence of (VI) among the breakdown products of (I), which at first sight appears puzzling owing to the relative sizes of the two molecules, can thus be plausibly explained as a result of the recombination of (III) and (V).

The occurrence of (VI) is of significance in that its isolation after treating mixtures of mustard gas and its analogues with sodium thiomethoxide would at first sight seem to provide evidence for the presence of the related chloro-compound (VIII) in the original mixtures. In Parts I and II of this series, however, two routes have now been described by which (VI) can be formed from mustard gas; the isolation of small amounts of (VI) must not therefore be taken as proof of the presence of (VIII).

## EXPERIMENTAL.

The Pyrolysis of 2 : 2'-Dimethylthiodiethyl Sulphide (I).—The thioether (redistilled, m. p. 24.3°; 40 to 80 g. in different experiments) was put into a 100 c.c. Claisen flask fitted with an 8-inch fractionating column (Vigreux type); it was then heated with a flame, the heating being adjusted to give a slow distillation (distillation temperature between 100° and 150°; initial liquid temperature *ca.* 250°). The heating was continued for 2½ hours, then the distillate and residue were combined and fractionated. The following fractions were isolated:

(a) Methylthiol was present in all experiments, and could be collected in a cold trap; yield 3–5 g. from 50 g. of (I). This compound was recognised by odour and b. p. (6°); by distillation into aqueous mercuric cyanide, mercury thiomethoxide was deposited [colourless plates from dioxan, m. p. and mixed m. p. 170° (decomp.)].

(b) The fraction, b. p. 40–80° [5–8 g. from 50 g. of (I)], on redistillation yielded *methyl vinyl sulphide* (IV), b. p. 69–70° (Found: S, 43.0. C<sub>3</sub>H<sub>6</sub>S requires S, 43.2%). This compound was a colourless oil, showing no signs of polymerisation on storage. It was mixed with phenylthiol (1 equiv.); reaction took place with evolution of heat, and was completed by heating at 100° for 15 minutes. Distillation of the product gave *1-phenylthio-2-methylthioethane* as a colourless oil, b. p. 130°/3 mm.; yield, after one distillation, 80% (Found: S, 34.8. C<sub>9</sub>H<sub>12</sub>S<sub>2</sub> requires S, 34.8%). On oxidation with perhydrol and acetic acid, *1-phenylsulphonyl-2-methylsulphonylethane* was deposited in 90% yield; colourless prisms from aqueous acetic acid, m. p. 172° (Found: S, 25.85. C<sub>9</sub>H<sub>12</sub>O<sub>4</sub>S<sub>2</sub> requires S, 25.8%).

If this fraction, b. p. 40–80°, were left overnight before being redistilled it was found to contain 1 : 2-dimethylthioethane (VII), b. p. 60°/5 mm. (cf. Ewerlöf, *Ber.*, 1871, 4, 716). This compound on oxidation with perhydrol and acetic acid gave 1 : 2-dimethylsulphonylethane, colourless plates from water, m. p. 190° (Found: S, 34.45. Calc. for C<sub>4</sub>H<sub>10</sub>O<sub>4</sub>S<sub>2</sub>: S, 34.4%). Otto, *loc. cit.*, gives m. p. 190°.

(c) A fraction, b. p. 40–125°/5 mm. [15 to 22 g. from 50 g. of (I)]. This apparently consisted of a large number of compounds, the separation of which proved difficult; nor were the results obtained in different experiments always the same. The following fractions were at one time or other obtained boiling over a fairly narrow range.

(i) A fraction, b. p. *ca.* 90°/55 mm., containing a thiol was always obtained. The SH value was variable, varying from 15.5% to 40.5% in different experiments; it is thought that the fraction consisted partly of 2-methylthioethylthiol (Moggridge, in the press); this compound requires SH, 30.5%; possible contaminants would be 1 : 2-dimethylthioethane (see above) and 1 : 2-dithioethane. In several experiments the  $\alpha$ -naphthyl carbamate of 2-methylthioethylthiol, m. p. and mixed m. p. 119° (Moggridge, in the press), was isolated after treating the fraction with  $\alpha$ -naphthyl isocyanate.

(ii) A fraction, b. p. *ca.* 90°/5 mm., containing dithian, which crystallised in the condenser on re-distillation; m. p. and mixed m. p. 111° (cf. Masson, *J.*, 1886, 49, 234). The remaining material in this fraction was never isolated in a state of purity.

(iii) In two experiments a fraction, b. p. 102–104°/2 mm., was obtained as a colourless oil (Found: S, 50.0%), giving on oxidation with perhydrol-acetic acid (cf. Part I) a sulphone, needles from water or glacial acetic acid, m. p. 168° (Found: S, 33.3%). The original compound did not reduce iodine; the sulphone was not soluble in aqueous alkali, and no satisfactory product could be isolated after the action of sodium ethoxide and methyl iodide; it therefore appeared that it did not contain a disulphonylmethane grouping. No sign of this compound was observed in later experiments; and further work on its structure was prevented by lack of material.

(d) (I), b. p. 135°/5 mm., was recovered unchanged in all experiments; crude yield, 10–15 g. from 50 g. of starting material. It was identified by conversion into its sulphone, m. p. 265°.

(e) 1 : 2-Di-(2-methylthioethylthio)ethane (VI) was isolated from the distillation residue after several distillations followed by recrystallisations; yield of material, m. p. 64°, 0.03 g. from 50 g. of (I). The compound was identified by mixed m. p. with a synthetic specimen.

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RESEARCH ESTABLISHMENT, SUTTON OAK.

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