## 380. *Some Reactions of Ethylene Sulphide, and a New Method of Preparation of Vicinal Dithiols.*

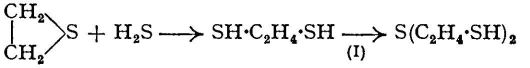
By E. M. Meade and F. N. Woodward.

Ethylene sulphide (I) has been shown to resemble ethylene oxide in many of its reactions. The ring is easily opened by the action of hydrogen chloride, chloroacetyl chloride and bromide, methane- and *n*-pentane-thiol, and hydrogen sulphide to give 2-chloroethanethiol, 2-chloro- and 2-bromo-ethylthiolochloroacetate, 2-methyl- and 2-*n*-amyl-thioethanethiols, and a mixture of ethylene dithiol (II) and 2 : 2′-dimercaptodiethyl sulphide (III), respectively. The last reaction can be modified for the continuous production of (II).

Ethylene sulphide, prepared by the interaction of chloroethyl thiocyanate and aqueous sodium sulphide (Delépine, *Compt. rend.*, 1920, **171**, 36), of 2-chloroethanethiol and aqueous sodium hydrogen carbonate (U.S.P. 2,183,860), or of thiourea or a water-soluble thiocyanate and ethylene oxide in the presence of an alkali chloride or carbonate (U.S.P. 2,094,837; Canad. P. 392,681; B.P. 465,662), has been but little investigated.

Delépine and Eschenbrenner (*Bull. Soc. chim.*, 1923, **33**, 703) found that (I) resembles ethylene oxide in many of its reactions. Nitric acid oxidised it to the acids $SO_3H\cdot CH_2\cdot CO_2H$ and $SO_3H\cdot[CH_2]_2\cdot S\cdot CH_2\cdot CO_2H$, and excess of hydrochloric acid yields a mixture of 2-chloroethanethiol, 2-chloroethylthioethanethiol, and dithian. Similarly, hydrobromic acid affords 2-bromoethanethiol.

In view of the known ease of opening of the ethylene oxide (preceding paper) and the ethyleneimine ring (*Ber.*, 1897, **30**, 2497) by the action of hydrogen sulphide, it was considered probable that (I) would behave similarly to afford (II) and (III) :



$$\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>S + H_2S \longrightarrow SH\cdot C_2H_4\cdot SH \xrightarrow[(I)]{} S(C_2H_4\cdot SH)_2$$

(I.) (II.) (III.)

$CH_2Cl\cdot CH_2\cdot S\cdot CO\cdot CH_2Cl$

(IV.)

This was found to be the case, the reaction going smoothly in methanol solution at 60°. The yields obtained in a single experiment were 49% of (II), 16% of (III), and 4% of residue [calculated as $(\cdot CH_2\cdot S\cdot C_2H_4\cdot SH)_2$]. The reaction was also carried out satisfactorily with stirring in the continuous convertor described in the preceding paper, affording a 50% yield of (II) when thiodiglycol was used as solvent. The physical characteristics of (I), (II), and (III) have been determined, as have those of 2-chloroethanethiol, which is more readily obtained by the interaction of (I) with hydrogen chloride than by means of hydrochloric acid as advocated by Bennett (*J.*, 1922, **121**, 2139); it was found to be much more stable than previously recorded by Bennett and by Delépine and Eschenbrenner. (I) reacts with sodium *n*-amyl sulphide to give a mixture of 2-n-*amylthioethanethiol* (75%) and what is presumably 2-n-*amylthioethylthioethanethiol*, $C_5H_{11}\cdot S\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot SH$ (25%). With sodium methyl sulphide, 2-methylthioethanethiol is formed, whilst with chloroacetyl chloride or bromide, 2-*chloroethyl thiolo-chloroacetate* (IV) and -bromoacetate are produced.

### Experimental.

*Ethylene Sulphide* (I).—Prepared essentially as described in B.P. 465,662, from ethylene oxide (60 g). and potassium thiocyanate (90 g.) in water (90 g.) at −5° to −10°, (I) was obtained in 27% yield, b. p. 54—55·5°, and had the following characteristics : $d_{4^\circ}^{20^\circ}$ 1·0113, $n_D^{20^\circ}$ 1·4946, $[R_L]_D$ 17·32 (Calc. : 17·21) (Found : S, 52·7. Calc. for $C_2H_4S$ : S, 53·2%).

2-*Chloroethanethiol*.—Pure distilled (I) (12 c.c.) in dry ether (200 c.c.) was saturated with dry hydrogen chloride during 20 mins. at −10°. After removal of the solvent, the residue distilled at about 80°/290 m m. On redistillation, 8 g. of the chlorothiol were obtained, b. p. 113—113·5°/760 mm. having the following physical characteristics : $d_{4^\circ}^{20^\circ}$ 1·1826, $n_D^{20^\circ}$ 1·4929, $[R_L]_D$ 23·86 (Calc. : 23·99) (Bennett, *loc. cit.*, gives b. p. 125—126°, $d_{4^\circ}^{20^\circ}$ 1·203, $n_D^{20^\circ}$ 1·5289, $[R_L]_D$ 24·74) (Found : SH, 34·0; Cl, 36·8. Calc. for $C_2H_5ClS$ : SH, 34·2; Cl, 36·8%).

2-*Chloroethyl Thiolochloroacetate*.—To distilled (I) (6 c.c.) in ether (25 c.c.) was added chloroacetyl chloride (8·4 c.c.) and the mixture refluxed for 2½ hrs. After removal of solvent, the product was distilled, and the middle fraction (8·1 g.), b. p. 85—90°/3 mm., was redistilled to give the pure *ester*, b. p.

83°/3 mm. It had the following characteristics : $d_{4^\circ}^{20^\circ}$ 1·3917, $n_{\mathrm{D}}^{20^\circ}$ 1·5295, $[R_L]_{\mathrm{D}}$ 38·74 (Calc. : 38·39) (Found : Cl, 40·7, 40·9. $C_4H_6OCl_2S$ requires Cl, 41·0%).

2-*Bromoethyl Thiolochloroacetate*.—This ester, b. p. 107—110°/7 mm., prepared similarly from chloroacetyl bromide, had $d_{4^\circ}^{20^\circ}$ 1·6965, $n_{\mathrm{D}}^{20^\circ}$ 1·5603, $[R_L]_{\mathrm{D}}$ 41·46 (Calc. : 41·43).

2-n-*Amylthioethanethiol*.—Distilled (I) (1·1 g.), sealed in a glass ampoule, was broken under a solution of *n*-pentanethiol (3 g.) in alcoholic sodium ethoxide (Na, 0·6 g; EtOH, 25 c.c.). The reaction was exothermic, and after 0·5 hr., glacial acetic acid (4 c.c.) was added together with water (75 c.c.). The aqueous solution was extracted with chloroform, and the chloroform layer was dried and distilled, giving 1·02 g. of impure *thiol*, b. p. 105°/5 mm. (Found : SH, 38·3. $C_7H_{16}S_2$ requires SH, 40·2%), and 0·33 g. of a liquid, b. p. 150°/4 mm.

2-*Methylthioethanethiol*.—A mixture of (I) in twice its volume of alcohol and a 150% excess of sodium methyl sulphide in alcohol was refluxed for 0·25 hr., and the solvent removed by distillation. The residue after cooling and acidification (dilute acetic acid) was extracted with chloroform. After removal of the solvent from the extract, distillation gave the *thiol*, b. p. 82°/40 mm., in 40% yield (Found : SH, 30·5. $C_3H_8S_2$ required SH, 30·5%).

*Ethylenedithiol* (II) *and* 2 : 2′-*Dimercaptodiethyl Sulphide* (III).—Methanol (750 c.c.) was saturated (3·5N) with hydrogen sulphide at room temperature, the solution made up to 1 l. (1·32 g.-mol. of $H_2S$), and (I) (48 g.; 0·8 g.-mol.) added. The mixture was heated at 60° for two days (time required for complete reaction as indicated by pressure change) in a stoppered bottle fitted with a sealed manometer. After removal of the alcohol, distillation gave (*a*) 36·9 g., b. p. 60°/43 mm. to 80°/10 mm.; (*b*) 9·5 g., b. p. 80°/10 mm. to 140°/12 mm.; (*c*) an undistillable residue (2·2 g.). Fraction (*a*) on redistillation gave (II), b. p. 65°/44 mm., 73°/61 mm., $d_{4^\circ}^{24^\circ}$ 1·1200, $n_{\mathrm{D}}^{20^\circ}$ 1·5497, $[R_L]_{\mathrm{D}}$ 26·70 (Calc. : 26·82) (Fasbender, *Ber.*, 1887, **20**, 461, gives b. p. 148°, $d_{4^\circ}^{24^\circ}$ 1·123), in 49% yield (Found : SH, 67·8. Calc. for $C_2H_6S_2$ : SH, 68·9%); and fraction (*b*) gave (III), b. p. 102—107°/3 mm., $d_{4^\circ}^{20^\circ}$ 1·1662, $n_{\mathrm{D}}^{20^\circ}$ 1·5807, $[R_L]_{\mathrm{D}}$ 44·08 (Calc. : 44·02) (Meadow and Reid, *J. Amer. Chem. Soc.*, 1934, **56**, 2177, give b. p. 135—136°/10 mm., m. p. −12·5°), in 15% yield (Found : S, 63·0. Calc. for $C_4H_{10}S_3$ : S, 63·4%).

When (I), dissolved in thiodiglycol (200 c.c.), was subjected to a stream of hydrogen sulphide (10 l./hr.) at 45° and stirred in the reaction vessel described in the preceding paper, (II) was obtained continuously (50% yield); b. p. 85°/120 mm., 145°/760 mm.

Thanks are due to the Chief Scientist, Ministry of Supply, for permission to publish this paper, and to Dr. G. H. Whiting and Messrs. K. H. Jack and D. Nightingale for technical assistance.

H.M. RESEARCH ESTABLISHMENT, SUTTON OAK.

[*Received, October 8th*, 1947.]