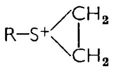
776. *The Acid-catalysed Decomposition of Hydroxyethyl Sulphides.*

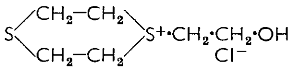
By D. Welti and D. Whittaker.

The reaction between thiodiglycol and dilute hydrochloric acid has been studied. The reaction differs from that of thiodiglycol with concentrated hydrochloric acid, since it does not produce 2,2′-dichlorodiethyl sulphide; instead, the main product is 2-chloroethyl 2-hyroxyethyl sulphide; small quantities of 1,4-dithian, 1,4-thioxan, and acetaldehyde are also formed. Under similar conditions, ethyl 2-hydroxyethyl sulphide yields 1,2-di(ethylthio)ethane and ethyl chloride. Thiodiglycol forms 1,4-dithian when refluxed with perchloric or sulphuric acid, indicating that it is not necessarily formed by way of the sulphonium salt.

Hydrolysis of 2,2′-dichlorodiethyl sulphide has been shown by Bartlett and Swain[1] to proceed in two steps, each involving the formation of the ion, namely, (I; R = $CH_2{\cdot}CH_2Cl$) in the first and (I; R = $CH_2{\cdot}CH_2{\cdot}OH$) in the second. In neutral aqueous solution, the ion (I) may react with water to give the hydroxyethyl sulphide, or with a chloride ion produced in the first step of the reaction to regenerate the chloroethyl sulphide. In alkaline solution, 2,2′-dichlorodiethyl sulphide undergoes elimination to give divinyl sulphide.[2,3]

(I)

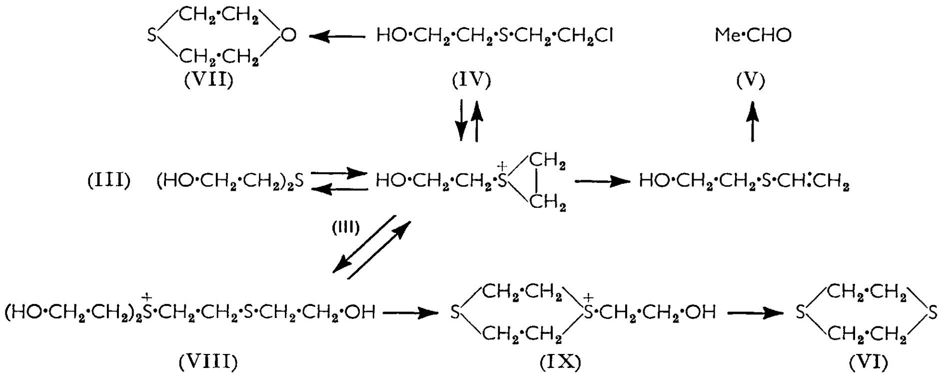




(II)

Although the hydrolysis of 2,2′-dichlorodiethyl sulphide has been the subject of many investigations, the reverse reaction has been studied infrequently. Clarke[4] demonstrated that 2,2′-dichlorodiethyl sulphide could be prepared by refluxing a solution of thiodiglycol in concentrated hydrochloric acid. The reaction of thiodiglycol with dilute hydrochloric acid gives different products at different concentrations of thiodiglycol.[3] In high concentration thiodiglycol gives a mixture of sulphonium chlorides from which 1-2′-hydroxyethyl-1,4-dithianium chloride (II) has been isolated, but in low concentration does not produce detectable quantities of sulphonium chlorides.

Reaction of Thiodiglycol.—We have found that the equilibrium mixture of thiodiglycol (III) and 2-chloroethyl 2-hydroxyethyl sulphide (IV) which was obtained by refluxing thiodiglycol with dilute hydrochloric acid reacted slowly at the b. p. to give acetaldehyde (V), 1,4-dithian (VI), and 1,4-thioxan (VII). It did not form any 2,2′-dichlorodiethyl sulphide during 48 hours' refluxing. When the equilibrium mixture or 2-chloroethyl



---

[1] Bartlett and Swain, *J. Amer. Chem. Soc.*, 1949, **71**, 1406.

[2] Bales and Nickelson, *J.*, 1923, **123**, 2486.

[3] Davies and Oxford, *J.*, 1931, 224.

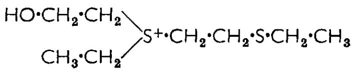
[4] Clarke, *J.*, 1912, **101**, 1583.

2-hydroxyethyl sulphide was treated with aqueous alkali, hydrogen chloride was eliminated from the latter, giving 2-hydroxyethyl vinyl sulphide. With dilute sulphuric acid thiodiglycol formed only 1,4-dithian and acetaldehyde. The formation of acetaldehyde indicates that thiodiglycol undergoes slow elimination in acid solution, the ion (I; $R = CH_2{\cdot}CH_2{\cdot}OH$) losing a proton to give 2-hydroxyethyl vinyl sulphide, which, in acid solution, would undergo hydrolysis to give acetaldehyde.[5,6] This sequence has been checked by refluxing a suspension of 2-hydroxyethyl vinyl sulphide in dilute hydrochloric acid; the reaction produced acetaldehyde, though much of the sulphide decomposed to a brown tar. Experiments with ethylene glycol and 2-mercaptoethanol, the two probable products of fission of the C–S bond of thiodiglycol, have shown that neither decomposes to acetaldehyde under the conditions of the reaction.

Hydrolysis of 2-chloroethyl 2-hydroxyethyl sulphide in aqueous solution is rapid at 25°, so that the rate of formation of this compound from thiodiglycol must exceed the rate of elimination of water from thiodiglycol by several powers of ten.

The production of 1,4-dithian from thiodiglycol requires the condensation of at least two molecules of thiodiglycol. Davies and Oxford[3] have shown that the reaction of concentrated solutions of thiodiglycol in dilute hydrochloric acid gives the chloride (II), which is probably the precursor of 1,4-dithian under these conditions,[7] but reaction of thiodiglycol in the presence of dilute perchloric or sulphuric acids cannot proceed through a sulphonium salt. Under these conditions, the first step of the reaction is probably the reaction of a neutral thiodiglycol molecule with the ion (I; $R = CH_2{\cdot}CH_2{\cdot}OH$) to give the ion (VIII). Comparison with the work of Davies and Oxford[3] suggests that this ion then forms the ion (IX) which decomposes to 1,4-dithian.

The ion (IX) may be formed from the ion (VIII) by an internal cyclisation involving the hydroxyl group on the carbon atom in the ε-position to the sulphonium ion centre, resulting in elimination of ethylene glycol. In support we find that acid-catalysed decomposition of ethyl 2-hydroxyethyl sulphide probably takes place through the ion (X),



$$(HO{\cdot}CH_2{\cdot}CH_2)(CH_3{\cdot}CH_2)S^+{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_3$$

(X)

but does not produce 1,4-dithian even at high concentrations of the hydroxyethyl sulphide, suggesting that the presence of a hydroxyl group on the carbon atom in the position ε to the sulphonium ion centre is a necessary condition for the formation of 1,4-dithian.

An alternative route from (VIII) to (IX) might involve formation of 1,2-di-(2-hydroxyethylthio)ethane from (VIII), followed by protonation of this substance and loss of water to give the ion (I; $R = CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}OH$), which can then cyclise to (IX). This route has been disproved by preparing 1,2-di-(2-hydroxyethylthio)ethane, and showing that it produces polymeric ethylene sulphide, which was not detected in the reaction of thiodiglycol, in addition to 1,4-dithian, when refluxed with dilute hydrochloric acid.

The reaction between thiodiglycol and dilute hydrochloric acid produces traces of 1,4-thioxan, but this compound has not been detected in the reaction of thiodiglycol with dilute sulphuric acid, suggesting that it is formed from 2-chloroethyl 2-hydroxyethyl sulphide rather than from any of the ions discussed previously. Fuson and Ziegler[8] found that 2-chloroethyl 2-hydroxyethyl sulphide and alcoholic alkali produce some 1,4-thioxan, but insufficient evidence is available on the reactions in either acid or alkaline medium to permit comparison between the two.

With concentrated hydrochloric acid thiodiglycol produces 2,2′-dichlorodiethyl sulphide,[4] but not acetaldehyde or 1,4-dithian.

---

[5] Fitt and Owen, *J.*, 1957, 2250.
[6] Tarbell and Lovett, *J. Amer. Chem. Soc.*, 1956, **78**, 2259.
[7] Ray and Levine, *J. Org. Chem.*, 1937, **2**, 267.
[8] Fuson and Ziegler, *J. Org. Chem.*, 1946, **11**, 510.

Reaction of Ethyl 2-Hydroxyethyl Sulphide.—With dilute hydrochloric acid ethyl-2-hydroxyethyl sulphide reacts differently from thiodiglycol. No free chloride has been isolated, suggesting that any chloride produced reacts rapidly with the free hydroxyethyl sulphide, to give the sulphonium chloride. The main products are 1,2-di(ethylthio)ethane and ethyl chloride; a trace of diethyl disulphide is also produced. The products indicate that the main reaction proceeds through the ion (X), a mechanism analogous to that proposed by Fitt and Owen [5] for the acid-catalysed decomposition of 2-hydroxyethyl methyl sulphide.

With dilute sulphuric or dilute perchloric acid ethyl 2-hydroxyethyl sulphide gives products similar to those produced in the reaction with dilute hydrochloric acid, indicating that (X) may be formed through the ion (I; $R = CH_2{\cdot}CH_3$) or the chloride. The ion (X) can decompose by any of three routes,[7] reacting with water or hydrochloric acid:

$$(a)\ (X) \longrightarrow HO{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_3 + HO{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_3 \text{ or } Cl{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_3$$

$$(b)\ (X) \longrightarrow CH_3{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_3 + HO{\cdot}CH_2{\cdot}CH_2{\cdot}OH \text{ or } Cl{\cdot}CH_2{\cdot}CH_2{\cdot}OH$$

$$(c)\ (X) \longrightarrow HO{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_3 + HO{\cdot}CH_2{\cdot}CH_3 \text{ or } Cl{\cdot}CH_2{\cdot}CH_3$$

Attempts to isolate a pure sample of 1-ethylthio-2-(2-hydroxyethylthio)ethane from the reaction mixture have not been successful, as the water-soluble component of the product is readily decomposed by heat.

The diethyl disulphide formed probably arises by oxidation of ethanethiol, but it is not evident how this was formed. There is no evidence of elimination of water from ethyl 2-hydroxyethyl sulphide to give ethyl vinyl sulphide, which would produce ethanethiol on hydrolysis, so it seems probable that some of the thiol was formed by fission of the C–S bond of ethyl 2-hydroxyethyl sulphide. This reaction should also produce some 2-mercaptoethanol, which Bennett [9] has shown to decompose in dilute hydrochloric acid to give polymeric ethylene sulphide, but in the presence of ethyl 2-hydroxyethyl sulphide reaction with this substance may be faster than dehydration.

The rapid reaction of the ion (I; $R = CH_2{\cdot}CH_3$) with a molecule of the free substrate to give the ion (X) indicates that this ion is considerably less stable than the ion (I; $R = CH_2{\cdot}CH_2{\cdot}OH$). The reactions of the ions (VIII) and (X) are also influenced by the presence of hydroxyl groups, so that no direct comparison of the reaction mechanisms of thiodiglycol and ethyl 2-hydroxyethyl sulphide can be made.

EXPERIMENTAL

Thiodiglycol.—Commercial thiodiglycol distilled at 140—144°/6 mm. to give a colourless syrup (lit.,[10] b. p. 137°/5 mm.). Gas–liquid chromatography on a column of 15% of polyethylene glycol adipate on Embacel at 150° gave a single peak.

1,2-*Di*-(2-*hydroxyethylthio*)*ethane.*—1,2-Di-(2-hydroxyethylthio)ethane was prepared by reaction between the sodium derivative of ethane-1,2-dithiol and ethylene chlorohydrin. After recrystallisation from acetone, it had m. p. 59—61°, b. p. 100°/2 mm. (lit.,[11] m. p. 64°) (Found: C, 39·7; H, 7·6; S, 35·4. Calc. for $C_6H_{14}O_2S_2$: C, 39·6; H, 7·7; S, 35·2%).

Ethyl 2-*Hydroxyethyl Sulphide.*—This sulphide was prepared by reaction of ethanethiol with ethylene oxide in methanol containing a catalytic quantity of sodium. The method is similar to that used by Adams and his co-workers [12] for preparing mercapto-sulphides from olefin sulphides (cf. refs. 13, 14). The product had b. p. 75—76°/12 mm. (lit.,[14,15] 79·5°/14 mm., 81°/20 mm.). Gas–liquid chromatography as above at 100° showed it to be 95% pure (Found: C, 45·7; H, 9·4. Calc. for $C_4H_{10}OS$: C, 45·3; H, 9·4%). The product was identical with a

---

[9] Bennett, *J.*, 1922, **121**, 2139.

[10] Ross, *J. Amer. Chem. Soc.*, 1946, **68**, 1484.

[11] Bennett and Whincop, *J.*, 1921, **119**, 1860.

[12] Adams, Doyle, Hatt, Holland, Hunter, Mansford, Nayler, and Queen, *J.*, 1960, 2649; Gilman and Fullhart, *J. Amer. Chem. Soc.*, 1949, **71**, 1478.

[13] Nenitzescu and Scarlatescu, *Ber.*, 1935, **68**, 587.

[14] Culvenor, Davies, and Heath, *J.*, 1949, 278.

[15] Fehér and Vogelbruch, *Chem. Ber.*, 1958, **91**, 996.

sample, b. p. 49—51°/3 mm., prepared by reaction of sodium ethyl sulphide with ethylene chlorohydrin.[15]

1,2-*Di*(*ethylthio*)*ethane*.—Prepared from sodium ethyl sulphide and 1,2-dichloroethane,[15] this had b. p. 48—54°/0·2 mm. (lit.,[15] b. p. 56°/0·5 mm.). Gas–liquid chromatography as above at 100° (40 ml. of argon per min.) gave a single peak after 28 min. (Found: C, 48·0; H, 9·6. Calc. for $C_6H_{14}S_2$: C, 48·0; H, 9·3%).

1,4-*Dithian*.—1,4-Dithian, m. p. 111° (lit.,[16] m. p. 112°), was supplied by Dr. W. A. Swindin, of Unilever Research Laboratory, Port Sunlight.

1,4-*Thioxan*.—Commercial 1,4-thioxan was shown by gas–liquid chromatography as above at 100° to be 95% pure. With hydrogen peroxide in glacial acetic acid containing 5% of concentrated hydrochloric acid it gave the sulphone, m. p. 131—133° (lit.,[17] m. p. 130°).

Reaction of Hydroxyethyl Sulphides.—Initial studies of each reaction were carried out by refluxing 15 ml. of the sulphide with 135 ml. of ~10% hydrochloric acid for 8 hr. under a condenser, connected to a trap immersed in a solid carbon dioxide–alcohol (calcium chloride guard-tube). During some experiments in which acetaldehyde was known to be produced, the emergent gases passed through a saturated solution of 2,4-dinitrophenylhydrazine hydrochloride in 10% hydrochloric acid but no hydrazone was formed. Two batches of hydrochloric acid were used, one 3·79M, the other 3·85M (the difference did not affect the reaction products).

Reaction of Thiodiglycol with Dilute Hydrochloric Acid.—Thiodiglycol (18 g.) was refluxed with 10% hydrochloric acid (135 ml.) for 8 hr.

Adding 2,4-dinitrophenylhydrazine reagent to the trap gave acetaldehyde 2,4-dinitrophenylhydrazone (0·3 g.), m. p. 145—146° (lit.[18] 146°). Recrystallisation from alcohol gave the other form, m. p. 165° (lit.,[18,19] 167°), $\lambda_{max.}$ 360 mμ (in 95% EtOH), having the correct infrared spectrum.

The infrared spectrum of a carbon tetrachloride solution of the trap contents showed that the solution contained 1,4-thioxan in addition to acetaldehyde. Attempts to confirm this by oxidation with hydrogen peroxide in acetic acid containing 5% of concentrated hydrochloric acid were not successful, probably because of the small quantity of thioxan produced. The intensity of the infrared spectrum suggests that ~50 mg. are produced during 8 hr.

During the reaction, crystals of 1,4-dithian (0·1 g.) were deposited in the condenser. These had the correct infrared spectrum and m. p. and mixed m. p. 110—111° (from acetone) (lit.,[16] 112°) (Found: C, 40·2; H, 6·8. Calc. for $C_4H_8S_2$: C, 40·0; H, 6·7%).

The residue from the reaction was extracted with chloroform (3 × 200 ml.), washed with water (100 ml.), and decolorised with Norite. Removal of the chloroform left ~1 ml. of 2-chloroethyl 2-hydroxyethyl sulphide, n_D^{23} 1·521 (lit.,[8,20] n_D^{20} 1·5188, $n_D^{24·5}$ 1·5205). Analysis (Found: C, 33·3; H, 5·5; Cl, 24·0; S, 23·1. Calc. for C_4H_9ClOS: C, 34·2; H, 6·4; Cl, 25·2; S, 22·7%) showed that the material was not pure. Treatment with aqueous 40% potassium hydroxide at 60° gave an oil, a chloroform extract of which was washed with water. Removing the solvent under a vacuum gave an oil $\nu_{max.}$ 3387 (OH), 1584s, 3091w, 3010w, 961w, and 870w cm.$^{-1}$, characteristic of a vinyl group next to a sulphur atom (Mikawa [21] reports that ethyl vinyl sulphide has $\nu_{max.}$ 1585 cm.$^{-1}$, probably due to the vinyl group).

The unsaturated material was distilled at 114°/10 mm., separating the volatile part from a residue, the infrared spectrum of which suggested that it was a polymeric form of the volatile material. The distillate was identified as 2-*hydroxyethyl vinyl sulphide* by its infrared spectrum and analysis (Found: C, 46·2; H, 7·6; S, 31·3. C_4H_8OS requires C, 46·2; H, 7·7; S, 30·8%). The molecular weight was found to be 104 by mass-spectrometry (strong peaks m/e 105 and 106 disappear on lowering the potential of the spectrometer from 70 to 7 v and may be formed by ion-molecule reactions). The identification of 2-hydroxyethyl vinyl sulphide confirms the view that the main product of this reaction was 2-chloroethyl 2-hydroxyethyl sulphide. The nature of the impurities in the original sample is unknown.

Formation of 1,4-*Dithian from Thiodiglycol*.—Yields of 1,4-dithian formed with varying

---

[16] Mansfeld, *Ber.*, 1886, **19**, 700.
[17] Price and Bullitt, *J. Org. Chem.*, 1947, **12**, 242.
[18] Ingold, Pritchard, and Smith, *J.*, 1934, 79.
[19] Braude and Jones, *J.*, 1945, 498.
[20] Rueggeberg, Cook, and Reid, *J. Org. Chem.*, 1948, **13**, 114.
[21] Mikawa, *Bull. Chem. Soc. Japan*, 1956, **29**, 110.

concentrations of thiodiglycol in hydrochloric and other acids are given in Table 1. The reaction with sulphuric acid produced acetaldehyde, identified by the m. p. and infrared spectrum of its 2,4-dinitrophenylhydrazone, but did not produce any 1,4-thioxan; no attempt was made to detect 1,4-thioxan or acetaldehyde after the reaction with perchloric acid.

TABLE 1.

Acid	Vol. of 4N-acid (ml.)	Wt. of thiodiglycol (g.)	Time of refluxing (hr.)	Yield of 1,4-dithian g.)
HCl	135	18	8	0·1
HCl	100	60	8	1·2
HCl	750	60	8	0·2
$HClO_4$	100	60	24	3·0
H_2SO_4	100	60	24	3·0

Experiments on Acetaldehyde Formation.—(*a*) Ethylene glycol or 2-mercaptoethanol (15 ml.) was refluxed with 10% hydrochloric acid (135 ml.). After 8 hours' refluxing, the contents of the trap did not react with 2,4-dinitrophenylhydrazine reagent. (*b*) 2-Hydroxyethyl vinyl sulphide (10 ml.) (an undistilled preparation from the alkaline hydrolysis of the product of the reaction between thiodiglycol and dilute hydrochloric acid) was shaken with 10% hydrochloric acid (140 ml.). Addition of 2,4-dinitrophenylhydrazine reagent to 5 ml. of this suspension did not produce a precipitate. The suspension was refluxed for 8 hr., then addition of 2,4-dinitrophenylhydrazine reagent to the trap gave a precipitate which was identified by its infrared spectrum as acetaldehyde 2,4-dinitrophenylhydrazone. After recrystallisation from ethanol, it had m. p. 164—166°, $\lambda_{max.}$ 360 mμ (in 95% EtOH).

The residue from this reaction contained a tar and a white solid, m. p. 122—124°, which was identified by its infrared spectrum as polymeric ethylene sulphide. Recorded m. p.s of this vary; Bennett [9] reports 177—180°, while Hurd and Wilkinson [22] report 158—165°. We have obtained values from 102° to 170°, depending on the method of preparation of the samples. The infrared spectra of all these samples are, however, identical. This compound was not detected in the reaction of thiodiglycol with acid, but was probably produced in this experiment by dehydration of 2-mercaptoethanol formed during the experiment.[9] This substance reacts with thiodiglycol to give long-chain hydroxyethyl sulphides.[23]

Reaction of Thiodiglycol with Concentrated Hydrochloric Acid.[4]—In this work the carbon dioxide–alcohol trap was replaced by a bubbler containing 2,4-dinitrophenylhydrazine reagent. When thiodiglycol (18 g.) was refluxed with concentrated hydrochloric acid (135 ml.), the solution quickly became turbid, and a heavy oil separated. After 8 hours' refluxing, crude 2,2′-dichlorodiethyl sulphide was separated, washed with water, and distilled at 67°/0·9 mm. (Found: C, 30·1; H, 5·4; Cl, 43·7; S, 20·1. Calc. for $C_4H_8Cl_2S$: C, 30·1; H, 5·0; Cl, 44·6; S, 20·1%). The 2,4-dinitrophenylhydrazine reagent in the bubbler did not afford a precipitate. The reaction did not produce a detectable amount of 1,4-dithian.

Reaction of 1,2-*Di*-(2-*hydroxyethylthio*)*ethane with Dilute Hydrochloric Acid.*—1,2-Di-(2-hydroxyethylthio)ethane (15 g.) was reflxed with 10% hydrochloric acid (135 ml.) for 8 hr. On adding 2,4-dinitrophenylhydrazine reagent to the cold trap, no precipitate was formed. White crystals (1·1 g.) deposited on the condenser were identified by their infrared spectrum as 1,4-dithian, m. p. and mixed m. p. 110—111°. The residue contained a white precipitate, almost insoluble in all common solvents. It had m. p. 167—170° and was identified as polymeric ethylene sulphide by its infrared spectrum.

Reaction of Ethyl 2-*Hydroxyethyl Sulphide with Dilute Hydrochloric Acid.*—Ethyl 2-hydroxyethyl sulphide (15 g.) was refluxed with 10% hydrochloric acid (135 ml.) for 8 hr. The contents of the trap did not react with 2,4-dinitrophenylhydrazine reagent, but, when shaken with water, the aqueous layer gave a purple colour with sodium nitroprusside after treatment with potassium cyanide (test for a disulphide). The main component of the trap contents was identified as ethyl chloride by comparison of its infrared spectra in carbon tetrachloride and carbon disulphide with those of authentic samples. The identification was confirmed by mass-spectrometric examination of the product.

Mass-spectrometry of a sample from which most of the ethyl chloride had been allowed to evaporate gave a spectrum which, though partly obscured by residual ethyl chloride, and

---

[22] Hurd and Wilkinson, *J. Amer. Chem. Soc.*, 1949, **71**, 3429.

[23] Gasson, McCombie, Williams, and Woodward, *J.*, 1948, 44.

possibly other impurities, had strong peaks at *m/e* values of 66, 94, and 122, characteristic of diethyl disulphide.

The residue from the reaction consisted of two phases. The upper layer, ~4 ml. of an oil with a very unpleasant sickly-sweet smell, was separated, washed with water, then distilled at 48—55°/0·2 mm. Analysis by gas–liquid chromatography as above at 100° (40 ml. of argon per min.) gave a single peak after 28 min. It was identified as 1,2-di(ethylthio)ethane by its infrared spectrum (Found: C, 48·0; H, 9·4; S, 42·6. Calc. for $C_6H_{14}S_2$: C, 48·0; H, 9·3; S, 42·7%). The aqueous phase of the residue contained an oil which could be extracted with chloroform but readily decomposed on distillation or analysis by gas–liquid chromatography. The infrared spectrum showed some similarity to that of ethyl 2-hydroxyethyl sulphide but differed from it in detail (Found: C, 44·8; H, 9·0; S, 34·5. Calc. for a 1 : 1 mixture of $C_4H_{10}OS$ and $C_6H_{14}OS_2$: C, 45·1; H, 9·0; S, 34·4%).

Formation of 1,2-*Di*(*ethylthio*)*ethane from Ethyl* 2-*Hydroxyethyl Sulphide.*—Decomposition of ethyl 2-hydroxyethyl sulphide in dilute sulphuric acid and dilute perchloric acid gives 1,2-di(ethylthio)ethane. The results are given in Table 2.

TABLE 2.

Acid	Vol. (ml.) of 4N-acid	Wt. (g.) of $EtS{\cdot}[CH_2]_2{\cdot}OH$	Time of refluxing (hr.)	Yield (g.) of $(EtS{\cdot}CH_2)_2$
HCl	135	15	8	4·0
H_2SO_4	135	15	24	0·5
$HClO_4$	135	15	24	0·5

Attempt to Obtain 1,4-*Dithian by Reaction of Ethyl* 2-*Hydroxyethyl Sulphide.*—This sulphide (50 g.) and 10% hydrochloric acid (100 ml.) were refluxed together for 8 hr. The reaction produced 1,2-di(ethylthio)ethane and ethyl chloride, but not 1,4-dithian.

Reaction of 2-*Mercaptoethanol with Dilute Hydrochloric Acid.*—Commercial 2-mercaptoethanol (15 ml.) was refluxed with 10% hydrochloric acid (135 ml.) for 8 hr. The contents of the trap did not then react with 2,4-dinitrophenylhydrazine. The main product of the reaction was polymeric ethylene sulphide, m. p. 151°, identified by its infrared spectrum and insolubility in most organic solvents. The reaction also produced a small quantity (0·2 g.) of 1,4-dithian, m. p. and mixed m. p. 110°, the identity being confirmed by comparison of the infrared spectrum. Bennett [9] obtained polymeric ethylene sulphide from this reaction, and noted a pungent smell which he assumed to be monomeric ethylene sulphide, but this experiment indicates that it was probably 1,4-dithian.

Reaction of 2-*Mercaptoethanol with Dilute Hydrochloric Acid in the Presence of Ethyl* 2-*Hydroxyethyl Sulphide.*—A mixture of ethyl 2-hydroxyethyl sulphide (10 ml.), 2-mercaptoethanol (2 ml.), and 10% hydrochloric acid (140 ml.) remained clear after 8 hours' refluxing, showing that the reaction had not produced any polymeric ethylene sulphide; when the quantity of 2-mercaptoethanol used was increased to 5 ml., a precipitate of polymeric ethylene sulphide was obtained after 8 hours' refluxing.

Spectroscopic Measurements.—The infrared spectra were recorded linearly in $cm.^{-1}$ between 650 and 3650 $cm.^{-1}$ with a Unicam S.P. 100 double-beam infrared spectrometer equipped with a sodium chloride prism-grating double monochromator (1500 lines per inch from 650 to 2150 $cm.^{-1}$, and 3000 lines per inch from 2150 to 3650 $cm.^{-1}$) operated under dry nitrogen. The spectra were scanned at 190 $cm.^{-1}$ per min. Owing to the fast scanning speed, we cannot quote an accuracy of better than ± 2 $cm.^{-1}$ though it was generally better than that.

The ultraviolet spectra were recorded on a Unicam S.P. 700 spectrophotometer. Any errors greater than 1 mμ are due to the difficulty of assessing the actual position of broad maxima.

The mass spectra were obtained on an A.E.I. M.S. 2H mass spectrometer.

Gas chromatography.—Gas-chromatographic measurements were made on a Pye Argon gas chromatograph.

The authors thank Dr. T. H. Shuttleworth and Mr. D. P. Barrett, of Unilever Research Laboratory, Port Sunlight, for interpretation of the mass-spectrometric data, and Misses J. A. Airey, V. Kay, C. K. Kemp-Small and S. Sayer for technical assistance.

UNILEVER RESEARCH LABORATORY, COLWORTH HOUSE,
SHARNBROOK, BEDFORD.

[*Received, March* 26*th*, 1962.]