XXX.—*Formation of Sulphonium Chlorides and of Unsaturated Substances by the Action of Water and of Aqueous Alcoholic Potash on ββ′-Dichlorodiethyl Sulphide.*

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THE hydrolysis of ββ′-dichlorodiethyl sulphide (I) has formed the subject of numerous investigations and it has generally been assumed that the reaction occurs in two stages:

(1) $S(C_2H_4Cl)_2$ (I) + H_2O ⟶ $C_2H_4Cl{\cdot}S{\cdot}C_2H_4{\cdot}OH$ (II) + HCl
(2) $C_2H_4Cl{\cdot}S{\cdot}C_2H_4{\cdot}OH$ + H_2O ⟶ $S(C_2H_4{\cdot}OH)_2$ (III) + HCl

It is probable, however, that the assumed intermediate (II) has not yet been isolated (compare Wilson, Fuller, and Schur, *J. Amer. Chem. Soc.*, 1922, **44**, 2762, 2867). Bales and Nickelson (J., 1922, **121**, 2137; 1923, **123**, 2486), studying the action of aqueous-alcoholic potash on ββ′-dichlorodiethyl sulphide, isolated a liquid, b. p. 152—154°, to which they assigned the constitution (II), but, as explained later, this substance appears to be β-chloroethyl vinyl sulphide. Our attempts to prepare β-chloro-β′-hydroxydiethyl sulphide (II) from the sodium salt of monothioethylene glycol and ethylene dichloride (compare Bennett and Whincop, J., 1921, **119**, 1862) and from β-chloroethyl mercaptan and ethylene oxide failed. The last-named reaction was not studied very closely, chiefly on account of the inaccessibility of β-chloroethyl mercaptan, but ethylene chlorohydrin appeared to be the only volatile liquid formed.

An attempt has also been made to obtain β-chloro-β′-hydroxydiethyl sulphide directly from ββ′-dichlorodiethyl sulphide by evaporating a solution of the latter in the minimum amount of boiling water at a low temperature under diminished pressure. The product was a syrup, insoluble in chloroform and acetone (hence neither II nor III) but readily soluble in cold water to give a solution containing much chloride ion. In previous work on the hydrolysis of (I) a large excess of water has usually been employed. Under these conditions the conversion into thiodiglycol (III) is almost quantitative, but it is now found that when the amount of boiling water is greatly reduced, for example, to about thrice the volume of the chloro-sulphide, the reaction takes an unexpected course. Little free thiodiglycol or other chloroform-soluble substance can be isolated, but the solution contains hydrochloric acid and a complex mixture of sulphonium chlorides of two distinct

types, (*a*) those whose aqueous solutions yield hydrochloric acid on boiling and form an insoluble oil (mostly I) when heated with concentrated hydrochloric acid, and (*b*) those whose aqueous solutions are stable to heat and do not yield an insoluble oil with hydrochloric acid. Chlorides of type (*b*) are the chief products only when the amount of water used is as small as possible. Only one of the sulphonium chlorides present in the syrup obtained by evaporation of the solution has been isolated in a state of purity, namely, 1 : 4-*dithian* 1-β-*hydroxyethochloride* (VI; type *b*), identical with one of the products of the interaction of ethylene bis-β-hydroxyethyl sulphide (XI) and ethylene chlorohydrin, and also of ethylene chlorohydrin and 1 : 4-dithian. The last-named synthesis places its constitution beyond doubt. Similar syrupy mixtures of sulphonium chlorides (containing VI) can also be obtained in the reverse way by heating ββ′-dihydroxydiethyl sulphide with dilute hydrochloric acid under suitable conditions (p. 233).

According to formula (VI) two C_2H_4S residues have united during hydrolysis. Examples of similar condensations have been recorded by Bell, Bennett, and Hock (J., 1927, 1803), and Phillips, Davies, and Mumford (J., 1929, 540). By the mechanism suggested there, the compound (VI) can be obtained theoretically from (III) and (I) or (II), from (II) and (I), or from two molecules of (II). The first possibility can be ruled out definitely, since the interaction of (III) and (I) gives *sulphidobis*-β-*hydroxydiethyl sulphide* 1 : 3-*di*-β-*hydroxyethochloride* * (IX; a sulphonium chloride of type *a*), in which two molecules of the former have united with one of the latter. An attempt to prepare (IX) from sulphidobis-β-hydroxydiethyl sulphide, $S(C_2H_4{\cdot}S{\cdot}C_2H_4{\cdot}OH)_2$ (Bennett and Whincop, *loc. cit.*), and ethylene chlorohydrin led to the isolation of two sulphonium chlorides, *viz.*, (VI) and a substance which is probably the isomeride of (IX), *viz.*, *sulphidobis*-β-*hydroxydiethyl sulphide* 1 : 2-*di*-β-*hydroxyethochloride* (VIII).

Thiodiglycol (III), unlike (I), unites readily with methyl iodide and other alkyl and aryl halides, and with ethylene chlorohydrin to give *tri*-β-*hydroxyethylsulphonium chloride* (XII); also, unlike any other sulphide investigated here, it forms a crystalline sulphonium chloride with (I) itself, as mentioned above. It is thus clear why all attempts to isolate β-chloro-β′-hydroxydiethyl sulphide (II) by hydrolysis of (I) have failed, for, even if it were formed momentarily, it might unite with itself and most certainly would combine with (III) to form sulphonium chlorides. Although the conditions of hydrolysis favour the suggestion that the chlorohydroxy-sulphide

* The sulphur atoms are numbered 1, 2, and 3, starting from one end of the chain.

(II) is the main source of sulphonium chloride formation, it is almost certain that the dihydroxy-compound (III) also takes part, and if it is further assumed that any compound of the form $R{\cdot}S{\cdot}C_2H_4{\cdot}OH$ so arising may by virtue of its reactive sulphur atom unite with any compound present containing the group C_2H_4Cl, it follows that a large number of sulphonium chlorides may be formed and that the syrupy hydrolysis product may well be a complex mixture. The scheme on p. 227 outlines some of the possibilities (unknown compounds being enclosed in parentheses). The substances (XII) and (IX) have been prepared by other methods (see above) but have not actually been isolated from the hydrolysis syrup.

In order that (VI) (with the skeleton $S<^{C_2H_4}_{C_2H_4}>S{\cdot}C_2H_4{\cdot}$) may arise from $2S(C_2H_4{\cdot})_2$, it seems essential to assume the splitting off of either ethylene chlorohydrin or ethylene dichloride at some intermediate stage, *e.g.*, from (IV) and (X) respectively. Neither was detected among the hydrolysis products, but the former might have combined with (III) to give (XII). Since ethylene dichloride does not unite with thiodiglycol to form a sulphonium chloride, it would appear that it was not formed during the hydrolysis. The yield of (VI) is increased by reducing the relative amount of water, clearly because the intermediates have then a better chance of reacting with each other, and it is quite probable that (VI) may be reached by more than one route, *e.g.*, along routes (*a*) I $\longrightarrow$ II $\longrightarrow$ IV $\longrightarrow$ V $\longrightarrow$ VI and (*b*) I $\longrightarrow$ II $\longrightarrow$ III $\longrightarrow$ VII $\longrightarrow$ VIII $\longrightarrow$ V $\longrightarrow$ VI. This view is strongly supported by the formation of (VI) from ethylene chlorohydrin and ethylene bis-β-hydroxyethyl sulphide (XI), probably along the route XI $\longrightarrow$ VII $\longrightarrow$ VIII $\longrightarrow$ V $\longrightarrow$ VI (compare *b* above), and also by its formation together with (VIII) from ethylene chlorohydrin and sulphidobis-β-hydroxydiethyl sulphide.

Since most of the theoretically possible intermediate compounds contain two or three atoms of sulphur, it might be expected that corresponding dichloro-di- and -tri-sulphides might be formed together with (I) when the hydrolysis syrup is heated with concentrated hydrochloric acid. In one such experiment, ethylene bis-β-chloroethyl sulphide ($C_2H_4Cl{\cdot}S{\cdot}C_2H_4{\cdot}S{\cdot}C_2H_4Cl$) was in fact isolated in small yield, in all probability being derived from (V).

The introduction of gaseous hydrogen chloride into anhydrous ββ′-dihydroxydiethyl sulphide at 100° gives rise to no sulphonium chlorides but to a distillable liquid, chiefly (I), and an almost equal amount of an undistillable oil, which on treatment with alcoholic sodium phenoxide yields a crystalline *diphenoxy*-derivative, $C_{20}H_{26}O_3S_2$. The main constituent of the parent undistillable oil

(I.) S(C2H4Cl)2
H2O
[C2H4Cl·S·C2H4·OH] (II.) + HCl
H2O
S(C2H4·OH)2 (III.) + HCl
III + II
+C2H4Cl·OH
S(C2H4·OH)3 (XII.)
III + I
I + II
II + II
(IV.)
(X.)
Loss of C2H4Cl·OH
Loss of C2H4Cl·OH
(V.)
Loss of S(C2H4·OH)2 and C2H4Cl·OH
(IX.)
(VII.)
VII + II
+C2H4Cl·OH
(XI.)
+C2H4Cl·OH
(VIII.)
(VI.) (compare Bennett, Heathcoat, and Mosses, J., 1929, 2567).

is therefore probably *oxidobis-β-chlorodiethyl sulphide*, $C_8H_{16}OCl_2S_2$, formed from (II) by loss of water :

$$2C_2H_4Cl\cdot S\cdot C_2H_4\cdot OH \longrightarrow (C_2H_4Cl\cdot S\cdot C_2H_4)_2O + H_2O^*$$

A parallel may be found in the production of $(EtO\cdot C_2H_4\cdot S\cdot C_2H_4)_2O$ from β-ethoxy-β′-hydroxydiethyl sulphide by the action of zinc chloride (Kretov, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 2345). Sulphonium chloride formation is, however, encountered again when thionyl chloride reacts with a large excess of thiodiglycol (III), and attempts to prepare β-chloro-β′-hydroxydiethyl sulphide by this method failed.

There remains to be considered the compound, b. p. 152—154°, which Bales and Nickelson (*loc. cit.*) obtained by the action of aqueous-alcoholic potash on (I) and which, when treated with phosphorus trichloride, apparently was reconverted into (I). A comparison of the physical constants of their product with those of (I) and (III) gave rise to doubt as to the validity of their conclusions and the present authors found that by the action of potassium hydroxide (1 mol.) in 20% aqueous alcohol ββ′-dichlorodiethyl sulphide was incompletely converted into a mixture of divinyl sulphide and *β-chloroethyl vinyl sulphide* (XIII), b. p. 151·5—152·5°/764 mm., which readily absorbed hydrogen chloride without formation of water to give αβ′-dichlorodiethyl sulphide (XIV).

$$(I) \xrightarrow{-HCl} CH_2{:}CH\cdot S\cdot C_2H_4Cl\ (XIII.) \xrightarrow{+HCl} CHMeCl\cdot S\cdot C_2H_4Cl\ (XIV.)$$

Employing a large excess of aqueous alcoholic potash, we have obtained results largely in agreement with those of Kretov (*loc. cit.*), who has exhaustively studied the action of zinc dust and alcohol on (I), but in addition *β-ethoxyethyl vinyl sulphide* has been isolated.

Experimental.

ββ′-Dihydroxydiethyl sulphide (thiodiglycol) (III) was prepared by a modification of Gomberg's method (*J. Amer. Chem. Soc.*, 1919, **41**, 1414). It is a colourless viscous oil, b. p. 130°/2 mm., $d_4^{20°}$ 1·1821, readily soluble in water, ethyl acetate, alcohol, acetone, and chloroform and very sparingly soluble in ether, benzene, and carbon tetrachloride.

The *diphenylcarbamate* (6·6 g.), prepared from the sulphide (2 g.)

* The scheme $S(C_2H_4\cdot OH)_2 - H_2O \longrightarrow S\langle{}^{C_2H_4}_{C_2H_4}\rangle O \xrightarrow{+\text{I or II}}$ $(Cl \text{ or } OH)\cdot C_2H_4\cdot S\cdot C_2H_4\cdot SCl\langle{}^{C_2H_4}_{C_2H_4}\rangle O \xrightarrow{HCl} C_2H_4Cl\cdot S\cdot C_2H_4\cdot S\cdot C_2H_4\cdot O\cdot C_2H_4Cl$ provides an alternative structure for the undistillable chloro-sulphide, but is improbable in view of the fact that *ββ′*-dichlorodiethyl sulphide, although miscible with 1 : 4-thioxan, does not react with it to any appreciable extent even at 140°.

and phenylcarbimide (5 g.) on the water-bath, separated from benzene as a felted mass of long silky needles, m. p. 128·5—129·5° (Found :* C, 60·4; H, 5·6; N, 7·6. $C_{18}H_{20}O_4N_2S$ requires C, 60·0; H, 5·6; N, 7·8%). The methiodide is a viscous, uncrystallisable, red oil, insoluble in chloroform. Its neutral aqueous solution develops no acidity on boiling. The p-*toluenesulphilimine* (18 g.), obtained by keeping aqueous solutions of the sulphide (12 g. in 12 c.c.) and chloramine-T (36 g. in 100 c.c.) together overnight, was crystallised from benzene and twice from chloroform. It formed colourless needles, m. p. 86—87° after slight softening at 83° [Found :* C, 42·7; H, 6·0. $CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}N{:}S(C_2H_4{\cdot}OH)_2,H_2O$ requires C, 42·7; H, 6·1%]. It is moderately easily soluble in cold water, alcohol, and acetone and sparingly soluble in cold benzene, chloroform, and ethyl acetate.

Tri-β-hydroxyethylsulphonium Chloride (XII).—A mixture of ββ′-dihydroxydiethyl sulphide (5 g.) and 30·8% aqueous ethylene chlorohydrin (1, 2, or 3 mols.) was heated on the water-bath for about 13 hours and the water and excess of chlorohydrin were then removed under reduced pressure. The residual colourless oil solidified on cooling or on addition of chloroform and separated from alcohol in clusters of hard prismatic crystals, m. p. 125—126° (Found :* C, 35·6; H, 7·4; Cl, 17·2. $C_6H_{15}O_3ClS$ requires C, 35·6; H, 7·4; Cl, 17·5%). It is almost insoluble in hot chloroform, carbon tetrachloride, acetone, benzene, and ether. The yield appeared to be greatest (7·2 g.) when 3 mols. of aqueous chlorohydrin were used, and was considerably diminished when equimolecular proportions of anhydrous materials were heated for much longer periods. In all cases the crystalline solid was accompanied by an oil insoluble in chloroform, but the amount was greater when anhydrous chlorohydrin was used. Both solid and oil are readily soluble in water, and their solutions give an immediate precipitate of silver chloride with aqueous silver nitrate. The oil, which appeared to be a more complex sulphonium chloride, was not examined further.

Tri-β-hydroxyethylsulphonium chloride develops no acidity when dissolved in water, and its chlorine content can be estimated volumetrically. It is soluble in concentrated hydrochloric acid, but no ββ′-dichlorodiethyl sulphide is formed on prolonged boiling.

The Action of ββ′-Dichloro- on ββ′-Dihydroxy-diethyl Sulphide. Formation of Sulphidobis-β-hydroxydiethyl Sulphide 1 : 3-*Di-β-hydroxyethochloride* (IX).—Complete miscibility of the two interactants takes place only after several days with frequent shaking;

* All analyses so marked are micro-analyses made by Dr. Ing. A. Schoeller, of Berlin.

a syrup denser than the chloro-sulphide is then obtained which slowly crystallises when seeded with the solid *sulphonium chloride* prepared by the following method:—A mixture of the chloro-sulphide (10·16 g.; 1 mol.) and the dihydroxy-sulphide (23·4 g.; 3 mols.) was heated at 65—75° for 6 hours after being shaken when hot to effect homogeneity. The excess of thiodiglycol was then removed by six extractions with much chloroform, leaving a very viscous oil which, after being freed from chloroform, slowly crystallised during several weeks. After many crystallisations from alcohol, clusters of non-hygroscopic, colourless, flat needles, m. p. 101·5—103°, were obtained (Found*: C, 35·5; H, 7·0; S, 23·5; Cl, 17·5. $C_{12}H_{28}O_4Cl_2S_3$ requires C, 35·7; H, 6·9; S, 23·8; Cl, 17·6%).

A better, if more troublesome, method is to use a large excess of the chloro-sulphide and to continue the heating for 10 hours with frequent and vigorous shaking, unchanged material being removed first by decantation and then by extraction of the syrupy residue with acetone. The addition compound $C_2H_4Cl{\cdot}S{\cdot}C_2H_4{\cdot}SCl(C_2H_4{\cdot}OH)_2$ was not detected under these or any other conditions.

ββ′-Dichlorodiethyl sulphide does not form additive compounds when heated at 80° for six hours with diethyl sulphide, sulphidobis-β-hydroxydiethyl sulphide, ethylenebis-β-hydroxyethyl sulphide, 1 : 4-dithian or 1 : 4-thioxan.

The new sulphonium chloride is very sparingly soluble in acetone, somewhat sparingly soluble in cold alcohol, insoluble in most other organic solvents, but very readily soluble in cold water to give a neutral solution containing the theoretical amount of chloridion. An equivalent amount of hydrion is, however, quickly produced on boiling, and 0·3 equivalent is liberated when its 1% aqueous solution is kept at 15—20° for 3 weeks. It behaves exactly like thiodiglycol when heated with little or much hydrochloric acid, but, unlike this substance, yields only ββ′-dichlorodiethyl sulphide with hydrogen chloride at 100° (compare p. 231). The mercurichloride is an oil, and the chloroplatinate a yellow amorphous solid, m. p. 133—134°, insoluble in all the usual solvents.

The Action of Ethylene Chlorohydrin on Sulphidobis-β-hydroxydiethyl Sulphide. Probable Formation of Sulphidobis-β-hydroxydiethyl Sulphide 1 : 2-*Di*-β-*hydroxyethochloride* (VIII).—A solution of sulphidobis-β-hydroxydiethyl sulphide (Bennett and Whincop, *loc. cit.*) (19 g.; 1 mol.) in ethylene chlorohydrin (62 g.; 10 mols.) was heated at 100° for 14 hours. The product, when shaken with chloroform (500 c.c.), yielded a brown chloroform-insoluble oil (2 g.) which solidified on treatment with ether. By fractional crystallisation from alcohol, two sulphonium chlorides were obtained. The higher-melting (m. p. 160—167°) and more sparingly soluble

chloride was probably 1 : 4-dithian 1-β-hydroxyethochloride (below) and the other, which formed long, slender, colourless needles, m. p. 120—121·5°, from alcohol–acetone, undoubtedly depressed the m. p. of the sulphonium chloride (IX). It is probable, therefore, that it has the constitution assigned (VIII) (Found : Cl, 17·5. $C_{12}H_{28}O_4Cl_2S_3$ requires Cl, 17·6%).

1 : 4-*Dithian* 1-β-*Hydroxyethochloride* (VI).—(*a*) Ethylenebis-β-hydroxyethyl sulphide (20 g.) and ethylene chlorohydrin (55 g.; 5 mols.) were heated on the water-bath for 8 hours. The brown reaction mixture was heated under reduced pressure to remove the excess of chlorohydrin and volatile reaction products. The addition of chloroform to the residue furnished a precipitate (3 g.) embedded in a small amount of oil. After repeated crystallisation from alcohol, it formed flat needles, m. p. 175°, which did not depress the m. p. of the product obtained by method (*b*). Removal of the solvent from the chloroform liquors furnished a brown oil, which gave a gelatinous precipitate (2·5 g.) on treatment with water. This was not examined further.

Ethylenebis-β-hydroxyethyl sulphide was unaffected by ethylene dichloride even after 18 hours' heating on the water-bath.

(*b*) *From ethylene chlorohydrin and* 1 : 4-*dithian.* A solution of 1 : 4-dithian (10 g.) in ethylene chlorohydrin (30 c.c.) was kept at 100° for 28 hours (further heating diminishes the yield by side reactions). The reaction mixture was diluted with much chloroform ; the *monosulphonium chloride* was then precipitated almost pure (5 g., m. p. 170°). One crystallisation from alcohol sufficed to raise the m. p. to 175° (Found : Cl, 17·4. $C_6H_{13}OClS_2$ requires Cl, 17·7%).

The *mercurichloride*, prepared from aqueous solutions of the sulphonium chloride and mercuric chloride, crystallised from hot alcohol, in which the reaction product was not completely soluble, a gummy residue remaining, in long colourless needles, m. p. 95—96° [Found :* Cl, 21·5. $(C_6H_{13}OClS_2)_2,HgCl_2$ requires Cl, 21·1%].

Action of Hydrogen Chloride on ββ′-*Dihydroxydiethyl Sulphide at* 100°. *Formation of* ββ′-*Dichlorodiethyl Sulphide* (I) *and Oxidobis*-β-*chlorodiethyl Sulphide.*—Dry hydrogen chloride was led into ββ′-dihydroxydiethyl sulphide (160 g.) at 100—106°. Water did not separate until the absorption was nearly complete. Distillation of the bottom layer (180 g., m. p. about 0°) furnished a volatile fraction of almost pure ββ′-dichlorodiethyl sulphide (56%) and a more viscous residue (44%), which could not be distilled at 152°/1 mm. and was insoluble in cold water [Found : Cl (as HCl by hydrolysis by boiling water), 24·0; Cl (by Carius), 23·7; S, 25·7. $C_8H_{16}OCl_2S_2$ requires Cl, 27·0; S, 24·3. $C_8H_{16}Cl_2S_3$ requires Cl, 25·5; S, 34·4%].

The phenoxy-derivative. Crude oxidobis-β-chlorodiethyl sulphide

(6·4 g.) was added to a solution of phenol (5 g.) in sodium ethoxide (sodium, 1·25 g., and absolute alcohol, 140 c.c.). The mixture was boiled under reflux for 1 hour, sodium chloride being precipitated almost immediately. By addition of water (70 c.c.) a yellow oil was thrown down, which partly solidified after thorough and repeated washing with water. Several crystallisations from light petroleum (b. p. 60—80°) furnished colourless needles, m. p. 55—57°, which depressed the m. p. of ββ′-diphenoxydiethyl sulphide, m. p. 54° (Found :* C, 62·8; H, 7·0; S, 17·4. $C_{20}H_{26}O_3S_2$ requires C, 63·5; H, 6·9; S, 16·9. $C_{20}H_{26}O_2S_3$ requires C, 60·9; H, 6·6; S, 24·4%). It is readily soluble in all the usual solvents except light petroleum.

Hydrolysis of ββ′-Dichlorodiethyl Sulphide by 2—6 Volumes of Boiling Water. Formation of a Mixture of Sulphonium Chlorides.—The pure chloro-sulphide, m. p. 14·4°, was added drop by drop during 3½ hours to the requisite volume of water, boiling vigorously under reflux (oil-bath at 130°), the boiling being continued for 6 hours in all. The minimum amount of cold water required to dissolve 1 vol. of the chloro-sulphide under these conditions is 2·25 vols. After cooling, removal of unchanged material (if any), filtration, and withdrawal of an aliquot portion for analysis, the remainder was evaporated to dryness at 60—70°/10—15 mm.

The liquid before evaporation contained negligible amounts of thiodiglycol, unchanged material, and other chloroform-soluble substances, whilst during evaporation a little dithian was obtained at the commencement and a small but appreciable amount of ββ′-dichlorodiethyl sulphide towards the end. The results tabulated below show the remarkable differences in the properties of the hydrolysis liquid and syrup obtained when the amount of water is merely increased from the minimum (*Y*, 2·25 vols.) to 3 vols. (*Z*). When 6 vols. of water are used, the hydrolysis syrup contains no 1 : 4-dithian 1-β-hydroxyethochloride (see *a* below).

	Y.	*Z*.
Density.....	1·12 at 15°	1·10 at 15°
1. Total chloridion content of hydrolysis liquid (estimated gravimetrically).....	16·0%	13·1%
2. Chlorine present as free HCl in aqueous liquid (estimated by titration with 0·1*N*-NaOH).	11·5%	9·9%
3. Chlorine present in form of sulphonium chlorides, whose Cl is hydrolysed to HCl by 250 pts. of boiling water (estimated by titration with 0·1*N*-NaOH).....	2·0%	2·4%
4. Chlorine present in form of sulphonium chlorides not hydrolysed to HCl as in 3, *i.e.*, 1 − (2 + 3).	2·5%	0·8%
5. Yield of crude syrup by evaporation.....	30%	about 30%
6. Yield of crude ββ′-dichlorodiethyl sulphide by treating the syrup in 5 with 12 vols of conc. hydrochloric acid at 100° (compare *b* below).	17% of wt. of syrup (m. p. 13·0°)	70% of wt. of syrup (m. p. 12·2°)

(*a*) *Isolation of* 1 : 4-*dithian* 1-β-*hydroxyethochloride.* The hydrolysis was carried out as above, 2·25 vols. of water being used, and the above sulphonium chloride, m. p. 170—173°, was isolated either by keeping the acetone-washed syrup on a porous tile in a desiccator for several weeks, or preferably by dissolving it in about 5 vols. of boiling alcohol, filtering the solution, and seeding it when cold. Two further crystallisations from alcohol furnished the pure material, identical in all respects with the product obtained by the methods described on p. 231 (Found :* C, 35·6; H, 6·6; Cl, 17·7. $C_6H_{13}OClS_2$ requires C, 35·9; H, 6·5; Cl, 17·7%).

(*b*) *Conversion into* ββ′-*dichlorodiethyl sulphide and ethylenebis-*β-*chloroethyl sulphide.* The latter substance was isolated only when a relatively small proportion of hydrochloric acid was used.

A solution of the syrup (49 g.; obtained by hydrolysis with 4 vols. of water) in concentrated hydrochloric acid (150 c.c.; *d* 1·14) was heated at 100° for 40 minutes. When cold, the bottom layer was separated, and united with the residue obtained by extracting the aqueous layer twice with carbon tetrachloride and subsequently removing the solvent. The total yield of crude oil was 42 g., m. p. about 7°. This, on distillation, furnished ββ′-dichlorodiethyl sulphide (35 g.) and a dark-coloured undistillable residue, which partly solidified at 0° and from which a small quantity (1 g.) of nearly pure ethylenebis-β-chloroethyl sulphide, m. p. 51—54° (Bennett and Whincop, *loc. cit.*, record m. p. 54°), was isolated after spreading on a porous tile (Found : Cl, 31·2. Calc. for $C_6H_{12}Cl_2S_2$: Cl, 32·4%). Its vesicant action was equal to that of authentic ethylenebis-β-chloroethyl sulphide.

If 10 vols. of hydrochloric acid are used, ββ′-dichlorodiethyl sulphide is the sole product. A number of experiments were also carried out on the action of relatively small amounts of concentrated hydrochloric acid on thiodiglycol at 100°, but in no case was ethylenebis-β-chloroethyl sulphide detected, although in one instance (2·8 vols. of hydrochloric acid, *d* 1·16, to 1 vol. of thiodiglycol) the m. p. of the crude oil was as low as 10·2°.

Formation of 1 : 4-*Dithian* 1-β-*Hydroxyethochloride* (VI) *and Other Sulphonium Chlorides from* ββ′-*Dihydroxydiethyl Sulphide and Dilute Hydrochloric Acid.*—The dihydroxy-sulphide (21 g.; 1 mol.; 1 vol.) was dissolved in a mixture of concentrated hydrochloric acid (35 c.c., *d* 1·16; *i.e.*, 2 mols. HCl) and water (16 c.c.; total amount of water, 2·5 vols.) and boiled under reflux for 5 hours. The pale yellow solution, which contained only traces of chloroform-soluble products, was separated from a little ββ′-dichlorodiethyl sulphide and evaporated to dryness at 60—70°/10 mm. From the mixture of sulphonium chlorides thus obtained, pure 1 : 4-dithian 1-β-hydroxy-

ethochloride was isolated by shaking with acetone and crystallisation from alcohol.

The initial concentration of the dihydroxy-sulphide is the most important factor in the formation of sulphonium chlorides by this method: from the syrup produced from ββ′-dihydroxydiethyl sulphide (1 vol.; 1 mol.) and hydrogen chloride (2 mols.) in water (3 vols. in all) still less of the above solid could be obtained. When a large excess of dilute hydrochloric acid of the same strength was used, no sulphonium chlorides were formed at all, whilst if insufficient dilute acid of the same strength was used, the resulting syrup undoubtedly contained sulphonium chloride, since the total chloridion content exceeded considerably the free hydrochloric acid content.

Hydrolysis of ββ′-Dichlorodiethyl Sulphide (1 *Mol.*) *with* 20% *Aqueous-alcoholic Potassium Hydroxide.—(a) Using* 4 *mols. of potassium hydroxide.* Pure ββ′-dichlorodiethyl sulphide, m. p. 14·4° (100 g.; 79 c.c.), was slowly added down the condenser during 20 minutes to a solution of potassium hydroxide (141 g.; 4 mols.) in a mixture of water (120 c.c.) and alcohol (480 c.c.) boiling under reflux (oil-bath at 110°). After refluxing for a further 30 minutes, the mixture was distilled until the vapour temperature reached 95°. The distillate was poured into water (7 vols.), and the mixture of divinyl and β-ethoxyethyl vinyl sulphides (top layer) was separated, dried over anhydrous sodium sulphate for a few hours, and distilled *at once* through an efficient fractionating column. The divinyl sulphide (35 g.) was distilled at 80 mm., leaving a residue which began to polymerise at 100°; the distillation was therefore quickly carried to completion at 15 mm. (β-ethoxyethyl vinyl sulphide fraction, *ca.* 3 g.).

The undistilled residue from the reaction was filtered from salt, and both filtrate and salt were exhaustively extracted with ether. The red mobile oil (8 g.) obtained from the dried ethereal extract, when fractionated through an efficient column at 4 mm., furnished a little β-ethoxyethyl vinyl sulphide, ββ′-diethoxydiethyl sulphide (4 g., b. p. 101—102°/4mm.), and β-ethoxy-β′-hydroxydiethyl sulphide (1 g., b. p. 117·5°/4 mm.). The undistilled residue (2 g.) was not further examined.

Divinyl sulphide, $S(CH{:}CH_2)_2$, b. p. 85°, is a colourless, highly refractive, mobile oil when freshly distilled. It is no longer completely miscible with alcohol after a few hours, becomes more and more viscous, and changes after about a month into a translucent jelly, which still contains some unpolymerised sulphide and is soluble n chloroform and partly soluble in benzene and convertible by acetone or alcohol into a gum. According to Bales and Nickelson (*loc. cit.*) divinyl sulphide polymerises in 48 hours to an opaque jelly

soluble only in carbon disulphide, but in our experience this description applies rather to crude undistilled divinyl sulphide, which polymerises in less than a week to an opaque jelly convertible by alcohol or acetone into an amorphous friable solid.

Freshly distilled divinyl sulphide readily forms a *sulphilimine*, m. p. 91—93°, large hexagonal prisms from alcohol, when shaken with excess of 10% aqueous chloramine-T at 30° (Found :* C, 51·6; H, 5·0. $C_{11}H_{13}O_2NS_2$ requires C, 5 ·8; H, 5·1%).

β-*Ethoxyethyl vinyl sulphide*, $CH_2{:}CH{\cdot}S{\cdot}C_2H_4{\cdot}OEt$, b. p. 65°/8 mm., $d_4^{20°}$ 0·9532, is a colourless mobile liquid with a curious, pungent, camphor-like odour. It slowly darkens on keeping (Found : C, 54·1; H, 8·9. $C_6H_{12}OS$ requires C, 54·5; H, 9·1%). It yields a gummy uncrystallisable sulphilimine, but a well-defined mercurichloride, tiny leaflets, m. p. 152—153°, from alcohol, satisfactory analytical figures for which could not be obtained. ββ′-Diethoxydiethyl sulphide, b. p. 101—102°/4 mm., was identified by its density ($d_4^{20°}$ 0·9658), its almost ethereal odour, and by its readily obtained mercurichloride, m. p. 93—94° (Kretov, *loc. cit.*, records m. p. 93—93·5°), moderately soluble in cold alcohol. When it is shaken with 10% aqueous chloramine-T, an oily product is obtained from which toluene-*p*-sulphonamide can be separated.

(*b*) *Using* 1 *mol. of potassium hydroxide. Isolation of* β-*chloroethyl vinyl sulphide* (XIII). A solution of potassium hydroxide (35·5 g.) in water–alcohol (1 : 4 by volume, 175·5 c.c.) was placed in a distillation flask fitted with a condenser and dropping-funnel containing ββ′-dichlorodiethyl sulphide (100 g.). About 1/6th was added to the cold alcoholic potassium hydroxide, and the mixture heated until reaction commenced (oil-bath at 105—110°); the remaining dichloro-sulphide was then added as quickly as possible without allowing the reaction to get out of control. The bath temperature was then gradually raised to 160°, the distillate poured into water, and the oil collected, dried over calcium chloride, and fractionated. From the crude product (212 g. from 12 such experiments), after discarding the more volatile fractions, were obtained crude unchanged ββ′-dichlorodiethyl sulphide (56 g.), b. p. 80—129°/51 mm., m. p. 3°, and β-*chloroethyl vinyl sulphide* (87 g.), b. p. 71—72°/50 mm. (Found : C, 39·2; H, 5·8; Cl, 28·6, 28·7; S, 25·9, 26·1. C_4H_7ClS requires C, 39·2; H, 5·7; Cl, 29·0; S, 26·2%). The derived *sulphilimine*, clusters of needles from toluene, had m. p. 101·5—103° (Found :* C, 45·5; H, 4·6; Cl, 12·3. $C_{11}H_{14}O_2NClS_2$ requires C, 45·3; H, 4·8; Cl, 12·2%).

The mercurichloride is amorphous and when heated begins to shrink at 95°, commences to evolve a gas without marked decomposition, and blackens at 150° with copious evolution of gas. It is

only sparingly soluble in the usual solvents and appears to be decomposed by some, *e.g.*, hot benzene, toluene, and xylene.

αβ′-Dichlorodiethyl Sulphide (XIV).—A rapid current of dry hydrogen chloride was passed into β-chloroethyl vinyl sulphide (43·6 g.) contained in a bubbler fitted with a sintered glass inlet. Absorption of the gas took place readily and quantitatively (13·9 g.; ½ hour) with evolution of heat, and when the liquid became warm, it was cooled in ice-water. The excess of hydrogen chloride (1·9 g.) was removed from the wine-red reaction product by means of a current of dry air, and the pale yellow liquid obtained was fractionated through a Raschig column, the main fraction (about 41 g.) boiling at 67—69°/9 mm. On refractionation it distilled at 68—69°/9 mm. (Found : C, 31·2; H, 5·1; Cl, 41·7, 41·8; S, 21·4. $C_4H_8Cl_2S$ requires C, 30·2; H, 5·1; Cl, 44·6; S, 20·1%). The analytical figures, which remained constant after several redistillations, show that the substance contains presumably a little unchanged β-chloroethyl vinyl sulphide.

αβ′-Dichlorodiethyl sulphide when freshly distilled is a colourless mobile oil with a piercing odour quite distinct from that of its αα′- and ββ′-isomerides. It develops a brown colour on standing, and a dark-coloured residue is generally left behind on distillation at 9 mm. pressure, together with a small amount of silvery needles, m. p. 121° (indefinite), in the neck of the flask and in the condenser.

The only pure product isolated from the action of aqueous chloramine-T was toluene-*p*-sulphonamide, m. p. 136—137°, but a very unstable sulphilimine appeared to be formed which decomposed on attempted crystallisation from hot benzene.

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