CCXXXVI.—*Decomposition of some Halogenated Sulphides, and the Nature of the "Polymeric" Ethylene Sulphides.*

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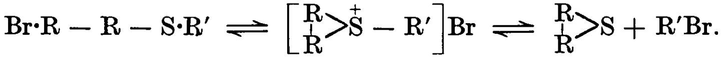
THE union of an alkyl halide with an alkyl sulphide to produce a sulphonium salt is a reversible reaction, and unsymmetrical sulphonium halides may thus dissociate to yield compounds distinct from those used in their preparation :

$$R_2S + R'I \rightleftharpoons [R_2R'S]I \rightleftharpoons RR'S + RI$$

(Cahours, *Ber.*, 1875, **8**, 825; Klinger and Maassen, *Annalen*, 1889, **252**, 241).

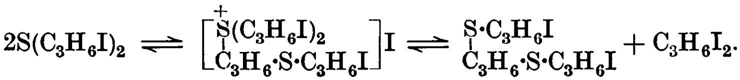
An exactly analogous change was detected in an examination of some δ-substituted sulphides (this vol., p. 477) when a δ-bromobutyl sulphide was found to be transformed by internal salt formation into a cyclic sulphonium salt, $\left[\begin{matrix}CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2\end{matrix}\!>\overset{+}{S}\cdot C_4H_8\cdot OH\right]Br$, which dissociated, on heating, with liberation of the cyclic tetramethylene sulphide :



$$Br\cdot R - R - S\cdot R' \rightleftharpoons \left[\begin{matrix}R \\ | \\ R\end{matrix}\!>\overset{+}{S} - R'\right]Br \rightleftharpoons \begin{matrix}R \\ | \\ R\end{matrix}\!>S + R'Br.$$

It appeared probable that a similar tendency to the formation of sulphonium salts by self-addition would be a property common to all classes of halogenated sulphides. No such tendency has hitherto been recognised, but we find that some observations of our own on β- and γ-halogenated sulphides and one or two anomalies recorded in the literature may be explained as the results of such processes of reversible sulphonium salt formation.

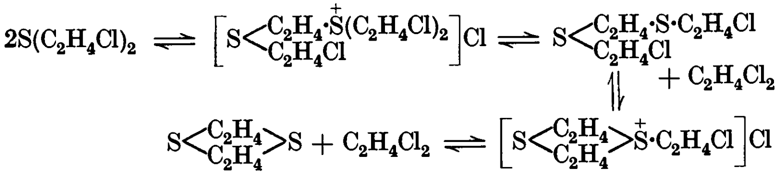
The self-addition of a halogenated sulphide might evidently be intermolecular or intramolecular. The latter type of reaction involves ring closure, and it may be anticipated that it will only be in evidence when a five- or six-membered ring is concerned, as in the case of the δ-bromo-sulphide. An indication of intermolecular addition in a γ-halogenated sulphide was obtained when γγ′-dichlorodipropyl sulphide was converted by the action of sodium iodide into the corresponding di-iodo-sulphide. The latter decomposed, on keeping, with liberation of trimethylene iodide in quantity, whilst a dark, viscous material was deposited which contained ionic iodine and was probably a mixture of complex substances. This may be explained as follows :



$$2S(C_3H_6I)_2 \rightleftharpoons \left[\begin{matrix}\overset{+}{S}(C_3H_6I)_2 \\ | \\ C_3H_6\cdot S\cdot C_3H_6I\end{matrix}\right]I \rightleftharpoons \begin{matrix}S\cdot C_3H_6I \\ | \\ C_3H_6\cdot S\cdot C_3H_6I\end{matrix} + C_3H_6I_2.$$

The more complex di-iodo-sulphide on the right may undergo further changes of the same kind so that a mixture of substances results.

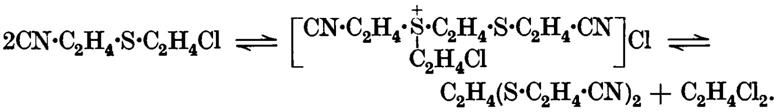
It is known that most specimens of ββ′-dichlorodiethyl sulphide contain dithian (see, *e.g.*, Davies, J., 1920, **117**, 299), but the reason for its presence has never been elucidated. It has usually been regarded as an impurity introduced at the time of preparation, but there is now no doubt that the proportion of dithian in samples of dichlorodiethyl sulphide increases greatly with the time of keeping. The production of dithian can be explained as due to a series of reactions involving both the intermolecular and the intramolecular type of addition, thus,



$$\begin{array}{ccccc} 2S(C_2H_4Cl)_2 & \rightleftharpoons & \left[S{<}^{C_2H_4\cdot\overset{+}{S}(C_2H_4Cl)_2}_{C_2H_4Cl}\right]Cl & \rightleftharpoons & S{<}^{C_2H_4\cdot S\cdot C_2H_4Cl}_{C_2H_4Cl} \\ &&&& \updownarrows \quad + C_2H_4Cl_2 \\ && S{<}^{C_2H_4}_{C_2H_4}{>}S + C_2H_4Cl_2 & \rightleftharpoons & \left[S{<}^{C_2H_4}_{C_2H_4}{>}\overset{+}{S}\cdot C_2H_4Cl\right]Cl \end{array}$$

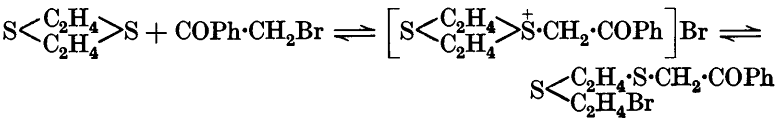
ethylene dichloride being a second substance produced in the process. We have tested the truth of this scheme of reactions, as far as possible, and have directly confirmed the formation of both dithian and ethylene dichloride in quantity from pure dichlorodiethyl sulphide heated at 180° for 18 hours. A similar reaction doubtless occurs more slowly at the ordinary temperature. If these reactions are reversible at each stage (as shown), the action of ethylene dichloride upon dithian should conversely to some extent yield dichlorodiethyl sulphide, although the amount present in the final equilibrium mixture might be small. We find that dithian heated at 180° with an excess of ethylene dichloride yields a highly vesicant liquid, and the presence of dichlorodiethyl sulphide is proved by the isolation of the crystalline ββ′-diphenoxydiethyl sulphide (Helfrich and Reid, *J. Amer. Chem. Soc.*, 1920, **42**, 1208).

The curious observation of Davies (*loc. cit.*) that potassium cyanide acts on dichlorodiethyl sulphide to furnish the dinitrile, $CN\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot CN$, is intelligible from the same point of view. This dinitrile is a by-product evidently derived from an intermediate mononitrile as follows :



$$2CN\cdot C_2H_4\cdot S\cdot C_2H_4Cl \rightleftharpoons \left[CN\cdot C_2H_4\cdot \underset{C_2H_4Cl}{\overset{+}{S}}\cdot C_2H_4\cdot S\cdot C_2H_4\cdot CN\right]Cl \rightleftharpoons C_2H_4(S\cdot C_2H_4\cdot CN)_2 + C_2H_4Cl_2.$$

The formation and dissociation of a sulphonium salt also explains the anomaly noticed by Clarke (J., 1912, **101**, 1794) in the reaction of phenacyl bromide with dithian. The amount of ionic bromine, observed at intervals by titration, was found to rise at first as expected, but then diminished rapidly. This is clearly evidence of the opening of a ring as follows,

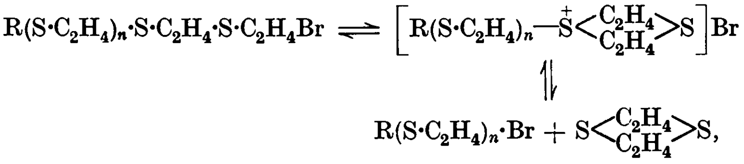


$$S{<}^{C_2H_4}_{C_2H_4}{>}S + COPh\cdot CH_2Br \rightleftharpoons \left[S{<}^{C_2H_4}_{C_2H_4}{>}\overset{+}{S}\cdot CH_2\cdot COPh\right]Br \rightleftharpoons S{<}^{C_2H_4\cdot S\cdot CH_2\cdot COPh}_{C_2H_4Br}$$

the bromo-sulphide on the right containing no ionic bromine.

The Nature of the " Polymeric " Ethylene Sulphides.—The reactions discussed above throw a new light on the nature of the "polymeric" ethylene sulphides, which are produced in a variety of reactions, such as the action of alkali sulphides on ethylene dichloride, ethylene dibromide or dichlorodiethyl sulphide, and by the dehydration of monothioethylene glycol. It is probable that they are all mixtures of substances of high molecular weight having a long open-chain structure of the type $\mathrm{A(S{\cdot}C_2H_4)_n{\cdot}S{\cdot}B}$, where A and B may be such groups as $\mathrm{-C_2H_4{\cdot}OH}$, $\mathrm{-CH{:}CH_2}$, or $\mathrm{-C_2H_4Br}$ (Bennett and Whincop, J., 1921, **119**, 1861; *Nature*, 1926, **118**, 555; compare Staudinger, *Helv. Chim. Acta*, 1925, **8**, 67). The composition of these products is approximately that of a polymeride of ethylene sulphide (as is required by the formula provided that *n* be large), but it has long been known that variable amounts of bromine may be present (Crafts, *Annalen*, 1863, **128**, 220). The recent observations of Sir P. C. Rây and K. C. Bose-Rây (*J. Indian Chem. Soc.*, 1926, **3**, 75) support the idea of the occurrence of such long-chain bromopolyethylene polysulphides.

Two classes of "polymeric" ethylene sulphides were clearly distinguished by V. Meyer (*Ber.*, 1886, **19**, 3262): I, those which when heated did not yield dithian, and II, those which were readily degraded to dithian when heated alone or in solution in various solvents at high temperatures. The latter type of behaviour is to be expected in a bromo-polysulphide, owing to internal self-addition according to the scheme



$$\mathrm{R(S{\cdot}C_2H_4)_n{\cdot}S{\cdot}C_2H_4{\cdot}S{\cdot}C_2H_4Br} \rightleftharpoons \left[\mathrm{R(S{\cdot}C_2H_4)_n{-}\overset{+}{S}{<}\substack{C_2H_4\\C_2H_4}{>}S}\right]\mathrm{Br}$$

$$\Big\updownarrow$$

$$\mathrm{R(S{\cdot}C_2H_4)_n{\cdot}Br + S{<}\substack{C_2H_4\\C_2H_4}{>}S},$$

and repetitions of the process will liberate successive molecules of dithian, each cycle of changes being analogous to the reactions involved in the decomposition of dichlorodiethyl sulphide.

The existence of the "polymerides" of class I and their failure to yield dithian by a similar process will evidently be accounted for if they contain no halogen, since this is indispensable to sulphonium salt formation, and we find that, as far as evidence is available, "polymerides" which do not contain halogen do in fact belong to this class. Thus the material of Löwig and Weidmann (*Annalen*, 1840, **36**, 321) was found by Crafts (*loc. cit.*) to be free from halogen and to give no dithian on heating. We have confirmed the complete absence of halogen from a specimen of "polymeride" of class I prepared from ethylene dibromide, whilst products of class I from monothioethylene glycol were made from halogen-free materials

(J., 1922, **121**, 2144). These facts support our suggestion that it is the absence or the presence of halogen which determines the chemical differences between " polymerides " of class I and class II. In those of class I the terminal groups in the molecule are probably either $-C_2H_4{\cdot}OH$ or $-CH{:}CH_2$. Such substances would be likely to react with hydrogen bromide or with ethylene dibromide to yield halogenated polysulphides by such reactions as the following :

$$R{\cdot}S{\cdot}C_2H_4{\cdot}OH + HBr = R{\cdot}S{\cdot}C_2H_4Br + H_2O;\ R{\cdot}S{\cdot}CH{:}CH_2 + HBr = R{\cdot}S{\cdot}C_2H_4Br;\ R{\cdot}S{\cdot}R' + C_2H_4Br_2 = R{\cdot}S{\cdot}C_2H_4Br + R'Br.$$

The products would then be liable to the process of degradation with liberation of dithian. This anticipation also has been verified : " polymerides " of class I yield dithian when heated in boiling phenol, provided that hydrogen bromide or ethylene dibromide be added.

The simpler substances $S(C_2H_4{\cdot}OH)_2$, $C_2H_4(S{\cdot}C_2H_4{\cdot}OH)_2$, and $S(C_2H_4{\cdot}S{\cdot}C_2H_4{\cdot}OH)_2$ previously described (Bennett and Whincop, *loc. cit.*), which are not easily decomposed when heated alone, have now been found, as expected, to yield dithian readily when they are heated with a boiling solution of hydrogen bromide in phenol. These three dihydroxy-sulphides are the simplest members of a homologous series of substances, the higher members of which are doubtless present in " polymeric " ethylene sulphides of class I.

EXPERIMENTAL.

Action of Sodium Iodide on γγ'-Dichlorodipropyl Sulphide.—The pure dichloro-sulphide was heated in acetone solution with sodium iodide (3 mols.) until sodium chloride was no longer precipitated. The solution was concentrated, and the crude *γγ'-di-iododipropyl sulphide* thrown out as a heavy oil by dilution. This substance did not crystallise and could not be distilled without decomposition. When kept for several weeks at the ordinary temperature, the liquid deposited a dark resinous material which slowly hardened, but retained pockets of a heavy mobile oil. The solid could not be crystallised; it was partly soluble in water, the solution containing ionic iodine.

The oil was separated, and distilled at 120—130°/50 mm. It was identified as trimethylene di-iodide by direct comparison and by its ready conversion on heating with a solution of sodium phenoxide in phenol into αγ-diphenoxypropane, of which the m. p., 59—60°, was unaltered by admixture of an authentic specimen.

Decomposition of ββ'-Dichlorodiethyl Sulphide.—Freshly redistilled dichlorodiethyl sulphide (2·5 g.) was heated in a sealed tube for 18 hours in the vapour of boiling phenol. When the tube was opened, a volatile liquid was noticed. The contents of the tube were mixed with an excess of aniline and heated at 100° for an hour and then at the boiling point for a further hour. The excess of aniline and the dithian were removed in a current of steam and the distillate was acidified to dissolve the aniline. The precipitate (0·5 g.; 50% of the theoretical yield) had m. p. 111°, not depressed by admixture of pure 1 : 4-dithian.

The residue from the steam distillation was extracted with ether, and the ether evaporated. The residual oil gave a crystalline sulphate when warmed with sulphuric acid (50%). This salt was crystallised from the filtered solution, and the base liberated from it by ammonia was crystallised from paraffin (b. p. 60°) and identified as ethylenediphenyldiamine, m. p. 60°, not depressed by admixture of an authentic specimen. This proves that the tube must have contained ethylene dichloride when opened.

The Action of Ethylene Dichloride upon Dithian.—Dithian (0·5 g.) and ethylene dichloride (5 c.c.) were heated in a sealed tube for 12 hours at 180°. Evaporation of the ethylene dichloride left a brown oil, which had a strong vesicant action. It was heated with an excess of alcoholic sodium phenoxide, and the solution was acidified and distilled in steam. The residual oil was removed in ether, and the latter evaporated. The viscous residue deposited crystals, which were drained on porous earthenware and recrystallised from paraffin of low b. p. This substance had m. p. 54°, not depressed by admixture of an authentic specimen of $\beta\beta'$-diphenoxydiethyl sulphide. The two substances were also found by microscopic examination to crystallise identically from ethyl alcohol in bunches of needles with a straight extinction.

Degradation of " Polymeric " Ethylene Sulphide of Class I.—The specimen of " polymeride " was made by the action of alkali sulphide on ethylene dibromide, and had been freed from all trace of " polymeride " of class II by heating in phenol. It gave no dithian when dry-distilled or when heated in boiling phenol for several hours. Repeated tests proved the absence of halogen from this material.

The " polymeride " (30 g.) was heated at 130° for 1 hour with ethylene dibromide (18 g.; 1/5 mol.). Phenol (60 g.) was then added, and the mixture boiled for 3 hours. Addition of an excess of aqueous sodium hydroxide left a crystalline precipitate identified as dithian (6·7 g.).

The " polymeride " (15 g.) was boiled for 2 hours with phenol (60 g.) saturated with hydrogen bromide, and dithian was isolated as before (5 g.).

Production of Dithian from Simpler Hydroxy-sulphides.—Thiodiglycol, ethylenebis-β-hydroxyethyl sulphide, and sulphidobis-β-hydroxydiethyl sulphide were each boiled for 2 hours with phenol saturated with hydrogen bromide, and the mixture was separated as before. In each case, dithian was identified, the yield from the last-named substance being nearly 50% by weight.

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