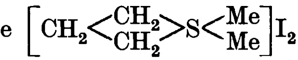
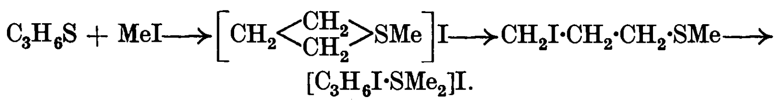
CCCXXXIV.—*The Nature of the Supposed Dimethiodide of Trimethylene Sulphide.*

By GEORGE MACDONALD BENNETT and ALFRED LOUIS HOCK.

IN reviewing the organic compounds of nitrogen and sulphur from the point of view of the octet theory, Langmuir (*J. Amer. Chem. Soc.*, 1920, **42**, 274) mentioned the dimethiodide of trimethylene sulphide (Grischkevitsch-Trochimovski, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 880) as the only substance known of the type $[SR_4]I_2$, the sulphur atom forming the centre of a positive bivalent ion. Although this compound can be satisfactorily formulated in accordance with the electronic theory of valency, no reason was apparent why this (together with the corresponding derivative of 2-methyltetramethylene sulphide) should have been the only dimethiodide of a sulphide to be isolated. We thought it desirable, therefore, to examine the substance in greater detail and to prepare other salts derived from this novel type of ion.

In the course of these experiments, we have found that the substance does not possess the structure  $\left[CH_2{<}\substack{CH_2\\CH_2}{>}S{<}\substack{Me\\Me}\right]I_2$ attributed to it. It was stated explicitly by Grischkevitsch-Trochimovski that the two atoms of iodine in the molecule of the compound are equally ionic, but we were led to doubt this by the observation that only half the iodine is immediately precipitated by silver nitrate in cold aqueous solution, the rest being thrown down when the solution is boiled. This indicates the presence in the molecule of one atom of iodine in the ionic condition and a second atom highly reactive but not actually ionised. In agreement with this view, a solution of the supposed dimethiodide, after being shaken with an excess of silver chloride, yielded a *chloroplatinate*, $[CH_2I{\cdot}CH_2{\cdot}CH_2{\cdot}SMe_2]_2PtCl_6$, and a *chloroaurate*, $[CH_2I{\cdot}CH_2{\cdot}CH_2{\cdot}SMe_2]AuCl_4$, each with iodine still present in the molecule.

The compound produced by the addition of methyl iodide to trimethylene sulphide is therefore dimethyl-γ-iodopropylsulphonium iodide. Its formation is readily interpreted as due to reversible sulphonium salt formation (compare Bell, Bennett, and Hock, this vol., p. 1803). The strain in the four-membered ring will cause the monomethiodide, which must presumably be first formed, to pass over by intramolecular dissociation into methyl γ-iodopropyl sulphide, which will then combine with a second molecular proportion of methyl iodide :



$$C_3H_6S + MeI \longrightarrow \left[CH_2{<}\begin{matrix}CH_2\\ CH_2\end{matrix}{>}SMe\right]I \longrightarrow CH_2I{\cdot}CH_2{\cdot}CH_2{\cdot}SMe \longrightarrow [C_3H_6I{\cdot}SMe_2]I.$$

Independent confirmation of the structure of the compound in question has also been obtained by synthesis. Methyl γ-hydroxypropyl sulphide, prepared by methylating γ-hydroxypropyl mercaptan (Rojahn and Lemme, *Arch. Pharm.*, 1925, **263**, 612), yielded an oily methiodide which reacted rapidly with hydrogen iodide to yield dimethyl-γ-iodopropylsulphonium iodide, identical with the supposed dimethiodide of trimethylene sulphide.

It follows also that the " dimethiodide " of 2-methyltrimethylene sulphide is either dimethyl-γ-iodo-α-methylpropylsulphonium iodide or dimethyl-γ-iodo-*n*-butylsulphonium iodide.

There is thus no reason to believe that a dimethiodide of a sulphide can exist. Although the electronic formula of such a substance would be analogous to that of a sulphone, $R_2\overset{+}{\underset{+}{S}}{<}\begin{matrix}\overset{-}{O}\\ \underset{-}{O}\end{matrix}$, the relative difficulty of formation of the former is easily understood. The conversion of a methiodide into a dimethiodide would be opposed by a large force, since it would involve the addition of a second equal charge to a sulphur atom already bearing a full free positive charge. This force must prevent the formation of a dimethiodide of a monosulphide, for similar forces make the addition of a second molecule of methyl iodide difficult or impossible even in the case of such substances as 1 : 4-dithian and pyrazine, where there are present in the molecule two distinct atoms of sulphur or nitrogen at which addition might occur. The relative ease with which a sulphoxide is converted into a sulphone, on the other hand, results from the diminution in these compounds of the field due to each positive charge by the influence of the free negative charge on the adjacent oxygen atom.

EXPERIMENTAL.

Preparation of Trimethylene Sulphide.—An improved yield of trimethylene sulphide was obtained thus : A solution of sodium sulphide (80 g. of the hydrate) in water (80 c.c.) and alcohol (100 c.c.) was divided into unequal portions, one-third being boiled in a flask under reflux whilst the remaining two-thirds and trimethylene dibromide (50 g.) were simultaneously introduced from dropping-funnels over a period of ½ hour. The mixture was boiled for a further ½ hour, cooled, diluted, and extracted with ether (5 times). The ethereal solution was dried, and distilled through a Widmer column (the sulphide being volatile with ether) (Yield : 7—9 g.).

The dimethiodide, produced by keeping a mixture of the sulphide and an excess of methyl iodide for 24 hours, crystallised well from absolute ethyl alcohol; m. p. 97—98° (Found: I, 70·4. Calc.: I, 70·9%). The proportion of iodine found by precipitation with an excess of silver nitrate in cold aqueous solution was 33·3, 33·6, and 41·6% after 5, 15, and 120 minutes, respectively, whilst rapid titration gave a mean value of 33·3% (Calc. for one atom of iodine per molecule, 35·4%).

Action of Silver Chloride on the Iodide.—The iodide (1·7 g.) dissolved in cold water (25 c.c.) was shaken with freshly precipitated silver chloride (2 mols.) for 15 minutes, and the solution filtered. Addition of platinic chloride then precipitated a *chloroplatinate*, as an ochre-coloured powder which evolved much iodine on heating (Found: Pt, 22·7, 22·3. $C_{10}H_{24}Cl_6I_2S_2Pt$ requires Pt, 22·4%), and of auric chloride a *chloroaurate*, as a canary-yellow powder which evolved much iodine on ignition (Found: Au, 34·5. $C_5H_{12}Cl_4ISAu$ requires Au, 34·6%).

Attempts to isolate a crystalline picrate, mercuri-iodide, or oxalate were unsuccessful.

Action of Dimethylaniline on the Iodide.—When the iodide was heated at 100° with dimethylaniline (1 equiv. or more), a good yield of dimethylaniline methiodide, m. p. 215—217° (decomp.), was obtained (Found: I, 48·2. Calc.: I, 48·3%).

Synthesis of Dimethyl-γ-iodopropylsulphonium Iodide.—γ-Hydroxypropyl mercaptan (27 g.) was methylated by dissolving it in alkali (35 g. of sodium hydroxide in 150 c.c. of water) and adding methyl sulphate (44 g.). The mixture was heated at 100° for 1 hour, cooled, acidified with acetic acid, and extracted with ether. The extract was dried, evaporated, and finally fractionated under diminished pressure. *Methyl γ-hydroxypropyl sulphide* was thus obtained as a colourless oil, b. p. 102°/24 mm., $d_{4^\circ}^{20^\circ}$ (vac.) 1·030 (Found: C, 45·05; H, 9·4. $C_4H_{10}OS$ requires C, 45·3; H, 9·4%). When this substance was dissolved in an excess of methyl iodide, heat was developed and an oil began at once to separate. After 6 hours, the excess of methyl iodide was decanted from the crude *dimethyl-γ-hydroxypropylsulphonium iodide*, which was not further purified. It was covered with dry xylene and dry hydrogen iodide was passed in at 100° for a short time. The xylene was then decanted, and the residue, when inoculated with a trace of the "dimethiodide" of trimethylene sulphide, crystallised at once. After crystallisation from alcohol, *dimethyl-γ-iodopropylsulphonium iodide* was obtained in colourless needles of m. p. 97·5°, not depressed by admixture of the "dimethiodide" of trimethylene sulphide

(Found: by precipitation in cold solution, I, 32·2; in boiling solution, 70·4. Calc.: I, 70·9%).

The authors wish to express their thanks to Mr. G. A. Birkett for translating the Russian memoir on which this work was based.

THE UNIVERSITY, SHEFFIELD. [*Received, August* 11*th*, 1927.]