

281. *The Selenoaldehydes. Part I. "Selenoformaldehyde"*
(Trimethylene Triselenide) and its Chlorination Products.

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Three products of the interaction of hydrogen selenide and formaldehyde are described. Two of them are solids and have been previously reported; the third is a liquid which appears to have been hitherto unmentioned. The name selenoformaldehyde, previously applied to the two solid products, is not compatible with their properties and trimethylene triselenide is proposed as an alternative.

Chlorination of the higher-melting form of trimethylene triselenide, resulting in the isolation of bischloromethyl selenide, bischloromethyl diselenide, and chloromethylselenenyl chloride, is also described.

ACCORDING to the concentration of hydrochloric acid present, one or another of three products is obtained on passing hydrogen selenide into aqueous solutions of formaldehyde. At high acid concentrations, a light-yellow powder, m. p. *ca.* 200°, is produced, at medium acid concentrations, a pasty solid, m. p. <100°, and at low acid concentrations or in neutral solution a heavy, colourless, unpleasant-smelling oil.

The first two products have been prepared by earlier workers (Vanino and Schinner, *J. pr. Chem.*, 1915, [iii], **91**, 116; Bradt and Valkenburgh, *Proc. Indiana Acad. Sci.*, 1929, **39**, 165; Pearson, Purcell, and Saigh, *J.*, 1938, 409), but the oil has not been previously recorded, though sulphur analogues have been described (Baumann, *Ber.*, 1890, **23**, 60; Pinner, *Ber.*, 1871, **4**, 257). The inter-relations of these materials are still being investigated and will form the subject of a later publication.

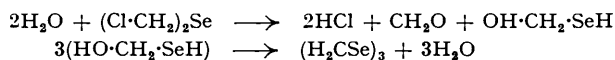
The work recorded here is only concerned with the higher-melting solid. This compound is relatively unreactive, is unaffected by boiling concentrated hydrochloric acid and aqueous caustic alkalis, is only slowly, but completely, decomposed by hot concentrated sulphuric acid, and shows no signs of reaction with the standard reagents used for the detection of carbonyl groups. It is insoluble in water and only sparingly soluble in most organic solvents. It is, however, sufficiently soluble in xylene and in chlorobenzene to allow it to be purified by recrystallisation from these solvents. The purified product consists of practically odourless, white, needle-like crystals, m. p. 210°. Analytical figures correspond with the formula $(\text{CH}_2\text{Se})_x$. Vanino and Schinner obtained similar figures and unfortunately named this compound selenoformaldehyde and this terminology still persists. When, however, the properties of formaldehyde and trithioformaldehyde are reviewed in conjunction with the relative bond strengths of singly- and double-bonded oxygen, sulphur, and selenium, it seems highly unlikely that monomeric selenoaldehydes should exist at all; this substance is therefore probably a polymer, and molecular-weight determinations in boiling xylene indicate that it is, in fact, a trimer. It is probably cyclic, similar in structure to trioxymethylene and trithioformaldehyde, and thus to be considered rather as a cyclic selenide than as an analogue of formaldehyde. It exhibits no properties similar to those of the aldehydes and its chemical behaviour resembles that of the simple organic selenides, for example, in the formation of insoluble addition compounds with many metallic salts (Pearson, Purcell, and Saigh, *loc. cit.*). The name trimethylene triselenide is therefore more in accord with its probable structure and properties.

Attempts were made to carry out a controlled oxidation of trimethylene triselenide, in a manner similar to that used by Bell and Bennett (*J.*, 1929, 15) in the preparation of sulphoxides from trithioformaldehyde. Hydrogen peroxide and nitric acid were used and the conditions were widely varied, but without success, only hydrated selenious and selenic acids being isolated.

Chlorination, first accomplished by passing gaseous chlorine into a well-stirred suspension of trimethylene triselenide in carbon tetrachloride, gave, in addition to elementary selenium and unidentifiable gummy substances, bischloromethyl selenide, bischloromethyl diselenide, and chloromethylselenenyl chloride.

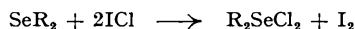
It was found later that chlorination with selenium monochloride gave the same products. If the proportion of chlorinating agent used was kept at a minimum, bischloromethyl selenide and diselenide only, were isolated, but, if excess was used, the product consisted almost entirely of the selenenyl chloride.

Bischloromethyl selenide is a pale yellow mobile liquid with a smell surprisingly reminiscent of the simpler chlorinated hydrocarbons. It is fairly stable to heat and can be distilled unchanged at atmospheric pressure (b. p. 42°/2 mm., 180°/760 mm.). It is insoluble in water but miscible with most organic solvents. Boiling water attacks it but little, and it can be distilled from strong aqueous sodium hydroxide. However, it is hydrolysed fairly readily to formaldehyde and trimethylene triselenide by boiling aqueous solutions of sodium hydrogen carbonate or borate, the latter being the more effective :



This may be compared with similar reactions of the analogous sulphur compounds (Bloch and Hohn, *Ber.*, 1922, **55**, 53).

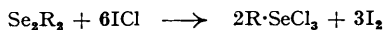
Treatment with aqueous potassium iodide liberates no iodine, indicating that chlorine is not directly attached to selenium, and this is confirmed by treatment with iodine monochloride, which liberates two equivalents of iodine per atom of selenium :



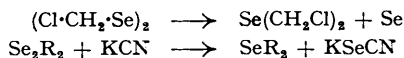
Bischloromethyl diselenide is a heavy golden-yellow oil, which does not wet glass. In odour it slightly resembles the organic selenides. It has b. p. 97°/1.5 mm., but it is impossible to measure the boiling point at atmospheric pressure, owing to extensive decomposition, at elevated temperatures, to selenium and bischloromethyl selenide in fair yield. The diselenide

is insoluble in water, and sparingly soluble in methyl alcohol, but readily soluble in the less polar organic solvents. Like the selenide it is hydrolysed with some difficulty. The hydrolytic products are sticky intractable solids.

No iodine is produced on treatment with aqueous potassium iodide, and three equivalents of iodine per atom of selenium are liberated on treatment with iodine monochloride, thus confirming the presence of the diselenide link :

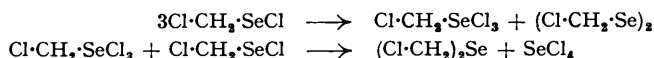


This linkage is somewhat labile: in addition to the thermal decomposition, treatment with potassium cyanide gives an evil-smelling mixture from which potassium selenocyanate and bischloromethyl selenide can be isolated :



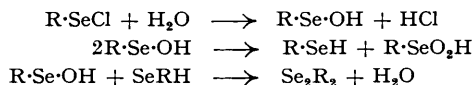
The latter reaction resembles the attack on the disulphide linkage by potassium cyanide, described by Farnworth and Speakman (*Nature*, 1949, **163**, 798). The diselenide link is also readily cleaved by halogens: e.g., treatment with chlorine gives an almost theoretical yield of the selenenyl chloride.

Chloromethylselenenyl chloride is a dark red heavy oil, b. p. $52^\circ/1.5$ mm., which does not wet glass and has a smell resembling that of burnt gunpowder. It is soluble in most organic solvents but insoluble in water, by which it is, however, rapidly hydrolysed. It is much less stable and more reactive than the two compounds described above. When it is kept for several weeks, black crystals of selenium are deposited and hydrogen chloride is evolved. On heating, disproportionation occurs and this renders the purification of the material somewhat difficult, as bischloromethyl selenide and diselenide continue to distil even on repeated fractionation at pressures as low as 0.5 mm. This behaviour may be represented as resulting from the simultaneous occurrence of the two reactions :



Foster (*Rec. Trav. chim.*, 1934, **53**, 405) found a similar disproportionation on heating arylselenium halides.

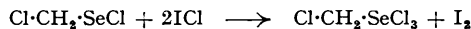
The hydrolysis products obtained on treating chloromethylselenenyl chloride with water or dilute alkali include a sticky, so far unidentifiable yellowish-white solid, red selenium, and bischloromethyl diselenide. Behagel and Siebert (*Ber.*, 1933, **66 B**, 708) found a similar production of diselenides on hydrolysis of the arylselenenyl chlorides and suggested the following mechanism :



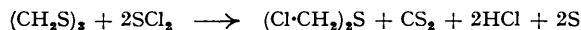
The direct attachment of a chlorine atom to selenium in this compound is indicated by the liberation of one equivalent of iodine per atom of selenium on treatment with aqueous potassium iodide :



and this is supported by the production of two equivalents of iodine by interaction with iodine monochloride :



From the fact that on treating trithioformaldehyde with sulphur dichloride they obtained an almost quantitative yield of products according to the equation



Mann and Pope (*J.*, 1923, 1172) appear to adduce some support for a cyclic structure for trithioformaldehyde. A similar suggestion that bischloromethyl selenide obtained by the chlorination of trimethylene triselenide is formed from the fragments of the triselenacyclohexane ring is attractive. However, if this is accepted, difficulties immediately arise with respect to the explanation of the formation of bischloromethyl diselenide. Also, it must be remembered that the chlorination of monomeric carbon diselenide (Ives, Pittman, and Wardlaw, *J.*, 1947, 1080) gives rise to a series of compounds exactly analogous with those described in this paper. It is therefore necessary to conclude that chlorination of trimethylene triselenide offers little support for a ring structure for this compound.

It seems highly likely that the initial product in the chlorination is chloromethylselenenyl chloride, which, in the absence of excess of chlorinating agent readily loses chlorine with the formation of the diselenide, and that the bischloromethyl selenide which may be subsequently obtained is produced by the disproportionation of this compound in the distillation necessary for purification.

EXPERIMENTAL.

Interaction of Formaldehyde and Hydrogen Selenide.—(a) *In strongly acid solution* (Vanino and Schinner, *loc. cit.*). Hydrogen selenide was passed over the surface of a well-stirred mixture of 36% formaldehyde (30 g.) and concentrated hydrochloric acid (90 ml.) in an air-free apparatus, until no more absorption occurred. The white solid which formed was filtered off and washed free from hydrogen selenide with a large quantity of water, followed by alcohol and then by ether. It was dried in a vacuum-desiccator for several weeks. Yield, 30 g. Recrystallisation twice from xylene gave trimethylene triselenide as white needles, m. p. 210°, unchanged on further recrystallisation [Found: Se, 84.4%; *M* (ebullioscopic in xylene), 262. Calc. for $(\text{CH}_2\text{Se})_3$: Se, 85.0%; *M*, 279). Unless it was adequately dried, the compound appeared not to be soluble in either xylene or chlorobenzene.

(b) *At medium acid concentration.* The previous experiment was repeated using a mixture of 36% formaldehyde (30 g.), concentrated hydrochloric acid (30 ml.), and water (60 ml.). A white evil-smelling pasty solid was obtained. This was repeatedly washed with alcohol and then with acetone and dried in a vacuum desiccator. This substance could not be recrystallised from any of the common organic solvents. It had m. p. 70–74°, but, when the substance was kept, the m. p. slowly rose to 165° (Found: Se, 79.3%). On vacuum-sublimation (<0.0001 mm.), a very small deposit of glittering white needles, m. p. 210°, was obtained in close vicinity to the solid, and an evil-smelling dirty yellow oil was deposited in small amount on the cooled receiver.

(c) *In neutral solution.* Experiment (a) was repeated using a mixture of 36% formaldehyde (30 g.) and water (90 ml.). After some hours a clear, colourless oil was formed below the aqueous phase. This was separated, but could not be purified by distillation, even at very low pressures, as extensive decomposition took place with the production of a golden-yellow, stinking, involatile oil. Analyses were therefore made on the impure product (Found: Se, 73.2%).

Chlorination of Trimethylene Triselenide.—(a) *With chlorine.* Dry chlorine was passed into a well-stirred suspension of trimethylene triselenide in anhydrous carbon tetrachloride, cooled in a freezing mixture. Initially the suspension appeared to thicken and then the white solid became yellow and dissolved, leaving a gummy deposit including red selenium. Much heat was evolved at this stage and the carbon tetrachloride layer became deep yellow. Further chlorination caused a darkening of this colour to a deep red. The course of this reaction could not be adequately followed by weighing owing to the considerable side reactions, but the colour of the carbon tetrachloride layer was a good index of the extent of chlorination. Chlorination was stopped at the desired stage, the mixture filtered, and the bulk of the carbon tetrachloride distilled off at atmospheric pressure. The residual oil was fractionally distilled in an all-glass apparatus at 1–2 mm. The table gives the results of three typical experiments.

$(\text{CH}_2\text{Se})_3$, g.	Colour of CCl_4 layer.	Pale yellow	Dark red	Intermediate fraction, g.	Deep yellow
		fraction, b. p. 39–42°/2 mm., g.	fraction, b. p. 44–50°/1.5 mm., g.		fraction, b. p. 96–100°/1.5 mm., g.
133	Reddish-yellow	none	24.0	17	22.0
148	Deep red	none	80.0	none	none
85	Deep yellow	7.7	none	12.0	28.1

In all cases the temperature rose very slowly between fractions. Careful redistillation gave three products of constant b. p.: (i) *Bischloromethyl selenide*, a pale yellow mobile liquid, b. p. 42°/2 mm. [Found: Se, 44.1; Cl, 40.1; C, 13.3; H, 2.1%; *M* (cryoscopic in C_6H_6), 180. $\text{C}_2\text{H}_4\text{Cl}_2\text{Se}$ requires Se, 44.4; Cl, 39.8; C, 13.4; H, 2.2%; *M*, 178.2]. (ii) *Chloromethylselenenyl chloride*, a dark red heavy oil, b. p. 52°/1.5 mm. A fairly pure sample could be obtained by rapid distillation of the substance with excess of chlorinating agent through a very short column [Found: Se, 48.0; Cl, 41.9%; *M* (cryoscopic in C_6H_6), 195. $\text{CH}_2\text{Cl}_2\text{Se}$ requires Se, 48.2; Cl, 43.2%; *M*, 164]. (iii) *Bischloromethyl diselenide*, a golden-yellow, heavy oil, b. p. 97°/1.5 mm. [Found: Se, 60.9; Cl, 27.2; C, 10.0; H, 2.4%; *M* (ebullioscopic in C_6H_6), 258. $\text{C}_2\text{H}_4\text{Cl}_2\text{Se}_2$ requires Se, 61.5; Cl, 27.6; C, 9.3; H, 1.6%; *M*, 256.4].

(b) *With selenium monochloride.* As in the chlorinations with chlorine, the products depended on the relative proportions of the reactants. Two typical experiments are therefore described.

(i) Finely divided trimethylene triselenide (15 g.) was shaken for 30 minutes with selenium monochloride (34 g.) dissolved in anhydrous carbon tetrachloride (50 ml.). On filtration and removal of the solvent a dark red oil was obtained. This, on fractional distillation, gave a heavy red liquid (8 g.), b. p. 52°/1.5 mm., identical in properties and analysis with chloromethylselenenyl chloride obtained in (a).

(ii) Use of trimethylene triselenide (60 g.) and selenium monochloride (70 g.) and fractionation gave a light-yellow liquid (5 g.), b. p. 43°/2 mm., and a golden-yellow oil (12 g.), b. p. 96°/1.5 mm., identical with the bischloromethyl selenide and diselenide previously obtained.

Hydrolysis of Bischloromethyl Selenide.—Several grams of bischloromethyl selenide were refluxed with a 1% aqueous solution of borax. On passage of the vapours evolved into an alcoholic solution of dimedon and into a solution of 2:4-dinitrophenylhydrazine in dilute hydrochloric acid, crystalline derivatives were obtained. These on recrystallisation gave m. p.s 186° and 164° respectively, which correspond with the m. p.s of the derivatives formed by formaldehyde with these two reagents. A white solid, which was also formed by the treatment with borax, was washed free from boric acid with warm water, and dried. Preliminary examination showed that it was almost undoubtedly trimethylene triselenide. It was, therefore, refluxed with concentrated hydrochloric acid to convert it into the

high-melting form, washed with water, and thoroughly dried. Recrystallisation gave colourless white needles, m. p. 200° (Found: Se, 83.5. Calc. for $C_2H_4Se_2$: Se, 85.0%).

A similar hydrolysis was carried out quantitatively, using 0.7% aqueous sodium hydrogen carbonate in place of borax. A 70% yield of trimethylene triselenide, based on the selenium taken, was obtained and practically the whole of the chlorine was recovered from the aqueous phase.

Hydrolysis of Chloromethylselenenyl Chloride.—Chloromethylselenenyl chloride (10 g.) was thoroughly shaken with distilled water (200 ml.), a golden yellow oil contaminated with a little red selenium being formed. This was extracted with carbon tetrachloride and on fractional distillation of this extract 5 g. of an oil, b. p. 96°/1.5 mm., were obtained (Found: Se, 61.0. Calc. for $C_2H_4Cl_2Se_2$: Se, 61.5%). Evaporation of the supernatant aqueous layer gave a sticky yellowish-white solid which was not amenable to investigation.

Treatment of Bischloromethyl Diselenide with Potassium Cyanide.—To a solution of the diselenide (10 g.) in acetone was added, with constant stirring, potassium cyanide (2.5 g.) dissolved in methyl alcohol. The buff-coloured precipitate which formed was then filtered off and the major portion of the solvent was removed by evaporation under reduced pressure on a water-bath. The evil-smelling, sticky syrup thus obtained was treated with a fresh portion of acetone and the insoluble material filtered off. This consisted mainly of potassium selenocyanate. Fractional distillation of the filtrate gave a light-yellow liquid (1.5 g.), b. p. 178°/760 mm., identified as bischloromethyl selenide by refluxing it with zinc dust in ethyl alcohol. A white solid was obtained, which, on recrystallisation from nitrobenzene gave colourless needle-shaped crystals, m. p. 173°, identical (m. p. and mixed m. p.) with the crystals obtained by a similar treatment of a sample of the bischloromethyl selenide obtained from the chlorination experiments.

Analytical Procedures.—Selenium. A weighed quantity of the substance was placed in an all-glass distillation apparatus fitted with a tap funnel. Several ml. of saturated aqueous silver nitrate were added and the mixture was gently warmed. Reaction then occurred with the formation of black silver selenide and nitrous fumes. When this reaction appeared to be complete, 100 ml. of concentrated hydrobromic acid were added from the tap funnel and the bulk of this acid was then slowly distilled, the condenser being vertical, with its open end dipping just below the surface of a little hydrobromic acid. The selenium in the distillate, present as selenium tetrabromide, was precipitated by treatment with sulphur dioxide until the first appearance of colloidal red selenium, the reduction then being completed by the addition of several g. of hydroxylamine hydrochloride and boiling. The precipitated selenium was separated in the usual manner and weighed.

Halogens. Halogen was determined by the modified Dains method (*J. Amer. Chem. Soc.*, 1920, **42**, 1574) described by Ives, Pittman, and Wardlaw (*J.*, 1947, 1080). This was further modified, however, removal of selenium by boiling with dilute sulphuric acid being replaced by reduction with sulphur dioxide, followed by filtration.

Carbon and hydrogen were determined by Drs. Weiler and Strauss, Oxford.

Action of Potassium Iodide and Iodine Monochloride on Selenium Compounds.—The technique used was that described by McCullough, Campbell, and Krilanovich (*Ind. Eng. Chem., Anal.*, 1946, **18**, 638).

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