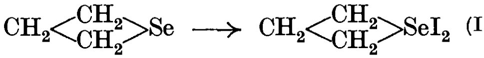
CXC.—*Heterocyclic Systems Containing Selenium. Part III.* cyclo*Selenopropane.*

By Gilbert T. Morgan and Francis Hereward Burstall.

Whereas the interaction of the requisite alkylene dibromide and sodium selenide leads readily to the production in good yields of cyclic selenohydrocarbons containing five- or six-membered rings (J., 1929, 1096, 2197), yet trimethylene dibromide and sodium selenide furnish only a small proportion of cyclo*selenopropane* (I), the main product being a six-fold *polymeride* (III) resulting by aggregations of simpler four-membered unsaturated radicals, $^{-}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}Se^{-}$.

*cyclo*Selenopropane (I), a colourless liquid with a more pungent odour than those of *cyclo*selenobutane and *cyclo*selenopentane, resembles these selenohydrocarbons in yielding a characteristic deep purple *di-iodide* (II) and a white crystalline *mercurichloride*,

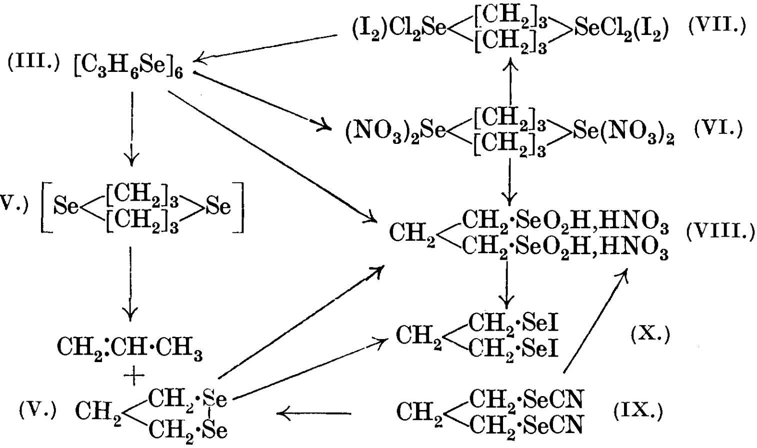
(I.)  (II.)

$$CH_2{<}^{CH_2}_{CH_2}{>}Se \longrightarrow CH_2{<}^{CH_2}_{CH_2}{>}SeI_2$$

but differs from the two higher cyclic homologues in its tendency to give gummy ill-defined materials.

The amorphous saponaceous polymeride obtained from these gummy residues decomposes on heating, but without elimination of selenium, into propylene and the more stable *cyclo*trimethylene diselenide (V). This reaction suggests that at the higher temperature the polymeride has undergone partial depolymerisation with the intermediate formation of *cyclo*hexamethylene 1 : 5-diselenide (IV). Dilute nitric acid does not rupture the polymeric complex but oxidises its selenium atoms with formation of a *nitrate* (VI), a water-soluble and readily decomposable compound which by double decomposition with hydrochloric acid gives rise to the corresponding *chloride* (VII) : this is reduced by sodium metabisulphite to the original polymeride. Hot concentrated nitric acid attacks the polymeride, yielding *trimethylenediselenious acid dinitrate* (VIII), and oxalic acid, the latter compound being in all probability an oxidation product of the malonic acid originally formed by ring fission. The dinitrate (VI) is also obtained by oxidation with nitric acid of either *cyclo*trimethylene diselenide (V) or trimethylenediselenocyanate (IX). These two selenium derivatives (V and IX) were first isolated by Hagelberg (*Ber.*, 1890, **23**, 1090).

The following series of reactions is completed by the action of hydriodic acid on the trimethylenediselenious acid dinitrate, which gives rise to dark red *trimethylenediseleno-di-iodide* (X), also obtained by adding iodine to *cyclo*trimethylene diselenide.



(III.) $[C_3H_6Se]_6$

(IV.) $\left[Se<^{[CH_2]_3}_{[CH_2]_3}>Se\right]$

$CH_2{:}CH\cdot CH_3$ +

(V.) $CH_2<^{CH_2\cdot Se}_{CH_2\cdot Se}$

(VI.) $(NO_3)_2Se<^{[CH_2]_3}_{[CH_2]_3}>Se(NO_3)_2$

(VII.) $(I_2)Cl_2Se<^{[CH_2]_3}_{[CH_2]_3}>SeCl_2(I_2)$

(VIII.) $CH_2<^{CH_2\cdot SeO_2H,HNO_3}_{CH_2\cdot SeO_2H,HNO_3}$

(IX.) $CH_2<^{CH_2\cdot SeCN}_{CH_2\cdot SeCN}$

(X.) $CH_2<^{CH_2\cdot SeI}_{CH_2\cdot SeI}$

Earlier attempts to implicate sulphur in a four-membered heterocyclic ring resulted in products which are in the main analogous with the derivatives now recorded in the case of selenium.

Grischkevitsch-Trochimovski (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 880) obtained *cyclo*thiopropane, b. p. 93—94°/752 mm., from trimethylene dibromide and sodium sulphite, and this monomeric substance was accompanied by a polymeride, m. p. *ca.* 85°, which had previously been obtained by Mansfield (*Ber.*, 1886, **19**, 696), who assigned to his compound the molecular formula $(C_3H_6)_3S_3$. Autenrieth and Wolff (*Ber.*, 1899, **32**, 1390), by the action of trimethylene dibromide on the disodium derivative of trimethylene dimercaptan, prepared *cyclo*hexamethylene-1 : 5-disulphide as a colourless oil.

EXPERIMENTAL.

cyclo*Selenopropane* (I).—Freshly distilled trimethylene dibromide (40 g.) was added to an alcoholic suspension (350 c.c.) of sodium selenide prepared from 24 g. of aluminium selenide, 11 g. of sodium and 9 c.c. of water in the presence of hydrogen. The mixture was left for some hours at room temperature and the stream of hydrogen maintained to ensure adequate agitation and to prevent aerial oxidation. The alcoholic solution, filtered from precipitated sodium bromide and yellow gum, was distilled under diminished pressure; the distillate was rectified until a colourless alcoholic solution was obtained. This solution was then poured into a large excess of water (1000 c.c. of water for each 100 c.c. of alcoholic solution), and the aqueous-alcoholic solution repeatedly extracted with petroleum (b. p. 40—60°). The petroleum extracts were dried over calcium chloride and the solvent distilled; the residue was distilled under diminished pressure and finally rectified in a stream of carbon dioxide under ordinary pressure. A considerable quantity of the oil polymerised to a yellow gum during these distillations. cyclo*Selenopropane* was thus obtained as a colourless limpid oil of exceedingly powerful and penetrating odour. The vapour has an irritant effect on the mucous membrane of the nose. It boiled at 118—119°/779 mm.; $n_{D}^{15^\circ}$ 1·5612; $d_{4^\circ}^{20^\circ}$ 1·525; $d_{4^\circ}^{29^\circ}$ 1·510; $d_{4^\circ}^{37{\cdot}5^\circ}$ 1·498; $d_{4^\circ}^{47^\circ}$ 1·484, whence $d_{4^\circ}^{t^\circ} = 1{\cdot}554 - 0{\cdot}001493t$ (Found: C, 29·2; H, 5·0; Se, 65·0. C_3H_6Se requires C, 29·7; H, 4·95; Se, 65·3%). The selenohydrocarbon was insoluble in water but was miscible in all proportions with organic media. *cyclo*Selenopropane was completely volatile in the vapours of alcohol or ether and to a small extent in the vapours of other volatile solvents. It remained unchanged when kept in a cool dark place. Mineral acids caused rapid polymerisation of this cyclic selenohydrocarbon.

cyclo*Selenipropane* 1 : 1-*Di-iodide* (II).—Addition of alcoholic iodine to an alcoholic solution of *cyclo*selenopropane caused the separation of two products. The less soluble *material*, present in larger quantity, a polymerised condition of the di-iodide, formed an amorphous purple deposit insoluble in all organic media; it softened at 87° and then remained liquid [Found: I, 67·4. $(C_3H_6I_2Se)_x$ requires I, 67·7%].

The more soluble monomeric *di-iodide* separated in deep purple, hair-like needles, m. p. 98°. Although soluble in acetone, benzene or chloroform, this di-iodide dissolved only sparingly in alcohol and was insoluble in cold water. It decomposed slowly on exposure to light (Found: C, 9·8; H, 1·55; Se, 20·4; I, 67·9; *M*, in acetone, 369. $C_3H_6I_2Se$ requires C, 9·6; H, 1·6; Se, 21·1; I, 67·7%; *M*, 375).

On grinding the foregoing monomeric di-iodide with water and silver oxide a colourless neutral solution of the dihydroxide resulted, but this soon decomposed with formation of a yellow solid, m. p. 73—74°. Aqueous sodium metabisulphite reduced the di-iodide with difficulty and the presence of *cyclo*selenopropane was detected by its odour. A small quantity of yellow polymeride separated slowly from solution.

cyclo*Selenopropane mercurichloride*, $C_3H_6{>}Se,HgCl_2$, separated when alcoholic solutions of mercuric chloride and *cyclo*selenopropane were mixed. The white crystalline precipitate, after being washed with alcohol and dried over sulphuric acid, decomposed at 105° after shrinking at 80° (Found: Hg, 50·8; Cl, 18·4. $C_3H_6Cl_2SeHg$ requires Hg, 51·1; Cl, 18·1%). This mercurichloride was insoluble in water and organic solvents, but aqueous caustic alkalis decomposed it, liberating *cyclo*selenopropane. When heated, the mercurichloride gave mercuric selenide and trimethylene dichloride. Addition of methyl iodide to an alcoholic solution of *cyclo*selenopropane and cautious evaporation of the mixture led to the production of a brown oil, from which, however, no crystalline methiodide could be isolated.

The Polymeride (III).—The yellow gum separating from the original alcoholic solution of *cyclo*selenopropane was washed with water to remove sodium bromide and dissolved in chloroform. Evaporation of the dried solution left a deep reddish gum, which was extracted with boiling acetone until the extracts were colourless. The residual gum then solidified to a pale yellow, soap-like substance, m. p. 38—40° [Found: C, 29·7; H, 4·9; Se, 65·0; *M*, ebullioscopic in benzene, 738, 836. $C_{18}H_{36}Se_6$ requires C, 29·7; H, 4·95; Se, 65·3%; *M*, 727]. This complex substance was insoluble in water or alcohol and sparingly so in acetone, but dissolved readily in warm chloroform or benzene. From its solution in the last two solvents the halogens precipitated coloured unstable additive compounds whereas methyl iodide gave a dark gum. When this *polyselenide* was gently heated, selenium was not eliminated but a considerable amount of frothing took place and the evolved gas when passed through bromine water furnished propylene dibromide, b. p. 140—141° (Found: Br, 78·6. Calc.: Br, 79·15%). The residue consisted of *cyclo*trimethylenediselenide, identified by comparison with an authentic specimen made by the general method of preparation for these diselenides (*v. infra*).

The Nitrate (VI).—Warm 2*N*-nitric acid dissolved the polymeride and deposited on cooling a white microcrystalline *nitrate*, which was washed with 2*N*-nitric acid (Found: Se, 31·8. $C_6H_{12}O_{12}N_4Se_2$ requires Se, 32·3%). This nitrate, which dissolved readily in water to a strongly acid solution, decomposed slowly with evolution of nitrous fumes, leaving a residue of yellow gum; it decomposed rapidly at 87°.

The corresponding *chloride* (VII) was precipitated when concentrated hydrochloric acid was added to a solution of the foregoing nitrate (Found: C, 18·3; H, 3·3; Cl, 36·2. $C_6H_{12}Cl_4Se_2$ requires C, 18·7; H, 3·1; Cl, 36·9%). Although moderately easily soluble in water, this white microcrystalline chloride dissolved only sparingly in hydrochloric acid and was insoluble in alcohol or acetone. On addition of aqueous sodium metabisulphite to its aqueous solution a yellow amorphous precipitate of the polymeride was deposited.

The gummy iodide was obtained when potassium iodide solution was added to a solution of the foregoing nitrate which had been neutralised with aqueous sodium acetate. It was sparingly soluble in most common organic solvents but could not be obtained in a state of purity. It decomposed indefinitely above 100°.

Hot concentrated nitric acid reacted violently with the polymeride and the resulting clear colourless solution after evaporation and cooling deposited oxalic acid, m. p. 100° (Found: C, 18·8; H, 4·9. Calc.: C, 19·0; H, 4·8%).

Trimethylenediselenodi-iodide (X).—After separation of the oxalic acid the viscid residue was freed from mineral acid by sodium acetate; addition of a concentrated solution of potassium iodide then precipitated the brick-red di-iodide arising from the reducing action of hydriodic acid on trimethylenediselenious acid. *Trimethylenediselenodi-iodide*, also obtained by treating a chloroform solution of *cyclo*trimethylene diselenide with iodine, dissolved in warm chloroform or benzene but very sparingly in acetone or alcohol; it melted to a red liquid at 124° (Found: C, 8·1; H, 1·2; Se, 34·5; I, 55·7. $C_3H_6I_2Se_2$ requires C, 7·9; H, 1·3; Se, 34·9; I, 55·9%).

Trimethylenediselenocyanate (IX) was readily prepared by heating trimethylene dibromide (1 mol.) and potassium selenocyanate (2 mols.) in acetone. The dark filtrate from precipitated potassium bromide was obtained as an oil which subsequently solidified and was obtained in thin colourless prisms, m. p. 53°, by crystallisation from aqueous acetone. Hagelberg (*loc. cit.*) gave m. p. 51° (Found: Se, 62·5. Calc.: Se, 62·7%). This diselenocyanate, which remained undecomposed on keeping, possessed a faint and characteristic odour.

*cyclo*Trimethylene diselenide (V), obtained as a yellow amorphous precipitate when air was aspirated through an alcoholic soda solution of the foregoing diselenocyanate, was purified by crystallisation from acetone or chloroform; m. p. 59°. Hagelberg (*loc. cit.*) gave m. p. 54·5° (Found: Se, 78·9; *M*, ebullioscopic in benzene, 225. Calc. for $C_3H_6Se_2$: Se, 79·1%; *M*, 200). This diselenide distilled undecomposed when heated under diminished pressure. Its chloroform solution gave with iodine a red precipitate of trimethylenediselenodi-iodide, m. p. 124° (*vide supra*).

Trimethylenediselenious Acid Dinitrate (VIII).—The foregoing diselenocyanate and diselenide both dissolved readily in nitric acid and the concentrated solution deposited a mass of white needles, which were recrystallised from nitric acid (Found: Se, 40·2. $C_3H_{10}O_{10}N_2Se_2$ requires Se, 40·4%). The *dinitrate* decomposed at 112°; it dissolved easily in water and this solution when treated successively with sodium acetate and potassium iodide gave a brick-red precipitate of trimethylenediselenodi-iodide, m. p. 124°.

CHEMICAL RESEARCH LABORATORY,
TEDDINGTON, MIDDLESEX.

[*Received, May 9th*, 1930.]