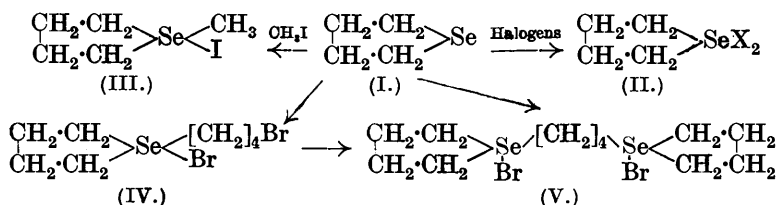


CXLVI.—*Heterocyclic Systems containing Selenium.*
Part I. cycloSelenobutane (Tetrahydro-selenophen).

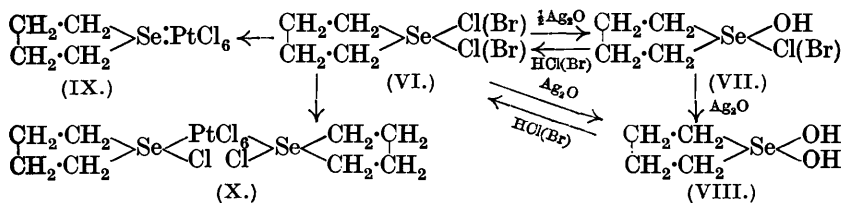
By GILBERT T. MORGAN and FRANCIS HEREWARD BURSTALL.

In the course of a systematic investigation on cyclic derivatives of selenium we have prepared cyclo-selenobutane (*tetrahydro-selenophen*; formula I) by condensing tetramethylene dibromide and sodium selenide, using special precautions to avoid oxidation of the alkali selenide. This reaction is applicable to the production of other cyclic systems containing selenium, but the present communication deals only with a description of *cyclo-selenobutane* and its derivatives.

As a compound containing bivalent selenium, *cyclo-selenobutane* exhibits considerable residual affinity. It combines additively with mercuric chloride and the halogens and with alkyl halides and alkylene dihalides. These reactions are summarised in the following diagram :



The three crystalline *cyclo-selenobutane 1:1-dihalides* (II) show a decrease in solubility in organic media and a colour gradation (colourless–yellow–purple–black) as the atomic weight of the halogen increases. The solubility of these dihalides in non-hydrolysing organic media points to a non-polar character, but in hot water the dichloride and dibromide dissolve to give strongly acid solutions from which they crystallise unchanged on cooling. These reactions suggest a change in the molecular structure of the dissolved dihalides on which some light is thrown by the experiments indicated in the following diagram :



Moist silver oxide with excess of dichloride or dibromide (VI) yields a *cyclo-selenobutane 1-hydroxychloride* or *1-hydroxybromide*

(VII). These hydroxyhalides are colourless crystalline salts which dissolve freely in water, yielding acid solutions, but are almost insoluble in non-hydrolysing solvents. By addition of the appropriate hydrogen halide they are reconverted into dichloride or dibromide.

With excess of silver oxide the foregoing hydroxyhalides and dihalides yield *cycloselenibutane* 1 : 1-dihydroxide (VIII), a very soluble hygroscopic substance which dissolves in water to a feebly acid solution (p_H 6.0 to 6.2) and behaves as an amphoteric hydroxide.

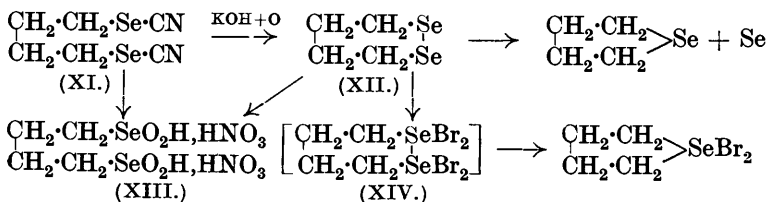
In cold dilute solution combination occurs between molecular proportions of the dichloride and platinum chloride so that a simple chloroplatinate (IX) is formed which, although sparingly soluble in water, dissolves in the ordinary organic media, including the alcohols, acetone, benzene, and chloroform. With warm concentrated solutions a more complex chloroplatinate (X) is obtained, which is readily soluble in water or alcohol, but insoluble in acetone, benzene, and other organic media.

cycloSelenibutane 1-chloroplatinate (IX) behaves like the non-polar *cycloselenibutane* dihalides in dissolving in non-hydrolysing organic media, whereas *bis*-1-chlorocycloselenibutane 1-chloroplatinate (X) is evidently a polar compound, dissolving in water and corresponding with the hydrolysed forms of the dihalides in aqueous solution.

Water-soluble selenonium salts are produced when *cycloselenobutane* combines with alkyl halides and alkylene dihalides. With methyl iodide *cycloselenibutane* 1-methiodide is produced, whereas the interaction with $\alpha\delta$ -butylene dibromide proceeds in two stages, giving successively 1- δ -bromobutylcycloselenibutane 1-bromide (IV) and tetramethylene- $\alpha\delta$ -biscycloselenibutane 1 : 1'-dibromide (V). These selenium salts furnish neutral aqueous or alcoholic solutions, from which silver nitrate readily precipitates the halogen ion.

An alternative method of obtaining *cycloselenobutane* and its derivatives has been devised starting from tetramethylene dibromide and potassium selenocyanate, which interact smoothly to yield tetramethylene diselenocyanate (XI). Hydrolysis of this substance by alcoholic potash or soda, accompanied by aerial oxidation, leads to cyclotetramethylene diselenide (cyclodiselenobutane; XII) and when heated the diselenide loses half its selenium and passes into *cycloselenobutane*, whereas bromine and the diselenide interact to give *cycloselenibutane* dibromide, the eliminated selenium being obtained as such or as its monobromide according to the amount of bromine employed. This conversion of diselenide into *cycloselenibutane* dibromide is preceded by the intermediate formation of an

unstable orange tetrabromide (XIV). The structure of this cyclic diselenide is revealed by its quantitative conversion with excess of nitric acid into *tetramethylenediseleninic acid dinitrate* (XIII), a substance which is also obtained on heating tetramethylene diselenocyanate (XI) with the same oxidising agent.



We are indebted to Dr. Sugden for his kind assistance in the following determination of the parachor of *cycloselenobutane*.

t	10°	20°	30°	40°
Surface tension, γ	41.28	39.53	38.07	37.14
Density, D	1.493	1.478	1.463	1.452
Parachor	229.4	229.3	229.5	229.8
Mean	229.5	Calculated	227.3	

These results show that *cycloselenobutane* is quite normal as regards its parachor.

Literature contains two references to the sulphur analogue of *cycloselenobutane*, which was first obtained by von Braun and Trümpler (*Ber.*, 1910, **43**, 545) on condensing tetramethylene iodide with sodium sulphide. Later Grischkevitch-Trochimovski (*J. Russ. Chem. Soc.*, 1916, **48**, 901) repeated the preparation, confirmed the boiling point, determined the physical constants, and investigated its chemical properties.

Recent papers by Briscoe and Peel (*J.*, 1928, 1741, 2628) on the isolation and description of selenophen furnish data employed in the following comparison of the physical constants of the two pairs of five-membered heterocyclic rings :

Physical properties.	Thiophen (Landolt Börnstein).	Tetrahydrothiophen (G.T.).	Selenophen (B. & P.).	Tetrahydro-selenophen.
B. p. ...	87°/770 mm.	118—119°	110°/752 mm.	135—136°/770 mm.
D	1.0704 ₄ ^{15°}	0.9607 ₄ ^{18°}	1.5307 ₄ ^{18°}	1.484 ₄ ^{15°}
n	1.5298/18°	1.4871/15°	1.568/15°	1.5510/18°
γ	33.5/0°	—	36.49/15°	40.40/15°

Hydrogenation of the thiophen ring raises the boiling point by about 30°, and a similar difference (35°) is observed between the boiling points of selenophen and its tetrahydro-derivative. These regularities are also supported by the boiling point (113—114°) recorded for selenophen by Mazza and Solazzo (*Rend. Accad. Sci. fis. mat. Napoli*, 1927, **33**, 236).

EXPERIMENTAL.

I. *cycloSelenobutane* (*Tetrahydro-selenophen*) (I).— $\alpha\delta$ -Tetramethylene glycol was prepared by reducing ethyl succinate with sodium in anhydrous alcohol, the average yield being *ca.* 50% (compare Müller, *Monatsh.*, 1928, **49**, 27), and this glycol was converted into $\alpha\delta$ -tetramethylene dibromide (b. p. 96°/50 mm.) by interaction with dry hydrogen bromide.

Hydrogen selenide, generated by the action of water on 14.5 g. of aluminium selenide, and hydrogen were passed into alcoholic soda made from 6.9 g. of sodium, 250 c.c. of alcohol, and 6 c.c. of water. Colourless sodium selenide separated and when all the hydrogen selenide had been introduced the alcohol was distilled away and cold water was added together with 25 g. of $\alpha\delta$ -tetramethylene dibromide (32.5 g. are required by theory, but excess of sodium selenide is desirable).

The mixture was heated at 80° in a current of hydrogen, which prevented oxidation and kept the liquid agitated. After 4 hours the *cyclo-selenobutane* was dissolved in carbon tetrachloride, and this extract dried over calcium chloride. Sufficient bromine was then added to convert the selenohydrocarbon into dibromide (yield, 75% of the theoretical). *cycloSelenobutane*, regenerated by prolonged stirring of the dibromide with water and four times its weight of sodium metabisulphite, was dried over calcium chloride and distilled under reduced pressure. It was noticed that the selenium compound dissolved a considerable amount of sulphur dioxide, which was liberated on heating. The final rectification was effected under ordinary pressure in a stream of carbon dioxide. *cycloSelenobutane* was thus obtained as a colourless to faintly yellow liquid, b. p. 90—91°/172 mm. and 135—136°/770 mm., d^{15} 1.484: densities at other temperatures are given by the expression $D_t = 1.5060 - 0.001354t$. It possessed a very pungent and somewhat unpleasant odour (Found: C, 35.3; H, 6.1; Se, 58.2, 58.35. C_4H_8Se requires C, 35.5; H, 6.0; Se, 58.55%).

Although insoluble in water, the selenohydrocarbon was volatile in steam or in the vapours of alcohol and ether. It was miscible in all proportions with organic solvents. Cold concentrated sulphuric acid gave no coloration, but on warming yellow to red tints were developed. Although *cyclo-selenobutane* was only very slowly oxidised in air, hydrogen peroxide promoted oxidation. Aqueous permanganate ruptured the ring, as also did fuming nitric acid, whereas the moderately concentrated acid gave *cyclo-selenobutane* 1:1-dinitrate.

II. *Additive Compounds of cycloSelenobutane*.—*cycloSelenobutane mercurichloride*, $C_4H_8Se, HgCl_2$, crystallised in colourless needles

from a warm alcoholic solution of *cycloselenobutane* and mercuric chloride; it melted to an opaque white liquid at 146° (Found : Cl, 17.2. $C_4H_8Cl_2SeHg$ requires Cl, 17.4%).

cycloSelenibutane 1 : 1-dichloride (II) crystallised in colourless plates when chlorine was passed into a carbon tetrachloride solution of *cycloselenobutane*: it melted at $88-89^{\circ}$ (Found : Cl, 34.4. $C_4H_8Cl_2Se$ requires Cl, 34.4%). This dichloride was soluble in chloroform, benzene, or acetone; it dissolved sparingly in alcohol or hot water to a strongly acid solution from which, on cooling, it separated unchanged.

cycloSelenibutane 1 : 1-dibromide (II), also prepared by direct addition of its generators, crystallised from benzene, carbon tetrachloride or hot water in lustrous yellow needles, m. p. 92° (Found : C, 16.2; H, 2.7; Br, 54.4; Se, 26.7. $C_4H_8Br_2Se$ requires C, 16.3; H, 2.7; Br, 54.2; Se, 26.8%).

The *perbromide*, $C_4H_8SeBr_2Br_5$, separated in crimson prismatic crystals when concentrated chloroform solutions of bromine and the preceding dibromide were mixed. From dilute solutions it was obtained in large tabular crystals which, although stable in contact with their mother-liquor, decomposed slowly in the air or more quickly on heating, leaving a residue of the dibromide. Acetone also removed five atomic proportions of bromine from this perbromide (Found : Br, 79.7. $C_4H_8Br_7Se$ requires Br, 80.5%).

cycloSelenibutane 1 : 1-di-iodide (II) separated in lustrous purplish-black crystals, m. p. $99-100^{\circ}$, when carbon tetrachloride solutions of its generators were mixed (Found : I, 65.4. $C_4H_8I_2Se$ requires I, 65.25%). This di-iodide is only sparingly soluble in organic media and practically insoluble in hot water.

cycloSelenibutane 1 : 1-dihydroxide (VIII) was produced in aqueous solution when the corresponding dibromide was treated with excess of freshly prepared silver oxide. On evaporation of the filtered solution on the water-bath and finally in a vacuum desiccator, colourless highly hygroscopic crystals were obtained. This aqueous solution was neutral to litmus (p_H 6.0—6.2) and addition of aqueous hydrogen halide regenerated the corresponding 1 : 1-dihalide.

cycloSelenibutane 1-hydroxy-1-bromide (VII). When *cycloselenobutane* 1 : 1-dibromide was treated with sufficient silver oxide to remove only half its bromine or when equimolecular proportions of 1 : 1-dihydroxide and 1 : 1-dibromide were mixed in aqueous solution, this liquid on concentration over sulphuric acid yielded colourless crystalline *hydroxybromide*, which was freed from any unchanged dibromide by washing with benzene (Found : C, 20.7; H, 3.7; Br, 34.5. C_4H_8OBrSe requires C, 20.7; H, 3.9; Br, 34.4%).

This hydroxybromide decomposed slowly on keeping, and on

heating decomposition set in at 99—100°; it was almost insoluble in non-hydrolytic solvents and its aqueous solution was strongly acidic.

cycloSelenibutane 1-hydroxy-1-chloride (VII), prepared in a similar manner to the foregoing hydroxybromide, was a stable crystalline compound readily soluble in water to a strongly acid solution; it decomposed at 116° (Found: Cl, 18.9. C_4H_9OClSe requires Cl, 18.9%).

cycloSelenibutane 1-chloroplatinate (IX) separated slowly in yellow needles from cold dilute aqueous solutions of *cycloSelenobutane 1:1-dichloride* and chloroplatinic acid; it decomposed at 230° (Found: Pt, 35.7. $C_4H_8Cl_2SePt$ requires Pt, 35.9%).

Bis-1-chlorocycloSelenibutane 1-chloroplatinate (X). Platinic chloride was added to a warm concentrated solution containing excess of *cycloSelenobutane 1:1-dichloride*. After further evaporation and cooling, orange crystals of the complex salt separated which after drying were washed with warm acetone to remove any unchanged dichloride (Found: Pt, 26.3; Cl, 37.3. $C_8H_{16}Cl_2Se_2Pt$ requires Pt, 26.0; Cl, 37.9%). This complex salt melted and decomposed at 179°.

III. *Alkyl and Alkylene Salts of cycloSelenobutane*.—*cycloSelenibutane 1-methiodide* (III). On mixing 27 parts of *cycloSelenobutane* and 27 parts of methyl iodide heat was generated and the *methiodide* was produced, which crystallised from hot water in colourless needles (Found: I, 45.5. $C_5H_{11}ISe$ requires I, 45.8%). On heating in an open tube, this iodide sublimed slowly at about 150°, but in a closed tube it melted at 174°.

1-δ-BromobutylcycloSelenibutane 1-bromide (IV). When *cycloSelenobutane* was left in contact with an excess of $\alpha\delta$ -tetramethylene dibromide, a colourless glassy compound separated in the course of a few days. After removal of the excess of tetramethylene dibromide and washing with light petroleum, the residue was dissolved in water and the solution evaporated over sulphuric acid. The residual gum crystallised slowly; m. p. 65—66° (Found: Br, 45.3. $C_8H_{16}Br_2Se$ requires Br, 45.5%).

Tetramethylene-αδ-biscycloSelenibutane 1:1'-dibromide (V). A mixture of *cycloSelenobutane*, $\alpha\delta$ -tetramethylene dibromide, and water was heated at 90° in a sealed tube with occasional shaking until no more material dissolved in the aqueous layer. This solution was then evaporated over sulphuric acid until the complex *dibromide* separated in colourless prisms, which were dried on porous tile in a vacuum; m. p. 95—96° (Found: Br, 32.9. $C_{12}H_{24}Br_2Se_2$ requires Br, 32.85%).

IV. *Alternative Formations of cycloSelenobutane*.—*Tetramethylene*

$\alpha\delta$ -diselenocyanate (XI). Potassium selenocyanate (14.4 g.) and 10.8 g. of $\alpha\delta$ -tetramethylene dibromide were heated in acetone solution under reflux for several hours. The filtrate from potassium bromide was evaporated, and water added to the residue; the diselenocyanate then separated as a heavy pale yellow oil which slowly solidified (yield, practically quantitative) and was obtained in white flakes, m. p. 40° , by crystallisation from aqueous acetone (Found: C, 27.25; H, 3.2; Se, 59.5. $C_6H_8N_2Se_2$ requires C, 27.0; H, 3.0; Se, 59.45%).

This diselenocyanate, which possessed a penetrating and nauseous odour, decomposed slowly on keeping. Although readily soluble in the ordinary organic media, it was insoluble in water.

cycloTetramethylene diselenide (cyclodiselenobutane) (XII). An alcoholic solution of 5.0 g. of tetramethylene $\alpha\delta$ -diselenocyanate was added to alcoholic soda made by dissolving 1.5 g. of sodium in 100 c.c. of alcohol. The yellow liquid was decanted from any precipitate and diluted with 400 c.c. of water, and air bubbled through it for several hours. The diselenide, which separated as a yellow powder, sparingly soluble in alcohol or acetone, was washed successively with water and acetone. It dissolved readily in benzene or chloroform and separated from the latter solvent as a yellow gum which subsequently solidified (Found: C, 22.2; H, 3.8; Se, 73.8. $C_4H_8Se_2$ requires C, 22.4; H, 3.8; Se, 73.9%). This diselenide was quite stable on keeping and melted to a yellow liquid at 41 – 42° ; when strongly heated, it decomposed, giving cycloselenobutane, identified by its characteristic odour and by the formation of cycloselenibutane 1 : 1-dibromide.

When the deep red chloroform solution of cycloTetramethylene diselenide (1 mol.) and bromine (2 mols.) was allowed to evaporate at the ordinary temperature, the residue obtained consisted of cycloselenibutane 1 : 1-dibromide (m. p. 92°), black elemental selenium, and tarry material. The dibromide was extracted with carbon tetrachloride. The yield calculated on the resulting dibromide and on selenium recovered was 40% and upwards according to the time of evaporation.

With excess of bromine (4 mols.) an orange precipitate was deposited from the chloroform solution which appeared to be cycloTetramethylene diselenide tetrabromide (XIV) but was so readily decomposed that it could not be analysed. The transformation to cycloselenibutane 1 : 1-dibromide proceeded as before, but the selenium eliminated was obtained as selenium monobromide. The yield of dibromide was not appreciably different from that of the preceding preparation with less bromine.

$\alpha\delta$ -Tetramethylenediseleninic acid dinitrate (XIII) separated in

colourless crystals when $\alpha\delta$ -tetramethylene diselenocyanate or *cyclotetramethylene* diselenide was dissolved in warm nitric acid (1 part of concentrated acid : 1 of water) (Found : Se, 38.9. $C_4H_{12}O_{10}N_2Se_2$ requires Se, 39.0%). At 136° this complex acid decomposed with explosive violence and liberation of selenium.

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