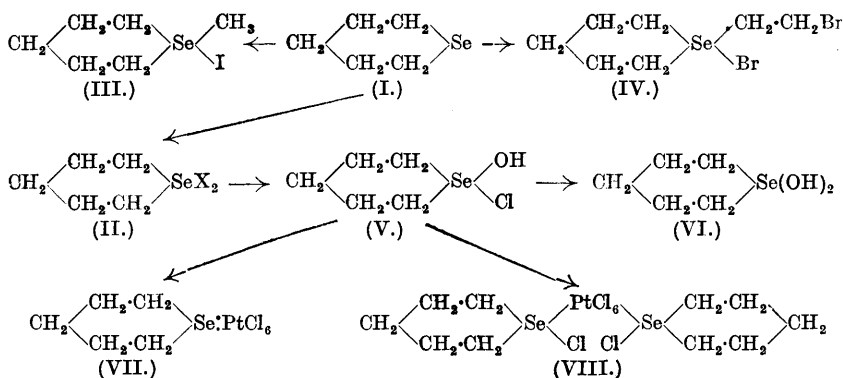


CCLXXXI.—*Heterocyclic Systems containing Selenium.*
Part II. cycloSelenopentane.

By GILBERT T. MORGAN and FRANCIS HEREWARD BURSTALL.

THE six-membered analogue of this series, *cycloselenopentane*, has been prepared by a method similar to that employed for *cyclo-selenobutane* (this vol., p. 1096) and the physical and chemical properties of the two selenopolymethylenes have been compared. These two selenohydrocarbons are very similar, but the derivatives of the new six-membered ring system made by addition of various reagents to the selenium atom are somewhat less stable than those of the five-membered ring. Combinations with methyl iodide, ethylene dibromide, and the halogens are summarised in the following diagram :



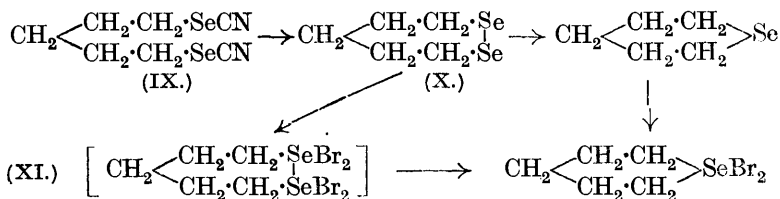
The crystalline cycloselenipentane 1:1-dihalides (II) dissolve easily in non-hydrolysing solvents: the dichloride and dibromide are also soluble in hot water and crystallise unchanged from the strongly acid solutions. It is noteworthy that cycloselenipentane 1:1-di-iodide was only obtained in purple-black prisms which correspond with the more stable darker β -form of cyclotelluripentane 1:1-di-iodide (Morgan and Burgess, J., 1928, 328).

Silver oxide converts the dichloride successively into cycloselenipentane 1-hydroxychloride (V) and the dihydroxide (VI): the former is a white crystalline substance soluble in water to an acid solution but insoluble in non-hydrolysing solvents, whereas the latter is a hygroscopic substance dissolving readily in water to an almost neutral solution. In dilute solutions chloroplatinic acid and cycloselenipentane 1:1-dichloride give cycloselenipentane 1-chloroplatinate (VII), soluble in organic media, and in stronger solutions bis-1-chlorocycloselenipentane 1-chloroplatinate (VIII), a polar compound insoluble in organic media but soluble in water.

Methyl iodide and ethylene dibromide both furnish water-soluble selenonium salts with cycloselenopentane; the former gives cycloselenipentane 1-methiodide (III) and the latter, 1- β -bromoethylcycloselenipentane 1-bromide (IV). No compound containing two molecules of cycloselenopentane and one molecule of ethylene dibromide was produced and in this respect the addition differed from the interactions of cycloselenobutane and cyclotelluropentane with tetramethylene dibromide and pentamethylene dibromide respectively (*loc. cit.*).

An alternative method of preparing cycloselenopentane follows that already given for cycloselenobutane. Pentamethylene dibromide and potassium selenocyanate react to give pentamethylene diselenocyanate (IX), which is converted into cyclopentamethylene diselenide (cyclodiselenopentane, X) by alcoholic potash and aerial

oxidation. On heating, the foregoing diselenide loses half its selenium and gives *cyclo*selenopentane. Bromine and the diselenide yield *cyclo*selenopentane 1 : 1-dibromide : the conversion is preceded by the formation of an unstable tetrabromide (XI).



The determination of the parachor shows that *cyclo*selenopentane is a normal liquid. The atomic constant for selenium was taken as 62.5 (Sugden and Henley, this vol., p. 1058).

<i>t</i>	12.5°	22.0°	32.1°	42.3°
Density (<i>D</i>)	1.409	1.397	1.384	1.372
Surface tension (γ)	38.76	37.33	35.93	34.59
Parachor	264.5	264.1	264.0	264.1
Mean parachor	264.2 (calc., 263.6).			

The foregoing observations on *cyclo*selenopentane complete the description of a series of analogous ring compounds including all members of the oxygen-sulphur group of elements :

Pentamethylene oxide (*cyclo*oxy-pentane), described by Demjanow (*J. Russ. Phys. Chem. Soc.*, 1890, **22**, 389) and later by Höchstetter (*Monatsh.*, 1902, **23**, 1071); b. p. 81—82°/760 mm., d_4^{20} : 0.8800.

Pentamethylene sulphide (*cyclo*thiopentane), first obtained by von Braun and von Trümpler (*Ber.*, 1910, **43**, 545) and studied more fully by Grischkevitch-Trochimovski (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 928); b. p. 141—142°/747 mm., d_4^{20} : 0.9943.

*cyclo*Selenopentane (*vide infra*), b. p. 158°/759 mm.

*cyclo*Telluropentane, recently described by Morgan and Burgess (*loc. cit.*); b. p. 82—83°/12 mm.

EXPERIMENTAL.

*cyclo*Selenopentane (I).—Hydrogen selenide, generated by the action of water on 14.5 parts 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 27.0 g. of $\alpha\alpha$ -pentamethylene dibromide (36.0 g. are required by theory).

The mixture was heated to 80° in a current of hydrogen, which prevented oxidation and kept the liquid agitated. After 4 hours the *cyclo*selenopentane mixed with unchanged dibromide and

impurities was dissolved in carbon tetrachloride, and this extract dried over calcium chloride. Sufficient bromine was then added to convert the selenohydrocarbon into its dibromide (yield, 45% of the theoretical). *cycloSelenopentane*, regenerated by stirring of the purified dibromide with water and four times its weight of sodium metabisulphite, was dried over calcium chloride and distilled under ordinary pressure in a stream of carbon dioxide. It was thus obtained as a colourless or very faintly yellow liquid, b. p. $158^{\circ}/759$ mm., n_D^{18} 1.5475, d_4^{25} 1.409, d_4^{20} 1.399, d_4^{26} 1.392, d_4^{22} 1.384, whence $d_4^{25} = 1.424 - 0.001236t$. It possessed a pungent and rather unpleasant odour (Found: C, 40.0; H, 7.0; Se, 53.3. $C_5H_{10}Se$ requires C, 40.2; H, 6.9; Se, 53.0%).

Although insoluble in water, the selenohydrocarbon was volatile in steam and in the vapours of alcohol and ether and was, furthermore, miscible in all proportions with organic solvents. Concentrated sulphuric acid gave yellow to red tints on warming. Whereas *cycloselenopentane* was oxidised only slowly in air, potassium permanganate in aqueous solution caused rupture of the ring, as did also fuming nitric acid; moderately concentrated nitric acid, however, gave *cycloselenipentane* 1 : 1-dinitrate.

cycloSelenopentane mercurichloride, $C_5H_{10}Se, HgCl_2$, crystallised in white feathery needles from a hot alcoholic solution of the selenohydrocarbon and mercuric chloride; it melted to an opaque white liquid at $175-176^{\circ}$ (Found: Cl, 16.7. $C_5H_{10}Cl_2SeHg$ requires Cl, 16.85%).

cycloSelenipentane 1 : 1-dichloride (II) crystallised in white needles melting at 103° when chlorine was passed into a carbon tetrachloride solution of *cycloselenopentane* (Found: Cl, 31.9. $C_5H_{10}Cl_2Se$ requires Cl, 32.2%). Although this dichloride was easily soluble in benzene, chloroform, and acetone, it dissolved only sparingly in alcohol or petroleum.

cycloSelenipentane 1 : 1-dibromide (II), prepared by direct addition of its generators, crystallised from benzene, carbon tetrachloride or hot water in small, bright yellow needles melting at $117-118^{\circ}$ to a deep red liquid (Found: Br, 51.5. $C_5H_{10}Br_2Se$ requires Br, 51.7%).

The *perbromide*, $C_5H_{10}SeBr_2, Br_5$, separated in small, crimson, prismatic crystals when concentrated solutions of bromine and the foregoing dibromide were mixed; it decomposed very readily in air, leaving a residue of the dibromide (Found: Br, 78.4. $C_5H_{10}Br_7Se$ requires Br, 78.9%).

cycloSelenipentane 1 : 1-di-iodide (II) separated in large, almost black, prismatic crystals (m. p. 114°) when solutions of its generators were mixed. The finely ground di-iodide was deep red and its solutions in benzene, chloroform, or acetone, in which it was readily

soluble, had the same colour even on warming (Found : I, 62.75. $C_5H_{10}I_2Se$ requires I, 63.0%). This di-iodide was practically insoluble in water.

cycloSelenipentane 1 : 1-dihydroxide (VI) was produced when an aqueous solution of the corresponding dichloride or 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. The aqueous solution was practically neutral (p_H 6.0—6.2) and addition of aqueous hydrogen halide regenerated the corresponding 1 : 1-dihalide.

cycloSelenipentane 1-hydroxy-1-chloride (V). An aqueous solution of *cyclo*selenipentane 1 : 1-dichloride was treated with sufficient silver oxide to remove only half its chlorine, or equimolecular proportions of the 1 : 1-dihydroxide and 1 : 1-dichloride were mixed in aqueous solution. The resulting liquid was concentrated over sulphuric acid and the colourless crystalline *hydroxychloride* which separated was washed with benzene; it decomposed at 110—111° (Found : C, 29.6; H, 5.5; Cl, 17.3. $C_5H_{11}OClSe$ requires C, 29.75; H, 5.5; Cl, 17.6%).

cycloSelenipentane 1-chloroplatinate (VII) separated very slowly in small yield as a pale yellow, microcrystalline powder from a cold, very dilute aqueous solution of *cyclo*selenipentane 1 : 1-dichloride and chloroplatinic acid; it decomposed at 216° after shrinking at 190°. It was almost insoluble in water but dissolved in chloroform and benzene (Found : Pt, 34.8. $C_5H_{10}Cl_6SePt$ requires Pt, 35.0%).

Bis-1-chlorocyclo*selenipentane* 1-chloroplatinate (VIII). Chloroplatinic acid was added to a hot, moderately concentrated solution of *cyclo*selenipentane 1 : 1-dichloride; the sparingly soluble, orange crystalline *salt* separated on cooling and was recrystallised from hot water (Found : Pt, 24.8; Cl, 36.2. $C_{10}H_{20}Cl_8Se_2Pt$ requires Pt, 25.1; Cl, 36.5%).

This complex salt was insoluble in organic solvents with the exception of alcohol, and on heating it decomposed at 160°.

cycloSelenipentane 1-methiodide (III). When a slight excess of methyl iodide was added to *cyclo*selenopentane, heat was generated and the solid *methiodide* was produced; it crystallised from water in white needles (Found : I, 43.55. $C_6H_{13}ISe$ requires I, 43.6%). On heating in an open tube, the methiodide slowly sublimed without melting at 160°, but in a closed tube it melted to a colourless liquid at 165—166°.

1- β -Bromoethyl*cyclo*selenipentane 1-Bromide (IV).—A mixture of *cyclo*selenopentane, ethylene dibromide, and water was heated for a week in a sealed tube at 100° until no more material dissolved in

the aqueous layer. The aqueous solution was then evaporated over sulphuric acid, the *dibromide* being obtained as a colourless glass. Crystallisation from alcohol-acetone gave the compound in small, white, very hygroscopic needles, m. p. 88° (Found: Br, 46.8. $C_7H_{14}Br_2Se$ requires Br, 47.4%). This complex bromide decomposed slowly on keeping.

Alternative Formation of cycloSelenopentane.— $\alpha\epsilon$ -*Pentamethylene diselenocyanate* (IX). Potassium selenocyanate (14.4 g.) and pentamethylene dibromide (11.5 g.) were heated in acetone solution for several hours. The filtrate from potassium bromide was evaporated, and water added to the residue; the *diselenocyanate* then separated as a dark oil (yield, almost quantitative). Since the *diselenocyanate* could not be solidified, and decomposed on distillation, it was purified by precipitating a benzene solution with petroleum (Found: Se, 56.5. $C_7H_{10}N_2Se_2$ requires Se, 56.5%). The viscous *diselenocyanate* possessed the intense nauseating odour characteristic of this group of substances.

cycloPentamethylene diselenide (*cyclodiselenopentane*). An alcoholic solution of the foregoing *diselenocyanate* (7 g.) was added slowly to 50 c.c. of alcohol containing 3.0 g. of caustic potash. The brown oil which slowly separated was dissolved in benzene, and was obtained on evaporation as a yellow uncrystallisable gum (Found: C, 26.1; H, 4.4; Se, 69.2. $C_5H_{10}Se_2$ requires C, 26.3; H, 4.4; Se, 69.3%). The *diselenide* was quite stable on keeping. When heated strongly, it decomposed, giving *cycloselenopentane*, identified by the formation of *cycloselenipentane* 1:1-dibromide. When the deep red chloroform solution of *cyclopentamethylene diselenide* (1 mol.) and bromine (2 mols.) was allowed to evaporate freely at the ordinary temperature, the residue obtained contained *cycloselenipentane* 1:1-dibromide, black elemental selenium, and tarry material (yield of dibromide, 61% of the theoretical). When an excess of bromine was used (4 mols.), a yellowish-orange precipitate was obtained, probably consisting of *cyclopentamethylene diselenide tetrabromide* (XI), but this unstable substance decomposed with the production of *cycloselenipentane* 1:1-dibromide.

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[Received, July 2nd, 1929.]