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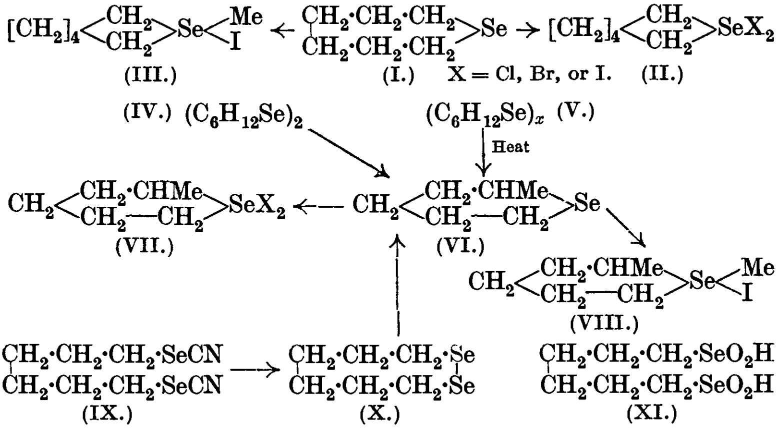
# XXIII.—*Heterocyclic Systems containing Selenium. Part IV.* cyclo*Selenohexane.*

By GILBERT T. MORGAN and FRANCIS HEREWARD BURSTALL.

THE interaction of sodium selenide and αζ-hexamethylene dibromide in alcoholic media leads to the formation of only a small proportion of monomeric cyclo*selenohexane* (I), since the main product is a mixture of at least two polymeric forms. Accordingly this reaction is comparable with that which takes place between trimethylene dibromide and sodium selenide which was outlined in Part III (J., 1930, 1497). *cyclo*Selenohexane, a pungent oil, has, however, a greater stability than the four-membered cyclic selenohydrocarbon. It furnishes cyclo*selenidihalides* of type (II) and these dihalides resemble, in general, the corresponding dihalides of *cyclo*selenobutane and *cyclo*selenopentane (J., 1929, 1096, 2197).



Methyl iodide gives the water-soluble cyclo*selenihexane* 1-*methiodide* (III), and mercuric chloride furnishes a characteristic cyclo*seleno-hexane mercurichloride.*

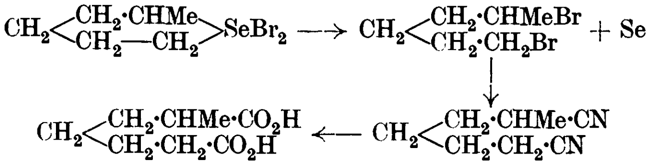
A determination of the parachor of *cyclo*selenohexane shows that this substance is a normal liquid.

| | | | |
|---|---|---|---|
| *t* | 19·5° | 35·0° | 46·0° |
| Density (*D*) | 1·358 | 1·343 | 1·331 |
| Surface tension ($\gamma$) | 39·85 | 38·01 | 36·73 |
| Parachor | 302·2 | 301·9 | 302·1 |

Mean parachor 302·1 (calc., 303·1)

The structural constant for a seven-membered ring is taken as 6·6 (Sugden, " The Parachor and Valency," p. 40).

Two well-defined individuals have been obtained from the saponaceous mixture of polymerides which accompanies *cyclo*selenohexane; the first compound crystallising from the more soluble portion of the polymeride is a white, highly crystalline *dimeride* (IV), while the second, present in much larger quantity, is a waxy, readily fusible solid of high molecular weight (V). Both these polymerides furnish *dibromides* which are each reducible to the original polymeride. On being heated, these polymeric selenohydrocarbons remain stable to above 200° and then depolymerise, without loss of selenium, into 2-*methyl*cyclo*selenopentane* (VI), which contains a new six-membered ring. This selenohydrocarbon is a pungent oil which furnishes liquid 2-*methyl*cyclo*selenipentane* 1 : 1-*dihalides* (VII), a water-soluble *methiodide* (VIII), and a well-defined *mercurichloride.* The stability of 2-methyl*cyclo*selenopentane is comparable with that of *cyclo*selenopentane, but the additive compounds of the former cyclic selenide are less stable than those of the latter, a difference which may be due to steric effect produced by the α-methyl group. A clue to the constitution of 2-methyl*cyclo*selenopentane is obtained by the action of heat on 2-methyl*cyclo*selenipentane 1 : 1-dibromide, which loses elemental selenium and yields β-methylpentamethylene dibromide. This dibromide is converted successively into the corresponding dinitrile and α-methylpimelic acid, the latter being identified as its dianilide.



$$CH_2<\begin{matrix}CH_2\cdot CHMe\\ CH_2—CH_2\end{matrix}>SeBr_2 \longrightarrow CH_2<\begin{matrix}CH_2\cdot CHMeBr\\ CH_2\cdot CH_2Br\end{matrix} + Se$$

$$\downarrow$$

$$CH_2<\begin{matrix}CH_2\cdot CHMe\cdot CO_2H\\ CH_2\cdot CH_2\cdot CO_2H\end{matrix} \longleftarrow CH_2<\begin{matrix}CH_2\cdot CHMe\cdot CN\\ CH_2\cdot CH_2\cdot CN\end{matrix}$$

An alternative method of preparing 2-methyl*cyclo*selenopentane starts from hexamethylene dibromide and potassium selenocyanate, which interact smoothly to yield *hexamethylene diselenocyanate* (IX). Hydrolysis of this substance by alcoholic alkali, followed by aerial oxidation, leads to cyclo*hexamethylene* 1 : 8-*diselenide* (cyclo*diselenohexane*, X). This diselenide, which is not a simple monomeric substance, is decomposed by bromine into hexamethylene dibromide and selenium, an effect which differs from that of bromine on *cyclo*tetramethylene diselenide and *cyclo*pentamethylene diselenide. By the action of heat this diselenide (X) furnishes 2-methyl*cyclo*selenopentane with loss of one atom of selenium. When treated with nitric acid, the foregoing diselenide and hexamethylene diselenocyanate both give *hexamethylenediselenious acid* (XI).

The parachor of 2-methyl*cyclo*selenopentane indicates that this substance is quite normal.

| | | | |
|---|---|---|---|
| $t$ | 19·5° | 35·0° | 46·0° |
| Density ($D$) | 1·290 | 1·273 | 1·261 |
| Surface tension ($\gamma$) | 33·49 | 31·43 | 30·53 |
| Parachor | 304·5 | 303·8 | 304·4 |

Mean parachor 304·2 (calc., 302·6)

The sulphur analogues of *cyclo*selenohexane and 2-methyl*cyclo*selenopentane have been prepared by Grischkevitsch-Trochimovski (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 944, 928), who recorded the physical and chemical properties of these cyclic thiohydrocarbons.

## EXPERIMENTAL.

cyclo*Selenohexane* (I).—αζ-Hexamethylene glycol, prepared by reducing diethyl adipate with sodium in anhydrous alcohol (compare Müller and Sauerwald, *Monatsh.*, 1927, **48**, 521), was converted by hydrogen bromide into αζ-hexamethylene dibromide (b. p. 127—130°/25 mm.). An alcoholic suspension of sodium selenide was prepared by passing hydrogen selenide, generated by the action of dilute sulphuric acid on aluminium selenide (18 g.), into a solution of sodium (6·9 g.) in alcohol (250 c.c.) and water (9 c.c.) in a hydrogen atmosphere. Hexamethylene dibromide (32 g.) was added, and the mixture refluxed for 2 hours. The alcoholic filtrate from sodium bromide and yellow polymerides was distilled under reduced pressure, and the distillate rectified until a colourless solution resulted. A slight excess of an alcoholic solution of iodine was added; reddish-purple crystals of cyclo*selenihexane* 1 : 1-*di-iodide* (1·8 g.) then slowly separated and a further quantity (0·3 g.) was obtained on evaporation of the mother-liquor. cyclo*Selenohexane*, regenerated by stirring and warming the di-iodide with an excess of aqueous sodium metabisulphite, was dried over calcium chloride and rectified by distillation under diminished pressure and was thus obtained as a colourless liquid having a penetrating but not unpleasant odour, b. p. 105—106°/68 mm., 188—190°/756 mm.; $n_D^{18^\circ}$ 1·5470; $d_{4^\circ}^{24\cdot5^\circ}$ 1·353; $d_{4^\circ}^{37^\circ}$ 1·341; $d_{4^\circ}^{44^\circ}$ 1·334; $d_{4^\circ}^{54^\circ}$ 1·323; whence $d_{4^\circ}^{t^\circ} = 1{\cdot}378 - 0{\cdot}00101t$ (Found: C, 43·9; H, 7·45; Se, 48·4. $C_6H_{12}Se$ requires C, 44·1; H, 7·4; Se, 48·5%). Although the selenohydrocarbon was insoluble in water, it was miscible in all proportions with organic solvents and was volatile in the vapours of alcohol and ether. It dissolved in cold concentrated sulphuric acid and yellow to red tints developed on warming. *cyclo*Selenohexane could be kept without change in a cool dark place and it was not oxidised by air.

cyclo*Selenohexane mercurichloride*, $C_6H_{12}Se,HgCl_2$, separated in sparingly soluble, white, flaky crystals when alcoholic solutions of its generators were mixed; it melted at 193—194° (decomp.) (Found: Cl, 16·3. $C_6H_{12}Cl_2SeHg$ requires Cl, 16·3%). This characteristic mercurichloride was insoluble in water and most organic solvents except alcohol; aqueous caustic alkalis regenerated *cyclo*selenohexane.

cyclo*Selenihexane* 1 : 1-*di-iodide* (II) was obtained in small reddish-purple needles, m. p. 82°, from alcoholic solutions of its generators (*vide supra*), and was recrystallised from carbon tetrachloride or benzene (Found: Se, 18·65; I, 61·1. $C_6H_{12}I_2Se$ requires Se, 19·0; I, 60·85%).

cyclo*Selenihexane* 1 : 1-*dibromide* (II) with the following dichloride was prepared in a similar way to the di-iodide. It separated from carbon tetrachloride in yellow prismatic crystals, m. p. 118—119° (Found: Br, 49·4. $C_6H_{12}Br_2Se$ requires Br, 49·5%). This dibromide decomposed slowly, forming hexamethylene dibromide and leaving a residue of selenium.

cyclo*Selenohexane* 1 : 1-*dichloride* (II) separated in small white crystals, m. p. 78°, from carbon tetrachloride solution (Found: Cl, 30·1. $C_6H_{12}Cl_2Se$ requires Cl, 30·3%). The dichloride and dibromide were soluble in most organic solvents and dissolved in water, giving acid solutions.

cyclo*Selenihexane* 1-*methiodide* was readily prepared from *cyclo*selenohexane and methyl iodide. It crystallised from aqueous acetone in white prisms decomposing at 149—150°; it was insoluble in organic solvents except alcohol (Found: I, 41·7. $C_7H_{15}ISe$ requires I, 41·6%).

### *Polymeric* cyclo*Selenohexanes.*

The yellow gummy solid mixed with sodium bromide which had

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ated to dryness. When the residue was thoroughly extracted with petroleum (b. p. 60—80°), it yielded two fractions of differing solubility (19 g.) and a dark brown, insoluble varnish which was not further investigated.

*Dimeride*, $(C_6H_{12}Se)_2$ (IV).—The more soluble fraction, separating in white needles mixed with an oily impurity, was recrystallised from hot acetone, whereupon the dimeride separated in white acicular prisms [Found: C, 44·2; H, 7·4; Se, 48·3; *M* (in boiling benzene), 335. $(C_6H_{12}Se)_2$ requires C, 44·1; H, 7·4; Se, 48·5; *M*, 336·6].

requires Br, 49·5%]. This complex dibromide decomposed slowly and melted to a red liquid at 94—95° (decomp.). Aqueous sodium metabisulphite reduced it to the original polyselenide and warm dilute nitric acid converted it into a colourless viscid oxidation product which separated on cooling. Whereas this polymeride was insoluble in water and only sparingly so in alcohol, it dissolved easily in the common organic solvents. Concentrated sulphuric acid developed a red tint on warming, but 2*N*-caustic alkalis had no action.

2-*Methyl*cyclo*selenopentane* (VI).—The foregoing polymeride melted to a clear yellow liquid at 36—37° and showed considerable stability at higher temperatures, but depolymerisation commenced at about 220° without loss of selenium and a dark yellow oil distilled. When this pyrolysis was carried out under 30 mm. pressure with purified polymeride, practically no residue remained. The distillate was fractionated under reduced pressure.

2-*Methyl*cyclo*selenopentane* was a colourless to pale yellow liquid having a characteristic penetrating odour, b. p. 90°/65 mm., 169—171°/764 mm.; $n_{D}^{18^\circ}$ 1·5205; $d_{4^\circ}^{22^\circ}$ 1·287; $d_{4^\circ}^{31^\circ}$ 1·278; $d_{4^\circ}^{40^\circ}$ 1·267; $d_{4^\circ}^{50^\circ}$ 1·257; whence $d_{4^\circ}^{t^\circ} = 1{\cdot}3115 - 0{\cdot}00111t$ (Found: C, 43·9; H, 7·4; Se, 48·6. $C_6H_{12}Se$ requires C, 44·1; H, 7·4; Se, 48·5%).

Although insoluble in water 2-methyl*cyclo*selenopentane was miscible in all proportions with organic solvents; moreover it was volatile in the vapours of steam, alcohol, and ether. Sulphuric acid gave yellow to red tints on warming, whereas nitric acid furnished a crystalline nitrate. Acid or alkaline permanganate ruptured the ring, but a single acid could not be isolated from the oxidised mixture. 2*N*-Caustic alkalis had no action on 2-methyl*cyclo*selenopentane.

The halogen addition products with 2-methyl*cyclo*selenopentane were liquid or gummy; the dichloride a colourless liquid, the *dibromide* a reddish-yellow gum (Found: Br, 49·0. $C_6H_{12}Br_2Se$ requires Br, 49·5%), and the di-iodide a deep red gum.

*Constitution of* 2-*Methyl*cyclo*selenopentane*.—The foregoing dibromide was heated under diminished pressure until decomposition ensued and a distillate of β-methylpentamethylene dibromide was collected, leaving a residue of metallic selenium. The latter dibromide was converted by boiling with aqueous-alcoholic potassium cyanide into the corresponding dinitrile, which was hydrolysed to α-methylpimelic acid by boiling with concentrated hydrochloric acid. The acid solution was neutralised with sodium carbonate and evaporated to dryness, and the residue acidified and extracted with ether. Evaporation left a gummy dibasic acid, which was converted without further purification into the dianilide, m. p. 161—162°, by boiling with aniline. An authentic sample of the dianilide was prepared by Einhorn and Ehret's method (*Annalen*, 1897, **295**, 175) from *o*-cresotinic acid, which was converted successively into dibromo-*o*-cresotinic acid and α-methylpimelic acid. The latter gave a dianilide, melting at 165° alone and at 162° when mixed with the above specimen.

2-*Methyl*cyclo*selenopentane mercurichloride* separated when concentrated alcoholic solutions of its generators were mixed. Recrystallisation afforded the mercurichloride in small white needles, m. p. 112° to a colourless liquid (Found: Hg, 45·8; Cl, 16·2. $C_6H_{12}Cl_2SeHg$ requires Hg, 46·1; Cl, 16·3%). Aqueous caustic soda regenerated the selenohydrocarbon.

2-*Methyl*cyclo*selenopentane* 1-*Methiodide* (VIII).—This water-soluble product was readily prepared by warming 2-methyl*cyclo*-selenopentane with methyl iodide. The white microcrystalline powder was washed with acetone and crystallised from water; m. p. 164° (decomp.) (Found: I, 41·5. $C_7H_{15}ISe$ requires I, 41·6%).

*Alternative Formation of* 2-*Methyl*cyclo*selenopentane.—Hexamethylene αζ-diselenocyanate* (IX). Potassium selenocyanate (14·4 g.) and αζ-hexamethylene dibromide (12·2 g.) were heated in acetone solution under reflux for several hours. The filtrate from potassium bromide was evaporated, and water added to the residue. The deep yellow, viscid oil was dissolved in benzene and dried with calcium chloride. The filtered solution was poured into a large excess of petroleum (b. p. 40—60°); the *diselenocyanate* then separated as a thick yellow oil. Any solvent remaining after the separation of the diselenocyanate was removed by heating under reduced pressure (Found: C, 32·35; H, 4·1; Se, 53·8. $C_8H_{12}N_2Se_2$ requires C, 32·3; H, 4·1; Se, 53·8%). This selenocyanate did not solidify and decomposed on distillation; it was insoluble in water and only sparingly soluble in petroleum but dissolved in most organic media. It possessed the penetrating and nauseous odour characteristic of this group of compounds.

cyclo*Hexamethylene* 1 : 8-*Diselenide* (cyclo*Diselenohexane*, X).—The foregoing diselenocyanate (5·0 g.), dissolved in alcohol (50 c.c.), was added to a solution of sodium (2 g.) in 100 c.c. of alcohol. The yellow mixture was poured into a large excess of water through which air was aspirated. The precipitated brown oil was extracted with chloroform and dried; the solvent was evaporated to furnish brown *diselenide*, which slowly solidified in a desiccator at 0° (Found: C, 29·6; H, 5·0; Se, 65·8. $C_6H_{12}Se_2$ requires C, 29·7; H, 5·0; Se, 65·3%). A molecular-weight determination indicated that this diselenide was a highly polymerised substance. When a chloroform solution of the diselenide was treated with bromine, no immediate reaction occurred but selenium was slowly deposited with formation of hexamethylene dibromide.

When this diselenide was heated, it melted rather indefinitely at 40° and showed no further change until at about 250° it decomposed with loss of selenium and formation of 2-methyl*cyclo*selenopentane, identified by its boiling point (169—171°) and by its characteristic mercurichloride, m. p. 112°.

*Hexamethylenediselenious acid* (XI) was isolated when the foregoing diselenide or diselenocyanate was dissolved in warm nitric acid (1 conc. acid : 1 water); it crystallised from water in small white needles, decomposing at 147° (Found: Se, 50·4. $C_6H_{14}O_4Se_2$ requires Se, 51·35%).

CHEMICAL RESEARCH LABORATORY,
TEDDINGTON, MIDDLESEX.

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