Cyclische seleniumverbindingen
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IX. SUMMARY OF RESULTS.

This thesis describes the preparation of selenacyclobutanes (rings composed of one selenium and three carbon atoms) by the interaction of alcoholic potassium selenide and trimethylene bromides with a quarternary central carbon atom.

Potassium selenide and 1,3-dibromopropane give a poor yield of selenacyclobutane. The main reaction product is a polymeride. Tetramethyltetrabromomethane, 2,2-dimethyl-1,3-dibromopropane and 1,1-dibromomethylcyclohexane react with potassium selenide, giving a good yield of 2,6-diselena-4-spiroheptane (I), 3,3-dimethylselenacyclobutane (II) and 2-selena-4-spirononane (III).

These bromides only react with an alcoholic solution of potassium selenide on heating, whereas trimethylene bromide does so at room temperature.

Tetrabromotetramethylmethane is 75% converted, when boiled for half an hour with alcoholic potassium selenide, a polymeride not being formed. It is difficult to separate the product, 2,6-diselena-4-spiroheptane from unchanged tetrabromotetramethylmethane; the purification by means of the additive compound with mercuric chloride causes great losses.

2,2-Dimethyl-1,3-dibromopropane is completely converted by boiling it for four hours with alcoholic potassium selenide, and a 40% yield of 3,3-dimethylselenacyclobutane can be isolated from the reaction mixture.

1,1-Dibromomethyl-cyclohexane is prepared from the corresponding diol and phosphorus tribromide. It reacts with alcoholic potassium selenide more slowly than dimethyldibromopropane, but 2-selena-4-spirononane (III) nevertheless was obtained in excellent yield (68%).

Thus, as with thiacyclobutane and 3,3-dimethylthiacyclobutane, the yields of selenacyclobutane compounds are much higher, if the hydrocarbon ring is easily formed in a similar ring or with a cyclohexane ring.

The substituted selenacyclobutanes are more stable than selenacyclobutane.

2,6-Diselena-4-spiroheptane is a m.p. 67°C. The crystals are isomeric with dithiospiroheptane (b.p. 56°C/40 mm; 138-4-spiromunane (b.p. 103.5–104°C) liquids with a pungent odour, which is that of selenacyclobutane.

2-Phenyl-2-methyl-1,3-dibromopropane that reacted readily at room temperature. The main product was a hydrocarbon (b.p. 114.5°C, IV). The constitution of the oxidation to 2-phenyl-2-methylpropane was studied. 4,4-Dimethyl-1,2-diselenacyclopentanone from 2,2-dimethyl-1,3-dibromopropane gives a pleasant, pungent odour.

The compounds prepared by using different organic solvents as brown liquids with a pungent odour, which is that of selenacyclobutane.

OF RESULTS.

Preparation of selenacyclobutanes and three carbon atoms) by the selenide and trimethylene bromides atom.

Propane give a poor yield of ion product is a polymeride 1). 2-dimethyl-1,3-dibromopropane react with potassium selenide, 1-spiroheptane (I), 3,3-dimethyl-4-spiroheptane (II).

Alcoholic solution of potassium ylene bromide does so at room temperature 75% converted, when boiled sium selenide, a polymeride not rate the product, 2,6-diselenacyclohexane (b.p. 56°/40 mm; 138-138.5°/750 mm) and 2-selenacyclohexane (b.p. 103.5-104°/13 mm) are stable, colourless liquids with a pungent odour, which, however, is not so nauseating as that of selenacyclobutane.

2-Phenyl-2-methyl-1,3-dibromopropane behaved differently, in that it reacted readily at room temperature with potassium selenide. The main product was a hydrocarbon C_{10}H_{12}, accompanied by a by-product 4-phenyl-4-methyl-1,2-diselenacyclopentane (m.p. 114-114.5°, IV). The constitution of this compound was confirmed by oxidation to 2-phenyl-2-methylpropane-1,3-diseleninic acid. In this connection a statement of Franke 1) is of interest, that in phenylmethylidibromopropane the bromine atoms are bound less firmly than in aliphatic dialkytrimethylene bromides.

4,4-Dimethyl-1,2-diselenacyclopentane (m.p. 34°, V) is obtained from 2,2-dimethyl-1,3-dibromopropane through the corresponding diselenocyanate.

\[
\begin{align*}
\text{C}_6\text{H}_6 & \text{C}_6\text{H}_5 & \text{CH}_2 - \text{Se} & \text{CH}_2 - \text{Se} \\
\text{CH}_3 & & \text{CH}_2 - \text{Se} & \text{CH}_2 - \text{Se}
\end{align*}
\]

These two diselenacyclopentane compounds crystallize from different organic solvents as brown needles or plates with an unpleasant, pungent odour.

The compounds prepared by us contain bivalent selenium atoms, and thus show residual affinity. The addition reactions with several reagents were studied.

1) Franke, Monatsh. 34, 1895 (1913).
2,6-Diselena-4-spiroheptane gives an addition compound with two mols. mercuric chloride, and with iodine it gives an unstable tetraiodide.

With an excess of methyl iodide a crystalline monoselenium compound is formed:

\[
\text{Se}\begin{array}{c}
\text{CH}_2
\\
\text{Se} \text{(CH}_2\text{)}_2
\\
\text{CH}_2
\end{array}
\text{I}
\]

The behaviour of 3,3-dimethylselenacyclobutane and 2-selena-4-spiirononane with several reagents is almost similar. Mercuric chloride and mercuric bromide furnish nearly insoluble addition compounds. With two molecules of methyl iodide, the selenacyclobutane ring opens. Thus dimethylselenacycl obtane gives crystalline 3-ido-2,2-dimethyl-propyl-dimethylselenonium iodide. The structure of this compound proved to be:

\[(\text{CH}_3)_2\text{C}((\text{CH}_2\text{Br})\text{CH}_2\text{Se})\text{I}\]

With excess of chlorine or bromine the selenacyclobutane ring also opens and tetrahalides are formed:

\[\text{R'R'C}((\text{CH}_2\text{Se})\text{R'})\text{Se} + 2 \text{Hg}_2 = \text{R'R'C}((\text{CH}_2\text{Hg})\text{Se})\text{Hg}_2\]

These halides dissolve in water, yielding acid solutions. The necessary quantity of silver hydroxide converts them into the corresponding seleninic acids. In this way the following seleninic acids have been obtained.

3-bromo-2,2-dimethylpropaneseleninic acid:
\[(\text{CH}_3)_2\text{C}((\text{CH}_2\text{Br})\text{CH}_2\text{Se})\text{O}_2\text{H}\]

3-chloro-2,2-dimethylpropaneseleninic acid:
\[(\text{CH}_3)_2\text{C}((\text{CH}_2\text{Cl})\text{CH}_2\text{Se})\text{O}_2\text{H}\]

1-bromomethyl-1-methylseleninic acid cyclohexane:
\[
\text{CH}_3\begin{array}{c}
\text{CH}_2
\\
\text{Br}
\end{array} \text{CH}_3
\]

1-chloromethyl-1-methylseleninic acid cyclohexane:
\[
\text{CH}_3\begin{array}{c}
\text{CH}_2
\\
\text{Cl}
\end{array} \text{CH}_3
\]

All these seleninic acids are white crystalline compounds.

If the sodium salts of these acids are used, the precipitated silver halide is precipitated, and the selenolate, obtained by oxidation of 3,3-dimethylselenooxide. Oxidation of 4-phenyl-4-methylselenocyclohexane gives the following seleninic acids:

\[2,2\text{-dimethylpropane-1,3-diseleninic acid:} (\text{CH}_3)_2\text{C}((\text{CH}_2\text{Se})\text{CH}_2)\text{O}_2\text{H}\]

\[2\text{-phenyl-2-methylpropane-1,3-diseleninic acid:} (\text{C}_9\text{H}_8)_2\text{C}((\text{CH}_2\text{Se})\text{CH}_2)\text{O}_2\text{H}\]

These compounds add two dinitrates. Both diseleninic acids are less soluble than the seleninic acid of phenylmethylpropanediseleninic acid, being less soluble than the dimethyl derivative being readily soluble. By the recrystallization of the dinitrate from hot water, the dinitrate, being less soluble than the diseleninic acid, is converted into the corresponding seleninic acid.

By the interaction of 2,2-difunctional bromine, a tetrabromide \[(\text{CH}_3)_2\text{C}((\text{CH}_2\text{SeBr})\text{CH}_2)\text{Br}\]

LIST OF NE

Cyclic mono- and diselenium chlorides:
\[
\begin{array}{l}
\text{CH}_3 \hspace{1cm} \text{CH}_3 \\
\text{CH}_3 \hspace{1cm} \text{CH}_3
\end{array}
\]

3,3-dimethylselenacyclobutane; 2-selenao-4-spiirononane
\[
\begin{array}{l}
\text{Se} \hspace{1cm} \text{Se} \\
\text{CH}_3 \hspace{1cm} \text{CH}_3
\end{array}
\]

2,6-diselena-4-spiroheptane
\[
\begin{array}{l}
\text{Se} \hspace{1cm} \text{Se} \\
\text{CH}_3 \hspace{1cm} \text{CH}_3
\end{array}
\]

2,6-diselena-4-spiroheptane gives an addition compound with two mols. mercuric chloride, and with iodine it gives an unstable tetraiodide.
gives an addition compound with iodine it gives an unstable crystalline monoselenium compound.

\[
\text{CH}_2\text{Se} (\text{CH}_3)_2 \quad \text{I}
\]

Selenacyclobutane and 2-selena-4-nts is almost similar. Mercuric furnishes nearly insoluble addition of methyl iodide, the selenacyclo-selenacyclobutane gives crystalline dilylselenium iodide. The structure of the selenacyclobutane ring is:

\[
\text{RR'}\text{C} (\text{CH}_2\text{Hlg}) (\text{CH}_2\text{SeHlg})_2
\]

ter, yielding acid solutions. The trioxide converts them into the this way the following seleninic acid:

\[
\text{CH}_2\text{SeO}_2\text{H}
\]

enic acid:

\[
(\text{CH}_3)_2\text{C} (\text{CH}_2\text{SeO}_2\text{H})_2
\]

tic acid:

\[
(\text{CH}_3)_2\text{C} (\text{CH}_2\text{SeO}_2\text{H})_2
\]

cyclohexane:

\[
\text{CH}_3\text{Br}
\]

cyclohexane:

\[
\text{CH}_3\text{Cl}
\]

These compounds add two molecules of nitric acid, forming dinitrates. Both diseleninic acids crystallize as colourless needles. The solubilities of these compounds in water are different, the dimethyl derivative being readily soluble, whereas the phenylmethyl compound dissolves sparingly and may be recrystallized from hot water. By the recrystallization of dimethylpropanodiseleninic acid dinitrate from hot water, the dinitrate separates, because it is less soluble than the diseleninic acid itself. When, however, the dinitrate of phenylmethylpropanodiseleninic acid is similarly treated, the free acid, being less soluble than the dinitrate, crystallizes out.

By the interaction of 2,2-dimethylpropylenediselenocyanate and bromine, a tetrabromide \((\text{CH}_3)_2\text{C} (\text{CH}_2\text{SeBr}) (\text{CH}_2\text{SeBr})_3\)

and a dibromide \((\text{CH}_3)_2\text{C} (\text{CH}_2\text{SeBr})_2\)

are obtained.

**LIST OF NEW COMPOUNDS.**

**Cyclic mono- and diselenium compounds.**

\[
\begin{align*}
\text{CH}_3 \quad &\text{C} \quad \text{CH}_3 \\
\text{CH}_3 \quad &\text{C} \quad \text{CH}_3 \\
\text{CH}_3 \quad &\text{C} \quad \text{CH}_3 \\
\text{CH}_3 \quad &\text{C} \quad \text{CH}_3 \\
\end{align*}
\]

3,3-dimethylselenocyclobutane; b.p. \(56^\circ/40 \text{ mm} \); 138—138.5°/750 mm.

\[
\begin{align*}
\text{CH}_3 \quad &\text{C} \quad \text{CH}_3 \\
\text{CH}_3 \quad &\text{C} \quad \text{CH}_3 \\
\text{CH}_3 \quad &\text{C} \quad \text{CH}_3 \\
\text{CH}_3 \quad &\text{C} \quad \text{CH}_3 \\
\end{align*}
\]

2-selena-4-spirohexanone; b.p. 103.5—104°/13 mm.

\[
\begin{align*}
\text{CH}_3 \quad &\text{C} \quad \text{CH}_3 \\
\text{CH}_3 \quad &\text{C} \quad \text{CH}_3 \\
\text{CH}_3 \quad &\text{C} \quad \text{CH}_3 \\
\text{CH}_3 \quad &\text{C} \quad \text{CH}_3 \\
\end{align*}
\]

2,6-diselena-4-spiroheptane; m.p. 67°.