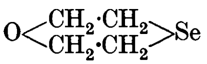
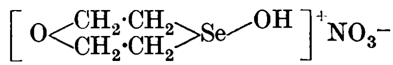
XXXV.—*Syntheses with ββ'-Dichlorodiethyl Ether. Part II. Heterocyclic Compounds containing Two Members of the Oxygen Group in the Ring.* 1 : 4-*Selenoxan and its Derivatives.*

By Charles Stanley Gibson and John Dobney Andrew Johnson.

The preparation and the properties of ββ'-dichlorodiethyl selenide and its derivatives have been investigated by Gibson and coworkers (J., 1920, **117**, 1453; 1925, **127**, 1877). 1 : 4-*Selenoxan* (I), produced by the action of sodium selenide on ββ'-dichloro-* or ββ'-di-iodo-diethyl ether (compare J., 1930, 2526), affords another substance in which the chemical and physical properties of selenium in organic compounds can be conveniently investigated. It is a colourless liquid analogous in general properties to *cyclo*selenobutane

(I.) 

$\mathrm{O}{<}\genfrac{}{}{0pt}{}{\mathrm{CH_2{\cdot}CH_2}}{\mathrm{CH_2{\cdot}CH_2}}{>}\mathrm{Se}$

 (II.)

$\left[\mathrm{O}{<}\genfrac{}{}{0pt}{}{\mathrm{CH_2{\cdot}CH_2}}{\mathrm{CH_2{\cdot}CH_2}}{>}\mathrm{Se}{\diagup}^{\mathrm{OH}}\right]^{+}\mathrm{NO_3}^{-}$

and *cyclo*selenopentane (Morgan and Burstall, J., 1929, 1096, 2197). The fact that the observed mean value of its parachor, kindly determined by Dr. S. Sugden, agrees closely with the calculated value is a further confirmation of the accuracy of the representative value of the atomic parachor of selenium being 62·5. The following table shows the variation in some physical constants among four related organic selenium compounds :

	$[P]$ obs.	$[P]$ calc.	B. p.	M. p.	$[R_L]_D$.†
*cyclo*Selenobutane	229·5	227·3	135—136°/770 mm.	—	29·11
Selenophen	210·6	205·8	150°	− 38°	28·04 (Briscoe and Peel, J., 1928, 1741)
*cyclo*Selenopentane	264·2	263·6	158°/759 mm.	—	33·79
1 : 4-Selenoxan	245·2	244·6	168°/763 mm.	− 21·5°	30·60

† From the observed value of the molecular refraction, $[R]$, of pentamethylene oxide, the atomic refraction of selenium is computed to be 10·5. The atomic refractions of selenium deduced from the above four compounds in order are 10·6, 10·5, 10·7, and 10·5 respectively, giving an average value 10·57. The atomic refractions of neighbouring elements in the Periodic Classification are in agreement with this value : germanium (9·29), arsenic (10·7, deduced from the chloride), and bromine (8·865).

When 1 : 4-selenoxan is treated with nitric acid under conditions which lead to the production of a sulphoxide from a sulphide, no oxide is produced but a crystalline salt, the *hydroxynitrate* (II), is

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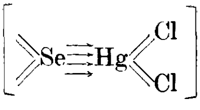
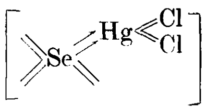
* The m. p. of ββ'-dichlorodiethyl ether is − 44° and not − 24·5° as recorded in Part I. ββ'-Di-iododiethyl ether has m. p. − 19°.

obtained. There is no tendency to form a dinitrate; even when the dihydroxide, which could not be obtained crystalline, was treated with an excess of nitric acid the same hydroxynitrate was obtained. Although soluble in moderately concentrated mineral acids, selenoxan does not form salts by direct addition. It readily yields a *methiodide*, which behaves as a salt, a *mercurichloride*, a *chloroaurate* (V), and a *chloroplatinate* (VI), the last two compounds being formed from 1 : 4-selenoxan dichloride and auric and platinic chlorides respectively. The mercurichloride is not appreciably ionised in aqueous solution and its constitution may be represented either by (III), in which the mercury atom has acquired a complete octet by sharing the two lone pairs of electrons of the selenium atom, or by (IV), in which the mercury atom has a sextet, the selenium sharing only one of its lone pairs.


(III.)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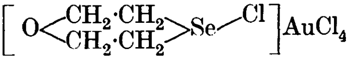
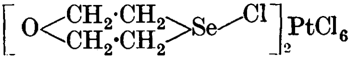
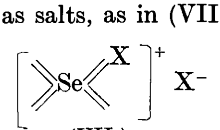
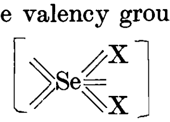
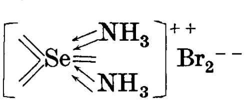

$\left[\mathrm{O}<\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{Se{-}Cl}\right]\mathrm{AuCl_4}$
(V.)


$\left[\mathrm{O}<\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{Se{-}Cl}\right]_2\mathrm{PtCl_6}$
(VI.)

1 : 4-*Selenoxan dichloride* (colourless; m. p. 127—129°, decomp.), *dibromide* (yellow; m. p. 132°, decomp.), and *di-iodide* (deep violet; m. p. 106—107°) are obtained from selenoxan and the appropriate halogen. They show the same sequence of colours as the corresponding dihalides of *cyclo*seleno-butane and -pentane. The di-iodide has a normal molecular weight in nitrobenzene solution. It is very sparingly soluble in water, but the chloride and bromide are moderately easily soluble, the solutions containing ionised halogen. This may indicate ionisation, but the acidic nature of the solutions indicates that some hydrolysis, at any rate, has taken place. As salts, their constitution may be represented by (VII), the valency group of the selenium being an octet. If they are not represented as salts, as in (VIII), the valency group of the selenium atom is a decet (or an octet if the selenium–halogen linkages are singlets). Both halogen atoms attached to the selenium in these dihalides are easily replaceable by the hydroxyl group and this, together with the fact that, for example, the dibromide is soluble both in water and in benzene, indicates that the 1 : 4-selenoxan dihalides are potential sources of both forms (VII) and (VIII) depending on the


(VII.)


(VIII.)


(IX.)

solvent; the melting points of these compounds being in the order dichloride>dibromide>di-iodide is in favour of their being considered as salts.

The compound formed by passing dry ammonia into a benzene solution of 1 : 4-selenoxan dibromide is of special interest. It has the composition $C_4H_8OCl_2Se,2NH_3$, is colourless, insoluble in ordinary organic solvents, and is decomposed by water. To this compound different constitutional formulæ may be given and in any of them it is impossible for the selenium atom to preserve its octet unless singlet linkages are present. If it is a bromide of a univalent radical, the selenium atom has a duodecet in its valency group, as a bromide of a bivalent radical the selenium atom has a decet (IX), as a neutral substance the selenium atom has a quattuordecet. If the selenium atom and the ammonia groups are connected by singlet linkages, the selenium atom has correspondingly a decet, an octet, and a duodecet in the types of compound mentioned.

Similar compounds are formed between 1 : 4-selenoxan dibromide and pyridine, piperidine and aniline respectively, and when ammonia is passed into a benzene solution of the dichloride, but none of these was found suitable for investigation. The co-ordination compound of the dibromide with ethylenediamine yielded ethylenediamine dihydrobromide on treatment with aqueous alcohol.

EXPERIMENTAL.

1 : 4-*Selenoxan* (I).—Hydrogen selenide prepared by slowly dropping water on to small lumps of aluminium selenide (60 g.) was passed, together with hydrogen, into alcoholic sodium hydroxide prepared from sodium (27·6 g.), water (24 c.c.), and ethyl alcohol (1 litre). Colourless sodium selenide separated from the deeply coloured solution. The alcohol was distilled off on the water-bath, the residue dissolved in water (440 c.c.), ββ′-dichlorodiethyl ether (22·9 g.) or ββ′-di-iododiethyl ether (52·2 g.) added, and the mixture boiled for 4½ hours while hydrogen was passed through it. The cold solution was extracted five times with carbon tetrachloride, and this solution, filtered as often as necessary from precipitated selenium, was dried with calcium chloride and evaporated to about 450 c.c. (The distillate contained appreciable quantities of the required substance, which was recovered by converting it into the dibromide as described below.) After cooling, the orange-coloured solution was treated with a solution of bromine in carbon tetrachloride (1 vol. bromine : 10 vols. CCl_4—about 75 c.c. of this solution being required) until no further yellow precipitate was formed. After standing for one hour, the yellow solid was filtered off and recrystallised from either benzene or carbon tetrachloride. The

mother-liquor from the bromination gave, on further bromination, a tarry precipitate which was not investigated. Unless the original bromination is carried out carefully, this tarry material contaminates the main product and subsequent purification is difficult. The *dibromide* (see below) was reduced by shaking it at intervals during one hour with a solution of sodium metabisulphite or sodium hydrosulphite (80 g. in 150 c.c. of water for each 18 g. of the dibromide), the *selenoxan* being precipitated as an oil. It was extracted with carbon tetrachloride, and the solution dried with calcium chloride and evaporated on the water-bath. (The distillate was treated with bromine solution, and a little dibromide recovered. This is a convenient way of avoiding loss of selenoxan.) The residue was distilled under reduced pressure and the following constants of the pure substance were determined : b. p. 66°/22 mm., 69·5°/26 mm., 167·5—168·5°/763 mm.; m. p. $-$ 21·5°; $n_{\mathrm{D}}^{20^\circ}$ 1·5480; $d_{4^\circ}^{16^\circ}$ 1·575, $d_{4^\circ}^{23\cdot5^\circ}$ 1·565, $d_{4^\circ}^{35^\circ}$ 1·549, $d_{4^\circ}^{43^\circ}$ 1·539 (whence $d_{4^\circ}^{t^\circ} = 1\cdot597 - 0\cdot00135t$); γ^{17° 42·08, $\gamma^{28\cdot5^\circ}$ 40·80, $\gamma^{35\cdot5^\circ}$ 39·75, γ^{44° 38·67 dynes/cm.;* $[R_L]_{\mathrm{D}} = 30\cdot60$ (Found : C, 32·1; H, 5·5; Se, 52·3, 52·2, 51·5. C_4H_8OSe requires C, 31·7; H, 5·3; Se, 52·4%). The yield was variable, depending largely on the quality of the aluminium selenide, but 33—40% yields of the dibromide were readily obtained. From 164 g. of the dibromide, 60 g. of pure 1 : 4-selenoxan were obtained together with 7 g. of the dibromide recovered in the manner indicated.

1 : 4-Selenoxan is a colourless liquid with a characteristic and penetrating but not unpleasant odour. It is soluble in the usual organic solvents and volatile in the vapour of carbon tetrachloride; it is sparingly soluble in water. With stannic chloride it yields a white crystalline compound decomposed by atmospheric moisture. It showed no signs of compound formation with thionyl chloride, arsenious chloride, or ammonia.

1 : 4-*Selenoxan Hydroxynitrate* (II).—When nitric acid (*d* 1·42; 8 c.c.) is added rapidly to the selenoxan (4·85 g.), a deep red solution is momentarily formed and almost immediately oxidation takes place with explosive violence, the liquid, on cooling, depositing the *hydroxynitrate* in colourless massive prisms. This is recrystallised twice from a *little* water and dried under reduced pressure over potassium hydroxide (Found : N, 6·2. $C_4H_9O_5NSe$ requires N, 6·1%). It decomposes at 140—141° and detonates on being heated in a sealed tube over a small flame. Its aqueous solution gives an immediate precipitate of the dibromide (below) with a solution of hydrobromic acid in the cold, whereas selenoxan, dissolved in dilute nitric acid, gives no precipitate with hydrobromic acid unless the

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* Densities and surface tensions were kindly determined by Dr. S. Sugden in connexion with the evaluation of the parachor of 1 : 4-selenoxan (see above).

mixture is boiled. In the latter case bromine is produced which then reacts with the selenoxan.

The hydroxynitrate is also prepared by adding cold nitric acid (*d* 1·42) and a little water to the dihydroxide (see below). Heat is evolved and from the mixture, on cooling, the hydroxynitrate is deposited in colourless massive prisms identical with the substance described above (Found : N, 6·6%).

Selenoxan dichloride (VII), prepared by passing chlorine into the selenoxan (10 g.) dissolved in carbon tetrachloride (80 c.c.), crystallises from benzene in colourless needles, m. p. 127—129° (decomp. after slight softening and darkening from 122°) (Found, by titration : Cl, 31·4. $C_4H_8OCl_2Se$ requires Cl, 31·9%).

The *dibromide*, prepared by adding a 10% solution of bromine in carbon tetrachloride to a solution of the selenoxan in the same solvent, crystallised from benzene or carbon tetrachloride in yellow prismatic needles, m. p. 132° (decomp.) (Found : C, 15·3, 15·7; H, 2·7, 2·8; Br, 51·4. $C_4H_8OBr_2Se$ requires C, 15·4; H, 2·6; Br, 51·4%). It is somewhat soluble in cold benzene and very soluble in the hot solvent. It is sparingly soluble in the following hot and cold solvents : carbon tetrachloride, ethyl alcohol, *cyclo*hexane, acetone. It is somewhat more soluble in chloroform and is insoluble in ether and in ligroin (b. p. 60—80°). It dissolves in water on warming, the solution being colourless and acid, and nothing separates from this on cooling; the original dibromide is, however, precipitated on addition of concentrated hydrobromic acid to the aqueous solution. An aqueous solution of the dichloride behaves similarly with concentrated hydrochloric acid. An aqueous solution of the dibromide gave a precipitate of silver bromide with silver nitrate solution both in the presence and in the absence of nitric acid. Concordant, but low, results were obtained on titrating the ionised bromine. Aqueous solutions of the dichloride and of the dibromide gave precipitates of the di-iodide with an aqueous solution of potassium iodide.

The *di-iodide*, prepared from the selenoxan (1·51 g.) in carbon tetrachloride (10 c.c.) and iodine (2·54 g.) in carbon tetrachloride (120 c.c.), crystallised in violet plates, m. p. 106—107°, from solution in benzene, in which it is most soluble. It is very sparingly soluble in water and in the ordinary organic solvents (Found : I, 62·1; *M*, in nitrobenzene, 415. $C_4H_8OI_2Se$ requires I, 62·6%; *M*, 405).

1 : 4-*Selenoxan methiodide* was prepared (a) by mixing selenoxan (2·0 g.) and methyl iodide (3·0 g.) in absolute alcohol (6·0 c.c.) and filtering off the crystalline material after 5 hours, and, better (b) by keeping a mixture of selenoxan (1·45 g.) and methyl iodide (1·50 g.) for 2 hours and recrystallising the solid rapidly from alcohol

It crystallises in colourless needles, m. p. 171° (Found: I, 43·15. $C_5H_{11}OISe$ requires I, 43·3%). It is soluble in water and this solution shows the presence of ionised iodine, but attempts to titrate the iodine did not yield satisfactory results.

The *mercurichloride* (III or IV) is precipitated on adding an aqueous solution of mercuric chloride (2·7%, 110 c.c.) to a solution of the selenoxan (1·5 g.) in alcohol (20 c.c.). Crystallised from a large volume of alcohol, it is obtained in colourless needles, m. p. 179° (to a clear liquid). It is insoluble in all the ordinary solvents except alcohol and it does not appear to be appreciably ionised in aqueous solution (Found: Cl, 16·7. $C_4H_8OCl_2SeHg$ requires Cl, 16·8%).

When the dibromide (4 g.) in aqueous solution (110 c.c.) was shaken with moist silver oxide from silver nitrate (17·5 g.), silver bromide was formed. The residue on evaporation of the filtrate, first on the water-bath and finally over potassium hydroxide in a desiccator, was an oil which could not be induced to crystallise and was contaminated with a little silver. It was highly hygroscopic, and when treated with the appropriate halogen acid the selenoxan dihalides were obtained. The preparation of the hydroxynitrate from this dihydroxide has been described above.

1 : 4-*Selenoxan chloroaurate* (V) was prepared by adding an excess of a concentrated aqueous solution of auric chloride to 1 : 4-selenoxan dichloride (0·37 g.) in water (2·5 c.c.). On recrystallisation from water it was obtained in golden-yellow needles, decomposing at 142—144° (Found: Au, 38·3. $C_4H_8OCl_5SeAu$ requires Au, 37·5%).

1 : 4-*Selenoxan chloroplatinate* (VI) was prepared similarly, a cold solution of platinic chloride (0·6 g.) in water (3·0 c.c.) and 1 : 4-selenoxan dichloride (0·4 g.) in water (4 c.c.) being used. It separated in small orange-yellow prisms, m. p. 149° (decomp.) (Found: C, 12·8, 12·8; H, 3·1, 3·0; Se, 20·5; Pt, 25·1. $C_8H_{10}O_2Cl_8Se_2Pt$ requires C, 12·3; H, 2·1; Se, 20·2; Pt, 25·0%). It is difficult to explain the high analytical figure for the hydrogen content.

Ammino-derivative of 1 : 4-*Selenoxan Dibromide* (IX).—Dry ammonia was passed into a slightly warm solution of the dibromide (2 g.) in benzene (40 c.c.) until the colour of the solution was discharged, a white precipitate separating. This was washed thoroughly with dry benzene and dried in air on clean porous porcelain. It was insoluble in the ordinary organic solvents and highly soluble in cold water. It had no definite melting point, beginning to froth at 93° and turning brownish-yellow at 130° (Found: N, 7·85; Br, 44·25; atomic ratio N/Br, 1·013. $C_4H_{14}ON_2Br_2Se$ requires N, 8·1; Br, 46·3%; atomic ratio N/Br, 1·000).

A sulphilimine derivative of selenoxan could not be prepared, although some oxidation by means of chloramine-T took place. A hot solution of potassium permanganate was reduced by selenoxan, but no product of a definite character was isolated.

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