

CCXCVIII.—*The Quadrivalency of Selenium. Part II.*
The Simple Halogen Derivatives and the Dihydr-
oxide of 4-Acetamidodiphenyl Selenide.

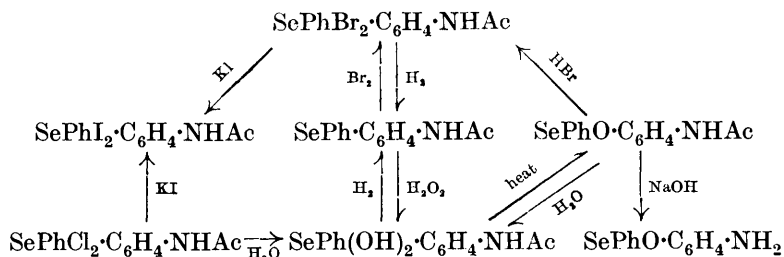
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THE primary object of this investigation was to prepare and attempt the resolution of 4-aminodiphenyl selenoxide. This selenoxide can be prepared indirectly from 4-aminodiphenyl selenide, which is formed by the interaction of benzeneseleninic acid with aniline,

but it proved to be unstable in the presence of acids and hence its resolution could not be attempted. 4-Acetamidodiphenyl selenide, however, reacts with halogens in acetic acid solution to give well-defined, highly coloured, crystalline dihalogen derivatives, the chemical properties of which have been studied in order to compare and contrast them with those of the dihalogen derivatives of semi-aromatic and aliphatic selenides. When heated, the *dichloride* and also the *dibromide* are converted into selenides with halogenated aromatic nuclei. The corresponding *di-iodide*, however, under the same treatment evolves iodine and, indeed, even when exposed to the air at the ordinary temperature, gradually reverts to the selenide.

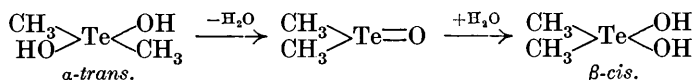
An aqueous solution of potassium bromide converts the dichloride into the dibromide, and this with an aqueous solution of 2 mols. of potassium iodide yields the di-iodide. Each of the three dihalogen compounds can be recrystallised from glacial acetic acid, but only the di-iodide is sufficiently soluble in ethyl alcohol to be recrystallised from this solvent. When the di-iodide is treated with a suitable amount of dry ether, a less highly coloured substance remains undissolved, which proves to be the selenide. Similarly, the selenide is deposited when an ethereal solution of the di-iodide is concentrated. The di-iodide in ethereal solution therefore dissociates into iodine and the selenide.

Water, or more rapidly dilute alkalis, converts the dichloride and dibromide into the *dihydroxide*. Boiling water, however, is without action on the di-iodide which with sodium hydroxide yields its parent selenide. By the action of moist silver oxide, the di-iodide can be made to yield the dihydroxide, which is nevertheless contaminated with some selenide, the latter being the sole product when the di-iodide is treated with warm aqueous solutions of either potassium iodide or sodium thiosulphate. These reactions can be summarised as follows :



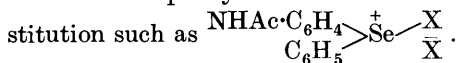
4-Acetamidodiphenyl selenide dihydroxide can also be obtained by the action of hydrogen peroxide on the selenide, and can be recrystallised from hot water. On fusion (147—148°) it loses water,

and the corresponding selenoxide is formed, which, when heated more strongly, darkens, suddenly evolves oxygen, and leaves a fluid mass of pure 4-acetamidodiphenyl selenide. This behaviour is in marked contrast to that of 4-amino-4'-methylidiphenyl sulphoxide which can be heated well above its m. p. without showing any sign of decomposition. At a lower temperature and pressure, 4-acetamidodiphenyl selenide dihydroxide loses water in a manner which is strongly reminiscent of the conversion of α -dimethyltellurium dihydroxide into a telluroxide (Vernon, J., 1920, **117**, 86, 889). By the action of the halogen acids on aqueous solutions of this telluroxide, Vernon obtained dimethyltellurium dihalides, which differed in chemical and physical properties from the corresponding dihalogen compounds obtained from aqueous solutions of the β -dimethyltellurium dihydroxide; he concluded that the four groups of the isomeric dimethyltellurium dihydroxides were in the same plane as the central tellurium atom, and that the α -base was the *trans*-isomeride, whilst the telluroxide after recombination with water gave the *cis*-isomeride.



No analogous change occurs, however, when 4-acetamidodiphenyl selenide dihydroxide loses water, since the same dihalogen compounds were obtained from the dihydroxide as from the selenoxide. These dihalogen compounds were also identical with those prepared from 4-acetamidodiphenyl selenide by the direct addition of halogen.

The behaviour of the dihalogen derivatives and dihydroxide of 4-acetamidodiphenyl selenide is therefore consistent with a constitution such as



It may be pointed out, however, that during all the reactions described, the selenide molecule remains intact and in no instance is a carbon-selenium bond broken. The ease with which 4-acetamidodiphenyl selenoxide loses oxygen is noteworthy as suggesting, but in no way proving, that oxygen may be linked to selenium by a linking weaker than a semipolar double bond.

EXPERIMENTAL.

4-Aminodiphenyl selenide was prepared by heating a mixture of benzeneseleninic acid (20 g.) and aniline (80 c.c.) at 110–115° for 6 hours. After removal of the unchanged aniline in a current of steam, the dark-coloured residue was extracted with hot dilute hydrochloric acid. On addition of sodium carbonate to the acid

extract, the selenide was precipitated as a pink, microcrystalline powder (yield, 12—15 g.). 4-Aminodiphenyl selenide separates from aqueous alcohol (norit) in clusters of almost colourless, prismatic needles, m. p. 93—94° (Found : N, 5·7. $C_{12}H_{11}NSe$ requires N, 5·6%). The base is readily soluble in hot dilute hydrochloric acid, and on cooling, the *hydrochloride* separates as small, feathery needles, m. p. 159° (Found : HCl, by titration, 13·0. $C_{12}H_{12}NSeCl$ requires HCl, 12·9%). Addition of sodium carbonate solution to the hydrochloride regenerates the pure base.

By the interaction of aniline and benzenesulphinic acid, Hinsberg (*Ber.*, 1908, **41**, 113) obtained 4-aminodiphenyl sulphoxide. The foregoing reaction of benzeneseleninic acid doubtless proceeds by the same mechanism, but the selenoxide produced is reduced to the selenide by the excess of aniline.

4-Acetamidodiphenyl selenide was prepared by warming together 4-aminodiphenyl selenide (3·8 g.) and acetic anhydride (4 c.c.). The product (4·2 g.) separated from aqueous alcohol in glistening leaflets, m. p. 169—170° (Found : C, 58·2; H, 5·0; N, 4·8. $C_{14}H_{13}ONSe$ requires C, 57·9; H, 4·4; N, 4·8%). 4-Acetamidodiphenyl selenide decomposes when heated with mineral acids. It undergoes hydrolysis smoothly, however, under the following conditions : A solution of the selenide (2 g.) in alcohol (10 c.c.) was heated under reflux with 3*N*-sodium hydroxide solution (10 c.c.) for 6 hours; on cooling, the regenerated base (1·65 g.) crystallised from the reaction mixture, and after crystallisation from alcohol, had m. p. 93—94°.

4-Acetamidodiphenyl Selenide Dihydroxide.—To a cooled mixture of 4-acetamidodiphenyl selenide (5·8 g.) and glacial acetic acid (10 c.c.), perhydrol (4 c.c.) was gradually added; the *dihydroxide* (5·7 g.) separated from the resulting clear solution on standing, and after crystallisation from boiling water (700 c.c.) had m. p. 147—148° (decomp.) (Found : C, 51·9; H, 5·0; N, 4·3. $C_{14}H_{15}O_3NSe$ requires C, 51·9; H, 4·6; N, 4·3%). When a large excess of perhydrol was used the same compound was obtained, and no trace of the corresponding selenone could be detected. When heated for a few minutes with zinc dust and glacial acetic acid 4-acetamidodiphenyl selenide dihydroxide was quantitatively reduced to the corresponding selenide. It dissolved in warm *N*/2-hydrochloric acid, and when the solution was heated on the steam-bath for an hour glistening leaflets of 4-acetamidodiphenyl selenide separated. Some of the dissolved dihydroxide reappeared as tarry material and the solution possessed oxidising properties, consistent with the view that it contained hypochlorous acid which had resulted from the dissociation of a selenide hydroxychloride. 4-Acetamidodiphenyl

selenide dihydroxide was melted over a small flame and the colourless liquid heated until there was no further loss of moisture (Found : H_2O , 5.56. Calc. : 5.55%). When the horny mass thus obtained was heated more strongly, it darkened, suddenly evolved a gas, and the residual fluid became crystalline on cooling. By recrystallisation from alcohol, this residue was obtained as colourless leaflets (1.0 g.), m. p. 166—168°, either alone or when mixed with 4-acetamidodiphenyl selenide.

4-Acetamidodiphenyl Selenoxide.—4-Acetamidodiphenyl selenide dihydroxide (4 g.) when heated under a pressure of 20 mm. effervesced vigorously at 120—130° and became fluid. After 20 minutes, the effervescence ceased and the liquid crystallised although its temperature was 130°. The solid, 4-acetamidodiphenyl selenoxide, was recrystallised from dry chloroform and obtained as small, ill-defined crystals, m. p. 144—146° (Found : C, 54.8; H, 4.6; N, 4.6. $\text{C}_{14}\text{H}_{13}\text{O}_2\text{NSe}$ requires C, 54.9; H, 4.3; N, 4.6%). Unlike the original dihydroxy-compound, the selenoxide does not decompose on melting: the m. p. of the dihydroxy-compound is really the temperature at which it loses water at ordinary pressure.

When a hot aqueous-alcoholic solution of 4-acetamidodiphenyl selenoxide was cooled, crystals of the corresponding dihydroxide, m. p. 147—148° (decomp.), were deposited. The dihalides, obtained in quantitative yields by the addition of concentrated solutions of hydrochloric, hydrobromic, or hydriodic acid to a warm solution of the selenoxide in glacial acetic acid, were identical with the dihalides obtained in a similar manner from the corresponding dihydroxide.

4-Aminodiphenyl selenoxide was prepared by heating a solution of 4-acetamidodiphenyl selenide dihydroxide (1.7 g.) in alcohol (15 c.c.) with sodium hydroxide solution (10 c.c. of 3N) for 6 hours; on cooling, the selenoxide (1.3 g.) separated as glistening needles, m. p. 188—189° (decomp.) (Found : C, 54.4; H, 4.1; N, 5.4; Se, 30.4. $\text{C}_{12}\text{H}_{11}\text{ONSe}$ requires C, 54.6; H, 4.2; N, 5.3; Se, 30.0%). This compound was also prepared from 4-aminodiphenyl selenide as follows: The selenide (7.5 g.), dissolved in acetone (30 c.c.), was mixed with perhydrol (4.5 c.c.), and the crystals (5.2 g.) which separated on standing were filtered off and washed with acetone (m. p. 180—181°). They were recrystallised, together with a second crop (0.6 g.) obtained from the filtrate, from methyl alcohol, and then had m. p. 187—189° either alone or when mixed with the selenoxide prepared from 4-acetamidodiphenyl selenide dihydroxide as described above. 4-Aminodiphenyl selenoxide was quantitatively reduced to the corresponding selenide by treatment with zinc dust and a solution of sodium hydroxide.

Reaction with dilute hydrochloric acid. The finely-powdered

selenoxide (1 g.) was triturated with dilute hydrochloric acid (50 c.c. of $N/2$). The reaction mixture was filtered, and from the acid filtrate 4-aminodiphenyl selenide (0.2 g.), m. p. 93—94°, was precipitated by the addition of sodium bicarbonate. No crystalline product could be isolated from the tarry, insoluble material.

4-Acetamidodiphenyl selenide dichloride was prepared by the addition of a mixture of concentrated aqueous hydrochloric acid (2 c.c.) and acetic acid (3 c.c.) to a warm solution of the dihydroxide (1.53 g.) in glacial acetic acid (4 c.c.); the dichloride which separated crystallised from acetic acid (30 c.c.) as almost colourless, bulky, feathery needles (1.6 g.), which turned yellow about 125° and had m. p. 131—132° (Found: Cl, 19.6. $C_{14}H_{13}ONCl_2Se$ requires Cl, 19.6%). When chlorine was passed into a solution of 4-acetamidodiphenyl selenide in acetic acid, a white, crystalline compound was precipitated, m. p. 186—187°, which contained chlorine not displaceable by the action of aqueous sodium hydroxide. Even when the equivalent amount of chlorine, dissolved in acetic acid, was added to an acetic acid solution of the selenide, the product obtained melted indefinitely at 110—120°. Thus chlorine, in contradistinction to bromine and iodine, appears to react with the acetamido-group. By treatment either with much water or with dilute sodium hydroxide solution, the dichloride was converted quantitatively into the dihydroxide, whilst when triturated with a cold, concentrated, aqueous solution of potassium bromide (2 mols.), it was rapidly and quantitatively converted into the brightly coloured dibromide.

4-Acetamidodiphenyl selenide dibromide was prepared by mixing solutions of bromine (1.8 g.) and 4-acetamidodiphenyl selenide (3.5 g.) in acetic acid (95 c.c. in all); hemispherical clusters of small red needles (5.05 g.) separated rapidly. After recrystallisation from warm glacial acetic acid, the dibromide turned bright red at 100° and melted to a deep red liquid at 135—136° (Found: C, 37.2; H, 3.9; N, 3.1; Br, 35.1. $C_{14}H_{13}ONBr_2Se$ requires C, 37.3; H, 2.9; N, 3.1; Br, 35.4%). When zinc dust was added to a suspension of the dibromide in acetic acid, 4-acetamidodiphenyl selenide was obtained. On grinding with sodium hydroxide solution (35 c.c. of 3N), the highly coloured dibromide (17.6 g.) was converted into the colourless dihydroxide (10 g.), m. p. 147—148°, with evolution of steam. The same reaction was effected, only more slowly, by the use of cold water. Hydrobromic acid was evolved when 4-acetamidodiphenyl selenide dibromide was heated at its m. p. for $\frac{1}{2}$ hour; the resulting deep red paste was washed with ether, and the insoluble grey powder was crystallised from alcohol, from which it separates as colourless, glistening needles, m. p. 167°.

This *compound* contains bromine but gives no precipitate when heated with alcoholic silver nitrate solution (Found: Br, 34.7. $C_{14}H_{11}ONBr_2Se$ requires Br, 35.2%); the bromine had therefore migrated from the selenium atom to one of the benzene nuclei, producing, probably, 3:5-dibromo-4-acetamidodiphenyl selenide.

4-Acetamidodiphenyl selenide di-iodide. (a) A solution of iodine (1.3 g.) in warm acetic acid (29 c.c.) was added to a solution of 4-acetamidodiphenyl selenide (1.45 g.) in acetic acid (30 c.c.); after a few minutes, the *di-iodide* separated in bulky rosettes of fine needles (2.3 g.), m. p. 144—145° (decomp.) (Found: I, by titration, 46.6. $C_{14}H_{13}ONI_2Se$ requires I, 46.7%). (b) Concentrated aqueous hydriodic acid (10 c.c.) was added to a warm solution of the dihydroxide (0.8 g.) in acetic acid (10 c.c.), and the di-iodide (1.0 g.), m. p. 144—145° (decomp.) either alone or when mixed with the compound prepared as described under (a) or (c), was obtained. Furthermore, when 4-acetamidodiphenyl selenoxide was used in the above experiment in place of the dihydroxide, an identical di-iodide was obtained. (c) The dibromide (1.12 g.) was triturated with a solution of potassium iodide (0.83 g.; 2 mols.) in water (1 c.c.) during 20 minutes; the orange dibromide gradually changed to the chocolate-brown di-iodide, which was washed with water and recrystallised from alcohol or acetic acid.

4-Acetamidodiphenyl selenide di-iodide, when heated at its m. p. for an hour, gave a copious sublimate of iodine, whilst the residue, after crystallisation from aqueous alcohol, had m. p. 93—94° either alone or when mixed with 4-acetamidodiphenyl selenide. This change proceeds slowly at ordinary temperatures: a specimen of the di-iodide exposed to the air was found to have changed completely to the selenide after 10 days.