CCXCVII.—*The Quadrivalency of Selenium. Part I. 4-Carboxydiphenyl and* p-*Carboxyphenyl Methyl Selenoxides.*

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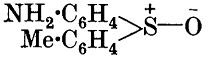
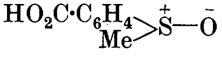
The resolution of 4′-amino-4-methyldiphenyl sulphoxide (I) and *m*-carboxyphenyl methyl sulphoxide (II) into their optically active forms (Harrison, Kenyon, and Phillips, J., 1926, 2079) provided conclusive experimental evidence that the double bond between sulphur and oxygen in these compounds is unsymmetrical and can

(I.)



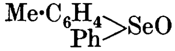
$$\begin{matrix}\mathrm{NH_2{\cdot}C_6H_4}\\ \mathrm{Me{\cdot}C_6H_4}\end{matrix}{>}\overset{+}{\mathrm{S}}{-}\overset{-}{\mathrm{O}}$$



$$\begin{matrix}\mathrm{HO_2C{\cdot}C_6H_4}\\ \mathrm{Me}\end{matrix}{>}\overset{+}{\mathrm{S}}{-}\overset{-}{\mathrm{O}}$$

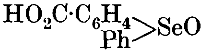
(II.)

therefore be considered to be a semipolar double bond. In order to obtain evidence as to the nature of the bonds linking the selenium and oxygen atoms of selenoxides, attempts have now been made to resolve *phenyl* p-*tolyl selenoxide* (III), 4-*carboxydiphenyl selenoxide* (IV), and p-*carboxyphenyl methyl selenoxide* (V), but they



$$\begin{matrix}\mathrm{Me{\cdot}C_6H_4}\\ \mathrm{Ph}\end{matrix}{>}\mathrm{SeO}$$

(III.)



$$\begin{matrix}\mathrm{HO_2C{\cdot}C_6H_4}\\ \mathrm{Ph}\end{matrix}{>}\mathrm{SeO}$$

(IV.)

$$\begin{matrix}\mathrm{HO_2C{\cdot}C_6H_4}\\ \mathrm{Me}\end{matrix}{>}\mathrm{SeO}$$

(V.)

have been unsuccessful. This failure was unexpected since the sulphoxides were resolved without difficulty, and the resolution of *dl*-phenylmethylselenetine *d*-bromocamphorsulphonate by Pope and Neville (J., 1902, **81**, 1552) proves that quadrivalent selenium has a tetrahedral environment.

The chemical evidence at our disposal suggests that the linking between the selenium and oxygen atoms may be partly polar in character. For example, the selenoxides now described, to a greater degree even than the sulphoxides of similar constitution, are much more soluble in acids than in water.

The selenoxides, however, differ from sulphoxides in one important respect. Sulphoxides are so readily oxidised with potassium permanganate to the corresponding sulphones that it is often difficult, even when mild oxidising reagents are used, to arrest the oxidation of a sulphide at the sulphoxide stage. It is noteworthy, therefore, that the selenoxides described could not be oxidised to selenones by potassium permanganate, and also that with the exception of diphenyl selenone (Krafft and Vorster, *Ber.*, 1893, **26**, 2820), which has the properties of a peroxide and hence differs considerably from its inert sulphur analogue, no reference to the isolation of selenones can be found in the literature. This particular reluctance on the part of a selenium atom, linked to two univalent groups and to oxygen, to pass to the sexavalent condition is also illustrated by the crystallisation of benzeneseleninic acid as a nitrate from moderately concentrated nitric acid (which would oxidise benzenesulphinic acid to the sulphonic acid); moreover, although the interaction of ethyl iodide and silver sulphite leads to the formation of the unsymmetrical ethyl ethanesulphonate, yet silver selenite, under the same conditions, yields the symmetrical diethyl selenite (Michaelis and Landmann, *Annalen*, 1887, **241**, 150).

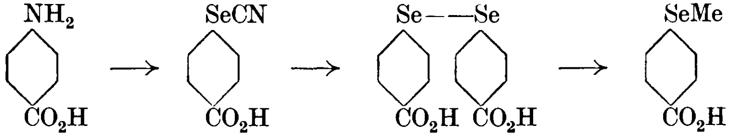
It can therefore be concluded that the linking between the selenium and oxygen atoms of a selenoxide may be partly polar in character, but at the same time may tend to utilise or render inert the remaining combining capacity of the selenium atom in a manner which suggests that the linking may not be an unsymmetrical semipolar double bond. The partly polar character of the linking might be accounted for by assuming that the oxygen atom is linked to the selenium atom by two semipolar single bonds (Prideaux, *Chem. and Ind.*, 1923, **42**, 672; Sugden, J., 1927, 1173); until the electronic structure of such bonds is precisely defined, however, it is difficult to visualise why two such bonds, when exerted together towards the same atom, should differ from a semipolar double bond, and further, why, by exerting two semipolar single bonds, the selenium atom should lose combining capacity.

These difficulties could be overcome by assuming that two selenium electrons and one oxygen electron are concerned with the formation of each semipolar single bond, but that only one of the electrons—a selenium electron—is shared by both atoms, the remaining selenium electron and oxygen electron of the trio being assumed to be in some way essential for the formation of a semipolar single bond and no longer available for purposes of reaction. By the aid of these assumptions it would be possible to explain, not only the reluctance on the part of the selenium atom to become sexavalent, but also the possible symmetrical disposition of the oxygen atom in space with respect to the remainder of the selenoxide molecule. To determine whether this hypothesis is valid other selenoxides are being prepared and investigated.

Phenyl *p*-tolyl selenoxide was prepared by the action of alkalis on phenyl *p*-tolyl·selenide dibromide. On cooling warm solutions of this selenoxide in aqueous solutions of *d*-camphorsulphonic acid, indefinite mixtures of the two separated, and the selenoxide recovered from the mother-liquors was optically inactive; but when equimolecular proportions were mixed in warm, dry ethyl acetate crystals were deposited which, by titration, were found to agree closely in composition with that demanded for the *d*-camphorsulphonate of the selenoxide. The rotatory powers of these " salts " in dry ethyl acetate were, however, identical with the rotatory powers of the solutions obtained by dissolving *d*-camphorsulphonic acid and the selenoxide in ethyl acetate in the same proportions as they occurred in the " salts."

4-Carboxydiphenyl selenoxide was prepared by the oxidation of phenyl *p*-tolyl selenide with an excess of potassium permanganate, and was not contaminated by the corresponding selenone. It gave well-defined, crystalline salts with brucine, *l*-menthylamine, and *d*-α-phenylethylamine, the properties of the salts being unchanged by repeated crystallisation from various solvents. The selenoxide regenerated from the salts was, in every instance, optically inactive. Although, when free, 4-carboxydiphenyl selenoxide does not form a dihydroxide, its salt with *d*-α-phenylethylamine was carefully examined after it had been in contact with water or wet solvents, in order to make certain that the failure to obtain resolution was not due to the addition of water to the possibly unsymmetrical selenoxide, giving rise to a symmetrical dihydroxide. No evidence for such combination could be obtained, and no change in the rotatory power of a dry specimen of this salt could be produced by recrystallising it from dry ethyl acetate.

p-Carboxyphenyl methyl selenoxide was prepared from the dibromide of the corresponding selenide, which was synthesised according to the following scheme. It gave a brucine salt which furnished no evidence that it was a mixture of stereoisomerides.



EXPERIMENTAL.

Phenyl p-*tolyl selenide* was obtained by the method used by Krafft and Vorster (*loc. cit.*) for the preparation of diphenyl selenide. Phenyl *p*-tolyl sulphone (116 g.), which has m. p. 127—128° and not 124·5° as quoted in the literature, and powdered selenium (40 g.) were heated in a metal-bath until there was an active evolution of sulphur dioxide: after 2—3 hours the temperature was raised, and phenyl *p*-tolyl selenide distilled at 305—312°. By redistillation it was obtained as an almost odourless, pale yellow, mobile liquid, b. p. 175—178°/20 mm.; yield 35 g. (Found: C, 63·2; H, 4·9. $C_{13}H_{12}Se$ requires C, 63·1; H, 4·8%). The *dibromide* was prepared by the addition of bromine (6·5 g.) to a cooled solution of the selenide (10 g.) in carbon disulphide (20 c.c.). After standing for an hour, the crystalline material (14 g., m. p. 143—144°) was removed by filtration and recrystallised from carbon disulphide whereby it was obtained as long, orange-red, glistening needles, m. p. 149—150° (Found: Br, 39·2. $C_{13}H_{12}SeBr_2$ requires Br, 39·4%).

Phenyl p-*tolyl selenoxide* was readily obtained by trituration of the dibromide (7·5 g.) with sodium hydroxide solution (15 c.c. of 15%) until the reddish-brown paste became converted into a white, granular powder; this was filtered off, washed, dried, and crystallised from benzene, from which it separated in clusters of feathery needles,

m. p. 131—133°; yield 4 g. The selenoxide was also prepared directly from the selenide by the action of a boiling solution of potassium permanganate. When the theoretical amount of potassium permanganate was used the yield of selenoxide was only about 25% because further oxidation of a portion of the material to 4-carboxydiphenyl selenoxide took place and therefore a considerable proportion of the selenide was recovered unchanged. Phenyl *p*-tolyl selenoxide prepared in this way had m. p. 131—133° either alone or when mixed with that prepared from the dibromide (Found : C, 59·7; H, 4·5. $C_{13}H_{12}OSe$ requires C, 59·3; H, 4·5%). The selenoxide, when triturated with saturated aqueous hydrobromic acid, was rapidly transformed into the orange-red dibromide, which after crystallisation from carbon disulphide had m. p. 149—150° (decomp.) either alone or when mixed with the dibromide prepared directly from the selenide.

Attempted Resolution of Phenyl p-*Tolyl Selenoxide by Means of* d-*Camphorsulphonic Acid.*—Phenyl *p*-tolyl selenoxide (1·3 g.) was added to a solution of *d*-camphorsulphonic acid (3 g.) in water (5 c.c.), and the mixture heated on the steam-bath for a few minutes until solution was almost complete. After cooling, the crystalline material was filtered off and found to consist of almost pure selenoxide which was optically inactive. The recovered selenoxide was therefore dissolved in a solution of *d*-camphorsulphonic acid (2 g.) in ethyl alcohol (12 c.c.), and the solution allowed to crystallise. After decomposition of the filtrate with sodium carbonate, 0·18 g. of selenoxide was obtained which proved to be optically inactive.

The selenoxide (2·6 g.) and *d*-camphorsulphonic acid (2·3 g.) were dissolved in hot, dry ethyl acetate. The crystals which separated on cooling the resulting clear solution had α_{5461} + 0·32° in dry ethyl acetate ($c = 1{\cdot}1175$; $l = 2{\cdot}0$), whence $[\alpha]_{5461}$ + 14·3°. By titration, 0·2235 g. of the crystals was found to contain 0·0908 g. of *d*-camphorsulphonic acid, whereas if the crystals had been the pure salt of the selenoxide they should have contained 0·1045 g. of the acid. A solution prepared by making up 0·1327 g. of the selenoxide and 0·0908 g. of *d*-camphorsulphonic acid to 20 c.c. with dry ethyl acetate had α_{5461} + 0·33° ($l = 2{\cdot}0$) whence $[\alpha]_{5461}$ + 14·7°. Hence it was concluded that no resolution of the selenoxide was taking place. The filtrate from the crystals described above deposited on standing a second crop which had α_{5461} + 0·30° in dry ethyl acetate ($c = 1{\cdot}0725$; $l = 2{\cdot}0$) whence $[\alpha]_{5461}$ + 13·9°. This second crop contained slightly more than the theoretical quantity of *d*-camphorsulphonic acid, since 0·2847 g. contained 0·1409 g. of acid (theory requires 0·1331 g.).

4-*Carboxydiphenyl selenoxide* was prepared by boiling an aqueous suspension of phenyl *p*-tolyl selenide and potassium permanganate for several hours. The manganese mud was dissolved and the 4-carboxydiphenyl selenoxide precipitated by the passage of sulphur dioxide. The reaction mixture was filtered and the insoluble portion macerated with dilute sodium carbonate solution. In this way, the products of the oxidation were separated into phenyl *p*-tolyl selenoxide and 4-carboxydiphenyl selenoxide. On the addition of dilute sulphuric acid to the sodium carbonate extract, 4-carboxydiphenyl selenoxide separated and was obtained, after crystallisation from alcohol, as a microcrystalline powder, m. p. 253—255° (decomp.) (Found : C, 53·5; H, 3·4; equiv., by titration, 292. $C_{13}H_{10}O_3Se$ requires C, 53·2; H, 3·4%; equiv., 293).

4-*Carboxydiphenyl selenide* was prepared by warming a mixture of 4-carboxydiphenyl selenoxide (0·5 g.), acetic acid (15 c.c.), and zinc dust (0·3 g.) on a steam-bath for 3 hours. The hot filtered solution was diluted with water and the selenide (0·25 g.) separated as pale yellow, glistening leaflets, m. p. 182—184° (without decomp.) (Found : equiv., by titration, 279. $C_{13}H_{10}O_2Se$ requires equiv., 277).

4-*Carboxydiphenyl selenide dibromide* was prepared (*a*) by the addition of aqueous hydrobromic acid to a warm solution of 4-carboxydiphenyl selenoxide (0·5 g.) in acetic acid, from which it separated as yellow, microcrystalline needles (0·6 g.), which turn deep red and soften between 180—190° and melt at 208—210°; (*b*) by the addition of a solution of bromine (0·13 g.) in carbon tetrachloride (1 c.c.) to a warm solution of 4-carboxydiphenyl selenide (0·21 g.) in the same solvent (50 c.c.). The dibromide (0·28 g.), m. p. 205—207°, crystallised on cooling the mixed solutions (0·1534 g. neutralised 0·0560 g. KOH on decomposition. Calc. : 0·0588 g.).

Attempted Resolution of 4-*Carboxydiphenyl Selenoxide*.—The *brucine* salt of 4-carboxydiphenyl selenoxide was prepared in warm acetone solution, from which it separated on cooling as very small needles, m. p. 130° (decomp.). The *strychnine* salt was too unstable to be of service. The l-*menthylamine* salt crystallised from alcohol in needles, m. p. 220—222° (decomp.). Its rotatory power, $[\alpha]_{5461}$ $-$ 16·4° ($c = 0{\cdot}8415$ in ethyl alcohol; $l = 2{\cdot}0$), and m. p. remained unchanged after repeated crystallisation from alcohol. The d-α-*phenylethylamine* salt was prepared in aqueous solution, from which it separated in clusters of feathery needles, m. p. 194—195° (decomp.). Recrystallisation from alcohol, water, or ethyl acetate caused no change in either its m. p. or its rotatory power, which was $[\alpha]_{5461}$ $-$ 12·7° ($c = 1{\cdot}139$ in pyridine; $l = 2{\cdot}0$). This salt was also heated at 98°/15 mm., but such treatment did not cause it to lose weight or to change in rotatory power.

4 : 4′-*Dicarboxydiphenyl diselenide* was prepared by the method used by Bauer (*Ber.*, 1913, **46**, 92) for the preparation of analogous compounds. To a vigorously stirred, cooled solution of *p*-aminobenzoic acid (46 g.) in water (750 c.c.) and concentrated hydrochloric acid (83 c.c.), sodium nitrite solution (230 c.c. of 10%) was added. After 30 minutes, the solution was made alkaline to Congo-red by the addition of potassium acetate, and a solution of potassium selenocyanate (96 c.c. of 50%) was then gradually added. After the mixture had been stirred for 3 hours, the light brown, insoluble material was removed by filtration; it consisted mainly of an inseparable mixture of *p*-carboxyphenyl selenocyanate contaminated with 4 : 4′-dicarboxydiphenyl diselenide. In order to convert the selenocyanate into the diselenide, the mixture was dissolved in 2*N*-sodium hydroxide solution, and the solution boiled for an hour, cooled, filtered and acidified. The precipitated 4 : 4′-dicarboxydiphenyl diselenide (32 g.) separated from methyl alcohol as a pale yellow, microcrystalline powder, m. p. 297° (Found : C, 42·1; H, 2·5. $C_{14}H_{10}O_4Se_2$ requires C, 42·0; H, 2·5%).

p-*Carboxyphenyl methyl selenide.* To a gently boiling solution of 4 : 4′-dicarboxydiphenyl diselenide (40 g.) in aqueous sodium hydroxide (240 c.c. of 10%), sodium hydrosulphite (80 g.) (or zinc dust, 12 g.) was gradually added. To the filtered and cooled solution, methyl sulphate (13 c.c.) was added in small portions with agitation, and after 1 hour the crude p-*carboxyphenyl methyl selenide* was precipitated by the addition of acid. When dry, it was extracted with benzene, in which the chief impurity, the diselenide, is insoluble; 20 g. separated from hot benzene as a pale yellow, microcrystalline powder, m. p. 174° (Found : C, 44·8; H, 3·8. $C_8H_8O_2Se$ requires C, 44·6; H, 3·7%). The *dibromide* was prepared by the addition of a solution of bromine (9·6 g.) in acetic acid (50 c.c.) to a slightly warm solution of the selenide (12·80 g.) in acetic acid (200 c.c.). The addition compound (22·4 g.) rapidly separated as small orange-red needles, which, after washing with acetic acid, turned a deep red above 170° and had m. p. 198—199° (Found : Br, 42·3. $C_8H_8O_2SeBr_2$ requires Br, 42·7%).

p-*Carboxyphenyl methyl selenoxide* was obtained (*a*) by triturating the dibromide (22·4 g.) with water (60 c.c.) and a few c.c. of 3*N*-sodium hydroxide solution until the suspension had turned completely white, the liquor being acid to Congo-red, removing the selenoxide (9·80 g.) by filtration, washing with water and drying, m. p. 170° (indef.); (*b*) by the addition of hydrogen peroxide (5 c.c. of 30%) to a solution of *p*-carboxyphenyl methyl selenide (10·2 g.) in methyl alcohol (300 c.c.), and filtering the crystals (10 g.) of *p*-carboxyphenyl methyl selenoxide which separated over-night.

It crystallised from alcohol in small, hard, irregular prisms, m. p. 183—184° (decomp.) (Found : C, 41·2; H, 3·7. $C_8H_8O_3Se$ requires C, 41·6; H, 3·5%), and the molten product rapidly set to a yellow solid which remelted about 250°.

The *brucine* salt of *p*-carboxyphenyl methyl selenoxide had m. p. 105—110° (see below); it was very soluble in cold alcohol, and when recrystallised from a hot mixture of alcohol and acetone was obtained with m. p. 151—153°. On investigation, it was found that during the recrystallisation the selenoxide had become partly reduced to the selenide and that the alkaloidal salt (m. p. 151—153°) was a mixture of the brucine salts of the selenoxide and the selenide. Accordingly the brucine salt was prepared in cold absolute ethyl alcohol and the solution allowed to concentrate in a desiccator until a suitable amount (m. p. 105—110°, decomp.) had separated. From this salt the selenoxide (m. p. 183—184°, decomp.) could be obtained by decomposition with alkalis and acidification of the alkaline extract with acetic acid. Similarly, by the addition of dilute sodium carbonate solution to the filtrate from the brucine salt, aqueous solutions of the sodium salt of *p*-carboxyphenyl methyl selenoxide were prepared. These solutions after repeated extraction with chloroform to remove dissolved brucine were found to be either optically inactive or in some cases to give a rotation of the order $\alpha_{5461} + 0{\cdot}02°—0{\cdot}04°$, *i.e.*, within the limits of experimental error. The various solutions of the sodium salt yielded *p*-carboxyphenyl methyl selenoxide (as shown by its m. p., and by conversion into the dibromide by means of hydrobromic acid) which was optically inactive in either aqueous or ethyl-alcoholic solution. The brucine salt of *p*-carboxyphenyl methyl selenoxide is optically inactive to light of λ_{5461} and has $[\alpha]_{5870} + 2{\cdot}5°$ ($l = 2{\cdot}0$; $c = 0{\cdot}9864$ in ethyl alcohol).

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