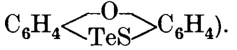
LXVI.—*Cyclic Organo-metallic Compounds. Part V. Phenoxselenine and Phenoxthionine from Phenoxtellurine. Selenylium and Thionylium Compounds.*

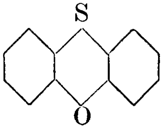
By HARRY DUGALD KEITH DREW.

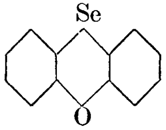
PHENOXTHIONINE (I) was discovered by Mauthner (*Ber.*, 1906, **39**, 1344), who prepared it by a lengthy process from sodium thiopyrocatechol and 3-chloro-2 : 4-dinitrobenzoic acid. Phenoxselenine (II) has not hitherto been described.

The author's process for the preparation of phenoxtellurine (Part I; J., 1926, 223), *viz.*, condensation between diphenyl ether and the tetrachloride of the metalloid, followed by reduction with alkali bisulphite, cannot be applied in the case of phenoxthionine, and was fruitless in that of phenoxselenine, owing to the chlorinating action of selenium tetrachloride. It is now found, however, that phenoxtellurine may readily be transformed either to phenoxthionine or to phenoxselenine.

When phenoxtellurine is heated with an atomic proportion of sulphur, the red solution becomes greenish-brown (probably owing to the formation of the sulphide  $C_6H_4{<}\genfrac{}{}{0pt}{}{O}{TeS}{>}C_6H_4$). An exothermic reaction then ensues; crystalline tellurium is set free, and is replaced by sulphur. The resulting phenoxthionine contains about 7% of unchanged phenoxtellurine, from which it is easily separated.

(I.)





(II.)

When selenium is employed instead of sulphur, the product consists of phenoxselenine (2 mols.) and phenoxtellurine (1 mol.). This mixture (or molecular complex) cannot be resolved by crystallisation, but pure *phenoxselenine* may be obtained from it quantitatively by transformation to the mixed dibromides, followed by warming with acetone.

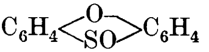
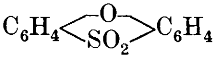
Phenoxtellurine is totally recoverable from its dibromide, and therefore the foregoing reactions afford quantitative yields in the sense that the whole of the initial phenoxtellurine can ultimately be converted either into phenoxthionine or into phenoxselenine. The bulk of the tellurium can be recovered and used again.

The processes are probably applicable generally to the nuclear-substituted derivatives of phenoxtellurine. For example, 2-chloro-8-methylphenoxtellurine behaves towards sulphur in a manner similar to that of phenoxtellurine. The nitrophenoxtellurines, which decompose explosively when heated with sulphur, afford an exception to this rule.

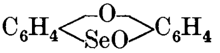
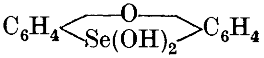
The following table shows a comparison between some of the properties of the foregoing substances:

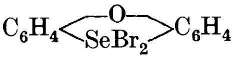
Substance.	Colour.	M. p.	Colour in sulphuric acid.
Phenoxthionine	Colourless	58°	Intense violet
Phenoxselenine	Colourless	88	Intense olive-green; violet on dilution or warming (reversible)
Phenoxtellurine	Yellow (from alcohol); orange (from acetic acid or acetone)	79	Deep purplish-red

The three compounds, taken in pairs, form mixed crystals inseparable by solvents. Normal depression of melting point is therefore not shown by the mixtures. In fact, an admixture of all three compounds in about equal proportions melts between 55° and 85°. A similar relationship had been noticed previously (J., 1921, **119**, 1063) in the case of the crystalline acetylacetonates of aluminium, gallium, and indium—where the metallic atoms are related in the periodic table of the elements in the same manner as sulphur, selenium, and tellurium.

Phenoxthionine yields an *oxide*,  $C_6H_4\genfrac{<}{>}{0pt}{}{\text{O}}{\text{SO}}C_6H_4$ (III), (m. p. 158—159°), which gives with sulphuric acid a violet coloration, becoming deep blue on warming (irreversible). Further oxidation affords the dioxide,  $C_6H_4\genfrac{<}{>}{0pt}{}{\text{O}}{\text{SO}_2}C_6H_4$ (IV) (m. p. 147—148°), which gives no sulphuric acid coloration. This substance has already been prepared by Mauthner, who, however, gives m. p. 140—141° and states that a blue coloration is produced with sulphuric acid. His product was evidently contaminated with the oxide (III).

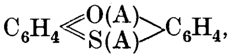
Phenoxthionine does not form a dichloride, dibromide, or diacetate.

Phenoxselenine forms an *oxide*,  $C_6H_4\genfrac{<}{>}{0pt}{}{\text{O}}{\text{SeO}}C_6H_4$ (V), which is soluble both in organic solvents and in water, separating from the latter as the crystalline neutral *dihydroxide*,  $C_6H_4\genfrac{<}{>}{0pt}{}{\text{O}}{\text{Se(OH)}_2}C_6H_4$ (VI). These substances give deep violet solutions in sulphuric acid, which become permanently blue on being warmed.

Phenoxselenine forms a yellow *dichloride*, and a red *dibromide*,  $C_6H_4\genfrac{<}{>}{0pt}{}{\text{O}}{\text{SeBr}_2}C_6H_4$ (VII), and these compounds differ from the corresponding halides of phenoxtellurine (which are colourless and yellow respectively) in that they are halogenating agents towards such substances as acetone. Phenoxselenine forms only an unstable acetate, readily hydrolysed to the oxide.

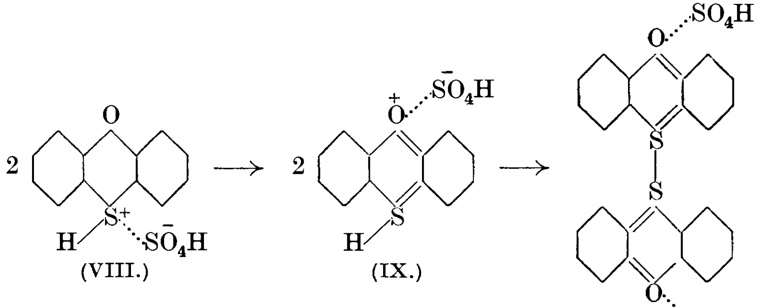
The oxides (III) and (V) differ remarkably in that, whereas phenoxthionine oxide is only sparingly soluble in water, may be distilled unchanged, does not catalytically decompose hydrogen peroxide, and is not reduced by alkali bisulphite, phenoxselenine oxide is extremely soluble in water, quantitatively loses oxygen on being heated above its melting point, liberates oxygen from hydrogen peroxide, and is at once reduced by alkali bisulphite in the cold.

Thionylium and Selenylium Compounds.

Hilditch and Smiles (J., 1911, **99**, 408) ascribed the intense colour of the sulphuric acid solutions of phenoxthionines and their oxides to the presence of thionium salts of the type  $C_6H_4{<}\begin{smallmatrix} O(A) \\ S(A) \end{smallmatrix}{>}C_6H_4$, where A stands for an acid radical. The following experiments show, however, that thionylium compounds (analogous to the tellurylium compounds) are in reality responsible.

When the intensely violet sulphuric acid solution of phenoxthionine is allowed to stand during three hours, until sulphur dioxide ceases to be produced, and is then decomposed with ice, half of the original phenoxthionine is recovered as the oxide (donor), the remaining half being recovered unchanged (acceptor). The coloured solution must therefore have been a homogeneous solution of a diphenoxthionylium compound, doubtless (by analogy with the corresponding tellurylium compound) in combination with sulphuric acid molecules.

It may be postulated that an additive compound * with sulphuric acid (VIII) is first produced and that this is transformed to the quinonoid form (IX) by the migration of its anion. Two molecules of (IX) are then oxidised by sulphuric acid to form a single molecule of *diphenoxthionylium dibisulphate* (X). The transformation of (IX) to (X) is thus similar in principle to the oxidation by sulphuric acid of thiophenol to diphenyl disulphide (Stenhouse, *Annalen*, 1869, **149**, 251).



(VIII.) (IX.) (X.)

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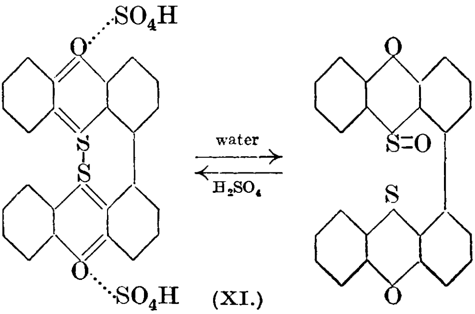
* Throughout the paper, dotted bonds indicate polar linkings.

On the above view, the change is seen to involve the transfer of an electron across the central ring of each phenoxthionine nucleus from oxygen to sulphur. The reaction may, however, be expressed in still simpler terms, if the suggestion (J., 1926, 3062) be adopted that reducing agents are substances which exchange electrons for anions. In that case, each molecule of the reducing agent, phenoxthionine, parts with an electron to sulphuric acid, receiving in exchange the bisulphate anion; the lost electron is then " replaced " by sharing (through the sulphur atoms) with another similar residue, giving (X). The nascent hydrogen, generated on receipt of the electron by a sulphuric acid molecule, is regarded as being directly removed by the excess of sulphuric acid.

It is a striking fact that a thionylium compound is produced when phenoxthionine oxide (III) is dissolved in sulphuric acid. The violet solutions of the oxide invariably yield phenoxthionine when decomposed by ice. Sulphuric acid acts, therefore, both as an oxidising agent towards the free sulphide and as a reducing agent towards its oxide, the reaction apparently ceasing when the thionylium state has been attained.

In the case of the oxide, however, secondary reactions ensue. Fresh solutions of phenoxthionine oxide in cold sulphuric acid give both phenoxthionine and its oxide after treatment with ice; but from solutions allowed to stand during 2 hours oxide can no longer be recovered, the products then consisting of phenoxthionine equivalent to about one-third of the original oxide, together with a yellow amorphous product. This substance, which is not a sulphonic acid, gives an intensely blue colour with sulphuric acid and is therefore probably a nuclear-oxidation product of a thionylium compound, *e.g.*, (XI).

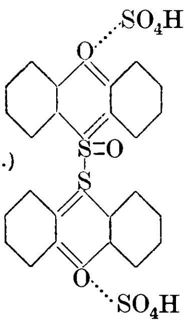


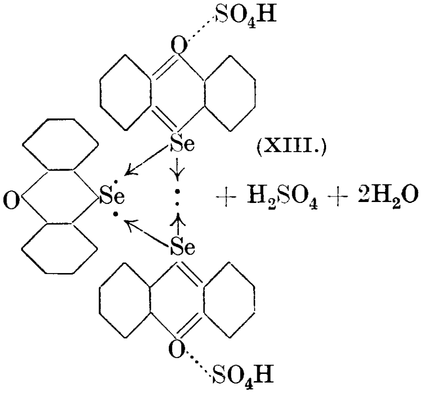
(XI.)

When a solution of phenoxthionine oxide in sulphuric acid is warmed on the water-bath, the violet colour changes to a permanent blue; and the blue solution, diluted with water, yields phenoxthionine equivalent to only about one-quarter of the original oxide, the remaining product being similar to the above amorphous substance.

It is clear, therefore, that, although the action of sulphuric acid upon phenoxthionine oxide is complex, it invariably gives rise to thionylium compounds, which in part survive even when the solution is heated. Probably the first reaction consists in the formation of the oxythionylium compound (XII), a proportion of which loses persulphuric acid, giving the thionylium compound (X); while the remainder undergoes inner oxidation to (XI). The argument receives support from the fact that Fries and Volk (*Ber.*, 1909, **42**, 1170) have detected the formation of persulphuric acid when dimethylthianthrene oxide is dissolved in sulphuric acid.

(XII.)





(XIII.)

$+ H_2SO_4 + 2H_2O$

Thionylium compounds are extremely sensitive to moisture, and are dissociated by acetic acid and by ether. Attempts to isolate them have proved fruitless.

Selenylium compounds, however, are less readily decomposed by water and it has been possible to isolate one of them in a pure crystalline condition.

The deep olive-green solution of phenoxselenine in cold sulphuric acid, decomposed by ice after 2 hours, gives only phenoxselenine (57·4% of the original weight) and phenoxselenine oxide (equivalent to 41·2% of phenoxselenine). The green solution may thus consist of triphenoxselenylium dibisulphate together with rather less than a molecular proportion of diphenoxselenylium dibisulphate, both probably in combination with sulphuric acid molecules.

Cautious dilution of such a solution with water gives two kinds of crystals, which are respectively deep copper-red (A) and dark purple (B). Conditions can be chosen in which only (A) is formed, but (B) has not been obtained free from (A). Recrystallisation from acetic acid does not alter the composition of (A), but crystallisation of the mixture of (A) and (B) from acetic acid containing a drop of sulphuric acid transforms the whole into (A).

The red crystals consist of *triphenoxselenylium dibisulphate sulphuric acid dihydrate* (XIII; compare VIII in Part IV of this series; preceding paper). When decomposed by water, this substance gives only sulphuric acid, phenoxselenine (46·7%), and phenoxselenine oxide (equivalent to 23·0% phenoxselenine). Thus it contains two molecular proportions of phenoxselenine in the acceptor and one in the donor condition. Moreover, it yields 69·7% of total phenoxselenine, as against 69·35% demanded by theory.

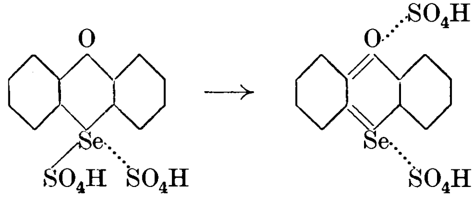
The total sulphuric acid in this compound may be determined accurately by titration, whereas such is not the case with the tellurylium compounds, the sulphates of phenoxtellurine being less easily hydrolysed.

Compound (XIII) gives in acetic acid an intensely green solution which becomes almost colourless when warmed, and violet when heated to a higher temperature. Small amounts of added sulphuric acid increase the intensities of the colours. The feebly coloured solution may consist of the dissociated constituents (sulphuric acid, phenoxselenine, and phenoxselenine oxide); whereas the violet solution probably contains an oxyselenylium compound, analogous to (XII). The green solution contains the undissociated compound. This view is supported by the fact that the sulphuric acid solution of phenoxselenine oxide is violet, becoming permanently blue on being heated. The changes are analogous to those given by phenoxthionine oxide.

The purple crystals (B) consist either of a diphenoxselenylium compound or of the above substance (XIII) deprived of the molecule of attached sulphuric acid.

Phenoxselenine dibromide (VII) evolves hydrogen bromide when dissolved in concentrated sulphuric acid, giving a yellow solution which becomes orange-red on being warmed. On further warming, the solution becomes violet and then permanently blue. A similar behaviour is shown by the dichloride. The yellow colour is probably due to the formation of phenoxselenine dibisulphate (XIV), which becomes orange-red when it assumes the quinonoid con-

(XIV.)



(XV.)

dition (XV). Transformation to the oxyselenylium state (analogous to XII), with the accompanying changes already suggested, produces the violet colour, and inner oxidation to a complex (analogous to XI) represents the blue stage.

Phenoxtellurine dibisulphate gives blue or blue-black substances with warm phenoxthionine and with phenoxselenine in the cold, showing that mixed -ylium compounds, less stable than the tellurylium compounds, exist. The oxides of phenoxselenine and phenoxthionine act as acceptors towards phenoxtellurine dibisulphate when warmed, mixed oxy-ylium compounds probably being formed.

The study of thionylium, selenylium, and tellurylium compounds shows that, having regard to the three elements in their quadrivalent states, sulphur may be associated in its compounds with 18 or with 20 electrons, selenium with 36 or with 38 electrons, and tellurium with 54 or with 56 electrons. The tendency to become associated with the higher number of electrons decreases in the order Te, Se, S, as is shown by the diminishing stability of the corresponding -ylium compounds in the presence of water or organic solvents. It may be inferred that the tendency of oxygen to become associated with 12 electrons is even less than the tendency of sulphur to become associated with 20, but the possibility that -ylium compounds of oxygen are capable of existence in strongly acid solutions is by no means excluded.

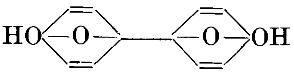
The stability of the oxides of phenoxthionine, phenoxselenine, and phenoxtellurine towards heat appears to decrease in the order S, Se, Te, but that of the dihalides, towards substances capable of halogenation and towards mineral acids, decreases in the order Te, Se, S. The stability towards heat of the dihydroxides appears to decrease in the order Te, Se, S; and the stability towards hydrolytic agents of such salts as the diacetates, dibisulphates, and dinitrates decreases in the same order.

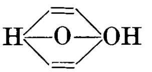
The existence of -ylium salts makes it probable that " dimeric " structures of analogous nature are associated with the changes undergone by the thianthrens (Fries and Volk, *loc. cit.*), and by other substances containing similar ring systems.

Quinhydrones.

The compounds of the quinhydrone type simulate in many respects the behaviour of the tellurylium compounds, and it is accordingly suggested that the former substances possess a carbonylium structure. Quinhydrone itself, for example, may on this hypothesis be formulated as (XVI), its generator, quinol, being regarded as able to assume the carbonium phase (XVII). The latter molecule would be capable of passing to (XVI) either by direct oxidation or by union with quinone. Replacement of the mobile hydrogen atom in (XVII) by an alkyl group would be expected to diminish the tendency towards quinhydrone formation, on account of the reluctance of the alkyl radical to assume a charge; and this accords with the experience that quinol dialkyl ethers form only unstable quinhydrones.

(XVI.)

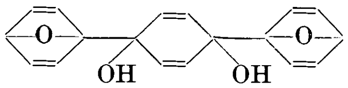




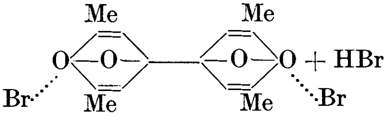
(XVII.)

The same considerations would apply to the compounds formed by diamines and alkylated diamines with quinones and quinone-imines, which would contain an imino-bridge. In the alkylated diamines, however, the alkyl groups would be more electropositive than those in the ethers. The *p*-quinonoid oxygen- or imino-bridge, unlike the simple *p*-bridge, is in conformity with stereochemical requirements for formulæ consisting of open chains of quinonoid benzene nuclei (*e.g.*, XVI), but not for closed chains of such nuclei. In cases of the latter type, perhaps, for example, in that of the compound of benzidine and quinonedi-imine, the bridge may be regarded as opened by the formation of a dipole. That the carbon–carbon linking in such a compound as (XVI) would be prone to ready disruption is rendered exceedingly probable by the recent work of Conant (*J. Amer. Chem. Soc.*, 1927, **49**, 2080). It has been shown, too, by Goldschmidt and Christmann (*Ber.*, 1924, **57**, 711) that a pair of salt-forming hydroxyl groups still exists in quinhydrone, for the deep blue sodium salt of this substance was isolated in the solid state. This is in agreement with the formulations now proposed.

For phenoquinone the formula (XVIII) is suggested; and in the pyrone series, Hantzsch and Denstorff's perbromide of dimethylpyrone hydrobromide (*Annalen*, 1906, **349**, 39) may be regarded as possessing the structure (XIX), the donor in this case being the dimethylpyrone dibromide (XX) and the acceptor dimethylpyrone

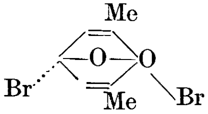


(XVIII.)

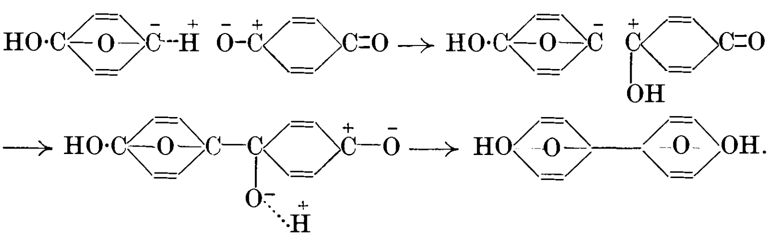


(XIX.)

(XX.)

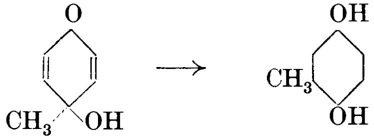


itself (compare Collie and Klein, J., 1927, 2162). The donor therefore parts with an anion, as in the case of the phenoxtellurine and similar salts; whereas, in the formation of true quinhydrones, the donor is probably to be regarded as parting with a kation. Since in some instances aromatic hydrocarbons, such as durene and hexamethylbenzene, form quinhydrones with suitable quinones, the substituted benzene nucleus must be capable of parting with charged hydrogen or alkyl. It may be noted that a mixture of a quinone with a quinol of another series contains the quinone of the latter series (Siegmund, *J. pr. Chem.*, 1915, **92**, 342), so that it is evident that hydrogen exchange occurs from quinol to quinone in accord with the scheme outlined above. In all of the cases cited, the negatively charged oxygen atom of the quinone or other ketone (or the nitrogen atom of the quinoneimine) is regarded as receiving the kation, the nuclei then joining owing to the attraction between the negative and the positive carbon atoms. The suggested process may be illustrated as follows for the formation of quinhydrone :



In toluquinol (XXI), the carbon–carbon linking is unstable, the compound isomerising in presence of alkali to (XXII) (compare Bamberger, *Annalen*, 1912, **390**, 164).

(XXI.)



(XXII.)

EXPERIMENTAL.

Phenoxthionine (I).—Phenoxtellurine (3 g.) and sulphur (0·35 to 0·4 g.) were heated together until reaction set in. This having ceased, the organic product was boiled during 10 minutes, and then distilled; or it was cooled and extracted by ether or chloroform. The product (2·1 g.) separated from acetic acid in pale yellow needles, m. p. 57—58°, unaltered by further crystallisation. The crystals contained 6—7% of unaltered phenoxtellurine (Found : C, 69·8, 70·0; H, 3·9, 4·0%). Purification was effected by dissolving the substance in chloroform, adding a few drops of bromine, filtering the solution, and allowing the solvent to evaporate; the residue was then warmed with a little acetone (which was allowed to evaporate), taken up in ether, and filtered. From alcohol, it formed inch-long, colourless, refractive, prismatic needles or plates, m. p. 58° after slight shrinkage from 56°. Mauthner (*loc. cit.*) gives m. p. 60—61°; but purification of the present author's product by several methods failed to raise the melting point (Found: C, 71·7, 71·8; H, 4·1, 4·0. Calc. for $C_{12}H_8OS$: C, 72·0; H, 4·0%).

Phenoxthionine oxide (III) is prepared by adding a slight excess of hydrogen peroxide to a glacial acetic acid solution of phenoxthionine, warming the mixture for a few minutes, and diluting it somewhat with water. The oxide forms colourless massive needles or prisms from acetic acid or benzene, is rather sparingly soluble in hot water to a neutral solution, and does not form a hydroxide. It forms phenoxthionine when treated with zinc dust and acetic acid; and is reduced also by warm acetic–hydrochloric acids, evolving chlorine, which partly chlorinates the resulting phenoxthionine. It melts at 158—159°, and gives a deep violet coloration in warm, syrupy phosphoric acid (Found: C, 66·8; H, 3·7. $C_{12}H_8O_2S$ requires C, 66·7; H, 3·7%).

Phenoxthionine dioxide (IV) is prepared by the prolonged action of hydrogen peroxide upon phenoxthionine in glacial acetic acid, or by the action of chromic acid or potassium permanganate. It forms long, colourless needles, m. p. 147—148°, from dilute acetic acid, and is unaltered even when dissolved in hot sulphuric acid. It is very resistant to reducing agents and appears quite unaffected by hot acetic–hydrochloric acids (Found: C, 61·9; H, 3·3; S, 13·4. $C_{12}H_8O_3S$ requires C, 62·05; H, 3·5; S, 13·8%).

Action of Sulphuric Acid upon Phenoxthionine.—Phenoxthionine (0·3752 g.) was dissolved in cold concentrated sulphuric acid (5 c.c.). The deep violet solution was kept for 3 hours, the evolved sulphur dioxide being drawn off under reduced pressure. The solution was then cooled in ice and salt, and decomposed by ice (30 g.). The colourless suspension was filtered, and the filtrate extracted with chloroform; the filter-paper was washed with chloroform. The total amount of solid recovered (dried over phosphorus pentoxide) was 0·3798 g. From it the phenoxthionine (0·1891 g., m. p. 57—58°) was extracted quantitatively by cold light petroleum (b. p. 40—60°). The residue of almost pure phenoxthionine oxide (m. p. 155—156°, after one crystallisation from dilute acetic acid) amounted to 0·1875 g. These results show that phenoxthionine and its oxide are present in molecular proportion in the coloured solution. Moreover, these two substances must be combined, since neither is stable towards sulphuric acid in the free condition. A *thionylium compound* (X) is therefore present.

Action of Sulphuric Acid on Phenoxthionine Oxide.—(1) Phenoxthionine oxide (0·3902 g.) was dissolved in concentrated sulphuric acid (5 c.c.); sulphur dioxide was not evolved, nor was the evolution of oxygen detected. The intensely purplish-violet solution was kept during 2 hours and then decomposed with ice (20 g.). The recovered brown solid gave pure phenoxthionine (0·1247 g.) on extraction with cold petroleum. The brown insoluble residue (0·2658 g.), probably containing a little phenoxthionine oxide, could not be separated into pure constituents. The more sparingly soluble portion, left after extraction with cold acetone, was a brown, amorphous solid, m. p. 215—220° (decomp.), which gave an intensely blue coloration with cold sulphuric acid. This substance is considered to be a complex of the type represented in formula (XI). It is clear that the phenoxthionine recovered could not have been present as such in the sulphuric acid solution, otherwise sulphur dioxide would have been evolved. The experiment thus showed that a thionylium compound was produced.

(2) Phenoxthionine oxide (0·3215 g.) in concentrated sulphuric acid (4 c.c.) was heated on a water-bath during ½ hour, until the violet colour became blue; some sulphur dioxide was liberated. Decomposition with water led to the isolation of pure phenoxthionine (0·0883 g.). The remaining product was similar to the amorphous substance in (1).

(3) When a solution of phenoxthionine oxide, similar to that in (1) above, was kept for only 5 minutes before decomposition with ice, both phenoxthionine and phenoxthionine oxide were isolated from it in the pure condition, but a proportion of the amorphous substance was nevertheless produced.

Phenoxselenine (II).—Phenoxtellurine (3 g.) and powdered black selenium (0·9—1·3 g.) were mixed and heated so that the phenoxtellurine boiled gently during ½ to 1 hour. The organic product (2·6 g.) was distilled, or extracted with ether or chloroform. It crystallised from acetic acid in long, sulphur-yellow needles, m. p. 82—84°, and was a mixture or compound containing about 2 mols. of phenoxselenine to 1 mol. of phenoxtellurine (Found : C, 54·9, 55·1; H, 3·1, 3·2%). It was resolved into its constituents by dissolving it in cold chloroform and adding a slight excess of bromine, collecting the mixed dibromides, and boiling them with acetone for a few minutes under reflux. The acetone and bromoacetone were allowed to evaporate, and the residue was taken up in ether and filtered from the insoluble phenoxtellurine dibromide. The ethereal solution left almost pure phenoxselenine. *Phenoxselenine* separates from alcohol or acetic acid in long, colourless, refractive, rectangular prisms, m. p. 87—88°, which have a faint odour of rose leaves (Found: C, 58·2; H, 3·3; Se, 31·1. $C_{12}H_8OSe$ requires C, 58·3;

H, 3·25; Se, 32·0%). It forms halides when treated with the halogen elements, dissolved in chloroform.

Phenoxselenine dichloride crystallises in light yellow, glistening plates, m. p. 127° (decomp.), from acetic acid. *Phenoxselenine dibromide* (VII) forms orange-red spangles, m. p. 147—148° (decomp.), from acetic acid. These halides give no coloration when ground with phenoxtellurine, even on being warmed.

Phenoxselenine oxide (V) was prepared by dissolving phenoxselenine in warm glacial acetic acid and adding a slight excess of hydrogen peroxide. The solution of the unstable diacetate was allowed to evaporate in the air, the crude product dissolved in a little hot water, and the solution allowed to cool undisturbed and then rapidly extracted with its own bulk of ether (to remove traces of unchanged phenoxselenine). The aqueous layer now crystallised, on scratching, in inch-long, slender, colourless needles of *phenoxselenine dihydroxide* (VI), very readily soluble in water (Found for air-dried substance: C, 51·25; H, 3·8. $C_{12}H_{10}O_3Se$ requires C, 51·2; H, 3·6%). The dihydroxide loses a molecule of water when dried at 100° in a vacuum over phosphorus pentoxide (Found, using 60 mg. of substance: loss of H_2O, 7·4. Calc., 6·4%), forming *phenoxselenine oxide* (V), a colourless, crystalline powder, m. p. 171—172°. Water changes it again to the dihydroxide, the aqueous solution of which is neutral. Above its melting point, the oxide is quantitatively transformed to phenoxselenine. Both the oxide and the dihydroxide vigorously decomposed hydrogen peroxide in glacial acetic acid solution (Found for the vacuum-dried oxide: C, 54·4; H, 3·15. $C_{12}H_8O_2Se$ requires C, 54·7; H, 3·05%). The dihydroxide is devoid of special bactericidal activity.

Action of Sulphuric Acid on Phenoxselenine.—The deep olive-green solution of phenoxselenine (0·2490 g.) in concentrated sulphuric acid (4 c.c.) evolved sulphur dioxide. After 2 hours, it was cooled in ice–salt and completely decomposed by ice. The colourless precipitate was filtered off, dried, and extracted by chloroform, the chloroform solution being then warmed with water; the solvent was allowed to evaporate, and the dried residue extracted by cold light petroleum (b. p. 40—60°), to free it from a little insoluble phenoxselenine oxide, which was then added to the aqueous solution. The petroleum left almost pure phenoxselenine (0·1429 g.), m. p. 85—88°, representing the acceptor portion. The aqueous solution and washings were then reduced with potassium metabisulphite and the donor portion of phenoxselenine (m. p. 85—88°) was estimated as before: found, 0·1025 g. The donor portion cannot in this case be estimated as phenoxselenine oxide, owing to the great solubility of this compound in water.

Triphenoxselenylium Dibisulphate Sulphuric Acid Dihydrate (XIII).—*Preparation.* (1) The deep greenish-black solution of phenoxselenine (1 g.) in concentrated sulphuric acid (6 c.c.) was warmed gently during 5 minutes, sulphur dioxide escaping. To the cooled liquid, water (4 c.c.) was gradually added with stirring. After 36 hours, the copper-red crystals were filtered off through sintered glass, and rapidly spread on dried porous plate in a desiccator. The mother-liquor gave a further crop of the crystals when treated with more water (3 c.c.).

(2) Phenoxselenine (0·8 g.) in concentrated sulphuric acid (7 c.c.) was left during 3 hours and then treated with water (7 c.c.). After standing, the liquid deposited a crop of the copper-red crystals. The mother-liquor, treated with more water (4 c.c.), now gave on standing a mixture of the copper-red crystals with bronzed-purple crystals. On recrystallisation from hot glacial acetic acid containing a few drops of sulphuric acid, this mixture gave only the copper-red crystals.

The triphenoxselenylium compound forms large, deep copper-red, rectangular tablets from acetic acid, the crystals giving a purplish-black powder. In a sealed tube, the powder changes near 155°, and then melts at 168° to a deep greenish-black liquid. The solution in sulphuric acid is olive-green, becoming violet on dilution or warming (reversible change). The substance is stable in moist air for only a few hours, being then gradually hydroxylated with loss of colour. Analysis showed that the substance was unaltered (merely purified) by crystallisation from acetic acid (Found in unrecrystallised substance: C, 38·8; H, 3·15. Found in substance crystallised from acetic acid alone: C, 40·5; H, 3·3; S, 8·6. Found in substance crystallised from acetic acid containing sulphuric acid: C, 40·4; H, 3·1; S, 8·65. $C_{36}H_{32}O_{17}S_3Se_3$ requires C, 40·4; H, 3·0; S, 9·0%).

Hydroxylation of the Triphenoxselenylium Compound.—On treatment with cold water the substance breaks up quantitatively into sulphuric acid, phenoxselenine, and phenoxselenine oxide.

(1) Specimen crystallised from acetic acid alone: 0·2576 g., treated with 10 c.c. of water and titrated in presence of methyl-orange, required 13·8 c.c. of *N*/10-sodium carbonate. The acceptor phenoxselenine (m. p. 87—88°) was extracted with ether: found, 0·1200 g. Hence 1 g. requires 53·6 c.c. of *N*/10-alkali; and acceptor phenoxselenine amounts to 46·6%.

(2) Specimen crystallised from acetic acid containing a few drops of sulphuric acid: 0·5237 g., treated with 20 c.c. of water, required 28·2 c.c. of *N*/10-caustic soda. The acceptor phenoxselenine (m. p. 87—88°) amounted to 0·2446 g. The aqueous liquid was reduced

with potassium metabisulphite, and the donor phenoxselenine (m. p. 87—88°) extracted with chloroform : found, 0·1205 g. Hence 1 g. requires 53·9 c.c. of *N*/10-alkali ; acceptor phenoxselenine amounts to 46·7% ; donor phenoxselenine to 23·0% ; and total phenoxselenine to 69·7%.

From the formula $C_{36}H_{32}O_{17}S_3Se_3$ is calculated : 1 g. requires 56·1 c.c. of *N*/10-alkali ; acceptor phenoxselenine, 46·2% ; donor phenoxselenine, 23·1% ; and total phenoxselenine, 69·35%.

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