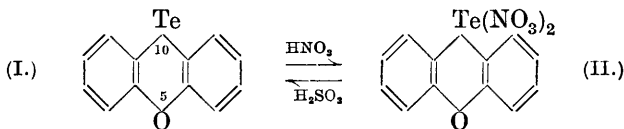


CCCCIX.—*Cyclic Organo-metallic Compounds. Part II. Tellurylium Compounds, a New Series of Intensely Coloured Tellurium Derivatives. The Migration of Anions in Solids.*

By HARRY DUGALD KEITH DREW.

WHEN phenoxtellurine (I) is treated with nitric acid under conditions which preclude nitration of the nucleus, it becomes intensely bluish-violet and is then transformed to colourless phenoxtellurine dinitrate (II; see this vol., p. 223). Reduction of the dinitrate with sulphurous acid gives a similar bluish-violet, intermediate substance, which is ultimately transformed completely to yellow phenoxtellurine. Each of the following processes, therefore, gives rise to an intensely coloured compound :



An insight was obtained into the nature of the phenomenon when it was found that the intense violet colour was developed on merely mixing and rubbing together the dry substances (I and II) between glass surfaces. The action of such solvents as water, alcohol, ether, benzene, and chloroform discharged the colour, reproducing the original substances, which could be recovered and

recombined. A glass rod coated with a film of the violet substance became colourless on being plunged into ether vapour, the colour returning on withdrawal into the air.

A series of nitro- and dinitro-derivatives of substance (II), of which 2-nitrophenoxtellurine 10 : 10-dinitrate and 2 : 8-dinitrophenoxtellurine 10 : 10-dinitrate are examples, was next prepared; and it was found that these substances produced similar violet compounds when combined with phenoxtellurine or with a nitro- or dinitro-derivative thereof, although, owing to steric or other hindrance, not every pair could be caused to interact (see table, p. 3066).

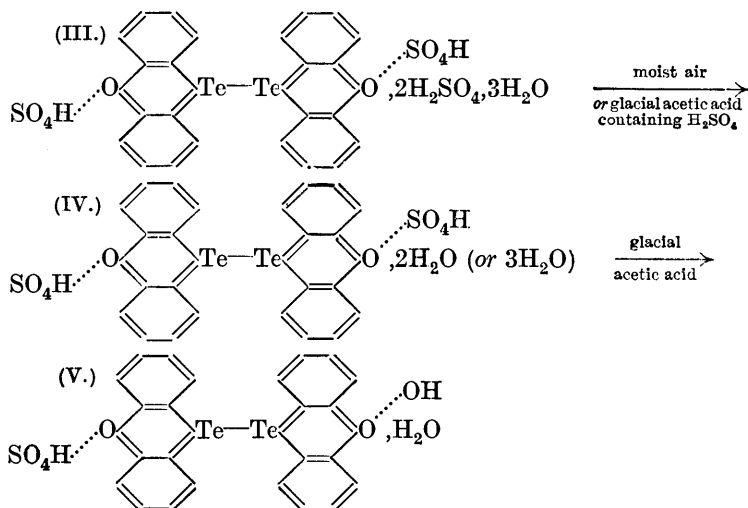
It was therefore evident that the reaction between a dinitrate, of type similar to (II), and its reduction product, of type similar to (I), occasions generally the formation of an intensely coloured substance. The object of the subsequent investigation was to elucidate the mechanism of this remarkable reaction and to find the extent of its applicability to salts other than the dinitrates.

The foregoing methods were inconvenient for the production of the coloured substances in a pure state, since the complexes containing nitrate groups underwent considerable decomposition in the most favourable solvent medium, *viz.*, warm glacial acetic acid. The possibility of substituting the less oxidising bisulphate radical for the nitrate radical was therefore examined.

The author had previously noted (*loc. cit.*) the production of an intensely red colour when phenoxtellurine was dissolved in concentrated sulphuric acid. This reaction is accompanied by the evolution of sulphur dioxide, pointing to the intermediate production of a sulphate of phenoxtellurine. To isolate the colouring matter, water was cautiously mixed in small proportion with the red solution, and the liquid allowed to stand. There separated bright red crystals of *diphenoxtellurylium dibisulphate disulphuric acid trihydrate* (III). On exposure on porous tile to moist air, this hygroscopic substance loses the attached "free" sulphuric acid, and becomes transformed quantitatively into an intensely violet-blue substance having a greenish-bronze reflex, *viz.*, *diphenoxtellurylium dibisulphate di- or tri-hydrate* (IV), in which the conditions of drying determine the final degree of hydration.

Similarly, when the red solution of phenoxtellurine in concentrated sulphuric acid was diluted with a greater proportion of water, the colour changed from red to blue with eventual production of a violet precipitate; and the latter, when crystallised from glacial acetic acid, was transformed into *diphenoxtellurylium hydroxybisulphate monohydrate* (V), which separated in copper-coloured needles giving a violet-black powder. The change was evidently

due to the removal of part of the water followed by hydroxylation of one of the bisulphate radicals of the intermediate compound (IV).



(The dotted bonds in the above and the following formulæ indicate polar linkings.)

Crystallisation of the red compound (III) from glacial acetic acid likewise resulted in the almost quantitative production of compound (V), "free" sulphuric acid and water being removed, part of the latter then producing hydroxylation. When, however, compound (III) was dissolved in acetic anhydride, which would have the effect of permanently removing the water, it was decomposed without production of (V), behaviour which confirms the foregoing view of the change in glacial acetic acid.

The above changes and the additional reactions indicated in the following statement show that the transformation of the three compounds (III, IV, and V) can be carried out in either direction :

- (i) Crystallisation of (III) from glacial acetic acid containing a little conc. H₂SO₄ yields (IV).
- (ii) Crystallisation of (V) from glacial acetic acid containing considerable conc. H₂SO₄ yields (III).
- (iii) The action of (I) on glacial acetic acid containing a little conc. H₂SO₄ yields (IV), together with SO₂.
- (iv) The action of (I) on glacial acetic acid containing more conc. H₂SO₄ yields (III), together with SO₂.

Each of the compounds (III), (IV), and (V) is decomposed into its constituents by an excess of water. The reaction is quantitative in a rough sense; and it has been shown that approximately equimolecular proportions of phenoxtellurine and its (hydroxylated

salt are produced in each case, these substances being readily separable. It thus becomes clear why the gradual addition of water to a solution of phenoxtellurine in concentrated sulphuric acid changes the red colour to blue and violet and finally leaves only a pale yellow turbidity due to phenoxtellurine.

Each of the nitro- and dinitro-substituted phenoxtellurines yields an intensely coloured violet or greenish-violet substance when its red solution in sulphuric acid is cautiously diluted with water. The same holds even in the case of 2 : 8-diaminophenoxtellurine.

Compound (V) shows remarkable behaviour in glacial acetic acid solution. It is practically insoluble in the cold; but in the hot solvent it gives intense cherry-red solutions which become very pale yellow when diluted with more solvent. Solutions sufficiently dilute to be nearly colourless when hot develop intense cherry-red colorations on cooling, whilst more concentrated solutions become cherry-red and then deep violet-blue on cooling, owing to the deposition of the finely-divided solid. Compound (IV) shows similar behaviour.

It will be clear that, on the foregoing hypothesis, the violet compounds (IV and V) result from a combination of phenoxtellurine and its dibisulphate or hydroxybisulphate. To confirm this view, it was necessary to combine these constituents directly.

To obtain the sulphate, it was found best to prepare first *phenoxtellurine* 10 : 10-diacetate, $O \left\langle \begin{array}{c} C_6H_4 \\ C_6H_4 \end{array} \right\rangle Te(O \cdot CO \cdot CH_3)_2$ (VI). This was readily obtained, in the form of colourless needles soluble in organic solvents, by the action (i) of hydrogen peroxide, or (ii) of sodium nitrite, upon a glacial acetic acid solution of phenoxtellurine; and these reactions were found to be of general application to the members of the phenoxtellurine and *cyclotelluropentanedione* series of tellurides.

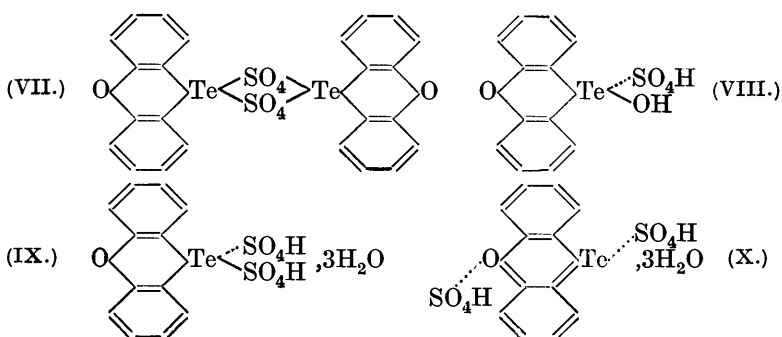
The use of an excess of hydrogen peroxide occasions the production of *phenoxtellurone*, an insoluble white powder (see experimental section).

When a solution of phenoxtellurine diacetate (VI) in boiling water was treated with sulphuric acid, a crystalline sulphate separated, which, on recrystallisation from sulphuric acid, gave crystals whose composition depended upon the concentration of acid present. With the minimum of sulphuric acid necessary to cause precipitation, almost colourless needles of *phenoxtellurine sulphate* (VII; or, less probably, its monomeric form) separated. This substance occasioned little, if any, development of colour with phenoxtellurine.

From more strongly acid solutions, cream-coloured crystals were

obtained, approximating in composition to a complex compound (see experimental section) containing phenoxtellurine hydroxybisulphate (VIII). This substance (or mixture) gave considerable development of violet colour when rubbed with phenoxtellurine.

When, however, the crude sulphate was dissolved in warm concentrated sulphuric acid, and a relatively small proportion of water added, the orange solution crystallised on cooling to a mass of yellow plates, which, after being drained on clay in a desiccator, became transformed into pale yellow *phenoxtellurine dibisulphate trihydrate* (IX), obtained in a pure state.



This substance combined with tellurides to form intensely violet products. With phenoxtellurine, either in the dry state or in presence of glacial acetic acid, compound (IV) was produced; and, from it, compounds identical with (III) and (V) were readily obtained in the pure condition.

These syntheses demonstrate the truth of the initial hypothesis.

Phenoxtellurine dibisulphate, unlike the dinitrate and diacetate, is yellow. Its solution in sulphuric acid is bright yellow, or orange-red when hot or concentrated. For this reason, formula (X) must be considered as an alternative to formula (IX), or, at least, as representing a possible phase. In any case, phenoxtellurine dibisulphate behaves as a salt, and must be considered to possess one anion in the phase represented by (IX), and possibly two anions in that represented by (X).

When phenoxtellurine diacetate is treated with syrupy phosphoric acid or with a concentrated solution of perchloric acid, salts are obtained which resemble the dinitrate and dibisulphate in that they give rise to intensely coloured tellurylium compounds (although of a bluer shade) when combined with tellurides. The salts are probably di-dihydrogen phosphates and diperchlorates, respectively. They and the derived tellurylium compounds are extremely sensitive to moisture.

Telluride salts containing nitrate, bisulphate, dihydrogen phosphate, or perchlorate radicals therefore possess an anion, and, when this migrates from tellurium (as in X), a further anion may develop. The tellurium atom in these cases is satisfied with one polar and three non-polar bonds; but where chloride, bromide, or acetate radicals are present, the compounds are non-polar and do not give rise to coloured complexes. The tellurium atom is here associated with four non-polar bonds. Quadrivalent tellurium can thus be associated with 54 or with 56 electrons.

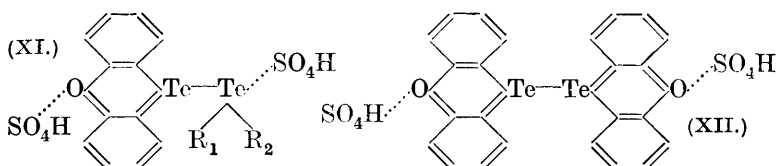
When phenoxtellurine dibisulphate (IX) is treated with hot aqueous barium chloride, it gives 10:10-dichlorophenoxtellurine (*loc. cit.*), from which the dibisulphate is regenerated by warming with concentrated sulphuric acid. The latter reaction gives a further general method for the preparation of the dibisulphates of the phenoxtellurine series.

Mechanism of the Development of the Coloured Complex.

A large number of experiments have shown that a coloured complex of this series is developed only by the interaction of a telluride and a salt of the type already indicated. The author considers it probable that the process involves *the migration of an anion from the salt member to the reduced (telluride) member of the pair of generators*, accompanied by union of the two residues.

The salt member (*e.g.*, II) would thus become the "donor" of an acid radical, the reduced member (*e.g.*, I) being the "acceptor." For the sake of brevity, these terms will be employed in the following discussion. The presence of the phenoxtellurine ring system in one member of this pair of generators is essential.

Evidence has been obtained that coloured complexes of the type shown in (XI), in which the right-hand member may be any



organic telluride or sulphide, are capable of existence; but these substances are so readily dissociated that it has hitherto proved impossible to isolate any of them in a pure condition.

Each of the coloured complexes so far obtained in a pure state belongs to the type (XII), in which occur two phenoxtellurine (or substituted phenoxtellurine) rings.

The following table shows the types of substances capable of

producing coloured complexes by interaction with acceptors or donors of the phenoxtellurine series.

Donors.

Salts of phenoxtellurine, etc.
 Salts of *cyclotelluropentanediones*.
 Salts of diethyl sulphide (not isolated).
 Basic tellurium nitrate or sulphate.
 Concentrated nitric or sulphuric acid.

Acceptors.

Phenoxtellurine, etc.
*cyclo*Telluropentanediones.
 Tellurodiacetic acid.
 Ditellurodiacetic acid.
 Diethyl sulphide.
 Hydrogen sulphide.
 Sulphurous acid.
 Base metals (Fe, Cu, Na, etc.).
 1 : 2-Dihydroxybenzenes (pyrogallol).

* The majority of the *cyclotelluropentanediones* can be employed only in the dry way, since the mixed products are decomposed by hot acetic acid with liberation of tellurium. Only the products from 4 : 4-dialkyl*cyclo*-telluropentanediones are stable to acetic acid.

The reactions of tellurides with phenoxtellurine dibisulphate afford a very delicate test for the presence of these substances.

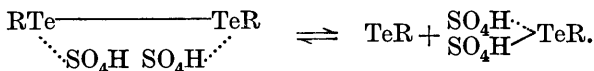
These apparently unrelated reactions are unified by adopting the hypothesis that in every case of interaction between a donor and an acceptor there occurs *an exchange of anions from the former for an equal number of electrons from the latter*. The exchange is followed by the union of the two residues with production of the coloured complex, the extent to which this is formed being governed by the prevailing conditions of temperature and concentration as well as by the nature of the interactants.

Substances which act as donors or acceptors but do not themselves enter into the molecule of the resulting complex are intermediary suppliers or receivers of anions. They create donors or acceptors, respectively, of the phenoxtellurine series.

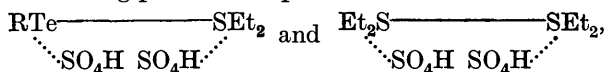
Thus, between diethyl sulphide and phenoxtellurine dibisulphate there is set up the equilibrium :



where R represents the bivalent carbon grouping of phenoxtellurine. Free phenoxtellurine is therefore present in the system and unites with its dibisulphate to give the violet complex, which is in turn in equilibrium with its constituents :



The two remaining possible complexes, *viz.*,



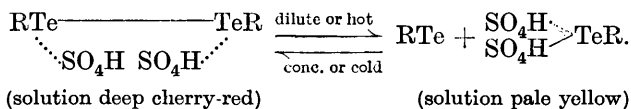
are similarly in equilibrium with their constituents. Naturally, the tendency towards formation of some of the possible complexes

will be small or nil and will in general be governed by the affinities of the active atoms (Te and S in the above case) for anions and by the tendency of these atoms to unite together.

The system in dilute solution is therefore equivalent to one in which there are present in equilibrium only the uncharged substances RTe and Et_2S and the ions $\bar{S}O_4H, RTe^+(SO_4H)$ and $Et_2\bar{S}(SO_4H)$.

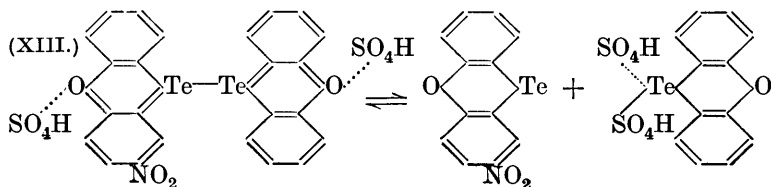
That this is so has been shown by a variety of experiments; e.g., (i) in the above case, phenoxtellurine dibisulphate becomes violet in gaseous diethyl sulphide; excess of the gas (or presence of liquid diethyl sulphide) changes the colour to red; the violet solid loses diethyl sulphide and becomes pale yellow when removed from the gas. Crystallisation of the violet solid from glacial acetic acid gives only compound (V) in small yield. If phenoxtellurine dibisulphate is exposed on clay to the vapour of diethyl sulphide, a part of it remains permanently violet, showing that a small proportion of $Et_2S(SO_4H)_2$ has been absorbed by the clay, its removal disturbing the normal equilibrium. (ii) The combination of a pair R^1Te and $R^2Te(SO_4H)_2$ gives the same result as that of the reversed pair, R^2Te and $R^1Te(SO_4H)_2$. Thus 4-ethylcyclo-telluropentanedione and phenoxtellurine dibisulphate, when combined as solids or in acetic acid, give the same violet complex (IV or V) as does the combination of 4-ethylcyclo-telluropentanedione dibisulphate and phenoxtellurine.

A parallel result occurs when R^1Te and R^2Te represent two different members of the phenoxtellurine series. (iii) The behaviour in glacial acetic acid solution of compound (IV) precisely corresponds with the scheme :



The colour of hot dilute solutions is of the same order of intensity as that of phenoxtellurine alone.

Moreover, when the analogous compound (XIII) is similarly treated, hot dilute solutions show the much enhanced yellow colour due to free 2-nitrophenoxtellurine.



(iv) When a subsidiary reaction can occur to disturb the equilibrium, there is the expected quantitative production of a violet complex. Thus, gaseous or dissolved hydrogen sulphide almost completely converts phenoxtellurine dibisulphate into a violet complex (IV or V), because the intermediate compound $\text{H}_2\text{S}(\text{SO}_4\text{H})_2$ changes rapidly to sulphur and sulphuric acid. Diethyl sulphide, however, has no permanent action, because the corresponding compound $\text{Et}_2\text{S}(\text{SO}_4\text{H})_2$ cannot undergo such a change. Similarly, liquid or gaseous sulphur dioxide has no action upon phenoxtellurine dibisulphate, but the addition of water causes conversion into the violet complex. The compound $\text{SO}_2(\text{SO}_4\text{H})_2$ is stable; while the hydrated substance, $\text{SO}(\text{OH})_2(\text{SO}_4\text{H})_2$, undergoes change to sulphur trioxide and sulphuric acid. It is not suggested that compounds such as $\text{SO}_2(\text{SO}_4\text{H})_2$ are present in more than a minute proportion. The smallest proportion would suffice were the compound immediately removed by a subsidiary reaction.

The reverse phenomenon is seen in the action of sulphuric and nitric acids upon phenoxtellurine. The acids supply anions to tellurium in exchange for electrons, leaving nascent (uncharged) hydrogen, which is removed by its subsidiary reducing action upon the excess of acid.

Reducing agents are thus pictured as those which can supply electrons and receive anions, oxidising agents receiving electrons and supplying anions. (Compare the oxidising action of nitrous acid upon phenoxtellurine, see p. 3057, in which hyponitrous acid or nitric oxide is doubtless formed.)

Some of the phenomena seem to suggest that acceptors in solution are to some extent separated from their unshared valency electrons (extra-valency electrons).

It is suggested that basic tellurium nitrate, which is known to have the empirical formula $2\text{TeO}_2 \cdot \text{HNO}_3$, has the structure $\text{OTe} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{Te} \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{NO}_3 \end{array}$, and that the donor prepared by the author from tellurium tetrachloride and concentrated sulphuric acid is the analogous bisulphate or dibisulphate.

In the case of *o*-dihydroxybenzenes (pyrogallol), the oxygen atoms probably receive the anions, which are immediately removed by a subsidiary reaction, such as the formation of *o*-quinones and sulphuric acid.

Colour Development with Metals.

On rubbing phenoxtellurine dibisulphate (IX) upon porous tile with a steel knife, a surprising development of intense violet colour was noted. The same action occurred with all the other base metals tried (Na, Al, Fe, Ni, Cu, Zn, Sn, As, Sb), used either in

the form of polished strips or as powder, but no effect was produced with the noble metals (Ag, Pt, Au, and also Hg); sulphur and tellurium were also devoid of action. The reaction can therefore be used to distinguish base from noble metals.

The members of the phenoxtellurine dinitrate series behave generally in the same manner, but the corresponding salts of those tellurides which do not contain a phenoxtellurine ring produce no colorations with the metals.

The base metals exhibit selective action towards different anions. Iron, for example, produces a coloration with both dinitrate and dibisulphate of phenoxtellurine; copper or nickel, only with the latter salt. These reactions therefore afford a rough indication of the relative attractions of different metals for certain anions.

The base metals do not enter into the molecule of the violet substances which they produce in this manner. The action of the metallic particles is to remove anions, in exchange for electrons, from the salt molecules, forming free phenoxtellurine, which then combines with unchanged salt to produce substances (IV) and (V). Salts of the metals are thus present in equilibrium with the violet tellurium compounds, and in the case of the dibisulphate the balance is controlled by the proportion of water present. This is rendered visible in the action of iron upon phenoxtellurine dibisulphate, for the violet mixture becomes red when dried on clay in a desiccator, but the violet colour is restored on exposure to moist air. In this alternation, which can be repeated indefinitely, the red stage denotes the presence of compound (III), and the violet that of compound (IV) or (V). The hydrated iron sulphate or basic sulphate present must therefore have a greater affinity for sulphuric acid than the corresponding anhydrous iron salt, the affinity of compound (IV) for sulphuric acid being intermediate between these two values. When nickel is substituted for iron, reversibility is no longer manifest, the violet stage being permanent.

The above view of the action of base metals upon the salts of phenoxtellurine is supported by the fact that the violet mixtures produced by the action of such metals are decomposed by water with liberation of "free" phenoxtellurine, which is obtained in a pure state by extraction with ether.

Pairs containing Mixed Nuclei.

A preliminary study has been made of the action between phenoxtellurine dibisulphate and 2-nitrophenoxtellurine. The violet-blue product, when crystallised from glacial acetic acid, was found to be a mixture of the complex derived from 2-nitrophenoxtellurine with the salt of phenoxtellurine, together with a much smaller

proportion of the complex derived from phenoxtellurine and its salt. 2-Nitrophenoxtellurine did not occur as a donor, two of the possible four coloured complexes being thus eliminated. The reversed pair (2-nitrophenoxtellurine dibisulphate and phenoxtellurine) gave an exactly similar product.

The tellurium atom in phenoxtellurine has thus a much greater affinity for bisulphate radicals than has that in 2-nitrophenoxtellurine.

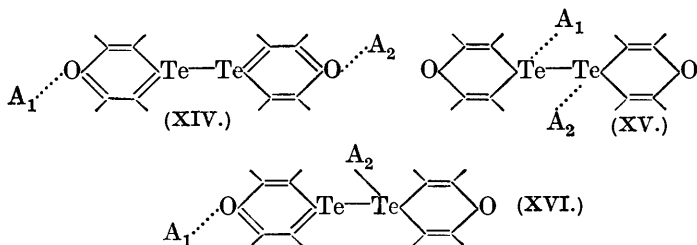
This behaviour affords a means of pitting, as it were, two differently combined tellurium atoms against one another in contest for a series of anions, and enables, for example, the effect of different ring substituents upon the electropositeness of the tellurium atom in phenoxtellurine to be assessed.

The method of examining a coloured complex consists in treating it with water, when the acceptor is set free and can be extracted by ether; the residual salt can then be reduced by adding potassium bisulphite, and the nucleus of the donor again extracted by ether. The products are insoluble in water, so that fresh equilibria cannot presumably be set up.

The addition of a molecular proportion of phenoxtellurine dibisulphate, which is insoluble in ether, to 2:4-diethylcyclo-telluropentanedione dissolved in ether led to the precipitation of blue complexes and the rapid removal of the *cyclo*telluropentanedione from solution, its place being supplied by free phenoxtellurine. The tellurium atom of this *cyclo*telluropentanedione has therefore a much greater affinity for bisulphate radicals than has that of phenoxtellurine.

These methods should yield results of value in the study of the polarity of groups.

Colour production among the tellurylium compounds is ascribed to the occurrence of the structure (XIV), in which A_1 and A_2



represent HSO_4 , ClO_4 , NO_3 , H_2PO_4 , or OH radicals; but it should be pointed out that structures (XV) and (XVI) are possible alternatives. Again, tellurium might conceivably be joined to "oxonium" oxygen, or the two oxygen atoms might be united. These

formulæ, however, do not reflect so well as (XIV) the fact that the presence of the phenoxtellurine ring is essential, such substances as diphenyl ether yielding no coloured complexes.

The reason why A_1 and A_2 cannot represent Cl, Br, or $\text{CH}_3\cdot\text{CO}\cdot\text{O}$ is probably the very small tendency of these radicals to ionise when united with tellurium. The tendency nevertheless exists, for reduction is possible in these instances when a subsidiary reaction can occur.

It is noteworthy that each of the mobile acid radicals possesses doubly-bonded oxygen. The nitrate ion appears to be mobile even in reaction between dry solids (phenoxtellurine and its anhydrous dinitrate).

Phenothioxin, which gives an intensely violet solution in concentrated sulphuric acid, probably forms a series of coloured salts, and it is hoped to apply to that problem the experimental methods developed in the present paper. The foregoing principles have also possible application in many other directions. The author desires to reserve for the present the study of this subject.

EXPERIMENTAL.

Phenoxtellurine 10 : 10-dinitrate (II), large, colourless needles or glistening plates, m. p. 258° (efferv.), was prepared by crystallising phenoxtellurine (1 g.) from nitric acid (105 c.c., made by diluting 2 vols. of the concentrated acid with 1 vol. of water). It is stable in moist air, but is slowly hydroxylated by water (Found : C, 34.4; * H, 2.0.* $\text{C}_{12}\text{H}_8\text{O}_7\text{N}_2\text{Te}$ requires C, 34.3; H, 1.9%).

The following were similarly prepared from the nitro-derivatives of phenoxtellurine :

2-Nitrophenoxtellurine 10 : 10-dinitrate formed minute, colourless needles, m. p. $196\text{--}197^\circ$ (efferv.), from dilute nitric acid and was slowly decomposed by moist air (Found : N, 8.2.* $\text{C}_{12}\text{H}_7\text{O}_9\text{N}_3\text{Te}$ requires N, 9.1%).

2 : 8-Dinitrophenoxtellurine 10 : 10-dinitrate crystallised from concentrated nitric acid in large, colourless, serrated needles, m. p. 259° (efferv.). It was slowly decomposed by moist air (Found : N, 10.0.* $\text{C}_{12}\text{H}_6\text{O}_{11}\text{N}_4\text{Te}$ requires N, 11.0%).

When a 4-nitro-group was present in the phenoxtellurine ring, basic nitrates appeared to be produced, for which the following constitutions are conjectured :

4-Nitro-10-hydroxyphenoxtellurine 10-nitrate monohydrate crystallised from dilute nitric acid in minute, white rods, m. p. 243° (decomp.) (Found : N, 6.3.* $\text{C}_{12}\text{H}_{10}\text{O}_8\text{N}_2\text{Te}$ requires N, 6.4%).

4 : 8-Dinitro-10-hydroxyphenoxtellurine 10-nitrate monohydrate

* Indicates a figure obtained by micro-analysis.

separated from concentrated nitric acid in small, white needles, which decomposed violently at 237—239° (Found : C, 30.4* ; H, 1.9* ; N, 8.9,* 9.1,* 9.2.* $C_{12}H_9O_{10}N_3Te$ requires C, 29.9 ; H, 1.9 ; N, 8.7%).

Reduction of the above nitrates and basic nitrates showed that further nitration of the nucleus had not occurred during the treatment with nitric acid.

Note.—The micro-Dumas method of analysis for nitrogen, which was employed to obtain the above figures, appears to give results which are only approximate for tellurium compounds containing nitrate groups. The results are recorded, therefore, merely for reference. The method is accurate when applied to tellurium compounds containing the whole of the nitrogen in the form of nitro-groups.

The nitrates were unaffected by liquid sulphur dioxide, but the addition of a trace of water to the mixture caused in several cases the instant development of a violet colour, which changed to the yellow or orange of the reduction product on the addition of more water. The permanence and intensity of the violet coloration varied among different members of the series.

The following phenomena were noted on rubbing together between glass surfaces the substances indicated :

Acceptor.	Donor (in form of nitrate or basic nitrate).	Colour produced.
Phenoxtellurine.	Phenoxtellurine.	Intense violet.
2-Nitrophenoxtellurine.	Phenoxtellurine.	" "
Phenoxtellurine.	2 : 8-Dinitrophenoxtellurine.	Feeble violet.
2-Nitrophenoxtellurine.	2-Nitrophenoxtellurine.	Rather feeble violet.
2 : 8-Dinitrophenoxtellurine.	Phenoxtellurine.	None.
2 : 8-Dinitrophenoxtellurine.	2 : 8-Dinitrophenoxtellurine.	None.
Phenoxtellurine.	4 : 8-Dinitrophenoxtellurine.	Intense violet.
4 : 8-Dinitrophenoxtellurine.	4 : 8-Dinitrophenoxtellurine.	None.

These results clearly indicate the inhibitory effect of an accumulation of nitro-groups upon the ease of development of the coloured compounds, especially when the nitro-groups are in the 2- and 8-positions (*i.e.*, meta- to the tellurium atom). That this effect is due less to a depression of mobility of the nitrate ion than to a depression of receptiveness in the tellurium atom of the acceptor is shown by the fact that the effect is greater when the nitro-groups are in the acceptor than when they are in the donor of the same pair. In other words, the presence of nitro-groups in the acceptor depresses the mobility of the electron available for exchange.

Diphenoxtellurylium dibisulphate disulphuric acid trihydrate (III) was prepared by the following methods : (1) *Action of sulphuric*

* Indicates a figure obtained by micro-analysis.

acid on phenoxtellurine. Phenoxtellurine (6 g.) was dissolved in concentrated sulphuric acid (40 c.c.), and the intensely red solution kept for $\frac{1}{2}$ hour, sulphur dioxide escaping. The liquid was then cooled in ice and salt, and water (25 c.c.) gradually stirred in. After about an hour, the red crystals were filtered off through sintered glass and kept on porous tile in a desiccator. The same substance was produced when 1.1 g. of phenoxtellurine was treated with 15 c.c. of concentrated sulphuric acid and 10 c.c. of water. The yield is about 94% of the theoretical [Found: C, 27.5; H, 2.9; O, 32.5 (by diff.); S, 12.6; Te, 24.5. $C_{24}H_{28}O_{21}S_4Te_2$ requires C, 27.8; H, 2.7; O, 32.5; S, 12.4; Te, 24.6%]. The red crystals were hygroscopic, becoming moist with sulphuric acid and gaining about 30% of their weight of water when exposed to air for several days in a glass dish. When exposed on clay, the substance lost sulphuric acid and was transformed quantitatively into the greenish-violet compound (IV). Gaseous ammonia occasioned a similar change. When the red crystals (0.544 g.) were treated with cold water (15 c.c.), decomposition ensued and phenoxtellurine (0.13 g.; calc., 0.155 g.) became extractable by ether. The residue, after reduction by aqueous potassium bisulphite, gave a further molecular proportion of phenoxtellurine (0.155 g.; calc., 0.155 g.). The red crystals had no definite melting point, becoming slowly blue-black near 100° and decomposing indefinitely near 165° to a black mass which became violet above about 235° but did not melt.

(2) Phenoxtellurine was dissolved in glacial acetic acid, and a considerable proportion of concentrated sulphuric acid containing a little water added; the red crystals separated on keeping.

(3) When either of the violet substances (IV and V) was treated with sulphuric acid containing a little water, or with acetic-sulphuric acid, the red crystals were produced, provided the concentration of sulphuric acid was sufficiently high.

(4) The same result was obtained by mixing phenoxtellurine and its hydrated dibisulphate (IX) in glacial acetic acid and adding a little concentrated sulphuric acid.

Diphenoxtellurylium hydroxybisulphate monohydrate (V) was prepared (1) by dissolving phenoxtellurine in warm glacial acetic acid and adding a few drops of concentrated sulphuric acid, the intensely coloured solution crystallising on cooling; (2) by crystallising the red substance (III) or the greenish-violet substance (IV) several times from glacial acetic acid, with filtration through sintered glass, if necessary; (3) by warming together, in glacial acetic acid, phenoxtellurine and its hydrated dibisulphate (IX) and recrystallising the product from glacial acetic acid; (4) by dissolving phenoxtellurine in concentrated sulphuric acid, cautiously stirring in water until

the solution began to deposit a blue precipitate, allowing it to stand, and then collecting the precipitate and crystallising it from glacial acetic acid; (5) by grinding together phenoxtellurine and its hydroxybisulphate or dibisulphate and recrystallising the product from glacial acetic acid.

The product forms copper-coloured flakes or rosettes of needles giving a violet-black powder. It has no definite melting point, losing colour gradually at 205—245° and forming phenoxtellurine and a whitish solid which is unmelted at 300°. Heated at 100° in a vacuum, it does not lose its molecule of combined water. The change on heating represents a decomposition into phenoxtellurine and its hydroxybisulphate, since partial redevelopment of violet colour occurs on cooling and grinding the whitish mixture.

The compound is decomposed only slowly by ether and other organic solvents (contrast the similar substances containing nitrate radicals, which are decomposed much more rapidly), but it is quickly disrupted by cold water; *e.g.*, 0.404 g., on being shaken with 10 c.c. of water, generated a molecular proportion of free phenoxtellurine (0.186 g.; calc., 0.166 g.), which was extractable by ether [Found: C, 39.7, 39.6, 39.6; H, 2.6, 2.5, 2.9; O, 17.5 (by diff., in a single sample); S, 4.0, 4.9; Te, 35.1. $C_{24}H_{20}O_8STe_2$ requires C, 39.8; H, 2.8; O, 17.7; S, 4.4; Te, 35.25%].

When pure, the substance gives in hot glacial acetic acid a clear solution which is colourless when dilute and intensely cherry-red when concentrated. Cold solutions are much more coloured than hot solutions of the same concentration. Solutions in glacial acetic acid immediately reduce anhydrous ferric chloride. The compound dissolves in syrupy phosphoric acid to an intensely blue solution.

Diphenoxtellurylium dibisulphate di- or tri-hydrate (IV) is best prepared by leaving the powdered red substance (III) on porous tile in moist air for a few days, with occasional turning. A deep bluish-black, stable, crystalline powder, with greenish reflex, remains. It may also be prepared by any of the methods indicated for the hydroxy-compound (V), if the product be crystallised finally from glacial acetic acid containing a little concentrated sulphuric acid (too great a proportion of sulphuric acid leads to the production of III). Two different samples were prepared by the first method, one being apparently a di- and the other a tri-hydrate; the difference is probably due to a slight variation in the conditions during drying [Found, for sample prepared by transforming V to III and then exposing this to air and finally drying it on clay in a desiccator during 2 days: C, 34.5; H, 2.9. $C_{24}H_{24}O_{13}S_2Te_2$ (the trihydrate) requires C, 34.35; H, 2.85%. Found, for sample

prepared by crystallising III from glacial acetic acid containing 4% by volume of concentrated sulphuric acid, and then exposing the product on clay and finally drying it in a vacuum over sulphuric acid during 12 hours : C, 35.3; H, 2.8; O, 22.9 (by diff.); S, 7.3; Te, 31.7. $C_{24}H_{22}O_{12}S_2Te_2$ (the dihydrate) requires C, 35.1; H, 2.7; O, 23.3; S, 7.8; Te, 31.05%. The dihydrate seemed slowly to absorb moisture when exposed to the air. Both the di- and the tri-hydrate were decomposed by cold water, first into sulphuric acid and compound (V), and finally into phenoxtellurine and its basic bisulphate.

Phenoxtellurine 10 : 10-Diacetate (VI).—A solution of phenoxtellurine in hot glacial acetic acid was allowed to cool and then aqueous hydrogen peroxide was stirred in drop by drop until the yellow colour of the solution was discharged. The solution was heated to boiling and treated with sufficient water to produce a faint turbidity; the diacetate slowly separated in long, colourless needles. Concentration of the mother-liquor gave a further crop, the total yield being more than 90% of the theoretical. The substance is soluble in hot water with hydrolysis, sparingly soluble in ether or petroleum, and easily soluble in hot benzene, from which it crystallises readily. It gave no coloration when ground with phenoxtellurine or with metals (Found : C, 46.5; H, 3.4. $C_{16}H_{14}O_5Te$ requires C, 46.4; H, 3.4%). The diacetate melts with effervescence at 205—207°. It is readily reduced to phenoxtellurine by aqueous alkali bisulphites.

Phenoxtellurone, $O\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle TeO_2$.—When phenoxtellurine is dissolved in acetone and treated with an excess of 30% aqueous hydrogen peroxide, a white, amorphous precipitate is thrown down. The same result occurs if an excess of hydrogen peroxide be used in the preparation of phenoxtellurine diacetate. The substance, which is insoluble in water or acetone but soluble in hot glacial acetic acid, is reduced to the tellurous state by concentrated sulphuric or hydrochloric acid, oxygen or chlorine being evolved with production of a salt of phenoxtellurine. Hydriodic acid promotes a similar reduction, with liberation of iodine. The product is insoluble in dilute mineral acids but is soluble in aqueous caustic alkali. After heating in a vacuum at 110° during an hour, it had the composition of the half-anhydride of the semi-ortho-form of the tellurone, *viz.*, $O\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle Te(O)(OH)\cdot O\cdot(OH)(O)Te\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle O$ (Found : C, 42.5; H, 2.7. $C_{24}H_{18}O_7Te_2$ requires C, 42.8; H, 2.7%).

Sulphates of Phenoxtellurine.—Phenoxtellurine 10 : 10-diacetate (7.1 g.) was heated with 300 c.c. of water, nearly all dissolving.

To the hot solution was added a mixture of 100 c.c. of water and 100 c.c. of concentrated sulphuric acid, and the whole was heated to the boiling point. The clear solution obtained, on cooling, gave 6.5 g. of cream-coloured crystals.

Portions of this substance were then crystallised from sulphuric acid of various concentrations, and the products examined: (i) The material was dissolved in a large volume of boiling water, and to the cold solution a minimum of sulphuric acid was added to effect separation of crystals. The liquid slowly deposited *phenoxtellurine sulphate* (VII) in thin, almost colourless, very refractive needles, which became slightly cream-coloured on drying on clay in a vacuum during a day (Found: C, 36.5, 36.7; H, 2.4, 2.5. $C_{24}H_{16}O_{10}S_2Te_2$ requires C, 36.8; H, 2.05%). This substance developed only a trace of colour when ground with phenoxtellurine.

(ii) The material was dissolved in a boiling mixture of 1 vol. of concentrated sulphuric acid and 1.22 vols. of water. Voluminous cream-coloured flakes separated, and these, after being drained on clay and then heated during 5 hours at about 115° in a vacuum (loss = 2.4%), gave analytical figures which corresponded with a mixture or *compound* containing two molecular proportions of phenoxtellurine hydroxybisulphate (VIII) and one of phenoxtellurine dibisulphate, together with a molecule of water [Found: C, 32.3, 32.35; H, 2.6, 2.6; O, 26.5 (by diff.); S, 9.4; Te, 29.1. $C_{36}H_{32}O_{22}S_4Te_3$ requires C, 32.55; H, 2.4; O, 26.5; S, 9.65; Te, 28.8%]. The substance gave a violet colour when ground with phenoxtellurine. Its solution in concentrated sulphuric acid was orange-red.

(iii) When the material was dissolved, with gentle warming, in concentrated sulphuric acid (1.7 g. to 10 c.c. of acid) and the clear orange-red solution treated with the minimum of water (about 1 c.c.) sufficing to cause slow separation of crystals, bright yellow, glistening plates were obtained. When filtered off rapidly through sintered glass and drained on clay in a vacuum, the crystals changed to a creamy-yellow powder of *phenoxtellurine dibisulphate trihydrate* (IX) [Found: C, 26.4; H, 3.0; O, 34.5 (by diff.); S, 12.2; Te, 23.9. $C_{12}H_{16}O_{12}S_2Te$ requires C, 26.5; H, 2.9; O, 35.3; S, 11.8; Te, 23.5%]. The substance gave an intense violet coloration with phenoxtellurine and other tellurides, or with iron and other base metals. Its solution in sulphuric acid became intensely red-brown on addition of hydrogen peroxide.

Each of the above sulphates of phenoxtellurine, when reduced by alkali bisulphite, gave phenoxtellurine as the sole organic product, showing that in no case had nuclear sulphonation occurred.

Note on the Analysis of Aromatic Tellurium Compounds containing

Sulphur.—It was found necessary, in determining sulphur and tellurium in the same sample, to adopt the following procedure: The sample was heated with fuming nitric acid during 24 hours at 250—280° in a Carius tube, the contents of the tube dissolved in about 100 c.c. of concentrated hydrochloric acid, and the solution evaporated to a few c.c. on the water-bath. The residue was taken up in dilute hydrochloric acid (about 200 c.c.), with filtration from traces of glass or silica if necessary. Sulphur was estimated by digestion during 12 hours with a slight excess of barium chloride. The liquid (filtrate from barium sulphate) was then freed from excess of barium by digesting it similarly with a slight excess of sulphuric acid and evaporated completely on the water-bath, and tellurium was estimated in the residue by the usual method.

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