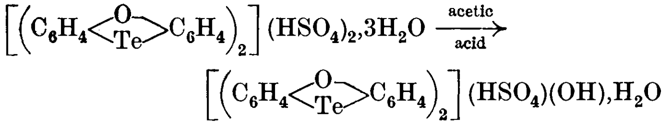
LXV.—*Cyclic Organo-metallic Compounds. Part IV. Tellurylium Compounds* (continued).

By HARRY DUGALD KEITH DREW.

WHEN hydrated diphenoxtellurylium dibisulphate (I), or the complex (IV) which it forms with two molecules of sulphuric acid, is crystallised from glacial acetic acid, it is transformed to a deeply coloured, bronzed substance which was described (J., 1926, 3055) as diphenoxtellurylium hydroxybisulphate monohydrate (II) :



$$\text{(I.)}\quad \left[\left(C_6H_4{<}\genfrac{}{}{0pt}{}{O}{Te}{>}C_6H_4\right)_2\right](HSO_4)_2,3H_2O \xrightarrow[\text{acid}]{\text{acetic}} \left[\left(C_6H_4{<}\genfrac{}{}{0pt}{}{O}{Te}{>}C_6H_4\right)_2\right](HSO_4)(OH),H_2O \quad \text{(II.)}$$

This substance (II) is decomposed by water into the constituent donor and acceptor, a reaction which was stated to be only approximately quantitative (*loc. cit.*), since the author obtained 46% of phenoxtellurine as acceptor instead of 40·9% demanded by theory. The method of analysis has now been improved, and, as a result, it is found that the decomposition by water is quantitative and that the true percentage of phenoxtellurine present as acceptor in the above compound is 53·5. The percentage of phenoxtellurine present in the donor form (not previously estimated) has been determined as 27·9. Two molecular proportions of phenoxtellurine are therefore present in the acceptor condition to one in the donor, and the substance formerly represented as (II) must now be described as *triphenoxtellurylium dibisulphate*, having the empirical formula (III).

The ultimate analytical figures calculated from the revised formula approximate closely to those required by the old formula and are in equally good agreement with the figures previously obtained by actual experiment :

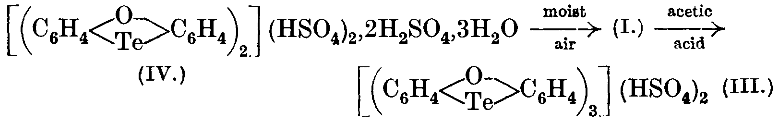
%.	Old formula.	New formula.	Found (*loc. cit.*).
C	39·8	40·0	39·7, 39·6, 39·6
H	2·8	2·4	2·6, 2·5, 2·9
O	17·7	16·3	17·5
S	4·4	5·9	4·0, 4·9
Te	35·25	35·4	35·1

Whereas, however, the old formulation requires equal amounts (40·9%) of phenoxtellurine in donor and acceptor, the new formula requires 54·7% in the acceptor and 27·3% in the donor, figures which agree with those found by experiment.

The method has been applied also to the parent compounds of the series, with the result that the structures previously assigned to them have been confirmed :

	% Phenoxtellurine			
	in acceptor.		in donor.	
Compound.	Calc.	Found.	Calc.	Found.
Diphenoxtellurylium dibisulphate disulphuric acid trihydrate (IV)	28·5	28·7	28·5	27·8
Diphenoxtellurylium dibisulphate trihydrate (I)	35·2	34·9	35·2	35·6

The changes undergone by these substances can therefore be expressed empirically in the following simple manner :

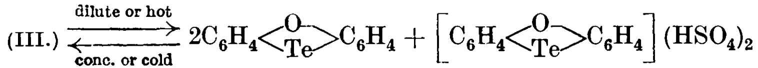


$$\left[\left(C_6H_4{<}\begin{matrix}O\\Te\end{matrix}{>}C_6H_4\right)_2\right](HSO_4)_2,2H_2SO_4,3H_2O \xrightarrow[\text{air}]{\text{moist}} \text{(I.)} \xrightarrow[\text{acid}]{\text{acetic}} \left[\left(C_6H_4{<}\begin{matrix}O\\Te\end{matrix}{>}C_6H_4\right)_3\right](HSO_4)_2$$

(IV.) (III.)

Whereas the transformation of (IV) to (I) involves, as previously given, merely the removal of two molecules of sulphuric acid, that of (I) to (III) involves the elimination, from two molecules of (I), of three molecules of water and one molecule of trihydrated phenoxtellurine dibisulphate. This reaction can only occur after dissociation of (I) into its constituent donor and acceptor, a change which has already been shown to take place in glacial acetic acid solution (*loc. cit.*, p. 3061). Recrystallisation of (IV) or of (I) from hot acetic acid was already known to lead to the separation of a residue of basic phenoxtellurine sulphate, a phenomenon previously attributed to partial hydrolysis by moisture.

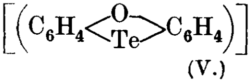
The new view of the transformation in acetic acid solution does not affect the theoretical considerations dealt with in the previous paper. The colour change undergone by the solution of compound (III) in acetic acid can be expressed by the equilibrium :



$$\text{(III.)} \underset{\text{conc. or cold}}{\overset{\text{dilute or hot}}{\rightleftarrows}} 2C_6H_4{<}\begin{matrix}O\\Te\end{matrix}{>}C_6H_4 + \left[C_6H_4{<}\begin{matrix}O\\Te\end{matrix}{>}C_6H_4\right](HSO_4)_2$$

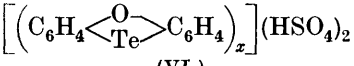
(soln. deep cherry-red) (soln. pale yellow)

Since phenoxtellurine dibisulphate trihydrate may be represented by the simple formula (V), there exists a series of compounds of the



$\left[\left(C_6H_4{<}\substack{O\\Te}{>}C_6H_4\right)\right](HSO_4)_2,3H_2O$

(V.)

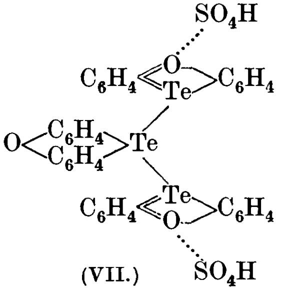


$\left[\left(C_6H_4{<}\substack{O\\Te}{>}C_6H_4\right)_x\right](HSO_4)_2$

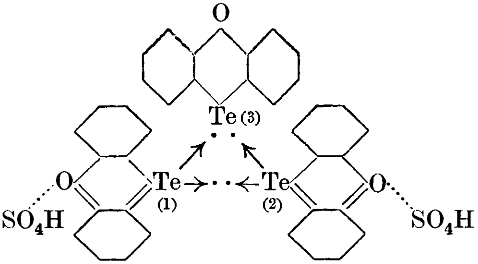
(VI.)

type (VI) in which x may be 1, 2, or 3, the various members of the series being associated with different addenda (H_2SO_4 or H_2O), or, as in (III), having no addendum. The molecule of each of these substances contains two anions, which make their appearance in a single molecule of the donor when the compound is decomposed by water, the remaining phenoxtellurine appearing as the acceptor. The ratio of phenoxtellurine in the acceptor to that in the donor is therefore $(x - 1) : 1$.

Expanded formulæ have already been given (*loc. cit.*) for compounds (I), (IV), and (V); it remains to consider compound (III). In this substance the third molecule of phenoxtellurine might be regarded as an addendum substituting $3H_2O$ in the formula of (I). It is considered probable, however, that the three tellurium atoms are actually linked together, either in a chain (VII) or in a ring (VIII). Of these alternatives, the second is preferred, since in it the three phenoxtellurine residues are equivalently situated if the formula be regarded as potentially dynamic. In the phase represented, the tellurium atoms marked (1) and (2) supply each an electron to affix tellurium atom (3), whilst they are themselves united by means of a non-polar bond (the dots show the binding electrons, and the arrows indicate the atoms whence these electrons originate; the dotted bonds represent polar linkings). At all phases of the formula, each of the three tellurium atoms is seen to be associated with 56, and each oxygen and carbon atom is associated with 10, electrons.



(VII.)



(VIII.)

This view is seen to involve the suggestion that three atoms may be held together by the sharing of 4 electrons.

Thomason and the author (J., 1927, 119) described a compound which, from ultimate analysis, they considered a complex of phenoxtellurine and 2-chloro-8-methylphenoxtellurine in molecularly equivalent proportion. This substance has now been separated into its constituents by the fractional precipitation of its chloroform solution with bromine. The phenoxtellurine is precipitated first, as the dibromide. Hence the introduction of the above nuclear substituents depresses the affinity of the tellurium atom for bromine.

The di-α-bromocamphor-π-sulphonate of chloromethylphenoxtellurine was prepared, but could not be purified owing to its tendency to hydrolyse. It yields brilliantly coloured tellurylium compounds with phenoxtellurine or substituted phenoxtellurines, so that it is necessary to add the α-bromocamphor-π-sulphonic acid anion to the list of mobile anions already given (J., 1926, 3064). From this list, for reasons which will now be apparent, the OH anion should be deleted.

EXPERIMENTAL.

Estimation of the Percentage of Phenoxtellurine present as Donor and as Acceptor in Tellurylium Compounds.—(1) *Triphenoxtellurylium dibisulphate* (III). The sample (0·5277 g.) was shaken in a stoppered extraction funnel with cold water (15 c.c.) and several times with chloroform. The filtered chloroform was allowed to evaporate at the ordinary temperature (loss of phenoxtellurine occurs at more elevated temperatures). The white aqueous suspension, treated with an excess of potassium metabisulphite, gave phenoxtellurine, which was extracted with chloroform (Found : phenoxtellurine as acceptor, 53·5 ; as donor, 27·9. Calc. for $C_{36}H_{26}O_{11}S_2Te_3$: phenoxtellurine as acceptor, 54·7 ; as donor, 27·3%).

(2) *Diphenoxtellurylium dibisulphate disulphuric acid trihydrate* (IV). The sample (0·5369 g.) was reduced with aqueous potassium metabisulphite, and the total phenoxtellurine extracted with chloroform : found, 0·3038 g. A second sample (1·7844 g.) was treated with cold water (50 c.c.) and nearly neutralised with *N*-sodium carbonate (12·9 c.c.). The acceptor phenoxtellurine was then estimated as before (Found : phenoxtellurine as acceptor, 28·75 ; as donor, 27·85. Calc. for $C_{24}H_{28}O_{21}S_4Te_2$: phenoxtellurine as acceptor, 28·55 ; as donor, 28·55%).

(3) *Diphenoxtellurylium dibisulphate trihydrate* (I). In a first sample (0·3380 g.), the total phenoxtellurine was estimated as above : found, 0·2383 g. A second sample (0·5261 g.) was treated with cold water (50 c.c.) and *N*/10-sodium carbonate (19 c.c.) as in (2) (Found : phenoxtellurine as acceptor, 34·9 ; as donor, 35·6. Calc. for $C_{24}H_{24}O_{13}S_2Te_2$: phenoxtellurine as acceptor, 35·2 ; as donor, 35·2%). In every case, the recovered phenoxtellurine was found to be pure.

Molecular Compound of Phenoxtellurine and Chloromethylphenoxtellurine : Separation into its Constituents.—The compound (8·4 g.) m. p. 59° (J. 1927, 119), was dissolved in chloroform (12 c.c.), and a solution of 2·1 g. of bromine in 20 c.c. of chloroform gradually added. Phenoxtellurine dibromide (6·4 g.) separated, and this gave on reduction phenoxtellurine which was pure after one crystallisation. The chloroform mother-liquor was precipitated again by 0·4 g. of bromine in 5 c.c. of chloroform, giving a mixture of the two dibromides. The chloroform mother-liquor from this was precipitated by 1·7 g. of bromine, yielding *chloromethylphenoxtellurine dibromide*, a yellow, crystalline substance which is very sparingly soluble in chloroform; m. p. 315° (decomp.). Its reduction by aqueous potassium metabisulphite takes place only very slowly compared with that of phenoxtellurine dibromide. The product (3·2 g.), consisting of *chloromethylphenoxtellurine*, crystallises from alcohol in minute, pale yellow, prismatic needles, m. p. 46—47° (Found : C, 45·2 ; H, 2·5. $C_{13}H_9OClTe$ requires C, 45·3 ; H, 2·6%). It is very soluble in organic solvents but insoluble in water. It forms a *dichloride*, pale yellow prisms, m. p. 300° (decomp.), from xylene ; a *diacetate*, colourless needles, m. p. 230—232° (with frothing), from acetic acid ; and a *dibisulphate*, cream-coloured scales, which acts as a donor towards tellurides, giving deep purplish-black tellurylium compounds.

Chloromethylphenoxtellurine dissolved in cold concentrated sulphuric acid to a deep maroon-red solution which evolved sulphur dioxide. On treating the solution with a little water and crystallising the resulting minute, dark red crystals from acetic acid, a dark blue-black, crystalline powder having a greenish-bronze lustre was obtained. A solution of this *tellurylium compound* in acetic acid had an intense reddish-purple colour, which became pale yellow on dilution or heating (reversible change).

The foregoing procedure for the separation of the complex compound into its constituents enables the yield of phenoxtellurine (obtained by the method described in J., 1926, pp. 230—231) to be increased, since the reduced by-products from that process can be further worked up for phenoxtellurine by treatment with bromine in chloroform solution.

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