XXXIII.—*Cyclic Organo-metallic Compounds. Part I. Compounds of Tellurium.*

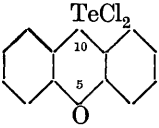
By Harry Dugald Keith Drew.

The present work has for its object the investigation of cyclic organo-metallic compounds (*i.e.*, compounds in which a metallic atom is united directly to carbon atoms, taking part therewith in ring formation), few of which have hitherto been synthesised.

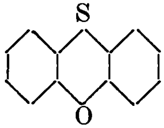
Tellurium tetrachloride and diphenyl ether slowly but almost completely condense when heated together in chloroform solution. Hydrogen chloride is evolved and a yellow telluritrichloride is formed in which the group $-TeCl_3$ has replaced a hydrogen atom of one of the aromatic nuclei. This substance is p-*phenoxyphenyltelluritrichloride* (I), $PhO{\cdot}C_6H_4{\cdot}TeCl_3$, since on reduction with aqueous potassium metabisulphite it becomes transformed to a purplish-red, crystalline substance, pp′-*diphenoxydiphenyl ditelluride* (II), $PhO{\cdot}C_6H_4{\cdot}Te{:}Te{\cdot}C_6H_4{\cdot}OPh$, which shows a normal molecular weight in freezing benzene.

The formation of these substances demonstrates that the tellurium atom can be caused to enter an aromatic nucleus without the aid of Grignard reagents (compare Morgan and Drew, J., 1925, **127**, 2307). That the group $-TeCl_3$ enters the aromatic nucleus almost exclusively in one position was shown by the absence of an isomeric telluritrichloride from the by-products of this condensation and by the homogeneity of the ditelluride resulting upon reduction.

The telluritrichloride (I) melts at 156°, but if it is heated to about 200° a further (intramolecular) condensation occurs; a molecule of hydrogen chloride is evolved, and a colourless, crystalline, cyclic compound, 10 : 10-*dichlorophenoxtellurine* (III), is produced. That this substance contains the tellurium atom in a di-ortho-position relatively to the oxygen atom is indicated both from stereochemical considerations and by the existence of structurally analogous compounds of sulphur (IV) and of arsenic (V), of which the constitutions must be regarded as established (compare, for example, Turner and Sheppard, J., 1925, **127**, 544). Additional evidence upon this point is afforded by the ready reduction of the telluridichloride (III) to a yellow, crystalline, cyclic substance, *phenoxtellurine* (VI), of such marked chemical and physical stability



(III.)



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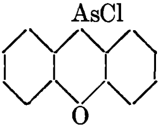

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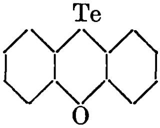
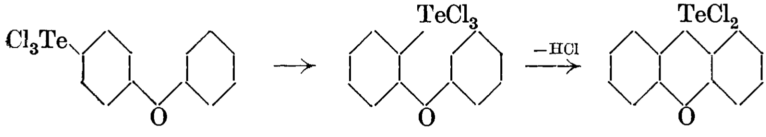


(VI.)

that there seems no doubt as to the nature of its tricyclic structure. This substance, which shows a normal molecular weight in freezing benzene, resembles somewhat closely the colourless sulphur analogue, phenoxthin or phenothioxin (IV; Mauthner, *Ber.*, 1906, **39**, 1344), in both physical and chemical properties. It has, for example, a delicate floral odour suggesting rose-water, whereas phenoxthin is described as having a geraniol smell; and both substances develop intense colorations with concentrated sulphuric acid. Phenoxtellurine readily adds on bromine or iodine in chloroform solution, yielding primrose-yellow 10 : 10-*dibromophenoxtellurine* and red 10 : 10-*di-iodophenoxtellurine*, respectively; while the action of warm nitric acid converts it into colourless *phenoxtellurine* 10 : 10-*dinitrate*.

The formation of a cyclic tellurium compound from the telluritrichloride (I) suggests that the latter must in reality be the *o*-compound (VII). Since, however, it has been shown (Morgan and Drew, *loc. cit.*) that in the analogous condensation with phenetole the group $-TeCl_3$ takes up exclusively a para-position with respect to ethoxyl, a para-orientation with respect to the phenoxy-group in the present case also would be anticipated. There remains thus the probability that the telluritrichloride is actually the *p*-compound (I), and that, on being heated above its melting point, it suffers a preliminary isomeric change into the *o*-compound (VII), which can then undergo the inner condensation :—



(VII.)

In an endeavour to test this possibility, the action of concentrated nitric acid upon the ditelluride (II) was tried. The telluritrinitrate, $PhO\cdot C_6H_4\cdot Te(NO_3)_3$, was first produced and then the tellurium atom displaced, *pp'*-dinitrodiphenyl ether (m. p. 143°) being formed; no *o*-nitro-compound was isolated. Of the two obvious mechanisms of displacement of the tellurium atom, *viz.*,

(1) $PhO\cdot C_6H_4\cdot Te(NO_3)_3+HO\cdot NO_2=Te(NO_3)_3\cdot OH+PhO\cdot C_6H_4\cdot NO_2$, and (2) $PhO\cdot C_6H_4\cdot Te(NO_3)_3 + H\cdot NO_3 = Te(NO_3)_4 + PhO\cdot C_6H_5$, the more probable would appear to be (1); and, if this is the case, the production of a *p*-nitro-compound of diphenyl ether proves the structure of the telluritrichloride and of the ditelluride derived from it. The possibility of mechanism (2), in which diphenyl ether is first liberated and then nitrated, cannot, however, be ignored with safety.

On the whole, the weight of evidence seems to be in favour of the para-structure; and accordingly it is considered best to adopt, for the present, the formulæ I and II for the telluritrichloride and ditelluride respectively, and to assume the transformation of the *p*-telluritrichloride into its *o*-isomeride as an intermediate step in the synthesis of the cyclic dichloride (III).

The best method of preparing 10 : 10-dichlorophenoxtellurine, giving a yield of 50%, is to heat at about 200° a mixture of tellurium tetrachloride and diphenyl ether in molecular proportions. The reaction proceeds in two stages, marked evolution of hydrogen chloride occurring first near 120° and then again near 200°. These stages apparently represent respectively the formation of the telluritrichloride and its transformation to the cyclic telluridichloride. The hypothetical preliminary isomeric change of the *p*- to the *o*-telluritrichloride must then occur between the temperature of the melting point of the telluritrichloride and the higher temperature, *i.e.*, between about 160° and 200°, a separate experiment having shown that the presence of chloroform in the preliminary stages of the above reaction had no effect upon the nature of the ultimate product.

Accordingly, an attempt was made to isolate the *o*-telluritrichloride by heating the supposed *p*-telluritrichloride to about 160° in an atmosphere of nitrogen. From the glassy product, which was a complex mixture containing a proportion of regenerated tellurium tetrachloride, a substance was obtained which had the properties of a telluritrichloride and yet was not identical with the initial material. This compound, which crystallised from benzene in almost colourless, pearly flakes decomposing at 125°, was possibly the *o*-telluritrichloride (VII), since it was easily reduced to a red substance possessing the characteristics of a ditelluride. Neither of these compounds was obtained in a pure condition, however, and their identity with the above structures has not been definitely established.

A colourless non-cyclic telluridichloride occurs as a by-product in the condensation of tellurium tetrachloride and diphenyl ether in chloroform solution; and this substance results also when the telluritrichloride (I) is heated with an excess of diphenyl ether at about 160°, hydrogen chloride being set free. This telluridichloride must therefore be pp′-*diphenoxydiphenyltelluridichloride* (VIII), $PhO{\cdot}C_6H_4{\cdot}TeCl_2{\cdot}C_6H_4{\cdot}OPh$.

Here again the di-para-orientation is considered the more probable, since the substance is formed in small amount even at the low temperature of a condensation in chloroform. Owing, however, to the uncertainty attaching to the conditions under which the hypothetical change of the tellurium atom from the *p*- to the *o*-position occurs, a di-ortho-, or even a para-ortho-structure is not definitely excluded.

The non-cyclic telluridichloride (VIII) was unchanged by the action of heat at 210°, and its formation was therefore unconnected with the production of the cyclic telluridichloride (III). It was of interest, therefore, to find that the latter was the main product of the action of heat at 200° upon a mixture of tellurium tetrachloride and a large excess (3½ mols.) of diphenyl ether, for this result seems to supply further evidence in favour of the hypothetical isomeric change of the *p*- to the *o*-telluritrichloride; since, in the absence of this transformation, it would be expected that the whole of the telluritrichloride would be changed at 200° into the non-cyclic telluridichloride (VIII), a reaction which is fairly rapid even at 160°. The production of the *o*-telluritrichloride must therefore accelerate rapidly at temperatures approaching 200°.

Leaving aside the question of orientation, we have thus the following series of changes which have been realised experimentally, with the temperatures at which the reactions are appreciably rapid :—

$$\mathrm{TeCl_4 + C_6H_5{\cdot}OPh \xrightarrow[\text{(with or without CHCl}_3\text{)}]{120^\circ} HCl + TeCl_3(C_6H_4{\cdot}OPh)};$$

$$\mathrm{TeCl_3(C_6H_4{\cdot}OPh) + C_6H_5{\cdot}OPh \xrightarrow{160^\circ} HCl + TeCl_2(C_6H_4{\cdot}OPh)_2};$$

$$\mathrm{TeCl_3(C_6H_4{\cdot}OPh) \xrightarrow{200^\circ} HCl + TeCl_2(C_6H_4{\cdot}O{\cdot}C_6H_4)};$$

$$\mathrm{TeCl_4 + C_6H_5{\cdot}OPh \xrightarrow{200^\circ} 2HCl + TeCl_2(C_6H_4{\cdot}O{\cdot}C_6H_4)}.$$

It is probable that *pp*′-diphenoxydiphenyltelluridichloride (VIII) is always formed, at least in minor quantities, when tellurium tetrachloride and diphenyl ether are heated together; but this telluridichloride is not readily separated from the resinous or colloidal by-products associated with it in the reaction-mixture.

Attempts are being made to clear up the uncertainty which exists regarding the orientations of the foregoing substances; and, in addition, the author is investigating the analogues and derivatives of phenoxtellurine and similar compounds containing other metals and metalloids.

EXPERIMENTAL.

Condensation of Tellurium Tetrachloride with Diphenyl Ether in presence of Chloroform.—Four experiments were carried out, with proportions of diphenyl ether ranging from 1 to 1½ mols. per mol. of tellurium tetrachloride and with amounts of chloroform varying between 0·6 and 2 c.c. per g. of the tetrachloride; the times of heating were between 8 and 26 hours. The optimum experiment only will be described in detail: 23·8 g. of tellurium tetrachloride, 18·7 g.

(1¼ mols.) of diphenyl ether, and 15 c.c. of dry chloroform were heated under reflux during 26 hours, moist air being excluded. Hydrogen chloride was evolved and all the tellurium tetrachloride dissolved in about 1½ hours. The yellow trichloride that was gradually deposited from the intensely orange-brown solution was recrystallised from boiling dried chloroform; the mother-liquor on concentration to a syrup gave further crops of trichloride, which were recrystallised as before (total yield, 31·5 g. or 90%). The final syrup, on long standing in a desiccator, gave the dichloride (0·5 g.) in large, colourless prisms, which were recrystallised from ethyl alcohol or acetone. In this and in other experiments the separating trichloride was practically pure. Portions of it were subjected to careful fractionation from boiling dry chloroform, in an attempt to detect the presence of a possible isomeric trichloride. The melting points and mixed melting points of the recrystallised first and final fractions were always practically identical. Slight differences sometimes observed were traced to the presence of small amounts of the dichloride.

p-*Phenoxyphenyltelluritrichloride* (I) separates from its yellow solution in chloroform or carbon tetrachloride in opaque, nodular rosettes of very small, pale yellow needles. The rosettes crumble, on drying, to a creamy yellow, crystalline powder. The substance melts at 156—157° to a transparent, yellow liquid, but never quite sharply, usually softening from about 154°, behaviour which suggests a partial change near the melting point. The compound is almost insoluble in light petroleum, sparingly soluble in hot carbon tetrachloride, but more soluble in hot chloroform or benzene. It is readily hydroxylated by water or hydroxylic organic solvents (Found: C, 35·6; H, 2·3; Cl, 26·6. $C_{12}H_9OCl_3Te$ requires C, 35·75; H, 2·25; Cl, 26·4%).

pp′-*Diphenoxydiphenyltelluridichloride* (VIII), a by-product in the foregoing condensation, was best prepared by heating 3·9 g. (1 mol.) of the above trichloride and 1·7 g. (1 mol.) of diphenyl ether together at 140—165° during 6 hours, moist air being excluded and a slow current of nitrogen maintained in the apparatus. Hydrogen chloride was evolved even at 145°. The hard, semi-crystalline mass was extracted with ether, the ether removed, and the resulting semi-solid triturated successively with light petroleum and ethyl alcohol, and filtered. There remained 2·8 g. of crude dichloride containing an amorphous impurity, readily soluble in chloroform, benzene or acetone, from which it was found difficult to free the dichloride. Purification was finally effected by fractional solution in cold benzene, followed by crystallisation of the least soluble fraction from benzene–light petroleum (b. p. 40—60°).

When two molecular proportions of diphenyl ether were employed and the heating was conducted during 10 hours at 115—150°, a similar product (1·1 g. from 1·5 g. of trichloride) was obtained, which yielded the dichloride on purification by means of carbon tetrachloride and ether. When quite pure, the dichloride separated from boiling methyl or ethyl alcohol in transparent, colourless, prismatic needles, which became slightly pink on keeping. The solutions in hot alcohol of impure specimens always became cloudy, on cooling, before crystallisation set in. The dichloride melted without decomposition at 157—158°, and depressed the almost identical melting point of the trichloride to about 120°. It was much more easily soluble than the trichloride in organic solvents, being readily soluble in cold benzene, chloroform or ether; but it was insoluble in light petroleum, and only moderately easily soluble in hot ethyl alcohol. The halogen atoms were firmly bound in this substance, which remained unaffected by cold aqueous potash, although it was decomposed by the boiling reagent with liberation of diphenyl ether (Found: Cl, 13·15. $C_{24}H_{18}O_2Cl_2Te$ requires Cl, 13·2%).

When this dichloride was heated at 210° during an hour, it remained unchanged, no trace of diphenyl ether or of cyclic telluridichloride being produced.

pp'-*Diphenoxydiphenyl Ditelluride* (II).—The trichloride (7 g.) was reduced with 50 c.c. of ice-cold water and 11·6 g. (3 mols.) of powdered potassium metabisulphite, which was slowly added during $\frac{3}{4}$ hour, the mixture being stirred mechanically. Sulphur dioxide was evolved, and a soft red mass produced. The reduction was completed by grinding the whole in a glass mortar during a further $\frac{1}{2}$ hour. The deep purple, crystalline product was filtered off, washed with water, and dried in a vacuum; the yield of crude product (5·3 g.) was quantitative. The substance was then rapidly crystallised from hot light petroleum (b. p. 40—60°) saturated with sulphur dioxide, two crystallisations producing the analytically pure ditelluride. Careful examination of the mother-liquors failed to reveal the presence of an isomeride.

pp'-*Diphenoxydiphenyl ditelluride* separates from petroleum or alcohol in clusters of minute, bronzed, brownish-violet or purplish-red needles, which dissolve in organic solvents to dark red solutions. It commences to soften at 85° and melts to a deep red liquid at 87—88°. It is easily soluble in benzene, chloroform, carbon tetrachloride, ether, or acetone, only moderately easily soluble in light petroleum or alcohol, and insoluble in water [Found: C, 48·55; H, 3·05; Te, 43·1; M, cryoscopic in benzene, 579 ($c = 1{\cdot}39$), 595 ($c = 2{\cdot}04$). $C_{24}H_{18}O_2Te_2$ requires C, 48·55; H, 3·05; Te, 43·0%; M, 593].

Great difficulty was at first experienced in purifying this substance sufficiently for analysis. Although it crystallised well from ethyl or methyl alcohol and from acetone or ether, the crystals were persistently low in carbon content (Found : C, 47·6, 47·6, 47·5, 48·05 ; H, 3·1, 3·2, 3·1, 3·15%). Finally the impurity was isolated : it consisted of a white, amorphous oxide, which was slowly reduced by aqueous potassium metabisulphite or aqueous sulphur dioxide to the ditelluride. In solution the ditelluride slowly precipitates this oxide when exposed to the air. With bromine in cold chloroform solution the ditelluride reacts to form a yellow *bromide* melting near 180° and readily soluble in hot chloroform. This substance is probably the analogue of the trichloride, since it is again reduced to the ditelluride by aqueous alkali bisulphites. With warm concentrated nitric acid the ditelluride yields ultimately *pp′*-dinitrodiphenyl ether (needles from alcohol; m. p. 142—143°).

Preparation of 10 : 10-*Dichlorophenoxtellurine.*—(1) *Action of heat on* p-*phenoxyphenyltelluritrichloride.* The trichloride (1·4 g.) was heated gradually during $4\frac{3}{4}$ hours, from 150° to 210°; hydrogen chloride was slowly evolved. The cooled melt was extracted with ether; a substance sensitive to moisture (probably tellurium tetrachloride) was then found to be present. The residue from the ether extraction, on crystallisation from boiling toluene, yielded 0·4 g. (or 33%) of the pure cyclic telluridichloride, identical with the following product in (2).

When the trichloride (5·6 g.) was heated at a lower temperature (150—160°) during 2 hours in a current of nitrogen, a lesser proportion of hydrogen chloride was evolved. On cooling, the melt solidified to a brown glass, which was powdered and dissolved in hot dry chloroform. The solution, kept out of contact with moist air, deposited pale pinkish-white micro-needles (0·5 g.) of a telluritrichloride (probably corresponding with formula VII) which, however, still contained traces of tellurium tetrachloride (Found : Cl, 27·3 ; whereas formula VII requires Cl, 26·4%). Recrystallised from hot benzene, the compound formed a voluminous mass of almost colourless, nacreous flakes, decomposing near 125° with darkening and evolution of hydrogen chloride. It was readily reduced by aqueous potassium metabisulphite to a red substance (probably the ditelluride), which was soluble in benzene but easily oxidised by the air, while in solution, to a less soluble substance.

The main product of the above reaction was a glutinous mixture containing free tellurium tetrachloride.

(2) *Action of heat upon an equimolecular mixture of tellurium tetrachloride and diphenyl ether.* Six experiments under varying condi-

tions were carried out, but the yield of cyclic dichloride seemed almost constant (about 50%). The following is a typical experiment: Tellurium tetrachloride (11·1 g.) and diphenyl ether (7·0 g.) were heated together in a flask with a long air-condenser, carrying a moisture guard-tube, a slow current of nitrogen being bubbled through the melt (this was not essential, however). The temperature was raised slowly from 100° to 240° over a period of 13 hours, when hydrogen chloride was evolved, mainly during two maximal phases, the first occurring near 120° and the second near 200°. The melt gradually thickened and after about 8 hours partly solidified even at 190°, but remelted as the temperature rose. The cooled melt finally set to a crystalline cake, which was ground to a loose brown powder. The powder was stirred with ether, filtered off, dissolved in acetone, and filtered from 0·8 g. of free tellurium. Evaporation of the acetone left 9·4 g. of the fairly pure cyclic dichloride (62%); but, on further purification of the product in a Soxhlet apparatus with toluene, the yield fell to 48%.

Keeping the temperature below 220°, reducing the time of heating to 5 hours, adding a little chloroform at the commencement of heating, and other similar modifications produced no important variation in the yield.

The material obtained by evaporating the ethereal extracts of the product contained free diphenyl ether or chlorinated diphenyl ether, as well as soluble tellurium compounds which could not be isolated from the viscous residues.

10 : 10-*Dichlorophenoxtellurine* (III) crystallises from boiling toluene in colourless, nacreous platelets, which melt without decomposition at 265° to a transparent, yellow liquid. At 100° the crystalline solid is yellow, but reverts to the colourless form on cooling. It is extremely stable to heat and can be vaporised without undergoing much decomposition; is almost insoluble in ether or petroleum, sparingly soluble in chloroform or ethyl alcohol, rather more soluble in benzene or toluene, and easily soluble in acetone. It is slowly hydrolysed by boiling water, a white oxide resulting. Boiling aqueous potash detaches the tellurium atom and generates diphenyl ether. The solution in cold concentrated sulphuric acid is yellow (Found: C, 39·8; H, 2·2; Cl, 19·3. $C_{12}H_8OCl_2Te$ requires C, 39·3; H, 2·2; Cl, 19·35%).

Phenoxtellurine (VI).—The powdered dichloride (4 g.) was reduced at 0° with 25 c.c. of water and 4·8 g. (2 mols.) of potassium metabisulphite, slowly added with stirring, when sulphur dioxide was evolved. The yellow product was ground beneath the liquid in a glass mortar during an hour to complete the reduction, and the solid was then filtered off, washed with water, and dried. The yield (3·2 g.) was nearly theoretical. The product was recrystallised from light petroleum (b. p. 40—60°).

Phenoxtellurine separates from hot petroleum in long, spear-like needles and from the cold solvent in large, transparent prisms, both forms being lemon-yellow to orange in colour, melting without decomposition at 78—79°, and having a delicate floral odour. The compound is very stable to heat and can be vaporised unchanged. It is insoluble in water, but easily soluble in ethyl alcohol, ether, benzene, or carbon tetrachloride to yellow solutions. It dissolves in cold concentrated sulphuric acid to a deep purplish-red solution, and is stable towards hot concentrated hydrochloric acid or dilute aqueous caustic soda [Found: C, 48·7; H, 2·9; Te, 43·4; *M*, cryoscopic in benzene, 287 ($c = 1{\cdot}25$), 294 ($c = 2{\cdot}18$). $C_{12}H_8OTe$ requires C, 48·7; H, 2·7; Te, 43·1%; *M*, 295·5].

Warm concentrated nitric acid does not immediately cause nuclear nitration of phenoxtellurine, but produces the 10:10-*dinitrate*, which forms colourless needles decomposing near 258°. Bromine and iodine in chloroform solution readily yield respectively the 10:10-*dibromide*, bright yellow spangles from chloroform or primrose-yellow prisms from toluene (decomposing at 290°), and the 10:10-*di-iodide*, red spangles (decomposing indefinitely, mainly near 270°).

Action of Heat upon Mixtures of Tellurium Tetrachloride and Diphenyl Ether in Various Proportions.—(1) When it was attempted to introduce two $-TeCl_3$ groups into the molecule of diphenyl ether by using 2 mols. of tellurium tetrachloride to 1 mol. of the aromatic ether and heating at 120° during 6 hours, only the telluritrichloride was obtained, part of the tellurium tetrachloride remaining unaltered.

(2) Tellurium tetrachloride and 2 mols. of diphenyl ether, heated at 110° to 180° during 8 hours, yielded only a mixture of a trichloride and the cyclic dichloride.

(3) Tellurium tetrachloride (1 mol.) and diphenyl ether ($3\frac{1}{2}$ mols.), heated at 110° to 210° during 16 hours, gave a yield of 42% of 10:10-dichlorophenoxtellurine, showing that the tendency towards formation of this cyclic dichloride is maintained even in presence of a large excess of diphenyl ether.

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