

XX.—*Cyclic Organo-metallic Compounds. Part III.*
Nitro- and Amino-derivatives of Phenoxtellurine.

By HARRY DUGALD KEITH DREW and REUBEN WILLIAM THOMASON.

IN the thiazines and oxazines, of which methylene-blue and Meldola's blue are examples, respectively, the central ring contains the odd-valent element nitrogen, together with sulphur or oxygen. In phenoxtellurine, nitrogen is replaced by the even-valent element tellurium. Having regard, therefore, to the uncertainty which still prevails as to the distribution of bonds in the coloured salts of the first-mentioned series, it was considered desirable to investigate the properties of the amino-derivatives of phenoxtellurine (I) from the point of view of possible colour-development among their salts. For, in that event, the coloured substances of the phenoxtellurine series must of necessity consist of dimeric molecules, or must contain each an extra acid radical, in order to simulate the structures ascribed to methylene-blue and the like.

An attempt to condense 2-nitrodiphenyl ether with tellurium tetrachloride led to profound decomposition, phenolic substances being produced. Since, in addition, the condensation of amino-compounds with tellurium tetrachloride is generally unfavourable, it was decided to prepare the aminophenoxtellurines by direct nitration of phenoxtellurine, followed by reduction of the nitro-compounds. This method proved practicable.

When phenoxtellurine is treated with nitric acid, it is first

quantitatively transformed by an oxidising reaction to the 10:10-dinitrate. Under suitable conditions, this action is then followed by nitration of the nucleus. Nitro-dinitrates, or nitro-basic-nitrates, of phenoxtellurine are thus produced; and these, on reduction by alkali bisulphite, are quantitatively transformed to nitro-derivatives of phenoxtellurine. The latter can then be reduced, by means of tin and hydrochloric acid, to the corresponding amino-derivatives.

Treatment of phenoxtellurine with ordinary concentrated nitric acid (*d* 1.42) leads chiefly to the formation of mononitro-derivatives, the main product consisting of 2-nitrophenoxtellurine (II), the by-product being 4-nitrophenoxtellurine (III).

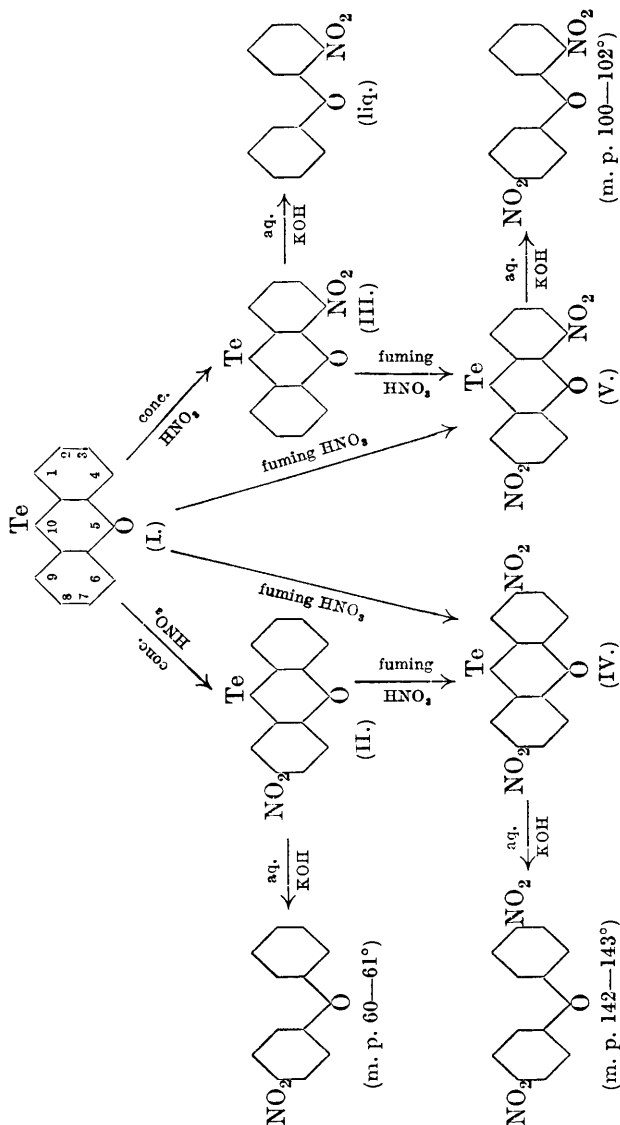
By the use of boiling fuming nitric acid, a second nitro-group is caused to enter the nucleus, and there are obtained, after reduction of the salts, 2:8-dinitrophenoxtellurine (IV) as main product and 4:8-dinitrophenoxtellurine (V) as by-product. A small proportion of 4:6-dinitrophenoxtellurine is doubtless also produced, but this substance has not yet been isolated.

The phenoxtellurine nucleus offers considerable resistance to further nitration, and tri- or higher nitro-derivatives were not obtained.

The nitro- and dinitro-phenoxtellurines are well-crystallised, yellow to orange-red substances, soluble in organic solvents, and possessed of considerable stability. The proof of the orientation of the nitro-groups therein was supplied in a simple manner by extending to these compounds the observation previously made, in the case of phenoxtellurine itself, that the 10:10-dichlorides, -dinitrates, and other similar salts are decomposed by warm aqueous potash in a manner leading to replacement of the tellurium atom by two atoms of hydrogen, potassium tellurite and the appropriate substitution product of diphenyl ether being generated in each case. Identification of the latter affords unequivocal information as to the structure of the phenoxtellurine derivative itself, except when substituents are present in positions relatively *meta*- to the ether oxygen atom (*i.e.*, in positions 1, 3, 7, or 9). So far, no such doubtful cases have been encountered. Inspection of the formulations given below will make clear the foregoing argument.

The nitrodiphenyl ethers produced from (II), (IV) and (V) by the action of potash were known crystalline substances having characteristic melting points, and the methods by which they have already been synthesised leave no doubt regarding their structure. The 2-nitrodiphenyl ether resulting from (III), however, is a liquid. The proof of the orientation of the nitro-group was therefore supplied by further nitration to (V). Confirmation of the struc-

ture of (II) was obtained by similar further nitration to (IV). The following scheme illustrates the methods employed :



The separation of the nitro-derivatives of phenoxtellurine is complicated by the existence of a series of addition compounds between the various members. Some of these occur in well-defined

crystals of characteristic appearance; and repeated crystallisation from certain organic solvents fails to disrupt them, although other solvents effect complete or partial separation into the constituent substances. In the cases observed, a molecule of each of two nitro-derivatives may be combined; or two molecules of one derivative may unite with a single molecule of a second. Thus, two molecules of (IV) unite with a molecule of (II) to form a complex crystallising from acetone in orange-red prisms; whilst a molecule of (IV) unites with a molecule of (II) to form a complex separating from alcohol in yellow, hexagonal plates. Phenox-tellurine itself unites with a molecular proportion of 2-chloro-8-methylphenox-tellurine to form a remarkable *compound*, which crystallises unchanged, from petroleum or ethyl alcohol, in well-defined, yellow needles having a perfectly sharp melting point. This substance is always found associated with phenox-tellurine when the latter is prepared from ordinary (solid) diphenyl ether and tellurium tetrachloride, owing, we are of an opinion, to the presence of *p*-cresol in the material from which the diphenyl ether is made.

That these additive compounds are not the result of union between the bivalent tellurium atoms of several molecules is indicated by the fact that the corresponding complex 10:10-dichlorides and dinitrates, containing only quadrivalent tellurium, may in some cases be recrystallised substantially unchanged.

A point of interest emerging from the study of the nitration of phenox-tellurine is that the orienting influence of the tellurium atom, in the form of the group $>\text{Te}(\text{NO}_2)_2$, on the entering nitro-groups is negligible in comparison with that of the ether oxygen atom, unless, indeed, the telluridinitrate group be considered *meta*-directive, in which case the separate influences of the two directive groups would be reinforcing. As would be expected, the entry of a second nitro-group into the phenox-tellurine ring occurs mainly, if not exclusively, in the unnitrate phenylene group.

Incidentally, the results afford confirmation of the structure of phenox-tellurine itself, since they indicate that the tellurium and oxygen atoms in that substance are attached to the phenylene groups in mutually *di-ortho*-positions.

The foregoing nitro-derivatives are readily reduced by means of tin and hydrochloric acid, 2-*amino*-, 2:8-*diamino*-, and 4:8-*di-amino-phenox-tellurine* being thus produced. These substances are crystalline, stable, and appreciably soluble in water. Their hydrochlorides are readily diazotised or tetrazotised, giving yellow to red diazonium salts which may be coupled with reactive phenols, etc., to produce azo-dyes and pigments. The amines themselves have no special bactericidal action.

The action of boiling aqueous potash or soda upon the amines replaces tellurium by two atoms of hydrogen, yielding the corresponding amino-derivatives of diphenyl ether. From the latter, the amino-substituted phenoxtellurines are sharply distinguished by their instant action upon phenoxtellurine dibisulphate, mere traces of the telluride and the phenoxtellurine salt sufficing to produce, when rubbed together, the brilliant violet colour characteristic of diphenoxtellurylium salts (J., 1926, 3054).

Examination of the foregoing organic derivatives of tellurium, several of which have been carefully fractionated and repeatedly analysed, has yielded no evidence that tellurium is a complex (compare Brauner, J., 1895, 67, 549). On the contrary, the results point to the probability that the accepted atomic weight for tellurium represents that of a single element (mixture of isotopes).

EXPERIMENTAL.

Complex By-product in the Preparation of Phenoxtellurine.—When 183 g. of tellurium tetrachloride were condensed with diphenyl ether in the manner previously described (*loc. cit.*), 178 g. of crude 10:10-dichlorophenoxtellurine were obtained. This, when reduced without further purification, yielded 14 g. of free tellurium, 80 g. of pure phenoxtellurine, and 20 g. of a complex by-product which closely resembled phenoxtellurine in general properties. The by-product was separated from phenoxtellurine by crystallisation from light petroleum (b. p. 40—60°), remaining in the first mother-liquor. Subsequent purification was effected from ethyl alcohol. A complete separation of these two substances is obtained with surprising ease.

The *by-product* is a compound of a molecule of phenoxtellurine with one molecule of 2(?) -chloro-8(?) -methylphenoxtellurine. It results from the presence in the diphenyl ether of a small proportion of phenyl *p*(?) -tolyl ether, which is chlorinated by tellurium tetrachloride, the product becoming transformed into 2(?) -chloro-8(?) -methylphenoxtellurine, which then unites with phenoxtellurine. It separates from ethyl or methyl alcohol, or from petroleum, in bushes of well-defined, light yellow needles with chiselled ends, and melts sharply at 59°. Conversion into the dinitrate by means of dilute nitric acid does not effect resolution of this substance into its constituents, since it is recovered unchanged on reduction of the recrystallised product. Partial separation may be obtained, however, by repeated fractionation of the 10:10-dichloride from chloroform. Nucleus nitration results in disintegration of the complex, nitro-derivatives of phenoxtellurine becoming isolable. In benzene solution, the compound is com-

pletely resolved into its constituents, although it is reformed when the solution is concentrated [Found : *M* (cryoscopic), 284, 287, 295. Calc., *M*, 319.8].

Mixtures of the complex substance with phenoxtellurine melt indefinitely between 59° and 79°. Removal of tellurium, by boiling with aqueous potash, gave a heavy oil which contained diphenyl ether but did not solidify. This was probably a mixture of diphenyl ether with *p*-chlorophenyl *p*-tolyl ether [Found : C, 47.05, 47.0; H, 2.9, 2.7; Cl, 5.3, 5.4; TeO, 44.9 (by diff.). $C_{25}H_{17}O_2ClTe_2$ requires C, 46.9; H, 2.65; Cl, 5.55; TeO, 44.9%]. For comparison, analyses were carried out on specimens of phenoxtellurine prepared in the same experiment (Found : C, 48.6, 48.8, 48.5; H, 2.9, 2.85, 2.8. $C_{12}H_8OTe$ requires C, 48.7; H, 2.7%).

Nitration of Phenoxtellurine.—(1) *Preparation of mononitrophenoxtellurines.* Powdered phenoxtellurine (4.5 g.) was added slowly to 70 c.c. of nitric acid (*d* 1.42), and the orange-red solution obtained after 10 minutes' boiling yielded, after 2 days, opaque, white needles (5.7 g., after being dried over soda-lime). The mother-liquor, concentrated on the water-bath, yielded further solid (0.9 g.) which, on reduction, gave chiefly 2 : 8-dinitrophenoxtellurine.

The main crop (5.7 g. above), when reduced by 30 c.c. of water and 5.7 g. of potassium metabisulphite, was transformed into a dark paste. The yellow ethereal extract of this, when allowed to evaporate on a wide surface, left yellow needles (A) surrounded by orange-red flakes (B). These two products were separated mechanically and each was crystallised from acetone. The orange-red flakes (B) gave slender, yellow crystals of 2 : 8-dinitrophenoxtellurine, together with massive, red prisms melting gradually from 145° to 220°. The latter substance was a *compound* containing two molecular proportions of 2 : 8-dinitrophenoxtellurine and one proportion of 2-nitrophenoxtellurine, into which it was separated by fractionation from ethyl alcohol (Found : N, 6.0. $C_{36}H_{19}O_{13}N_5Te_3$ requires N, 6.3%). From acetone, the complex could be recrystallised almost unchanged.

The yellow needles (A) gave a first crop of crystals, part of which dissolved more readily than the remainder in hot ethyl alcohol. The soluble portion separated from alcohol in silky, bright yellow needles of 2-nitrophenoxtellurine (II), m. p. 129° (Found : C, 42.2; H, 2.25; N, 4.25. $C_{12}H_7O_3N_1Te$ requires C, 42.3; H, 2.05; N, 4.1%). The less soluble portion separated from hot alcohol in glistening, bright yellow spangles, consisting of thin, hexagonal prisms. This substance was a *compound* of 2 : 8-dinitro- and 2-nitrophenoxtellurines in molecular proportion (Found : N, 5.7. $C_{24}H_{13}O_8N_3Te_2$ requires N, 5.8%). The complex could be recrystallised unchanged

from alcohol, but was partly disrupted by acetone. It melted gradually between 145° and 185° .

The acetone mother-liquor from A, allowed to evaporate very slowly, gave small, yellow needles of impure 2-nitrophenoxtellurine, together with massive, lemon-yellow prisms. The prisms, sorted out by hand and recrystallised from ethyl alcohol, gave pale lemon-yellow prisms or needles of 4-nitrophenoxtellurine (III), m. p. 104° (Found : C, 42.4; H, 2.2; N, 4.2%).

(2) *Preparation of dinitrophenoxtellurines.* Powdered phenoxtellurine (4.3 g.) was added gradually to 25 c.c. of nitric acid (d 1.50), cooled in ice and salt. The mixture was then heated on a water-bath during $\frac{1}{2}$ hour. The cooled solution was precipitated by addition of water and the white solid was removed and recrystallised from boiling nitric acid (d 1.42). The first crop (3.9 g.), when crystallised again from nitric acid, gave large, colourless, serrated needles (2.9 g.) which, on reduction with aqueous potassium metabisulphite, yielded pure 2 : 8-dinitrophenoxtellurine (IV), m. p. 228° . This substance crystallised from acetone in large, hexagonal, orange prisms, or from ethyl alcohol in smaller, yellow prisms. It was more sparingly soluble in organic solvents than the foregoing mononitrophenoxtellurines (Found : C, 37.9; H, 1.85; N, 7.3. $C_{12}H_6O_5N_2Te$ requires C, 37.4; H, 1.55; N, 7.3%).

The nitric acid mother-liquor from the above first crop was diluted with water and the white precipitate (4.2 g.) was boiled with 20 c.c. of fuming nitric acid during 2 hours. Precipitation by water and crystallisation of the precipitate from concentrated nitric acid gave a further crop of the above serrated needles. The nitric acid mother-liquor from this crop slowly deposited a second substance in minute, white rods. This, after recrystallisation in a similar manner from concentrated nitric acid, yielded, on reduction with aqueous potassium metabisulphite, pure 4 : 8-dinitrophenoxtellurine (V), m. p. $197-198^{\circ}$. This substance crystallised from benzene in long, thin, golden, lath-like needles containing $\frac{1}{2}C_6H_6$ (Found : loss of benzene at 100° , 9.2. Calc., 9.3%). The benzene was slowly lost in the air, the dinitro-compound remaining as a salmon-red, crystalline powder (Found : C, 37.0; H, 1.9; N, 7.3%). The substance separated from ethyl alcohol in minute, red crystals. It was generally only sparingly soluble in organic solvents.

Although the basic nitrate of 4 : 8-dinitrophenoxtellurine is much less easily soluble in nitric acid than is the dinitrate of 2 : 8-dinitrophenoxtellurine, the former tends to remain in supersaturated solution while the latter crystallises readily.

Many other experiments on the nitration of phenoxtellurine with nitric acid under a variety of conditions led to the conclusion

that the reaction cannot be controlled so as to produce mononitro-compounds only, lesser proportions of dinitro-compounds invariably being present. On the other hand, conditions are readily chosen in which only dinitro-compounds are produced. Fuming nitric acid, at atmospheric pressure, seems to be incapable of introducing more than two nitro-groups into the phenoxtellurine nucleus. Nitration in presence of auxiliary acids has not yet been tried.

Nitration of 2-Nitrophenoxtellurine.—A solution of 2-nitrophenoxtellurine in fuming nitric acid was boiled during $2\frac{1}{2}$ hours. Separation of the products in the manner already described yielded crystals which, on reduction, gave pure 2 : 8-dinitrophenoxtellurine. The mother-liquor contained a substance which furnished, on reduction, a mixture of 2 : 8- and 4 : 8-dinitrophenoxtellurine. The latter, present only in very small proportion, was not isolated but was characterised by its colour change on crystallisation from benzene and exposure of the crystals to air.

Nitration of 4-Nitrophenoxtellurine.—Finely powdered 4-nitrophenoxtellurine (0.4 g.) was added slowly to cold fuming nitric acid (5 c.c.). The solution was boiled during 2 hours, and water was then added until a turbidity appeared. The white solid which subsequently separated was reduced with aqueous potassium metabisulphite, furnishing, after crystallisation from benzene, pure 4 : 8-dinitrophenoxtellurine (V), m. p. 198° , in 60% yield. The mother-liquor contained another nitro-compound, probably 4 : 6-dinitrophenoxtellurine, but the proportion was too small to allow of its isolation.

Conversion of Nitro-derivatives of Phenoxtellurine into Nitro-derivatives of Diphenyl Ether.—2-Nitrophenoxtellurine was converted into its dinitrate by means of nitric acid, and the crystals were boiled for a few minutes with 50% aqueous potash. Extraction by a mixture of ether and benzene furnished a solid which, after one crystallisation from ethyl alcohol, gave 4-nitrodiphenyl ether in very pale yellowish-white, flat plates, m. p. $60-61^{\circ}$.

4-Nitrophenoxtellurine was converted into its 10 : 10-dibromide (pale yellow crystals, melting and decomposing at 302°), which was then boiled with 30% aqueous potash. Extraction with ether gave *o*-nitrodiphenyl ether, a pleasant-smelling oil which did not solidify on keeping.

2 : 8-Dinitrophenoxtellurine, similarly converted into its dinitrate and boiled with 30% aqueous potash, yielded a solid which, after one crystallisation from alcohol, gave pale yellowish-white needles of 4 : 4'-dinitrodiphenyl ether, m. p. $142-143^{\circ}$.

4 : 8-Dinitrophenoxtellurine was converted into the basic nitrate,

and the latter boiled with 50% aqueous potash for a few minutes; the mixture was diluted with an equal bulk of water and then further heated at 100° for an hour. Extraction with much benzene gave 2:4'-dinitrodiphenyl ether, large, brittle, glassy, brownish prisms, m. p. 100—102°, from alcohol.

Amino-derivatives of Phenoxtellurine.—*2-Aminophenoxtellurine.* Finely powdered 2-nitrophenoxtellurine (2 g.) was heated on a water-bath during several hours with a large excess of tin and concentrated hydrochloric acid, until the yellow colour of the nitro-compound had disappeared. After filtration, the solid and filtrate were treated separately with cold caustic soda solution, and the liberated amine was extracted with chloroform in a Soxhlet apparatus. The amine was converted into the hydrochloride, which crystallised from water in small, very pale yellow needles. The addition of caustic soda to this solid gave *2-aminophenoxtellurine*, which crystallised from aqueous alcohol in pinkish-white needles, m. p. 157° (Found: N, 4.65. $C_{12}H_9ONTe$ requires N, 4.5%). Proof of orientation of this amine was shown by boiling it with aqueous potash, 4-aminodiphenyl ether (colourless needles from alcohol; m. p. 84°) being obtained.

By diazotising 2-aminophenoxtellurine at 0°, a pale yellow solution was obtained; and this, on coupling with alkaline β -naphthol, gave an insoluble, red azo-dye.

2:8-Diaminophenoxtellurine.—Finely ground 2:8-dinitrophenoxtellurine (3.8 g.) was heated with tin and concentrated hydrochloric acid on the water-bath, the red powder gradually becoming yellow; it was necessary to decant the clear liquid occasionally and grind the solid. The sparingly soluble hydrochloride of the amine was collected and treated with caustic soda. The amine thus formed was filtered off and extracted with chloroform, the cooled extract yielding 2:8-*diaminophenoxtellurine*, which crystallised from alcohol in lemon-yellow needles, m. p. 198° (Found: C, 44.3; H, 3.05; N, 8.6. $C_{12}H_{10}ON_2Te$ requires C, 44.2; H, 3.05; N, 8.6%). This diamine is slightly soluble in water and yields a hydrochloride which crystallises from hot water in long, yellow needles. Tetrazotisation causes the formation of a blood-red solution which yields an insoluble red azo-dye with alkaline β -naphthol.

4:8-Diaminophenoxtellurine. When 4:8-dinitrophenoxtellurine was similarly treated with tin and hydrochloric acid, the reduction proceeded much more rapidly. After the orange colour had disappeared, the hydrochloride was separated and crystallised from water. The action of caustic soda liberated 4:8-*diaminophenoxtellurine*, which crystallised from aqueous alcohol or water in faintly yellow, feathery needles or mica-like plates, m. p. 156° (Found:

C, 44.15; H, 3.0; N, 8.65%). On tetrazotisation, the diamine yielded a bright red diazonium chloride, which formed a red azo-dye with alkaline β -naphthol.

UNIVERSITY OF BIRMINGHAM,
EDCBASTON.

[Received, November 12th, 1926.]
