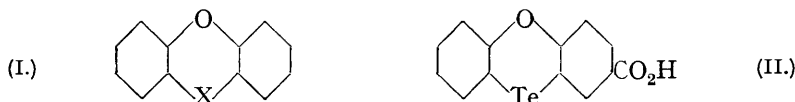


### 10. *The Configuration of Heterocyclic Compounds. Part VII.* *Some Derivatives of Phenoxtellurine.*

By ISHBEL G. M. CAMPBELL and E. E. TURNER.

The valencies extending outwards from the six carbon atoms in benzene are in one plane with the centres of those six atoms. The radii of (combined) atoms are now known to a considerable degree of accuracy. Without making any further assumptions, it is possible to work out the probable configuration of the phenoxtellurine molecule (I, X = Te). This is shown to be least strained when it is folded about the oxygen-tellurium axis, and therefore phenoxtellurine-2-carboxylic acid (II) can be represented as existing in mirror-image forms. The calculations do not permit an estimate to be made of the stability of these folded forms, and, in fact, attempts to obtain the acid in optically active forms have failed. It is probable, therefore, that the phenoxtellurine molecule, although folded, is flexible.

THE present communication describes the completion of one aspect of the investigation of the series represented by formula (I), in which X is sulphur, selenium, or tellurium,



the cases of sulphur and selenium having been dealt with already (Bennett, Lesslie, and Turner, J., 1937, 444; Thompson and Turner, preceding paper).

The following table shows the mathematical relationships existing in phenoxtellurine (I, X = Te) between the oxygen angle ( $\theta$ ), the tellurium angle ( $\phi$ ), and the consequent angle of fold ( $\psi$ ), the radii of oxygen, tellurium, and aromatic carbon being taken as 0.66, 1.37, and 0.70 Å., respectively :

$\theta$ .....	90°	110°	120°	130°	140°	142°
$\phi$ .....	68.5	81.5	87.0	92.5	97.0	97.5
$\psi$ .....	97.0	120.0	132.5	147.0	167.0	180

Since oxygen, when linking two aromatic nuclei, is known to prefer a valency angle somewhat greater than 120° (Sutton and Hampson, *Trans. Faraday Soc.*, 1935, **31**, 945), it is probable that  $\psi$  for the phenoxtellurine molecule lies between 135° and 145°, although this preferred, folded configuration may not be rigid. In connexion with the valency angle of tellurium, it may be noted that the dipole moments of diphenyl sulphide, selenide, and telluride are (approximately) 1.5, 1.4, and  $1.1 \times 10^{-18}$  e.s.u., respectively (Bergmann, Engel, and Sandor, *Z. physikal. Chem.*, 1930, *B*, **10**, 397). In the absence of information as to the dipole moment of the unknown tellurium analogue of thianthren and selenanthren, we cannot assess the valency angle of tellurium satisfactorily.

The only available test of stable configuration is the one we have applied in previous work in this series, namely, that of optical activity of suitably substituted derivatives. We have therefore attempted to resolve 2-aminophenoxtellurine and *phenoxtellurine-2-carboxylic acid* (II). The base was not very satisfactory material for investigation, but the acid gave a number of excellent salts with active bases, and because of our conviction that the essentials of our general hypothesis were correct, we only accepted the result we now publish, *viz.*, our failure to resolve the acid, when we felt that there were no further profitable experiments we could perform. Unfortunately, the method of fractional precipitation of salts is impracticable in this case, because of the relative solubilities of the acid and its salts.

*2-Aminophenoxtellurine hydrogen d-tartrate* was crystallised repeatedly from alcohol, and of the 30 g. of salt under examination, 14 different samples were examined polarimetrically. The salt had  $[\alpha]_{5791}^{20} + 2.45^\circ$  in absolute ethyl alcohol, no appreciable deviations from this value being recorded. No induction effects could be produced. The recovered base was always inactive. The *d-camphorsulphonate* crystallised well from

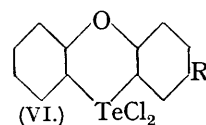
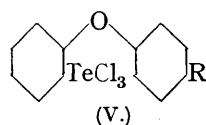
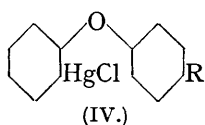
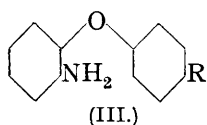
alcohol or from aqueous acetone and had  $[\alpha]_{5791}^{20} + 15.0^\circ$  in absolute ethyl alcohol. It showed no tendency to resolve.

Phenoxtellurine-2-carboxylic acid gave a well-defined *nor-d-ψ-ephedrine* salt, of which 49 g. were available. Sixteen crops taken from an extended series of crystallisations were examined polarimetrically and no important deviation from  $[\alpha]_{5791}^{20} + 16.7^\circ$  (in absolute ethyl alcohol) was recorded. The *strychnine* salt, of which 33 g. were submitted to exhaustive fractional crystallisation, had a constant value of  $[\alpha]_{5791}^{20} + 5.5^\circ$ , in chloroform. The *quinine* salt remained unchanged although 20 g. of it were repeatedly crystallised from alcohol. It had  $[\alpha]_{5791}^{20} + 125^\circ$  in chloroform, in which solvent it was stable only in the dark. Fractional crystallisation of 32 g. of the *cinchonidine* salt led to no appreciable change in rotation from  $[\alpha]_{5791}^{20} - 58.5^\circ$  in absolute ethyl alcohol. The *d-α-phenylethylamine* salt (23 g.) was similarly unresolvable, having  $[\alpha]_{5791}^{20} + 4.0^\circ$  in methyl alcohol. No specimen of acid regenerated from any crop of the salts was optically active, and no asymmetric induction effects were producible. Partial esterification of the acid with *l*-menthol did not lead to an active specimen.

We regard these results as indicating that the acid cannot be resolved, and therefore, that, although it has a folded configuration, the folding is unstable, as it is in thianthren, so that interconversion of the *d*- and the *l*-form is extremely rapid.

When this work was begun, the only phenoxtellurine derivatives known were those described by Drew (J., 1926, 223, 3054; 1927, 116), including a substance, m. p. 46—47°, which he regarded as 2-chloro-8-methylphenoxtellurine. In order to obtain a phenoxtellurinecarboxylic acid, we first condensed 4-chloro-4'-methyldiphenyl ether with tellurium tetrachloride, which, as Drew found, chlorinates phenyl *p*-tolyl ether itself. The yield of 2-chloro-8-methylphenoxtellurine, m. p. 67—68°, was small and it was impossible to obtain a practicable method of oxidising this compound to the carboxylic acid.

After various other methods had been investigated, we succeeded in devising a convenient synthesis of phenoxtellurines. The easily prepared amino-ether (III; R = Me) was diazotised and converted into the *chloromercuri*-compound (IV; R = Me) by Nesmejanow's method (*Ber.*, 1929, 62, 1010; 1934, 67, 130). When a chloroform solution



of this and tellurium tetrachloride was boiled for some time, the *telluritrichloride* (V; R = Me) was formed in good yield. This compound readily passed into 2-methylphenoxtellurine 10 : 10-dichloride (VI; R = Me) when heated, and reduction of this dichloride gave 2-methylphenoxtellurine.

Oxidation of a methyl group in a phenoxtellurine being impracticable as a route to a carboxylic acid, we applied the new synthesis to 2-amino-4'-carboxydiphenyl ether (III; R = CO<sub>2</sub>H). The process worked excellently, provided acetonitrile was used as solvent for the reaction (IV) → (V).

#### EXPERIMENTAL.

*2-Nitrophenoxtellurine*.—Phenoxtellurine (50 g.), prepared by Drew's method (*loc. cit.*), was gradually added to a mixture of 330 c.c. of nitric acid (*d* 1.5) and 500 c.c. of glacial acetic acid at the ordinary temperature. The mixture was heated on the boiling water-bath until the dinitrate had completely dissolved (1½ hours), and the solution was then poured into much water containing ice. The precipitated dinitrate was immediately reduced with 60 g. of potassium anhydrosulphite and 200 c.c. of water. The gummy mass obtained was extracted with chloroform and the extract was dried and evaporated. The residue, when crystallised from alcohol-acetone, gave 11.5 g. of pure 2-nitrophenoxtellurine as yellow needles, m. p. 128—129°.

2-Aminophenoxtellurine could not be obtained by catalytic reduction under pressure, apparently owing to poisoning of the platinum oxide used, but was prepared in 65% yield by Drew's method (*loc. cit.*).

**2-Aminophenoxtellurine Hydrogen d-Tartrate.**—A solution of 10 g. of tartaric acid in 100 c.c. of absolute alcohol was added to one of 20.7 g. of aminophenoxtellurine in 350 c.c. of hot absolute alcohol. On cooling, 24.2 g. of the *sal* separated as rosettes of small flat needles, and on concentrating the mother-liquor two further crops of 4 g. and 2 g., severally. These crops had  $[\alpha]_{5791}^{20} + 2.48^\circ$ ,  $+ 2.06^\circ$ , and  $+ 2.02^\circ$ , in absolute ethyl alcohol, respectively, and melted at 158—159° (decomp.). The first fraction was recrystallised from alcohol 7 times and then had  $[\alpha]_{5791}^{20} + 2.45^\circ$  (Found: C, 40.9; H, 3.6.  $C_{16}H_{15}O_7N_2Te$  requires C, 41.7; H, 3.3%). This crop gave rise to an inactive specimen of 2-aminophenoxtellurine, as did two other crops obtained during further fractionation. In all, 14 crops were examined polarimetrically and showed no difference in rotation except when they were obtained from concentrated mother-liquors and were dark in colour. Such crops had  $[\alpha]_{5791}^{20}$  as high as  $+ 3.15^\circ$ , but no significance is attached to this slightly higher figure.

**2-Aminophenoxtellurine d-Camphorsulphonate.**—Equivalent solutions of the base (15.5 g.) and acid (11.6 g.) in hot alcohol were mixed (total volume, 400 c.c.). On cooling, rosettes of pale yellow needles, m. p. 182—185° (decomp.), separated (8.1 g.). By successive concentrations of the mother-liquor, 14.5 g. and 1.7 g. of salt were obtained. A fourth crop was too highly coloured for polarimetric examination, but the first three crops had  $[\alpha]_{5791}^{20} + 14.0^\circ$ ,  $+ 14.4^\circ$ , and  $+ 15.6^\circ$ , respectively, in absolute ethyl alcohol. The third fraction, treated with ammonia, gave inactive base. The first fraction was recrystallised from aqueous acetone and gave 2 crops with  $[\alpha]_{5791}^{20} + 15.3^\circ$  and  $+ 14.3^\circ$ , a further crystallisation of the first of these crops leading to  $[\alpha]_{5791}^{20} + 15.0^\circ$  (Found: C, 46.7; H, 4.8.  $C_{22}H_{25}O_5N_2STe$  requires C, 48.6; H, 4.6%).

**2-Chloro-8-methylphenoxtellurine.**—4-Nitro-4'-methylphenyl ether, prepared from *p*-chloronitrobenzene and *p*-cresol by the usual method, was reduced with iron and acidified water at 100°, and the 4-amino-ether converted (65% yield) by the Sandmeyer process into 4-chloro-4'-methylphenyl ether (b. p. 168°/14 mm.; leaflets, m. p. 54°, from alcohol). Condensation of the chloro-ether with tellurium tetrachloride at 200°, or at 200—250°, gave very poor yields of 2-chloro-8-methylphenoxtellurine 10 : 10-dichloride. This was most conveniently prepared by heating 22 g. of the ether with 27 g. of tellurium tetrachloride for 3 hours at 160° and then for 8 hours at 200—240°. The brittle, dark red mass obtained on cooling was powdered, and extracted with ether until free from chloro-ether. The residue (40 g.) was crystallised from chloroform, in which much of it was insoluble. Tellurium (12 g.) was also isolated. In this way, 6 g. of reddish-brown microcrystalline dichloride, m. p. 284°, were obtained, and this was moistened with acetone and reduced with potassium anhydrosulphite and water. The resulting brown powder, when crystallised from alcohol, gave 2-chloro-8-methylphenoxtellurine as yellow needles, m. p. 67—68° (Found: C, 45.4; H, 2.7.  $C_{13}H_9OCITe$  requires C, 45.3; H, 2.6%).

**2-Chloromercuri-4'-methylphenyl Ether.**—The basis of the process used was the method of Nesmejanow (*loc. cit.*). 2-Amino-4'-methylphenyl ether (47 g.) was diazotised in hydrochloric acid with 14 g. of sodium nitrite, and the concentrated solution added, with stirring, to a solution of 54 g. of mercuric chloride in 54 c.c. of concentrated hydrochloric acid, to which 50 g. of ice had been added. The pale yellow crystalline precipitate of the diazomercuric chloride was filtered off, washed successively with water, alcohol, and ether, and then dried in the air. It was suspended in 400 c.c. of pure acetone at  $- 60^\circ$ , and treated with copper powder freshly prepared from 120 g. of copper sulphate crystals and 26 g. of zinc dust. The rate of decomposition regulated the yield, which was highest when the reaction mixture was kept at  $- 60^\circ$  for 12 hours, and then allowed slowly to attain the ordinary temperature during another 12 hours. The mixture was then filtered, and the residue extracted with hot acetone. The combined acetone extracts were concentrated to 200 c.c., and, on cooling, the *chloromercuri*-compound separated in stout needles. It was recrystallised from alcohol and then formed long, white, feathery needles, m. p. 140° (yield, 48 g.; 57%). It distils unchanged at 250—255°/15 mm. (Found: Hg, 47.7; Cl, 8.5.  $C_{13}H_{11}OCIHg$  requires Hg, 47.8; Cl, 8.5%).

**4'-Methylphenyl Ether 2-Telluritrichloride.**—To a solution of 41.9 g. of the mercurichloride in 300 c.c. of dry chloroform, 26 g. of tellurium tetrachloride (*i.e.*, slightly less than the calculated quantity) were added, and the whole was boiled under reflux for 1.5 hours. On cooling, mercuric chloride separated and was filtered off (25 g.). The filtrate was concentrated to 70 c.c., and, when kept, deposited 33 g. of the almost pure *telluritrichloride*, which was recrystallised from chloroform and obtained in massive yellow prisms or octahedra, m. p. 180—185° (decomp.) (yield, 80%) (Found: C, 36.3; H, 2.7.  $C_{13}H_{11}OCl_3Te$  requires C, 37.1; H, 2.6%).

*2-Methylphenoxtellurine 10 : 10-Dichloride*.—The trichloride (16.8 g.) was heated for 0.5 hour in a large test-tube in a bath at 200—240°, with continual stirring. The deep red solid obtained on cooling was ground, and crystallised from acetone. The *dichloride* separated in pale yellow plates, m. p. 274—275° (12.2 g.; 80% yield) (Found: C, 41.5; H, 2.7.  $C_{13}H_{10}OCl_2Te$  requires C, 41.0; H, 2.6%). A little tellurium was always formed.

*2-Methylphenoxtellurine*.—The dichloride was slowly reduced by potassium anhydrosulphite in presence of water, the mixture being ground at intervals during 24 hours. *2-Methylphenox-tellurine* was then obtained in 93% yield. It tended to separate as an oil from solutions in light petroleum, but addition of a little alcohol prevented oil-formation and gave rosettes of needles, m. p. 50—52° (Found: C, 51.7; H, 3.55.  $C_{13}H_{10}OTe$  requires C, 50.4; H, 3.2%). The 2-methylphenoxtellurine could not be oxidised with neutral or alkaline permanganate, or with chromic and acetic acids. The bulk of the material was destroyed and only small quantities of the telluroxide carboxylic acid were formed. Oxidation of the tellurine to the tellurone by means of hydrogen peroxide in acetone solution, followed by oxidation as above, also gave poor yields.

*2-Amino-4'-carboxydiphenyl Ether*.—2-Nitro-4'-methyldiphenyl ether was reduced to the amino-ether by the wet iron method, the base acetylated, and the 2-acetamido-4'-methyldiphenyl ether oxidised with neutral permanganate (Thompson and Turner, *loc. cit.*).

*2-Chloromercuri-4'-carboxydiphenyl Ether*.—The hydrochloride of 2-amino-4'-carboxydiphenyl ether (53 g.) was diazotised in hydrochloric acid, the final volume being about 350 c.c. The diazonium salt always crystallised out, and in order to keep the solution as concentrated as possible, it was filtered off and redissolved in the least quantity of ice-cold water, in which it is considerably more soluble than in the dilute acid from which it separated. The solution was brought into reaction with mercuric chloride exactly as above, and the resulting pale yellow, microcrystalline diazomercuric chloride treated as before. It was suspended in 350 c.c. of pure acetone at -60° (some of the salt dissolved) and treated with copper powder (2 atoms). The evolution of nitrogen started very briskly, but the yield of chloromercuri-compound reached a maximum when the reaction was allowed to take 48 hours. The mixture was then filtered, and the solid residue extracted several times with 100 c.c. portions of boiling acetone. The acetone was partly removed from the extract, and the chloromercuri-compound allowed to crystallise from about 200 c.c. of solution. It retained a greenish colour even after several crystallisations from acetone or alcohol, and the trace of copper responsible for this was removed by dissolving the product in sodium hydrogen carbonate solution and reprecipitating it with hydrochloric acid. The *chloromercuri*-compound then separated from alcohol in slender, pale buff-coloured needles, m. p. 220° (decomp.) (Found: Hg, 44.0; Cl, 8.1.  $C_{13}H_9O_3ClHg$  requires Hg, 44.6; Cl, 7.9%).

*4'-Carboxydiphenyl Ether 2-Telluritrichloride*.—Interaction between the chloromercuri-compound and tellurium tetrachloride did not take place in boiling chloroform, benzene, or toluene, probably owing to the insolubility of the mercury derivative. Acetonitrile or dioxan can be used as solvent, but the former is more suitable in view of the extreme solubility of the product in dioxan.

The chloromercuri-compound (22.5 g.) was dissolved in 350 c.c. of hot acetonitrile, and 13 g. of tellurium tetrachloride (slightly less than the calculated quantity) added. A deep red colour was immediately produced, and though this became less intense as the reaction proceeded, after 4 or 5 hours' boiling under reflux the solution was still highly coloured. The acetonitrile was partly distilled off, and the product allowed to crystallise from about 80 c.c. of solution. The mercuric chloride remained in the mother-liquor. The trichloride is almost insoluble in most non-hydroxylic solvents, but crystallises from acetonitrile in very small prisms, m. p. 205—206° (decomp.) (Found: C, 35.55; H, 2.4.  $C_{13}H_9O_3TeCl_3$  requires C, 34.9; H, 2.0%).

*2-Carboxyphenoxtellurine 10 : 10-Dichloride*.—The trichloride was heated for 0.5 hour at 220—240°. Hydrogen chloride was evolved vigorously, and the colour gradually changed from dark red to greyish-brown. The mass was allowed to cool, powdered, and crystallised from acetone. A 62% yield of the pure *dichloride* was obtained, as white leaflets, m. p. 319° (Found: C, 38.0; H, 2.0.  $C_{13}H_8O_3TeCl_2$  requires C, 38.0; H, 1.95%).

*Phenoxtellurine-2-carboxylic Acid*.—The dichloride (20.5 g.) was dissolved in a solution of 20 g. of sodium carbonate in 300 c.c. of water; the filtered solution was cooled to 0°, and reduced with 25 g. of potassium anhydrosulphite dissolved in the minimum of water. The colour changed from pale brown to a vivid yellow, and plates of the sodium salt of the reduced acid separated. Reduction at the ordinary temperature gave a dark product. The reaction

mixture was finally warmed to 40°, in order to dissolve the sodium salt, and the acid was precipitated with acetic acid. Mineral acids can only be used for the precipitation when there is a large excess of anhydrosulphite present, for otherwise the deep blue colour of tellurylium salts immediately appears. The acid was crystallised from alcohol or acetone. It forms heavy, bright yellow prisms, m. p. 231—233° (Found: C, 46.0; H, 2.7.  $C_{13}H_8O_3Te$  requires C, 45.9; H, 2.4%).

*Decarboxylation of Phenoxtellurine-2-carboxylic Acid.*—A solution of 1 g. of the acid in 30 c.c. of dry quinoline was boiled for an hour in presence of a little copper-bronze. The cooled mixture was poured into dilute acetic acid. The crystalline deposit which was soon formed was removed, washed with dilute acetic acid and with water, and extracted with sodium carbonate solution. From the alkaline solution, 0.5 g. of unchanged acid was recovered, and by crystallising the alkali-insoluble material twice from light petroleum, 0.2 g. of phenoxtellurine was obtained. It melted at 77—79°, either alone or when mixed with pure phenoxtellurine.

*Experiments on the Resolution of Phenoxtellurine-2-carboxylic Acid.*—(a) *Nor-d-ψ-ephedrine salt.* A hot solution of 13.3 g. of nor-d-ψ-ephedrine in 50% aqueous alcohol was added to a suspension of 30 g. of the acid in the same hot solvent. The filtered solution obtained (550 c.c.) deposited pale yellow, flat needles (49 g.) of the trihydrate of the salt. Vacuum desiccation raised the m. p. from 76—80° to 130—140°, and further drying at 100° to 144—145° (Found: loss, 9.7 g.  $C_{22}H_{21}O_4N_2Te \cdot 3H_2O$  requires  $3H_2O$ , 9.9 g. Found in anhydrous salt: C, 53.6; H, 4.7.  $C_{22}H_{21}O_4N_2Te$  requires C, 53.8; H, 4.3%). The salt was very soluble in all solvents except light petroleum, and was therefore crystallised from aqueous alcohol and air-dried to the trihydrate. Two crops obtained during the preparation of the salt had  $[\alpha]_{5791}^{20} + 16.8^\circ$  and  $+ 16.9^\circ$  in absolute ethyl alcohol. The first crop was recrystallised from aqueous alcohol 4 times: the rotation was then  $+ 16.8^\circ$ . Acid recovered from the last fraction was inactive. The mother-liquors were worked up and gave crops with rotations between  $+ 16.7^\circ$  and  $+ 17.0^\circ$ . In all, 16 crops were examined polarimetrically ( $l = 2$ ;  $c = 2.5$ ).

(b) *Strychnine salt.* The acid (16.98 g.) and strychnine (16.7 g.) were dissolved separately in absolute alcohol and the hot solutions mixed (1000 c.c.). The salt which separated on cooling in an ice chest was not crystalline and was solvated, but crystallisation at the ordinary temperature gave rosettes of needles, m. p. 198—200° (decomp.) (Found: C, 60.6; H, 4.6.  $C_{34}H_{30}O_5N_2Te$  requires C, 60.6; H, 4.5%). The salt could only be crystallised from ethyl alcohol. Four crops obtained during the preparation were examined. The first (13.5 g.) after being crystallised 6 times changed in  $[\alpha]_{5791}^{20}$  only from  $- 14.5^\circ$  to  $- 17.2^\circ$ ; the second (7.5 g.) from  $- 14.4^\circ$  to  $- 15.9^\circ$ ; the third (9.0 g.) from  $- 14.6^\circ$  to  $- 15.3^\circ$  (in chloroform) during 2 crystallisations. Such crops as were decomposed gave inactive acid. The higher rotations were found to be due to separation of free strychnine together with the salt.

(c) *Quinine salt.* The acid (10.2 g.) and quinine (9.72 g.) were dissolved separately in hot alcohol and the solutions mixed. The salt separated in rosettes of hard glistening needles, m. p. 211° (Found: C, 59.5; H, 4.9.  $C_{33}H_{32}O_5N_2Te$  requires C, 59.7; H, 4.8%). The three crops obtained weighed 16.0, 2.25, and 0.8 g. and had respectively  $[\alpha]_{5791}^{20} - 119.4^\circ$ ,  $- 122.3^\circ$ , and  $- 121.6^\circ$  in chloroform. After 3 recrystallisations from absolute alcohol the first crop had  $[\alpha]_{5791}^{20} - 125.1^\circ$ . The acid liberated from it was inactive. The rotations of 12 crops were determined, and ranged from  $- 114^\circ$  to  $- 126^\circ$ , low figures being associated with partial decomposition of the salt in presence of light.

(d) *Cinchonidine salt.* Hot alcoholic solutions of 14.7 g. of cinchonidine and 16.9 g. of acid were mixed. From 500 c.c. of solution 17.8 g. of needles separated with m. p. 206° and  $[\alpha]_{5791}^{20} - 59.4^\circ$  (Found: C, 60.2; H, 5.0.  $C_{32}H_{30}O_4N_2Te$  requires C, 60.6; H, 4.7%). A second fraction of 4 g. had  $[\alpha]_{5791}^{20} - 59.1^\circ$ . Recrystallisation of the first crop gave three fractions with  $[\alpha]_{5791}^{20} - 58.9^\circ$ ,  $- 57.9^\circ$ , and  $- 57.8^\circ$ . In all, eight crops were examined, and several were decomposed, giving inactive acid.

(e) *d-α-Phenylethylamine salt.* When a hot solution of 6.05 g. of base in 50 c.c. of alcohol was added to one of 16.98 g. of acid in 400 c.c. of alcohol, salt separated, and was redissolved after adding 150 c.c. of alcohol. Four fractions of salt separated in turn. These weighed 12.5, 4.5, 2.5, and 2 g., and had  $[\alpha]_{5791}^{20} + 3.97^\circ$ ,  $+ 4.19^\circ$ ,  $+ 3.90^\circ$ , and  $+ 3.85^\circ$ , respectively. The first fraction was recrystallised twice from alcohol and then had m. p. 205° and  $[\alpha]_{5791}^{20} + 4.05^\circ$ . Three further crystallisations from methyl alcohol gave 1.8 g. with  $[\alpha]_{5791}^{20} + 3.88^\circ$ . Inactive acid was obtained from more than one crop. The original second and third fractions were together crystallised from acetone, giving  $[\alpha]_{5791}^{20} + 4.09^\circ$ , and the new crop was then crystallised from methyl alcohol, the rotation finally being  $+ 4.04^\circ$ . The rotations of 11

crops of different origins were actually determined, and ranged from  $+3.80^\circ$  to  $+4.19^\circ$  ( $l = 2$ ;  $c = 1$ ; methyl alcohol) (Found : C, 54.6; H, 4.2.  $C_{22}H_{21}O_3N$ Te requires C, 54.7; H, 4.1%).

*Partial Esterification of Phenoxtellurinecarboxylic Acid with l-Menthol.*—The acid (3.4 g.) and *l*-menthol (5 g.) were heated together under reflux for 7—8 hours. The whole was dissolved in ether, and the ethereal solution extracted with sodium carbonate solution, from which 1.0 g. of acid was subsequently recovered. The ethereal solution was steam-distilled, and when the product was free from menthol it was crystallised from alcohol. The *l*-menthyl ester was so obtained as yellow prisms, m. p.  $123$ — $125^\circ$ . It was recrystallised twice from alcohol and once from acetone, but the crops varied in  $[\alpha]_{579.1}^{20}$  only from  $-51.9^\circ$  to  $-52.2^\circ$  in acetone (Found : C, 57.6; H, 5.6.  $C_{23}H_{26}O_3$ Te requires C, 57.8; H, 5.5%).

We thank Imperial Chemical Industries for a grant.

UNIVERSITY OF LONDON (BEDFORD COLLEGE).

[Received, November 27th, 1937.]

---