# CCLXXXIII.—*Interactions of Basic Tellurium Chloride and the Cresols.*

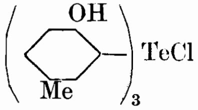
By GILBERT T. MORGAN and HENRY BURGESS.

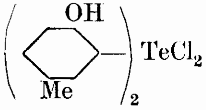
THIS investigation, which was undertaken with the object of producing organic tellurium compounds suitable for use in chemotherapy, has furnished results comparable with those obtained in an earlier study of the interactions of selenium oxychloride and phenols (Morgan and Burstall, J., 1928, 3260). The reagent employed in our experiments, which is prepared by the action of concentrated hydrochloric acid on tellurium oxynitrate, may approximate to the hydrochlorides indicated by Ditte (*Compt. rend.*, 1876, **83**, 336), but whatever may be its precise chemical constitution the material has a specific reaction on the three cresols different from that displayed by either tellurium tetrachloride or tellurium dioxide. Accordingly throughout this paper the expression " basic tellurium chloride " refers to the product prepared as in the opening paragraph of the experimental section, although we are aware that in the course of a systematic investigation of tellurium compounds Lenher was led to the view that anhydrous tellurium oxychloride does not exist (*J. Amer. Chem. Soc.*, 1909, **31**, 243); more recently a similar conclusion has been reached by Parker and Robinson (J., 1928, 2854).

The research was abandoned before a complete proof of the orientation of the entrant tellurium atoms had been established; from analogy, however, with the corresponding selenium compounds (*loc. cit.*) it seems highly probable that the derivatives of the three cresols have the constitutions indicated below.

In the condensation with *p*-cresol, tellurium probably enters the aromatic ring in the ortho-position with respect to the hydroxyl group, so that in addition to a complex intermediate compound there are formed: (1) *tri-2-hydroxytri-5-methyltriphenyltelluronium chloride* (I), a polar compound soluble in aqueous alcohol but almost insoluble in non-hydrolysing organic media such as chloroform, benzene, and carbon tetrachloride:

(I.)



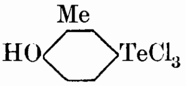


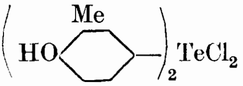
(II.)

(2) *di-2-hydroxydi-5-methyldiphenyl telluridichloride* (II), a non-polar compound soluble in chloroform, acetone, or alcohol. The latter derivative, which takes the place of di-2-hydroxydi-5-methyldiphenyl selenide in the selenium oxychloride condensation, illustrates the greater tendency for tellurium to retain its quadrivalency in such condensations.

In the interaction with *o*-cresol a product representing an earlier stage in the process can be isolated, namely, *4-hydroxy-3-methylphenyl tellurium trichloride* (III). This phase in the interaction has not hitherto been observed either with the other cresols or with the corresponding condensations between selenium oxychloride and the phenols.

(III.)



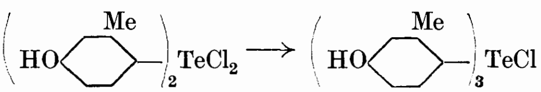


(IV.)

*o*-Cresol also gives rise to two isomeric *di-o-hydroxyditolyl telluridichlorides A* and *B*, one of which probably has the constitution indicated by formula (IV).

The condensation with *m*-cresol leads to *di-4-hydroxydi-2-methyldiphenyl telluridichloride* (V), which undergoes a remarkable change either on boiling with aqueous alcohol or when its solution in hot aqueous sodium carbonate is acidified, for by elimination of one-third of the tellurium from organic combination either of these processes leads to *tri-4-hydroxytri-2-methyltriphenyltelluronium chloride* (VI), a polar substance dissolving sparingly in hot water, more readily in the alcohols, but only sparingly in non-hydrolysing solvents.

(V.)



(VI.)

On reduction with aqueous alkali metabisulphite the foregoing telluridichloride gives *di-4-hydroxydi-2-methyldiphenyl telluride*, which is also obtained in very small yield by the action of this reducing agent on the product of the interaction of *m*-cresol and tellurium tetrachloride. The smallness of the yield indicates that in all probability the effective agent in this condensation is the small amount of basic tellurium chloride produced by the action of moisture on the tetrachloride.

## EXPERIMENTAL.

The basic tellurium chloride employed in the following condensations was prepared by oxidising tellurium with nitric acid (*d* 1·42), excess of this acid being removed by repeated evaporation with concentrated hydrochloric acid. After a final distillation on the water-bath under reduced pressure the residue, which usually retained traces of uncombined hydrogen chloride, was caused to interact with the three cresols in the following manner.

An excess of the cresol (2 to 4 mols.) having been added to the tellurium compound suspended in three times its weight of dry ether, the solvent was distilled away and the residual mixture maintained at 120—130° for *o*- or *m*-cresol and at 110—120° for *p*-cresol.

1. p-*Cresol Condensation.*—The three products arising from the foregoing condensation were extracted from the mixture by successive treatment with (*a*) benzene, (*b*) chloroform, and (*c*) alcohol, the dry solvent being employed in each case. The hot filtered benzene extract (*a*) deposited a pale sage, crystalline powder, decomp. 229—230°, which was insoluble in the common organic media and was freed from more soluble impurities by several extractions with hot benzene (Found: Cl, 15·4, 15·45; Te, 37·25. $C_{21}H_{21}O_4Cl_3Te_2$ requires Cl, 15·2; Te, 36·5%). These analyses indicate a complex *tri-2-hydroxytri-5-methyltriphenyltelluronium tellurium oxychloride*, $[(HO{\cdot}C_7H_6)_3Te]TeOCl_3$, somewhat analogous to dimethylpyrone tellurium oxychloride (Morgan and Drew, J., 1924, **125**, 751).

After its first separation from benzene the complex ditellurium compound was no longer soluble either in this solvent or in petroleum, carbon tetrachloride, or chloroform. Its original solubility in benzene was probably promoted by the presence in the crude condensation product of much unchanged *p*-cresol. The alcohols, however, decomposed the green substance into insoluble tellurium dioxide and a soluble white compound identified subsequently as tri-2-hydroxytri-5-methyltriphenyltelluronium chloride (I; see below).

*Di-2-hydroxydi-5-methyldiphenyl telluridichloride* (II). When the benzene mother-liquors from the foregoing sage-green substance were heated under 20 mm. pressure, unchanged *p*-cresol and solvent distilled over, leaving a black viscous tar. This was extracted with chloroform and the extract was added to the original chloroform extract (*b*) of the crude condensation product. The combined solutions were concentrated until on cooling a pink crystalline material separated, which after three crystallisations from chloroform was obtained in colourless compact crystals, decomp. 213—214° (Found: C, 40·6; H, 3·4; Cl, 16·7; Te, 31·1. $C_{14}H_{14}O_2Cl_2Te$ requires C, 40·7; H, 3·4; Cl, 17·2; Te, 30·9%). This complex *telluridichloride* was slightly more soluble in hot than in cold chloroform and dissolved readily in alcohol or acetone.

*Tri-2-hydroxytri-5-methyltriphenyltelluronium chloride* (I), $(HO\cdot C_7H_6)_3TeCl,2H_2O$, was obtained by precipitating with water both the original alcoholic extract (*c*) of the condensation mixture and the alcoholic extract of the sage-green complex tellurium oxychloride. These precipitates when crystallised from hot dilute alcohol were obtained in felted masses of colourless hair-like crystals melting somewhat indefinitely at 244—245° (decomp.) (Found: C, 48·9; H, 4·9; Cl, 6·8; Te, 23·9. $C_{21}H_{21}O_3ClTe,2H_2O$ requires C, 48·45; H, 4·85; Cl, 6·8; Te, 24·5%). The telluronium chloride was readily soluble in the hot alcohols but almost insoluble in benzene, chloroform, or carbon tetrachloride.

2. o-*Cresol Condensation.*—The crude condensation product was extracted successively with (*a*) light petroleum, (*b*) dry benzene, and (*c*) dry chloroform, the first solvent removing any unchanged *o*-cresol.

4-*Hydroxy*-3-*methylphenyltellurium trichloride* (III). The greyish-green insoluble residue from the foregoing extractions, when further extracted in a Soxhlet apparatus with dry chloroform containing 5% of alcohol, yielded olive-green crystals, decomp. 208—209° (Found: Cl, 31·0; Te, 36·4. $C_7H_7OCl_3Te$ requires Cl, 31·2; Te, 37·4%). This complex *trichloride* was insoluble in petroleum, benzene, carbon tetrachloride, or dry chloroform, but dissolved in the last solvent when containing a little absolute alcohol. It was decomposed by water or moist alcohol to products soluble in hot water.

*Isomeric di-*o*-hydroxyditolyl telluridichlorides* (IV). *Isomeride A.* The chloroform extract (*c*) of the crude condensation product on concentration and cooling gave a red solid which after repeated crystallisations from chloroform was obtained in well-defined, transparent, colourless, oblique prisms, decomp. 197—198° (Found: Cl, 17·4; Te, 30·8. $C_{14}H_{14}O_2Cl_2Te$ requires Cl, 17·2; Te, 30·9%).

*Isomeride B.* The benzene extract (*b*) of the crude condensation product when concentrated and cooled yielded a crop of the dichloride A, whereas the mother-liquor on addition of light petroleum gave a light grey solid which after repeated crystallisations from benzene separated in nodular, colourless, opaque crystals, decomp. 177—178° (mixed m. p. with A, 170—172°) (Found : Cl, 16·7 ; Te, 30·2%). This dichloride dissolved sparingly in petroleum or carbon tetrachloride, but was about ten times more soluble in benzene or chloroform than its isomeride A. It dissolved in water to an acid solution from which hydrochloric acid reprecipitated the original dichloride.

Unlike the following *m*-cresol derivative, these dichlorides are not readily transformed into triarylated tellurium chlorides by prolonged boiling with 95% alcohol or with aqueous sodium carbonate.

3. m-*Cresol Condensation.*—The dark semi-solid condensation product after extraction with carbon tetrachloride left an insoluble green solid, which on crystallisation from absolute alcohol furnished primrose-yellow crystals (Found : C, 41·0; H, 3·9; Cl, 17·0; Te, 30·6. $C_{14}H_{14}O_2Cl_2Te$ requires C, 40·7 ; H, 3·4 ; Cl, 17·2 ; Te, 30·9%).

*Di-4-hydroxydi-2-methyldiphenyl telluridichloride* (V) was almost insoluble in benzene, chloroform, carbon tetrachloride, or ethyl acetate, slightly soluble in acetone, and dissolved readily in hot absolute alcohol. It readily underwent transformation into telluronium chloride when treated as follows : (*a*) On refluxing with 95% alcohol, tellurium dioxide was precipitated and the tellurium dichloride passed into solution, whereas on boiling with absolute alcohol more than 90% of unchanged dichloride was recovered. (*b*) The dichloride was dissolved in hot aqueous sodium carbonate ; when the solution was acidified with hydrochloric acid, the telluronium chloride was precipitated quantitatively.

*Tri-4-hydroxytri-2-methyltriphenyltelluronium chloride* (VI), $(HO\cdot C_7H_6)_3TeCl,2H_2O$, crystallised from alcohol–petroleum in colourless, felted, feathery crystals, m. p. 184—185° (Found : C, 49·2; H, 4·8; Cl, 6·5; Te, 24·2; $H_2O$, 6·5. $C_{21}H_{21}O_3ClTe,2H_2O$ requires C, 48·45; H, 4·85; Cl, 6·8; Te, 24·5; $H_2O$, 6·9%). This telluronium chloride was slightly soluble in hot water to an acid solution. It dissolved readily in the alcohols but only sparingly in ether, acetone, or chloroform. It was insoluble in carbon tetrachloride, benzene, or petroleum.

The *sodium* derivative of *tri-4-hydroxytri-2-methyltriphenyltelluronium hydroxide*, $(NaO\cdot C_7H_6)_3Te\cdot OH$, was prepared by dissolving the telluronium chloride in warm 2*N*-sodium carbonate or 4*N*-sodium hydroxide. The colourless crystals which separated on cooling were washed with 50% alcohol (Found: Te, 24·1, 24·05; Na, 13·2. $C_{21}H_{19}O_4Na_3Te$ requires Te, 24·0; Na, 13·0%). The air-dried sodium salt melted sharply at 137—138° and resolidified on further heating. It was sparingly soluble in water to an alkaline solution.

*Di-4-hydroxydi-2-methyldiphenyl Telluride.*—Ethereal solutions of *m*-cresol (6·5 c.c.) and tellurium tetrachloride (5·5 g.) were mixed and subsequently heated for 2 hours on the water-bath. The resulting greenish-black oil was reduced with an ice-cold solution of 79% potassium metabisulphite, the product extracted rapidly with chloroform, and the filtered extract concentrated. During evaporation the colour of the solution diminished and addition of light petroleum gave felted colourless needles, which were recrystallised from carbon tetrachloride, and then melted at 143—144° (Found: C, 49·1; H, 4·2; Te, 36·8. $C_{14}H_{14}O_2Te$ requires C, 49·2; H, 4·1; Te, 37·3%). The *telluride*, which was thus obtained only in small yield (0·3 g.), dissolved sparingly in hot water to a faintly acid solution giving a wine-red coloration with alcoholic ferric chloride. It was readily soluble in chloroform, benzene, acetone, or alcohol and sparingly soluble in carbon tetrachloride or petroleum. On addition of mineral acid to an alkaline solution of this telluride a purple coloration was developed forthwith and rapidly disappeared, the original purple prisms of the precipitated telluride becoming colourless. This colour change can be repeated indefinitely.

The small yield of organic telluride obtained in the foregoing preparation suggested that this condensation was due, not to tellurium tetrachloride, but to a small amount of basic tellurium chloride formed through hydrolytic change. The reaction is certainly not due to tellurium dioxide, for this oxide was recovered unchanged after prolonged heating with *m*-cresol at 160—180°.

CHEMICAL RESEARCH LABORATORY,
TEDDINGTON, MIDDLESEX.

[*Received, August 22nd,* 1929.]