CXLVII.—*Interaction of Tellurium Tetrachloride and Dimethylaniline.*

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TELLURIUM tetrachloride and dimethylaniline combine in dry ethereal solution to form *bisdimethylaniline tellurium tetrachloride*, $(C_6H_5{\cdot}NMe_2)_2,TeCl_4$, a compound of similar type to the products previously obtained by combination of tellurium tetrabromide and various aromatic bases (Lowy and Dunbrook, *J. Amer. Chem. Soc.*, 1922, **44**, 614).

In the present instance the additive compound is accompanied by a small amount of a substitution product, 4 : 4′-*tetramethyldiaminodiphenyl telluridichloride*, $(NMe_2{\cdot}C_6H_4)_2TeCl_2$, which, however, is more conveniently obtained by digesting the tetrachloride in boiling water, the tellurium migrating into the rings in the para-positions with respect to the two nitrogen atoms. This orientation of tellurium is disclosed by the action of cold nitrous acid, tellurium being eliminated as dioxide and *p*-nitrosodimethylaniline produced. When reduced directly with alkali metabisulphite, the dichloride furnishes 4 : 4′-*tetramethyldiaminodiphenyl telluride*, which is also soluble in organic media and is slowly oxidised in the air.

After the conversion of the soluble tetrachloride additive compound into the insoluble dichloride by heating in aqueous solution the concentrated mother-liquor yields on addition of hydrogen chloride a double salt of dimethylaniline hydrochloride and tellurium tetrachloride which crystallises best from alcoholic hydrochloric acid as $(C_6H_5{\cdot}NMe_2,HCl)_3TeCl_4,C_2H_5{\cdot}OH$. This product resembles certain double salts containing tellurium tetrabromide and aromatic bases (Lowy and Dunbrook, *loc. cit.*) and the double halides of tellurium and the alkaloids (Lenher and Titus, *J. Amer. Chem. Soc.*, 1903, **25**, 730).

Preliminary experiments showed that in its interaction with tellurium tetrachloride *N*-methyldiphenylamine resembles dimethylaniline in yielding both an additive compound and a substitution product.

EXPERIMENTAL.

Bisdimethylaniline Tellurium Tetrachloride.—The bright red precipitate, which appeared on addition of 15·2 g. of tellurium tetrachloride, dissolved in 160 c.c. of dry ether, to 21 c.c. of dimethylaniline (3 mols.) in 200 c.c. of the same solvent, rapidly changed to a yellow crystalline solid, which was obtained in practically quantitative yield after washing with ether (Found: C, 37·4; H, 4·6; Cl, 27·8; Te, 24·7. $C_{16}H_{22}N_2Cl_4Te$ requires C, 37·5; H, 4·3; Cl, 27·7; Te, 24·9%).

Bisdimethylaniline tellurium tetrachloride became green at 137° and melted to a blue liquid at 144—145° with elimination of tellurium. It was insoluble in the common organic solvents except acetone and alcohols, which, however, decomposed it. Its bright yellow colour deepened on exposure to light and the substance slowly decomposed in moist air. It formed a colourless hydrochloride stable in dry air but decomposed by alkali with liberation of dimethylaniline.

4 : 4′-*Tetramethyldiaminodiphenyl telluridichloride* was isolated in small amount (0·1 g.) from the concentrated ethereal mother-liquor of the preceding preparation after removal of dimethylaniline with petroleum, but was best prepared by warming 28·5 g. of the foregoing additive compound with 200 c.c. of boiling water for 15 minutes; the initially clear solution then deposited a yellow precipitate, which was extracted with chloroform to separate the organic product from inorganic tellurium compounds. The dichloride which separated from its chloroform solution (yield, 8 g.) crystallised from acetone in well-defined, highly refractive, bright yellow plates or hexagonal prisms which turned blue at 181° and melted to a purple liquid at 188—189° (Found: C, 43·7; H, 4·4; Cl, 16·1; Te, 28·9. $C_{16}H_{20}N_2Cl_2Te$ requires C, 43·8; H, 4·6; Cl, 16·2; Te, 29·1%). The dichloride was readily soluble in chloroform or hot benzene, less soluble in acetone and only sparingly soluble in alcohol, ether, or carbon tetrachloride. It dissolved in concentrated sulphuric acid with effervescence, formed a hydrochloride (m. p. 136—137°), and, although insoluble in hot water, dissolved in warm aqueous alkalis to colourless solutions which deposited crystals on cooling. It underwent nitration and its nitro-derivative was reducible to a diazotisable base without elimination of tellurium.

The orientation of tellurium in this dichloride was determined by adding aqueous sodium nitrite (3 mols.) to 1 g. of the dichloride suspended in dilute hydrochloric acid at −5°, the temperature being finally raised to 5°: 0·30 g. of tellurium dioxide and 0·6 g. of *p*-nitrosodimethylaniline were collected, the yields of these products being 80% of the calculated quantities.

4 : 4′-*Tetramethyldiaminodiphenyl telluridi-iodide*,

$(NMe_2{\cdot}C_6H_4)_2TeI_2$,

readily obtained by refluxing the dichloride in acetone with a slight excess of sodium iodide, crystallised from chloroform–acetone in lustrous dark red prisms, melting and decomposing at 158—159° with evolution of gas (Found : I, 41·1. $C_{16}H_{20}N_2I_2Te$ requires I, 40·8%).

4 : 4′-*Tetramethyldiaminodiphenyl telluride*, $Te(C_6H_4{\cdot}NMe_2)_2$.—Potassium metabisulphite (2 g.) was added to a suspension of 0·8 g. of the dichloride in dilute acetone and after an hour the mixture was extracted with chloroform. Methyl alcohol was added to the dried and concentrated extract; and the solution, filtered from tellurium, was cooled on ice until pale olive-green crystals separated, m. p. 128—130° (Found : C, 52·1, 52·25; H, 6·1, 5·8; Te, 34·6. $C_{16}H_{20}N_2Te$ requires C, 52·2; H, 5·5; Te, 34·7%). This telluride was readily soluble in chloroform, acetone, or benzene, sparingly soluble in alcohol and insoluble in water. It oxidised slowly to a colourless insoluble solid. Even in cold solution it tended to deposit tellurium, and this separation probably caused the variability in colour (orange, orange-red and olive-green) of the various preparations.

Trisdimethylaniline Hydrochloride Tellurium Tetrachloride, $(C_6H_5{\cdot}NMe_2,HCl)_3TeCl_4,C_2H_5{\cdot}OH$.—In the foregoing preparation of 4 : 4′-tetramethyldiaminodiphenyl telluridichloride the aqueous mother-liquor on concentration yielded a residue, which crystallised from alcoholic hydrochloric acid in greenish-yellow, flattened needles, m. p. 119—121° (Found : C, 38·8, 39·0; H, 4·9, 5·0; Cl, 29·8, 31·35; Te, 15·7, 16·55. $C_{24}H_{36}N_3Cl_7Te,C_2H_5{\cdot}OH$ requires C, 39·6; H, 5·4; Cl, 31·5; Te, 16·2%). The alcohol present was identified by conversion into iodoform. This well-defined additive compound, which was readily soluble in water to an acid solution, was less soluble in alcohol. It was hygroscopic and decomposed by aqueous alkalis.

4 : 4′-*Diphenyldimethyldiaminodiphenyl Telluridichloride*,

$(C_6H_5{\cdot}NMe{\cdot}C_6H_4)_2TeCl_2$.

—Tellurium tetrachloride and *N*-methyldiphenylamine in ethereal solution yielded a black viscous oil hardening to an indigo-blue solid (yield, 80%), which was probably an additive compound similar to the first product of the interaction of the tetrachloride and dimethylaniline but not convertible into a dichlorotellurium derivative by the action of water (see p. 1104). The ethereal mother-liquor on concentration left, however, a small amount of viscous solid which after extraction with petroleum to remove *N*-methyldiphenylamine was crystallised repeatedly from acetone–alcohol (Found : C, 55·6 ; H, 4·5 ; Cl, 12·1 ; Te, 22·6. $C_{26}H_{24}N_2Cl_2Te$ requires C, 55·5 ; H, 4·3 ; Cl, 12·6 ; Te, 22·7%). This dichloride (yield, 5%) separated in well-defined, transparent, primrose-yellow, rhomboidal plates, m. p. 170—172° ; it was readily soluble in chloroform or hot acetone and sparingly soluble in alcohol, carbon tetrachloride, or light petroleum. On warming with concentrated sulphuric acid, it developed intense violet to blue colorations, and with nitric acid a deep wine-red tint.

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