CCCXLV.—*Bis*-p-*phenetyl Telluride and its Derivatives.*

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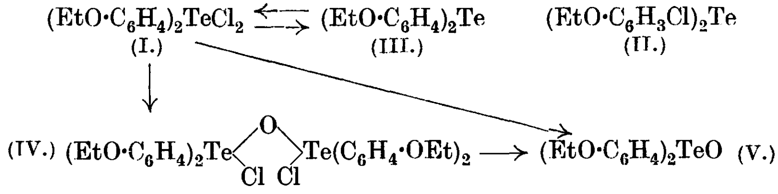
DURING an investigation on the parachor of tellurium (Burstall and Sugden, this vol., p. 229) it was found that the observed molecular parachor of bis-*p*-phenetyl telluridichloride (I) (Morgan and Drew, J., 1925, **127**, 2307) gave a value which suggested that this dichloride was a nuclear-substituted telluride (II). We have now confirmed the earlier view by preparing bis-*p*-phenetyl telluridichloride in a manner which leaves no doubt as to its constitution. *Bis*-p-*phenetyl telluride* (III), made by the Grignard reaction, readily adds on chlorine, forming a dichloro-derivative identical in all respects with the dichloride described by Morgan and Drew (*loc. cit.*).

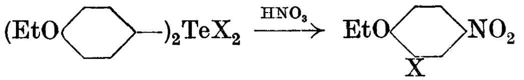


$$\underset{\text{(I.)}}{(EtO{\cdot}C_6H_4)_2TeCl_2} \rightleftarrows \underset{\text{(III.)}}{(EtO{\cdot}C_6H_4)_2Te} \qquad \underset{\text{(II.)}}{(EtO{\cdot}C_6H_3Cl)_2Te}$$

$$\text{(IV.)}\ (EtO{\cdot}C_6H_4)_2Te\overset{O}{\diagup\diagdown}Te(C_6H_4{\cdot}OEt)_2\ (Cl\ Cl) \longrightarrow (EtO{\cdot}C_6H_4)_2TeO\ \text{(V.)}$$

Bis-*p*-phenetyl telluridichloride is converted into *bis*-p-*phenetyl tellurioxychloride* (IV) by boiling with water, whereas warm aqueous caustic alkalis furnish *bis*-p-*phenetyl telluroxide* (V).

Bis-p-*phenetyl telluridibromide* and *bis*-p-*phenetyl telluridi-iodide* have also been prepared. Concentrated nitric acid decomposes these three telluridihalides with formation of varying proportions of *o*-halogenated *p*-nitrophenetoles, the yield being greatest in the case of *o*-iodo-*p*-nitrophenetole :



(X = Cl, Br, or I).

During the interaction of nitric acid and bis-*p*-phenetyl telluridibromide or di-iodide the mixture darkens owing to the transient liberation of the halogen and subsequently becomes decolorised. These colour changes support the view that this formation of *o*-halogeno-*p*-nitrophenetoles is due to successive reactions : liberation of halogen and subsequent halogenation. Similar migrations of halogens have been noted by other observers (Reverdin, *Ber.*, 1896, **29**, 2595; 1899, **32**, 160; G. M. Robinson, J., 1916, **109**, 1078). Moreover, direct bromination and iodination are promoted by the action of nitric acid (Datta and Chatterjee, *J. Amer. Chem. Soc.*, 1916. **38**, 2545; 1917, **39**, 435, 441).

p-*Anisyl*-p-*phenetyl telluridichloride*, m. p. 165—166°, produced on boiling *p*-phenetyl telluritrichloride with anisole, is readily reduced to p-*anisyl* p-*phenetyl telluride*. These compounds containing dissimilar aromatic radicals resemble closely their analogues of the anisyl and phenetyl series (Morgan and Kellett, J., 1926, 1080).

EXPERIMENTAL.

Bis-p-*phenetyl Telluride*.—*p*-Bromophenetole (63 g.), made by the Sandmeyer reaction from *p*-phenetidine, was added to 7·2 g. of clean magnesium suspended in dry ether. The mixture was gently warmed until practically all the magnesium had dissolved. The solution of the Grignard compound was decanted from any undissolved metal and added slowly to a suspension of tellurium dibromide (43 g.) in dry ether. The mixture was refluxed for several hours, cooled, and treated with ice. Hydrobromic acid was added to dissolve any precipitated basic magnesium salts, and the solution filtered from tellurium. The ethereal layer was dried over calcium chloride and evaporated to dryness. The dark brown gum containing the telluride mixed with impurities was extracted with petroleum (b. p. 40—60°) and the solid which separated on evaporation of this extract was crystallised repeatedly from alcohol. Pure *bis*-p-*phenetyl telluride* was obtained in white lustrous plates having a faint greenish tinge and melting at 64° (Found : C, 51·7; H, 5·0; Te, 34·4. $C_{16}H_{18}O_2Te$ requires C, 51·95; H, 4·9; Te, 34·5%). Although insoluble in water, the telluride dissolved easily in the common organic solvents; cold concentrated sulphuric acid developed a red coloration.

Bis-p-*phenetyl Telluridichloride*.—This dichloride has been obtained (*a*) by addition of chlorine to a solution of bis-*p*-phenetyl telluride in carbon tetrachloride, (*b*) by heating *p*-phenetyl telluritrichloride with excess of phenetole at 180—190° (Morgan and Drew, *loc. cit.*), and (*c*) by heating tellurium tetrachloride (1 mol.) with phenetole (4 mols.) at 180—190°. Each method gave a dichloride, melting at 108° either alone or in admixture with the other preparations (Found : Cl, 15·9. Calc., Cl, 16·1%). The three specimens of telluridichloride were reduced to bis-*p*-phenetyl telluride by zinc dust and acetic acid. When cautiously warmed with excess of nitric acid (*d* 1·4), the telluridichloride decomposed and *o*-chloro-*p*-nitrophenetole (m. p. 80°) was identified among the products of the reaction.

Bis-p-*phenetyl Tellurioxychloride*.—When the foregoing dichloride was heated to boiling in aqueous suspension, the crystals became opaque and a portion dissolved. On cooling, the filtrate yielded fluffy white crystals of the *oxychloride*, which dissolved in benzene, acetone, or alcohol and decomposed at 193° (Found: C, 46·4; H, 4·5; Cl, 8·4. $C_{32}H_{36}O_5Cl_2Te_2$ requires C, 46·4; H, 4·4; Cl, 8·6%).

Bis-p-*phenetyl telluridibromide* separated in lemon-yellow crystals when solutions of its generators were mixed. After recrystallisation from alcohol it melted at 127° (Found: Br, 30·2. $C_{16}H_{18}O_2Br_2Te$ requires Br, 30·2%). The dibromide was, however, not formed when *p*-phenetyl telluritribromide was heated with excess of phenetole or when phenetole and tellurium tetrabromide were heated at 180—190°; in both cases a mixture of bromophenetoles and metallic tellurium was obtained. When warmed with nitric acid (*d* 1·4), the dibromide decomposed and *o*-bromo-*p*-nitrophenetole, m. p. 98°, was isolated, the yield being about 40%.

Bis-p-*phenetyl telluridi-iodide*, m. p. 144°, separated from solutions of its generators in orange-red needles (Found: I, 40·8. $C_{16}H_{18}O_2I_2Te$ requires I, 40·7%). Decomposition with concentrated nitric acid resulted in the isolation of *o*-iodo-*p*-nitrophenetole, m. p. 96°, in excellent yield.

Bis-p-*phenetyl telluroxide*, a white microcrystalline substance decomposing at 181°, was formed when bis-*p*-phenetyl telluridichloride or dibromide was boiled with 2*N*-aqueous caustic alkali (Found: C, 49·6; H, 4·9. $C_{16}H_{18}O_3Te$ requires C, 49·8; H, 4·7%). Although insoluble in water, the oxide dissolved in alcohol and benzene; it separated from the solvents as an ill-defined powder.

p-*Anisyl*-p-*phenetyl Telluridichloride*.—*p*-Phenetyl telluritrichloride (1 mol.) was heated at 160° with anisole (4 mols.) for 6 hours. The cooled melt was treated with petroleum (b. p. 40—60°), and the residue crystallised repeatedly from alcohol; glistening white needles of the dichloride then separated, m. p. 165—166° (Found: Cl, 16·7; Te, 29·55. $C_{15}H_{16}O_2TeCl_2$ requires Cl, 16·6; Te, 29·85%).

p-*Anisyl* p-*Phenetyl Telluride*.—The foregoing dichloride was heated for an hour in glacial acetic acid with excess of zinc dust. The coloured filtrate was poured into water, and the precipitated *telluride* crystallised from alcohol; it then separated in glistening white needles having a faint greenish tinge (Found: C, 50·6; H, 4·6. $C_{15}H_{16}O_2Te$ requires C, 50·6; H, 4·5%). It melted to a clear liquid at 45°.

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