

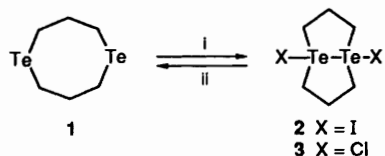
## Preparation and Characterization of a Four-coordinated Ditellurane Stabilized by a Transannular Tellurium–Tellurium Bond from 1,5-Ditelluracyclooctane: A New Multicentre Hypervalent Species

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1,5-Ditelluracyclooctane **1** reacted with halogens ( $I_2$  and  $Cl_2$ ) to give new dihalogenoditelluranes with a  $Te^{IV}-Te^{IV}$ . Reduction of the latter with aqueous NaOH, PhSH,  $Na_2S$  and  $Sml_2$  gave the neutral bis-telluride **1**.

Although the structural and theoretical features of hypervalent organosulfur compounds, sulfuranes, have been much studied, this is not so for multi-coordinated tellurium compounds.<sup>1–3</sup> Further, much less is known about the chemistry of bis-hypervalent bonds with two adjacent hypervalent bonding species.<sup>4</sup> Finally, no clear-cut example of an isolable ditellurane with a  $Te^{IV}-Te^{IV}$  bond has been hitherto reported. Recently, we reported that transannular interaction between the selenium and nitrogen atoms of *N*-methyl-5*H*,7*H*-dibenzo[*b,g*][1,5]-selenazocine produced the first hypervalent ammonioselenurane.<sup>5</sup> We have now studied an organotellurium hypervalent species formed by a transannular reaction in medium-sized cyclic bis-tellurides: new, isolable dihalogeno ditelluranes containing a  $Te^{IV}-Te^{IV}$  bond are described.

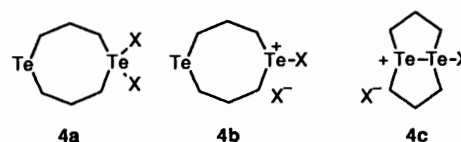
Treatment of the bis-telluride **1** with iodine (1 equiv.) gave the diiododitellurane **2** (Scheme 1), the structure of which was confirmed by multinuclear NMR spectroscopy, mass spectrometry,



**Scheme 1** Reagents: i,  $I_2$  or  $Cl_2$ ; ii, aq. NaOH, or PhSH, or  $Sml_2$ , or  $Na_2S$

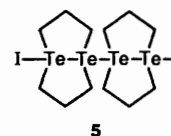
and elemental analysis. In the  $^{13}C$  NMR spectrum of **2** in  $(CD_3)_2SO$  the methylene carbon signals are shifted to  $\delta$  28.3 and 35.1 compared with those of **1** in  $CDCl_3$ ,  $\delta$  4.88 ( $J_{C-Te}$  158 Hz) and 34.1. Also, the  $^{125}Te$  NMR spectrum of **2** in  $Me_2SO$  shows a remarkable downfield shift to  $\delta$  706 from  $\delta$  164 (relative to  $Me_2Te$ ) for **1** in  $CHCl_3$ . The chemical shift of **2** in the  $^{125}Te$  NMR spectrum is in the range characteristic for hypervalent tellurium species.<sup>6</sup> Thus, structure **2** was assigned the ditellurane, rather than **4a**, **4b** or **4c**, on the basis of the following spectroscopic data. The  $^{125}Te$  chemical shift of **2** is a single signal whilst its  $^{13}C$  NMR spectrum has two signals; the NMR spectra of **4a–c** would be expected to exhibit two signals for the tellurium and three carbon chemical shifts for the  $^{13}C$ . The iodine of **2** is not ionic as evidenced by the lack of a signal for such an entity in the  $^{127}I$  NMR spectrum of **2** in  $Me_2SO$ . It is likely that the ditellurane **2** is formed *via* intermediate formation of **4a** or **4b**, or **4c** by remote tellurium participation.

Similarly, **1** reacted with  $Cl_2$  in  $CH_2Cl_2$  at room temperature to afford the dichloroditellurane **3** in quantitative yield, m.p. 165 °C (decomp.),  $m/z$  413.8441 (Calc. for  $C_6H_{12}Cl_2Te_2$ ;  $M$ , 413.8441). The  $^{125}Te$  NMR spectrum of **3** in  $Me_2SO$  shows a single resonance at 1008 ppm which is assigned to the tellurane structure.<sup>6</sup> The  $^{13}C$  NMR spectrum of **3** in  $(CD_3)_2SO$  exhibits



two resonances at  $\delta$  22.9 and 38.7 ( $J_{C-Te}$  208 Hz), while its  $^1H$  NMR spectrum shows signals at  $\delta$  2.47–2.57 (m, 4 H) and 3.20–3.32 (m, 8 H).

Interestingly, treatment of the telluride **1** (2 equiv.) with  $I_2$  in  $CCl_4$  at room temperature under an Ar atmosphere, precipitated the ditellurane dimer **5** as a yellow solid in quantitative yield. The  $^{13}C$  NMR spectrum of **5** in  $Me_2SO$  shows three resonances at  $\delta$  28.7, 35.0 and 41.2, while the  $^{125}Te$  NMR spectrum of **5** exhibits two tellurium signals at  $\delta$  509 and 697 in a 1:1 ratio. This is a new class of tellurane involving a multicentred bond.



It is noteworthy that the ditellurane **2** when treated with aqueous NaOH gave the telluride **1** in quantitative yield, whereas analogous treatment of the tellurane dimer **5** resulted in recovery of **5** (68%), little **1** (17%) being formed. Thiophenol (2 equiv.) reacted with **2** (1 equiv.) in the presence of triethylamine in MeCN under an Ar atmosphere at room temperature for 1 h to give diphenyl disulfide (80%) as the oxidation product and neutral **1** (76%) as the reduction product. Interestingly, **2** undergoes two-electron reduction to give **1** (88%) on treatment with samarium(II) iodide (2 equiv.),<sup>7</sup> as a one-electron reductant at room temperature. The dichloroditellurane **3** can be also reduced to the neutral telluride **1** (81%) on treatment with  $Na_2S$ .

Thus, transannular tellurium participation provides a new four-coordinated chalcogenide containing a two hypervalent atom bonding centre.

### Experimental

**Typical Procedure.**—To a solution of the bis-telluride **1**<sup>8</sup> (154 mg, 0.45 mmol) in benzene (10  $cm^3$ ) was added a solution of iodine (128 mg, 0.50 mmol) in benzene (15  $cm^3$ ), and the whole was stirred for 1 h at room temperature under an Ar atmosphere. The resulting yellow solid was filtered off and washed with benzene to give **2** (92%), m.p. 114–116 °C (decomp.);  $\delta_H[(CD_3)_2SO]$  2.01–4.20 (m, 12 H);  $m/z$  593, 595

and 597 (M<sup>+</sup>) (Found: C, 12.0; H, 1.8. C<sub>6</sub>H<sub>12</sub>Te<sub>2</sub>I<sub>2</sub> requires C, 12.15; H, 2.04%).

Compound **5** was prepared in a similar way to compound **2**: m.p. 103 °C (decomp.); δ<sub>H</sub>[(CD<sub>3</sub>)<sub>2</sub>SO] 2.10–3.80 (m, 24 H) (Found: C, 15.5; H, 2.2. C<sub>12</sub>H<sub>24</sub>Te<sub>4</sub>I<sub>2</sub> requires C, 15.45; H, 2.59%).

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