Reactivity of 1,1'-Spirobi(3*H*-2,1-benzoxatellurole)-3,3'-dione [10-Te-4(C2O2)] with Organic Phosphorus Reagents: The First Synthesis of a Tellurane with Two Carbon- and Two Sulfur-Tellurium Bonds, 1,1'-Spirobi(3*H*-2,1-benzothiatellurole)-3,3'-dione [10-Te-4(C2S2)]

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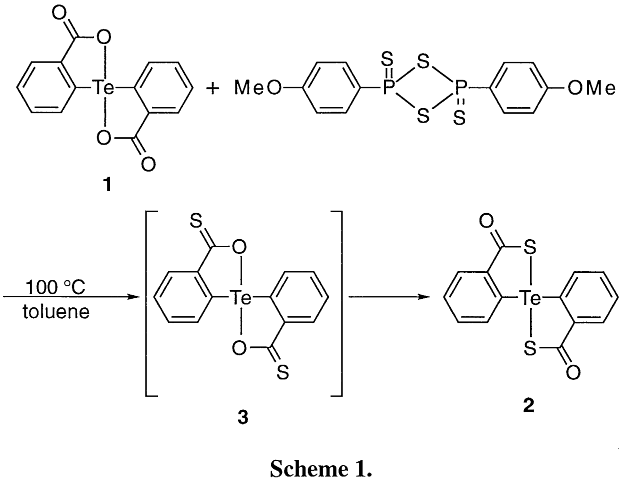
A new spirotellurane, 1,1'-spirobi(3*H*-2,1-benzothiatellurole)-3,3'-dione [10-Te-4(C2S2)] (**2**), having two sulfur atoms as the apical ligands and two carbon atoms as the equatorial ligands was obtained by the reaction of the spirotellurane **1** with Lawesson's reagent. The treatment of **2** with aqueous NaOH gave an unsymmetrical spirotellurane **4**. The telluranes **1** and **2** underwent ring-opening reactions on treatment with $P(NEt_2)_3$ to afford the telluride **6**.

Organic hypervalent compounds of chalcogens have received considerable attention in the past two decades.[1-3] In particular, synthesis and both the physical and chemical properties of various spirosulfuranes and spiroselenuranes have been extensively reported.[4] However, much less is known about those of spirotelluranes.[5] Recently, we reported the first synthesis and structural determination of 1,1'-spirobi(3*H*-2,1-benzoxatellurole)-3,3'-dione [10-Te-4(C2O2)] (**1**) which was found to be a very stable compound against hydrolysis.[6] We wish to report further results on the reactivity of spirotellurane **1**. This article describes the reactivity of spirotelluranes with organic phosphorus reagents, especially, the first isolation of spirotellurane **2** having two sulfur atoms as the apical ligands and the reactivity of compound **2**.

Previously, various attempts to synthesize chalcogenuranes having two sulfur and two carbon atoms as ligands resulted in failure.[7] We have found that the carbonyl group of the spirotellurane **1** readily reacted with nucleophiles,[8] and thus it was treated with Lawesson's reagent. To a solution of spirotellurane **1** (200 mg, 1.22 mmol) in anhydrous toluene (200 mL) was added Lawesson's reagent (495 mg, 1.23 mmol) under an Ar atmosphere. The mixture was stirred at 100 °C for 2 days. After the usual work-up, the residue was purified by silica-gel column chromatography to afford the 1,1'-spirobi(3H-2,1-benzothiatellurole)-3,3'-dione [10-Te-4 (C2S2)] (**2**) (83.4 mg, 0.207 mmol) in 17% yield as shown in Scheme 1.

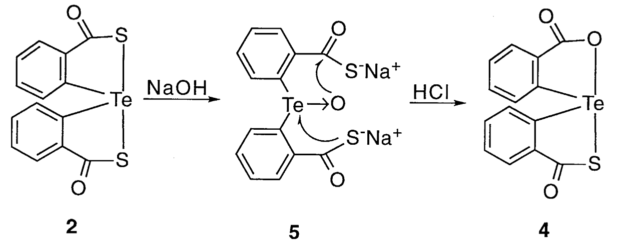


Scheme 1.

The spirotellurane **2** was characterized by spectroscopic and chemical means.[9] The ^{125}Te NMR spectrum of **2** in $CDCl_3$ shows a single peak at 743 ppm (relative to Me_2Te) in the region of tellurane structure. The ^{13}C NMR spectrum of **2** in $CDCl_3$ shows peaks at δ 126.9, 131.0, 132.1, 132.8, 134.9, 138.3, 195.2, which consist with a symmetric structure. Furthermore, the carbonyl carbon at δ 195.2 is attributable to thiol lactone structure. On the other hand, the mass spectrum of **2** shows clearly the parent peak at *m/z* 402 (M^+, 18.0%). Furthermore, the structure of spirotellurane **2** was evidenced from the UV-visible spectrum which exhibits an absorption band at λ_{max} = 293 nm (CH_2Cl_2) in the region of thiol lactone structure. On the other hand, the IR spectrum of **2** exhibits two strong absorption bands at 1634 and 1601 cm^{-1} which consist with the vibration of thiol lactone ring.

In order to explain the formation of **2** from **1**, we propose the following pathways: **1** is initially converted into a thiocarbonyl compound **3**. Subsequently, rearrangement from **3** takes place to give **2** (Scheme 1).

The reactivity of spirotellurane **2** was then investigated. Compound **2** was ready to decompose under irradiation with high pressure mercury lamp in marked contrast to the spirotellurane **1**. Furthermore, spirotellurane **2** was hydrolyzed slowly under aerial conditions, whereas spirotellurane **1** was quite stable to water. A solution of sodium hydroxide (200 mg) in water (1.0 mL) was added to spirotellurane **2** (30 mg, 0.075 mmol). This solution was neutralized with aqueous hydrochloric acid and white precipitates were separated from the solution by filtration to give asymmetric spirotellurane **4** (23 mg, 0.060 mmol) in 80% yield (Scheme 2).

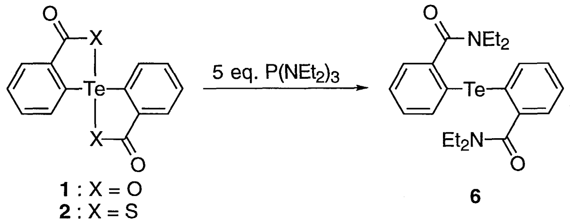


Scheme 2.

It is notable that the spirotelluranes **1** and **2** could not be obtained as reaction products. The structure of **4** was confirmed by ^{1}H, ^{13}C and ^{125}Te NMR spectroscopy, IR spectrum and elemental analysis.[10] The ^{125}Te NMR shift of spirotellurane **4** appears at 781 ppm ($CDCl_3$), which is an intermediate value between that of spirotellurane **1** (951 ppm in $CDCl_3$) and spirotellurane **2** (743 ppm in $CDCl_3$). In order to explain the formation of **4** from **2**, we propose the pathway as shown in

Scheme 2: **2** is initially converted into a telluroxide **5** because of the hydrolysis with aqueous sodium hydroxide. After neutralization, ring formation was occurred immediately to give the compound **4**. This reactivity of spirotellurane **2** toward hydrolysis is similar to the interaction of the spirotellurane **1** with aqueous NaOH.[6]

It is noteworthy that treatment of the spirotellurane **2** with $P(NEt_2)_3$ (2 equiv.) gave the telluride **6** (Scheme 3).[11]



Scheme 3.

The structure of **6** was confirmed by ^{1}H, ^{13}C, and ^{125}Te NMR spectroscopy, mass spectroscopy, and elemental analysis.[12]

Interestingly, the ^{1}H NMR spectrum of **6** shows that the ethyl proton signals vary with temperature, indicating that the free rotation of the C-N bonds on amide groups is restricted (Figure 1). Using the Shanan-Atidi equation $[\Delta G^{\ddagger} = 4.57 \times (273 + Tc) \times [9.97 + \log\{(273 + Tc) / \Delta Hz\}]]$[13] the energy barrier for the free rotation of the carbon-nitrogen bond in **6** was calculated to be 14.6 kcal/mol at 20 °C in $CDCl_3$.

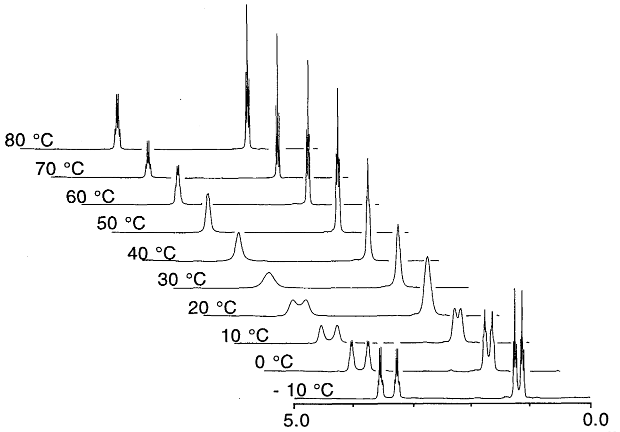


Figure 1. The VT ^{1}H NMR spectra of **6** (41.7 mM solution in $CDCl_3$).

Similarly, the tellurane **1** when treated with $P(NEt_2)_3$ gave the telluride **6** in 88% yield (Scheme 3).

The results described herein show formation of a new class of diaryl tellurane, S-apical tellurane **2**, although diaryl tellurane consisting of two apical sulfur atoms has never been reported. Further work is in progress to explore applications and advantages of the spirotelluranes with two carbon-tellurium and two sulfur-tellurium bonds.

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9 **2**: Mp 260°C; ^{1}H-NMR ($CDCl_3$) δ 7.33-7.77 (m, 4H), 8.14-8.17 (m, 2H), 8.77-8.80 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 126.9, 131.0, 132.1, 132.8, 134.9, 138.3, 195.2 ; ^{125}Te-NMR ($CDCl_3$) δ 743; ir 1634, 1601 (cm^{-1}); MS, *m/z* 402 (M^+, 18.0%). Anal. Found: C; 42.10, H; 2.09%. Calcd for $C_{14}H_8O_2S_2Te$: C; 42.04, H; 2.02%.

10 **4**: Mp 234°C; ^{1}H-NMR ($CDCl_3$) δ 7.69-7.87 (m, 4H), 8.04-8.07 (m, 1H), 8.25-8.29 (m, 2H), 8.43-8.46 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 127.7, 129.8, 130.4, 131.1, 131.4, 132.5, 133.3, 133.4, 134.0, 134.5, 135.8, 136.7, 169.3, 194.6; ^{125}Te-NMR ($CDCl_3$) δ 781; ir 1648 cm^{-1}. Anal. Found: C; 44.14, H; 2.10%. Calcd for $C_{14}H_8O_3STe$: C; 43.80, H; 2.10%.

11 Experimental procedure is as follows: To a solution of tellurane **2** (70.0 mg, 0.175 mmol) in 10 mL of CH_2Cl_2 was added 127 mg (0.523 mmol) of hexaethylphosphorous triamide, $P(NEt_2)_3$. The mixture was stirred for 14 h whence it turned orange. After work-up, the products were purified by HPLC to afford the telluride **6** (75 mg, 0.156 mmol) in 89% yield. Similar reactions of $P(NMe_2)_3$ with the lactone dimer of dimethylketene and dimethyl malonate were reported, see: W. G. Bentrude and W. D. Johnson, *Tetrahedron Lett.*, **46**, 4611 (1967); M. R. Burgada and M. M. Delépine, *Compt. Rend.*, **258**, 1532 (1964).

12 **6**: Mp 118-120°C; ^{1}H NMR ($CDCl_3$, -10 °C) δ 1.17 (t, J = 7.0 Hz, 6H), 1.26 (t, J = 7.0 Hz, 6H), 3.27 (q, J = 7.0 Hz, 4H), 3.55 (q, J = 7.0 Hz, 4H)7.11-7.27 (m, 2H), 7.26-7.28 (m, 4H), 7.64-7.67 (m, 2H); ^{13}C NMR ($CDCl_3$, -10 °C) δ 12.4, 14.1, 39.0, 42.9, 117.1, 126.1, 127.3, 129.5, 139.0, 142.5, 171.4; ^{125}Te NMR ($CDCl_3$) δ 632; ir 1612 cm^{-1}; MS, *m/z* 482 (M^+, 18.8%), 306 (M^+-176, 10.0%). Anal. Found: C, 55.21; H, 5.83; N, 5.84%. Calcd for $C_{22}H_{28}N_2O_2Te$: C, 55.04; H, 5.88; N, 5.84%.

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