Synthesis and Structural Determination of 1,1'-Spirobi(3*H*-2,1-benzoxatellurole)-3-one ([10-Te-4(C2O2)]): Conversion of Diacyloxyspirotellurane to Alkoxyspirotellurane by Reduction with Lithium Aluminium Hydride

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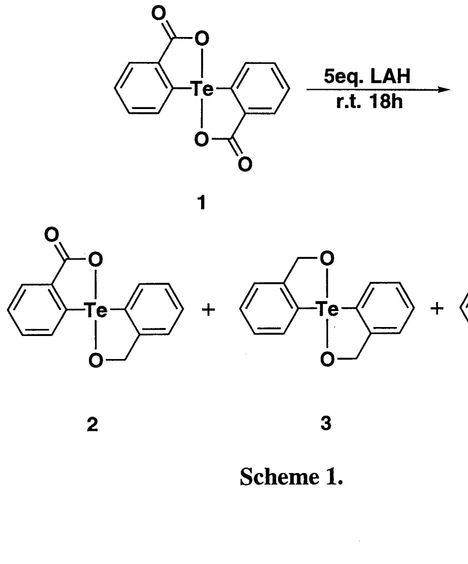
(Received January 18, 1996)

Selective reduction of the diacyloxyspirotellurane **1** with lithium aluminium hydride gave the acyloxyalkoxyspirotellurane **2** and dialkoxyspirotellurane **3**, respectively. The X-ray crystal structure analysis of **2** (R = 0.020) reveals distorted trigonal-bipyramidal geometry about tellurium, similar to structures previously determined for other spirotelluranes.

Organic hypervalent compounds of chalcogens have received considerable attention in the past two decades.[1-3] In particular, the synthesis and properties of various spirosulfuranes and spiroselenanes have been extensively reported.[4] However, much less is known about the physical and chemical properties of telluranes involving spirotelluranes.[5] Particulary, X-ray structural determination of spirotelluranes which have unsymmetrical apical ligands was quite rare. Recently, we reported the first synthesis and structural determination of 1,1'-spirobi(3H-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 paper describes the structural determination of unsymmetrical spirotellurane **2** and a new reaction mode for the chemoselective reduction of hypervalent chalcogen compounds, spirotellurane **1**.

During our investigation about the reactivity of spirotellurane **1**, we found that spirotellurane **1** react with neither H_2O and $BuNH_2$ as neutral nucleophiles nor *t*-BuOCl as an electrophile. Furthermore, we examined the reaction of spirotellurane **1** with hydride anion. It is notable that there are two reducible functional groups in diacyloxyspirotellurane **1**: one is the carbonyl group and another is the tetracoordinated tellurium (IV). Spirotellurane **1** was reduced chemoselectively by 5 equiv. of lithium aluminum hydride to afford new 1,1'-spirobi(3H-2,1-benzoxatellurole)-3-one (**2**) (23%) and 1,1'-spirobi(3H-2,1-benzoxatellurole) (**3**) (15%) and benzyl alcohol (**4**) (38%), respectively, as shown in Scheme 1.[7]



Scheme 1.

The structures of the spirotelluranes **2** and **3** were characterized by ^{1}H, ^{13}C, ^{125}Te NMR spectroscopy, mass spectroscopy and elemental analysis.[8] Particularly compound **2** is a first example of spirotellurane which has alkoxy and acyloxy groups as the apical ligands. The ^{125}Te NMR spectroscopy is a diagnostic method to estimate the structure of tellurium compounds. The ^{125}Te NMR shift of spirotellurane **2** appears at 1096 ppm ($CDCl_3$), which is an intermediate value between that of spirotellurane **1** (951 ppm in $CDCl_3$)[6] and spirotellurane **3** (1144 ppm in $CDCl_3$).[9] The ^{13}C NMR spectrum of **2** in $CDCl_3$ shows fourteen peaks at δ 74.4, 123.7, 128.6, 129.5, 130.0, 131.3, 131.9, 132.0, 132.3, 132.9, 133.6, 134.1, 147.5 and 170.7 which consist with an unsymmetrical structure. Furthermore, the ^{1}H NMR spectrum of **2** shows the methylene protons as one AB quartet observed at 5.59 and 5.73 ppm (J = 14.9 Hz), being consistent with a five-membered spiroring structure. On the other hand, the mass spectrum of **2** shows clearly the parent peak at m/z 356 (M^+, 5.4%) together with m/z 312 (M^+ - 44, 21.7%).

The structure of the compound **2** was finally determined by X-ray crystallographic analysis.[10] The molecular structure of spirotellurane **2**, similarly to other telluranes,[5,6,11] exhibits a considerably distorted trigonal bipyramidal (TBP) geometry about the central tellurium atom, where the more electronegative acyloxy and alkoxy ligands are in the apical positions with the two aryl carbons and the lone electron pair in the equatorial ones. The tellurane **2** was found to be composed of nearly identical two crystals. The ORTEP drawing of **2** is shown in Figure 1.

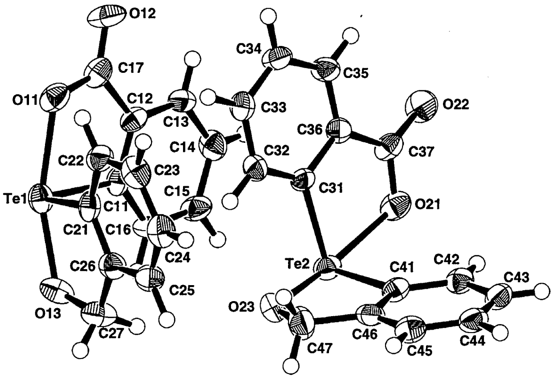


Figure 1. The ORTEP drawing of **2**.

The apical Te(1)-O(11), Te(1)-O(13), Te(2)-O(21) and Te(2)-O(23) bond distances are 2.188(5), 2.008(5), 2.187(5) and 1.991(6) Å, while the equatorial Te(1)-C(11), Te(1)-C(21), Te(2)-C(31) and Te(2)-C(41) bond lengths are 2.114(7), 2.081(6), 2.099(7) and 2.077(7) Å, respectively. The bond distances between tellurium and oxygen of the acyloxy groups were found to be longer than the sum of the tellurium and oxygen covalent radii (2.10 Å). On the other hand, the bond distances between tellurium and oxygen of the alkoxy groups were found to be slightly shorter than the sum of the tellurium and oxygen covalent radii. The bond distance of C-O (alkoxy group) bond is shorter than that of C-O (acyloxy group) bond, in good agreement with polarization of hypervalent O-Te-O bond. These tendency was observed in the bicyclic sulfurane which has alkoxy and acyloxy groups as the apical ligands.[12] Bond angles O(11)-Te(1)-O(13), O(21)-Te(2)-O(23), O(11)-Te(1)-C(11), O(11)-Te(1)-C(21), O(13)-Te(1)-C(11), O(13)-Te(1)-C(21), O(21)-Te(2)-C(31), O(21)-Te(2)-C(41), O(23)-Te(2)-C(31), O(23)-Te(2)-C(41), C(11)-Te(1)-C(21) and C(31)-Te(2)-C(41) are 162.1(2), 162.0(2), 76.7(3), 87.0(2), 90.7(3), 82.2(3), 77.5(2), 87.3(2), 89.6(2), 82.2(3), 98.2(3), and 98.5(3)°, indicating that **2** is a considerably distorted TBP structure which is nearly identical with that of tetraphenyltellurane reported by Ziolo and Titus.[13]

Furthermore, the effect of amount of $LiAlH_4$ was examined on the reduction of spirotellurane **1**. The product distribution on going from 0.5 equiv. of $LiAlH_4$ to 5.0 equiv. of $LiAlH_4$ is summarized in Table 1.

Table 1.

Entry	Equivalent of LAH	Yield (%)			
		1	**2**	**3**	**4**
1	0.5	90	0	0	0
2	1.2	90	trace	0	0
3	2.0	76	10	3	0
4	3.0	61	13	8	trace
5	4.0	0	20	20	40
6	5.0	0	23	15	38

The chemoselective reduction of the carbonyl groups occurred when spirotellurane **1** was treated with 2.0 equiv. of $LiAlH_4$ (Entry 3). The reduction of spirotellurane **1** took place at above 2.0 equiv. of $LiAlH_4$. On the other hand, the reaction of tellurane **1** with 4.0 equiv. of $LiAiH_4$ gave benzyl alcohol (40%) owing to the reduction of tetracoordinated tellurium (IV). From 4.0 equiv. to 5.0 equiv., the ratio of the products was little affected by varying the amount of $LiAlH_4$ (Entry 5 and 6).

The results described herein show molecular structure of the unsymmetrical spirotellurane and a new type of reaction of tellurane, although the tellurane consisting of acyloxy and alkoxy groups as apical groups has never been reported. Further work is in progress to explore applications and advantages of the unsymmetrical spirotelluranes and the chemoselective reduction of telluranes.

This work was supported by the Ministry of Education, Science and Culture, Japan [Priority area: Grant No. 07216211] and TARA Project fund.

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7 General procedures were shown in the following: a solution of 1,1'-spirobi(3H-2,1-benzoxatellurole)-3,3'-dione (**1**) (200 mg, 0.544 mmol) in dry THF (80 ml) was added dropwise to a suspension of lithium aluminium hydride (103 mg, 2.72 mmol) in dry THF (100 ml) at 0 °C. The whole mixture was stirred at room temperature for 18 h. After usual work-up the residue was purified by silica-gel column chromatography (methanol/chloroform 1:10) and HPLC to give the colorless crystal **2** (45 mg, 0.125 mmol, yield 23%), **3** (28 mg, 0.082 mmol, yield 15%) and **4** (45 mg, 0.413 mmol, yield 38%).

8 **2**: Mp 278 °C; ^{1}H-NMR ($CDCl_3$) δ 5.59, 5.73 (ABq, J = 14.9 Hz, 2H), 7.30-7.33 (m, 1H), 7.42-7.49 (m, 2H), 7.62-7.67 (m, 1H), 7.72-7.78 (m, 1H), 7.89-7.92 (m, 1H), 7.98-8.01 (m, 1H), 8.17-8.20 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 74.4, 123.7, 128.6, 129.5, 130.0, 131.3, 131.9, 132.0, 132.3, 132.9, 133.6, 134.1, 147.5, 170.7; ^{125}Te-NMR ($CDCl_3$) δ 1096; MS, m/z 356 (M^+, 5.4%), 312 (M^+ - 44, 21.7%). Anal. Calcd for $C_{14}H_{10}O_3Te$: C; 47.52, H; 2.85%. Found: C; 47.44, H; 2.65%. **3**: Mp 171 °C; ^{1}H-NMR ($CDCl_3$) δ 5.40 (s, 2H), 5.41 (s, 2H), 7.24-7.28 (m, 2H), 7.35-7.43 (m, 4H), 7.86-7.89 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 72.1, 124.1, 128.0, 128.4, 130.7, 131.1, 148.1; ^{125}Te-NMR ($CDCl_3$) δ 1144; MS, m/z 342 (M^+, 14.4%), 314 (M^+ - 28, 32.8%).

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10 Crystal data for **2**: $C_{14}H_{10}O_3Te$, FW = 353.83 single crystal with 0.30 x 0.20 x 0.10 mm^3, triclinic, space group $P1$, a = 7.546(1), b = 9.914(1), c = 10.092(2) Å, α = 59.42(6), β = 63.35(1), γ = 76.82(3)°, V = 581.0(3) Å^3, Z = 2, D_c = 2.022 $g\cdot cm^{-3}$, R = 0.020, R_w = 0.024, 2199 measured reflections, 2029 unique, 1999 observed ($I > 3.0\sigma(I)$). Hydrogen atoms were placed in calculated positions.

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