Organometallics **1994,** *13,* 3393–3395 3393

First X-ray Crystallographic Structure Determination of 2,2′-Biphenylylene-2-biphenylylphenoxytellurane ([10-Te-4(C3O)]) Formed during the Ring Opening Reaction of Bis(2,2′-biphenylylene)tellurane ([10-Te-4(C4)]) with Phenols

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Received May 12, 1994®

*Summary: Summary: Bis(2,2′-biphenylylene)tellurane (**1A**) undergoes a ring opening reaction on treatment with phenols to afford the oxytellurane [10-Te-4(C3O)] (**3A**). Structures of both telluranes (**1A**, **3A**) were determined by X-ray crystallographic analysis, revealing that they are distorted trigonal bipyramids.*

Studies on hypervalent organic compounds of chalcogenes (chalcogenanes) have attracted attention because they seem to open a new frontier in chemistry.[1,2] Particularly, earlier studies on the preparation of tetraphenyltellurane (**2A**) by Wittig[3] and bis(2,2′-biphenylylene)tellurane (**1A**)[4] and -selenane (**1B**)[5] by Hellwinkel apparently provided a new aspect in heteroatom chemistry,[6,7] while we have successfully achieved the first synthesis and structural determination of bis(2,2′-biphenylylene)sulfurane (**1C**).[8] These results provide the possibility for quantitative study of the stability and reactivity among these three chalcogenanes having identical ligands.[9,10] Recently, we found that both **1B** and **1C** react readily with alcohols, phenols, and thiols to give the coupling products quantitatively.[11,12] In the case of selenane (**1B**) on treatment with phenol, the intermediary formed oxyselenane [10-Se-4(C3O)] (**3B**) was detected by low temperature ^{77}Se, ^{1}H, and ^{13}C NMR spectroscopy but could not be isolated. Therefore, we undertook the reaction of the tellurane (**1A**) and phenols with the hope of isolating a new oxytellurane [10-Te-4(C3O)] (**3A**). This paper describes the first isolation of oxytellurane **3A** and its structural determination by X-ray crystallographic analysis.

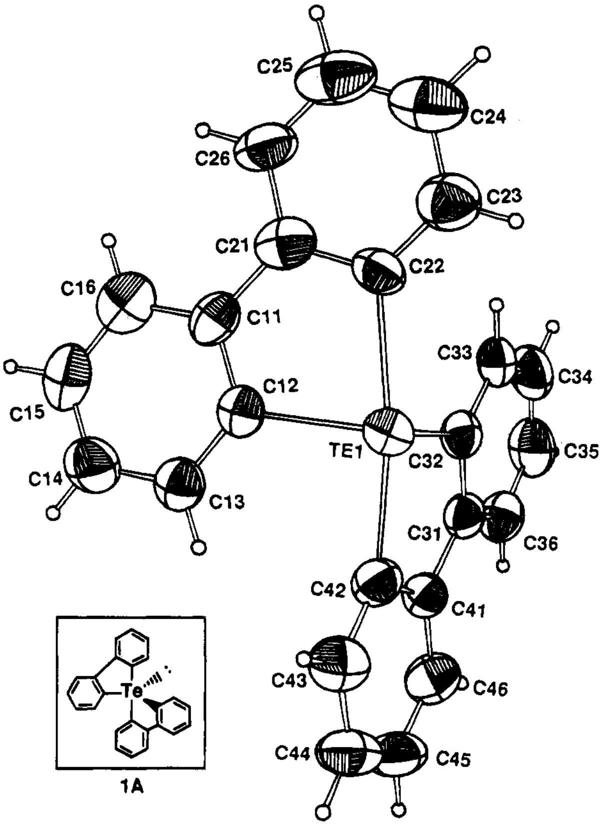

Figure 1. ORTEP view and atom-numbering scheme of **1A.** Selected bond distances (Å) and angles (deg) are as follows: Te(1)—C(22) = 2.244(9), Te(1)—C(42) = 2.235(9), Te(1)—C(12) = 2.144(8), Te(1)—C(32) = 2.137(9), C(11)—C(12) = 1.39(1), C(11)—C(16) = 1.38(1), C(11)—C(21) = 1.47(1), C(12)—C(13) = 1.38(1), C(13)—C(14) = 1.38(1), C(14)—C(15) = 1.36(2), C(15)—C(16) = 1.40(2), C(21)—C(22) = 1.39(1), C(21)—C(26) = 1.39(1), C(22)—C(23) = 1.37(1), C(23)—C(24) = 1.38(2), C(24)—C(25) = 1.38(2), C(25)—C(26) = 1.37(2), C(22)—Te(1)—C(42) = 159.0(4), C(12)—Te(1)—C(22) = 77.8(3), C(32)—Te(1)—C(42) = 77.4(3), C(22)—Te(1)—C(32) = 89.9(3), C(12)—Te(1)—C(42) = 90.3(3), C(12)—Te(1)—C(32) = 108.2(2), Te(1)—C(12)—C(11) = 115.1(6), Te(1)—C(22)—C(21) = 112.1(6), Te(1)—C(32)—C(31) = 115.8(6), Te(1)—C(42)—C(41) = 113.5(7).

® Abstract published in *Advance ACS Abstracts,* July 15, 1994.

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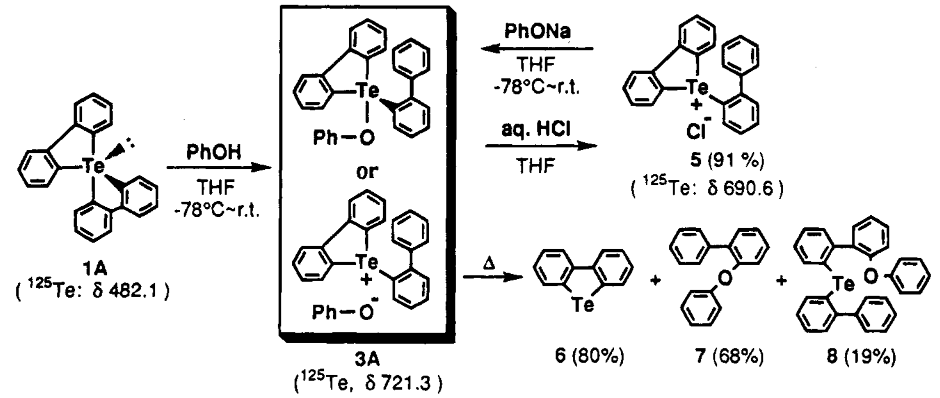
Scheme 1



Tellurane **1A** was prepared by Hellwinkel's procedure starting from tetrachlorotellurane and two equimolar amounts of 2,2′-dilithiobiphenyl in THF in 49% yield, mp 196–198 °C dec (lit. mp 205–214 °C).[4] The crystal structure of **1A** had not been determined and was confirmed by X-ray diffraction (Figure 1).[13] The apical Te(1)–C(22) and Te(1)–C(42) bond distances are 2.244(9) and 2.235(9) Å, while the equatorial Te(1)–C(12) and Te(1)–C(32) bond distances are 2.144(8) and 2.137(9) Å, respectively. Bond angles C(22)–Te(1)–C(42), C(12)–Te(1)–C(22), C(12)–Te(1)–C(32), and C(12)–Te(1)–C(42) are 159.0(4), 77.8(3), 108.2(3), 90.3(3)°, indicating that **1A** is a considerably distorted TBP structure which is nearly identical with that of tetraphenyltellurane (**2A**) reported by Ziolo and Titus.[14]

Tellurane **1A** was dissolved in dry THF at −78 °C and then one equimolar amount of phenol was added. After the solvent was evaporated, the residual powder was recrystallized from dry ether. Pale yellow crystals (**3A**) were obtained in 47% yield.[15] The structure of **3A** was identified by ^{1}H, ^{13}C, and ^{125}Te NMR, mass spectroscopy, and elemental analysis. Compound **3A** was quite stable thermally in marked contrast to the selenium analog and did not decompose even on heating at more than 100 °C for 10 h. At temperatures higher than 190 °C in situ, it decomposed to give the coupling products, dibenzotellurophene (**6**) (^{125}Te: δ 653.5, $CDCl_3$, 22 °C), 2-biphenylyl phenyl ether (**7**), and 2-(2-phenoxy)biphenylyl-2′-biphenylyl telluride (**8**) (Scheme 1). While several dioxytelluranes [10-Te-4(C2O2)] have been prepared,[16] preparation of an oxytellurane of the type [10-Te-4(C3O)] was reported by Wieber et al., from the reaction of triphenyltelluronium chloride and sodium alkoxides, but its structure was not determined.[17] By X-ray crystallographic analysis both triphenyltelluronium chloride and isocyanate are known to be onium salts,[18] and the present results seem to indicate that compound **3A** should be an onium structure.

Tellurane **1A** reacts with HCl at room temperature in chloroform to give chlorotelluronium salt **5** in 97% yield.[19] The telluronium salt (**5**) reacts further with sodium phenoxide to give **3A** which again gives **5** in aqueous HCl solution (Scheme 1).

^{125}Te NMR spectroscopy is a diagnostic method to estimate the structure of tellurium compounds.[20] The ^{125}Te NMR shift of tellurane **1A** appears at 481.6 ppm

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(13) Crystal data for **1A**: $C_{24}H_{16}Te$, $M = 432.10$, monoclinic, space group $P2_1/n$, $a = 4.540(1)$ Å, $b = 18.808(2)$ Å, $c = 20.226(1)$ Å, $\beta = 91.48(2)°$, $V = 1726.6$ Å^3, $D_c = 1.66$ g/cm^3, $Z = 4$, $F(000) = 848$, $\mu = 17.3$ cm^{-1}. A yellow rod crystal of dimensions 0.2 × 0.2 × 0.6 mm was used for measurements at 296 K on an Enraf Nonius CAD4 diffractometer employing graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) using the $\omega/2\theta$ scan technique. The structure was solved by direct methods. A total of 2804 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 226 variable parameters and converged with $R = 0.063$ and $R_w = 0.066$. All calculations were performed on a VAX computer using MolEN. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre.

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(15) To a solution of tellurane **1A** (104 mg, 0.24 mmol) in dry tetrahydrofuran (10 mL) was added distilled phenol (22.6 mg, 0.24 mmol) or *p*-nitrophenol (33.4 mg, 0.24 mmol), and the solution was stirred for 3 h in the presence of light under argon at room temperature. After removal of the solution the residue was recrystallized from dry ether under argon to give pale yellow crystals of **3A** (60.0 mg) in 47% yield and light yellow crystals of **4** (89.4 mg) in 65% yield. **3A**: mp 179–183 °C dec; ^{1}H NMR (270 MHz, $CDCl_3$, −20 °C) δ 6.62 (d, J = 7.6 Hz, 1H, 9-ArH), 6.64 (t, J = 7.6 Hz, 1H, 10-ArH), 7.11 (t, J = 7.6 Hz, 1H, 11-ArH), 7.25 (d, J = 7.6 Hz, 1H, 12-ArH), 7.30 (t, J = 7.6 Hz, 1H, 15-ArH), 7.32 (d, J = 7.6 Hz, 2H, 14-ArH), 7.33 (t, J = 7.6 Hz, 1H, 20-ArH), 7.47 (t, J = 7.6 Hz, 2H, 5-ArH), 7.48 (t, J = 7.6 Hz, 2H, 4-ArH), 7.48 (t, J = 7.6 Hz, 2H, 19-ArH), 7.56 (t, J = 7.6 Hz, 1H, 16-ArH), 7.56 (d, J = 7.6 Hz, 2H, 6-ArH), 7.69 (bd, 2H, 3-ArH), 7.84 (d, J = 7.6 Hz, 2H, 18-ArH); ^{13}C NMR (68 MHz, $CDCl_3$, −20 °C) δ 115.7, 120.8, 123.6, 128.8, 129.1, 129.1, 129.1, 129.3, 129.8, 130.0, 130.1, 130.6, 130.9, 130.9, 133.9, 134.5, 141.8, 143.9, 145.1, 164.6; ^{125}Te NMR (85 MHz, $CDCl_3$) δ 721.3; MS (m/z) 528 (M^+), 435 ($M^+ - 93$). Anal. Calcd for $C_{30}H_{22}OTe$: C, 68.49; H, 4.22%. Found: C, 68.31; H, 4.35%. **4**: mp 201–205 °C dec; ^{1}H NMR (270 MHz, $CDCl_3$, room temperature) δ 6.31 (d, J = 9.2 Hz, 2H, 18-ArH), 7.17 (t, J = 7.6 Hz, 1H, 11-ArH), 7.18 (d, J = 7.6 Hz, 1H, 12-ArH), 7.38 (d, J = 7.6 Hz, 1H, 9-ArH), 7.39 (t, J = 7.6 Hz, 1H, 10-ArH), 7.40 (t, J = 7.6 Hz, 2H, 5-ArH), 7.53 (d, J = 7.6 Hz, 2H, 14-ArH), 7.54 (t, J = 7.6 Hz, 1H, 16-ArH), 7.55 (t, J = 7.6 Hz, 2H, 15-ArH), 7.60 (t, J = 7.6 Hz, 2H, 4-ArH), 7.74 (d, J = 7.6 Hz, 2H, 3-ArH), 7.92 (b, J = 7.6 Hz, 2H, 6-ArH), 8.00 (d, J = 9.2 Hz 2H, 19-ArH); ^{13}C NMR (68 MHz, $CDCl_3$, room temperature) δ 119.3, 124.3, 126.8, 129.3, 129.4, 129.5, 129.6, 129.7, 130.4, 130.5, 130.9, 131.9, 134.4, 134.4, 135.4, 141.3, 144.6, 145.8, 145.8, 174.6; ^{125}Te NMR (85 MHz, $CDCl_3$) δ 718.0; MS (m/z) 586 ($M^+ + 13$), 573 (M^+), 435 ($M^+ - 138$). Anal. Calcd for $C_{30}H_{21}N_2O_3Te$: C, 63.09; H, 3.71; N, 2.45%. Found: C, 62.98; H, 3.55; N, 2.24%. Each chemical shifts were determined by two-dimensional shift correlation (^{1}H–^{1}H- and ^{13}C–^{1}H-COSY) spectra. All NMR spectra were recorded on a JEOL EX-270.

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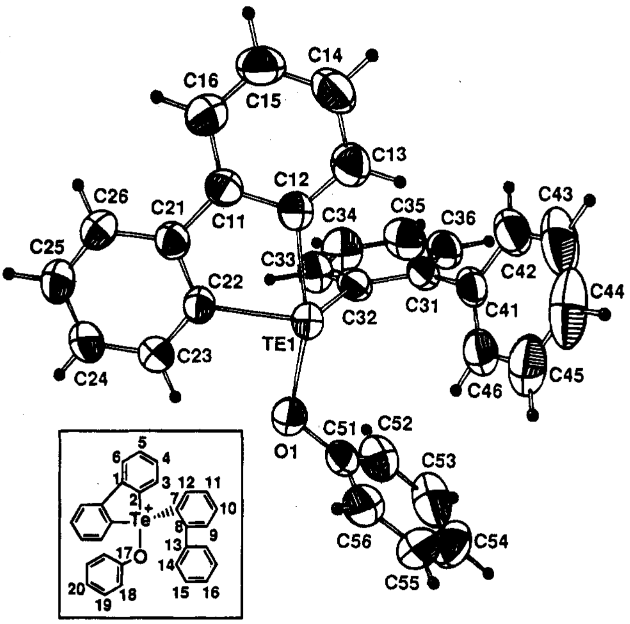
(19) **5**: mp 298–299 °C (lit. mp 269–270 °C); ^{1}H NMR (270 MHz, $CDCl_3$, room temperature) δ 7.14 (t, J = 8.1 Hz, 1H, 11-ArH), 7.18 (d, J = 8.1 Hz, 1H, 12-ArH), 7.35 (t, J = 8.1 Hz, 1H, 10-ArH), 7.35 (d, J = 7.6 Hz, 2H, 14-ArH), 7.39 (t, J = 7.6 Hz, 2H, 15-ArH), 7.56 (t, J = 7.6 Hz, 2H, 4-ArH), 7.61 (t, J = 7.6 Hz, 1H, 16-ArH), 7.69 (t, J = 7.6 Hz, 2H, 5-ArH), 7.83 (d, J = 7.6 Hz, 2H, 6-ArH), 7.84 (d, J = 7.6 Hz, 2H, 3-ArH), 7.88 (d, J = 8.1 Hz, 2H, 9-ArH); ^{13}C NMR (68 MHz, $CDCl_3$, room temperature) δ 124.3, 129.4, 129.6, 129.7, 129.7, 129.8, 130.2, 130.8, 130.8, 131.9, 132.9, 133.2, 134.7, 141.1, 143.9, 145.9; ^{125}Te NMR (85 MHz, $CDCl_3$, room temperature) δ 690.6. See ref 4.

(CDCl$_3$, 20 °C), while the spectra of **3A** and **5** are not very different and their chemical shifts are observed at 721.3 and 690.5 ppm, respectively. ^{125}Te NMR of tellurane covers a wide range, depending on the ligands attached at the Te atom, from 450 to 1600 ppm and hence determination of the structure by NMR is ambiguous. On the other hand, the mass spectrum of **3A** shows clearly the parent peak at m/z 528 (M$^+$, 0.2%) together with m/z 435 (M$^+$ − 137, 4.5%), while **5** does not show the parent peak at all. Therefore, these NMR and mass spectroscopic analyses do not give conclusive evidence for the structural determination of **3A**. The structure of the compound **3A** was finally determined by X-ray crystallographic analysis.[21] The ORTEP drawing of **3A** is shown in Figure 2.

As shown in Figure 2, the Te(1)—C(12) bond distance is longer than those of Te(1)—C(22) and Te(1)—C(32) while the Te(1)—O(1) bond distance is of a roughly identical value with that of the Te—O single bond (2.101 Å).[22] The bond angles O(1)—Te(1)—C(12) and C(22)—Te(1)—C(32) are 159.6(2) and 103.9(2)°, respectively (**3A**). Therefore, the structure of **3A** is obviously a distorted tellurane in which electronegative phenolic oxygen and one Te—C bond of dibenzotellurophene compose the apical bond and the rest of the C—Te bonds and the lone pair of electrons should be expanded at an equatorial plain of the molecule. Similarly, (p-nitrophenoxy)tellurane (**4**) was obtained as light yellow crystals in 65% yield on treatment of tellurane **1A** with p-nitrophenol.[15] p-Nitrophenoxy analog **4** shows the ^{125}Te NMR resonance at 718.0 ppm, and the mass spectrum also shows the parent peak at m/z 573 (M$^+$, 3.0%); hence, **4** also should have an oxytellurane structure [10-Te-4(C3O)].

On similar treatment, selenane and sulfurane (**1B**, **1C**) react with phenol to give the coupling products, o-phenoxybiphenyl and dibenzoselenophene or -thiophene, in quantitative yields. In the case of the reaction of selenane, formation of oxyselenane [10-Se-4(C3O)] was observed by ^{77}Se NMR at 0 °C, while the corresponding oxysulfurane was not detected by ^{1}H and ^{13}C NMR even at −100 °C. Therefore, the stability of oxychalcogenane [10-X-4(C3O)] (X = S, Se, Te) is identical with that of tetraphenylchalcogenanes.[10]



3A

Figure 2. ORTEP view and atom-numbering scheme of **3A**. Selected bond distances (Å) and angles (deg) are as follows: Te(1)—O(1) = 2.294(4), Te(1)—C(12) = 2.174(5), Te(1)—C(22) = 2.103(5), Te(1)—C(32) = 2.122(5), C(11)—C(12) = 1.391(7), C(11)—C(16) = 1.397(8), C(11)—C(21) = 1.471(8), C(12)—C(13) = 1.383(9), C(13)—C(14) = 1.383(9), C(14)—C(15) = 1.37(1), C(15)—C(16) = 1.37(1), C(21)—C(22) = 1.398(7), C(21)—C(26) = 1.398(8), C(22)—C(23) = 1.379(8), C(23)—C(24) = 1.384(8), C(24)—C(25) = 1.370(8), C(25)—C(26) = 1.37(1), O(1)—C(51) = 1.326(7), O(1)—Te(1)—C(12) = 159.6(2), O(1)—Te(1)—C(22) = 82.8(2), O(1)—Te(1)—C(32) = 83.6(2), C(12)—Te(1)—C(22) = 79.7(2), C(12)—Te(1)—C(32) = 90.4(2), C(22)—Te(1)—C(32) = 103.9(2), Te(1)—O(1)—C(51) = 115.0(3), Te(1)—C(12)—C(11) = 112.4(4), Te(1)—C(22)—C(21) = 113.4(4), Te(1)—C(32)—C(31) = 120.3(4), Te(1)—C(32)—C(33) = 119.1(4).

The present result provides a new procedure for the synthesis of various new telluranes, further work on which is currently underway in our laboratory.

Acknowledgment. This work was supported by the Ministery of Education, Science, and Culture, Japan [Priority area: Grant No. 05236205].

Supplementary Material Available: Textual presentation of experimental data and tables of crystal data, positional parameters, thermal parameters, root-mean-square amplitudes, and bond distances and angles (42 pages). Ordering information is given on any current masthead page.

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(21) Crystal data for **3A**: C$_{30}$H$_{22}$OTe, M = 526.11, triclinic, space group $P\bar{1}$, a = 8.938(1) Å, b = 10.174(1) Å, c = 12.954(1) Å, α = 98.42(1)°, β = 93.79(1)°, γ = 94.93(1)°, V = 1157.2 Å^3, D_c = 1.51 g/cm^3, Z = 2, F(000) = 524, μ = 13.0 cm^{-1}. A pale yellow rod crystal of dimensions 0.2 × 0.4 × 0.4 mm was used for measurements at 296 K on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) using the $\omega/2\theta$ scan technique. The structure was solved by direct methods. A total of 3734 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 289 variable parameters and converged with R = 0.044 and R_w = 0.046. All calculations were performed on a VAX computer using MolEN. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre.

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