Addition Reaction of *p*-Methoxyphenyltellurium Trichloride to 3-Hydroxy Alkynes

Gilson Zeni,[†] André Chieffi,[†] Rodrigo L. O. R. Cunha,[†]
Julio Zukerman-Schpector,[†] Hélio A. Stefani,[‡] and João V. Comasseto*[,†]

Instituto de Química, Universidade de São Paulo, Avenida Prof. Lineu Prestes, 748, São Paulo, 05508-900, Brazil, and Faculdade de Ciências Farmacêuticas, Universidade de São Paulo, Avenida Prof. Lineu Prestes, 580, São Paulo, 05501-010, Brazil

Received August 31, 1998

Summary: *The influence of the hydroxyl group in the regio- and stereochemistry of the reaction between p-methoxyphenyltellurium trichloride and 3-hydroxy alkynes is discussed. Mixtures of Z and E olefins, as well as products of opposed regiochemistry, are formed, depending on the structure of the substrate.*

Introduction

Vinylic tellurides are emerging as synthetic reagents.[1] The addition of nucleophilic tellurium species to alkynes, giving the *Z* isomer, is the most useful method to synthesize these vinyl organoelement compounds.[1] Electrophilic addition of the commercially available tellurium tetrachloride, or the easily prepared aryltellurium trichlorides,[2] to alkynes is another approach to access this class of compounds. However, very few reports on these reactions are available. The reaction of tellurium tetrachloride with alkynes gives 1-trichlorotelluro-2-cloroalkenes of *Z* configuration,[3] as recently demonstrated by X-ray analysis of the addition product of tellurium tetracloride to phenylacetylene.[4] Some years ago we reported our preliminary results on the addition of aryltellurium trichlorides to alkynes.[5] We found that this reaction gives (*Z*)-1-aryldichlorotelluro-2-chloroalkenes **1** as the main product, which can be obtained in isomerically pure form after recrystallization. X-ray analysis of several analogous aromatic derivatives, or their corresponding tellurides, confirmed the regio- and stereochemistry proposed.[6] The ^{1}H NMR analysis of the compounds described in our previous communication showed that the chemical shifts corresponding to the vinylic protons were in the range 7.54−7.79 ppm for all compounds, except for the ones containing a hydroxyl group at the allylic position, which absorbed in the range 6.95−6.98 ppm. To understand this behavior, crystal structures of such compounds were determined, showing that the compounds actually isolated were **2** and **3** (Figure 1).

Results and Discussion

The reaction of 1-ethynylcyclohexanol with *p*-methoxyphenyltellurium trichloride in refluxing benzene gave a mixture of products, as demonstrated by the ^{125}Te NMR spectrum of the crude reaction mixture (signals at 900, 897, 788, and 627 ppm, the most intense being the one at 900 ppm). The major product, a cyclic tellurium oxychloride **2**, was purified by recrystallization from chloroform/hexane, and its structure was determined by X-ray experiments (Figure 2). This result indicates that the regio- and stereochemistry is the reverse of that originally proposed in our previous communication.[5] NMR analysis is in accordance with the regiochemistry determined by X-ray experiment. HETCOR ^{1}H−^{13}C experiments do not show any correlation between the ^{13}C signal corresponding to the vinylic carbon linked to the tellurium atom (120 ppm, showing satellite bands with $^1J_{C-Te}$ of 350 Hz) and the ^{1}H signal corresponding to the vinylic hydrogen (7.05 ppm).

One of the products of the reaction between propargyl alcohol and *p*-methoxyphenyltellurium trichloride in refluxing benzene (**3**) was obtained in a similar way and also had the structure determined by X-ray analysis (Figure 3). However the cyclic oxychloride obtained has the opposite regiochemistry of the oxychloride obtained from the reaction with 1-ethynylcyclohexanol. The regiochemistry of **3** was also confirmed by NMR experiments. HETCOR ^{1}H−^{13}C shows a correlation between the ^{1}H signal corresponding to the vinylic hydrogen (7.14 ppm) and the ^{13}C signal corresponding to the carbon linked to the tellurium atom (120 ppm, showing satellite bands with $^1J_{C-Te}$ of 345 Hz).

The presence of the hydroxyl group in the starting alkynes has an important influence in the reaction of these compounds with *p*-methoxyphenyltellurium trichloride. The major products obtained from the addition of this reagent to aliphatic and aromatic alkynes are formed through a syn addition, probably involving a four-center mechanism (Scheme 1). When 3-hydroxy alkynes are used, products resulting from an anti addition are formed. These results can be rationalized in terms of an initial formation of a telluronium ion

* E-mail: jvcomass@quim.iq.usp.br.
[†] Instituto de Química.
[‡] Faculdade de Ciências Farmacêuticas.

(1) (a) Comasseto, J. V. *Rev. Heteroatom Chem.* **1993**, *9*, 61. (b) Comasseto, J. V.; Ling, L. W.; Petragnani, N.; Stefani, H. A. *Synthesis* **1997**, 373.
(2) Petragnani, N. *Tellurium in Organic Synthesis*; Academic Press: London, 1994.
(3) (a) Campos, M. M.; Petragnani, N. *Tetrahedron* **1962**, *18*, 527. (b) Uemura, S.; Miyoshi, H.; Okano, M. *Chem. Lett.* **1979**, 1357. (c) Chieffi, A.; Menezes, P. H.; Comasseto, J. V. *Organometallics* **1997**, *16*, 809.
(4) Zukerman-Schpector, J.; Comasseto, J. V. Unpublished.
(5) Comasseto, J. V.; Stefani, H. A.; Chieffi, A. *Organometallics* **1991**, *10*, 845.
(6) (a) Zukerman-Schpector, J.; Castellano, E. E.; Oliva, G.; Comasseto, J. V.; Stefani, H. A. *Acta Crystallogr.* **1991**, *C47*, 960. (b) Zukerman-Schpector, J.; Comasseto, J. V.; Stefani, H. A. *Acta Crystallogr.* **1995**, *C51*, 861. (c) Meyers, E. A.; Zingaro, R. A.; Comasseto, J. V.; Stefani, H. A.; Chieffi, A. *Z. Kristalogr.* **1995**, *210*, 306.

10.1021/om980738d CCC: $18.00
Publication on Web 01/29/1999

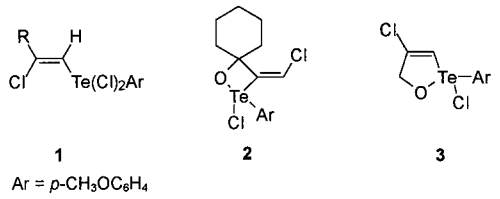


Figure 1.

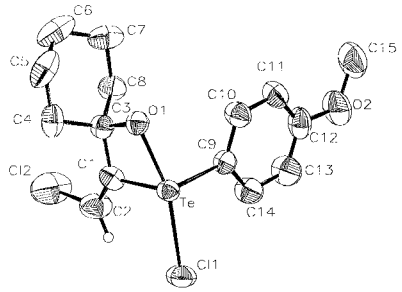


Figure 2. ZORTEP drawing of cyclic tellurium oxychloride **2**. Ellipsoids are shown at the 50% probability scale, except the H atom, which is at an arbitrary scale for the sake of clarity. Selected bond lengths (Å) and angles (deg): Te−O(1), 2.050(3); Te−C(1), 2.117(5); Te−C(9), 2.131(4); Te−C(1), 2.5643(12); O(1)−Te−C(1), 66.3(2); O(1)−Te−C(9), 92.15(14); C(1)−Te−C(9), 97.3(2); O(1)−Te−Cl(1), 157.26-(9); C(1)−Te−Cl(1), 91.01(13); C(9)−Te−Cl(1), 91.20(12).

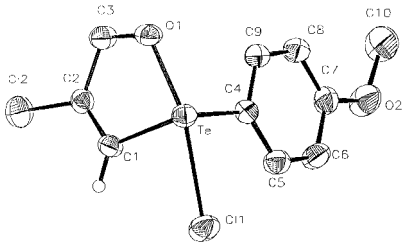
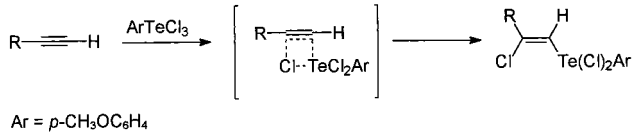


Figure 3. ZORTEP drawing of cyclic tellurium oxychloride **3**. Ellipsoids are shown at the 50% probability scale, except the H atom which is at an arbitrary scale for the sake of clarity. Selected bond lengths (Å) and angles (deg): Te−O(1), 2.034(2); Te−C(1), 2.084(3); Te−C(4), 2.132(3); Te−Cl(1), 2.5593(8); O(1)−Te−C(1), 80.54(10); O(1)−Te−C(4), 91.58(10); C(1)−Te−C(4), 98.68(11); O(1)−Te−Cl(1), 164.39-(6); C(1)−Te−Cl(1), 83.87(8); C(4)−Te−Cl(1), 91.43(8).

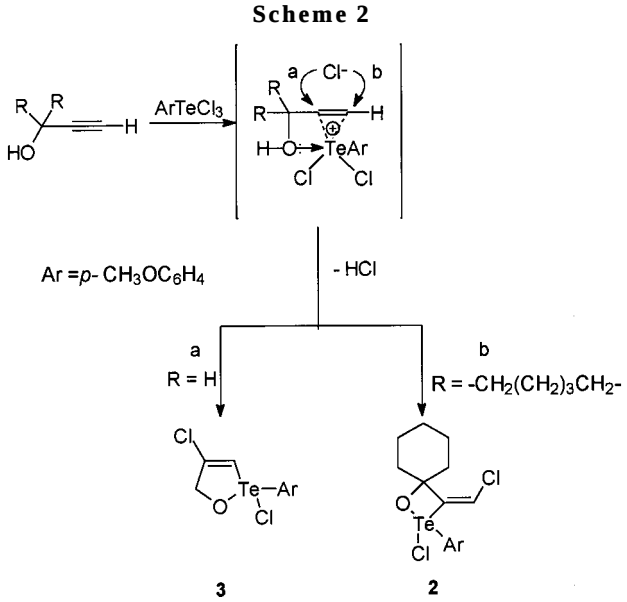
Scheme 1



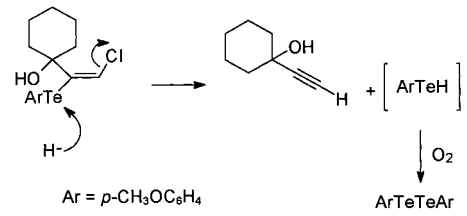
resulting from the attack of *p*-methoxyphenyltellurium trichloride to the triple bond which coordinates with the hydroxyl group. This telluronium ion can be opened by the chloride ion in two different ways: (a) when the propargylic position is not sterically hindered, the five-membered-ring cyclic oxychloride is formed; (b) when the propargylic position is sterically hindered, the four-membered-ring cyclic oxychloride is formed (Scheme 2).

Reduction of the oxychlorides **2** and **3** with stoichiometric amounts of sodium borohydride or excess sodium bissulfite gave the corresponding tellurides **4** and **5**. When a great excess of sodium borohydride was used, oxychlorides **2** and **3** were quantitatively transformed into di-*p*-methoxyphenyl ditelluride and the corresponding alkyne, presumably via the E_2 mechanism shown in Scheme 3. Similar results were obtained when the tellurides **4** and **5** were treated with sodium borohydride. These results support the stereochemistry proposed.

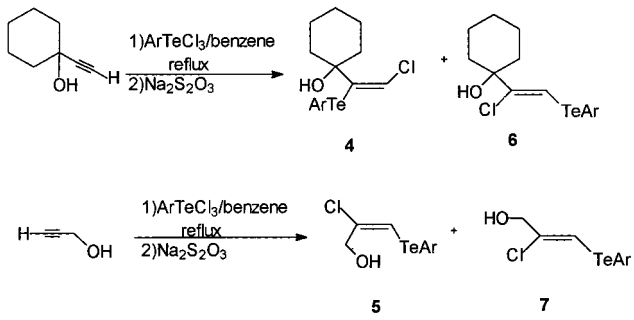
Scheme 2



Scheme 3



Scheme 4



Ar = *p*-$CH_3OC_6H_4$

Reduction of the crude mixture of the addition reaction with excess sodium bissulfite, followed by column chromatography in silica gel, allowed the separation of two isomers. Tellurides **4** and **7** were obtained as major isomers, and tellurides **5** and **6** as minor isomers (Scheme 4). In the case of compounds **4** and **6** the isomeric ratio of the tellurides is consistent with the isolation of compound **2** as the major isomer. The low yield of compound **4** can be attributed to some degree of elimination during the reduction of the crude mixture, since no isomerization of **4** was observed by stirring it in the presence of silica gel. In the case of compounds **5** and **7** however, the ratio of isomers is not consistent with the yield for compound **3** (65%). After reduction of the crude mixture, compound **5** was obtained in only

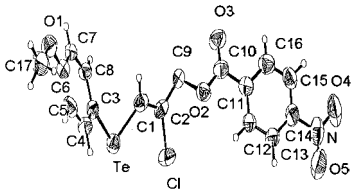


Figure 4. ZORTEP drawing of *p*-nitrobenzoate **8**. Ellipsoids are shown at the 50% probability scale, except the H atom, which are at an arbitrary scale for the sake of clarity. Selected bond lengths (Å) and angles (deg): Te−C(3), 2.085(7); Te−C(1), 12.088(7); C(3)−Te−C(1), 95.9(3).

20% yield, while compound **7** was isolated in 42% yield. In this case an isomerization is taking place. It was found that pure **5** was completely transformed into **7** after 2 h of stirring in a suspension of silica gel in a 1:1 mixture of hexane/ethyl acetate.

The regiochemistry of tellurides **6** and **7** was determined by NMR spectroscopy. HETCOR $^1H-^{13}C$ experiments showed a correlation between the ^{13}C peak attributed to the carbon linked to the tellurium atom (105 ppm for **6**, 106 ppm for **7**, both presenting satellite bands with $^1J_{C-Te}$ 306 Hz) and the ^1H peak attributed to the vinylic proton (6.99 ppm for **6** and 6.98 ppm for **7**). In addition, treatment of these compounds with excess sodium borohydride did not give the elimination product, suggesting that **6** and **7** have *Z* stereochemistry, which does not allow an E_2 elimination similar to that shown in Scheme 3.

To confirm the stereochemistry proposed, telluride **7** was transformed into the corresponding crystalline *p*-nitrobenzoate **8**, by reaction with *p*-nitrobenzoyl chloride. X-ray analysis of **8** confirmed the *Z* stereochemistry (Figure 4).

Conclusion

The presence of the hydroxyl group in the starting alkyne has an important influence in the reaction of these compounds with *p*-methoxyphenyltellurium trichloride. When 3-hydroxy alkynes were used, cyclic oxychlorides were formed through an anti addition, probably involving a telluronium ion giving the *E* isomer. A second isomer presenting the *Z* stereochemistry was formed through the four-center mechanism previously proposed.[5]

In view of the synthetic potential of the resulting adducts, studies are under way to control the regio- and stereochemistry of the reaction.

Experimental Section

^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were obtained on a Bruker DRX-500 spectrometer in $CDCl_3$ with TMS as the internal reference. IR spectra were recorded on a Perkin-Elmer 1600 spectrophotometer. Mass spectra were obtained on a GC/MS Hewlett-Packard 5988-8/5890 spectrometer, operating at 70 eV. Column chromatography was carried out with Merck silica gel (230−400 mesh) according to the procedure by Still and co-workers.[7] Thin-layer chromatography (TLC) was performed on silica gel 60 F-254 on aluminum foil. All solvents used were previously dried and distilled according to the usual methods.[8] Tellurium (200 mesh), propargyl alcohol, and 1-ethynylcyclohexanol were purchased from Aldrich. Aryltellurium trichloride[2,9] and tellurium tetrachloride[2,9] were prepared according to literature procedures.

Addition Reaction of *p*-Methoxyphenyltellurium Trichloride to 3-Hydroxy Alkynes. A solution of the 3-hydroxy alkyne (11 mmol) in dry benzene (10 mL) was added to a suspension of *p*-methoxyphenyltellurium trichloride (10 mmol, 3.40 g) in dry benzene (40 mL). The reaction mixture was refluxed for 8 h, during which the *p*-methoxyphenyltellurium trichloride was consumed, forming a clear yellow solution. The resulting solution was cooled to room temperature, diluted with ethyl acetate, and washed with a saturated NH_4Cl solution and brine. The solvent was evaporated under reduced pressure, and the residue was quickly chromatographed on SiO_2, using CCl_4 and $CHCl_3$/MeOH (5:1) as eluents. The resulting oil was crystallized from $CHCl_3$/hexane.

4-{2-Chloro-3-[chloromethylidene]-1-oxa-2λ-telluraspiro[3.5]non-2-yl}phenyl Methyl Ether (2). Yield: 3.07 g (72%). ^1H NMR: δ 8.27 (d, J = 8.85 Hz, 2 H), 7.12(d, J = 8.85 Hz, 2 H), 6.44 (s, 1 H), 3.89 (s, 3 H), 2.42−1.35 (m, 2 H), 2.02−1.99 (m, 2 H), 1.73−1.66 (m, 5 H), 1.31−1.28 (m, 1 H). ^{13}C NMR: δ 162.52, 159.11, 137.11, 125.44, 118.52, 116.02, 76.04, 55.56, 34.68, 24.58, 21.59. IR (KBr, film; cm^{-1}): 3030, 2950, 2927, 1585, 1485, 840. Anal. Calcd for $C_{15}H_{18}TeO_2Cl_2$: C, 42.11; H, 4.01. Found: C, 41.94; H, 4.18.

4-(2,4-Dichloro-2,5-dihydro-1,2λ-oxatellurol-2-yl)phenyl Methyl Ether (3). Yield: 2.33 g (65%); ^1H NMR: δ 7.91 (d, J = 8.8 Hz, 2 H), 7.14 (s, 1 H), 7.05 (d, J = 8.8 Hz, 2 H), 5.15 (d, J = 16.5 Hz, 1H), 4.92 (d, J = 16.5 Hz, 1 H), 3.86 (s, 3 H). ^{13}C NMR: δ 162.26, 151.37, 133.22, 124.97, 118.99, 115.58, 55.51, 11.54. IR (KBr, film; cm^{-1}): 3030, 2960, 1580, 1485, 830. Anal. Calcd for $C_{10}H_{10}TeO_2Cl_2$: C, 33.30; H, 2.79. Found: C, 33.56; H, 2.94.

Reduction of the Crude Mixture of the Addition Reaction of *p*-Methoxyphenyltellurium Trichloride to 3-Hydroxy Alkynes. To a solution of *p*-methoxyphenyltellurium trichloride (1.7 g, 5.0 mmol) in benzene (20 mL) was added the 3-hydroxy alkyne (5.0 mmol). After the addition, the mixture was refluxed for 8 h. The solvent was evaporated, and the residual oil was treated with $CHCl_3$ (30 mL) and a saturated aqueous solution of $Na_2S_2O_3$ (3 × 30 mL) and extracted with ethyl acetate (50 mL). The organic phase was dried with $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel column, eluting with hexane/ethyl acetate (9:1).

(*E*)-1-[2-Chloro-1-(4-methoxyphenyl)tellanyl]ethenylcyclohexanol (4). Yield: 0.86 g (40%). ^1H NMR: δ 7.73 (d, J = 8.5 Hz, 2 H), 6.81 (d, J = 8.5 Hz, 2 H), 5.17 (s, 1 H), 3.81 (s, 3 H), 2.40−2.34 (m, 3 H), 1.75−1.54 (m, 8 H); ^{13}C NMR: δ 160.40, 143.10, 143.04, 136.74, 115.84, 106.93, 103.74, 55.11, 33.10, 24.88, 21.59. LRMS *m*/*z* (relative intensity): 344 (18), 237 (10), 199 (100), 171 (27), 128 (15). IR (KBr, film; cm^{-1}): 3375, 3004, 2916, 2854, 1584, 1490, 1250, 821. Anal. Calcd for $C_{15}H_{19}TeO_2Cl$: C, 45.68; H, 4.86. Found: C, 45.79; H, 5.20.

(*E*)-2-Chloro-3-[(4-methoxyphenyl)tellanyl]-2-propen-1-ol (5). Yield: 0.27 g (20%); ^1H NMR: δ 7.73 (d, J = 8.4 Hz, 2 H), 6.80 (d, J = 8.4 Hz, 2 H), 5.89 (s, 1 H), 4.42 (d, J = 4.8 Hz, 2 H), 3.80 (s, 1 H), 2.48 (t, J = 5.8 Hz, 1 H). ^{13}C NMR: δ 160.34, 141,96, 124.20, 116.96, 115.37, 101.07, 62.99, 55.12. LRMS *m*/*z* (relative intensity): 326 (44), 235 (51), 198 (72), 163 (100). IR (KBr, film; cm^{-1}): 3363, 2928, 2839, 1587, 1490, 1285, 824. Anal. Calcd for $C_{10}H_{11}TeO_2Cl$: C, 36.82; H, 3.40. Found: C, 36.61; H, 3.22.

(*Z*)-1-[1-Chloro-2-(4-methoxyphenyl)tellanyl]ethenylcyclohexanol (6). Yield: 0.26 g (12%). ^1H NMR: δ 7.20 (d, J = 8.5 Hz, 2 H), 6.98 (s, 1 H), 6.79 (d, J = 8.5 Hz 2 H), 1.92 (s, 1 H), 1.76−1.65 (m, 5 H), 1.62−1.52 (m, 5 H). ^{13}C NMR: δ 160.06, 145.03, 140.96, 115.42, 105.84, 102.51, 75.66, 55.11,

(7) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(8) Perrin, D. D.; Armarego, W. K. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U.K., 1966.
(9) Irgolic, K. Y.; *Houben-Weyl−Methoden der Organishen Chemie*, 4th ed.; Georg Thieme: Stuttgart, 1990; Vol. E12b.

35.84, 25.24, 21.76. LRMS *m*/*z* (relative intensity): 344 (18), 237 (10), 199 (100), 171 (27), 128 (15). IR (KBr, film; cm^{-1}): 3473, 3002, 2929, 2856, 1586, 1490, 1248, 824. Anal. Calcd for $C_{15}H_{19}TeO_2Cl$: C, 45.68; H, 4.86. Found: C, 45.55; H, 4.56.

(*Z*)-2-Chloro-3-[(4-methoxyphenyl)tellanyl]-2-propen-1-ol (7). Yield: 0.76 g (47%). ^{1}H NMR: δ 7.68 (d, J = 8.4, 2 H), 6.97 (s, 1 H), 6.76 (d, J = 8.0, 2 H), 4.15 (s, 2 H), 3.06 (s, 1 H). ^{13}C NMR: δ 159.94, 140.82, 137.49, 115.38, 105.93, 101.81, 66.82, 55.07. LRMS *m*/*z* (relative intensity): 326 (56), 237 (36), 196 (49), 108 (100). IR (KBr, film; cm^{-1}): 3371, 2936, 2858, 1586, 1489, 1285, 823. Anal. Calcd for $C_{10}H_{11}TeO_2Cl$: C, 36.82; H, 3.40. Found: C, 36.59; H, 3.36.

(*Z*)-1-Chloro-2-[(4-methoxyphenyl)tellanyl]ethenyl-4-nitrobenzoate (8). The vinylic telluride **7** (0.65 g, 2 mmol) and *p*-nitrobenzoyl chloride (0.74 g, 4 mmol) in anhydrous pyridine (10 mL) were stirred at room temperature for 4 h. Then the mixture was diluted with saturated $NaHCO_3$ solution (10 mL) and with MeOH/H_2O (1:1), to give a solid product, which was recrystalized from MeOH/H_2O (1:1). Yield: 4.18 g (88%). ^{1}H NMR: δ 8.29 (d, 8.7 Hz, 2 H), 8.23 (d, 8.7 Hz, 2 H), 7.74 (d, 8.94 Hz, 2 H), 7.26 (s, 1 H), 6.81 (d, 8.5 Hz, 2 H), 4.98 (s, 2 H), 3.81 (s, 3 H). ^{13}C NMR δ 163.94, 160.46, 150.72, 141.21, 134.98, 131.64, 130.92, 123.59, 125.67, 114.56, 101.80, 68.64, 55.23. LRMS *m*/*z* (relative intensity): 474 (4), 347 (5), 237 (11), 181 (16), 150 (100), 104 (17). IR (KBr, film; cm^{-1}): 3035, 2950, 1733, 1586, 1525, 1271, 718. Anal. Calcd for $C_{17}H_{14}NO_5ClTe$: C, 42.95; H, 2.97. Found: C, 42.97; H, 2.88.

Isomerization Experiment. To a flask containing a suspension of silica gel (2 g) in a 1:1 mixture of hexane/ethyl acetate (20 mL) was added the telluride **5** (0.16 g, 0.5 mmol). The mixture was stirred for 2 h at room temperature, and the isomerization was monitored by GLC. After this time the mixture was filtered and the solvents were evaporated, affording telluride **7** in quantitative yield.

Crystal Data for 2: $C_{15}Cl_2H_{18}O_2Te$, M_r = 428.79, triclinic, space group $P\bar{1}$, a = 8.160(1) Å, b = 9.832(1) Å, c = 11.531(2) Å, α = 109.48(1)°, β = 101.44(1)°, γ = 94.18(1)°, V = 845.1(2) Å^3, Z = 2, D_c = 1.685 g cm^{-3}, μ(Mo Kα) = 2.074 mm^{-1}, irregular specimen max. and min. dimensions 0.40, 0.25 mm, 3130 unique reflections for 2.37° < θ < 25.57°; 2785 having $F > 2\sigma(F)$. Final results: R1 [$F > 2\sigma(F)$] = 0.0325, wR2 (F^2 all data) = 0.0895, and 182 parameters; S = 1.058. For **3**: $C_{10}Cl_2H_{10}O_2Te$, M_r = 360.68, monoclinic, space group $P2_1/n$; a = 14.000(1) Å, b = 5.7953(4) Å, c = 14.6148(8) Å, β = 92.910(5)°, V = 1184.2(1) Å^3, Z = 4, D_c = 2.023 g cm^{-3}, μ(Mo Kα) = 2.939 mm^{-1}, specimen 0.30 × 0.15 × 10 mm, 2405 unique reflections for 2.79° < θ < 26.29°; 2033 having $F > 2\sigma(F)$. Final results: R1 [$F > 2\sigma(F)$] = 0.0216, wR2 (F^2 all data) = 0.0565, and 137 parameters; S = 1.087. For **8**: $C_{17}ClH_{12}NO_5Te$, M_r = 473.33, orthorhombic, *Pbca*, a = 12.187(3) Å, b 7.840(3) Å, c = 38.204-(10) Å, V = 3650.2(19) Å^3, Z = 8, D_c = 1.723 g cm^{-3}, μ(Mo Kα) = 1.802 mm^{-1}, irregular specimen max. and min. dimensions 0.25, 0.15 mm, 3426 unique reflections for 2.71° < θ < 25,59°; 1609 having $F > 2\sigma(F)$. Final results: R1 [$F > 2\sigma(F)$] = 0.0445, wR2 (F^2 all data) = 0.1184, and 227 parameters; S = 1.000.

Other Conditions. Data at 291 K, Enraf-Nonius CAD-4 Mach 3 diffractometer, using graphite monochromatic Mo Kα radiation (λ = 0.710 73 Å) and $\omega/2\theta$ scans. *Lp* correction and semiempirical absorption corrections derived from ψ-scans were applied. Structural solution was by heavy-atom methods and refined by full-matrix least-squares based on F^2. Hydrogen atoms were located on stereochemical grounds and refined using a riding model with U(H) = 1.5U_{eq}(C) for methyl and 1.2U_{eq}(C) for other groups. For data collection and cell refinement the CAD-4 *Software* was used;[10] data reduction was performed using MolEN.[11] The program used to solve the structures was SHELXS86,[12] and SHELXL97[13] was used to refine them. The molecular graphics program ZORTEP[14] was used.

Acknowledgment. The authors acknowledge the following agencies for support: CNPq, FAPESP.

Supporting Information Available: Tables of crystallographic data, solution, data collection, and refinement details, positional and thermal parameters, and bond distances and angles for **2**, **3**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980738D

(10) Enraf-Nonius, CAD-4 Software, Version 5.0; Enraf-Noninus: Delft, The Netherlands, 1989.
(11) Frenz, B. A. *Computing in Crystallography*; Delft University Press: 1978; p 64.
(12) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(13) Sheldrick, G. M. *SHELX93, Program for the refinement of Crystal Structures*; University of Göttingen: Germany, 1993.
(14) Zsolnai, L. *ZORTEP*; University of Heidelberg: Germany, 1995.