Organometallics **1998,** *17,* 1901−1903 1901

Unexpected Reaction of 1-Butyltelluro-4-phenyl-1-buten-3-yne under Rupe Reaction Conditions

Miguel J. Dabdoub,* André Justino, and Palimécio G. Guerrero, Jr.

Laboratório de Síntese de Compostos Organocalcogênios, Departamento de Química, FFCLRP, Universidade de São Paulo, Av. Bandeirantes, 3900, Ribeirão Preto, SP Brasil

Julio Zukerman-Schpector

Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP Brasil

Received October 10, 1997

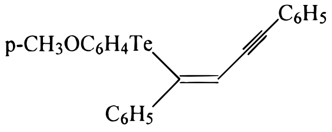
*Summary: Treatment of 1-butyltelluro-4-phenyl-1-buten-3-yne (**3**) with an aqueous solution of formic acid results in formation of the unexpected 2-phenyl-3-(4-phenylbut-3-yn-1-enyltelluro)tellurophene **5**. Formation of the expected α,β-unsaturated ketone β-telluro-substituted **4** was not observed by the reaction of **3** under Rupe reaction conditions. The structure of the product obtained was confirmed by X-ray diffraction of the dichlorotelluro derivative **6**.*

Introduction

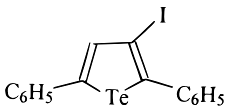
In the past decade, there has been remarkable interest in the synthesis of vinylic tellurium species and their synthetic applications.[1] However, limited reports on the synthesis of highly functionalized vinylic tellurides have appeared in the literature.[1] Synthesis of (*Z*)-*β*-(phenyltelluro)acrylate,[2] (*Z*)-*β*-(aryltelluro)acrylic acid derivatives,[3] (*Z*)-*β*-(aryltelluro)-α,*β*-unsaturated ketones,[4−6] and *β*-(organyltelluro)acroleins[7] by the hydrotelluration of appropriate acetylenic derivatives were described. The synthetic potential of these *β*-telluro-α,*β*-unsaturated carbonyl compounds has been demonstrated, since ethyl (*Z*)-*β*-(phenyltelluro)acrylate reacts with Grignard reagents catalyzed by nickel(II) or cobalt(II) phosphine complex to form carbon−carbon bonds[2] and the *β*-(organyltelluro)acroleins are transformed into the corresponding (organyltelluro)butadienes in good yields via a Wittig reaction.[7] We are interested in the synthesis of telluro carbonyl compounds and their biotransformations. In connection with other research currently underway in our laboratory, we attempted to develop a new method for the synthesis of *β*-butyltelluro-α,*β*-unsaturated ketones using the corresponding butyltelluroenynes[8−10] as starting materials. The Rupe reaction was the method of choice since it is generally agreed that rearrangement of tertiary α-acetylenic alcohols to α,*β*-unsaturated ketones proceeds through a dehydration−hydration sequence[11,12] with enynes as intermediates[12,13] when these reaction conditions are employed. Here, we describe our results on the reaction of 1-butyltelluro-4-phenyl-1-buten-3-yne[9] and the 1-butyltelluro-1,4-diphenyl-1-buten-3-yne[8] with an aqueous solution of formic acid under Rupe reaction conditions.

Results and Discussion

The hydrotelluration of symmetrical[8] or unsymmetrical[9] 1,4-bis(organyl)-1,3-butadiynes with dibutylditelluride and sodium borohydride in ethanol affords only (*Z*)-1-butyltelluro-1,4-bis(organyl)but-1-en-3-ynes. These compounds are easily transformed into the 3-iodo-2,5-diorganyltellurophenes when treated with iodine in petroleum ether.[10] We previously determined the structures of (*Z*)-1-(*p*-methoxyphenyltelluro)-1,4-diphenylbut-1-en-3-yne[10,14] (**1**) and 3-iodo-2,5-diphenyltellurophene[10,15] (**2**) by X-ray crystallography.



(1)



(2)

More recently, we observed that *β*-unsubstituted tellurophenes can be synthesized by a Te/Li exchange reaction on 1,4-bis(butyltelluro)-1,3-butadienes which were obtained from the corresponding 1,4-bis(butyltelluro)-1-buten-3-ynes.[16]

---

[1] For a review, see: Comasseto, J. V.; Ling, L. W.; Petragnani, N.; Stefani, H. A. *Synthesis* **1997**, 373.

[2] (a) Uemura, S.; Fukuzawa, S. *Tetrahedron Lett.* **1982**, *23*, 1181. (b) Uemura, S.; Fukuzawa, S.; Patil, S. R. *J. Organomet. Chem.* **1983**, *243*, 9.

[3] Detty, M. R.; Murray, B. J.; Smith, D. L.; Zumbulyadis, N. *J. Am. Chem. Soc.* **1983**, *105*, 875.

[4] Buzilova, S. R.; Vereshchagin, I. D.; Sadekov, I. D.; Minkin, V. I. *Zh. Obshch. Khim.* **1976**, *46*, 932.

[5] Buzilova, S. R.; Sadekov, I. D.; Lipovich, T. V.; Filippova, T. M.; Vereshchagin, L. I. *Zh. Obshch. Khim.* **1977**, *47*, 1999.

[6] Detty, M. R.; Luss, H. R.; McKelvey, J. M.; Geer, S. M. *J. Org. Chem.* **1986**, *51*, 1692.

[7] Mo, X.-S.; Huang, Y.-S. *Tetrahedron Lett.* **1995**, *36*, 3539.

[8] Dabdoub, M. J.; Dabdoub, V. B.; Comasseto, J. V. *Tetrahedron Lett.* **1992**, *33*, 7353.

[9] Dabdoub, M. J.; Dabdoub, V. B. *Tetrahedron* **1995**, *51*, 9839.

[10] Dabdoub, M. J.; Dabdoub, V. B.; Pereira, M. A.; Zukerman-Schpector, J. *J. Org. Chem.* **1996**, *61*, 9503.

[11] Hennion, G. F.; Davis, R. B.; Maloney, D. E. *J. Am. Chem. Soc.* **1956**, *78*, 3395.

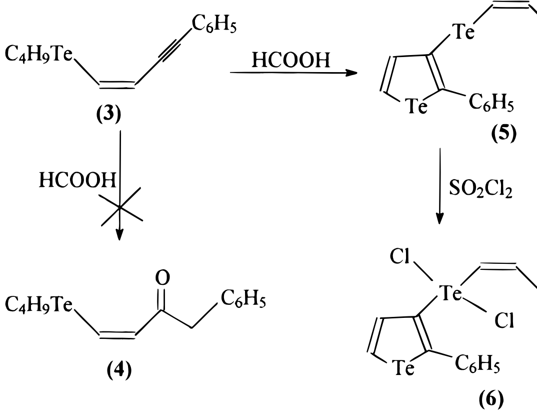
[12] For a review, see: Swaminathan, S.; Narayanan, V. *Chem. Rev.* **1971**, *71*, 429.

[13] Newman, M. S.; Goble, P. H. *J. Am. Chem. Soc.* **1960**, *82*, 4098.

[14] Zukerman-Schpector, J.; Caracelli, I.; Dabdoub, M. J.; Dabdoub, V. B. *J. Chem. Crystallogr.* **1996**, *26*, 379.

[15] Zukerman-Schpector, J.; Dabdoub, M. J.; Dabdoub, V. B.; Pereira, M. A. *Acta Crystallogr.* **1992**, *C48*, 767.

S0276-7333(97)00881-9 CCC: $15.00



In the present paper, we report the failure of our attempts to transform 1-butyltelluro-4-phenyl-1-buten-3-yne (**3**) into the corresponding α,β-unsaturated ketone β-telluro-substituted **4** by the Rupe reaction[12] using a 50% or 85% aqueous solution of formic acid. However, a very interesting result was obtained since the ^{1}H NMR spectrum showed the formation of a product which no longer contained the butyl group but only aromatic or vinylic hydrogens. Absorption corresponding to the carbonyl groups was not observed in the infrared spectrum, but a carbon−carbon triple bond was still present at 2184 cm^{-1}. The presence of a doublet at 8.93 ppm (J = 6.9 Hz) and another one at 7.98 ppm (J = 6.9 Hz) in the ^{1}H NMR spectrum indicated the presence of hydrogens with strong aromatic character,[10,16] probably bound to adjacent carbons. The two doublets that appear at 6.61 and 7.52 ppm showing a coupling constant of 10.4 Hz could be due to the presence of vinylic hydrogens bonded at one double bond of a cis configuration. On the basis of these results, the mass spectrum, and microanalysis, we propose that the obtained liquid product has the structure **5**.

A detailed analysis of the ^{1}H NMR spectrum showed that the trans isomer of compound **5** is formed as a side product since a doublet with J = 16.6 Hz appears at 6.56 ppm and another one with the same coupling constant at 7.58 ppm. The cis:trans ratio of the product obtained was 74:26, determined by ^{1}H NMR. The isomerization of the double bond is understandable since cationic species are involved in the reaction pathway.[12] However, the mechanism of the formation of **5** was not completely elucidated by us.

It should be noted that an extra tellurium atom is incorporated in the product, and there is no source of tellurium in the reaction other than the starting material **3**. In this way and considering a total conversion, 1.0 mmol of compound **3** could be transformed in only 0.5 mmol of compound **5**. The proposed structure was definitely confirmed after transformation of the liquid product obtained into a solid derivative that was obtained by treatment of **5** with sulfuryl chloride in petroleum ether at room temperature. The cis isomer (**6**) was obtained in pure form by recrystallization from hexane, and the structure of this derivative, obtained as yellow crystals (mp = 125−126 °C), was determined by X-ray crystallography (Figure 1), showing that only the acyclic tellurium atom undergoes chlorination, although examples of dihalogenation of the tellurium atom contained in tellurophenes are known.[10,17]

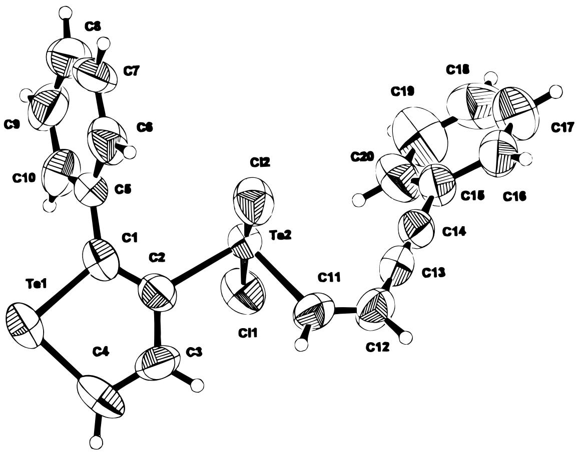
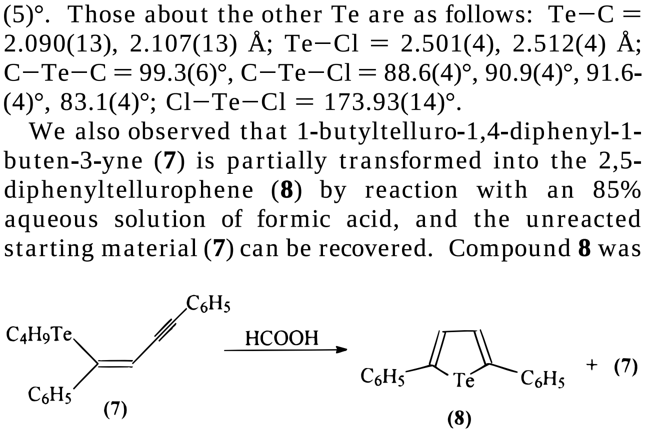


Figure 1. ORTEP drawing of compound **6**. Atoms are represented by ellipsoids corresponding to 50% probability.

The heterocyclic ring is essentially planar making dihedral angles of 69.4(4)° and 58.9(7)° with the phenyl rings. Selected distances and angle around the Te atom in the cycle are as follows: 2.088(12), 2.14(2) Å and 82.6(5)°. Those about the other Te are as follows: Te−C = 2.090(13), 2.107(13) Å; Te−Cl = 2.501(4), 2.512(4) Å; C−Te−C = 99.3(6)°, C−Te−Cl = 88.6(4)°, 90.9(4)°, 91.6(4)°, 83.1(4)°; Cl−Te−Cl = 173.93(14)°.

We also observed that 1-butyltelluro-1,4-diphenyl-1-buten-3-yne (**7**) is partially transformed into the 2,5-diphenyltellurophene (**8**) by reaction with an 85% aqueous solution of formic acid, and the unreacted starting material (**7**) can be recovered. Compound **8** was obtained in 41% yield after purification by flash chromatography using hexane as the eluent and identified by comparison (mp = 218−220 °C) with an authentic sample prepared as previously described.[17,18]



It is noteworthy that the abnormal formation of tellurophenes **5** and **8** is probably due to the presence of the phenyl groups in the structure of compounds **3** and **7** since preliminary results have shown that under Rupe reaction conditions 4-alkyl- and 1,4-dialkyl-substituted tellurobutenyne analogues to compounds **3** and **7** result in the formation of the desired β-telluro-substituted-α,β-unsaturated ketones. Studies on the scope and limitations of these reactions are underway in our laboratory, and the results will be published in due course.

Experimental Section

^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on an 80, a 200, or a 300 MHz spectrometer as noted. IR spectra were obtained with liquid films on a Perkin-Elmer

---

[16] Dabdoub, M. J.; Dabdoub, V. B. *Tetrahedron* **1997**, *53*, 4199.

[17] Mack, W. *Angew. Chem.* **1966**, *78*, 940; *Angew. Chem., Int. Engl. Ed.* **1966**, *5*, 896.

[18] Luppold, E.; Müller, E.; Winter, W. Z. *Naturforsh.* **1976**, *31B*, 1654.

1600-FT spectrometer. MS direct insertion spectra (EI) were measured at 70 eV. Elemental analyses were performed at the Instrumental Analysis Center of the Chemistry Institute, São Paulo University. Melting points are uncorrected. Ethanol (95%; Merck) was used without purification. Dibutylditelluride was prepared by the method reported in the literature.[19]

Synthesis of (*Z*)-1-Butyltelluro-4-phenyl-1-buten-3-yne (3). A solution of 1-phenyl-1,3-butadiyne (2.0 mmol) was obtained in situ by reaction of 2-hydroxy-2-methyl-6-phenyl-3,5-hexadiyne (0.368 g, 2.0 mmol) with solid NaOH (5.0 mg) in dry xylene (2.2 mL) at reflux for 10 min. The temperature was then allowed to reach room temperature, and 95% ethanol (30 mL) and dibutylditelluride (0.369 g, 1.0 mmol) were added. The reaction was run under 1 atm of N_2, and sodium borohydride (0.09 g, 2.5 mmol) was added. After the disappearance of the red color, the yellow-brown mixture was refluxed for 10 min, allowed to reach room temperature, diluted with ethyl acetate (70 mL) and washed with brine (4 × 30 mL). After the organic phase was dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel, using hexane as the mobile phase, to give the pure butyltelluroenyne **3** as a yellow oil. Yield 0.468 g (75%); GC/MS m/z 314(M^+) $C_{14}H_{16}$-Te, 256 ($M^+ - C_4H_9$), 128 (100.00); IR (neat, cm^{-1}) 690, 750, 1541, 1595, 2184; ^1H NMR (80 MHz, δ, $CDCl_3$) 0.93 (t, $J = 7.0$ Hz, 1H), 1.41 (sext, $J = 7.0$ Hz, 2H), 1.85 (quint, $J = 7.0$ Hz, 2H), 2.81 (t, $J = 7.0$ Hz, 2H), 6.61 (d, $J = 13.0$ Hz, 1H), 7.1−7.6 (m, 6H); ^{13}C NMR 6.2, 13.2, 24.7, 33.9, 89.5, 96.2, 117.3, 120.8, 123.0, 126.3, 128.1, 128.3, 131.1. Anal. Calcd for $C_{14}H_{16}Te$: C, 53.92; H, 5.17. Found: C, 54.33; H, 5.30.

Synthesis of (*Z*)-1-Butyltelluro-1,4-diphenyl-1-buten-3-yne (7). To a solution of 1,4-diphenyl-1,3-butadiyne (0.606 g, 3.0 mmol) and dibutylditelluride (0.553 g, 1.5 mmol) in 95% ethanol (20 mL) under N_2 was added sodium borohydride (0.046 g, 1.25 mmol) at room temperature. After the disappearance of the red color, the clear yellow mixture was refluxed for 2.5 h, allowed to reach room temperature, diluted with ethyl acetate (70 mL), and washed with brine (4 × 30 mL). After the organic phase was dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel, using hexane as the mobile phase, to give the pure butyltelluroenyne **7** as a yellow oil. Yield 1.036 g (89%); IR (cm^{-1}) 2175, 1596, 1475, 1437, 750, 688; GC/MS m/z 390 (14.01), 388 (12.32), 334 (11.01), 332 (11.34), 330 (7.22), 204 (62.67), 203 (93.48), 202 (100.00), 126 (5.54), 102 (12.89), 101 (12.77); ^1H NMR (200 MHz, δ, $CDCl_3$) 0.73 (t, $J = 7.0$ Hz, 3H), 1.22 (sext, $J = 7.0$ Hz, 2H), 1.56 (quint, $J = 7.0$ Hz, 2H), 2.48 (t, $J = 7.0$ Hz, 2H), 6.34 (s, 1H), 7.1−7.6 (m, 10H); ^{13}C NMR 8.7, 13.1, 24.8, 33.7, 90.3, 96.5, 116.0, 123.1, 127.7, 127.8, 128.1, 131.1, 137.0, 141.9. Anal. Calcd. for $C_{20}H_{20}Te$: C, 61.91; H, 5.15. Found: C, 61.79; H, 5.13.

Synthesis of 5 from Compound 3 under Rupe Reaction Conditions. (*Z*)-1-(Butyltelluro)-4-phenyl-1-buten-3-yne (0.311 g, 1.0 mmol) was dissolved in an 85% aqueous solution of formic acid (15 mL) and refluxed for 1.0 h. The resulting mixture was washed with a saturated $NaHCO_3$ solution until CO_2 evolution was no longer observed, the product was extracted with ethyl acetate (3 × 40 mL) and washed with water (3 × 40 mL), and the organic phase was dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on SiO_2 using hexane as the eluent. Compound **5** was obtained as an orange oil. Yield 0.198 g (78%); IR (cm^{-1}) 2184, 1592, 1486, 753, 692; MS m/z 510 (6.01), 385 (14.67), 384 (13.81), 383 (19.43), 382 (17.80), 381 (18.85), 315 (7.98), 314 (6.06), 313 (9.63), 303 (11.27), 302 (10.75), 255 (43.03), 254 (67.78), 253 (100.00), 252 (97.84), 202 (21.79), 128 (59.09), 127 (77.01), 126 (74.85); ^1H NMR (300 MHz, δ, $CDCl_3$) 6.61 (d, $J = 10.4$ Hz, 1H), 7.25−7.45 (m, 10H), 7.52 (d, $J = 10.4$ Hz, 1H), 7.98 (d, $J = 6.9$ Hz, 1H), 8.93 (d, $J = 6.9$ Hz, 1H); ^{13}C NMR 88.9, 117.0, 123.0, 124.3, 127.9, 128.0, 128.3, 128.4, 128.5, 128.8, 128.9, 129.0, 131.5, 147.4. Anal. Calcd for $C_{20}H_{14}Te_2$: C, 47.15; H, 2.77. Found: C, 46.84; H, 2.91.

Synthesis of 8 from Compound 7 under Rupe Reaction Conditions. (*Z*)-1-(Butyltelluro)-1,4-diphenyl-1-buten-3-yne (0.775 g, 2.0 mmol) was dissolved in an 85% aqueous solution of formic acid (30 mL) and refluxed for 1.0 h. The resulting mixture was washed with a saturated $NaHCO_3$ solution until CO_2 evolution was no longer observed, the product was extracted with ethyl acetate (3 × 50 mL) and washed with water (3 × 50 mL), and the organic phase was dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on SiO_2 using hexane as the eluent. The starting material **7** was partially recovered (0.155 g, 20%), and the 2,5-diphenyltellurophene **8** was obtained as a yellow solid. Mp 218−220 °C; yield 0.271 g (41%); GC/MS m/z 335 (10.79), 334 (65.02), 333 (10.94), 332 (59.09), 203 (100.00), 202 (65.84), 126 (6.06), 102 (40.71); ^1H NMR (80 MHz, δ, $CDCl_3$) 7.1−7.5 (m, 10H), 7.75 (s, 2H).

Synthesis of Dichlorotelluro Derivative 6 by Reaction of 5 with SO_2Cl_2. To a solution of compound **5** (1.02 g, 2.0 mmol), in petroleum ether (20 mL) under vigorous stirring at room temperature, sulfuryl chloride (0.18 mL) was added dropwise; the yellow solution turned colorless, and precipitation of a yellow solid was observed. After recrystallization from hexanes, compound **6** was obtained as yellow crystals. Mp 125−126 °C; yield 0.824 g (71%); ^1H NMR (500 MHz, δ, $CDCl_3$) 6.76 (d, $J = 9.9$ Hz, 1H), 7.32−7.42 (m, 2H), 7.45−7.56 (m, 6H), 7.60−7.63 (m, 2H), 7.87 (d, $J = 9.9$ Hz, 1H), 8.31 (d, $J = 7.2$ Hz, 1H), 9.15 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR 121.6, 124.6, 128.4, 128.5, 128.8, 129.0, 129.4, 129.5, 129.6, 129.9, 131.9, 132.0, 135.1, 137.5. Anal. Calcd for $C_{20}H_{14}Te_2Cl_2$: C, 41.39; H, 2.43. Found: C, 41.03; H, 2.36.

Acknowledgment. This research was supported by a Grant-in-Aid for Scientific research from FAPESP. Thanks are due to the Instrumental Analysis Center, Institute of Chemistry, São Paulo University, for providing elemental analyses, to Prof. Antonio Gilberto Ferreira (UFSCar) for providing the NMR facilities, and to Mr. Djalma Batista Gianetti for assistance in obtaining infrared and mass spectra.

Supporting Information Available: Full details for the X-ray crystal structure determination of compound **6** are provided, including a discussion of the results and tables with all data collection parameters and the refinement procedure (8 pages). Ordering information and is given on any current masthead page.

OM970881R

---

[19] Cava, M. P.; Engman, L. *Synth. Commun.* **1972**, *12*, 163.