Formation of the Transient Telluroketone (1*R*)-3-Telluroxocamphor and Its Dimerization to the Corresponding *syn*- and *anti*-1,3-Ditelluretanes

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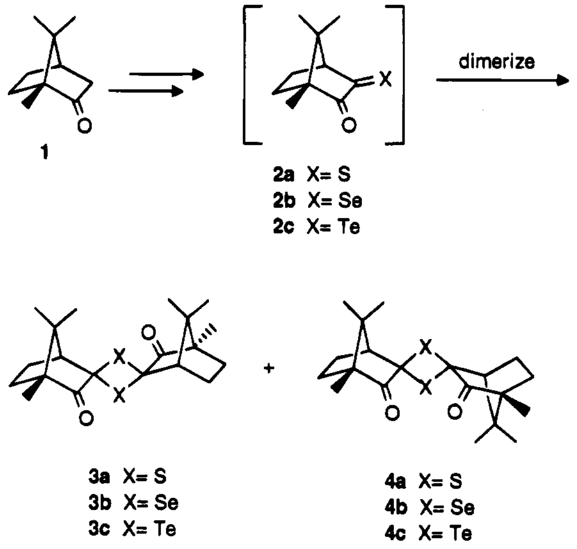
While a variety of tellurocarbonyl compounds are known,[1] only one relatively stable telluroketone has been prepared to date.[2] Several other telluroketones and telluroaldehydes have been isolated as complexes with transition metals[3] or trapped as Diels–Alder cycloadducts.[4] The cyclic dimers of a few tellurocarbonyl species have also been reported, including 2,4-alkylidene-1,3-ditelluretanes[5] (formally dimers of telluroketenes) and 2,2,4,4-tetrafluoro-1,3-ditelluretane (from $F_2C{=}Te$).[6] The dimerization of the 2-telluroketone derivative of adamantane appears to be the only example of a 1,3-ditelluretane produced from an authentic telluroketone.[4b] Recently we reported the generation of the 3-thio- and 3-selenoketone derivatives **2a,b** of (1*R*)-(+)-camphor (**1**),[7] and their immediate *in situ* conversion to the corresponding *anti*-1,3-dithietane **4a** and a mixture of *syn*- and *anti*-1,3-diselenetanes **3b** and **4b**, respectively (Scheme 1). However, the methods that were employed in the sulfur and selenium series proved unsuccessful in subsequent attempts to generate the corresponding telluroketone (1*R*)-3-telluroxocamphor (**2c**). We now report a new method for forming the latter compound as a transient intermediate and its *in situ* dimerization to **3c** and **4c**.

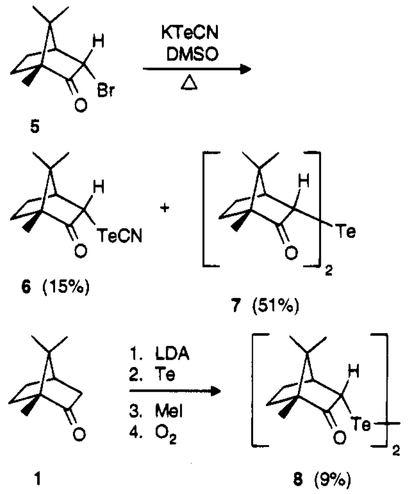
Scheme 1



Results and Discussion

In our previous work,[7] the thio- and selenoketones **2a,b** (and hence the dimers **4a, 3b** and **4b**) were formed by the base-catalyzed elimination of HCN from the corresponding 3-thio- and 3-selenocyanates,[8] or alternatively in the case of **2b**, by the treatment of camphor enolate with elemental selenium in the presence of an alkylating agent such as methyl iodide.[7] Silks and co-workers[9] recently demonstrated the substitution of α-haloketones, including 3-bromocamphor (**5**), with lithium arenetellurolates. By analogy, we investigated the reaction of KTeCN[10] with **5** in hot DMSO, but obtained a complex mixture of products, from which only 15% of the desired tellurocyanate **6**, as well as 51% of the telluride **7**, were isolated (Scheme 2). The preponderance of **7** may be the result of the known[11] disproportionation of aryl tellurocyanates to the corresponding tellurides and tellurium dicyanide, $Te(CN)_2$. The reaction of camphor enolate with elemental tellurium, in contrast to selenium, failed to undergo any substantial reaction even when subjected to ultrasound. Only a small amount of the ditelluride **8** was isolated and there was no evidence for the formation of the corresponding telluroketone or its dimerization products (Scheme 2). Reaction of the tellurocyanate **6** with various bases afforded complex mixtures of products and no observable quantities of the ditelluretanes.

Scheme 2



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[4] For example, see: (a) Erker, G.; Hock, R. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 179. (b) Segi, M.; Koyama, T.; Takata, Y.; Nakajima, T.; Suga, S. *J. Am. Chem. Soc.* **1989**, *111*, 8749.

[5] (a) Lakshmikantham, M. V.; Cava, M. P.; Albeck, M.; Engman, L.; Carroll, P.; Bergman, J.; Wudl, F. *Tetrahedron Lett.* **1981**, *22*, 4199. (b) Bender, S. L.; Haley, N. F.; Luss, H. R. *Tetrahedron Lett.* **1981**, *22*, 1495.

[6] (a) Boese, R.; Haas, A.; Limberg, C. *J. Chem. Soc., Chem. Commun.* **1991**, 1378. (b) Boese, R.; Haas, A.; Limberg, C. *J. Chem. Soc., Dalton Trans.* **1993**, 2547.

[7] Back, T. G.; Dyck, B. P.; Parvez, M. *J. Org. Chem.* **1995**, *60*, 703.

[8] This procedure has been previously used to produce other selenocarbonyl compounds from the corresponding selenocyanates: (a) Kirby, G. W.; Trethewey, A. N. *J. Chem. Soc., Chem. Commun.* **1986**, 1152. (b) Meinke, P. T.; Krafft, G. A. *J. Am. Chem. Soc.* **1988**, *110*, 8679.

[9] Silks, L. A., III; Odom, J. D.; Dunlap, R. B. *Synth. Commun.* **1991**, *21*, 1105.

[10] Spencer, H. K.; Lakshmikantham, M. V.; Cava, M. P. *J. Am. Chem. Soc.* **1977**, *99*, 1470.

[11] Engman, L. *J. Org. Chem.* **1983**, *48*, 2920.

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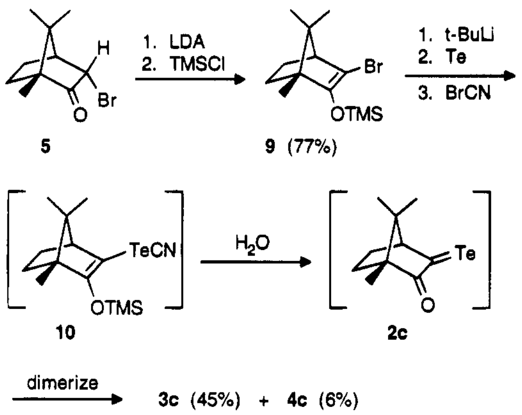
Scheme 3



In view of our failure to extend the methods that had been successful in forming products **2a,b** and dimers **4a**, **3b**, and **4b** to the corresponding tellurium compounds, we attempted to devise an alternative method to obtain the latter. The enol silyl ether of 3-bromocamphor (**9**) was easily obtained from 3-bromocamphor enolate and TMSCl.[12] Bromine–lithium exchange with t-BuLi, followed by reaction with elemental tellurium,[13] and cyanogen bromide then afforded the vinyl tellurocyanate **10**, which was not isolated but was hydrolyzed directly under anaerobic conditions to afford the isomeric *syn*- and *anti*-1,3-ditelluretanes **3c** and **4c** in yields of 45 and 6%, respectively. These ditelluretanes were presumably formed by dimerization of the telluroketone **2c** (Scheme 3). In addition to **3c** and **4c**, traces of the ditelluride **8**, telluride **7**, and tellurocyanate **6** were also detected (NMR) in the reaction mixture.

The 1,3-ditelluretanes were orange powders that could be both chromatographed and recrystallized and stored for extended periods in the dark, but decomposed in the presence of light and oxygen with deposition of elemental tellurium. Both isomers possess C_2 axes of symmetry which render the respective camphor moieties equivalent. In the *anti*-ditelluretane **4c** this axis is perpendicular to the four-membered ring and renders the two tellurium atoms equivalent, therefore giving rise to a single ^{125}Te-NMR resonance at δ 1375 ppm (relative to Me_2Te). However, in the *syn*-isomer **3c**, the C_2 axis passes through the two tellurium atoms and does not make them equivalent. Thus, two separate signals at δ 1552 and 1234 ppm are observed. An X-ray crystal structure confirmed the identity of **3c** and is included in the supporting information.[14]

Experimental Section

The ^{125}Te-NMR spectra were recorded at concentrations of ca. 0.03 M in $CDCl_3$ using diphenyl ditelluride as an external standard. Chemical shifts are reported relative to dimethyl telluride (δ 0 ppm) by assuming that the signal from the standard is at δ 421 ppm.[15] Mass spectra of all tellurium compounds showed the characteristic isotopic distribution, but only masses based upon ^{130}Te are reported. Elemental analyses and mass spectra were obtained by Ms. D. Fox and Dr. Q. Wu in the Chemical Instrumentation Laboratory at the University of Calgary.

Saturated aqueous solutions of NaCl and NH_4Cl were employed for washing organic solutions. (1*R*)-(+)-Camphor (**1**), (1*R*)-*endo*-3-bromocamphor (**5**), tellurium powder (200 mesh), BrCN, and KCN were purchased from commercial sources and used without further purification. Other reagents and solvents were purified or dried by standard methods as required. Preparation and purification of tellurium-containing products was generally performed under red light to minimize photodecomposition.[16] Chromatography was carried out on silica gel (230–400 mesh).

3-(*endo*-Tellurocyanato)camphor (6) and Di(*endo*-3-camphoryl) Telluride (7). Potassium cyanide (0.564 g, 8.66 mmol) and tellurium powder (1.106 g, 8.67 mg atom) were stirred together in 9 mL of DMSO at 100 °C for 2.5 h. Bromocamphor (**5**) (2.204 g, 9.54 mmol) in 9 mL of DMSO was added and stirring and heating at 100 °C was continued for another 3.5 h. The mixture was cooled, added to 80 mL of water, and extracted with 80 mL of ether. The ether was filtered (Celite), washed three times with water and aqueous NaCl, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was chromatographed (elution with 20% ethyl acetate–hexanes) to afford 1.043 g (51%, based on **5**) of the telluride **7**, followed by 0.407 g (15%, based on Te) of the tellurocyanate **6**.

Tellurocyanate **6**: R_f 0.24 (20% ethyl acetate–hexanes); mp 67–69 °C (from chloroform–hexanes); IR (Nujol) 2143, 1730, 1035, 757 cm^{-1}; ^{1}H-NMR (200 MHz) δ 5.24 (ddd, J = 4.6, 2.4, 0.8 Hz, 1 H), 2.37–2.33 (m, 1 H), 2.19–2.00 (m, 1 H), 1.91–1.71 (m, 2 H), 1.40 (ddd, J = 14.0, 9.1, 5.0 Hz, 1 H), 1.13 (s, 3 H), 1.02 (s, 3 H), 0.99 (s, 3 H); ^{13}C-NMR δ 215.4, 57.8, 49.1, 48.2, 43.1, 30.8, 26.5, 20.4, 20.0, 9.4; mass spectrum *m/z* (relative intensity) 307 (19, M$^+$), 151 (22), 123 (90), 83 (100); exact mass calcd for $C_{11}H_{15}NOTe$ 307.0218, found 307.0205. Anal. Calcd for $C_{11}H_{15}NOTe$: C, 43.34; H, 4.96; N, 4.59. Found: C, 42.80; H, 4.83; N, 4.50.

Telluride **7**: R_f 0.52 (20% ethyl acetate-hexanes); mp 69–73 °C (from ethanol); IR (Nujol) 1752, 1034, 768 cm^{-1}; ^{1}H-NMR (200 MHz) δ 4.63 (ddd, J = 4.8, 1.8, 0.8 Hz, 2 H), 2.33–2.28 (m, 2 H), 2.09 (ddd, J = 12.9, 9.2, 3.8 Hz, 2 H), 1.97–1.75 (m, 2 H), 1.70–1.62 (m, 2 H), 1.43 (ddd, J = 13.6, 9.1, 4.6 Hz, 2 H), 1.09 (s, 6 H), 0.98 (s, 6 H), 0.94 (s, 6 H); ^{13}C-NMR δ 212.4, 57.6, 53.8, 49.6, 45.9, 30.5, 22.4, 20.0, 19.9, 9.6; mass spectrum *m/z* (relative intensity) 432 (52, M$^+$), 281 (19), 151 (57), 123 (100). Attempts to obtain a high resolution mass spectrum were unsuccessful because of the lack of persistence of the molecular ion.

Di(*endo*-3-camphoryl) Ditelluride (8). Camphor (**1**) (1.01 g, 6.64 mmol) was added to a solution of LDA (7.87 mmol) in 10 mL of THF at −40 °C, and the resulting solution was stirred at this temperature for 90 min. Tellurium (0.95 g, 7.45 mg atom) was added, and the suspension was sonicated in an ice bath for 3 h. Iodomethane (0.88 mL, 14 mmol) was added, and the mixture was stirred at rt for 2 d. The mixture was poured into 50 mL of ether, filtered (Celite), washed three times with water and aqueous NaCl, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed (elution with 10% ethyl acetate–hexanes) to afford 0.168 g (9%, based on **1**) of the ditelluride **8** as a brown powder, R_f 0.40 (10% ethyl acetate–hexanes); mp 124–132 °C (from ethanol); IR (Nujol) 1722, 1033 cm^{-1}; ^{1}H-NMR (400 MHz) δ 5.05 (dd, J = 4.3, 2.5 Hz, 2 H), 2.33–2.31 (m, 2 H), 1.94–1.85 (m, 2 H), 1.75 (ddd, J = 13.2, 9.3, 3.9 Hz, 2 H), 1.65 (ddd, J = 14.1, 11.1, 3.4 Hz, 2 H), 1.39 (ddd, J = 13.9, 9.1, 5.0 Hz, 2 H), 1.07 (s, 6 H), 0.99 (s, 6 H), 0.94 (s, 6 H); ^{13}C-NMR δ 217.7, 57.3, 49.5, 46.9, 37.7, 29.9, 26.6, 20.2, 19.9, 9.9; mass spectrum *m/z* (relative intensity) 562 (0.2, M$^+$), 432 (3), 149 (86), 55 (100). Anal. Calcd for $C_{20}H_{30}O_2Te_2$: C, 43.08; H, 5.42. Found: C, 43.15; H, 5.43.

Trimethylsilyl Enol Ether of 3-Bromocamphor (9). Bromocamphor (**5**) (5.01 g, 21.7 mmol) was added to a solution of LDA (32.4 mmol) in 30 mL of THF, and the resulting mixture was stirred at −78 °C for 2 h. TMSCl (4.70 mL, 37.0 mmol)

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(12) The enol acetate of **5** has been previously prepared by a similar procedure: Joshi, G. C.; Chambers, W. D.; Warnhoff, E. W. *Tetrahedron Lett.* **1967**, 3613.

(13) For another example of tellurium insertion into vinyl lithium bonds, see: Wudl, F.; Aharon-Shalom, E. *J. Am. Chem. Soc.* **1982**, *104*, 1154.

(14) The authors have deposited atomic coordinates for structure **3c** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

(15) Granger, P.; Chapelle, S.; McWhinnie, W. R.; Al-Rubaie, A. *J. Organomet. Chem.* **1981**, *220*, 149.

(16) Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4438.

was added dropwise over 5 min, and the mixture was warmed to rt and stirred for 3 h. It was then concentrated, taken up in pentane, filtered, and again concentrated under reduced pressure. The residue was distilled *in vacuo* to afford 5.06 g (77%) of **9** as a colorless oil: bp 69−70 °C at 0.1 Torr; IR (film) 1643, 1252, 904, 847 cm^{-1}; ^{1}H-NMR (200 MHz) δ 2.30 (d, J = 3.4 Hz, 1 H), 1.88−1.78 (m, 1 H), 1.59−1.46 (m, 1 H), 1.32−1.19 (m, 2 H), 0.95 (s, 3 H), 0.93 (s, 3 H), 0.75 (s, 3 H), 0.28 (s, 9 H); ^{13}C-NMR δ 156.5, 96.2, 57.4, 55.4, 54.4, 32.2, 26.0, 19.7, 19.3, 10.4, 1.3; mass spectrum m/z (relative intensity) 304 (19, M$^+$), 276 (40), 223 (7), 195 (65), 73 (100); exact mass calcd for $C_{13}H_{23}BrOSi$ 304.0683, found 304.0672.

***syn*-1,3-Ditelluretane 3c and *anti*-1,3-Ditelluretane 4c.** t-BuLi (3.38 mmol) was added to a solution of 512 mg (1.69 mmol) of **9** in 5 mL of THF at −78 °C, and the mixture was stirred for 1 h. Tellurium powder (218 mg, 1.71 mg atom) was added, and the mixture was warmed to −15 °C and stirred for 4.5 h. Cyanogen bromide (198 mg, 1.87 mmol) in 1 mL of THF was added dropwise, the mixture was warmed to rt, and stirring was continued for 90 min. Deoxygenated water (5 mL) was added, and the mixture was stirred for 5 min. The mixture was poured into 50 mL of $CHCl_3$, washed six times with water and aqueous NaCl, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was chromatographed (elution with 20% ethyl acetate−hexanes) to afford 210 mg (45%) of the *syn*-ditelluretane **3c**, followed by 27 mg (6%) of its *anti* isomer **4c**.

syn-Ditelluretane **3c**: R_f 0.40 (30% ethyl acetate−hexanes); mp 201−204 °C dec (from ethanol); IR (Nujol) 1722, 1020, 999 cm^{-1}; ^{1}H-NMR (200 MHz) δ 3.15 (d, J = 4.2 Hz, 2 H), 1.82−1.63 (m, 2 H), 1.50−1.19 (m, 2 H), 1.15−1.00 (m, 4 H), 0.97 (s, 6 H), 0.93 (s, 6 H), 0.58 (s, 6 H); ^{13}C-NMR δ 220.0, 59.2, 56.8, 49.2, 28.4, 27.8, 21.2, 20.4, 10.2, −12.0;[17] ^{125}Te-NMR δ 1552, 1234; mass spectrum m/z (relative intensity) 560 (6, M$^+$), 430 (23), 319 (15), 279 (8), 149 (16), 123 (100); exact mass calcd for $C_{20}H_{28}O_2Te_2$ 556.0196, found 556.0228. Crystals suitable for X-ray diffraction were grown from $CHCl_3$.

anti-Ditelluretane **4c**: R_f 0.28 (30% ethyl acetate−hexanes); mp 198−204 °C dec (from ethanol); IR (Nujol) 1741, 1018, 997 cm^{-1}; ^{1}H-NMR (200 MHz) δ 2.88 (d, J = 4.2 Hz, 2 H), 1.73−1.56 (m, 2 H), 1.43 (ddd, J = 12.3, 12.3, 3.4 Hz, 2 H), 1.26−1.12 (m, 4 H), 0.97 (s, 12 H), 0.66 (s, 6 H); ^{13}C-NMR δ 218.2, 59.8, 56.7, 49.6, 28.4, 27.0, 21.2, 20.4, 10.2, −13.1;[17] ^{125}Te-NMR δ 1375; mass spectrum m/z (relative intensity) 560 (4, M$^+$), 430 (6), 319 (4), 279 (24), 149 (100), 123 (50); exact mass calcd for $C_{20}H_{28}O_2Te_2$ 556.0196, found 556.0163.

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Supporting Information Available: An ORTEP diagram of *syn*-1,3-ditelluretane **3c** and the ^{1}H- and ^{13}C-NMR spectra of compounds **3c**, **4c**, and **6−9** (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(17) For another example of the powerful shielding effect of tellurium substitution on ^{13}C-NMR resonances, see: Kohne, B.; Praefcke, K.; Zeisberg, R. *J. Organomet. Chem.* **1979**, *175*, 49.