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First Synthesis and Structure of Optically Pure Te-Chiral-Alkoxytelluranes

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Abstract: The first synthesis and isolation of optically pure Te-chiral-alkoxytelluranes **1** and **8** have been developed using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand. A distorted trigonal bipyramidal (TBP) structure of **1i** with *R* configuration was confirmed by the X-ray analysis. Copyright © 1996 Published by Elsevier Science Ltd

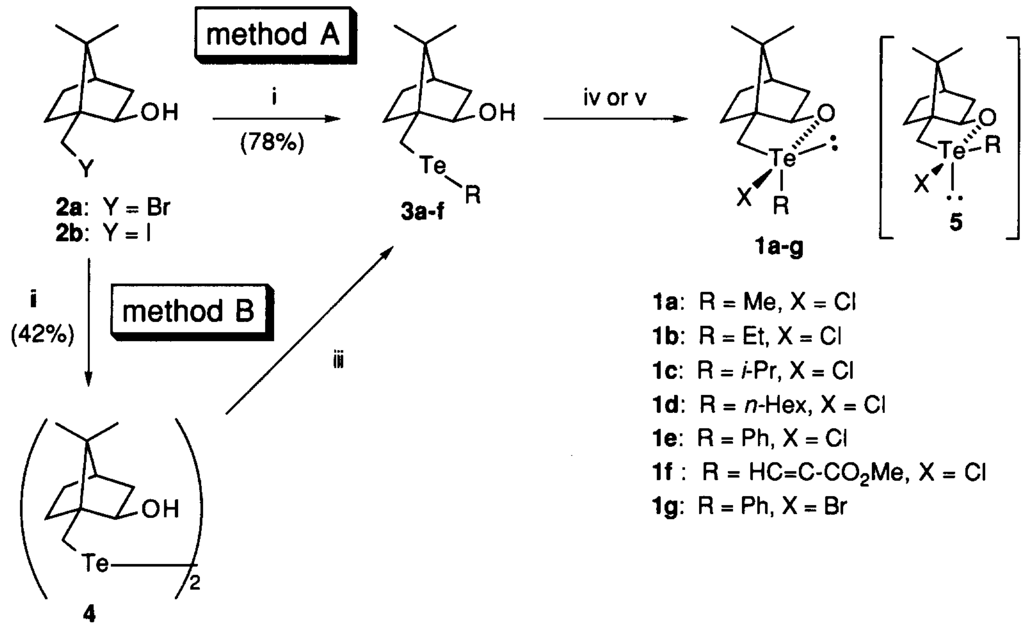
Although organotellurium compounds have attracted considerable interest in the field of organic synthesis,[1] little information is available on the stereochemical aspects of the tellurium compounds. The main reason is that there have been few reports concerning optically pure organotellurium compounds bearing a stereogenic tellurium.[2] Optically active telluronium salts[2a-c] and telluronium ylides[2d] have been obtained by optical resolution of the corresponding racemates. We report here the first synthesis of optically pure Te-chiral-10-Te-4 organotellurium species[3] (telluranes) **1** and **8** by using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand and the structure determination of **1** by X-ray analysis.

Tellurides **3** were prepared by two methods (Scheme 1 and Table 1): Method A; Reaction of (1*S*)-10-bromo-2-*exo*-borneol **2a**[4] or (1*S*)-10-iodo-2-*exo*-borneol **2b**[5] with sodium alkyl or aryltellurolate[6] generated *in situ* from $(RTe)_2$[7a] and $NaBH_4$. Method B; Formation[7b] of (1*S*)-bis(2-*exo*-bornyl) ditelluride **4** from (1*S*)-10-bromo-2-*exo*-borneol **2a** followed by reaction of **4** with $NaBH_4$ and various alkylating reagents (Me_2SO_4, EtBr and *i*-PrBr). Conjugate addition of sodium tellurolate, generated from **4**, to methyl propiolate gave (*E*)- and (*Z*)-α,β-unsaturated esters[8] **3f** (11% and 67% yield, respectively). Tellurides **3a-d** were used for the next reaction without purification because of their instability. Treatment of tellurides **3a-f** with *t*-BuOCl (CH_2Cl_2, 0 °C, 20 min) gave chlorotelluranes **1a-f** as exclusive products (86-97% yield from **3**). Bromotellurane **1g** was obtained as a single diastereomer (52% yield)[9] from the reaction of **3e** with *N*-bromosuccinimide (NBS) (CH_2Cl_2, room temperature, 30 min). IR, ^1H NMR and ^{13}C NMR spectra of **1e** and **1g** are very similar to each other. Halotelluranes **1a-g** were isolated and are stable even in air at room temperature.

Nucleophilic substitution of **1e** with 3 equiv. of NaBr (MeCN, room temperature, 7 h) gave bromotellurane **1g** (96% yield) (Scheme 2). Substitution of **1g** with NaI gave iodotellurane **1h** (98% yield). Treatment of **1e** with AgF gave fluorotellurane **1i** (85% yield).

The X-ray crystallographic analysis of **1i** indicated that it has a distorted TBP structure (*R*[10] configuration at the tellurium centre) (Figure 1).[11] Each apical-bond distance of Te–F [2.063(7) Å] and Te–O [1.998(7) Å] is similar to those of Te–F [2.006(2) Å][12a] of diphenyltellurium difluoride **6** and Te–O [2.077(2) and 2.082(2) Å][12b] of racemic 3,3,3',3'-tetrakis(trifluoromethyl)-1,1'-spirobi[3H-2,1-benzoxatellurole] **7**. The F–Te–O angle deviates by 13.2(3)° from linearity. This deviation increases in the order of diphenyltellurium difluoride

Scheme 1



1a: R = Me, X = Cl
1b: R = Et, X = Cl
1c: R = *i*-Pr, X = Cl
1d: R = *n*-Hex, X = Cl
1e: R = Ph, X = Cl
1f : R = HC=C-CO$_2$Me, X = Cl
1g: R = Ph, X = Br

i, (RTe)$_2$, NaBH$_4$, EtOH, Δ; ii, Te, thioureadioxide, NaOH, DMSO-H$_2$O, THF, Me(CH$_2$)$_{15}$N(Me)$_3$Br, 80 °C; iii, NaBH$_4$, alkylating reagent, EtOH, Δ; iv, *t*-BuOCl, CH$_2$Cl$_2$, 0 °C; v, NBS, CH$_2$Cl$_2$, room temperature.

Table 1. Synthesis of Halotelluranes **1**.

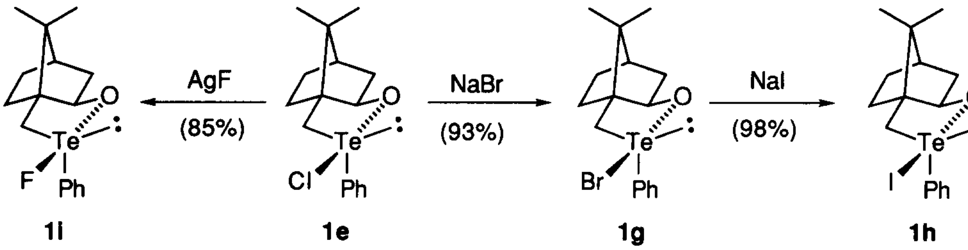
R	X	method (alkylating reagent)	yield of **3** (%)	yield of **1** (%)
Me	Cl	A	**3a** (65)	**1a** (95)
Me	Cl	B (Me$_2$SO$_4$)	**3a** (—)	**1a** (24[a])
Et	Cl	A	**3b** (80)	**1b** (93)
Et	Cl	B (EtBr)	**3b** (—)	**1b** (62[a])
i-Pr	Cl	A	**3c** (95)	**1c** (97)
i-Pr	Cl	B (*i*-PrBr)	**3c** (—)	**1c** (35[a])
n-Hex	Cl	A	**3d** (90)	**1d** (95)
Ph	Cl	A	**3e** (78)	**1e** (96)
HC=CCO$_2$Me	Cl	B (HC≡CCO$_2$Me)	**(*Z*)-3f** (67)	**(*Z*)-1f** (86)
			(*E*)-3f (11)	**(*E*)-1f** (97)
Ph	Br	A	**3e** (78)	**1g** (52)

[a] Yield from **4**.

6 [6.9(1)°][12a] < **1i** < 3,3,3',3'-tetrakis(trifluoromethyl)-1,1'-spirobi[3H-2,1-benzoxatellurole] **7** [19.47(7)°][12b]. Stereochemistry of the telluranes **1a-h** can be assigned as depicted in Schemes 1 and 2 by analogy with **1i** (^{1}H and ^{13}C NMR spectra). No tellurane **5** (Scheme 1), epimeric at the tellurium, was detected in these reactions.

Formation of telluranes **5** might be unfavorable because of steric repulsion between 7-methyl group of bornyl moiety and carbon ligand, R group.

Scheme 2



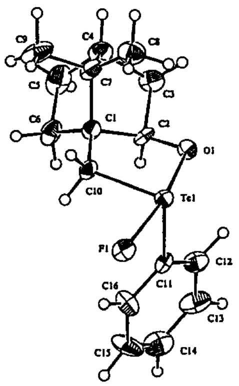
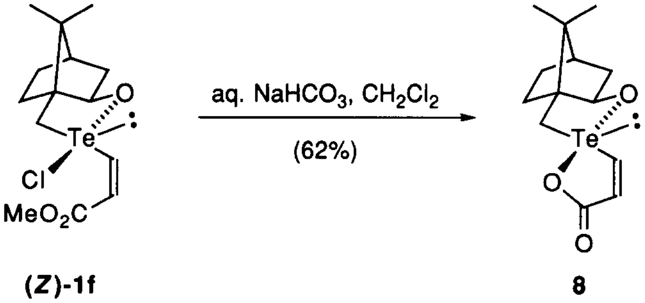


Figure 1. Perspective structure of **1i**.

In order to prepare a telluroxide, (*Z*)-**1f** was treated with aqueous $NaHCO_3$. Unexpectedly, a spirotellurane **8**[13] (62%) was obtained instead of a telluroxide. Successive hydrolysis of ester, dissociation of Te–Cl bond, and attack of the carboxylate anion to the resulting telluronium cation would give the spirotellurane **8**. This is the first chiral spirotellurane which has alkoxy and acyloxy groups as the apical ligands.[14]

Scheme 3



In conclusion, we have successfully accomplished the first synthesis of optically pure and isolable Te-chiral-telluranes **1** and **8**. The stability of **1** and **8** would be ascribed to protection of the stereogenic tellurium atom with bulky bornyl group as well as with five-membered ring. This concept of steric protection could be developed into the synthesis of other optically pure Te-chiral-telluranes and other hypervalent chalcogen compounds.[15] Furthermore, nucleophilic substitution reactions of these chiral telluranes will provide optically pure telluroxides and telluronium ylides, whose synthesis and reactions will open a new entry of organotellurium chemistry.

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7. (a) Haller W. S.; Irgolic, K. J. *J. Organometal. Chem.*, **1972**, *38*, 97-103. (b) Ferreira J. T. B.; de Oliveira, A. R. M.; Commasseto, J. V. *Synth. Commun.*, **1989**, *19*, 239-244.
8. Satisfactory analytical (combustion and high resolution mass) and spectral (IR, ^{1}H NMR, Mass) data were obtained for all new isolable compounds.
9. Isolated yield of **1g** was low compared to that of **1e** because it was difficult to separate **1g** from succinimide. Calculated yield of **1g** from **3e** was 100% from ^{1}H NMR spectrum of a crude reaction mixture.
10. Designation of absolute configuration at tetracoordinate tellurium (IV) was followed by an extension of the Cahn, Ingold, Prelog (CIP) *R-S* nomenclature proposed by Martin and Balthazor, see: Martin, J. C.; Balthazor, T. M. *J. Am. Chem. Soc.*, **1977**, *99*, 152-162.
11. Crystallographic data for **1i**: monoclinic, space group, P2$_1$ with a = 8.2316(6) Å, b = 7.582(1) Å, c = 12.6143(7) Å, β =102.742(5)°, V = 767.9(1) Å^3, and Z = 2 (d_{calcd} = 1.626 g cm^{-3}), μ (CuKα) = 153.21 cm^{-1} absorption corrected by ω scans; 1251 unique reflections; 1188 with $I > 3.00\sigma(I)$ were used in refinement; R = 3.8%, R_w = 5.2%. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge, CB2 1EZ (UK), on quoting the full journal citation.
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13. **8**: mp 146-147 °C; $[\alpha]_D^{26}$ -263.6 (*c* 1.10, CHCl$_3$); IR (KBr) 1644 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ: 0.91 (s, 3H, CH$_3$), 1.02 (s, 3H, CH$_3$), 1.04-1.97 (m, 7H), 2.60 and 3.55 (AB q, J = 13.2 Hz, 2H, 10-H), 4.06 (dd, J = 3.3, 6.6 Hz, 1H, 3-H), 7.43 (d, 1H, J = 7.1 Hz, vinyl-H), 7.50 (d, 1H, J = 7.1 Hz, vinyl-H). Similar reaction of **(*E*)-1f** afforded decomposed products.
14. Takaguchi and Furukawa have reported the synthesis of a racemic spirotellurane which has alkoxy and acyloxy groups as the apical ligands, see: Takaguchi, Y.; Furukawa, N. *Chem. Lett.*, **1996**, 365-366.
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