

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

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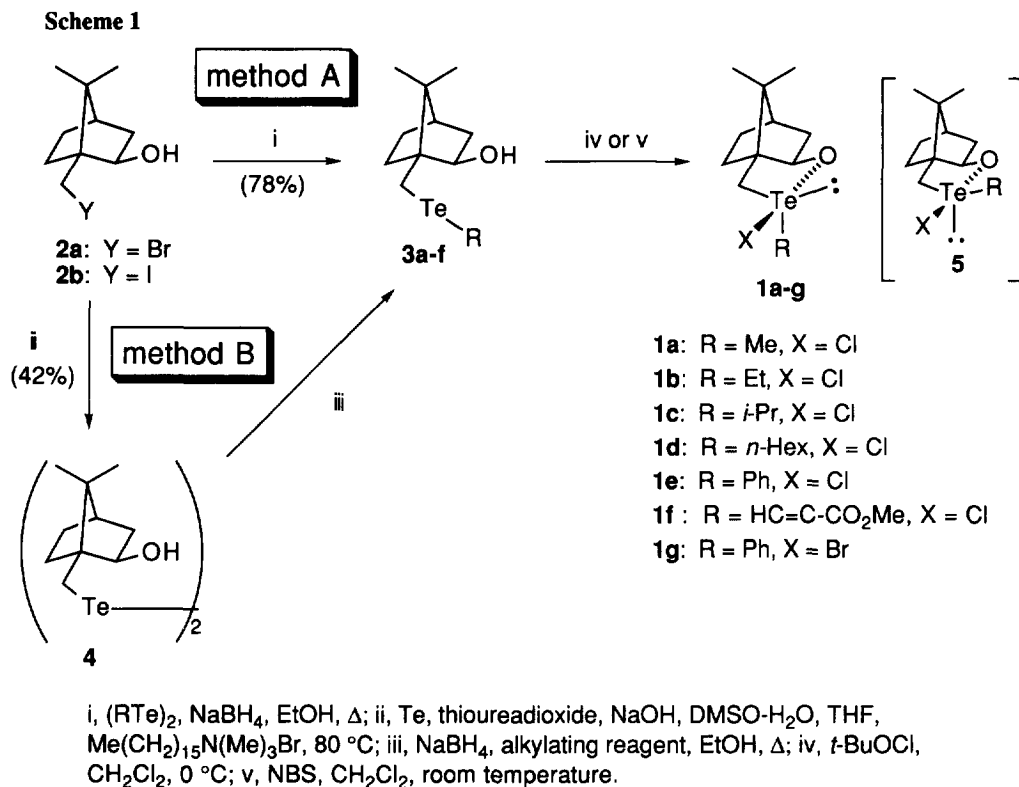
Abstract: The first synthesis and isolation of optically pure Te-chiral-alkoxytelluranes **1** and **8** have been developed using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand. A distorted trigonal bipyramidal (TBP) structure of **1i** with *R* configuration was confirmed by the X-ray analysis. 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 species³ (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 aryltellurolate⁶ generated *in situ* from (RTe)₂^{7a} and NaBH₄. 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 NaBH₄ and various alkylating reagents (Me₂SO₄, EtBr and *i*-PrBr). Conjugate addition of sodium tellurolate, generated from **4**, to methyl propiolate gave (*E*)- and (*Z*)- α,β -unsaturated esters⁸ **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 (CH₂Cl₂, 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) (CH₂Cl₂, room temperature, 30 min). IR, ¹H NMR and ¹³C 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

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

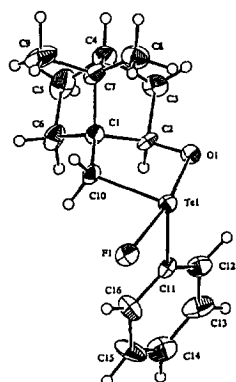
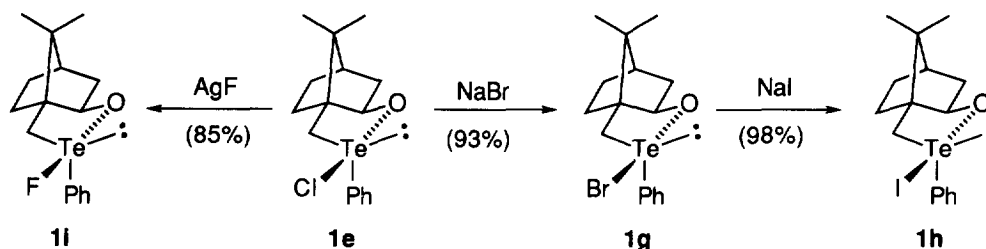
R	X	method (alkylating reagent)	yield of 3 (%)	yield of 1 (%)
Me	Cl	A	3a (65)	1a (95)
Me	Cl	B (Me ₂ SO ₄)	3a (—)	1a (24 ^a)
Et	Cl	A	3b (80)	1b (93)
Et	Cl	B (EtBr)	3b (—)	1b (62 ^a)
<i>i</i> -Pr	Cl	A	3c (95)	1c (97)
<i>i</i> -Pr	Cl	B (<i>i</i> -PrBr)	3c (—)	1c (35 ^a)
<i>n</i> -Hex	Cl	A	3d (90)	1d (95)
Ph	Cl	A	3e (78)	1e (96)
HC=CCO ₂ Me	Cl	B (HC≡CCO ₂ Me)	(<i>Z</i>)-3f (67) (<i>E</i>)-3f (11)	(<i>Z</i>)-1f (86) (<i>E</i>)-1f (97)
Ph	Br	A	3e (78)	1g (52)

^aYield from 4.

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

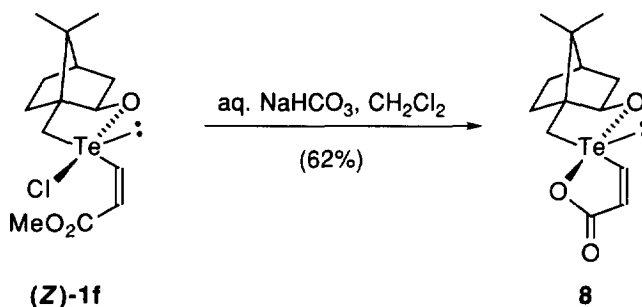
Formation of telluranes **5** might be unfavorable because of steric repulsion between 7-methyl group of bornyl moiety and carbon ligand, R group.

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 $\text{Te}-\text{Cl}$ 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.

Acknowledgement

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- Satisfactory analytical (combustion and high resolution mass) and spectral (IR, ¹H NMR, Mass) data were obtained for all new isolable compounds.
- 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 ¹H NMR spectrum of a crude reaction mixture.
- 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.
- Crystallographic data for **1i**: monoclinic, space group, P2₁ with *a* = 8.2316(6) Å, *b* = 7.582(1) Å, *c* = 12.6143(7) Å, β = 102.742(5)°, *V* = 767.9(1) Å³, 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* > 3.00σ(*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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- 8**: mp 146-147 °C; [α]_D²⁶ -263.6 (*c* 1.10, CHCl₃); IR (KBr) 1644 cm⁻¹ (C=O); ¹H NMR (CDCl₃) δ: 0.91 (s, 3H, CH₃), 1.02 (s, 3H, CH₃), 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.
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- (a) For stabilization of hypervalent species by a five membered ligand, see: Martin, J. C. *Science*, **1983**, *221*, 509-514. (b) We have developed this concept of steric protection into the first synthesis of optically pure selenuranes, see: Takahashi, T.; Kurose, N.; Kawanami, S.; Arai, Y.; Koizumi, T.; Shiro, M. *J. Org. Chem.*, **1994**, *59*, 3262-3264.

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