

First stereoselective synthesis of enantiomerically pure telluronium salts by the reaction of chiral halooxatelluranes with Grignard reagents

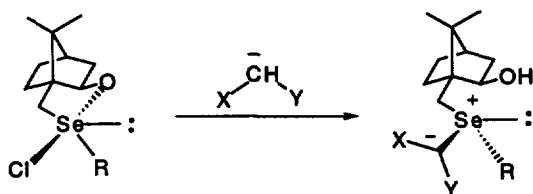
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Abstract: We prepared a series of enantiomerically pure benzyl and allyl telluronium salts **2** and **4**, using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand, in high yield and selectivity by the reaction of chiral haloalkoxytelluranes **1** and **3** with Grignard reagents. A sharp pyramidal structure with *S* absolute configuration at the tellurium atom was confirmed by an X-ray analysis of **2c**. © 1997 Published by Elsevier Science Ltd

Application of benzyl and allyl chalcogenonium salts in organic synthesis has attracted much attention over several decades. There are many examples of the application of sulfonium and selenonium salts, and recently some laboratories have reported their research on the reactions of telluronium analogues.^{1,2} Benzyl and allyl telluronium salts, which are precursors of telluronium ylides, react with carbonyl compounds on treatment with different bases to give secondary alcohols, alkenes, epoxides, and cyclopropanes.³ Many efforts have been made by several groups using racemic benzyl and allyl telluronium salts in this field. However, there is no report concerning the stereoselective synthesis of enantiomerically pure benzyl and allyl telluronium salts.

Very recently, Kamigata *et al.* reported their results on the synthesis of enantiomerically pure telluronium salts. They prepared chiral telluronium salts as optically stable compounds *via* resolution of the corresponding racemates by fractional recrystallization with a chiral anion followed by anion exchange.^{4c,d} During the study on the synthesis, reactions, and stereochemistry of chiral chalcogenuranes, we synthesized chiral halooxaselenuranes and halooxatelluranes in high yield and excellent selectivity by using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand.⁵ We have reported that the nucleophilic substitution reaction of the chloroselenuranes with active methylene compounds as carbon nucleophiles proceeded in a highly stereoselective manner with “retention of configuration” to give selenonium ylides as shown in Scheme 1.^{5b,6}



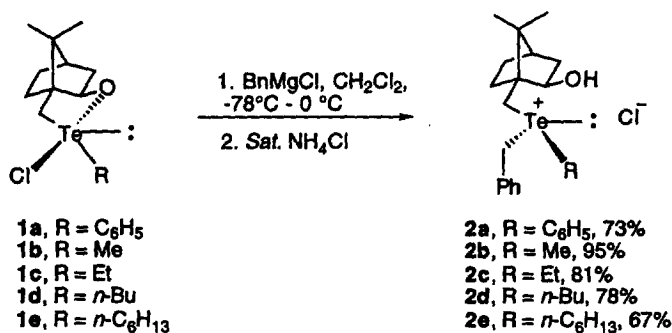
Scheme 1.

Herein, we report our results on the first stereoselective synthesis of enantiomerically pure benzyl and allyl telluronium salts by the reaction of chiral halooxatelluranes **1** and **3** with benzyl and

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allyl Grignard reagents, whose stereochemical outcome turned out to be, unexpectedly, “inversion of configuration” at the tellurium atom.⁶

Nucleophilic reaction of chiral chlorooxatellurane **1a**⁷ with 1.2 equiv. of benzylmagnesium chloride in CH₂Cl₂ (−78°C to 0°C) for *ca.* 2 h followed by the usual work-up gave telluronium chloride **2a** (73% yield) as a single diastereomer. The same reactions of benzylmagnesium chloride with telluranes **1b–e** were also performed and afforded telluronium salts **2b–e** as single diastereomers in good yield as shown in Scheme 2. The structures of these salts were determined by an X-ray crystallographic analysis of **2c**⁸ as shown in Figure 1, which indicated the reaction proceeded with “inversion of configuration” at the tellurium atom. Telluronium salt **2c** has a pyramidal geometrical structure with an *S* absolute configuration at the telluronium centre (Figure 1). Each bond distance of Te–C [2.16(1) Å, 2.13(2) Å, 2.15(1) Å] is of normal value, and the pyramidal geometry around the telluronium atom with an average value of C–Te–C angles of 89.8(7)° is even sharper than the reported ethylmethylphenyltelluronium salts.^{4c,d} Stereochemistry of other telluronium salts can be assigned as depicted by analogy with **2c** (¹H and ¹³C NMR spectra). No epimeric telluronium salt was detected in these reactions.



Scheme 2.

We also carried out reaction of telluranes **3** with allylmagnesium bromide.⁹ The bromotelluranes **3**^{5d} reacted with allylmagnesium bromide to give allyl telluronium salts **4** in moderate to good yield as single diastereomers after the usual workup (Scheme 3).¹⁰

Telluronium salts obtained here are optically and thermally stable, and no isomerization has been detected after standing the salts at room temperature for several weeks. It is noteworthy that the stereochemical result of this reaction is different from that of the reaction we previously reported (see Scheme 1). Thus, the reaction proceeded with “inversion of configuration”.

Although the detailed stereochemistry of the reaction is not clear at the present time, the reaction may proceed through the pathway as shown in Scheme 4. Initial chelation of Grignard reagents with

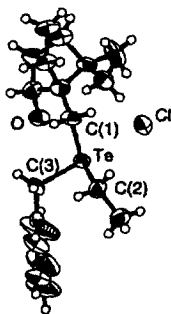
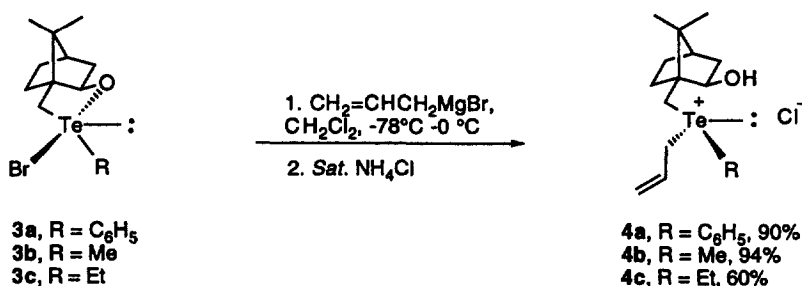
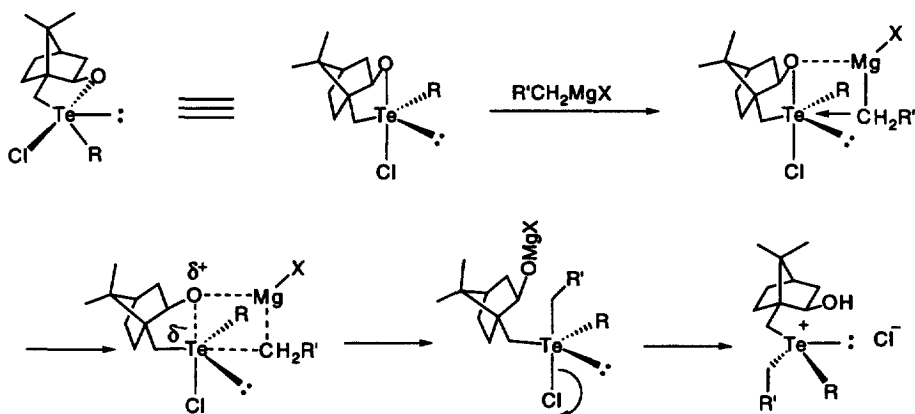


Figure 1.



Scheme 3.

the oxygen atom at the bornyl group made the oxygen less electronegative which induced the attack of the carbon anion from the direction as shown in Scheme 4. Cleavage of the Te–O bond followed by the dissociation of the Te–Cl bond afforded telluronium salts with “inversion of configuration” at the tellurium atom in high diastereoselectivity.



Scheme 4.

In conclusion, we developed a facile method for the synthesis of enantiomerically pure benzyl and allyl telluronium salts **2** and **4** using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand, by the reaction of chiral haloalkoxytelluranes **1** and **3** with Grignard reagent. This reaction has notable characteristics of high yield and excellent stereoselectivity. Furthermore, these enantiomerically pure telluronium salts are expected to be applied to asymmetric organic synthesis. The study on the synthesis of other chalcogenonium salts using this method are ongoing in our group.

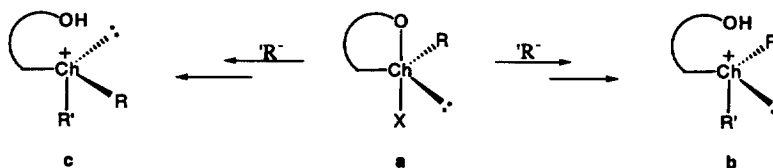
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- To express the stereochemical process of the reaction of chiral halooxachalcogenuranes with carbon anion clearly, we use the term “retention” as “the reaction of the halooxachalcogenurane (a) resulted in the formation of the chalcogenium compound (b)”. The formation of c is naturally considered as the “inversion” of configuration at the chalcogen atom.



- The structures as well as the absolute configuration at the telluronium centre of halooxatelluranes have been determined by X-ray crystallographic analysis.^{5d}
- Crystallographic data for **2c**: monoclinic, space group, C2 (#5) with $a=26.128(2)$ Å, $b=6.694(2)$ Å, $c=12.842(1)$ Å, $V=1998.1(6)$ Å³, and $Z=4$ ($d_{\text{calcd}}=1.451$ g cm⁻³), μ (MoK α)=16.23 cm⁻¹ absorption corrected by ω scans; 2479 unique reflections; 2056 with $I>3.00\sigma(I)$ were used in refinement; $R=6.1\%$, $R_w=7.9\%$. Selected bond lengths (Å) and angles (deg) are as follows: Te–C(1), 2.16(1); Te–C(2), 2.13(2); Te–C(3), 2.15(1); Te···O, 2.84(1); Te···Cl, 3.150(3); C(1)–Te–C(2), 93.5(7); C(1)–Te–C(3), 95.8(6); C(2)–Te–C(3), 80.1(7); Cl···Te···O, 87.8(3); Cl···Te–C(1), 90.9(4); Cl···Te–C(2), 110.7(5); Cl···Te–C(3), 167.0(5); O···Te–C(1), 69.4(6); O···Te–C(2), 155.4(6); O···Te–C(3), 84.1(5). Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, on quoting the full journal citation.

9. General procedure for the synthesis of telluronium salts: To a solution of tellurane (0.1 mmol) in CH_2Cl_2 (3 ml) was added a solution of RMgX (0.12 mmol, in THF or Et_2O) dropwise at -78°C under N_2 . The reaction mixture was stirred and allowed to warm up to 0°C during *ca.* 1 hr. Then the mixture was stirred at 0°C for 2 hr. The reaction mixture was worked up by addition of saturated aqueous NH_4Cl solution (2 ml), followed by extraction with CH_2Cl_2 (2×20 ml). The combined organic layer was washed with H_2O (1×4 ml) and brine (1×4 ml), dried over MgSO_4 , and then concentrated to dryness. Purification of the residue by recrystallization from hexane and CH_2Cl_2 afforded the product as a colorless crystal. Satisfactory analytical (combustion and high resolution mass) and spectral (IR, ^1H NMR, Mass) data were obtained for all new isolable compounds. Selected data for some compounds are as follows. **2c**: mp $145\text{--}146^\circ\text{C}$; $[\alpha]_{\text{D}}^{26} -93.30$ (c 2.30, CHCl_3); IR (KBr) 3204, 2943, 1627, 1454, 1073, 699 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 0.80 (s, 3H), 0.9–1.1 (m, 2H), 1.1 (s, 3H), 1.27–1.34 (m, 1H), 1.48 (t, 3H, $J=7.7$), 1.61–1.95 (m, 5H), 2.24 (d, 1H, $J=12.6$), 2.49 (d, 1H, $J=12.6$), 2.45–2.60 (m, 1H), 3.04–3.2 (m, 1H), 3.94 (dd, 1H, $J=3.3, 7.7$), 4.53 (d, 1H, $J=11.5$), 4.63 (d, 1H, $J=11.5$), 7.28–7.41 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ : 10.8, 20.7, 21.4, 22.9, 23.8, 27.3, 33.0, 34.5, 41.0, 45.6, 48.2, 50.1, 128.2, 129.0, 130.4, 132.6; Ms m/z : 374, 372, 370, 312, 310, 308, 250, 248, 246, 135, 91, 79, 67, 55; *Anal.* Calcd for $\text{C}_{19}\text{H}_{29}\text{ClOTe}$: C, 52.28; H, 6.70. Found: C, 52.05; H, 6.67. **4b**: mp $144\text{--}145^\circ\text{C}$; $[\alpha]_{\text{D}}^{26} -27.12$ (c 1.80, CHCl_3); IR (KBr) 3431, 2947, 1627, 1388, 1072 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 0.85 (s, 3H), 1.0–1.2 (m, 2H), 1.11 (s, 3H), 1.5–2.1 (m, 6H), 2.26 (s, 3H), 2.69 (d, 1H, $J=12.1$), 2.75 (d, 1H, $J=12.1$), 3.68–3.75 (m, 1H), 3.86–3.95 (m, 2H), 5.30–5.41 (m, 2H), 5.82–5.91 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ : 8.9, 20.8, 20.9, 25.3, 27.5, 30.5, 34.5, 40.7, 45.5, 48.4, 51.0, 77.1, 123.2, 128.3; Ms m/z : 324, 322, 320, 298, 296, 294, 265, 263, 261, 135, 107, 93, 79, 67, 55; *Anal.* Calcd for $\text{C}_{14}\text{H}_{25}\text{ClOTe}$: C, 45.15; H, 6.77. Found: C, 45.50; H, 6.73.
10. We confirmed that the absolute configuration of the compounds is not affected by work-up. Koizumi, T. *et al.*, unpublished results.

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