Synthesis and Absolute Configuration of Optically Active Telluronium Salts

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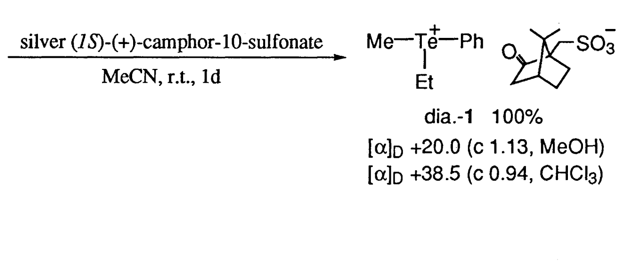
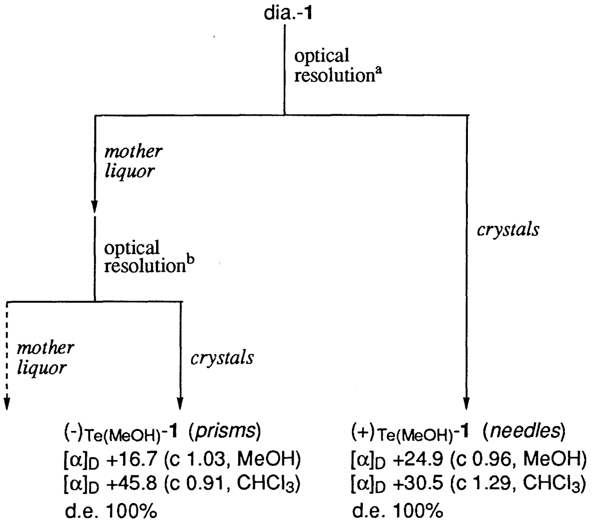
Enantiomerically pure ethylmethylphenyltelluronium salts were isolated by optical resolution from a diastereomeric mixture of ethylmethylphenyltelluronium (*1S*)-(+)-camphor-10-sulfonate and subsequent anion exchange reactions, and the absolute configurations were determined based on the X-ray crystallographic analysis of a diastereomeric isomer.

We have previously reported the synthesis and stereochemistry of optically active tricoordinate selenium compounds such as selenoxides,[1] selenonium imides,[2] selenonium ylides,[3] and selenonium salts.[4] Very recently, we also synthesized optically active telluronium ylides.[5] Telluronium salts are also tricoordinate tellurium compounds, and although two papers had been reported on the optically active telluronium salts several decades ago, and their optical purities and absolute configurations were unknown.[6,7] Since their reports, no paper has appeared maybe because it was described in the literatures that rapid racemization of the optically active telluronium salts took place in solution. We succeeded in isolating the diastereomerically and enantiomerically pure telluronium salts, in determining their absolute configurations based on the X-ray crystallographic analysis, and the stabilities for racemization were reexamined. Furthermore, optically active telluronium salts were found to show an interesting behavior on their specific rotations in solutions.

Diastereomeric mixture of ethylmethylphenyltelluronium (*1S*)-(+)-camphor-10-sulfonate (dia.-**1**) {mp 110-120 °C, $[\alpha]_D$ +20.0 (MeOH), $[\alpha]_D$ +38.5 ($CHCl_3$)} was synthesized by anion exchange reaction of the corresponding telluronium iodide prepared from methylphenyltelluride and a large excess amount of ethyl iodide (Scheme 1). Repeated recrystallization of dia.-**1** (8.6 g) from acetone-ether-hexane gave colorless needles of the optically pure telluronium salt isomer $(+)_{\mathrm{Te(MeOH)}}$-**1**[8] (1.1 g) {mp 145-146 °C, $[\alpha]_D$ +24.9 (MeOH)} (Figure 1). A small amount of another isomer $(-)_{\mathrm{Te(MeOH)}}$-**1** {mp 119-120 °C, $[\alpha]_D$ +16.7 (MeOH)} was also obtained as a diastereomerically pure form by recrystallization of the telluronium salt in the mother solution from acetone-ether. The optically active telluronium salt $(+)_{\mathrm{Te(MeOH)}}$-**1**, showing the positive specific rotation around the tellurium atom in methanol {$\Delta[\alpha]_D$ +4.9 (MeOH)},[9] indicated the negative sign of specific rotation caused by the chirality of the tellurium atom in chloroform {$\Delta[\alpha]_D$ -8.0 ($CHCl_3$)}. On the contrary, $(-)_{\mathrm{Te(MeOH)}}$-**1** showed the positive sign for the telluronium ion part in chloroform {$\Delta[\alpha]_D$ +7.3 ($CHCl_3$)}. This phenomenon was not observed in the case of the corresponding optically active sulfonium and selenonium salts.

Scheme 1.





[a]Recrystallization from acetone-ether-hexane
[b]Recrystallization from acetone-ether

Figure 1. Optical resolution of dia.-**1**.

The absolute configuration around the tellurium atom of $(+)_{\mathrm{Te(MeOH)}}$-**1** was determined to be *R*-form by the X-ray crystallographic analysis[10] based on the configuration of (*1S*)-(+)-camphor-10-sulfonate as an internal standard, shown in Figure 2. Therefore, that of $(-)_{\mathrm{Te(MeOH)}}$-**1** was assigned to be *S*-form. Bond lengths of the Te-C bonds are almost normal and the pyramidal geometry around the tellurium atom {C-Te-C: 95.2° (average)} is sharper than the normal tetrahedral geometry (109.5°). The distance between the tellurium atom and the closest oxygen atom of the sulfonate is 2.88 Å, which is remarkably longer than the sum of the covalent radii of tellurium and oxygen atoms (1.98 Å), truly indicating a salt structure and not hypervalent species.

Enantiomeric ethylmethylphenyltelluronium perchlorate (*R*)-(+)-**2** and tetrafluoroborate (*R*)-(+)-**3** were obtained by anion exchange reactions of (*R*)-$(+)_{\mathrm{Te(MeOH)}}$-**1** without loss of optical purities[11] (Scheme 2). The enantiomeric telluronium salts (*R*)-(+)-**2** and (*R*)-(+)-**3** showed the positive specific rotations both in methanol and chloroform, and change of the sign was not observed. The behavior of the specific rotations of the diastereomeric and enantiomeric telluronium salts in different solvents seems to depend on the solvation of the telluronium ion and the counter anion with solvents. Details are now under investigation.

Optically active telluronium salt (*R*)-(+)-**2** was found to be stable toward pyramidal inversion and no racemization was

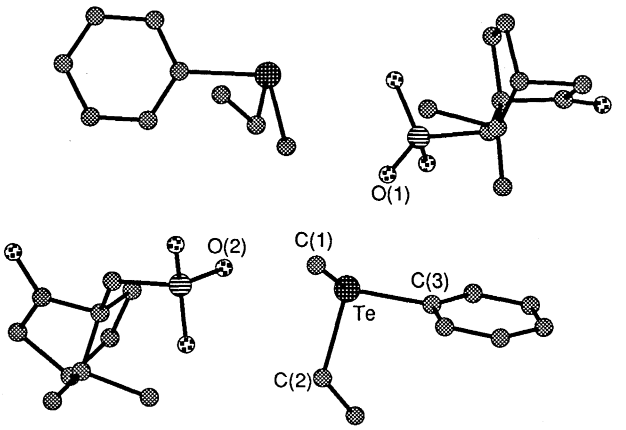
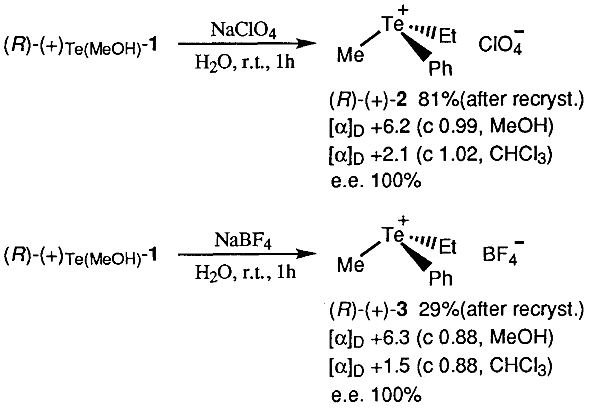


Figure 2. Crystal structure of (*R*)-(+)$_{Te(MeOH)}$-**1** (Hydrogen atoms are omitted). Selected bond distances (Å) and angles (°): Te-C(1) 2.128(10), Te-C(2) 2.173(10), Te-C(3) 2.117(8), Te-O(1) 2.88(1), Te-O(2) 3.05(1), C(1)-Te-C(2) 95.2(4), C(1)-Te-C(3) 96.6(4), C(2)-Te-C(3) 93.7(4).

Scheme 2.



(*R*)-(+)-**2** 81%(after recryst.)
$[\alpha]_D$ +6.2 (c 0.99, MeOH)
$[\alpha]_D$ +2.1 (c 1.02, $CHCl_3$)
e.e. 100%

(*R*)-(+)-**3** 29%(after recryst.)
$[\alpha]_D$ +6.3 (c 0.88, MeOH)
$[\alpha]_D$ +1.5 (c 0.88, $CHCl_3$)
e.e. 100%

observed in refluxing methanol for three days, whereas methylphenyl-*p*-tolyltelluronium salts[6] and 2-*p*-chlorophenacyltelluroisochromanium picrate[7] were reported to be optically unstable in solution even at room temperature. Furthermore, the pyramidal geometry of the telluronium salt was found to be more stable toward racemization than those of the sulfonium salts; optically active ethylmethylphenylsulfonium perchlorate was reported to racemize in methanol (50 °C: k = 2.88×10^{-5} sec^{-1}; 25 °C: k = 0.074×10^{-5} sec^{-1}).[12]

References and Notes

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8 (+)$_{Te(MeOH)}$ shows positive specific rotation around tellurium atom in methanol.
9 The values $\Delta[\alpha]_D$ show the differences between the $[\alpha]_D$ of the diastereomeric isomers and that of the diastereomeric mixture.
10 Crystal data for (*R*)-(+)$_{Te(MeOH)}$-**1**: Compound (*R*)-(+)$_{Te(MeOH)}$-**1** crystallized in the orthorhombic space group $P2_12_12_1$, with a = 11.767(3), b = 19.981(6), c = 8.826(4) Å, V = 2075(1) Å^3, Z = 4, and D_c = 1.54 g cm^{-3}. Data were collected on a Mac Science MXC18 four-circle diffractometer. Of the 2716 unique data collected with Mo-Kα radiation (λ = 0.7107 Å), the 2498 with $Fo > 3.0\sigma(Fo)$ were used in the least-squares refinement to yield R = 4.0%, R_w = 4.4%.
11 Optical purities were confirmed by measurements of ^{1}H-NMR spectra by using (*S*)-(-)-1,1'-bi-2-naphthol as an optically active shift reagent.
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