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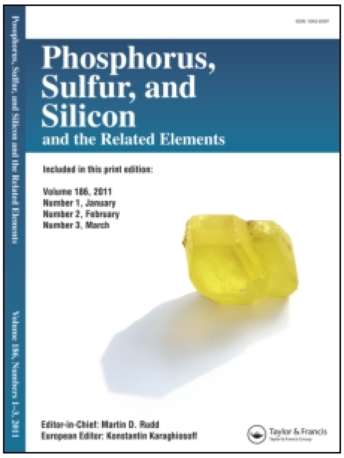

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Synthesis And Stereochemistry Of Optically Active Telluronium Salts

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SYNTHESIS AND STEREOCHEMISTRY OF OPTICALLY ACTIVE TELLURONIUM SALTS

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Enantiomerically pure telluronium salts (*R*)-**2**-**7** were isolated by optical resolution of a diastereomeric ethylmethylphenyltelluronium (*1S*)-(+)-camphor-10-sulfonate (dia.-**1**) followed by subsequent anion exchange reactions. Absolute configuration of the salts was determined based on X-ray crystallographic analysis. The optically active telluronium salts were found to show peculiar optical properties on their specific rotations and circular dichroism spectra in solutions.

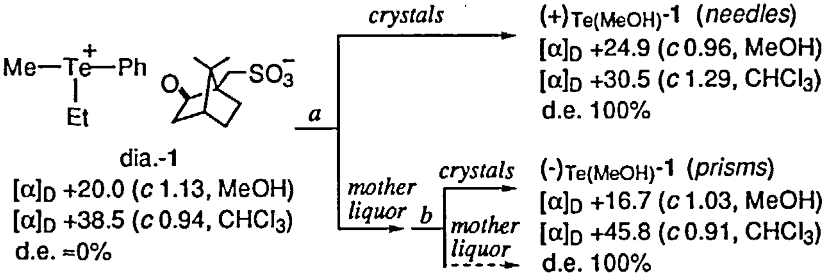
Keywords: telluronium salts, optically active compounds, stereochemistry, optical property, anion-cation interaction

INTRODUCTION

Only two papers had been reported on the optically active telluronium salts several decades ago, which optical purities and absolute configurations were unknown.[1,2] Since their reports, no paper has appeared maybe because it was described in the literatures that rapid racemization of the telluronium salts took place in solution. We succeeded in isolating the diastereomerically and enantiomerically pure telluronium salts and 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 and circular dichroism spectra in solutions, and anion-cation interaction in the crystalline state.[3]

RESULTS AND DISCUSSION

Repeated recrystallization of diastereomeric mixture of ethylmethylphenyltelluronium (*1S*)-(+)-camphor-10-sulfonate (dia.-**1**) (8.6 g) from acetone-ether-hexane gave colorless needles of the optically pure telluronium salt isomer (+)$_{\mathrm{Te(MeOH)}}$-**1** (1.1 g) (Scheme 1). A small amount of another isomer (-)$_{\mathrm{Te(MeOH)}}$-**1** was also obtained as a diastereomerically pure form by recrystallization of the telluronium salt in the mother solution from acetone-ether.

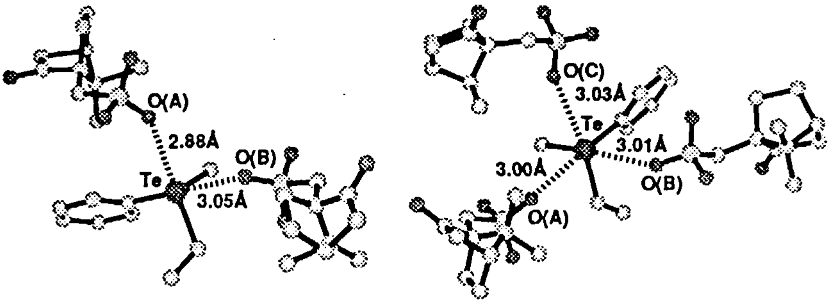


Scheme 1

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

Absolute configuration around the tellurium atom of (+)$_{\mathrm{Te(MeOH)}}$-**1** and (-)$_{\mathrm{Te(MeOH)}}$-**1** was determined to be *R*- and *S*-form, respectively, by the X-ray crystallographic analysis based on the configuration of (*1S*)-(+)-camphor-10-sulfonate as an internal standard, as shown in Figure 1. The tellurium atom of $(R)_{\mathrm{Te}}$-**1** interacts with two oxygen atoms in the crystalline state, and the three carbons and two oxygen atoms around the tellurium atom form a nearly square pyramidal geometry. On the other hand, crystal structure of the isomer $(S)_{\mathrm{Te}}$-**1** shows three interactions between the tellurium atom and the oxygen atoms, indicating octahedral geometry around the tellurium atom.

Enantiomerically pure (*R*)-ethylmethylphenyltelluronium perchlorate (*R*)-**2** was obtained in 81% yield by the anion exchange reaction of



$(R)_{Te}$-1 $(S)_{Te}$-1

FIGURE 1 Molecular structures of $(R)_{Te}$-1 and $(S)_{Te}$-1 showing anion-cation interactions with hydrogen atoms removed for clarity.

diastereomerically pure telluronium salt $(R)_{Te}$-1 with sodium perchlorate (Scheme 2). Optically pure (*R*)-ethylmethylphenyltelluronium tetrafluoroborate (*R*)-3, *p*-chlorobenzenesulfonate (*R*)-4, bornane-10-sulfonate (*R*)-5, tetraphenylborate (*R*)-6, and picrylsulfonate (*R*)-7 were also obtained by similar anion exchange reactions without loss of optical purities.

		$[\alpha]_D$ in MeOH	$[\alpha]_D$ in $CHCl_3$
(*R*)-2:	X = ClO_4	+6.2	+2.1
(*R*)-3:	X = BF_4	+6.3	+1.5
(*R*)-4:	X = *p*-$ClC_6H_4SO_3$	+5.7	-3.3
(*R*)-5:	X = 	+5.1	-6.6
(*R*)-6:	X = BPh_4	—	—
(*R*)-7:	X = $(NO_2)_3C_6H_2SO_3$	—	—

Scheme 2

Optically active telluronium perchlorate (*R*)-2 was found to be stable toward pyramidal inversion and no racemization was observed in refluxing methanol after three days, whereas methylphenyl-*p*-tolyltelluronium salts[1] and 2-*p*-chlorophenacyltelluroisochromanium picrate[2] were reported to be unstable toward racemization in solution even at room temperature. The pyramidal geometry of the telluronium salt (*R*)-2 was more stable toward racemization than that of the sulfonium salts; optically active ethylmethylphenylsulfonium perchlorate was reported to racemize in methanol even at room temperature (50 °C: $k = 2.88 \times 10^{-5}\ s^{-1}$; 25 °C: $k = 0.074 \times 10^{-5}\ s^{-1}$).[4] Telluronium salt (*R*)-**2** was also found to decompose in preference to racemization in methanol at 85 °C in a degassed sealed tube.

Optically pure telluronium salt $(R)_{Te}$-$(+)_{Te(MeOH)}$-**1**, showing dextrorotatory around the tellurium atom in methanol {$\Delta[\alpha]_D$ +4.9 (MeOH)}, indicated levorotatory in chloroform {$\Delta[\alpha]_D$ -8.0 ($CHCl_3$)}. The salt $(R)_{Te}$-**1** also showed dextrorotatory around the tellurium atom in other polar solvents such as ethanol, acetonitrile, and acetone ($\Delta[\alpha]_D$ +4.5, +1.9, and +1.6; respectively), and showed levorotatory in the less polar solvent, dichloromethane ($\Delta[\alpha]_D$ -6.7). The magnitude and direction of $\Delta[\alpha]_D$ of $(R)_{Te}$-**1** correspond to dielectric constants of the solvents used in measurements, except acetonitrile. To the contrary, $(S)_{Te}$-$(-)_{Te(MeOH)}$-**1** showed dextrorotatory around the tellurium atom in chloroform {$\Delta[\alpha]_D$ +7.3 ($CHCl_3$)}. This phenomenon was not observed in the cases of the corresponding sulfonium and selenonium salts. Enantiomerically pure telluronium salts (*R*)-**2**, (*R*)-**3**, (*R*)-**4**, and (*R*)-**5** showed dextrorotatory in methanol. However, in chloroform, the salts (*R*)-**4** and (*R*)-**5** showed levorotatory, whereas the salts (*R*)-**2** and (*R*)-**3** showed dextrorotatory. The values of specific rotation of (*R*)-**5** were found to change smoothly according to the concentration of methanol in mixed solvents (methanol/chloroform) {MeOH (0%): $[\alpha]_D$ -6.6 (*c* 1.0) ~ MeOH (100%): $[\alpha]_D$ +5.1 (*c* 1.0)}. Similar phenomenon was also observed on their circular dichroism spectra.

The characteristic optical behavior of the telluronium salts is considered to be caused by the strong solvation in polar solvents.

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