8032 *J. Org. Chem.* **1996,** *61,* 8032−8038

Syntheses and Peculiar Behavior in Solutions of Optically Active Telluronium Salts

Toshio Shimizu, Tomonari Urakubo, and Nobumasa Kamigata*

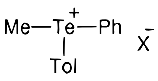
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Minami-ohsawa,
Hachioji, Tokyo 192-03, Japan

Received April 29, 1996⊗

A diastereomeric (epimeric) mixture of ethylmethylphenyltelluronium (1*S*)-(+)-camphor-10-sulfonate (dia.-**1**) was optically resolved by fractional recrystallization into the diastereomerically pure isomers $(R)_{\mathrm{Te}}$-**1** and $(S)_{\mathrm{Te}}$-**1**. The absolute configurations of the isomers were determined by the X-ray crystallographic analysis of $(R)_{\mathrm{Te}}$-**1**. Enantiomerically pure (*R*)-ethylmethylphenyltelluronium perchlorate, tetrafluoroborate, *p*-chlorobenzenesulfonate, bornane-10-sulfonate, tetraphenylborate, and picrylsulfonate (*R*)-**2**−**7** were isolated, respectively, by anion-exchange reactions of diastereomerically pure $(R)_{\mathrm{Te}}$-**1**. The optically active telluronium salts were found to show peculiar optical properties on their specific rotations and circular dichroism spectra in solutions compared with those of the corresponding sulfonium and selenonium salts. On the basis of NMR studies, the behavior on the optical properties of the optically active telluronium salts was found to be caused by a strong solvation in polar solvents.

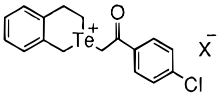
Introduction

Many optically active tricoordinate organic sulfur compounds have been synthesized and their properties and reactivities widely studied.[1−5] On the other hand, there are only a few reports on the synthesis and characterization of optically active tricoordinate selenium and tellurium compounds. The organic selenium and tellurium compounds can be also synthesized in optically pure form since selenium and tellurium are elements homologous with sulfur, and it is well known that many organoselenium and organotellurium compounds have structures similar to those of the corresponding sulfur compounds. Our recent interest has focused on the synthesis and stereochemistry of optically active tricoordinate chalcogen compounds. We have already reported the synthesis and stereochemistry of optically active selenonium salts,[6] selenonium ylides,[7] selenonium imides,[8] and selenoxides.[9] More recently, we have succeeded in resolving the optically active telluronium ylides.[10] Telluronium salts are also tricoordinate tellurium compounds; however, only two papers concerning optically active telluronium salts **I** and **II** were reported several decades ago and the optical purities and the absolute configurations of these compounds remained unknown.[11,12] We reported the isolation of the optically pure diastereomeric and enantiomeric telluronium salts **III** as a preliminary communication, and the absolute configurations were determined by the X-ray crystallographic analysis of one diastereomeric isomer.[13] Now, we report a full account of characteristics of specific rotations and circular dichroism spectra of the optically active telluronium salts, which are not observed on the corresponding optically active sulfonium and selenonium salts.

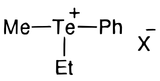


$\underset{\mathrm{Tol}}{\mathrm{Me{-}\overset{+}{Te}{-}Ph}}\ \ \bar{X}$

I



II



$\underset{\mathrm{Et}}{\mathrm{Me{-}\overset{+}{Te}{-}Ph}}\ \ \bar{X}$

III

Results and Discussion

Optical Resolution and Absolute Configuration of Diastereomeric Telluronium Salt. A diastereomeric mixture of ethylmethylphenyltelluronium (1*S*)-(+)-camphor-10-sulfonate (dia.-**1**), prepared from the corresponding telluronium iodide and silver (1*S*)-(+)-camphor-10-sulfonate, was optically resolved by repeated recrystallization from acetone−ether−hexane to give diastereomerically pure telluronium salt isomer $(+)_{\mathrm{Te(MeOH)}}$-**1**[14] as colorless needles (Scheme 1). A small amount of another isomer $(-)_{\mathrm{Te(MeOH)}}$-**1** was also obtained in a diastereomerically pure form by recrystalliza-

---

⊗ Abstract published in *Advance ACS Abstracts*, October 15, 1996.

[1] *The Chemistry of the Sulfonium Group*; Stirling, C. J. M., Patai, S., Eds.; Wiley: New York, 1981.

[2] Andersen, K. K.; Caret, R. L.; Ladd, D. L. *J. Org. Chem.* **1976**, *41*, 3096.

[3] (a) Campbell, S. J.; Darwish, D. *Can. J. Chem.* **1974**, *52*, 2953. (b) Moriyama, M.; Oae, S.; Numata, T.; Furukawa, N. *Chem. Ind. (London)* **1976**, 163.

[4] (a) Day, J.; Cram, D. J. *J. Am. Chem. Soc.* **1965**, ***87***, 4398. (b) Moriyama, M.; Yoshimura, T.; Furukawa, N.; Numata, T.; Oae, S. *Tetrahedron* **1976**, *32*, 3003.

[5] (a) Andersen, K. K.; Folly, J. W.; Perkins, T. I.; Gaffield, W.; Papanikolau, N. E. *J. Am. Chem. Soc.* **1964**, *86*, 5637. (b) Mislow, K.; Green, M. M.; Laur, P.; Melillo, J. T.; Simmons, T.; Ternary, A. L., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 1958. (c) Zhao, S.; Samuel, O.; Kagan, H. B. *Tetrahedron* **1987**, *43*, 5135.

[6] Kobayashi, M.; Koyabu, K.; Shimizu, T.; Umemura, K.; Matsuyama, H. *Chem. Lett.* **1986**, 2117.

[7] (a) Kamigata, N.; Nakamura, Y.; Matsuyama, H.; Shimizu, T. *Chem. Lett.* **1991**, 249. (b) Kamigata, N.; Nakamura, Y.; Kikuchi, K.; Ikemoto, I.; Shimizu, T.; Matsuyama, H. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1721. (c) Shimizu, T.; Matsuhisa, A.; Kamigata, N.; Ikuta, S. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1805.

[8] (a) Kamigata, N.; Taka, H.; Matsuhisa, A.; Matsuyama, H.; Shimizu, T. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2257. (b) Shimizu, T.; Seki, N.; Taka, H.; Kamigata, N. *J. Org. Chem.* **1996**, *61*, 6013.

[9] (a) Kamigata, N.; Shimizu, T. In *Reviews on Heteroatom Chemistry*; Oae, S., Ed.; Myu: Tokyo, 1991; Vol. 4, p 226 and references cited therein. (b) Shimizu, T.; Kobayashi, M. *Chem. Lett.* **1986**, 161. (c) Shimizu, T.; Kikuchi, K.; Ishikawa, Y.; Ikemoto, I.; Kobayashi, M.; Kamigata, N. *J. Chem. Soc., Perkin Trans. 1* **1989**, 597.

[10] Kamigata, N.; Matsuhisa, A.; Taka, H.; Shimizu, T. *J. Chem. Soc., Perkin Trans. 1* **1995**, 821.

[11] Lowry, T. M.; Gilbert, F. L. *J. Chem. Soc.* **1929**, 2867.

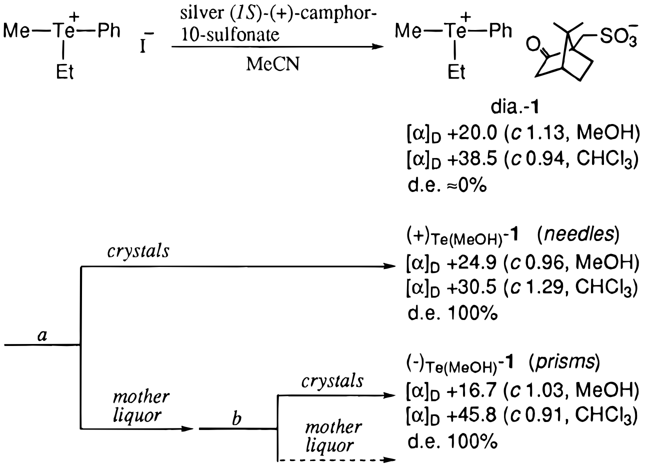
[12] Holliman, F. G.; Mann, F. G. *J. Chem. Soc.* **1945**, 37.

[13] Shimizu, T.; Urakubo, T.; Kamigata, N. *Chem. Lett.* **1996**, 297.

[14] The symbol, $(+)_{\mathrm{Te(MeOH)}}$, indicates positive specific rotation around the tellurium atom in methanol.

S0022-3263(96)00785-2 CCC: $12.00

Scheme 1[a]



[a] Key: (a) Recrystallization from acetone−ether−hexane. (b) Recrystallization from acetone−ether.

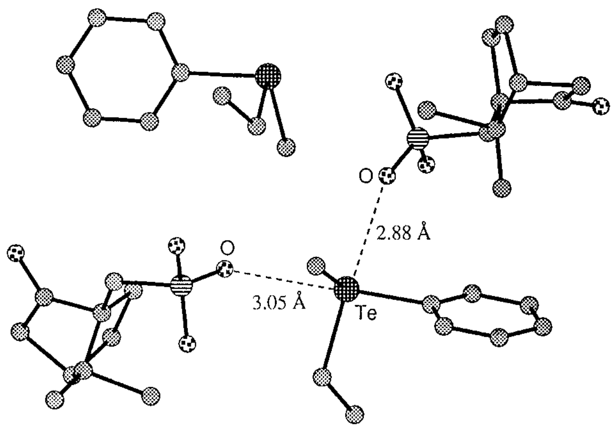
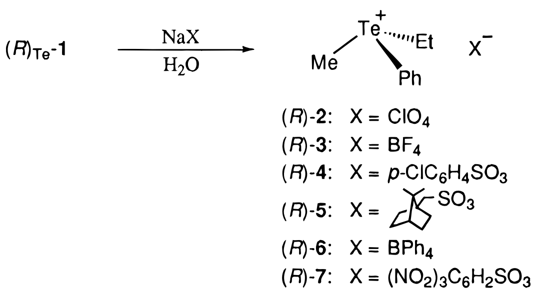


Figure 1. Crystal structure of $(R)_{\mathrm{Te}}$-$(+)_{\mathrm{Te(MeOH)}}$-**1**.[13] Hydrogens are removed for clarity.

tion from acetone−ether, of the telluronium salt remaining in the first mother solution. Optical purities of $(+)_{\mathrm{Te(MeOH)}}$-**1** and $(-)_{\mathrm{Te(MeOH)}}$-**1** were confirmed by comparison of ^{1}H-NMR spectra of the optical isomers with that of the diastereomeric mixture (dia.-**1**) in $CDCl_3$. Each optical isomer showed only one singlet signal ($(+)_{\mathrm{Te(MeOH)}}$-**1**: 2.69 ppm, $(-)_{\mathrm{Te(MeOH)}}$-**1**: 2.66 ppm) for the methyl group bonded to the tellurium atom on the ^{1}H-NMR spectrum, whereas two singlet signals were observed in almost equal intensity for the corresponding methyl groups of dia.-**1**. Furthermore, the methyl moiety in the ethyl group of each optically pure isomer showed one triplet signal ($(+)_{\mathrm{Te(MeOH)}}$-**1**: 1.45 ppm, 7.57 Hz; $(-)_{\mathrm{Te(MeOH)}}$-**1**: 1.47 ppm, 7.82 Hz), while the spectrum of dia.-**1** showed two sets of triplet signals corresponding to those of two optical isomers in $CDCl_3$.

Absolute configuration around the tellurium atom of $(+)_{\mathrm{Te(MeOH)}}$-**1** was determined to be the *R*-form by the X-ray crystallographic analysis based on the known configuration of (1*S*)-(+)-camphor-10-sulfonate as an internal standard (Figure 1).[13] Therefore, the configuration of $(-)_{\mathrm{Te(MeOH)}}$-**1** was assigned to be *S* around the tellurium atom. The tellurium atom of $(R)_{\mathrm{Te}}$-$(+)_{\mathrm{Te(MeOH)}}$-**1** was also found to interact with two oxygen atoms of the two sulfonate anions in the crystalline state, and the distances between the tellurium atom and the oxygen atoms were 2.88 and 3.05 Å, respectively.

Scheme 2



Transformation of Diastereomeric Telluronium Salts into Enantiomeric Telluronium Salts. Enantiomerically active (*R*)-ethylmethylphenyltelluronium perchlorate (*R*)-**2** was obtained in 81% yield by the anion-exchange reaction of diastereomerically pure telluronium salt $(R)_{\mathrm{Te}}$-**1** with sodium perchlorate (Scheme 2). The optical purity of (*R*)-**2** was determined to be 100% ee on the basis of the measurement of the ^{1}H-NMR spectrum by using (*S*)-(−)-1,1′-bi-2-naphthol as an optically active shift reagent. Optically active (*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 of optically pure $(R)_{\mathrm{Te}}$-**1** without loss of optical purities. Another enantiomeric isomer (*S*)-**2** was also obtained in 57% ee from the partially resolved $(S)_{\mathrm{Te}}$-**1**.

Thermal Stability of Optically Active Telluronium Salt. Optically active telluronium perchlorate (*R*)-**2** was found to be stable toward pyramidal inversion, and no racemization was observed in refluxing methanol after 3 days, whereas methylphenyl-*p*-tolyltelluronium salts[11] and 2-(*p*-chlorophenacyl)telluroisochromanium picrate[12] were reported to be unstable toward racemization in solution even at room temperature. Optically active telluronium salt (*R*)-**2** was also found to decompose in preference to racemization in methanol at 85 °C in a degassed sealed tube. The pyramidal geometry of the telluronium salt (*R*)-**2** was found to be 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}).[15]

Specific Rotations of Optically Active Telluronium Salts. Optically pure telluronium salt $(R)_{\mathrm{Te}}$-$(+)_{\mathrm{Te(MeOH)}}$-**1**, which was shown to dextrorotatory around the tellurium atom in methanol ($\Delta[\alpha]_D$ +4.9 (MeOH)),[16] was indicated to be levorotatory due to the chirality of the tellurium atom in chloroform ($\Delta[\alpha]_D$ −8.0 ($CHCl_3$)) (Table 1). The salt $(R)_{\mathrm{Te}}$-$(+)_{\mathrm{Te(MeOH)}}$-**1** was shown to be 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 levorotatory in the less polar solvent, dichloromethane ($\Delta[\alpha]_D$ −6.7). The magnitude and direction of $\Delta[\alpha]_D$ of **1** correspond to dielectric constants of the solvents used in measurements, except acetonitrile. On the contrary, $(S)_{\mathrm{Te}}$-$(-)_{\mathrm{Te(MeOH)}}$-**1** was shown to be 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 optically active sulfonium and selenonium

---

(15) Darwish, D.; Scott, C. E. *Can. J. Chem.* **1973**, *51*, 3647.

(16) The values $\Delta[\alpha]_D$ show the differences between the $[\alpha]_D$ of the diastereomeric isomers and that of the 1:1 diastereomeric mixture.

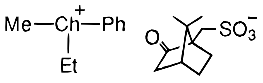
Table 1. Specific Rotations of Diastereomeric Chalcogen Onium Salts 8, 9, and 1

	$[\alpha]_D$				
chalcogen onium salt	*S*-form (de 100%)	$\Delta[\alpha]_D$	dia.-mix (de ≈ 0%)	$\Delta[\alpha]_D$	*R*-form (de 100%)
sulfonium salt **8**	+42.4 (*c* 1.03, MeOH) +65.4 (*c* 1.03, $CHCl_3$)	$\xleftarrow{+20.6}$ $\xleftarrow{+36.7}$	+21.8 (*c* 1.40, MeOH) +28.7 (*c* 1.15, $CHCl_3$)		
selenonium salt **9**			+23.2 (*c* 0.94, MeOH) +33.7 (*c* 1.11, $CHCl_3$)	$\xrightarrow{-10.3}$ $\xrightarrow{-27.1}$	+12.9 (*c* 0.97, MeOH) +6.6 (*c* 1.07, $CHCl_3$)
telluronium salt **1**	+16.7 (*c* 1.03, MeOH)	$\xleftarrow{-3.3}$	+20.0 (*c* 1.13, MeOH)	$\xrightarrow{+4.9}$	+24.9 (*c* 0.96, MeOH)
			+23.5 (*c* 1.04, EtOH)	$\xrightarrow{+4.5}$	+28.0 (*c* 1.23, EtOH)
			+26.6 (*c* 1.08, MeCN)	$\xrightarrow{+1.9}$	+28.5 (*c* 1.01, MeCN)
			+30.1 (*c* 1.29, acetone)	$\xrightarrow{+1.6}$	+31.7 (*c* 0.97, acetone)
			+34.4 (*c*, 1.12, CH_2Cl_2)	$\xrightarrow{-6.7}$	+27.7 (*c* 0.89, CH_2Cl_2)
	+45.8 (*c* 0.91, $CHCl_3$)	$\xleftarrow{+7.3}$	+38.5 (*c* 0.94, $CHCl_3$)	$\xrightarrow{-8.0}$	+30.5 (*c* 1.29, $CHCl_3$)

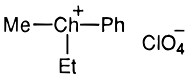
Table 2. Specific Rotations of Enantiomerically Pure Telluronium Salts (*R*)-2-5

	$[\alpha]_D$	
telluronium salt	in MeOH	in $CHCl_3$
(*R*)-**2**	+6.2 (*c* 0.99)	+2.1 (*c* 1.02)
(*R*)-**3**	+6.3 (*c* 0.88)	+1.5 (*c* 0.88)
(*R*)-**4**	+5.7 (*c* 0.99)	−3.3 (*c* 0.99)
(*R*)-**5**	+5.1 (*c* 0.97)	−6.6 (*c* 0.97)

salts **8**[17] and **9**,[6] where the *R*-isomers were shown to be levorotatory and the *S*-isomers were shown to be dextrorotatory around the chalcogen atoms in both methanol and chloroform. Therefore, the behavior on specific rotations of the telluronium salt **1** in polar solvents is found to be unusual among the chalcogen onium salts **8**, **9**, and **1**. Enantiomerically pure telluronium salts (*R*)-**2**, (*R*)-**3**, (*R*)-**4**, and (*R*)-**5** were shown to be dextrorotatory in methanol (Table 2). However, in chloroform, the salts (*R*)-**4** and (*R*)-**5** were shown to be levorotatory, whereas the salts (*R*)-**2** and (*R*)-**3** were shown to be dextrorotatory. The telluronium salts (*R*)-**6** and (*R*)-**7** were also shown to be dextrorotatory in acetone (+5.07 (*c* 0.80) and +5.44 (*c* 0.84), respectively), though the specific rotations of telluronium salts (*R*)-**6** and (*R*)-**7** could not be obtained in methanol and chloroform since these compounds were insoluble in both solvents of sufficient concentration to allow measurement. The values of specific rotations of (*R*)-**5** were found to change smoothly according to the concentration of methanol in mixed solvents (methanol/chloroform) as shown in Figure 2.



8: Ch = S
9: Ch = Se



10: Ch = S
11: Ch = Se

These novel observations concerning the specific rotations of the optically active telluronium salts can be explained as follows. Sulfonium and selenonium salts **8** and **9** show the specific rotations around the chalcogen atoms in the form with strong interaction of the chalcogen onium ions and the counteranions in both methanol and chloroform. Telluronium salts **1**, **4**, and **5**, possessing sulfonate moieties in the counteranions, also have interaction of the telluronium ions and the counteranions in chloroform. Therefore, optically active chalcogen onium salts **8**, **9**, **1**, **4**, and **5** with *R*-configurations show the same sign (negative) of specific rotation around the chalcogen atoms in chloroform. However, telluronium ions and the counteranions of $(R)_{Te}$-**1**, (*R*)-**4**, and (*R*)-**5** are solvated in methanol, and the specific rotations (positive) are influenced by the telluronium ion without strong interaction with the counteranions. Optically active telluronium salts (*R*)-**2** and (*R*)-**3** were shown to be dextrorotatory both in methanol and chloroform. This result is understandable in view of the fact that solvation of the cations and anions takes place even in chloroform. The size of the counteranions in the telluronium salts **2** and **3** is considered to be one reason for the facility of the solvation.

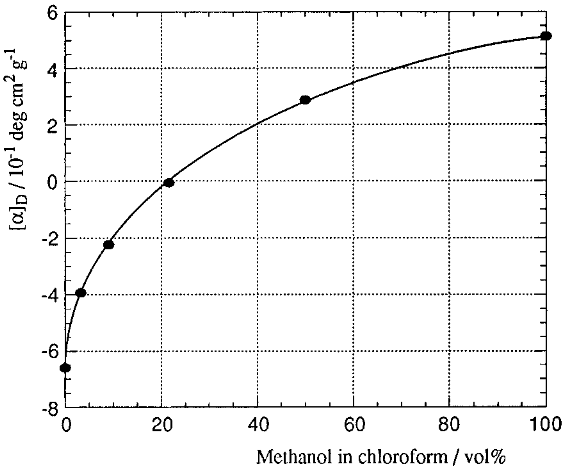


Figure 2. Solvent dependence of specific rotations of (*R*)-**5** in mixed solvents. Concentrations *c* are nearly 1.0.

Optically active telluronium perchlorate (*S*)-**2** (57% ee) was shown to be levorotatory in acetone ($[\alpha]_D$ −5.60 (*c* 1.03)), while the corresponding (*S*)-sulfonium and (*S*)-selenonium perchlorates (*S*)-**10**[17] and (*S*)-**11**[6] were indicated to be dextrorotatory in the same solvent ($[\alpha]_D$ +20.3 and +12.3, respectively). This result is also consistent with the above explanation. Furthermore, specific rotations of (*R*)-**5** were found to be strongly influenced by the concentration of the substrate in chloroform, shown in Figure 3, and the specific rotations inclined to positive direction in high concentration, whereas the specific rotations of (*R*)-**5** did not change in methanol in the range of similar concentrations.

Circular Dichroism Spectra of Optically Active Telluronium Salts. Diastereomerically pure telluronium salt $(R)_{Te}$-**1** showed positive first Cotton effect at 293 nm, positive second Cotton effect (shoulder) in the region of ca. 260−270 nm, and also positive third Cotton effect at the shorter wavelength on the circular dichroism

---

[17] (a) Kobayashi, M.; Umemura, K.; Watanabe, N.; Matsuyama, H. *Chem. Lett.* **1985**, 1067. (b) Umemura, K.; Matsuyama, H.; Watanabe, N.; Kobayashi, M.; Kamigata, N. *J. Org. Chem.* **1989**, *54*, 2374.

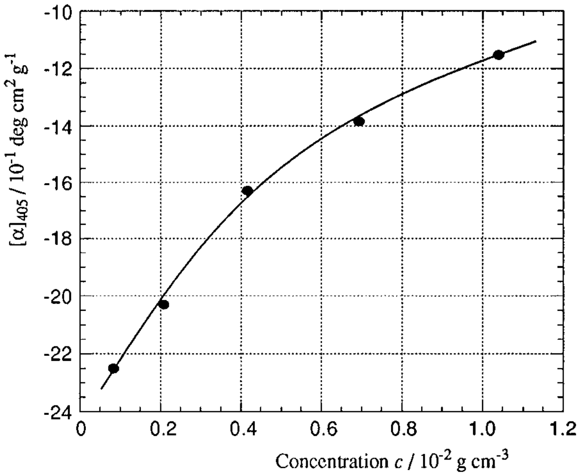


Figure 3. Concentration dependence of specific rotations of (*R*)-**5** in chloroform.

spectrum in methanol (Figure 4a). The salt $(R)_{Te}$-**1** also showed a positive first Cotton effect in chloroform. The telluronium salt $(S)_{Te}$-**1** showed a similar positive Cotton effect at 292 nm in methanol, but the corresponding second and third Cotton effects were negative. Therefore, the observed first Cotton effects for $(R)_{Te}$-**1** and $(S)_{Te}$-**1** at 293 and 292 nm are found to be caused by the common (*1S*)-(+)-camphor-10-sulfonate, and the second and third Cotton effects may be caused by the chiralities on the tellurium atoms. Enantiomerically pure telluronium perchlorate (*R*)-**2** showed positive Cotton effects in the region of 250−270 nm (benzenoid transition) and at 229 nm in methanol similar to that of $(R)_{Te}$-**1**, and (*S*)-**2** showed a symmetrical spectrum to that of (*R*)-**2** as shown in Figure 4b. The corresponding optically active sulfonium and selenonium perchlorates with *S*-configurations (*S*)-**10** and (*S*)-**11** showed negative Cotton effects in the region of 245−275 nm similar to those of (*S*)-**2**. However, the Cotton effects of (*S*)-**10** and (*S*)-**11** at the shorter wavelengths (around 220 nm) were positive, whereas the (*S*)-**2** showed negative Cotton effect in the same region. The behavior of the optically active telluronium salts on the circular dichroism spectra is peculiar compared with that of the sulfonium and selenonium salts and consistent with the explanation for the behavior on specific rotations of the chalcogen onium salts. Enantiomerically pure telluronium salts with *R*-configurations (*R*)-**3**, (*R*)-**4**, (*R*)-**5**, and (*R*)-**7** showed circular dichroism spectra similar to those of (*R*)-**2** as shown in Figure 4c. Moreover, the CD spectrum of (*R*)-**5** in chloroform was similar to that in methanol, while (*R*)-**5** showed different signs of the specific rotation in chloroform and methanol.

NMR Studies of Chalcogen Onium Salts. ^{1}H-NMR spectra of ethylmethylphenyl-sulfonium, -selenonium, and -telluronium perchlorates **10**, **11**, and **2** were compared in $CDCl_3$. The singlet signals of methyl protons neighboring the chalcogen atoms of the sulfonium and selenonium salts **10** and **11** were observed in a closed region (3.35 and 3.17 ppm, respectively) as shown in Figure 5 a. However, the singlet signal of the methyl protons for the telluronium salt **2** was observed at higher field (2.65 ppm). Methylene protons of **2** were also observed at higher field (3.29 ppm) than those of **10** and **11** (3.79 and 3.74 ppm, respectively). This result can be explained by the electronegativities of sulfur, selenium, and tellurium atoms (2.5, 2.4, and 2.1, respectively (Pauling)); i.e, the tellurium atom withdraws an electron from the neighboring carbon atoms more weakly than sulfur and selenium. The ^{13}C-NMR spectra of **10**, **11**, and **2** also showed a similar tendency in $CDCl_3$ (Figure 5b).[18]

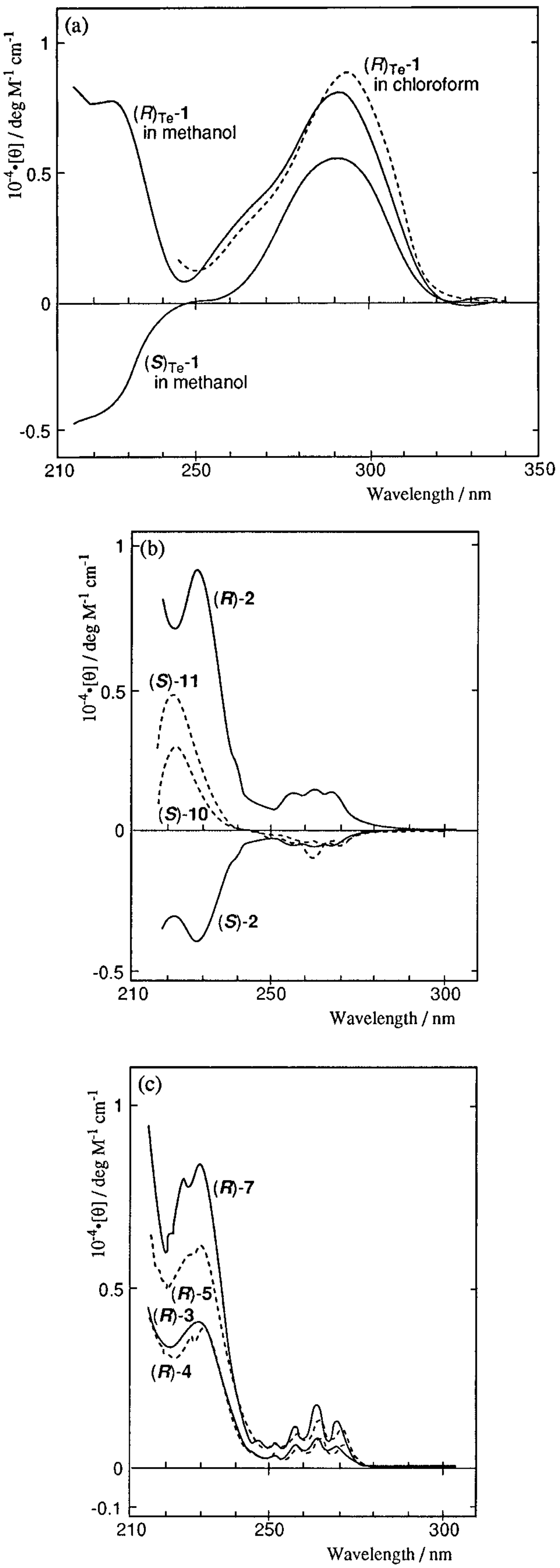


Figure 4. Circular dichroism spectra of (a) ethylmethylphenyltelluronium (*1S*)-(+)-camphor-10-sulfonates **1**; (b) ethylmethylphenylchalcogen-onium perchlorates **2**, **10**,[17] and **11**[6] in methanol; and (c) ethylmethylphenyltelluronium salts **3**, **4**, **5**, and **7** in methanol.

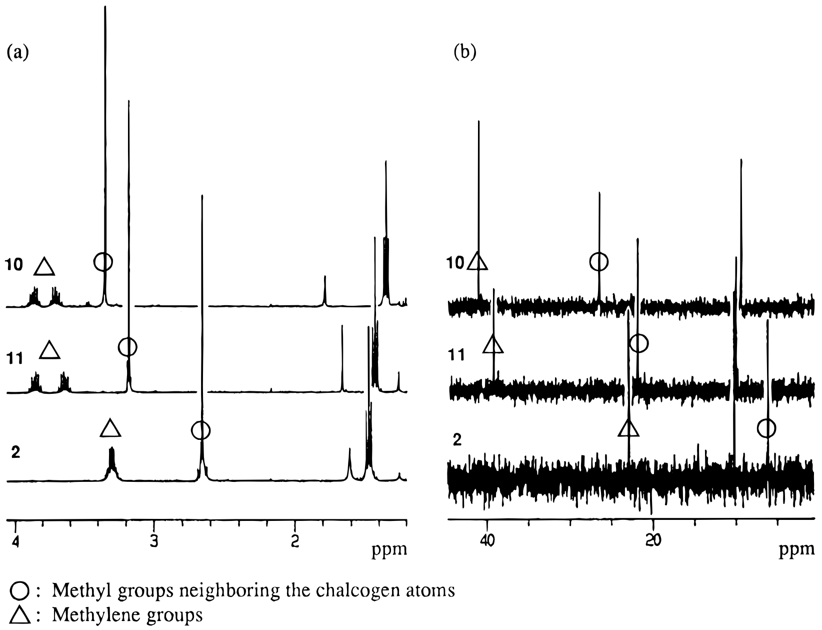


Figure 5. (a) ^{1}H-NMR spectra of ethylmethylphenylchalcogen-onium perchlorates **10**, **11**, and **2** in CDCl$_3$. (b) ^{13}C-NMR spectra of ethylmethylphenylchalcogen-onium perchlorates **10**, **11**, and **2** in CDCl$_3$.

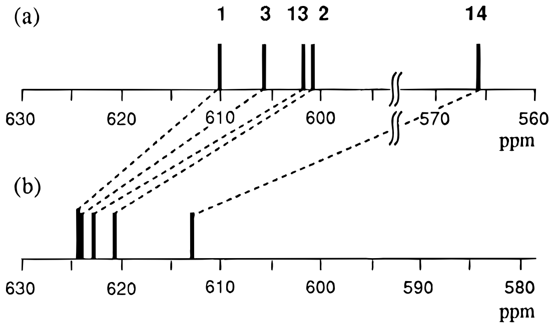


Figure 6. ^{125}Te-NMR spectra of ethylmethylphenyltelluronium salts **1**, **2**, **3**, **13**, and **14** (a) in CDCl$_3$ and (b) in CD$_3$OD.

The singlet signals (2.68 and 2.70 ppm) of diastereomeric mixture of **1** were observed separately on the ^{1}H-NMR spectrum in CDCl$_3$ and are assigned to methyl groups adjacent to the telluronium atoms of two diastereomeric isomers, while no separation was observed in CD$_3$OD. This result indicates that strong cation−anion interaction exists in the weak polar solvent (CDCl$_3$), and the interaction is inhibited in the polar solvent (CD$_3$OD) by the solvation.

The ^{125}Te-NMR spectra of ethylmethylphenyltelluronium (*1S*)-(+)-camphor-10-sulfonate, perchlorate, tetrafluoroborate, trifluoromethanesulfonate, and iodide **1**, **2**, **3**, **13**, and **14** were measured in both CDCl$_3$ and CD$_3$OD (Figure 6). The signals of ^{125}Te for the telluronium salts were observed in a wide region in CDCl$_3$, and the peak of the telluronium salt with iodide as a counteranion **14** was observed at an extremely separated position. In contrast, the peaks were observed in a restricted region in CD$_3$OD. This result also supports the theory that the cation−anion interactions were avoided by the polar solvents.

Behavior of the specific rotations and circular dichroism spectra anticipates existence of the hypervalent species. However, the ^{125}Te-NMR spectra deny the existence of the hypervalent Te-structures in solution because the hypervalent tellurium compounds with electron-withdrawing groups show their ^{125}Te-NMR chemical shifts at the lower field (~1000 ppm),[19] although there is no denying some contribution of the hypervalent Te-structures in solution.

Conclusion

Asymmetric telluronium ion with an optically active counteranion could be optically resolved into the diastereomerically pure isomers, and enantiomerically pure telluronium salts were isolated by anion-exchange reactions of the diastereomerically pure isomer. The absolute configurations of the optically active isomers were determined on the basis of the X-ray crystallographic analysis of one diastereomeric isomer. The optically active telluronium salts were found to show peculiar optical properties on their specific rotations and circular dichroism spectra in solutions compared with those of the corresponding sulfonium and selenonium salts. The behavior on the optical properties of the telluronium salts was found to be caused by the strong solvation in polar solvents based on NMR studies of the chalcogen onium salts.

Experimental Section

General Procedures. Melting points were determined on a Yamato MP-21 melting point apparatus and are uncorrected. IR spectra were measured on a Hitachi 260-10 infrared spectrophotometer and a JASCO FT/IR-5MP Fourier transform infrared spectrophotometer with samples as either neat liquids or KBr disks. UV−vis spectra were measured on a Shimadzu UV-160A UV−vis recording spectrophotometer. ^{1}H, ^{13}C, and ^{125}Te NMR spectra were determined on a JEOL JNM-EX-400 FT NMR spectrometer at 400, 100, and 126 MHz, respectively. The ^{1}H and ^{13}C NMR chemical shifts were referenced to Me$_4$Si as an internal standard, and *J* values are given in Hz. The ^{125}Te NMR chemical shifts were referenced to Me$_2$Te as an external standard. Optical rotations were measured on a JASCO DIP-370 digital polarimeter and are

---

(18) Each peak of ^{13}C-NMR spectra for **10**, **11**, and **2** was assigned on the basis of the C−H two-dimensional NMR spectrum, respectively.

(19) (a) Michalak, R. S.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7529. (b) Takaguchi, Y.; Furukawa, N. *Chem. Lett.* **1996**, 365.

given in units of 10^{-1} deg cm^2 g^{-1}, and CD spectra were recorded on JASCO J-40A and JASCO J-720Z digital polarimeters. TLC was performed with Merck Art. 5554 DC-Alufolien Kieselgel 60 F_{254}, Art. 5550 DC-Alufolien Aluminiumoxid 60 F_{254} neutral (Typ E), and Art. 5574 DC-Alufolien Cellulose F. Column chromatography was performed with Merck Aluminiumoxid 90 active basic (70/230 μm). All solvents were distilled and stored under nitrogen.

Materials. Optically active $(S)_S$-ethylmethylphenylsulfonium (*1S*)-(+)-camphor-10-sulfonate[6,15] ($(S)_S$-**8**), (*S*)-ethylmethylphenylsulfonium perchlorate[6,15] ((*S*)-**10**), $(R)_{Se}$-ethylmethylphenylselenonium (*1S*)-(+)-camphor-10-sulfonate[17] ($(R)_{Se}$-**9**), and (*S*)-ethylmethylphenylselenonium perchlorate[17] ((*S*)-**11**) were synthesized according to reported procedures.

Synthesis of Ethylmethylphenyltelluronium (*1S*)-(+)-Camphor-10-sulfonate (dia.-1). A mixture of methylphenyl telluride[20] (7.24 g, 33.0 mmol) and a large excess amount of ethyl iodide (103 g, 660 mmol) was stirred at room temperature for 5 days under nitrogen and dark conditions. The resulting precipitate was collected by filtration and washed with ether (100 mL). Recrystallization of the residue from acetone−ether−hexane gave ethylmethylphenyltelluronium iodide (**14**) (8.80 g, 71%) as colorless crystals: mp 131 °C dec (acetone−ether−hexane); ^{1}H-NMR (CDCl$_3$) δ 1.42 (t, 3H, $J = 7.81$ Hz), 2.73 (s, 3H), 3.43 (q, 2H, $J = 7.81$ Hz), 7.32−7.43 (m, 3H), 7.91−7.93 (m, 2H); ^{13}C-NMR (CDCl$_3$) δ 10.4, 11.4, 25.6, 120.6, 129.6, 130.4, 135.1; ^{125}Te-NMR (CDCl$_3$) δ 566; ^{125}Te-NMR (CD$_3$OD) δ 613; IR (KBr) ν_{max} 3051, 2962, 2924, 1574, 1476, 1435, 1311, 738, 690 cm^{-1}. Anal. Calcd for $C_9H_{13}TeI$: C, 28.77; H, 3.49. Found: C, 28.65; H, 3.81.

To an acetonitrile solution (450 mL) of ethylmethylphenyltelluronium iodide (**14**) (3.62 g, 9.64 mmol) under dark conditions was added silver (*1S*)-(+)-camphor-10-sulfonate (3.27 g, 9.64 mmol) prepared from (*1S*)-(+)-camphor-10-sulfonic acid and silver oxide(I). After the mixture was stirred at room temperature for 1 day, silver iodide was filtered off and the filtrate was concentrated. Treatment by means of short column chromatography (alumina/methanol) gave a diastereomeric mixture of ethylmethylphenyltelluronium (*1S*)-(+)-camphor-10-sulfonate (dia.-**1**) in quantitative yield (4.57 g): mp 110−120 °C (chloroform−ether); $[\alpha]_D$ +20.0 (*c* 1.13, MeOH), +38.5 (*c* 0.94, CHCl$_3$), +23.5 (*c* 1.04, EtOH), +26.6 (*c* 1.08, MeCN), +30.1 (*c* 1.29, acetone), +34.4 (*c* 1.12, CH$_2$Cl$_2$); ^{1}H-NMR (CDCl$_3$) δ 0.80 (s, 3H), 1.05 (s, 3H), 1.30−1.37 (m, 1H), 1.46 (t, 3/2H, $J = 7.57$ Hz), 1.47 (t, 3/2H, $J = 7.57$ Hz), 1.61−1.68 (m, 1H), 1.85 (d, 1H, $J = 18.55$ Hz), 1.95−2.03 (m, 2H), 2.26−2.33 (m, 1H), 2.62−2.70 (m, 1H), 2.68 (s, 3/2H), 2.70 (s, 3/2H), 2.72 (d, 1H, $J = 14.65$ Hz), 3.24 (d, 1H, $J = 14.65$ Hz), 3.27−3.39 (m, 2H), 7.49−7.53 (m, 3H), 7.69−7.71 (m, 2H); ^{13}C-NMR (CDCl$_3$) δ 8.5, 10.3, 19.8, 19.9, 24.5, 24.7, 27.0, 42.6, 43.0, 47.4, 47.9, 58.5, 121.2, 130.4, 131.6, 133.7, 217.1; ^{125}Te-NMR (CDCl$_3$) δ 610; ^{125}Te-NMR (CD$_3$OD) δ 624; IR (KBr) ν_{max} 3060, 2970, 2890, 1745, 1735, 1580, 1485, 1440, 1195, 1045, 740, 690 cm^{-1}; UV (MeOH) λ_{max} 221 (ϵ 9.7 × 10^3), 258 (ϵ 5.9 × 10^2), 264 (ϵ 6.9 × 10^2), 270 (ϵ 5.4 × 10^2) nm. Anal. Calcd for $C_{19}H_{28}O_4STe$: C, 47.53; H, 5.88. Found: C, 47.66; H, 6.12.

Optical Resolution of Ethylmethylphenyltelluronium (*1S*)-(+)-Camphor-10-sulfonate (dia.-1). Recrystallization of ethylmethylphenyltelluronium (*1S*)-(+)-camphor-10-sulfonate, dia.-**1** (8.63 g), from acetone−ether−hexane gave 4.41 g of crystals containing needles. After separation of the needles from the bulk, 2.20 g of the needles was further recrystallized from the acetone−ether−hexane solution to give optically pure diastereomeric telluronium salt $(R)_{Te}$-$(+)_{Te\text{-}(MeOH)}$-**1** (1.06 g) as colorless needles. Twice repeated recrystallization of telluronium salt, obtained from the mother liquor of the first recrystallization, from acetone−ether gave another diastereomerically pure telluronium salt $(S)_{Te}$-$(-)_{Te(MeOH)}$-**1** (95 mg) as colorless prisms. Optical purities of both telluronium salts were confirmed by the measurements of ^{1}H-NMR spectra, described in the text, and the absolute configurations were also determined on the basis of the X-ray crystallographic analysis of $(+)_{Te(MeOH)}$-**1**.[13]

Compound $(R)_{Te}$-**1**: mp 145−146 °C (acetone−ether−hexane); 100% de; $[\alpha]_D$ +24.9 (*c* 0.96, MeOH), +30.5 (*c* 1.29, CHCl$_3$), +28.0 (*c* 1.23, EtOH), +28.5 (*c* 1.01, MeCN), +31.7 (*c* 0.97, acetone), +27.7 (*c* 0.89, CH$_2$Cl$_2$); CD (MeOH) 293 ($[\theta]$ +8.0 × 10^3), 226 ($[\theta]$ +7.8 × 10^3) nm; CD (CHCl$_3$) 295 ($[\theta]$ +8.8 × 10^3) nm; ^{1}H-NMR (CDCl$_3$) δ 0.80 (s, 3H), 1.05 (s, 3H), 1.30−1.36 (m, 1H), 1.45 (t, 3H, $J = 7.57$ Hz), 1.62−1.69 (m, 1H), 1.85 (d, 1H, $J = 18.07$ Hz), 1.95−2.02 (m, 2H), 2.26−2.32 (m, 1H), 2.62−2.67 (m, 1H), 2.69 (s, 3H), 2.73 (d, 1H, $J = 14.41$ Hz), 3.24 (d, 1H, $J = 14.41$ Hz), 3.27−3.40 (m, 2H), 7.47−7.53 (m, 3H), 7.65−7.68 (m, 2H); ^{13}C-NMR (CDCl$_3$) δ 8.5, 10.3, 19.8, 19.9, 24.4, 24.5, 27.0, 42.6, 42.9, 47.3, 47.8, 58.5, 121.2, 130.3, 131.5, 133.7, 217.0; IR (KBr) ν_{max} 3055, 2970, 2885, 1745, 1735, 1575, 1485, 1440, 1190, 1045, 730, 685 cm^{-1}; UV (MeOH) λ_{max} 221 (ϵ 9.4 × 10^3), 258 (ϵ 5.9 × 10^2), 264 (ϵ 6.9 × 10^2), 270 (ϵ 5.3 × 10^2) nm. Anal. Calcd for $C_{19}H_{28}O_4STe$: C, 47.53; H, 5.88. Found: C, 47.50; H, 6.16.

Compound $(S)_{Te}$-**1**: mp 119−120 °C (acetone−ether); 100% de; $[\alpha]_D$ +16.7 (*c* 1.03, MeOH), +45.8 (*c* 0.91, CHCl$_3$); CD (MeOH) 292 ($[\theta]$ +5.4 × 10^3), 224 ($[\theta]$ −4.1 × 10^3) nm; ^{1}H-NMR (CDCl$_3$) δ 0.81 (s, 3H), 1.06 (s, 3H), 1.31−1.38 (m, 1H), 1.47 (t, 3H, $J = 7.82$ Hz), 1.67−1.74 (m, 1H), 1.85 (d, 1H, $J = 18.06$ Hz), 1.95−2.03 (m, 2H), 2.26−2.32 (m, 1H), 2.64−2.72 (m, 1H), 2.66 (s, 3H), 2.79 (d, 1H, $J = 14.41$ Hz), 3.27 (d, 1H, $J = 14.41$ Hz), 3.25−3.44 (m, 2H), 7.48−7.54 (m, 3H), 7.60−7.62 (m, 2H); ^{13}C-NMR (CDCl$_3$) δ 8.4, 10.3, 19.8, 19.9, 24.5, 24.6, 27.0, 42.6, 42.9, 47.3, 47.9, 58.5, 121.2, 130.3, 131.5, 133.7, 217.0; IR (KBr) ν_{max} 3050, 2955, 2885, 1745, 1730, 1575, 1480, 1435, 1190, 1040, 740, 690 cm^{-1}; UV (MeOH) λ_{max} 221 (ϵ 9.3 × 10^3), 258 (ϵ 5.8 × 10^2), 264 (ϵ 6.8 × 10^2), 270 (ϵ 5.3 × 10^2) nm. Anal. Calcd for $C_{19}H_{28}O_4STe$: C, 47.53; H, 5.88. Found: C, 47.47; H, 6.13.

Transformation of Diastereomeric Telluronium Salts into Enantiomeric Telluronium Salts. Enantiomerically pure (*R*)-telluronium salts were typically synthesized according to the following two methods. Method A. Diastereomeric telluronium salt $(R)_{Te}$-**1** or $(S)_{Te}$-**1** (ca. 1 mmol) was added to an aqueous solution of a ten-fold excess of the corresponding sodium salt (ca. 100 g L^{-1}). The mixture was stirred at room temperature for 1 h, and the resulting precipitate was extracted with dichloromethane. Purification was performed by recrystallization of the extracts. Method B. The resulting precipitate was collected by filtration and recrystallized.

(*R*)-Ethylmethylphenyltelluronium perchlorate (*R*)-**2** was obtained in 81% yield after recrystallization from dichloromethane−ether according to method A: mp 99−100 °C (dichloromethane−ether); 100% ee; $[\alpha]_D$ +6.24 (*c* 0.99, MeOH), +2.11 (*c* 1.02, CHCl$_3$); CD (MeOH) 271 ($[\theta]$ +1.0 × 10^3), 264 ($[\theta]$ +1.3 × 10^3), 258 ($[\theta]$ +9.6 × 10^2), 252 ($[\theta]$ +6.1 × 10^2), 229 ($[\theta]$ +6.1 × 10^3) nm; ^{1}H-NMR (CDCl$_3$) δ 1.46 (t, 3H, $J = 7.81$ Hz), 2.65 (s, 3H), 3.26−3.32 (m, 2H), 7.50−7.56 (m, 3H), 7.69−7.71 (m, 2H); ^{13}C-NMR (CDCl$_3$) δ 6.1, 10.2, 22.8, 117.2, 130.8, 132.3, 133.8; IR (KBr) ν_{max} 3050, 3000, 2950, 2875, 1580, 1480, 1440, 1220, 1100, 860, 740, 690 cm^{-1}; UV (MeOH) λ_{max} 222 (ϵ 1.1 × 10^4), 258 (ϵ 6.1 × 10^2), 264 (ϵ 7.1 × 10^2), 271 (ϵ 5.3 × 10^2) nm. Anal. Calcd for $C_9H_{13}O_4ClTe$: C, 31.04; H, 3.76. Found: C, 31.04; H, 4.01. The racemic perchlorate **2** showed ^{125}Te-NMR signal at 601 and 621 ppm in CDCl$_3$ and CD$_3$OD, respectively.

(*R*)-Ethylmethylphenyltelluronium tetrafluoroborate (*R*)-**3** was obtained in 29% yield after recrystallization from dichloromethane−ether according to method A: mp 83−84 °C (dichloromethane−ether); 100% ee; $[\alpha]_D$ +6.30 (*c* 0.88, MeOH), +1.45 (*c* 0.88, CHCl$_3$), +9.41 (*c* 0.87, acetone); CD (MeOH) 271 ($[\theta]$ +7.5 × 10^2), 264 ($[\theta]$ +9.6 × 10^2), 258 ($[\theta]$ +6.9 × 10^2), 251 ($[\theta]$ +4.4 × 10^2), 230 ($[\theta]$ +4.2 × 10^3) nm; ^{1}H-NMR (CDCl$_3$) δ 1.43 (t, 3H, $J = 7.81$ Hz), 2.61 (s, 3H), 3.22−3.28 (m, 2H), 7.49−7.56 (m, 3H), 7.68−7.70 (m, 2H); ^{13}C-NMR (CDCl$_3$) δ 5.4, 10.0, 22.3, 116.6, 130.7, 132.2, 133.6; ^{125}Te-NMR (CDCl$_3$) δ 606; ^{125}Te-NMR (CD$_3$OD) δ 624; IR (KBr) ν_{max} 3440 (br), 3050, 2970, 2940, 2875, 1580, 1480, 1435, 1205, 1070 (br), 1000, 860, 840, 730, 690 cm^{-1}; UV (MeOH) λ_{max} 222 (ϵ 8.3 × 10^3), 257 (ϵ 5.3 × 10^2), 264 (ϵ 6.1 × 10^2), 270 (ϵ 4.6 × 10^2) nm. Anal. Calcd for $C_9H_{13}BF_4Te$: C, 32.21; H, 3.90. Found: C, 32.33; H, 4.06.

(*R*)-Ethylmethylphenyltelluronium *p*-chlorobenzenesulfonate (*R*)-**4** was obtained in 64% yield after recrystallization from acetone−benzene−hexane according to method A: mp 105−

---

[20] Hope, E. G.; Kemmitt, T.; Levason, W. *Organometallics* **1988**, *7*, 78.

106 °C (acetone−benzene−hexane); 100% ee; $[\alpha]_D$ +5.66 (*c* 0.99, MeOH), −3.25 (*c* 0.99, $CHCl_3$); CD (MeOH) 271 ($[\theta]$ +6.7 × 10^2), 264 ($[\theta]$ +8.3 × 10^2), 257 ($[\theta]$ +5.7 × 10^2), 252 ($[\theta]$ +5.2 × 10^2), 230 ($[\theta]$ +3.9 × 10^3) nm; ^{1}H-NMR ($CDCl_3$) δ 1.40 (t, 3H, $J = 7.57$ Hz), 2.64 (s, 3H), 3.22−3.32 (m, 2H), 7.25−7.29 (m, 2H), 7.41−7.52 (m 3H), 7.64−7.70 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 7.8, 10.2, 23.6, 120.1, 127.5, 128.2, 130.3, 131.5, 133.6, 135.5, 144.2; IR (KBr) ν_{max} 3450 (br), 3090, 3050, 2975, 2940, 2870, 1575, 1480, 1440, 1395, 1225, 1180, 1130, 1090, 1040, 1010, 830, 760, 730, 685 cm^{-1}; UV (MeOH) λ_{max} 225 (ϵ 2.9 × 10^4), 259 (ϵ 1.0 × 10^3), 265 (ϵ 1.2 × 10^3), 270 (ϵ 8.5 × 10^2) nm. Anal. Calcd for $C_{15}H_{17}ClO_3STe$: C, 40.91; H, 3.89. Found: C, 40.83; H, 4.07.

(*R*)-Ethylmethylphenyltelluronium bornane-10-sulfonate (*R*)-**5** was obtained in 56% yield after recrystallization from acetone−ether−hexane according to method A: mp 157 °C dec (acetone−ether−hexane); 100% ee; $[\alpha]_D$ +5.14 (*c* 0.97, MeOH), −6.59 (*c* 0.97, $CHCl_3$); CD (MeOH) 271 ($[\theta]$ +1.2 × 10^3), 264 ($[\theta]$ +1.5 × 10^3), 258 ($[\theta]$ +1.1 × 10^3), 251 ($[\theta]$ +6.9 × 10^2), 229 ($[\theta]$ +6.8 × 10^3) nm; CD ($CHCl_3$) 272 ($[\theta]$ +1.7 × 10^3), 265 ($[\theta]$ +2.0 × 10^3), 258 ($[\theta]$ +1.5 × 10^3) nm; ^{1}H-NMR ($CDCl_3$) δ 0.77 (s, 6H), 1.04−1.14 (m, 2H), 1.45 (t, 3H, $J = 7.57$ Hz), 1.55−1.56 (m, 1H), 1.62−1.75 (m, 6H), 2.70 (s, 3H), 2.71 (s, 2H), 3.28−3.34 (m, 2H), 7.47−7.52 (m, 3H), 7.72−7.73 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 8.5, 10.4, 19.2, 24.0, 28.5, 33.3, 44.8, 46.2, 48.8, 54.9, 121.5, 130.2, 131.4, 133.8; IR (KBr) ν_{max} 3460, 3050, 2940, 2880, 1650, 1575, 1480, 1435, 1180 (br), 1150, 1045, 730, 685 cm^{-1}; UV (MeOH) λ_{max} 222 (ϵ 4.9 × 10^3), 258 (ϵ 2.9 × 10^2), 264 (ϵ 3.4 × 10^2), 270 (ϵ 2.5 × 10^2) nm. Anal. Calcd for $C_{19}H_{30}O_3STe$: C, 48.96; H, 6.49. Found: C, 48.93; H, 6.73.

(*R*)-Ethylmethylphenyltelluronium tetraphenylborate (*R*)-**6** was obtained in 57% yield after recrystallization from acetone−ether according to method B: mp 179−181 °C (acetone−ether); 100% ee; $[\alpha]_D$ +5.07 (*c* 0.80, acetone); ^{1}H-NMR (acetone-d_6) δ 1.50 (t, 3H, $J = 7.81$ Hz), 2.72 (s, 3H), 3.33 (q, 2H, $J = 7.81$ Hz), 6.76−6.80 (m, 4H), 6.91−6.94 (m, 8H), 7.32−7.37 (m, 8H), 7.61−7.68 (m, 3H), 7.88−7.90 (m, 2H); ^{13}C-NMR (acetone-d_6) δ 6.0, 10.2, 22.9, 118.9, 122.0, 125.8, 131.0, 132.8, 134.4, 136.7 ($J_{CCB} = 11.0$ Hz), 164.6 ($J_{CB} = 49.6$ Hz); IR (KBr) ν_{max} 3050, 3000, 2930, 1580, 1480, 1425, 1205, 1150, 1000, 850, 740, 730, 710, 700, 680 cm^{-1}. Anal. Calcd for $C_{33}H_{33}BTe$: C, 69.78; H, 5.86. Found: C, 69.73; H, 6.24.

(*R*)-Ethylmethylphenyltelluronium picrylsulfonate (*R*)-**7** was obtained in 55% yield after recrystallization from acetone−ether−hexane according to method B: mp 161 °C dec (acetone−ether−hexane); 100% ee; $[\alpha]_D$ +5.44 (*c* 0.84, acetone); CD (MeOH) 270 ($[\theta]$ +1.4 × 10^3), 264 ($[\theta]$ +1.7 × 10^3), 257 ($[\theta]$ +1.1 × 10^3), 252 ($[\theta]$ +7.3 × 10^2), 230 ($[\theta]$ +8.4 × 10^3) nm; ^{1}H-NMR (acetone-d_6) δ 1.44 (t, 3H, $J = 7.57$ Hz), 2.68 (s, 3H), 3.29 (q, 2H, $J = 7.57$ Hz), 7.52−7.59 (m, 3H), 7.88−7.90 (m, 2H), 8.62 (s, 2H); ^{13}C-NMR (acetone-d_6) δ 6.9, 10.9, 23.7, 120.4, 121.7, 121.9, 131.6, 133.2, 135.4; IR (KBr) ν_{max} 3075, 3030, 2940, 1605, 1550, 1485, 1440, 1360, 1260, 1245, 1215, 1125, 1070, 1035, 750, 720, 690 cm^{-1}; UV (MeOH) λ_{max} 257 (ϵ 1.0 × 10^4) nm. Anal. Calcd for $C_{15}H_{15}N_3O_9STe$: C, 33.30; H, 2.79; N, 7.77. Found: C, 33.42; H, 3.04; N, 7.83.

(*S*)-Ethylmethylphenyltelluronium perchlorate (*S*)-**2** was obtained in 63% yield, after recrystallization from dichloromethane−ether, according to method A from optically active telluronium salt $(S)_{Te}$-**1** (57% de): mp 101−104 °C (dichloromethane−ether); 57% ee; $[\alpha]_D$ −3.98 (*c* 0.92, MeOH), −0.30 (*c* 0.73, $CHCl_3$), −5.60 (*c* 1.03, acetone); CD (MeOH) 271 ($[\theta]$ −6.6 × 10^2), 264 ($[\theta]$ −8.7 × 10^2), 258 ($[\theta]$ −6.4 × 10^2), 252 ($[\theta]$ −4.1 × 10^2), 229 ($[\theta]$ −3.9 × 10^3) nm; ^{1}H-NMR ($CDCl_3$) δ 1.48 (t, 3H, $J = 7.81$ Hz), 2.67 (s, 3H), 3.27−3.34 (m, 2H), 7.51−7.58 (m, 3H), 7.68−7.71 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 6.1, 10.2, 23.0, 117.1, 130.8, 132.3, 133.7; IR (KBr) ν_{max} 3050, 2970, 2940, 2870, 1575, 1480, 1435, 1200, 1100 (br), 995, 855, 730, 685 cm^{-1}. Anal. Calcd for $C_9H_{13}O_4ClTe$: C, 31.04; H, 3.76. Found: C, 30.99; H, 3.94.

Ethylmethylphenyltelluronium Trifluoromethanesulfonate (13). To an acetonitrile solution (200 mL) of ethylmethylphenyltelluronium iodide (**14**) (1.39 g, 3.70 mmol) under dark conditions was added silver trifluoromethanesulfonate (955 mg, 3.70 mmol). After the mixture was stirred at room temperature for 1 h, silver iodide was filtered off and the filtrate was concentrated. Recrystallization from chloroform−ether, after treatment by means of short column chromatography (alumina/methanol), gave the telluronium salt **13** in 68% yield (997 mg) as colorless plates: mp 63−65 °C (chloroform−ether); ^{1}H-NMR ($CDCl_3$) δ 1.44 (t, 3H, $J = 7.81$ Hz), 2.61 (s, 3H), 3.23−3.29 (m, 2H), 7.49−7.57 (m, 3H), 7.69−7.71 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 6.7, 10.2, 23.2, 118.0, 130.6, 132.1, 133.8; ^{125}Te-NMR ($CDCl_3$) δ 602; ^{125}Te-NMR (CD_3OD) δ 623; IR (KBr) ν_{max} 3060, 3000, 2950, 2880, 1580, 1485, 1441, 1438, 1260 (br), 1165, 1030, 870, 732, 685 cm^{-1}. Anal. Calcd for $C_{10}H_{13}F_3O_3STe$: C, 30.19; H, 3.29. Found: C, 30.10; H, 3.53.

Acknowledgment. The authors are sincerely grateful to Dr. Takumi Konno and Professor Ken-ichi Okamoto at University of Tsukuba and Professor Takamichi Yamagishi at Tokyo Metropolitan University for the use of the circular dichroism spectrometer. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas and General Scientific Research from the Ministry of Education, Science and Culture, Japan.

JO960785K