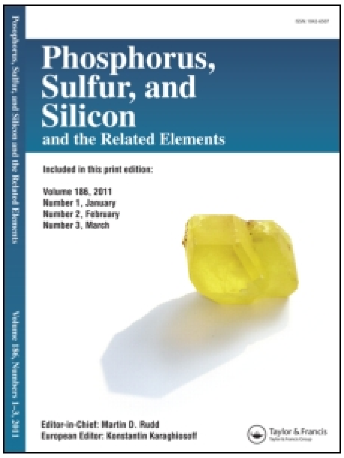

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Synthesis and Stereochemistry of Optically Active Selenium and Tellurium Compounds

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Synthesis and Stereochemistry of Optically Active Selenium and Tellurium Compounds

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The synthesis and stereochemistry of tricoordinated optically active selenium and tellurium compounds are described. Telluronium salts, telluronium imides, and seleninic acids were prepared and optically resolved by fractional recrystallization of diastereomeric mixtures or by chromatography using a chiral column of racemic mixtures. Diphenyl dichalcogenides also were optically resolved by chiral crystallization. Their absolute configurations were determined or estimated based on X-ray crystallographic analysis, specific rotations, and circular dichroism spectra. The kinetic studies and the mechanism for the racemization were also studied.

Keywords Absolute configuration; CD spectrum; diphenyl dichalcogenide; optical resolution; optically active compound; racemization; seleninic acid; specific rotation; stereochemistry; telluronium imide; telluronium salts; X-ray crystallographic analysis

INTRODUCTION

Many optically active tricoordinate sulfur compoundes have been synthesized and are used as chiral sources in asymmetric synthesis.[1–4] It is well known that many organoselenium and tellurium compounds have structures similar to those of the corresponding organosulfur compounds since selenium and tellurium are homologous with sulfur. However, studies on the synthesis and stereochemistry of optically active organoselenium and tellurium compounds have been limited in contrast to those of organosulfur compounds,[5–8] perhaps due to the instability of these chalcogen compounds. Recently, our interest has been focused on the isolation and stereochemistry of optically active tricoordinated organoselenium and tellurium compounds such as oxides, salts, imides, and ylides.[9–11] In these entries, optically active selenoxide,[12–15] selenonium salt,[16,17] telluronium salt,[18,19] selenonium

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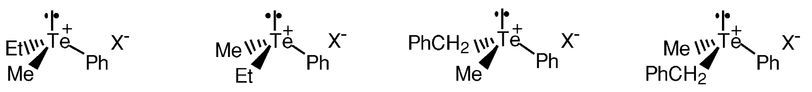
imide,[20–22] and selenonium ylide[23] had been reported; however, their optical purities were low or unknown, and their absolute configurations and properties had not been clarified in most cases. We have already succeeded in isolating optically pure, tricoordinated chalcogen compounds such as selenoxides,[24–30] telluroxides,[31–34] selenonium salts,[35] selenonium imide,[36–41] selenonium ylides,[42,43] and telluronium ylides,[44,45] stabilized by steric protection with bulky substituent (kinetic stabilization) or by intramolecular coordination of a Lewis base such as amino group to the chalcogen atom (thermodynamic stabilization) as stable crystalls and clarified their stereochemistry and configurational stability. This article describes a brief account of the synthesis, kinetics, and mechanism for the racemization of optically active telluronium salts,[46–48] telluronium imides,[49,50] seleninic acids,[51,52] and diphenyl dichalcogenides.[53]

Optically Active Telluronium Salts[46–48]

Diastereomeric mixtures of ethylmethylphenyltelluronium (Scheme 1) and benzylmethylphenyltelluronium (1*S*)-(+)-camphor-10-sulfonate {dia.-**1**: mp 110–120°C, $[\alpha]_D$ +20.0 (*c* 1.13, MeOH) and dia.-**2**: mp 97–99°C, $[\alpha]_D$ +15.8 (*c* 1.00, MeOH), respectively; X$^-$ = (1*S*)-(+)-camphor-10-sulfonate}, prepared from the corresponding telluronium iodide and silver (1*S*)-(+)-camphor-10-sulfonate were optically resolved by repeated recrystallization. Diastereomerically pure telluronium salt isomer (+)$_{\text{Te(MeOH)}}$-**1** was isolated as colorless needles from acetone-ether-hexane, and a small amount of another diastereomeric isomer (−)$_{\text{Te(MeOH)}}$-**1** was also obtained in optically pure form by recrystallization from acetone-ether of the telluronium salt remaining in the first mother solution. Similarly, diastereomerically pure telluronium salts (+)$_{\text{Te(MeOH)}}$-**2** and (−)$_{\text{Te(MeOH)}}$-**2** were obtained from dia.-**2**. The optical purities were determined by comparison of ^{1}H NMR spectra of the optical isomers with that of the corresponding diastereomeric mixture in CDCl$_3$.



(*R*)-(+)$_{\text{Te(MeOH)}}$-**1** (*needles*)
$[\alpha]_D$ +24.9 (*c* 0.96, MeOH)
mp 145-146 °C
de 100%

(*S*)-(-)$_{\text{Te(MeOH)}}$-**1** (*prisms*)
$[\alpha]_D$ +16.7 (*c* 1.03, MeOH)
mp 119-120 °C
de 100%

(*R*)-(+)$_{\text{Te(MeOH)}}$-**2** (*needles*)
$[\alpha]_D$ +80.0 (*c* 1.00, MeOH)
mp 113-115 °C
de 100%

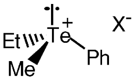
(*S*)-(-)$_{\text{Te(MeOH)}}$-**2** (*prisms*)
$[\alpha]_D$ -57.3 (*c* 1.00, MeOH)
mp 125-126 °C
de 100%

X$^-$ = (*1S*)-(+)-camphor-10-sulfonate

SCHEME 1

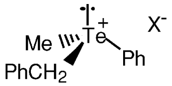
The absolute configurations around the tellurium atom of $(+)_{\mathrm{Te(MeOH)}}$-**1a** and $(-)_{\mathrm{Te(MeOH)}}$-**1b** were determined to be *R*- and *S*-forms, respectively, by the X-ray crystallographic analysis based on the known configuration of (1*S*)-(+)-camphor-10-sulfonate as an internal standard. Similarly, the absolute configuration of $(-)_{\mathrm{Te(MeOH)}}$-**1b** was determined to be *S*-form by the X-ray crystallographic analysis, and therefore the configurations of $(+)_{\mathrm{Te(MeOH)}}$-**1b** was assigned to be *R*-form.

Enantiomerically pure (*R*)-(+)-ethylmethylphenyltelluronium salts **3a–f** (Scheme 2) and (*S*)-(−)-benzylmethyl-phenyltelluronium salts **4a–d** were obtained by successful anion exchange reactions from optically pure telluronium salts $(R)_{\mathrm{Te}}$-$(+)_{\mathrm{Te(MeOH)}}$-**1** and $(S)_{\mathrm{Te}}$-$(-)_{\mathrm{Te(MeOH)}}$-**2**, respectively. This is the first example for isolation of enantiomerically pure telluronium salts.



(*R*)-(+)-**3**
ee 100%

3a: X = ClO_4
3b: X = BF_4
3c: X = *p*-$ClC_6H_4SO_3$
3d: X = borane-10-sulfonate
3e: X = BPh_4
3f: X = picrylsulfonate

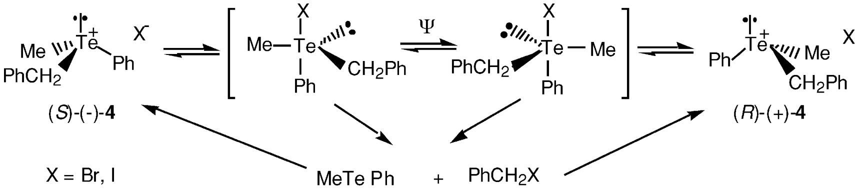


(*S*)-(-)-**4**
ee 100%

4a: X = BF_4
4b: X = *p*-$ClC_6H_4SO_3$
4c: X = Br
4d: X = I

SCHEME 2

The CD spectrum of (*R*)-(+)-**3** in methanol showed positive cotton effects in the region of 250–270 nm, and that of (*S*)-(−)-**4** showed negative cotton effects at 247 nm caused by the chiralities on the tellurium atom. Optically pure telluronium perchlorate (*R*)-(+)-**3a** was found to be stable toward pyramidal inversion, and no racemization was observed in solid state and in refluxing methanol after 3 days. Therefore, the pyramidal geometry of the telluronium salt (*R*)-(+)-**3a** was found to be much more stable toward racemization than that of the ethylmethylphenylsulfonium perchlorate which was reported to racemize in methanol even at room temperature.[54] Enantiomerically pure telluronium salts (*S*)-(−)-**4a** and (*S*)-(−)-**4b** were also stable toward racemization in solid state and in refluxing methanol; however, racemization was observed in the cases of telluronium salts (*S*)-(−)-**4c** and (*S*)-(−)-**4d** which have nucleophilic counter anion such as bromide and iodide in methanol and chloroform solution. The rates obeyed good first-order kinetics and the first-order rate constants at 27°C were as follows: (*S*)-(−)-**4c**: $k_1 = 2.99 \times 10^{-4}\ s^{-1}$ (in MeOH), $6.10 \times 10^{-3}\ s^{-1}$(in $CHCl_3$); (*S*)-(−)-**4d**: $k_1 = 4.50 \times 10^{-3}\ s^{-1}$(in MeOH), and $2.64 \times 10^{-1}\ s^{-1}$ (in $CHCl_3$). A plausible mechanism for the racemization is proposed as follows (Scheme 3). A hypervalent tellurane intermediate forms by the nucleophilic attack of halide ion on tellurium atom of **4** which undergoes



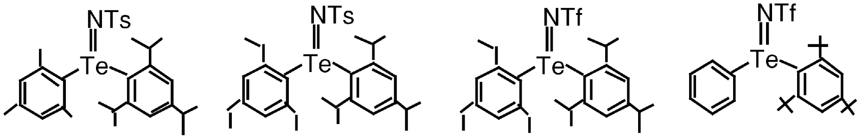
SCHEME 3

pseudo-rotation, and the successful ligand coupling of tellurane intermediate gives benzylhalide and methylphenyltelluride. Benzylhalide and methylphenyltelluride, once formed, react again to give racemic benzylmethylphenyltelluronium salt **4**.

Optical resolution of alkyldiaryltelluronium salt, methylphenyl-*p*-tolyltelluronium 3-bromocamphor-8-sulfonate, was first reported by Lowry and Gilbert in 1929, and they mentioned that the optical active compound was unstable toward epimerization and easily loosed the optical activity.[55] It was very strange for us why alkyldiaryltelluronium salt reported by Lowry and Gilbert was so unstable whereas our optically active dialkylaryltelluronium salt **1** and benzylmethylphenyltelluronium salt **2** were stable toward epimerization. Thus, we prepared alkyldiaryltelluronium salts such as methyl-1-naphthylphenyl-telluronium, mesitylmethylphenyltelluronium, and methylphenyl-2,4,6-triisopropylphenyltelluronium (1*S*)-(+)-camphor-10-sulfonates and attempted the optical resolution by repeated recrystallization under number of conditions; however, all of our trials failed and we could not obtain optically active alkyldiaryl-telluronium salts. Then, we prepared methylphenyl-*p*-tolyltelluronium 3-bromocamphor-8-sulfonate, the same compound reported by Lowry and Gilbert, and attempted the supplementary examination of optical resolution; however, much to my regret, we could not obtain optically active compound and reproduce their results in sprite of our efforts. Therefore, optical resolution of alkyldiaryl-telluronium salts is very difficult although the reason is not clear at the present time, and the result reported by Lowry and Gilbert is quite doubtful.

Optically Active Telluronium Imides[49]

Kinetically stabilized telluronium imide by bulky substituents such as mesityl 2,4,6-triisopropyl-phenyltelluronium *N*-toluene-4′-sulfonimide (**5**) and 2,4,6-triethylphenyl 2′,4′,6′-triisopropylphenyl-telluronium *N*-toluene-4″-sulfonimide (**6**) were synthesized by the reaction of the corresponding telluroxide with toluene-4-sulfonamide. However, a less bulky telluronium imide, phenyl 2,4,6-triisopropylphenyltelluronium *N*-toluene-4′-sulfonimide, could not be isolated because of facile hydrolysis although its formation was confirmed by ^{1}H NMR measurement of the reaction mixture. Similarly, 2,4,6-triethylphenyl 2′,4′,6′-triisopropylphenyltelluronium *N*-trifluoromethanesulfonimide (**7**) (Scheme 4) and phenyl 2,4,6-tri-*tert*-butyl-phenyltelluronium *N*-trifluoromethanesulfonimide (**8**) were synthesized.



5 **6** **7** **8**

SCHEME 4

Optical resolution of telluronium imide **5–8** was studied by HPLC on an analytical scale using a chiral column packed with cellulose carbamate derivative/silica gel and hexane/2-propanol as the mobile phase. Two peaks corresponding to each enantiomers were found in the chromatogram in the case of telluronium imides **6–8** (Figure 1) under the conditions; however, no peak corresponding to the telluronium imide was detected in the case of telluronium imide **5**. Telluronium imide **5**, having less bulky mesityl group, was found to hydrolyze in the column. The optical resolution of telluronium imides **6–8** was carried out on a preparative scale using same type of chiral column. Enantiomerically pure telluronium imides (+)-**6**, (+)-**7**, and (+)-**8** were obtained from the respective first fractions that were eluted, as shown in Table I. Optically pure (−)-**6**, (−)-**7**, and (−)-**8** were also obtained from the second-eluted portions by repeated chromatographic separations.

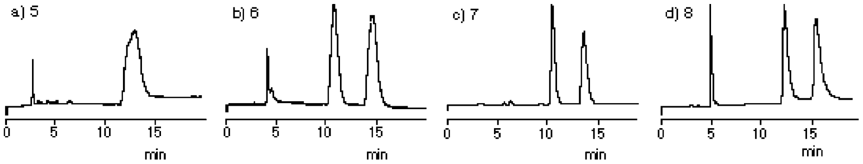
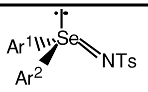


FIGURE 1 Opical resolution of telluronium imides **5–8** on a chiral column packed with cellulose carbamate derivative/silica gel (Daicel Chiralcel OD; 4.6 × 250 mm) by HPLC on an analytical scale at 25°C. (a) hexane/2-propanol (95/5); (b) hexane/2-propanol (90/10); (c) hexane/2-propanol (9820); (d) hexane/2-propanol (97/3).

TABLE I Optical Resolution and Specific Rotation of 6–8

Compound	First enantiomer		Second enantiomer	
	$[\alpha]_D$ (c)[a]	ee (%)	$[\alpha]_D$ (c)[a]	ee (%)
6	+55.0 (0.44)	100	−53.2 (0.65)	100
7	+79.0 (0.52)	100	−82.3 (0.20)	100
8	+57.6 (0.085)	100	−61.0 (0.050)	100



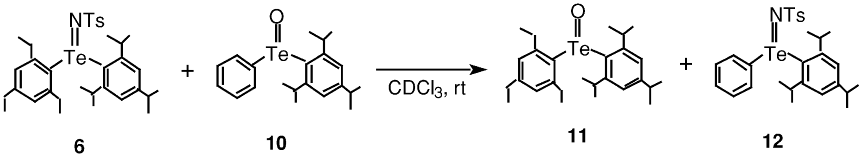
$Ar^1 = 2,4,6\text{-}(t\text{-}Bu)_3C_6H_2$
$Ar^2 = C_6H_5$

(*R*)-(+)-**9**

[a] Specific rotations were taken in acetonitrile at 25°C.

The CD spectra of optically pure telluronium imides (+)-**6**, (+)-**7**, and (+)-**8** showed positive cotton effects in acetonitrile at 285, 286, and 293 nm, respectively, and (−)-**6**, (−)-**7**, and (−)-**8** showed negative cotton effects in the corresponding regions. The first cotton effects showed good agreement with those of the optically pure selenium analogue; the CD spectrum of (*R*)-(+)-phenyl 2,4,6-tri-*tert*-butylphenyl-selenonium *N*-toluene-4′-sulfonimide (*R*)-(+)-**9** showed a positive first cotton effect at 272 nm, and that of the (*S*)-(−)-**9**-isomer showed a negative first Cotton effect at 272 nm, the absolute configuration of which was determined by X-ray crystallographic analysis of the (−)-isomer.[56] Based on a comparison of the optical properties, the absolute configuration of telluronium imides (+)-**6**, (+)-**7**, and (+)-**8** was assigned to be *R*-form and that of (−)-**6**, (−)-**7**, and (−)-**8** to *S*-form.

Optically active telluronium imide (*R*)-(+)-**6** was stable in the solid state under nitrogen; however, racemization was observed in solution. The decrease in the optical purity of (*R*)-(+)-**6** showed a good linear relationship with the first-order rate plots in chloroform that had been freshly distilled from calcium hydride ($k_1 = 6.67 \times 10^{-6} s^{-1}$ at 25°C). Pyramidal inversion is one possible mechanism of the racemization. However, the energy for the pyramidal inversion of a telluronium imide was calculated to be 54.4 kcal mol^{-1}.[57] Therefore, racemization *via* the pyramidal inversion was considered to be unlikely at least around room temperature. It was found that telluronium imides were easily hydrolyzed to give the corresponding telluroxides and amines. When racemic telluronium imide **6** and phenyl 2,4,6-triisopropylphenyl telluroxide (**10**) were stored in $CDCl_3$ at room temperature, both 2,4,6-triethylphenyl 2′,4′,6′-triisopropyl-phenyl telluroxide (**11**) and phenyl 2,4,6-triisopropylphenyltelluronium *N*-toluene-4′-sulfonimide (**12**) (Scheme 5) were found together with starting materials. Furthermore, a solution of phenyl 2,4,6-tri-*tert*-butylphenyl-telluroxide and trifluoromethanesulfonamide in $CDCl_3$ yielded telluronium imide **8**.



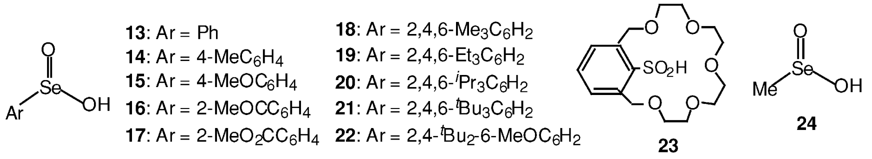
SCHEME 5

These results indicate that telluronium imides and telluroxides exist in equilibrium through hydrolysis of the imides and imination of the oxides. We have already clarified that optically active telluroxides readily racemize in the presence of a trace amount of water in the solvent despite careful purification.[31–34] Thus, we proposed a mechanism for the racemization of tellurinium imides involving the corresponding telluroxides, which are formed *in situ* by hydrolysis of the telluronium imides.

Optically Active Seleninic Acides[51,52]

Chalcogenic acids are also tricoordinated chalcogen compounds and are considered to be possible to resolve into their enantiomers; however, optically active chalcogenic acids have not yet been isolated. One reason for the lack of studies on chiral chalcogenic acids may be their facile racemization, and second reason is that there has been no superior technique for resolving these compounds into their enantiomers. We examined the optical resolution of various areneseleninic acids by means of liquid chromatography using a chiral column and found that seleninic acids could be optically resolved.

When racemic toluene-4-seleninic acid (**14**) was subjected to HPLC on an analytical scale at room temperature using a chiral column packed with amylose carbamate derivative/silica gel, two peaks corresponding to each enantiomers were observed on the chromatogram, although benzeneseleninic acid (**13**) was not resolved. The result indicates that the substituent on the aromatic ring is very important to the optical resolution and the hydrogen atom in seleninic acid is fixed to one oxygen atom. Then, optical resolution of racemic areneseleninic acid **15–22** (Scheme 6) into their inantiomers on a preparative scale was studied. In all cases, the first- and second-fractions containing the optical isomers were collected. However, optically active seleninic acids were completely racemized during the concentration of the solution. Therefore, the specific rotation and CD spectra of the enantiomers were measured in the eluate; the concentration was calculated based on the comparison of UV spectra with those of authentic racemic samples. This



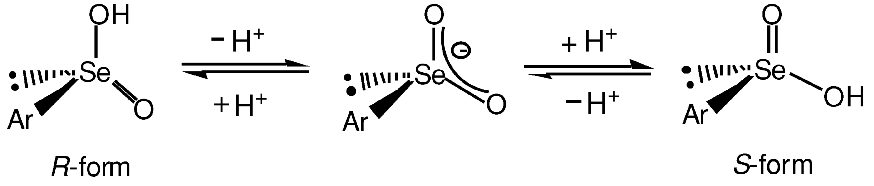
SCHEME 6

is the first example of the optical resolution of areneseleninic acids. We have succeeded in optical resolution of areneselenicic acids by means of chromatography using a chiral column but the optical isomer could not be isolated as a crystal, and therefore, the absolute configuration could not be determined by X-ray crystallographic analysis.

Areneseleninic acid **23** with a crown-ether ring, which is expected to be stabilized by intramolecular hydrogen bond and/or steric effect, was prepared, and chiral crysytals of each enantiomer of **23** were obtained by chiral crystallization from ether, respectively. The CD spectra of each enantiomer of **23** exhibited positive and negative cotton effects in the solid state (KBr disk) around 260 nm, respectively. The absolute configuration of **23**, which showed a negative Cotton effect, was determined to be *S*-form by X-ray crystallographic analysis. Thus, the absolute configuration of the optically active areneseleninic acids **18–22** with a negative cotton effect at around 250 nm was estimated to be *S* and that of the optical isomers with a positive cotton effect in the same region is *R*.

We have also succeeded in isolating enantiomeric pure methaneseleninic acid **24** as the single crystals by chiral crystallization, determined the absolute configuration by X-ray crystallographic analysis, and clarified the relationship between the CD spectra in solid state and the absolute configuration. The optically pure seleninic acid **24** was stable toward racemization in crystalline state but quite unstable in solvents; i.e., **24** was completely racemized within 5 s in chloroform.

A mechanism for the racemization of arene- and methaneseleninic acids in solutions is proposed *via* the corresponding seleninate anion (Scheme 7) with the extrusion of a proton in the presence of a trace



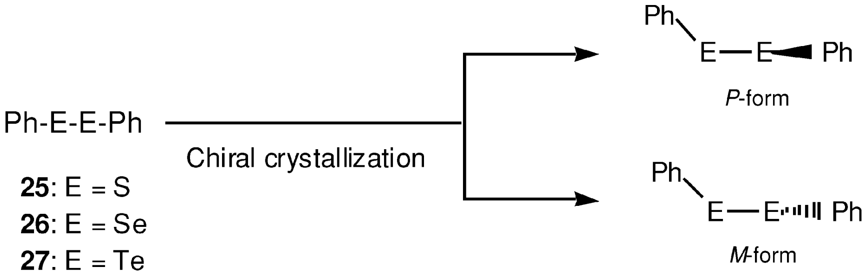
SCHEME 7

amount of water remaining in the solvent in spite of careful removal of water from the solvent.

Optically Active Diphenyl Dichalcogenides[53]

Disulfides are well known to show skewed structures in the crystalline and gas phase, except for disulfides with congested substituents, and many theoretical studies have indicated that such skewed geometries are global minima. Similar findings have been reported for diselenides and ditellurides. The skewed geometries of dichalcogenides have been explained on the basis of a gauche effect proposed by Wolfe. Therefore, dichalcogenides can be considered to exist in chiral *P*- and *M*-helical forms. However, the energy barriers for racemization by rotation of chalcogen-chalcogen bonds are not high enough, as estimated by theroretical and dynamic NMR studies, to isolate the optical isomers. Thus, racemization between *P*- and *M*-helical forms readily occurs in solution. On the other hand, the crystal structure of diphenyl disulfide, diselenide, and ditelluride have been determined by X-ray crystallographic analysis; all are orthorhombic and belong to the chiral space group $P2_12_12_1$.[58] The composition of one unit cell for diphenyl disulfide shows that the chirality of the crystal is due to the skewed structure of the diphenyl moiety, although the report does not mention the chirality. We have succeeded in the first isolation of simple optically pure dichalcogenides (diphenyl disulfide, diselenide, and ditelluride) in bulk without any configurational restriction by means of chiral crystallization. We have also clarified the relationship between the absolute configuration and the CD spectra in the crystalline state.

Recrystallization of diphenyl disulfide (**25**) from hot ethanol gave colorless needles in 74% recovery yield. The CD spectrum of the crystal (KBr disk made from a single crystal) showed a negative first Cotton effect at around 330 nm. However, the Cotton effect was not observed for the disulfide in solution due to racemization by the rapid rotation of the sulfur-sulfur bond. Facile racemization of diphenyl dichalcogenides in solution also has been supported by theoretical studies; energy barriers for racemization by rotation of diphenyl disulfide, diselenide, and ditelluride were calculated to be 8.6, 8.2, and 5.3 kcal mol^{-1} through the *cisoid* geometry and 5.4, 5.2, and 3.7 kcal mol^{-1} through the *transoid* geometry, respectively. When nine other pieces of crystal obtained from the same pot were subjected to measurement of the CD spectra in a similar manner, all of the crystals showed a negative first cotton effect in the same region. The result indicates that all of the crystals obtained in the pot are composed of the same stereoisomer of **25**. When recrystallization was repeated nine additional times, crystals that showed a positive cotton effect in the corresponding region were obtained in two cases, and the crystals in the same pot were composed of one stereoisomer on the basis of measurements of the CD spectra of 10 crystals selected at random. In crystallization, this phenomenon does not depend on the recovery yield (even over 50% yield), which means that chiral crystallization occurs in the pot.



SCHEME 8

Similarly, in the case of diphenyl diselenide (**26**) (Scheme 8), crystals showing a positive cotton effect and a negative cotton effect at around 375 nm in their CD spectra, respectively, were obtained, and crystals in the same pot were composed of a single stereoisomer in all the cases. However, in the case of diphenyl ditelluride (**27**), some of the crystals that precipitated from hot petroleum ether in a pot showed a positive first cotton effect at around 400 nm while others showed a negative cotton effect in the corresponding region, although sometimes crystals of only stereoisomer were obtained. When a single crystal of **27** which showed a positive first cotton effect was seeded in a petroleum ether solution of **27** in recrystallization, 10 pieces of crystal in the resulting precipitate all showed a positive cotton effect. Similarly, seeding of a crystal with a negative first cotton effect gave crystals with a negative cotton effect. These results mean that seeding a crystal with a known absolute configuration in crystallization can control the stereochemistry of chiral crystallization. This phenomenon was also observed in the case of **25** and **26**.

The absolute configuration of chiral **25** with a negative cotton effect was determined by X-ray crystallographic analysis at 120 K. As a result, **25** a negative first cotton effect in its CD spectrum was found to have a *P*-helical form. On the basis of the similarities of the first cotton effects of **26** and **27** with that of **25**, the structure of **26** and **27** with a negative first cotton effect can be assigned to be the *P*-form and with a positive cotton effect is the *M*-form. The relationship between the absolute configuration and CD spectra is summarized in Table II.

TABLE II Relationship Between Absolute Configuration and CD Spectra (KBr Disk) of Diphenyl Dichalcogenides

	Wave length/nm			
Compound	*P*-form		*M*-form	
25	−330	−270	+330	+270
26	−375	−265	+375	+265
27	−400	−290	+400	+290

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