Isolation and Stereochemistry of Optically Active Selenonium Imides

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Optical resolution of racemic diaryl selenonium-*N*-toluene-4′-sulfonimides (*rac*-**1a**−**d**) by liquid chromatography using an optically active column yielded optically pure selenonium imides. The absolute configuration around the selenium atom of (−)-2,4,6-tri-*tert*-butyldiphenylselenonium *N*-toluene-4′-sulfonimide [(−)-**1a**] was determined to be *S* by X-ray crystallographic analysis, and those of the other optically active selenonium imides were determined on the basis of their specific rotations and CD spectra. The kinetics of racemization by pyramidal inversion of the optically active selenonium imides (+)- and (−)-**1b** and **1d** were studied. The results indicated that the activation energy for the racemization of optically active selenonium imides was greater than those for sulfonium imides.

Introduction

Recently, our studies have focused on the synthesis and stereochemistry of optically active selenium and tellurium compounds.[1] Since selenium and tellurium are homologous to sulfur, many optically active sulfur compounds have been synthesized,[2,3] some of which have also been used for asymmetric synthesis.[4,5] However, until recently, there have been few studies on optically active selenium and tellurium compounds.[6−9] We have previously reported the synthesis and stereochemistry of optically active tricoordinated tetravalent selenium and tellurium compounds, such as selenoxides,[10,11] selenonium ylides,[12] selenonium salts,[13] telluronium ylides,[14] telluronium salts,[15] and telluroxides.[16] However, while selenonium imides are also tricoordinated tetravalent selenium compounds, there have been few reports on optically active selenonium imides. The first synthesis of an optically active selenonium imide was reported by Krasnov et al. in 1981,[17] but the specific rotation was very low, and the optical purity and absolute configuration were not determined. In 1994, we succeeded in isolating a diastereomerically pure selenonium imide by optical resolution of a diastereomeric selenonium imide with a *l*-menthyloxycarbonyl group as the chiral source and determined the absolute configuration by comparing the CD spectra of the optically active selenonium imide with those of sulfoxides, sulfonium imides, and selenoxides of known absolute configuration.[18] However, an attempt to transform the diastereomerically pure selenonium imide into the selenonium imide enantiomer by transesterification of the *l*-menthyl group into an achiral one failed. Later, optically active selenonium imide enantiomers were obtained in 80% ee by reacting optically pure selenoxide with toluene-*p*-sulfonamide[19] or in 20−36% ee by catalytic asymmetric imidation of selenide.[20] However,

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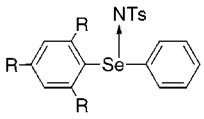
enantiomerically pure selenonium imides have not yet been isolated. We previously reported the optical resolution of racemic selenoxides[11] and telluroxides[16] into their enantiomers using liquid chromatography by means of optically active columns. In the present study, we succeeded in isolating enantiomerically pure diaryl selenonium imides **1a**−**d** by optical resolution using an optically active column. The absolute configurations of the optically active selenonium imides were determined by X-ray crystallographic analysis and their CD spectra. We also studied the kinetics of thermal racemization by pyramidal inversion of the selenonium imides.

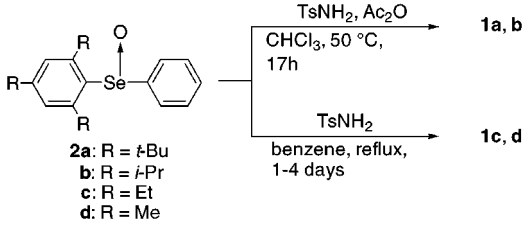


1a: R = *t*-Bu
b: R = *i*-Pr
c: R = Et
d: R = Me

Results and Discussion

Preparation of Racemic Selenonium Imides. Selenonium imides have been reported to be synthesized by reacting the corresponding selenoxide with sulfonamide in chloroform.[21] However, racemic 2,4,6-tri-*tert*-butyldiphenyl selenonium-*N*-toluene-4′-sulfonimide (*rac*-**1a**) and 2,4,6-triisopropyldiphenyl selenonium-*N*-toluene-4′-sulfonimide (*rac*-**1b**), both of which have bulky substituents, could not be obtained under these conditions.

Scheme 1. Preparation of Racemic Aryl Phenyl Selenonium Imides 1a−d



2a: R = *t*-Bu
b: R = *i*-Pr
c: R = Et
d: R = Me

Selenonium imides **1a** and **1b** were finally synthesized in yields of 86 and 91%, respectively, by reacting the corresponding selenoxides **2a** and **2b** with toluene-*p*-sulfonamide in the presence of acetic anhydride in chloroform (Scheme 1). 2,4,6-Triethyldiphenylselenonium *N*-toluene-4′-sulfonimide (*rac*-**1c**) and mesityl phenylselenonium *N*-toluene-4′-sulfonimide (*rac*-**1d**) were synthesized in quantitative yields by reacting the corresponding selenoxides **2c** and **2d** with toluene-*p*-sulfonamide in benzene. Selenonium imides **1a**−**d** were stable in the solid state and also in chloroform and methanol solution at room temperature, whereas diphenylselenonium *N*-toluene-4′-sulfonimide is reportedly moisture-sensitive.[21] These results mean that substituents at the ortho position of the aryl group, even a methyl group, are effective in preventing hydrolysis.

Optical Resolution of Selenonium Imides. Optical resolution of racemic selenonium imide *rac*-**1a** was attempted by high-performance liquid chromatography (HPLC) on an analytical scale using an optically active column (250 × 4.6 mm) packed with amylose carbamate derivative/silica gel. Selenonium imide *rac*-**1a** was resolved into two peaks that corresponded to the enantiomers (Figure 1). Similarly, selenonium imides *rac*-**1b**−**d** could also be separated into their enantiomers. Selenonium imide *rac*-**1a** showed the best peak resolution among **1a**−**d**, and the Rs value, which indicates the degree of peak resolution for the two enantiomers, was 1.38, as shown in Table 1. Selenonium imides **1b** and **1d** showed moderate peak resolution, with Rs values of 1.01 and 1.05, respectively. However, peak resolution of **1c** was not effective, and the Rs value was 0.71. Next, we attempted the optical resolution of racemic selenonium imide *rac*-**1a** on a preparative scale using a larger column (250 × 10 mm). Repeated resolution of the first and second fractions gave optically pure enantiomers, the optical purities of which were determined using the analytical column. The first eluted enantiomer had a positive specific rotation [(+)-**1a**; $[\alpha]_D$ +134.5 (*c* 0.57, $CHCl_3$)], and the second eluted enantiomer had a negative specific rotation [(−)-**1a**; $[\alpha]_D$ −131.9 (*c* 0.48, $CHCl_3$)]. Similarly, optically pure selenonium imides (+)-**1b**−**d**, (−)-**1b**, and (−)-**1d** were isolated, whereas optically active selenonium imide (−)-**1c** was obtained in 91% ee, perhaps due to tailing of the first eluted enantiomer.

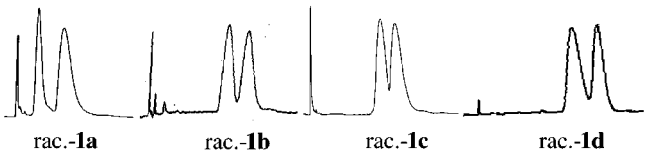
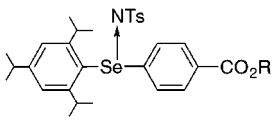


Figure 1. Chromatographic resolution of racemic aryl phenyl selenonium imides **1a**−**d** by means of HPLC using an optically active column.

Absolute Configuration of Selenonium Imides. The absolute configuration of optically active selenonium imide (−)-**1a** was determined by X-ray crystallographic analysis.[22] The ORTEP drawing of selenonium imide (−)-**1a** depicted an *S* configuration around the selenium atom, as shown in Figure 2. Therefore, the configuration around the selenium atom in (+)-**1a** was determined to be *R*. The CD spectrum of selenonium imide (*S*)-(−)-**1a** showed a negative first Cotton effect at around 287 nm in methanol, and that of selenonium imide (*R*)-(+)-**1a** showed a positive one in the same region, as shown in Figure 3. Optically active selenonium imides (−)-**1b**−**d** also showed negative Cotton effects at around 294 nm. Therefore, the absolute configurations of optically active selenonium imides with a negative specific rotation (−)-**1b**−**d** were assigned to be *S* by comparison of their CD spectra with that of selenonium imide (*S*)-(−)-**1a**. We previously reported the isolation of diastereoisomeric selenonium imide (−)-**3**[18] and enantioisomeric selenonium imide (−)-**4**,[19] and their absolute configurations have been assigned to be *S*, which showed CD spectra similar to those of (*S*)-(−)-**1a**−**d**.



$(S)_{Se}$-$(-)_{Se}$-**3**: R = *l*-menthyl
(*S*)-(−)-**4**: R = Me

The (*R*)-selenonium imides (*R*)-(+)-**1a**−**d** with positive specific rotations were eluted faster than (*S*)-(−)-**1a**−**d**

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Table 1. Chromatographic Resolution of Selenonium Imides 1a−d

		HPLC properties[b]			first enantiomer		second enantiomer	
selenonium imide	EtOH[a] (%)	k_1' [c]	α[d]	Rs[e]	$[\alpha]_D$ ($CHCl_3$)[f]	ee (%)[g]	$[\alpha]_D$ ($CHCl_3$)	ee (%)[g]
1a	10	1.79	2.25	1.38	+134.5 (c 0.57)	100	−131.9 (c 0.48)	100
1b	5	9.41	1.26	1.01	+167.1 (c 0.18)	100	−165.8 (c 0.19)	100
1c	10	8.98	1.21	0.71	+168.7 (c 0.63)	100	−146.0 (c 0.22)	91
1d	20	6.23	1.26	1.05	+199.6 (c 0.50)	100	−196.7 (c 0.46)	100

[a] The volume percentage of ethanol in hexane used as mobile phase. [b] Daicel CHIRALPAK AS column (250 × 4.6 mm) was used. [c] k_1' is the capacity ratio for the initially eluted enantiomer. [d] The chromatographic separability factor of the enantiomers, α, is the ratio of capacity ratios of two enantiomers. [e] Rs is the peak resolution of the two enantiomers. [f] The specific rotations were taken at 25−27 °C. [g] The optical purity was determined by HPLC analysis.

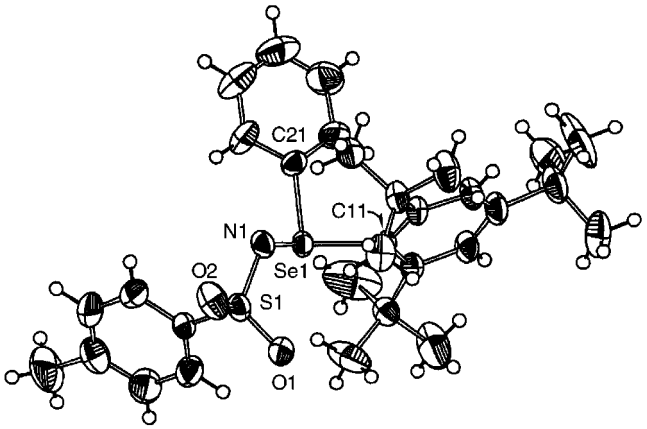


Figure 2. Crystal structure of (−)-**1a**. Absolute structure parameter: −0.008(9). Selected bond lengths (Å), bond angles (deg): Se(1)−N(1), 1.791(3); Se(1)−C(11), 1.985(3); Se(1)−C(21), 1.932(4); N(1)−Se(1)-C(11), 116.66(14); N(1)−Se(1)-C(21), 96.63(16); C(11)−Se(1)-C(21), 96.95(15). Displacement ellipsoids are shown at the 50% probability level; H atoms are drawn as small circles of arbitrary radii.

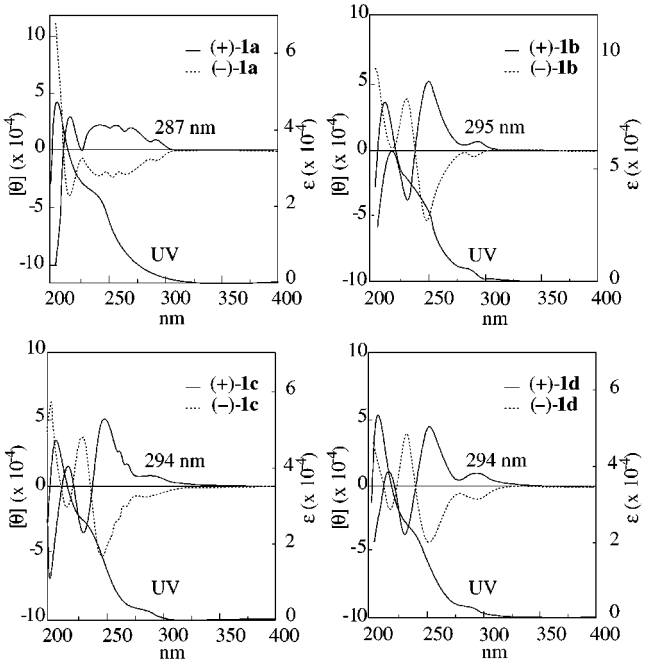


Figure 3. CD and UV spectra of optically active selenonium imides (+)- and (−)-**1a**−**d** in methanol.

in HPLC analysis. The relationship among the specific rotation, Cotton effect, and absolute configuration is summarized in Table 2.

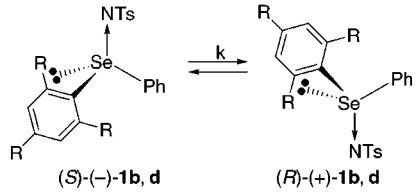
Racemization of Optically Active Selenonium Imides. The rate of racemization by pyramidal inversion

Table 2. Relationship among the Specific Rotation, CD Spectrum, and Absolute Configuration of Optically Active Selenonium Imides 1a−d

	first enantiomer			second enantiomer		
selenonium imide	sign of specific rotation[a]	sign of Cotton effect[b]	absolute config	sign of specific rotation	sign of Cotton effect[b]	absolute config
1a	+	+	*R*	−	−	*S*
1b	+	+	*R*	−	−	*S*
1c	+	+	*R*	−	−	*S*
1d	+	+	*R*	−	−	*S*

[a] $[\alpha]_D$ and $[\alpha]_{435}$ in chloroform. [b] The first Cotton effect at around 290 nm in methanol on the CD spectrum.

of the optically active selenonium imide was studied by heating a toluene solution of enantiomeric excess selenonium imide (*S*)-(−)-**1b** in a sealed tube. The racemization of selenonium imides (−)-**1b** and **1d** was observed at 130−145 °C, whereas that of (−)-4-chlorophenylmethylsulfonium *N*-toluene-4′-sulfonimide [(−)-**5**][23,24] and (−)-2-methoxydiphenyl sulfonium-*N*-toluene-4′-sulfonimide [(−)-**6**][23,24] was observed at lower temperature. The decrease in the optical purity of (*S*)-(−)-**1b**, as determined by HPLC analysis, showed a good linear relationship with the first-order rate plots at 130−145 °C. No difference was found in the ^{1}H NMR spectra of (−)-**1b** before and after the kinetic studies. These results indicate that the decrease in optical purity depends on racemization, and there is no thermal decomposition or hydrolysis under these conditions. Similarly, the rates of racemization of (*R*)-(+)-**1b** and (*R*)-(+)- and (*S*)-(−)-**1d** were also studied.



These results are summarized in Table 3 together with those of diastereoisomeric selenonium imides (+)-**3**[25] and sulfonium imides (−)-**5** and (−)-**6**. The results show that the selenonium imides are more stable than the sulfonium imides for racemization; i.e., the activation energies of the selenonium imides **1b** and **1d** are ca. 5 kcal/mol higher than that of the sulfonium imide (−)-**5**. There are

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Table 3. First-Order Rate Constants and Activation Parameters for the Racemization of Selenonium Imides 1b and 1d in Toluene

compd	T (°C)	$k \times 10^6$ (s^{-1})	E_a (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal K^{-1} mol^{-1})
(*R*)-(+)-**1b**	130	3.88			
	135	7.37			
	140	10.7	34.3	33.5	−0.7
	145	18.9			
(*S*)-(−)-**1b**	130	3.92			
	135	7.10			
	140	10.2	34.9	34.1	0.7
	145	19.8			
(*R*)-(+)-**1d**	130	1.93			
	135	3.52			
	140	5.55	34.8	34.0	−1.0
	145	9.37			
(*S*)-(−)-**1d**	130	1.95			
	135	3.43			
	140	5.57	34.4	33.6	−1.9
	145	9.21			
$(R)_{Se}$-$(+)_{Se}$-**3**	140	10.1	31.8	30.9	−7.4
(−)-**5**[a]	100	5.30	28.6	27.9	−3.6
(−)-**6**[b]	75	3.72			

[a] In benzene. [b] In $CHCl_3$.

at least two possible explanations for these results, one based on valence shell electron-pair repulsion and the other based on instability of the transition state of the selenonium imide, which requires an sp^2-hybridized orbital on the chalcogen atom. According to the former explanation, valence shell electron-pair repulsion in the selenonium imides is less than that in sulfonium imides since the C−Se bond is longer than the C−S bond and/or selenium is less electronegative than sulfur. Therefore, the electrons in the C−Se bond lie further from the selenium atom than those in the C−S bond lie from the sulfur atom. Accordingly, a higher reaction temperature is required for the pyramidal inversion of the selenonium imides than is needed for that of sulfonium imides.

Conclusions

We succeeded in isolating enantiomerically pure selenonium imides by optical resolution using an optically active column. The absolute configuration of selenonium imide (−)-**1a** was determined to be *S* by X-ray crystallographic analysis, and the absolute configuration of optically active selenonium imides (−)-**1b**−**d** was determined to be *S* by comparing the CD spectra of (−)-**1b**−**d** with that of (*S*)−(−)-**1a**. In the kinetic studies of selenonium imides **1b** and **1d**, racemization of the optically active selenonium imides by pyramidal inversion was observed at higher temperature than that of sulfonium imides. This study showed that the activation energy for the pyramidal inversion of selenonium imides is greater than those for sulfonium imides.

Experimental Section

General Methods. Benzene was distilled from sodium metal before use. Chloroform, hexane, and toluene were distilled from calcium hydride before use. Methanol and ethanol were distilled from magnesium cake and stored with 3A molecular sieves under nitrogen. TLC was performed with Merck Art. 5554 DC-Alufolien Kieselgel 60 F_{254}. Column chromatography was performed with Merck 7734 Kieselgel 60.

Materials. Aryl phenyl selenoxides (**2a**−**d**) were prepared according to the procedures in the literatures.[5,26]

2,4,6-Tri-*tert*-butyldiphenylselenonium *N*-Toluene-4′-sulfonimide (*rac*-1a). A chloroform solution (25 mL) of 2,4,6-tri-*tert*-butyldiphenyl selenoxide (**2a**) (2.1 g, 5.0 mmol), toluene-*p*-sulfonamide (0.9 g, 5.0 mmol), and acetic anhydride (0.7 g, 6.5 mmol) was stirred at 50 °C for 17 h. The solution was concentrated under reduced pressure followed by purification by silica gel column chromatography (eluent, dichloromethane/methanol 100:6) to give selenonium imide *rac*-**1a** (2.6 g, 91%): mp 136−138 °C; IR (KBr) 2956, 1276, 1135, 918, 697, 650 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.23 (9H, brs), 1.35 (9H, s), 1.59 (9H, brs), 2.35 (3H, s), 6.99−7.02 (2H, m), 7.17 and 7.87 (4H, ABq, J = 8.0 Hz), 7.26−7.36 (3H, m), 7.56 (2H, brs); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 31.1, 32.8, 34.3, 35.4, 123.0, 126.4, 127.1, 128.9, 129.4, 130.5, 131.7, 139.8, 140.9, 143.1, 154.5, 155.2; FAB-MS (3-nitrobenzyl alcohol) m/z 572 (^{80}Se, $M^+ + H$), 570 (^{78}Se, $M^+ + H$), 401; UV (MeOH) λ_{max} 239 (sh, ϵ 2.42 × 10^4), 206 (ϵ 4.88 × 10^4) nm. Anal. Calcd for $C_{31}H_{41}NO_2SSe$: C, 65.24; H, 7.24; N, 2.45. Found: C, 64.92; H, 7.19; N, 2.19.

2,4,6-Triisopropyldiphenylselenonium *N*-Toluene-4′-sulfonimide (*rac*-1b). A chloroform solution (25 mL) of 2,4,6-triisopropyldiphenyl selenoxide (**2b**) (1.1 g, 3.0 mmol), toluene-*p*-sulfonamide (0.5 g, 3.0 mmol), and acetic anhydride (0.5 g, 4.5 mmol) was stirred at 50 °C for 17 h. The solution was concentrated under reduced pressure followed by purification by silica gel column chromatography (eluent, dichloromethane/methanol 100:6) to give selenonium imide *rac*-**1b** (1.4 g, 86%): mp 171−173 °C; IR (KBr) 2965, 1272, 1132, 898, 688, 650 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.84 (6H, brs), 1.22 (6H, d, J = 7.0 Hz), 1.25 (3H, d, J = 7.0 Hz), 1.27 (3H, d, J = 7.0 Hz), 2.32 (3H, s), 2.89 (1H, hep., J = 7.0 Hz), 3.45 (2H, hep., J = 7.0 Hz), 7.05 (2H, s), 7.12 and 7.77 (4H, ABq, J = 8.0 Hz), 7.40−7.50 (3H, m), 7.50−7.70 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 23.1, 23.6, 25.2, 31.4, 34.3, 124.1, 126.1, 127.3, 128.9, 129.9, 130.3, 131.0, 135.5, 140.8, 143.1, 152.3, 154.3; MS (EI) m/z 529 (^{80}Se, M^+), 527 (^{78}Se, M^+), 359, 197, 119, 91; UV (MeOH) λ_{max} 286 (sh, ϵ 4.79 × 10^3), 234 (sh, ϵ 3.99 × 10^4), 209 (ϵ 7.66 × 10^4) nm. Anal. Calcd for $C_{28}H_{35}NO_2SSe$: C, 63.62; H, 6.67; N, 2.65. Found: C, 63.28; H, 6.61; N, 2.77.

2,4,6-Triethyldiphenylselenonium *N*-Toluene-4′-sulfonimide (*rac*-1c). A benzene solution (25 mL) of 2,4,6-triethyldiphenylselenoxide (**2c**) (3.3 g, 10 mmol) and toluene-*p*-sulfonamide (1.7 g, 10 mmol) was refluxed for 4 days on a Dean−Stark condenser equipped with 3A molecular sieves. The solution was concentrated under reduced pressure followed by purification by silica gel column chromatography (eluent, dichloromethane/methanol 100:6) to give selenonium imide *rac*-**1c** (4.8 g, quant): colorless viscous oil; IR (neat) 2971, 1265, 1133, 919, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.97 (6H, t, J = 7.6 Hz), 1.23 (3H, t, J = 7.6 Hz), 2.31 (3H, s), 2.62 (2H, q, J = 7.6 Hz), 2.66 (2H, qd, J = 7.6, 14.8 Hz), 2.84 (2H, qd, J = 7.6, 14.8 Hz), 6.93 (2H, s), 7.08 and 7.73 (4H, ABq, J = 8.1 Hz), 7.45−7.47 (3H, m), 7.59−7.62 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.0, 15.8, 21.3, 27.1, 28.6, 126.0, 127.4, 128.3, 128.8, 129.7, 130.0, 131.1, 134.5, 140.8, 142.8, 147.9, 149.6; MS (EI) m/z 487 (^{80}Se, M^+), 485 (^{78}Se, M^+), 320, 178, 128, 92; UV (MeOH) λ_{max} 286.4 (sh, ϵ 2.52 × 10^3), 232.6 (sh, ϵ 2.41 × 10^4), 206.8 (ϵ 4.39 × 10^4) nm. Anal. Calcd for $C_{25}H_{29}NO_2SSe$: C, 61.72; H, 6.01; N, 2.88. Found: C, 61.58; H, 6.01; N, 2.86.

2,4,6-Mesitylphenylselenonium *N*-Toluene-4′-sulfonimide (*rac*-1d). A benzene solution (25 mL) of 2,4,6-mesitylphenylselenoxide (**2d**) (2.9 g, 10 mmol) and toluene-*p*-sulfonamide (1.7 g, 10 mmol) was refluxed for 1 day on a Dean−Stark condenser equipped with 3A molecular sieves. The solution was concentrated under reduced pressure followed by purification by silica gel column chromatography (eluent, dichloromethane/methanol 100:6) to give selenonium imide *rac*-**1d** (4.5 g, quant): mp 122−123 °C; IR (KBr) 2960, 1276, 1140, 919, 684, 650 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.29 (3H, s), 2.31 (6H, s), 2.32 (3H, s), 6.85 (2H, s), 7.09 and 7.75 (4H, ABq, J = 8.0 Hz), 7.43−7.50 (3H, m), 7.56−7.61 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 21.1, 21.3, 125.9, 127.4, 128.9, 129.8, 130.0, 131.0, 131.2, 133.2, 140.9, 141.7, 142.8,

(26) Kobayashi, M.; Ohkubo, H.; Shimizu, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 503.

143.3; MS (EI) *m/z* 445 (^{80}Se, M$^+$), 443 (^{78}Se, M$^+$), 276, 194, 119, 91; UV (MeOH) λ_{max} 286.2 (sh, ϵ 3.66 × 10^3), 235.0 (sh, ϵ 2.38 × 10^4), 205.8 (ϵ 5.30 × 10^4) nm. Anal. Calcd. for $C_{22}H_{23}NO_2SSe$: C, 59.45; H, 5.22; N, 3.15. Found: C, 59.51; H, 5.28; N, 2.86.

HPLC Analysis of Selenonium Imides 1a−d by Using Optically Active Column. The enantiomeric excess (ee) for each optically active selenonium imide **1a**−**d** was determined by HPLC with an optically active column. The determination by HPLC was performed on a Daicel CHIRALPAK AS (250 × 4.6 mm) column packed with amylose carbamate derivative/silica gel. Hexane containing 5−25 vol % ethanol was used as the mobile phase at a flow rate of 1.0 mL min^{-1}.

Optical Resolution of Selenonium Imides *rac*-1a−d at Preparative Scale. Typically, the racemic selenonium imide (50 mg) was dissolved in dichloromethane (0.1 mL) followed by dilution in a eluent (0.5 mL). This solution was charged to the column (Daicel CHIRALPAK AS; 250 × 10 mm) and eluted with hexane containing 10 (for **1a**), 5 (for **1b**), 15 (for **1c**), and 20 (for **1d**) vol %, respectively, of ethanol at flow rate of 1.0 mL min^{-1}. Finally, optically pure selenonium imides were obtained at ca. 20 mg from the first eluent by repeated resolution (1−2 times) and at ca. 15 mg from the second eluent by repeated resolution (usually, 2−3 times), respectively.

Compound (*R*)-(+)-1a: 100% ee; mp 163−164 °C; IR (KBr) 2955, 1277, 1133, 922, 694, 645 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (9H, brs), 1.35 (9H, s), 1.59 (9H, brs), 2.35 (3H, s), 6.99−7.02 (2H, m), 7.17 and 7.87 (4H, ABq, J = 8.0 Hz), 7.26−7.36 (3H, m), 7.57 (2H, brs); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 31.0, 32.8, 34.3, 35.4, 123.0, 126.3, 127.1, 128.9, 129.4, 130.5, 131.7, 139.8, 140.9, 143.0, 154.5, 155.2; FAB-MS (3-nitrobenzyl alcohol) *m/z* 572 (^{80}Se, M$^+$ + H), 570 (^{78}Se, M$^+$ + H), 401; $[\alpha]_D$ +134.5 (c 0.57, $CHCl_3$), $[\alpha]_{435}$ +310.6 (c 0.54, $CHCl_3$); CD (MeOH) 286.4 ([θ] 1.18 × 10^4), 245.4 ([θ] 1.98 × 10^4), 232.0 ([θ] 3.21 × 10^3), 220.8 ([θ] 2.99 × 10^4), 204.0 ([θ] −9.31 × 10^4) nm. Anal. Calcd for $C_{31}H_{41}NO_2SSe$: C, 65.24; H, 7.24; N, 2.45. Found: C, 64.91; H, 7.14; N, 2.54.

Compound (*S*)-(−)-1a: 100% ee; mp 163−164 °C; IR (KBr) 2960, 1275, 1134, 920, 695, 630 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (9H, brs), 1.35 (9H, s), 1.59 (9H, brs), 2.35 (3H, s), 6.99−7.02 (2H, m), 7.17 and 7.87 (4H, ABq, J = 8.0 Hz), 7.27−7.36 (3H, m), 7.57 (2H, brs); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 31.1, 32.8, 34.5, 35.4, 129.8, 126.3, 127.1, 128.9, 129.4, 130.5, 131.7, 139.8, 140.9, 143.0, 154.5, 155.2; FAB-MS (3-nitrobenzyl alcohol) *m/z* 572 (^{80}Se, M$^+$ + H), 570 (^{78}Se, M$^+$ + H), 401; $[\alpha]_D$ −131.9 (c 0.48, $CHCl_3$), $[\alpha]_{435}$ −308.8 (c 0.48, $CHCl_3$); CD (MeOH) 286.6 ([θ] 1.22 × 10^4), 245.6 ([θ] −2.10 × 10^4), 230.4 ([θ] −3.85 × 10^3), 220.2 ([θ] −3.30 × 10^4), 206.0 ([θ] 9.03 × 10^4) nm. Anal. Calcd for $C_{31}H_{41}NO_2SSe$: C, 65.24; H, 7.24; N, 2.45. Found: C, 65.02; H, 7.15; N, 2.20.

Compound (*R*)-(+)-1b: 100% ee; mp 164−166 °C; IR (KBr) 2963, 1271, 1135, 903, 690, 645 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84 (6H, brs), 1.22 (6H, d, J = 7.0 Hz), 1.25 (3H, d, J = 7.0 Hz), 1.27 (3H, d, J = 7.0 Hz), 2.32 (3H, s), 2.89 (1H, hep., J = 7.0 Hz), 3.45 (2H, hep., J = 7.0 Hz), 7.05 (2H, s), 7.12 and 7.77 (4H, ABq, J = 8.0 Hz), 7.40−7.50 (3H, m), 7.50−7.70 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 23.1, 23.6, 25.2, 31.4, 34.3, 124.1, 126.1, 127.3, 128.9, 129.9, 130.3, 131.0, 135.5, 140.8, 143.1, 152.3, 154.3; MS (EI) *m/z* 529 (^{80}Se, M$^+$), 527 (^{78}Se, M$^+$), 359, 197, 119, 91; $[\alpha]_D$ +167.1 (c 0.18, $CHCl_3$), $[\alpha]_{435}$ +337.4 (c 0.18, $CHCl_3$); CD (MeOH) 295.8 ([θ] 4.61 × 10^3), 252.2 ([θ] 5.11 × 10^4), 233.4 ([θ] −3.77 × 10^4), 219.0 ([θ] −1.50 × 10^3), 206.4 ([θ] −6.06 × 10^4) nm. Anal. Calcd for $C_{28}H_{35}NO_2SSe$: C, 63.62; H, 6.67; N, 2.65. Found: C, 63.24; H, 6.64; N, 2.80.

Compound (*S*)-(−)-1b: 100% ee; mp 167−169 °C; IR (KBr) 2960, 1270, 1140, 900, 688, 651 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84 (6H, brs), 1.22 (6H, d, J = 7.0 Hz), 1.25 (3H, d, J = 7.0 Hz), 1.27 (3H, d, J = 7.0 Hz), 2.32 (3H, s), 2.89 (1H, hep., J = 7.0 Hz), 3.45 (2H, hep., J = 7.0 Hz), 7.05 (2H, s), 7.12 and 7.77 (4H, ABq, J = 8.0 Hz), 7.40−7.50 (3H, m), 7.50−7.70 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 23.1, 23.6, 25.2, 31.4, 34.3, 124.1, 126.1, 127.3, 128.9, 129.9, 130.3, 131.0, 135.5, 140.8, 143.1, 152.3, 154.3; MS (EI) *m/z* 529 (^{80}Se, M$^+$), 527 (^{78}Se, M$^+$), 359, 197, 119, 91; $[\alpha]_D$ −165.8 (c 0.19, $CHCl_3$), $[\alpha]_{435}$ −338.3 (c 0.19, $CHCl_3$); CD (MeOH) 293.4 ([θ] −4.89 × 10^3), 250.8 ([θ] −5.41 × 10^4), 232.2 ([θ] 3.74 × 10^4), 220.0 ([θ] −8.98 × 10^2), 204.8 ([θ] 6.15 × 10^4) nm. Anal. Calcd for $C_{28}H_{35}NO_2SSe$: C, 63.62; H, 6.67; N, 2.65. Found: C, 63.35; H, 6.53; N, 2.61.

Compound (*R*)-(+)-1c: 100% ee; colorless viscous oil; IR (neat) 2968, 1276, 1133, 921, 690 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (6H, t, J = 7.6 Hz), 1.24 (3H, t, J = 7.6 Hz), 2.31 (3H, s), 2.62 (2H, q, J = 7.6 Hz), 2.67 (2H, qd, J = 7.6, 14.8 Hz), 2.84 (2H, qd, J = 7.6, 14.8 Hz), 6.93 (2H, s), 7.08 and 7.73 (4H, ABq, J = 8.1 Hz), 7.44−7.47 (3H, m), 7.60−7.62 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.0, 15.8, 21.3, 27.1, 28.6, 126.1, 127.4, 128.3, 128.9, 129.8, 130.0, 131.1, 134.6, 140.8, 142.8, 147.9, 149.7; MS (EI) *m/z* 487 (^{80}Se, M$^+$), 485 (^{78}Se, M$^+$), 318, 176, 132, 91; $[\alpha]_D$ +168.7 (c 0.63, $CHCl_3$), $[\alpha]_{435}$ +384.2 (c 0.63, $CHCl_3$); CD (MeOH) 293.6 ([θ] 5.48 × 10^3), 250.6 ([θ] 4.07 × 10^4), 233.8 ([θ] −2.91 × 10^4), 220.1 ([θ] 1.18 × 10^4), 204.2 ([θ] −5.83 × 10^4) nm. Anal. Calcd for $C_{25}H_{29}NO_2SSe$: C, 61.72; H, 6.01; N, 2.88. Found: C, 61.47; H, 6.02; N, 2.93.

Compound (*S*)-(−)-1c: 91% ee; colorless viscous oil; IR (neat) 2970, 1276, 1132, 919, 690 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (6H, t, J = 7.6 Hz), 1.24 (3H, t, J = 7.6 Hz), 2.31 (3H, s), 2.62 (2H, q, J = 7.6 Hz), 2.67 (2H, qd, J = 7.6, 14.8 Hz), 2.84 (2H, qd, J = 7.6, 14.8 Hz), 6.93 (2H, s), 7.09 and 7.73 (4H, ABq, J = 8.1 Hz), 7.45−7.47 (3H, m), 7.60−7.62 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.0, 15.8, 21.3, 27.1, 28.6, 126.1, 127.4, 128.3, 128.9, 129.8, 130.0, 131.1, 134.6, 140.8, 142.8, 147.9, 149.7; MS (EI) *m/z* 487 (^{80}Se, M$^+$), 485 (^{78}Se, M$^+$), 318, 176, 131, 91; $[\alpha]_D$ −146.0 (c 0.22, $CHCl_3$), $[\alpha]_{435}$ −344.6 (c 0.22, $CHCl_3$); CD (MeOH) 291.8 ([θ] −4.81 × 10^3), 250.9 ([θ] −3.46 × 10^4), 232.7 ([θ] 2.48 × 10^4), 219.3 ([θ] −1.08 × 10^4), 205.5 ([θ] 4.20 × 10^4) nm. Anal. Calcd for $C_{25}H_{29}NO_2SSe$: C, 61.72; H, 6.01; N, 2.88. Found: C, 61.61; H, 6.05; N,2.92.

Compound (*R*)-(+)-1d: 100% ee; mp 143−144 °C; IR (KBr) 2960, 1276, 1135, 927, 685, 648 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.29 (3H, s), 2.31 (6H, s), 2.32 (3H, s), 6.84 (2H, s), 7.09 and 7.73 (4H, ABq, J = 8.0 Hz), 7.43−7.48 (3H, m), 7.56−7.60 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 21.1, 21.3, 125.9, 127.4, 128.8, 129.8, 130.0, 131.0, 131.2, 133.2, 140.8, 141.7, 142.8, 143.3; MS (EI) *m/z* 445 (^{80}Se, M$^+$), 443 (^{78}Se, M$^+$), 276, 195, 119, 91; $[\alpha]_D$ +199.6 (c 0.50, $CHCl_3$), $[\alpha]_{435}$ +460.4 (c 0.50, $CHCl_3$); CD (MeOH) 294.0 ([θ] 8.81 × 10^3), 252.7 ([θ] 4.31 × 10^4), 232.9 ([θ] −3.95 × 10^4) nm. Anal. Calcd for $C_{22}H_{23}NO_2SSe$: C, 59.45; H, 5.22; N, 3.15. Found: C, 59.43; H, 5.23; N, 2.88.

Compound (*S*)-(−)-1d: 100% ee; mp 142−143 °C; IR (KBr) 2960, 1276, 1135, 908, 680, 650 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.26 (3H, s), 2.30 (6H, s), 2.32 (3H, s), 6.85 (2H, s), 7.09 and 7.73 (4H, ABq, J = 8.0 Hz), 7.43−7.49 (3H, m), 7.56−7.61 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.7, 20.9, 21.1, 125.8, 127.3, 128.7, 129.6, 129.8, 130.9, 131.1, 133.0, 140.7, 141.5, 142.7, 143.2; MS (EI) *m/z* 445 (^{80}Se, M$^+$), 443 (^{78}Se, M$^+$), 276, 195, 119, 91; $[\alpha]_D$ −196.7 (c 0.46, $CHCl_3$), $[\alpha]_{435}$ −462.5 (c 0.46, $CHCl_3$); CD (MeOH) 294.1 ([θ] −8.78 × 10^3), 252.2 ([θ] −4.28 × 10^4), 233.2 ([θ] 3.63 × 10^4) nm. Anal. Calcd for $C_{22}H_{23}NO_2SSe$: C, 59.45; H, 5.22; N, 3.15. Found: C, 59.26; H, 5.17; N, 3.17.

Kinetic Studies of Racemization of Optically Active Selenonium Imides (*R*)-(+)- and (*S*)-(−)-1b and 1d. A toluene solution (2 mL) containing optically active selenonium imide (ca. 6 mmol) was heated at 130−145 °C. The enantiomeric excess (ee) was measured at adequate time intervals, and the rate for racemization was plotted to the first-order rate equation. The activation parameters were calculated by Arrhenius and Eyring absolute kinetic equations.

X-ray Analysis of (−)-1a.[22] X-ray data collection was carried out on a Rigaku AFC-5R diffractometer, and computations were performed on a SHELXL 97:[27] $C_{31}H_{41}NO_2SSe$ M_r = 570.67; monoclinic, space group $P2_1$; a = 10.8176(18) Å, b =

(27) Sheldrick, G. M. SHELXL 97: *Program for crystal structure determination*; University of Gottingen, Germany, 1997.

9.7701(13) Å, $c = 15.242(3)$ Å; $\beta = 108.832(18)°$; $V = 1524.6(4)$ Å^3, $Z = 2$, $\rho = 1.243$ g cm^{-3}, absolute structure parameter $= -0.008(9)$. Of the 7001 independent reflections, the 5804 reflections with $I > 2\sigma(I)$ were used in the least-squares refinement to yield $R[F^2 > 2\sigma(F^2)] = 0.0393$.

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Supporting Information Available: Detailed information of the X-ray crystallographic analysis of (*S*)-(−)-**1a** including structure diagram, crystal data, refinement, atomic coordinates, isotropic displacement parameter, bond length, and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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