Stereoselective Transformation of Optically Active Selenoxide into Optically Active Selenonium Imide

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Our studies have focused on the synthesis and stereochemistry of optically active organic selenium and tellurium compounds. So far, we have reported the synthesis and stereochemistry of optically active tricoordinate selenium compounds such as selenoxides,[1,2] selenonium ylides,[3] and selenonium salts.[4] Very recently, we also synthesized optically active telluronium ylides.[5] On the other hand, although selenonium imides are also tricoordinate selenium compounds, there have been few studies on the synthesis of optically active selenonium imides.[6] Moreover, their optical purities are unknown and their absolute configurations have not been clarified. Recently, we succeeded in isolating a diastereomerically pure selenonium imide through the optical resolution of the corresponding diastereomeric mixtures with an *l*-menthyloxycarbonyl group as the chiral source.[7] However, transformation of the diastereomerically pure selenonium imide into the selenonium imide enantiomer by transesterification of the *l*-menthyl ester group into an achiral one unfortunately failed because the imide structure was not stable under the reaction conditions. On the other hand, enantiomerically pure selenoxide could be obtained by a similar ester exchange reaction.[2] We report here the synthesis of optically active selenonium imide enantiomer through the transformation of optically active selenoxide. Furthermore, its absolute configuration was determined based on the specific rotation and the circular dichroism spectrum.

The dehydration of optically pure selenoxide (*S*)-(−)-**1** {$[\alpha]_D$ −84.3($CHCl_3$)}[2] with *p*-toluenesulfonamide ($TsNH_2$) in the presence of dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) at 80 °C in 1,1,2-trichloroethane gave optically active 4-(methoxycarbonyl)phenyl(2′,4′,6′-triisopropylphenyl)selenonium *N*-toluene-4″-sulfonimide {(−)-**2**} in 29% chemical yield. This reaction did not proceed at room temperature, and dehydration under acidic conditions (Ac_2O) failed due to rapid racemization of the optically active selenoxide,[8] even though the chemical yield was high.[7]

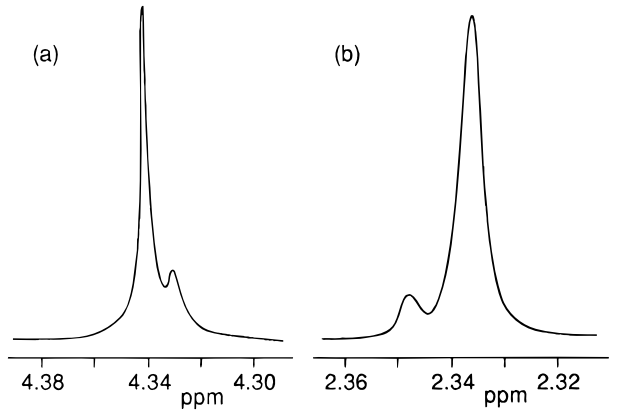


Figure 1. ^1H NMR spectra (400 MHz) for the methyl groups of the ester and *p*-tolyl moieties of (−)-**2** in the presence of $Eu(hfc)_3$ in $CDCl_3$: (a) methyl of ester; (b) methyl of *p*-tolyl.

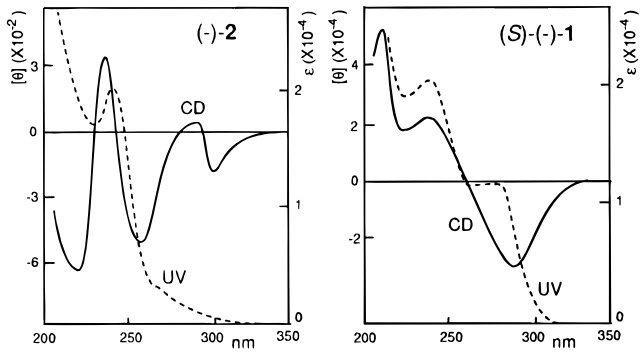
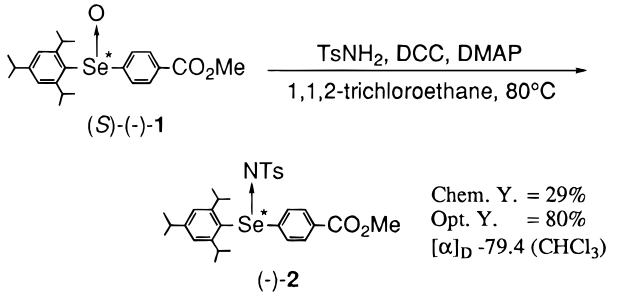


Figure 2. CD and UV spectra of optically active selenonium imide (−)-**2** and selenoxide (*S*)-(−)-**1** in methanol.



The selenonium imide (−)-**2** showed a negative specific rotation, and its optical purity was determined to be 80% by ^1H-NMR measurement using an optically active shift reagent {$Eu(hfc)_3$}. Splits of the methyl groups of both the ester and *p*-tolyl moieties were observed using the optically active shift reagent (Figure 1).

The circular dichroism spectrum of (−)-**2** is shown in Figure 2 together with that of optically active selenoxide (*S*)-(−)-**1**, the configuration of which has been clarified based on X-ray analysis.[2] The circular dichroism spectrum of (−)-**2** shows a negative first Cotton effect at 300 nm, and the spectrum of the selenoxide (*S*)-(−)-**1** also shows a negative sign as the first Cotton effect. The similarity of the signs of the specific rotation and the circular dichroism spectra of the selenonium imide (−)-**2** and the selenoxide (*S*)-(−)-**1** indicates a comparable stereochemistry because two substituents around the selenium atoms are the same and the third substituents are heteroatoms in both the imide and oxide. Therefore, the absolute configuration of the optically active sele-

(1) Kamigata, N.; Shimizu, T. *Rev. Heteroatom Chem.* **1991**, *4*, 226, and references cited therein.
(2) Shimizu, T.; Kikuchi, K.; Ishikawa, Y.; Ikemoto, I.; Kobayashi, M.; Kamigata, N. *J. Chem. Soc., Perkin Trans. 1* **1989**, 597.
(3) (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.
(4) Kobayashi, M.; Koyabu, K.; Shimizu, T.; Umemura, K.; Matsuyama, H. *Chem. Lett.* **1986**, 2117.
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(6) (a) Krasnov, V. P.; Naddaka, V. I.; Minkin, V. I. *Zh. Org. Khim.* **1981**, *17*, 445. (b) Davis, F. A.; Billmers, J. M.; Stringer, O. D. *Tetrahedron Lett.* **1983**, *24*, 3191.
(7) Kamigata, N.; Taka, H.; Matsuhisa, A.; Matsuyama, H.; Shimizu, T. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2257.
(8) Shimizu, T.; Kobayashi, M.; Kamigata, N. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3761.

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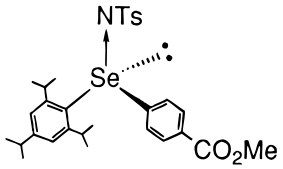
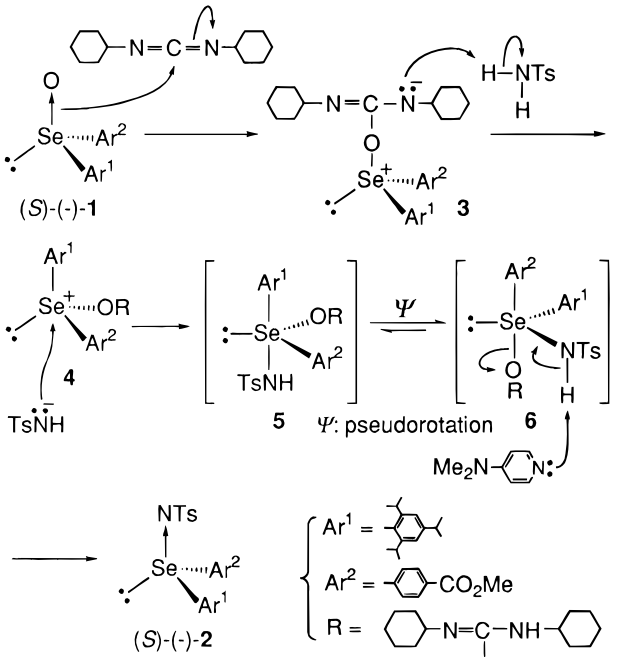
nonium imide (−)-**2** was estimated to be *S*-form and the transformation of selenoxide into selenonium imide proceeded with a retention of stereochemistry.



(*S*)-(-)-**2**

A plausible mechanism for this imide formation with a retention of stereochemistry is as follows. Reaction of (*S*)-(−)-selenoxide with DCC gives the intermediate **3**, and successive proton abstraction by nitrogen anion from tosylamide gives alkoxyselenonium ion **4** and tosylamide anion. The tosylamide anion attacks the selenium atom from the least sterically hindered direction (opposite the most bulky 2,4,6-triisopropylphenyl group) to give a hypervalent selenurane **5**. Selenurane **5** will rearrange to selenurane **6**, since it has been shown that a selenurane will rearrange into a more stable selenurane[9] by means of pseudorotation.[10] Thus, the electron-withdrawing alkoxy group rotates to the apical position. Selenurane **6** will undergo β-elimination[11] *via* proton abstraction by DMAP, and thus (*S*)-(−)-imide may be formed with an overall retention of stereochemistry.



Plausible Mechanism for Imide Formation

Experimental Section

Transformation of Optically Active Selenoxide into Optically Active Selenonium Imide. A mixture of selenoxide (*S*)-(−)-**1**[2] (215 mg, 0.50 mmol), *p*-toluenesulfonamide (111 mg, 0.65 mmol), dicyclohexylcarbodiimide (629 mg, 3.0 mmol), and 4-(dimethylamino)pyridine (33 mg, 0.25 mmol) was heated at 80 °C for 20 h in 1,1,2-trichloroethane (6 mL) under nitrogen. After removal of the solvent *in vacuo*, purification by alumina column chromatography (hexane/ethyl acetate = 3/1) followed by gel permeation chromatography (GPC) gave optically active selenonium imide (−)-**2** (85 mg, 29%): enantiomeric excess = 80%; mp 173−174 °C; $[\alpha]_D$ −79.4 (*c* 0.214, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.83 (broad s, 6H), 1.22 (d, 6H, J = 6.8 Hz), 1.25 (d, 6H, J = 6.8 Hz), 2.33 (s, 3H), 2.90 (hep, 1H, J = 6.8 Hz), 3.41 (hep, 1H, J = 6.8 Hz), 3.93 (s, 3H), 7.06 (s, 2H), 7.13 (d, 2H, J = 8.3 Hz), 7.69 (d, 2H, J = 8.3 Hz), 7.77 (d, 2H, J = 8.3 Hz), 8.11 (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 23.1, 23.6, 25.2, 31.6, 34.3, 52.5, 124.3, 126.1, 127.5, 129.0, 130.2, 130.8, 132.7, 140.9, 141.0, 142.9, 152.2, 154.7, 165.7; IR (KBr) 916, 1276, 1721, 2950 cm^{-1}; UV (MeOH) λ_{max} 242 nm (ϵ = 2.0×10^4); CD (MeOH) $[\theta]_{222}$ -6.28×10^2, $[\theta]_{234}$ $+3.11 \times 10^2$, $[\theta]_{257}$ -5.06×10^2, $[\theta]_{289}$ $+4.22 \times 10$, $[\theta]_{300}$ -1.92×10^2; MS *m*/*z* 587 (M^+, ^{80}Se), 418. Anal. Calcd for $C_{30}H_{37}NO_4SSe$: C, 61.42; H, 6.36; N, 2.39. Found: C, 61.42; H, 6.52; N, 2.45.

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(9) In general, selenurane is more stable when an electron-withdrawing group lies at the apical position.

(10) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(11) The leaving group is eliminated from the apical position of hypervalent selenurane.