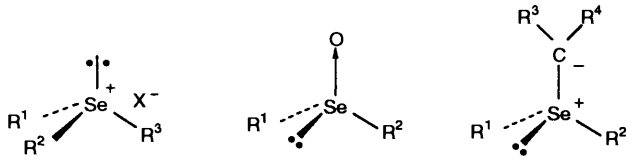
Synthesis and Stereochemistry of Optically Active Selenonium Imides

Nobumasa Kamigata,* Hideo Taka, Ayumi Matsuhisa, Haruo Matsuyama and Toshio Shimizu
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Minami-ohsawa, Hachioji, Tokyo 192-03, Japan

Diastereoisomeric mixtures of 4-[(−)-menthyloxycarbonyl]phenyl(methyl)selenonium-*N*-toluene-4′-sulfonimides (dia.-**1**) and 4-[(−)-menthyloxycarbonyl]phenyl(2′,4′,6′-triisopropylphenyl)selenonium-*N*-toluene-4″-sulfonimides (dia.-**7**) were synthesized. Optical resolution by the fractional recrystallization of dia.-**7** from methanol gave the optically pure (−)-selenonium imide as stable crystals. The absolute configuration around the selenium atom was determined to be *S* based on the CD spectra. The kinetics for the epimerization by pyramidal inversion of the optically active selenonium imide were studied.

Our interest has recently been focused on the synthesis and stereochemistry of optically active organic selenium compounds[1] since selenium is an element homologous with sulfur, and a number of optically active organic sulfur compounds have been synthesized,[2–5] some of which are utilized for asymmetric synthesis,[6] whereas little work has been reported on optically active selenium compounds.[7–10] More recently, we have



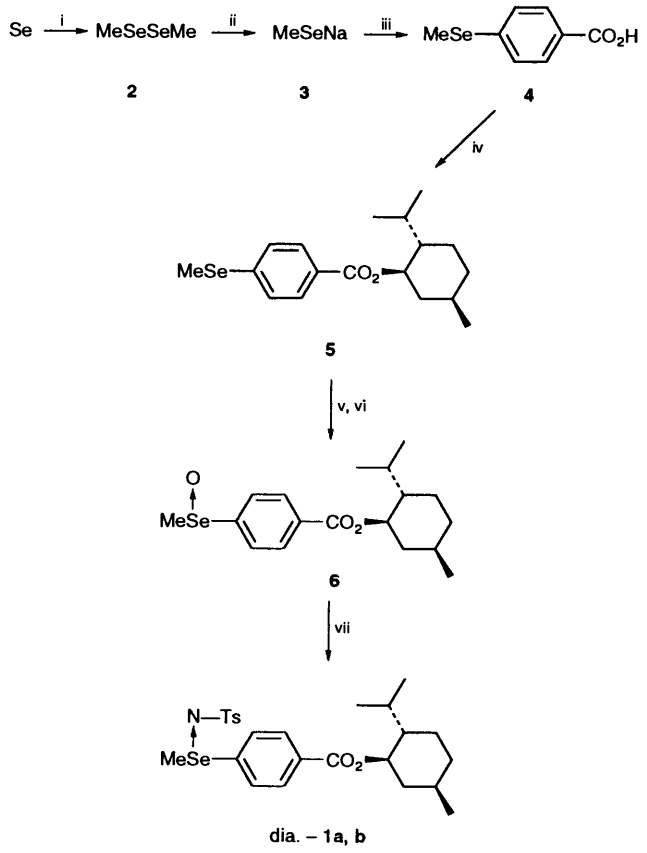
isolated some optically pure tricoordinate tetravalent selenium compounds such as selenonium salts,[11] selenoxides,[12,13] and selenonium ylides,[14] and have clarified their stereochemistry, reactivities, and physical properties. Selenonium imides are also tricoordinate tetravalent compounds and were expected to be isolated in optically active form since several optically active sulfonium imides are known.[2] Only one paper has appeared on the synthesis of optically active selenonium imides (by Krasnov *et al.*[8]); however, the optical purity was low and the absolute configuration was not determined. We isolated an optically pure selenonium imide by optical resolution of a diastereoisomeric selenonium imide, and studied its stereochemistry and kinetics of epimerization by pyramidal inversion, and the results are described herein.

Results and Discussion

The first preparation of selenonium imides was reported by Tamagaki and Sakaki in 1975 but those compounds were achiral.[15] The optically active selenonium imide prepared by Krasnov *et al.* was obtained by asymmetric induction. We planned to isolate an optically pure selenonium imide by optical resolution of diastereoisomeric selenonium imides. We therefore designed and synthesized asymmetric selenonium imides possessing a (−)-menthyl group as a chiral source for optical resolution and tried to resolve the selenonium imides by fractional recrystallization.

Syntheses and Optical Resolution of Selenonium Imides.—Diastereoisomeric 4-[(−)-menthyloxycarbonyl]phenyl(methyl)-selenonium-*N*-toluene-4′-sulfonimides (dia.-**1**) were synthesized by the following procedure. Reaction of sodium methaneselenolate **3**, prepared by the reduction of dimethyl diselenide **2** with sodium boranuide, with 4-iodobenzoic acid in the presence of copper powder in aq. sodium hydroxide and ethanol gave 4-(methylselanyl)benzoic acid **4** in 63% yield after reflux for 1 day.[16] (−)-Menthyl 4-(methylselanyl)benzoate **5** was prepared in 75% yield by treatment of the acid **4** with (−)-menthol in the presence of dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) in dichloromethane at room temperature for 24 h.[17] Oxidation of selenide **5** was achieved with *tert*-butyl hypochlorite in the presence of methanol and pyridine in dichloromethane to give a diastereoisomeric mixture of (−)-menthyl 4-(methylseleninyl)-benzoate **6** in 92% yield.[18] Reaction of compound **6** with toluene-*p*-sulfonamide in the presence of acetic anhydride in chloroform afforded a diastereoisomeric mixture of 4-[(−)-menthyloxycarbonyl]phenyl(methyl)selenonium-*N*-toluene-4′-sulfonimides (dia.-**1a**, **b**) in 70% yield (Scheme 1). The selenonium imides (dia.-**1a**, **b**) were sensitive to traces of water in the solvent and/or atmospheric moisture in the solid state. Therefore, diastereoisomers dia.-**1a**, **b** could not be resolved by fractional recrystallization to the diastereoisomerically excess form. Tamagaki *et al.* reported that selenonium imides possessing a bulky group could be isolated in stable form although almost all selenonium imides were unstable towards trace amounts of water and hydrolysed to the corresponding selenoxides and amines.[19] We therefore designed a selenonium imide having a bulky 2,4,6-triisopropylphenyl group to protect it from hydrolysis.

Diastereoisomeric 4-[(−)-menthyloxycarbonyl]phenyl(2′,4′,6′-triisopropylphenyl)selenonium-*N*-toluene-4″-sulfonimides (dia.-**7**) were synthesized by the following procedure. Reaction of potassium selenocyanate with 4-(ethoxycarbonyl)benzenediazonium chloride, prepared by the diazotization of ethyl 4-aminobenzoate, gave ethyl 4-(selenocyanato)benzoate **8** in 84% yield.[20] Ethyl 4-(2′,4′,6′-triisopropylphenylselanyl)benzoate **9** was prepared in 78% yield by the reaction of compound **8** with 2,4,6-triisopropylphenyllithium, prepared by treatment of 2,4,6-triisopropylphenyl bromide with butyllithium in tetrahydrofuran (THF) at −60 °C.[21] Hydrolysis of **9** by potassium hydroxide under reflux in methanol–water afforded 4-(2′,4′,6′-triisopropylphenylselanyl)benzoic acid **10** in quantitative yield. Treatment of the acid **10** with thionyl dichloride at 60 °C for 2 h and subsequent reaction with (−)-menthol in the presence of pyridine gave (−)-menthyl 4-(2′,4′,6′-triisopropylphenylselanyl)benzoate **11** in 98% yield. Oxidation of the selenide **11** was achieved with *tert*-butyl hypochlorite in the presence of methanol and pyridine in dichloromethane at −25 °C to give a diastereoisomeric mixture of (−)-menthyl 4-(2′,4′,6′-triisopropylphenylseleninyl)benzoate **12** in 86% yield.[18] Reaction of

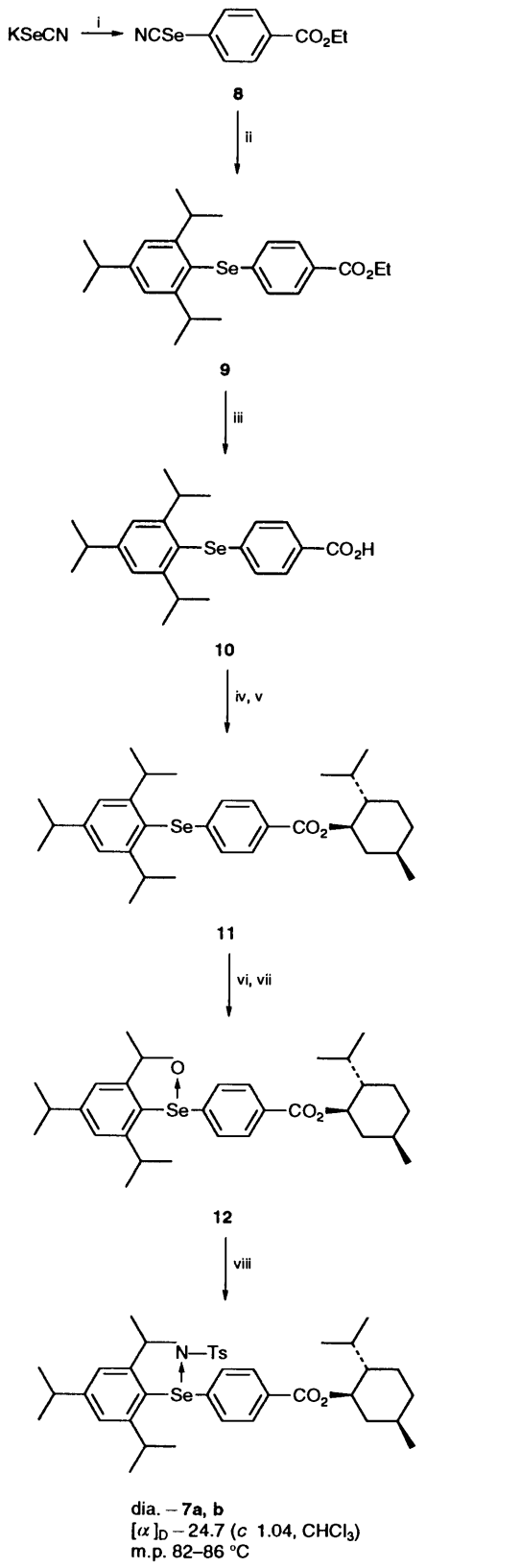


Scheme 1 *Reagents and conditions:* i, 80% N_2H_4, aq. NaOH, MeI; ii, $NaBH_4$, EtOH; iii, *p*-$IC_6H_4CO_2H$, Cu, aq. NaOH; iv, (−)-menthol, DCC, DMAP, CH_2Cl_2, room temp., 24 h; v, Bu^{t}OCl, pyridine, MeOH, CH_2Cl_2 −25 °C; vi. aq. NaOH; vii, $TsNH_2$, Ac_2O, $CHCl_3$, 50 °C

compound **12** with toluene-*p*-sulfonamide in the presence of acetic anhydride in chloroform at 50 °C for 17 h gave a diastereoisomeric mixture of 4-[(−)-menthyloxycarbonyl]-phenyl(2′,4′,6′-triisopropylphenyl)selenonium-*N*-toluene-4″-sulfonimides (dia.-**7a**, **b**) in 92% yield. The $[\alpha]_D$-value of the resulting selenonium imide (dia.**7a**, **b**) was -24.7×10^{-1} deg cm^2 g^{-1} (*c* 1.04, $CHCl_3$) and the m.p. was 82–86 °C (Scheme 2). The selenonium imide **7** was stable in the crystalline state and also in chloroform and methanol solution at room temperature.

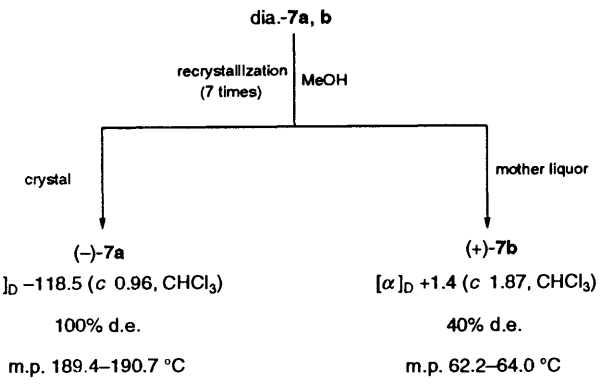
Diastereoisomeric mixture dia.-**7a**, **b** was optically resolved by fractional recrystallization from methanol. Diastereoisomerically pure (d.e. 100%) selenonium imide (−)-**7a** (600 mg) was obtained after seven fractional recrystallizations from the diastereoisomeric mixture dia.-**7a**, **b** (3.42 g). The optical purity was determined by ^{1}H NMR spectroscopy (400 MHz). The specific rotation and m.p. of diastereoisomerically pure imide (−)-**7a** were $[\alpha]_D$ -118.5×10^{-1} deg cm^2 g^{-1} (*c* 0.96, $CHCl_3$) and 189.4–190.7 °C, respectively. This is the first example of the isolation of an optically pure selenonium imide in a stable crystalline state. A diastereoisomerically excess of imide (+)-**7b** (700 mg) was obtained from the mother liquor, and showed $[\alpha]_D$ $+1.4 \times 10^{-1}$ deg cm^2 g^{-1} (*c* 1.87, $CHCl_3$) and m.p. 62.2–64.0 °C. The optical purity of compound (+)-**7b** was determined to be 40% d.e. by ^{1}H NMR spectroscopy. The results are summarized in Scheme 3.

Determination of the Optical Purity of Selenonium Imides (−)-**7a** *and* (+)-**7b** *by* ^{1}H *NMR Spectroscopy*. The isolated selenonium imide (−)-**7a** can be regarded as diastereoisomerically pure in a classical manner since the specific rotation and the m.p. became constant after seven recrystallizations (see



Scheme 2 *Reagents and conditions:* i, *p*-$EtO_2CC_6H_4N_2^+Cl^-$, water, 60 °C; ii, 2,4,6-$Pr^i_3C_6H_2Li$, THF, −78 °C; iii, KOH, aq. MeOH; iv, $SOCl_2$; v, (−)-menthol, pyridine; vi, Bu^{t}OCl, pyridine, MeOH, CH_2Cl_2, −25 °C; vii, aq. NaOH; viii, $TsNH_2$, Ac_2O, $CHCl_3$, 50 °C

above). To confirm that imide (−)-**7a** is really diastereoisomerically pure, we attempted to separate dia.-**7a**, **b** by HPLC using an optically active column; however, the diastereoisomeric



Scheme 3. Optical resolution of mixture dia.-**7a**, **b** by fractional recrystallization

mixture of selenonium imides dia.-**7a**, **b** could not be separated under the analytical conditions studied. We could therefore not determine the optical purity of isomers (−)-**7a** and (+)-**7b** by HPLC, so we tried to do so by ^{1}H NMR spectroscopy. The ^{1}H NMR signals of compounds (−)-**7a** and (+)-**7b** were expected to be observed at different chemical shifts since these two compounds are diastereoisomeric isomers; however, no difference was found in the ^{1}H NMR spectra obtained. The ^{1}H NMR spectrum of the diastereoisomeric mixture of selenonium imides (dia.-**7a**, **b**) was then measured in the presence of an optically active shift reagent, tris-[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) [Eu(hfc)$_3$; 25 mol% against dia.-**7a**, **b**] in chloroform. The singlet proton signal for the methyl group of the toluene-*p*-sulfonyl moiety and the singlet proton signal for aromatic hydrogens of the 2,4,6-triisopropylphenyl moiety were separated into two singlet signals, respectively, although these two kinds of proton signals were observed each as a singlet proton signal, respectively, in the absence of the optically active shift reagent [Fig. 1(a)]. The signal strengths for the two singlet signals of the methyl group and for the two singlet signals of the aromatic hydrogens in Fig. 1(a) were almost equal, and this means that imide dia.-**7a**, **b** is a 1:1 diastereoisomeric mixture. On the other hand, only one singlet proton signal for the methyl group of the toluene-*p*-sulfonyl moiety and only one singlet proton signal for aromatic hydrogens of the 2,4,6-triisopropylphenyl moiety were observed in the case of diastereoisomerically pure isomer (−)-**7a** in the presence of the same shift reagent [Fig. 1(b)]. Thus, the optical purity of selenonium imide (−)-**7a** was reconfirmed to be ~100% by the ^{1}H NMR technique using the optically active shift reagent. The proton signals for the methyl group of the toluene-*p*-sulfonyl moiety and for aromatic hydrogens of the 2,4,6-triisopropylphenyl moiety in (+)$_{rich}$-**7b** were also separated into two singlets in the presence of the shift reagent [Fig. 1(c)]. As shown in Fig. 1(c), it was found that both of the proton signals for the methyl group and the aromatic hydrogens appeared at lower magnetic fields for isomer (+)-**7b** and at higher magnetic fields for isomer (−)-**7b**. The optical purity of (+)$_{rich}$-**7b** was calculated to be 40% d.e. from the signal-strength ratio both for the methyl group and the aromatic hydrogens.

Attempt to Synthesize the Enantiomerically Pure Selenonium Imide.—The optically active selenonium imides thus obtained were diastereoisomerically pure selenonium imides containing two chiral moieties. If the (−)-menthyl moiety can be changed to an achiral group retaining the configuration of the chiral selenium atom, then the corresponding enantiomerically pure selenonium imide will be obtained. We therefore attempted the conversion of the menthyl esters into the enantiomeric selenonium imides by removal of the menthyl moiety using a

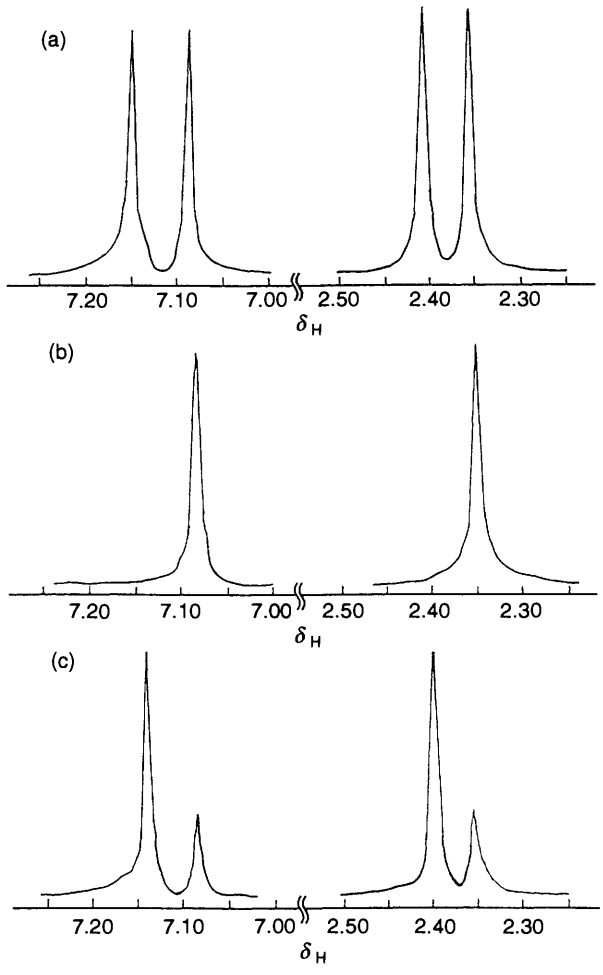
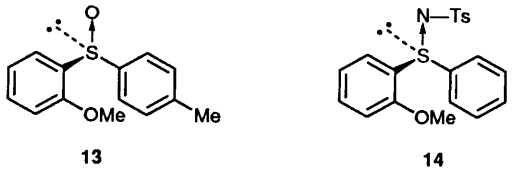


Fig. 1 ^{1}H NMR signals for the methyl group of the *N*-tosyl moiety and the aromatic hydrogens at the 3- and 5-position of the 2,4,6-triisopropylphenyl moiety in the presence of optically active shift reagent Eu(hfc)$_3$: (a) dia.-**7a**, **b**; (b) optically pure (−)-**7a**; (c) optically active (+)-**7b**

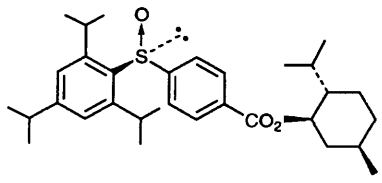
diastereoisomeric mixture of selenonium imide dia.-**7a**, **b** by the following four methods which are generally excellent for ester exchange: (a) ester exchange of dia.-**7a**, **b** in the presence of a catalytic amount of sulfuric acid in methanol under reflux for 48 h, (b) ester exchange of dia.-**7a**, **b** by sodium methoxide in methanol under reflux for 48 h,[22] (c) transesterification of dia.-**7a**, **b** with trimethylsilyl chloride and sodium iodide in acetonitrile at 80 °C for 4 h, and then reflux in methanol,[23] (d) transesterification of dia.-**7a**, **b** in the presence of cesium fluoride in methanol and dichloromethane at room temperature for 48 h.[24] However, all such attempts at transesterification of the (−)-menthyl moiety to an achiral group resulted in Se–N bond cleavage of the selenonium imide.

Determination of the Absolute Configurations of Isomers (−)-**7a** *and* (+)-**7b** *based on their CD Spectra.*—The CD spectrum of optically pure selenonium imide (−)-**7a** showed a negative first Cotton effect at 292 nm in methanol, and that of optically active selenonium imide (+)-**7b** showed a positive first Cotton effect at 292 nm as shown in Fig. 2(a). These results show that the first Cotton effect at 292 nm reflects the chirality of the selenium atom in the selenonium imide. The reported CD spectra of (*S*)-2-methoxyphenyl 4′-tolyl sulfoxide [(*S*)-**13**],[25] (*S*)-2-methoxyphenyl(phenyl)-*N*-tosylsulfonium imide [(*S*)-**14**],[25] and (*S*)-4-[(−)-menthyloxycarbonyl]phenyl 2,4,6-triisopropylphenyl selenoxide [(*S*)-**15**][12] are shown in Fig. 2(b). The CD spectrum of selenonium imide (−)-**7a** is quite similar to



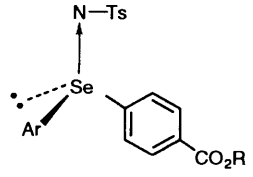
13

14



15

those of the sulfoxide, sulfonium imide, and selenoxide having an (*S*)-configuration and these three compounds show negative first Cotton effects at ~285 nm. Thus, the absolute configuration of the diastereoisomerically pure selenonium imide (−)-**7a** is determined to be *S* and that of the diastereoisomerically excess $(+)_{rich}$-**7b** is determined to be *R*, respectively. The relationships between the absolute configuration, specific rotation, and CD spectrum of optically active selenonium imide (−)-**7a** are summarized below.

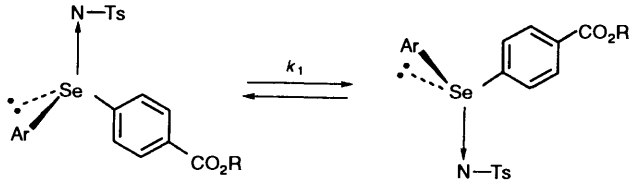


(*S*)-(−)-**7a** R = (−)-menthyl
Ar = 2,4,6-triisopropylphenyl

optical rotation: negative
CD spectrum: 292 and 252 nm (negative Cotton effect)
absolute configuration: *S*-form

The relationships between the absolute configuration, specific rotation, and CD spectrum of optically pure selenonium imide (−)-**7a**

Epimerization of Optically Active Selenonium Imide **7a**.—The rate of epimerization by pyramidal inversion of the optically active selenonium imide **7a** was studied by heating a solution of the diastereoisomerically excess selenonium imide (−)-**7a** in toluene in a sealed tube. The decrease in the optical purity as calculated from the specific rotation showed good linear relationship for first-order rate plots at 120–140 °C. No difference was found in the ^{1}H NMR spectra of selenonium imide (−)-**7a** before and after the kinetic studies, and the results mean that the decrease in specific rotation depends solely on the epimerization by pyramidal inversion and that there is no thermal decomposition or hydrolysis during the kinetic studies. The first-order rate constants for the epimerization of compound (−)-**7a** are summarized in Table 1 together with the activation energy and activation entropy calculated from the rate constants. The results show that selenonium imide is more stable than the sulfonium imide[26,27] towards epimerization by pyramidal inversion, and can be qualitatively interpreted as follows. The valence shell electron-pair repulsion in the selenonium imides is smaller than that in sulfonium imides since the carbon–selenium bond length is longer than the carbon–sulfur bond length and/or selenium is less electronegative than sulfur and therefore the electrons in the C–Se bond lie at a greater distance from selenium than they do from the sulfur in a C–S bond. A higher reaction temperature or activation energy accordingly is required for the pyramidal inversion of the selenonium imide.



(*S*)-(−)-**7a**

R = (−)-menthyl
Ar = 2,4,6-triisopropylphenyl

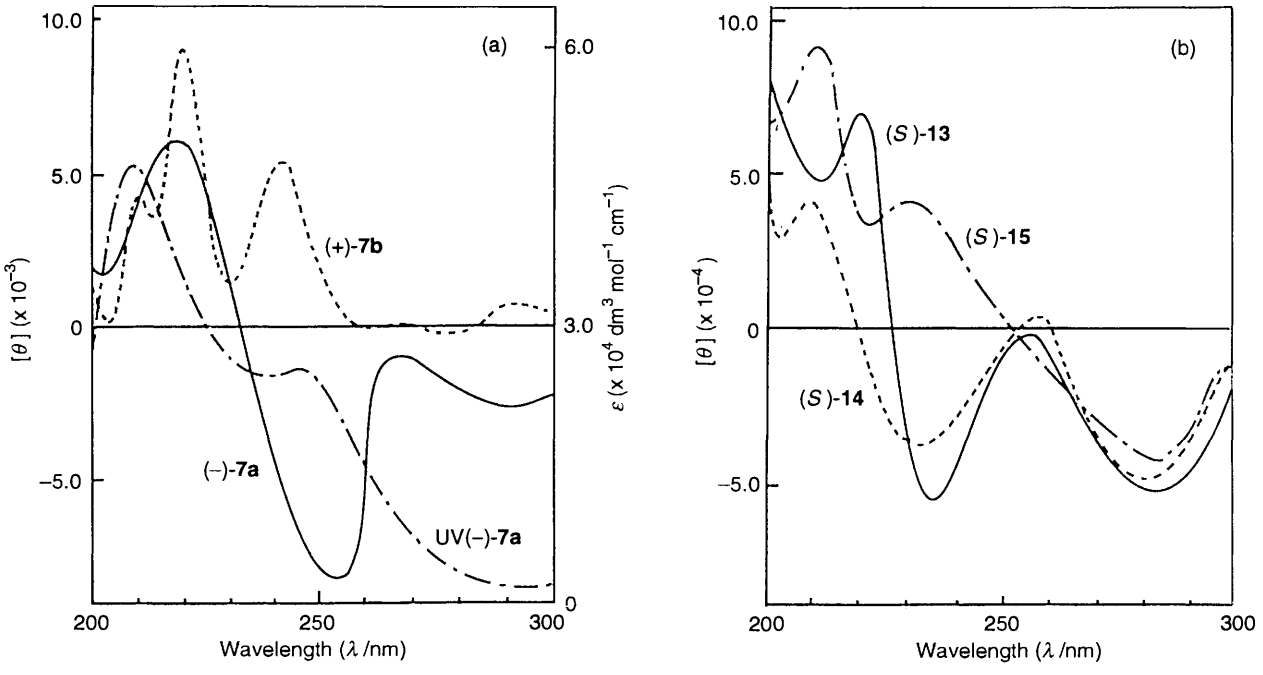


Fig. 2 CD spectra of selenonium imides (−)-**7a** and (+)-**7b**, (*S*)-2-methoxyphenyl 4-tolyl sulfoxide[25] (*S*)-**13**, (*S*)-2-methoxyphenyl(phenyl)-*N*-tosylsulfonium imide[25] (*S*)-**14**, and (*S*)- 4-[(−)-menthyloxycarbonyl]phenyl-2,4,6-triisopropylphenyl selenoxide[12] (*S*)-**15**

Table 1 First-order rate constants and activation parameters for the epimerization, by pyramidal inversion, of selenonium imide (−)-**7a**

Compound	Solvent	Temp. (T/°C)	k_1 (10^{-6} s^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)[c]
(*S*)-(−)-**7a**	toluene	120	1.49		
(*S*)-(−)-**7a**	toluene	130	2.96		
(*S*)-(−)-**7a**	toluene	135	6.88		
(*S*)-(−)-**7a**	toluene	140	10.1	30.9	−7.4
[a]	benzene	100	5.30	27.9	−3.6
[b]	chloroform	75	3.72		

[a] (−)-*p*-chlorophenyl(methyl)-*N*-tosylsulfonium imide.[26,27] [b] (−)-o-methoxyphenyl(phenyl)-*N*-tosylsulfonium imide.[26,27] [c] Entropy units.

Stability of the Selenonium Imide under Several Conditions.—The stability of the selenonium imide dia.-**7a**, **b** toward acid, base, and water was studied. To a solution containing a diastereoisomeric mixture of selenonium imide dia.-**7a**, **b** in methanol were added several drops of conc. sulfuric acid, and the solution was stirred at room temperature for 3 h; however, no difference was observed in the ^1H NMR spectrum. On the other hand, the selenonium imides dia.-**1a**, **b** were hydrolysed by atmospheric moistures and/or a trace amount of water in solvents. The results show that selenonium imides dia.-**7a**, **b** are stabilized by the bulky substituent. The selenonium imides dia.-**7a**, **b** were also stable toward silica gel column chromatography using a mixture of chloroform and methanol (20:1) as eluent.

To a methanolic solution of the selenonium imides dia.-**7a**, **b** were added a few grains of sodium hydroxide, and the mixture was stirred at room temperature for 1 day. The selenonium imide was found to be stable under these basic conditions, whereas the selenonium imides dia.-**1a**, **b** were found to be unstable when water was added to a solution of the selenonium imide in methanol under acidic, neutral, or basic conditions to give the corresponding selenoxide.

Experimental

M.p.s were determined on a Yamato MP-21 melting point apparatus or a Yanako MP-500D micro melting point apparatus, and are uncorrected. IR spectra were determined on a Hitachi 260–10 spectrophotometer or a JASCO FT/IR-5MP Fourier Transform Infrared spectrophotometer with samples as either neat liquids or KBr disks. UV spectra were measured on a Shimadzu UV-160A UV-Visible recording spectrophotometer or a UV-3101PC UV-VIS-NIR scanning spectrophotometer. ^1H NMR spectra were determined on a JEOL JNM-PMX60 SI (60 MHz) or a JEOL JNM-EX-400 FT NMR (400 MHz) spectrometer. ^{13}C NMR spectra were measured on a JEOL JNM-EX-400 FT NMR (100 MHz) spectrometer. The chemical shifts for ^1H and ^{13}C NMR spectra were referenced to Me_4Si as internal standard, and *J*-values are given in Hz. Mass spectra were measured on a JEOL JMS-AX505W spectrometer with JMA-DA5000 Mass Data System by the electron-impact (EI) ionizing technique at 20–70 eV. Optical rotations were measured on a JASCO DIP-140 digital polarimeter, and CD spectra were recorded on a JASCO J-40A spectrometer. $[\alpha]_D$-Values are given in units of 10^{-1} deg cm^2 g^{-1}. TLC and preparative TLC (PLC) were performed with Merck Art. 5554 DC-Alufolien Kieselgel 60 F_{254}. Column chromatography was performed with Wakogel C-200 and Daisogel IR-60 (63/210 μm). HPLC was performed using a Hitachi 655 liquid chromatograph with Daicel Chiralpak and Chiralcel columns. Gel-permeation chromatography (GPC) was performed using a JAI LC-08 or a JAI LC-908 recycling liquid chromatograph with two JAIGEL-1H columns (20 mm × 600 mm) and chloroform as eluent. All solvents were distilled and stored under nitrogen.

Synthesis of Diastereoisomeric 4-[(−)-*Menthyloxycarbonyl*]-*phenyl(methyl)selenonium*-N-*toluene*-4′-*sulfonimides* (dia.-**1a**, **b**).—Selenium powder (79 g, 1.0 mol) was added to a stirred aqueous solution of sodium hydroxide (60 g, 1.5 mol in 300 cm^3), and the mixture was cooled to 15–20 °C. To this mixture was added dropwise 80% hydrazine hydrate (65 g, 1.0 mol) over a period of 30 min, and the solution was stirred for an additional 6 h at 15–20 °C. After the evolution of nitrogen gas had ceased, to the solution containing sodium diselenide thus formed, was added dropwise iodomethane (142 g, 1.0 mol) over a period of 3 h. The end-point of the methylation was indicated by a sharp colour change from dark red to yellow. The mixture was diluted with water (1 dm^3), the organic layer was extracted with dichloromethane (100 cm^3 × 3), then the extract was washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was distilled at 155 °C to give dimethyl diselenide[28] **2** (55.2 g, 59%); ν_{max}(neat)/cm^{-1} 2890, 1404, 1255 and 885; $\delta_H(CDCl_3)$ 2.55 (6 H, s).

To a stirred solution of dimethyl diselenide **2** (1.88 g, 10 mmol) in ethanol (100 cm^3) cooled to −10 °C was slowly added sodium boranuide until the colour of the solution has been discharged, and the solution was then stirred for an additional 15 min at −10 °C. To this solution containing sodium methaneselenolate **3** were added copper powder (0.5 g), 4-iodobenzoic acid (4.72 g, 20 mmol) and aq. potassium hydroxide (5.60 g, 100 mmol in 50 cm^3), and the mixture was refluxed overnight.[16] The copper was filtered off and the solution was acidified to pH 1–2 by addition of dil. hydrochloric acid. The carboxylic acid liberated was collected by filtration and recrystallized from ethanol to afford 4-(methylselanyl)benzoic acid **4** (2.71 g, 63%), m.p. 162–163 °C; ν_{max}(neat)/cm^{-1} 2950–2550, 1680, 1585, 1410, 1300, 1180, 1065, 1010, 835 and 750; $\delta_H(CDCl_3)$ 2.39 (3 H, s), 7.40 and 7.93 (4 H, ABq, *J* 8.0) and 9.23 (1 H, br s).

A solution containing 4-(methylselanyl)benzoic acid **4** (3.85 g, 17.5 mmol), DCC (3.97 g, 19.3 mmol), DMAP (0.21 g, 1.75 mmol) and (−)-menthol (3.01 g, 19.3 mmol) in dichloromethane (90 cm^3) was stirred at room temperature for 24 h.[17] After the dicyclohexylurea formed during the reaction had been filtered off, the organic solution was washed successively with water (50 cm^3 × 3), 5% aq. acetic acid (50 cm^3 × 3), and water (50 cm^3 × 3), and was then dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure left a yellow residue, which was subjected to silica gel chromatography using a mixture of hexane and ethyl acetate (50:1) as eluent to give (−)-menthyl 4-(methylselanyl)benzoate **5** (4.65 g, 75%), m.p. 50–52 °C; ν_{max}(KBr)/cm^{-1} 2960–2870, 1710, 1595, 1460, 1395, 1280, 1110, 845 and 760; $\delta_H(CDCl_3)$ 0.73–2.03 (18 H, m), 2.33 (3 H, s), 4.89 (1 H, td, *J* 10.0 and 3.8) and 7.34 and 7.85 (4 H, ABq, *J* 8.2); *m/z* 354 (M^+, ^{80}Se), 218, 216, 199, 197, 184, 182, 171, 169, 156, 138, 123, 109 and 96.

To a solution containing (−)-menthyl 4-(methylselanyl)-benzoate **5** (5.72 g, 16.3 mmol), pyridine (1.29 g, 16.3 mmol) and methanol (2.61 g, 81.5 mmol) in dichloromethane (500 cm^3) cooled to −25 °C was slowly added a solution of *tert*-butyl hypochlorite (1.77 g, 16.3 mmol) in dichloromethane (80 cm^3), and the solution was stirred for an additional 30 min.[18] After the reaction mixture had been taken up with aq. sodium hydroxide (1.3 g in 80 cm^3), the organic layer was separated. The aqueous

layer was extracted with chloroform (30 cm^3 × 2), and the combined organic layer was dried over anhydrous magnesium sulfate. After the removal of the solvent and pyridine under reduced pressure (rotary evaporator and then a vacuum pump), the residue was subjected to silica gel chromatography with a mixture of chloroform and methanol (50:1) to give (−)-menthyl 4-(methylseleninyl)benzoate **6** (5.50 g, 92%), m.p. 145–146 °C; ν_{max}(KBr)/cm^{-1} 2950–2870, 1710, 1595, 1460, 1270, 1120, 820 and 760; δ_H($CDCl_3$) 0.76–2.03 (18 H, m), 2.60 (3 H, s), 4.93 (1 H, td, *J* 10.0 and 3.8) and 7.71 and 8.10 (4 H, ABq, *J* 7.8); *m/z* 371 (M^+ + 1, ^{80}Se), 369, 354, 352, 233, 231, 217, 215, 199, 197, 184, 171, 169, 156, 154, 138, 123, 109 and 96.

A solution containing (−)-menthyl 4-(methylseleninyl)-benzoate **6** (0.19 g, 0.5 mmol), toluene-*p*-sulfonamide (90 mg, 0.5 mmol) and acetic anhydride (80 mg, 0.65 mmol) in chloroform (10 cm^3) was stirred at 50 °C for 17 h. The solvent was removed under reduced pressure, and the residual solid was recrystallized from benzene–hexane to give a diastereoisomeric mixture of 4-[(−)-menthyloxycarbonyl]phenyl(methyl)-selenonium-*N*-toluene-4′-sulfonimide, dia.-**1a**, **b** (0.18 g, 70%); δ_H($CDCl_3$) 0.76–1.97 (18 H, m), 2.42 (3 H, s), 2.65 (3 H, s), 5.2–5.5 (1 H, m), 7.22 and 7.75 (4 H, ABq, *J* 7.8) and 7.75 and 8.14 (4 H, ABq, *J* 7.8); *m/z* 523 (M^+, ^{80}Se), 354 and 216. This compound was very unstable to moisture.

Synthesis of Diastereoisomeric 4-[(−)-*Menthyloxycarbonyl*]-*phenyl*(2′,4′,6′-*triisopropylphenyl*)*selenonium*-N-*toluene*-4″-*sulfonimides* (*dia.* **7a**, **b**).—4-(Ethoxycarbonyl)benzenediazonium chloride was prepared by diazotization of ethyl 4-aminobenzoate (24.8 g, 0.15 mol) by addition of conc. hydrochloric acid (53 cm^3) and water (90 cm^3), and then a solution of sodium nitrite (10.4 g, 0.15 mol) in water (90 cm^3) at 0–5 °C. After being stirred for 20 min at under 5 °C, the solution was neutralized by addition of sodium acetate (53 g).

To the solution of 4-(ethoxycarbonyl)benzenediazonium chloride was added dropwise aq. potassium selenocyanate (21.67 g, 0.15 mol in 50 cm^3) at 5 °C over a period of 10 min, and the solution was stirred for an additional 30 min at 60–70 °C.[20] The organic layer was extracted with chloroform (200 cm^3 × 3), then the extract was washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography with a mixture of hexane and dichloromethane (1:1) as eluent to give ethyl 4-(selenocyanato)benzoate **8** (32.1 g, 84%), m.p. 116–117 °C; ν_{max}(KBr)/cm^{-1} 2150, 1700 and 1280; δ_H($CDCl_3$) 1.41 (3 H, t, *J* 7.1), 4.40 (2 H, q, *J* 7.1) and 7.68 and 8.06 (4 H, ABq, *J* 8.5); *m/z* 255 (M^+, ^{80}Se), 227 and 210.

To a stirred solution of 2,4,6-triisopropylphenyl bromide (16.0 g, 56.5 mmol) in THF (100 cm^3) at −60 °C under nitrogen was added slowly a solution of butyllithium (45 cm^3 of 1.5 mol dm^{-3} hexane solution; 67.8 mmol) over a period of 20 min, and the solution was stirred for an additional 2 h. To this solution containing 2,4,6-triisopropylphenyllithium was added a solution of ethyl 4-(selenocyanato)benzoate **8** (14.3 g, 56.5 mmol) in THF (50 cm^3) over a period of 10 min at −60 °C, and the solution was stirred for an additional 2 h, then was allowed to warm slowly to room temperature.[21] Saturated brine (150 cm^3) was added to this solution, and the organic layer was separated. The aqueous layer was extracted with chloroform (150 cm^3 × 3) and the combined organic layer was washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was subjected to silica gel chromatography with a mixture of hexane and dichloromethane (1:1) to give ethyl 4-(2′,4′,6′-triisopropylphenylselanyl)benzoate **9** (18.9 g, 78%), m.p. 83–84 °C; ν_{max}(KBr)/cm^{-1} 2960, 1660 and 1265; δ_H($CDCl_3$) 1.15 (12 H, d, *J* 6.8), 1.30 (6 H, d, *J* 7.1), 1.35 (3 H, t, *J* 7.1), 2.94 (1 H, sept., *J* 6.8), 3.63 (2 H, sept., *J* 7.1), 4.32 (2 H, q, *J* 7.1), 7.12 (2 H, s) and 7.08 and 7.80 (4 H, ABq, *J* 8.3); *m/z* 432 (M^+, ^{80}Se), 299 and 230.

A solution of ethyl 4-(2′,4′,6′-triisopropylphenylselanyl)-benzoate **9** (29.0 g, 67 mmol), potassium hydroxide (18.8 g, 335 mmol), methanol (20 cm^3), and water (20 cm^3) was heated at reflux until the starting ester **9** had completely hydrolysed as checked by TLC (6 h was required). The solution was acidified to pH 1–2 by addition of hydrochloric acid, and the liberated solid was collected by filtration and dried over silica gel in a desiccator to afford 4-(2′,4′,6′-triisopropylphenylselanyl)-benzoic acid **10** (27.2 g, 100%). Recrystallization of the crude solid from ethanol to give pure acid **10** (21.1 g, 78%), m.p. 219–220 °C; ν_{max}(KBr)/cm^{-1} 2960, 1675 and 1285; δ_H($CDCl_3$) 1.11 (12 H, d, *J* 6.8), 1.29 (6 H, d, *J* 6.8), 2.93 (1 H, sept., *J* 6.8), 3.63 (2 H, sept., *J* 7.1), 7.10 (2 H, s) and 6.91 and 7.85 (4 H, ABq, *J* 8.3); *m/z* 404 (M^+, ^{80}Se), 389 and 187.

A mixture of 4-(2′,4′,6′-triisopropylphenylselanyl)benzoic acid **10** (6.06 g, 15 mmol) and thionyl dichloride (14.3 g) was heated at 60 °C and stirred for 2 h. After the remaining excess of unchanged thionyl dichloride had been removed completely on a rotary evaporator, pyridine (10 cm^3) was added to the reaction mixture by cooling with an ice–water-bath. To this pyridine solution containing 4-(2′,4′,6′-triisopropylphenyl-selanyl)benzoyl chloride was added dropwise a solution of (−)-menthol (6.09 g, 39 mmol) in pyridine (40 cm^3) at 0 °C over a period of 2 h, and the soluion was allowed to warm to room temperature and stirred overnight. Chloroform (100 cm^3) was added to the reaction mixture, and the organic solution was washed successively with water (100 cm^3 × 3), dil. hydrochloric acid (50 cm^3), and saturated aq. sodium carbonate (50 cm^3), and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave an organic residue, which was subjected to silica gel chromatography using a mixture of hexane and dichloromethane (4:1) as eluent to give (−)-menthyl 4-(2′,4′,6′-triisopropylphenylselanyl)benzoate **11** (7.93 g, 98%), m.p. 120–121 °C; ν_{max}(KBr)/cm^{-1} 2960, 1710 and 1590; δ_H($CDCl_3$) 0.71–2.33 (12 H, m), 0.89 (3 H, d, *J* 6.8), 0.90 (3 H, d, *J* 6.8), 1.15 (12 H, d, *J* 6.8), 1.30 (6 H, d, *J* 6.8), 2.94 (1 H, sept., *J* 6.8), 3.63 (2 H, sept., *J* 7.1), 3.63 (1 H, td, *J* 10.8 and 4.4), 7.12 (2 H, s) and 7.08 and 7.80 (4 H, ABq, *J* 8.3); *m/z* 542 (M^+, ^{80}Se), 404 and 203.

To a solution containing (−)-menthyl 4-(2′,4′,6′-triisopropyl-phenylselanyl)benzoate **11** (10.8 g, 20 mmol), pyridine (1.61 g, 20 mmol) and methanol (3.2 g, 100 mmol) in dichloromethane (500 cm^3) cooled to −25 °C under nitrogen was slowly added a solution of *tert*-butyl hypochlorite (4.34 g, 20 mmol) in dichloromethane (80 cm^3) over a period of 60 min, and the solution was stirred for an additional 30 min.[18] After the reaction mixture had been taken up with aq. sodium hydroxide (1.3 g in 80 cm^3), the organic layer was separated. The aqueous layer was extracted with chloroform (50 cm^3 × 3), and the combined organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent and pyridine under reduced pressure (rotary evaporator and then vacuum pump), the residue was subjected to silica gel chromatography with a mixture of chloroform and methanol (20:1) to give (−)-menthyl 4-(2′,4′,6′-triisopropylphenylseleninyl)benzoate **12** (19.1 g, 86%), m.p. 149–150 °C; ν_{max}(KBr)/cm^{-1} 2960, 1710 and 810; δ_H($CDCl_3$) 0.77–2.47 (12 H, m), 0.92 (6 H, d, *J* 6.4), 0.93 (6 H, d, *J* 6.4), 1.24 (6 H, d, *J* 6.8), 1.29 (6 H, d, *J* 6.8), 2.89 (1 H, sept., *J* 6.8), 3.72 (2 H, sept., *J* 6.8), 4.89–4.96 (1 H, m), 7.06 (2 H, s) and 7.66 and 8.11 (4 H, ABq, *J* 8.3); *m/z* 558 (M^+, ^{80}Se), 542 and 404.

A mixture of (−)-menthyl 4-(2′,4′,6′-triisopropylphenyl-seleninyl)benzoate **12** (0.56 g, 1.0 mmol), toluene-*p*-sulfonamide (0.17 g, 1.0 mmol) and acetic anhydride (0.13 g, 1.3 mmol) was stirred at 50 °C for 17 h. After confirmation that the starting selenoxide **12** and toluene-*p*-sulfonamide had been completely

consumed (TLC), the solvent was removed under reduced pressure, and then the residue was subjected to silica gel chromatography using a mixture of chloroform and methanol (20 : 1) as eluent to give a diastereoisomeric mixture of 4-[(−)-menthyloxycarbonyl]phenyl(2′,4′,6′-triisopropylphenyl)selenonium-*N*-toluene-4″-sulfonimide, dia.-**7a**, **b** (0.65 g, 92%); m.p. 82–86 °C; ν_{max}(KBr)/cm^{-1} 2950, 1715 and 910 (Se–N); δ_H($CDCl_3$) 0.77 (3 H, d, *J* 6.8), 0.85 (2 H, br s), 0.89–0.94 (7 H, m), 1.07–1.26 (18 H, m), 1.52–1.57 (2 H, m), 1.72–1.75 (2 H, m), 1.84–1.91 (1 H, m), 2.10–2.13 (1 H, m), 2.33 (3 H, s), 2.90 (1 H, sept., *J* 6.8), 3.42 (2 H, sept., *J* 6.8), 4.92 (1 H, td, *J* 10.7 and 4.4), 7.06 (2 H, s), 7.13 and 7.78 (4 H, ABq, *J* 8.3) and 7.60 and 8.10 (4 H, ABq, *J* 8.3); δ_C($CDCl_3$) 16.6, 20.7, 21.3, 22.0, 23.2, 23.7, 25.2, 26.7, 31.4, 31.6, 34.2, 34.3, 40.8, 47.2, 75.8, 124.4, 126.1, 127.4, 129.0, 130.1, 130.8, 133.4, 140.6, 141.0, 142.9, 152.2, 154.6 and 164.8: the assignments were performed by C–H COSY spectroscopy; $[\alpha]_D$ −24.7 (*c* 1.04, $CHCl_3$); *m*/*z* 711 (M^+, ^{80}Se), 542 and 404 [Found: *m*/*z*, 542.2668 (M^+ − NTs, ^{80}Se). Calc. for $C_{32}H_{46}O_2{}^{80}Se$: *m*/*z*, 542.2663]. The ratio of isomers (−)-**2a**:(+)-**2b** was determined to be 1:1 by ^{1}H NMR spectroscopy (400 MHz).

Optical Resolution of Selenonium Imides dia.-**1a**, **b** *and dia.*-**7a**, **b**.—A solution containing a diastereoisomeric mixture (3.42 g) of 4-[(−)-menthyloxycarbonyl]phenyl(2′,4′,6′-triisopropylphenyl)selenonium-*N*-toluene-4″-sulfonimides dia.-**7a**, **b** was optically resolved by fractional recrystallization from methanol. The specific rotation of crystalline selenonium imide (−)-**7a** became constant {$[\alpha]_D$ −118.5 (*c* 0.960, $CHCl_3$)} after seven fractional recrystallizations (isolated 600 mg), and the other diastereoisomer, (+)-**7b** (700 mg), was obtained from the mother liquor {$[\alpha]_D$ +1.4 (*c* 1.865, $CHCl_3$)}. The optical purity of isomer (−)-**7a**, $[\alpha]_D$ −118.2, was determined to be 100% d.e., whereas that of isomer (+)-**7b**, $[\alpha]_D$ +1.4, was 40% d.e. by ^{1}H NMR spectroscopy.

Similarly, a solution containing a diastereoisomeric mixture (0.15 g) of 4-[(−)-menthyloxycarbonyl]phenyl(methyl)selenonium-*N*-toluene-4′-sulfonimides dia.-**1a**, **b** was submitted to resolution by fractional recrystallization from methanol; however, in this case, all attempts to obtain a diastereoisomeric excess of selenonium imide failed since the imide was very unstable to moisture, and hydrolysed to selenoxide **6** and toluene-*p*-sulfonamide.

Compound (−)-**7a**: m.p. 189.4–190.7 °C; ν_{max}(KBr)/cm^{-1} 2960, 1710 and 910 (Se–N); δ_H($CDCl_3$) 0.73–2.13 (12 H, m), 0.90 (6 H, d, *J* 6.8), 0.93 (6 H, d, *J* 6.4), 1.23 (6 H, d, *J* 6.8), 1.25 (6 H, d, *J* 7.3), 2.33 (3 H, s), 2.90 (1 H, sept., *J* 6.8), 3.42 (2 H, sept., *J* 6.8), 4.92 (1 H, td, *J* 10.7 and 4.4), 7.06 (2 H, s), 7.13 and 7.78 (4 H, ABq, *J* 8.3) and 7.68 and 8.10 (4 H, ABq, *J* 8.3); δ_C($CDCl_3$) 16.6, 20.7, 21.3, 22.0, 23.1, 23.6, 25.2, 26.6, 31.4, 31.6, 34.2, 34.3, 40.8, 47.1, 75.8, 124.3, 126.1, 127.4, 129.0, 130.1, 130.7, 133.4, 140.5, 141.0, 142.9, 152.2, 154.6 and 164.7; $[\alpha]_D$ −118.5 (*c* 0.960, $CHCl_3$); *m*/*z* 711 (M^+, ^{80}Se), 542 and 404; λ_{max}(MeOH)/nm 243 (ε/dm^3 mol^{-1} cm^{-1} 2.7 × 10^4); CD (MeOH)/nm 220 ([θ] +7.74 × 10^3), 252 ([θ] −8.36 × 10^3) and 292 ([θ] −3.55 × 10^3) (Found: C, 65.7; H, 7.6; N, 1.8. Calc. for $C_{39}H_{53}NO_4SSe$: C, 65.89; H, 7.51; N, 1.97%).

Compound (+)-**7b**: m.p. 62.2–64.0 °C; ν_{max}(KBr)/cm^{-1} 2960, 1715, 1235 and 910 (Se–N); δ_H($CDCl_3$) 0.76–2.13 (12 H, m), 0.90 (6 H, d, *J* 6.8), 0.93 (6 H, d, *J* 6.4), 1.23 (6 H, d, *J* 6.8), 1.25 (6 H, d, *J* 7.3), 2.33 (3 H, s), 2.90 (1 H, sept., *J* 6.8), 3.42 (2 H, sept., *J* 6.4), 4.88–4.95 (1 H, m), 7.06 (2 H, s), 7.13 and 7.78 (4 H, ABq, *J* 8.3) and 7.67 and 8.10 (4 H, ABq, *J* 7.8); δ_C($CDCl_3$) 16.7, 20.7, 21.4, 22.0, 23.2, 23.7, 25.3, 26.7, 31.4, 31.6, 34.2, 34.4, 40.9, 47.2, 75.8, 124.5, 126.1, 126.5, 127.5, 129.1, 130.8, 133.4, 140.6, 141.1, 142.9, 152.3, 154.6 and 164.8; $[\alpha]_D$ +1.4 (*c* 1.870, $CHCl_3$); *m*/*z* 711 (M^+, ^{80}Se), 542 and 404 [Found: *m*/*z*, 542.2708 (M^+ − NTs, ^{80}Se). Calc. for $C_{32}H_{46}O_2{}^{80}Se$: *m*/*z*, 542.2663].

Attempt to Separate Compound dia.-**7a**, **b** *by HPLC using an Optically Active Column*.—A diastereoisomeric mixture of selenonium imide dia.-**7a**, **b** was subjected to HPLC using optically active columns for HPLC such as Daicel Chiralpak AS and AD, and Daicel Chiralcel OB, OB-H, OD, OF, OG and CA-1. The solvent systems as the eluent were hexane–propan-2-ol (95 : 5 to 99 : 1). In contrast to our expectations, isomers dia.-**7a**, **b** could not be separated under the conditions employed.

Kinetic Studies on the Epimerization of Optically Active Selenonium Imide (−)-**7a**.—A solution containing compound (−)-**2a** {100 mg; $[\alpha]_D$ −78.4 (*c* 1.00, toluene)} in toluene (10 cm^3) was heated at 120, 130, 135 and 140 °C. The specific rotation was measured at adequate time intervals, and the rates for epimerization by pyramidal inversion were plotted to the first-order rate equation. The activation parameters were calculated by Arrhenius and Eyring absolute kinetic equations. The ^{1}H NMR spectra of isomer (−)-**7a** were the same before and after the kinetic studies, and this means that only pyramidal inversion is occurring under the reaction conditions.

References

1 N. Kamigata and T. Shimizu, *Reviews on Heteroatom Chemistry*, ed. S. Oae, Myu, Tokyo, 1991, vol. 4, pp. 226–248.
2 J. Day and D. J. Cram, *J. Am. Chem. Soc.*, 1965, **87**, 4398; M. Moriyama, T. Yoshimura, N. Furukawa, T. Numata and S. Oae, *Tetrahedron*, 1976, **32**, 3003.
3 K. K. Andersen, J. W. Folly, T. I. Perkins, W. Gaffield and N. E. Papanikolau, *J. Am. Chem. Soc.*, 1964, **86** 5637; K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons and A. L. Ternary, Jr., *J. Am. Chem. Soc.*, 1965, **87**, 1958; S. Zhao, O. Samuel and H. B. Kagan, *Tetrahedron*, 1987, **43**, 5135.
4 K. K. Andersen, R. L. Caret and D. L. Ladd, *J. Org. Chem.*, 1976, **41**, 3096; K. K. Andersen, *The Chemistry of the Sulfonium Group*, ed. C. J. M. Stirling and S. Patai, Wiley, New York, 1981, pp. 229–266.
5 S. J. Campbell and D. Darwish, *Can. J. Chem.*, 1974, **52**, 2953; M. Moriyama, S. Oae, T. Numata and N. Furukawa, *Chem. Ind.*, 1976, 163.
6 G. Solladie, *Synthesis*, 1981, 185; K. Hiroi, *J. Synth. Org. Chem. Jpn.*, 1983, **41**, 925; G. Solladie, *Chimia*, 1984, **38**, 233; T. Koizumi, *J. Synth. Org. Chem. Jpn.*, 1986, **44**, 576; H. Kosugi, *J. Synth. Org. Chem. Jpn.*, 1987, **45**, 472.
7 W. J. Pope and A. Neville, *J. Chem. Soc.*, 1902, 1552; F. G. Holliman and F. G. Mann, *J. Chem. Soc.*, 1945, 37.
8 V. P. Krasnov, V. I. Naddaka and V. I. Minkin, *Zh. Org. Khim.*, 1981, **17**, 445.
9 K. Sakaki and S. Oae, *Tetrahedron Lett.*, 1976, 3703; F. A. Davis, J. M. Billmers and O. D. Stringer, *Tetrahedron Lett.*, 1983, **24**, 3191.
10 D. J. Procter and C. M. Rayner, *Tetrahedron Lett.*, 1994, **35**, 1449; N. Komatsu, T. Murakami, Y. Nishibayashi, T. Sugita and S. Uemura, *J. Org. Chem.*, 1993, **58**, 3697; F. A. Davis and R. T. Reddy, *J. Org. Chem.*, 1992, **57**, 2599; H. J. Reich and K. E. Yelm, *J. Org. Chem.*, 1991, **56**, 5672.
11 M. Kobayashi, K. Koyabu, T. Shimizu, K. Umemura and H. Matsuyama, *Chem. Lett.*, 1986, 2117.
12 T. Shimizu, K. Kikuchi, Y. Ishikawa, I. Ikemoto, M. Kobayashi and N. Kamigata, *J. Chem. Soc., Perkin Trans. 1*, 1989, 597.
13 T. Shimizu, M. Kobayashi and N. Kamigata, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2099; T. Shimizu and M. Kobayashi, *J. Org. Chem.*, 1987, **52**, 3399; *Bull. Chem. Soc. Jpn.*, 1986, **59**, 2654; *Chem. Lett.*, 1986, 161.
14 N. Kamigata, Y. Nakamura, H. Matsuyama and T. Shimizu, *Chem. Lett.*, 1991, 249; N. Kamigata, Y. Nakamura, K. Kikuchi, I. Ikemoto, T. Shimizu and H. Matsuyama, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1721.
15 S. Tamagaki and K. Sakaki, *Chem. Lett.*, 1975, 503.
16 K. Sindelar, E. Svatek, J. Metysova, J. Metys and M. Protiva, *Collect. Czech. Chem. Commun.*, 1969, **34**, 3792.
17 A. Hassner and V. Alexanian, *Tetrahedron Lett.*, 1978, 4475.
18 M. Kobayashi, H. Ohkubo and T. Shimizu, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 503.
19 S. Tamagaki, S. Oae and K. Sakaki, *Tetrahedron Lett.*, 1975, 649.

20 H. K. Spencer, M. V. Lakshmikantham and M. P. Cava, *J. Am. Chem. Soc.*, 1977, **99**, 1470.
21 B. Greenberg, E. S. Gould and W. Burlant, *J. Am. Chem. Soc*, 1956, **78**, 4028.
22 N. Kamigata and T. Shimizu, *J. Synth. Org. Chem. Jpn.*, 1990, **48**, 229.
23 G. A. Olah, S. C. Narang, G. F. Salem and B. G. B. Gupta, *Synthesis*, 1981, 142.
24 S. Shoda and T. Mukaiyama, *Chem. Lett.*, 1980, 391.
25 M. Moriyama, K. Kuriyama, T. Iwata, N. Furukawa, T. Numata and S. Oae, *Chem. Lett.*, 1976, 363.
26 N. Furukawa, K. Harada and S. Ooa, *Tetrahedron Lett.*, 1972, 1377.
27 M. Moriyama, N. Furukawa, T. Numata and S. Oae, *Chem. Lett.*, 1976, 275; *J. Chem. Soc., Perkin Trans. 2*, 1977, 1783.
28 L. Syper and J. Mlochowski, *Synthesis*, 1984, 439.

Paper 4/01695E
Received 22*nd March* 1994
Accepted 18*th April* 1994