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KINETIC STUDIES ON THE PYRAMIDAL INVERSION OF OPTICALLY ACTIVE SELENONIUM IMIDES

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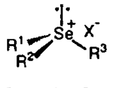
Kinetic studies were carried out on the thermal epimerization by pyramidal inversion of optically active (*S*)-$(-)_{\mathrm{Se}}$- and (*R*)-$(+)_{\mathrm{Se}}$-4-[(-)-menthyloxycarbonyl]phenyl(2′,4′,6′-triisopropylphenyl)selenonium-*N*-toluene-4″-sulphonimides (1). The first-order rate constants for the pyramidal inversion of (*S*)-$(-)_{\mathrm{Se}}$-1 and (*R*)-$(+)_{\mathrm{Se}}$-1 were determined and the activation enthalpies and entropies were calculated. A fairly large difference was found in the activation parameters between optically active (*S*)-$(-)_{\mathrm{Se}}$-1 and (*R*)-$(+)_{\mathrm{Se}}$-1, i.e. a large negative activation entropy was obtained in the case of (*R*)-$(+)_{\mathrm{Se}}$-1.

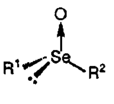
INTRODUCTION

A number of optically active tricoordinate tetravalent sulphur compounds such as sulphonium salts, sulphoxides, sulphonium imides and sulphonium ylides have been synthesized,[1–4] and kinetic studies on racemization by pyramidal inversion have been performed.[5,6] Tricoordinate tetravalent selenium compounds are also expected to be isolated in optically active form since selenium is homologous with sulphur; however, little work has been reported on the synthesis and stereochemistry of optically active selenium compounds.[7–10] Recently, we 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.

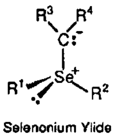
Selenonium imides are also tricoordinate tetravalent compounds and are expected to be isolated in optically active form. Only one paper has been appeared on the synthesis of optically active selenonium imide, by Krasnov *et al.*,[8] but the optical purity was low and the absolute configuration was not determined. We succeeded in isolating optically active selenonium imides by optical resolution of diastereoisomeric mixtures.[15] In this work, we studied the kinetics of the thermal epimerization by pyramidal inversion of optically active selenonium imides.



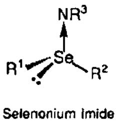
Selenonium Salt



Selenoxide



Selenonium Ylide

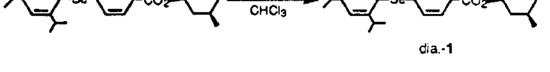


Selenonium Imide

RESULTS AND DISCUSSION

Diastereoisomeric 4-[(−)-menthyloxycarbonyl]phenyl (2′,4′,6′-triisopropylphenyl)selenonium-*N*-toluene-4″-sulphonimides (dia.-1) were synthesized by the following scheme. (-)-Menthyl 4-(2′,4′,6′-triisopropylphenyl-seleninyl)benzoate, prepared by the oxidation of (-)-menthyl 4-(2′,4′,6′-triisopropylphenyl-selanyl)benzoate, was treated with toluene-*p*-sulphonamide in the presence of acetic anhydride gave a 1 : 1 diastereoisomeric mixture of 4-[(−)-menthyloxycarbonyl]phenyl(2′,4′,6′-triisopropylphenyl) selenonium-*N*-toluene-4″-sulphonimides (dia.-1). Optically pure (*S*)-$(-)_{\mathrm{Se}}$-**1** was isolated as stable crystals by fractional recrystallizations of dia.-1 from methanol. Another diastereoisomer, (*R*)-$(+)_{\mathrm{Se}}$-**1** [40% diastereomeric excess (d.e.)], was obtained from the mother liquid.[15]

The rate of epimerization by pyramidal inversion of the optically active selenonium imide was studied by heating a toluene solution of the diastereomeric excess selenonium imide (*S*)-$(-)_{\mathrm{Se}}$-**1** in a sealed tube. The decrease in the optical purity calculated from the



dia.-1

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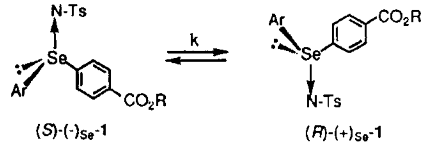

R = (-)-menthyl
Ar = 2,4,6-triisopropylphenyl

specific rotation showed a good linear relationship for the first-order rate plots at 120–140 °C. No difference was found in the ^{1}H NMR spectra of selenonium imide (S)-$(-)_{Se}$-**1** before and after the kinetic studies, and the results indicate that the decrease in the specific rotation depends solely on the epimerization by pyramidal inversion and there is no thermal decomposition or hydrolysis during the kinetic studies. Similarly, the rates of epimerization of (R)-$(+)_{Se}$-**1** was also studied. The first-order rate constants for the epimerization of (S)-$(-)_{Se}$-**1** and (R)-$(+)_{Se}$-**1** are summarized in Table 1 together with those of sulphonium imides[5] such as (-)-4-(chlorophenyl)methylsulphonium-*N*-toluene-4′-sulphonimide[(−)-**2**] and (−)-2-(methoxyphenyl)phenyl-*N*-toluene-4′-sulphonimide [(−)-**3**].

The epimerization by pyramidal inversion was observed at 120–140 °C whereas the racemization of the sulphonium imides (-)-**2** and (-)-**3** was observed at lower temperatures (75–100 °C). The results show that the selenonium imides are more stable than the sulphonium imides toward the epimerization by pyramidal inversion and this result can be qualitatively interpreted as follows. The valence shell electron-pair repulsion in the selenonium imides is smaller than that in sulphonium imides since the carbon–selenium bond length is longer than the carbon–sulphur bond length and/or the selenium atom is less electronegative than the sulphur atom and therefore the electrons in the C—Se bond lie at a greater distance from selenium than they do from the sulphur in a C—S bond. Accordingly, a higher reaction temperature or an activation energy is required for the pyramidal inversion of the selenonium imide.

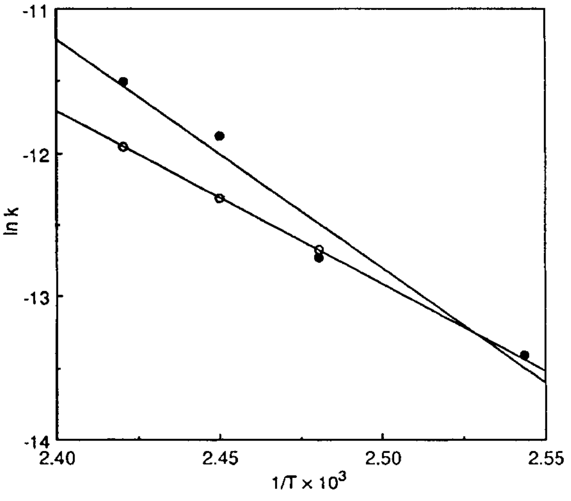

Figure 1. Arrhenius plots for the thermal epimerization of (●) (S)-$(-)_{Se}$-**1** and (○) (R)-$(+)_{Se}$-**1**

Figure 1 shows the Arrhenius plots of the rate constants given in Table 1, and the values of the activation enthalpies and the activation entropies were calculated from the rate constants. The activation enthalpy and the activation entropy for the epimerization by pyramidal inversion from (S)-$(-)_{Se}$-**1** to (R)-$(+)_{Se}$-**1** were 30·9 kcal mol^{-1} and −7·4 cal K^{-1} mol^{-1}, respectively, and the free energy of activation, $\Delta G_1^{\neq}$, was calculated to be 34·0 kcal mol^{-1} (1 kcal = 4·184 kJ). On the other hand, the activation enthalpy and the activation entropy for the epimerization from (R)-$(+)_{Se}$-**1** to (S)-$(-)_{Se}$-**1** were 23·2 kcal mol^{-1} and −26·8 cal K^{-1} mol^{-1}, respectively, and the free energy of activation, $\Delta G_2^{\neq}$, was calculated to be 34·3 kcal mol^{-1}. Thus, the difference in free energy of activation (ΔG^0) for the pyramidal inversion between from (S)-$(-)_{Se}$-**1** to (R)-$(+)_{Se}$-**1** and from (R)-$(+)_{Se}$-**1** to (S)-$(-)_{Se}$-**1** was calculated to be 0·3 kcal mol^{-1}. This

Table 1. First-order rate constants and activation parameters for the pyramidal inversion of (S)-$(-)_{Se}$-**1** and (R)-$(+)_{Se}$-**1**

Compound	Solvent	Temperature (°C)	$k \times 10^6$ (s^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal K^{-1} mol^{-1})	$\Delta G^{\neq}$ (kcal mol^{-1})
(S)-$(-)_{Se}$-**1**	Toluene	120	1·49			
(S)-$(-)_{Se}$-**1**	Toluene	130	2·96			
(S)-$(-)_{Se}$-**1**	Toluene	135	6·88			
(S)-$(-)_{Se}$-**1**	Toluene	140	10·1	30·9	−7·4	34·0
(R)-$(+)_{Se}$-**1**	Toluene	130	3·12			
(R)-$(+)_{Se}$-**1**	Toluene	135	4·49			
(R)-$(+)_{Se}$-**1**	Toluene	140	6·44	23·2	−26·8	34·3
(−)-**2**	Benzene	100	5·30	27·9	−3·6	
(-)-**3**	Chloroform	75	3·72			

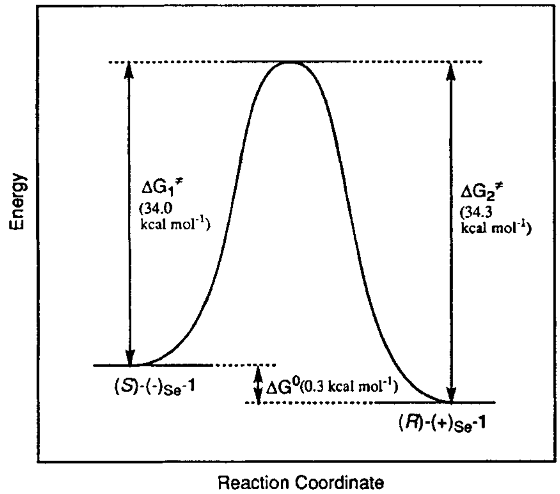

Figure 2. Energy relationship in the epimerization of (*S*)-$(-)_{Se}$-**1** and (*R*)-$(+)_{Se}$-**1**

means that the diastereoisomer (*S*)-$(-)_{Se}$-**1** is 0·3 kcal mol^{-1} higher in energy than the other diastereoisomer (*R*)-$(+)_{Se}$-**1**, since it is considered that the transition state in the epimerization by pyramidal inversion from (*S*)-$(-)_{Se}$-**1** to (*R*)-$(+)_{Se}$-**1** and from (*R*)-$(+)_{Se}$-**1** to (*S*)-$(-)_{Se}$-**1** is the same. These energy relationships are shown in Figure 2.

Interestingly, a fairly large difference was found in the activation parameters for the epimerization of (*S*)-$(-)_{Se}$-**1** and (*R*)-$(+)_{Se}$-**1**. In the epimerization of (*S*)-$(-)_{Se}$-**1**, the reaction is mainly controlled by the enthalpy. On the other hand, in the case of (*R*)-$(+)_{Se}$-**1**, the reaction is considerably affected by the entropy. These differences in the activation parameters between (*S*)-$(-)_{Se}$-**1** and (*R*)-$(+)_{Se}$-**1** are not unexpected since these two compounds are diastereomeric isomers, although it is not obvious how the (-)-menthyl moiety affected the activation parameters in the epimerization of (*S*)-$(-)_{Se}$-**1** and (*R*)-$(+)_{Se}$-**1** in spite of the (−)-menthyl moiety present at a fairly large distance from the reaction centre.

EXPERIMENTAL

A mixture of (−)-menthyl 4-(2′,4′,6′-triisopropylphenylseleninyl)benzoate (0·56 g, 1·0 mmol) and acetic anhydride (0·13 g, 1·3 mmol) in chloroform (10 cm^3) was stirred at 50 °C for 17 h. After confirmation that the starting selenoxide and toluene-*p*-sulphonamide had been completely consumed (TLC), the solvent was removed under reduced pressure and then the residue was subjected to silica gel chromatography using chloroform–methanol (20 : 1) as the eluent to give a diastereoisomeric mixture of 4-[(−)-menthyloxycarbonyl]phenyl(2′,4′,6′-triisopropylphenyl)selenonium-*N*-toluene-4″-sulphonimide, dia.-**1** (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(3H, d, *J*=6·8 Hz), 0·85 (2H, br s), 0·89–0·94 (7H, m), 1·07–1·26 (18H, m), 1·52–1·57 (2H, m), 1·72–1·75 (2H, m), 1·84–1·91 (1H, m), 2·10–2·13 (1H, m), 2·33 (3H, s), 2·90 (1H, sept., *J*=6·8 Hz), 3·42 (2H, sept., *J*=6·8 Hz), 4·92 (1H, td, *J*=10·7 and 4·4 Hz), 7·06 (2H, s), 7·13 and 7·78 (4H, ABq, *J*=8·3 Hz) and 7·68 and 8·10 (4H, ABq, *J*=8·3 Hz); 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; $[\alpha]_D$ −24·7(*c*, 1·04, CHCl$_3$); *m*/*z* 711 (M$^+$, ^{80}Se), 542 and 404.The diastereoisomeric mixture dia.-**1** (3·42 g) was optically resolved by fractional recrystallization from methanol, and optically pure (*S*)-$(-)_{Se}$-**1** (600 mg) was isolated after seven fractional recrystallizations. The optically active diastereoisomer (*R*)-$(+)_{Se}$-**1** (40% d.e.) was obtained from the mother liquid.

The physical and spectral data for (*S*)-$(-)_{Se}$-**1** were as follows: 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 (12H, m), 0·90 (6H, d, *J*=6·8 Hz), 0·93 (6H, d, *J*=6·4 Hz), 1·23 (6H, d, *J*=6·8 Hz), 1·25 (6H, d, *J*=7·3 Hz), 2·33 (3H, s), 2·90 (1H, sept., *J*=6·8 Hz), 3·42 (2H, sept., *J*=6·8 Hz), 4·92 (1H, td, *J*=10·7 and 4·4 Hz), 7·06 (2H, s), 7·13 and 7·78 (4H, ABq, *J*=8·3 Hz), and 7·68 and 8·10 (4H, ABq, *J*=8·3 Hz); 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 ($\varepsilon = 2{\cdot}7\times10^4$); circular dichroism spectrum (MeOH)/nm 220 ([θ] +7·74 × 10^3), 252 ([θ] −8·36 × 10^3), and 292 ([θ] −3·55 × 10^3); found C 65·66, H 7·59, N 1·80; calculated for $C_{39}H_{53}NO_4SSe$, C 65·89, H 7·51, N 1·97%. The physical and spectral data for (*R*)-$(+)_{Se}$-**1** were as follows: 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 (12H, m), 0·90 (6H, d, *J*=6·8 Hz), 0·93 (6H, d, *J*=6·4 Hz), 1·23 (6H, d, *J*=6·8 Hz), 1·25 (6H, d, *J*=7·3 Hz), 2·33 (3H, s), 2·90 (1H, sept., *J*=6·8 Hz), 3·42 (2H, sept., *J*=6·4 Hz), 4·88–4·95 (1H, m), 7·06 (2H, s), 7·13 and 7·78 (4H, ABq, *J*=8·3 Hz), 7·67 and 8·10 (4H, ABq, *J*=7·8 Hz); 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); calculated for $C_{32}H_{46}O_2{}^{80}Se$, *m*/*z* 542·2663].

Measurements of the rate for epimerization by pyramidal inversion of selenonium imides (S)-(−)$_{Se}$-**1** *and* (R)-(+)$_{Se}$-**1**. A solution containing (*S*)-(−)$_{Se}$-**1** {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 suitable time intervals, and the rates for the 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 (*S*)-(−)$_{Se}$-**1** and (*R*)-(+)$_{Se}$-**1** were the same before and after the kinetic studies, which indicates that only pyramidal inversion is occurring under the reaction conditions.

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