Synthesis and Stereochemistry of an Optically Active Selenonium Ylide. X-Ray Molecular Structure of $(+)_{Se}$-{4'-[(−)-Menthyloxycarbonyl]phenyl}(methyl)-selenonium 4,4-Dimethyl-2,6-dioxocyclohexylide

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Fractional recrystallization of diastereoisomeric {4'-[(−)-menthyloxycarbonyl]phenyl}(methyl)-selenonium 4,4-dimethyl-2,6-dioxocyclohexylide from hexane–diethyl ether gave the optically pure (+)-selenonium ylide as stable crystals. The absolute configuration around the selenium atom was determined to be *R* by X-ray crystallographic analysis. The epimerization of the optically active selenonium ylide by pyramidal inversion was studied.

It is widely known that many organoselenium compounds have structures similar to those of the corresponding organosulfur compounds since selenium is an element homologous with sulfur. However, studies on the syntheses and stereochemistry of organoselenium compounds are limited in contrast to those on organosulfur compounds. For example, a number of papers have reported optically active organosulfur compounds possessing a chiral sulfur centre, such as sulfoxides,[1–3] sulfilimines,[4,5] sulfonium salts,[6,7] and sulfonium ylides.[8,9] In particular, several synthetic methods for the syntheses of optically active sulfoxides have been developed, and numerous papers have reported on asymmetric syntheses utilizing these optically active sulfoxides as chiral sources.[10–13] Optically active selenium compounds such as selenoxides, selenilimines, selenonium salts and selenonium ylides are considered to be synthesized similarly to the corresponding organosulfur compounds. Among these compounds, optically active selenonium salts have been known for a long time.[14,15] In comparison, only a few papers on the synthesis of optically active selenilimines[16] and selenonium ylides[17] have recently appeared; however, their optical purities were low. More recently, we have synthesized optically pure selenonium salts[18] and selenoxide,[19] and have clarified their stereochemistry. We now report the synthesis of an optically pure selenonium ylide by fractional recrystallization of a diastereoisomeric selenonium ylide. The optically active selenonium ylide was found to be stable towards racemization, and the absolute configuration of the optically active selenonium ylide described is based on an X-ray crystallographic analysis and CD spectra.

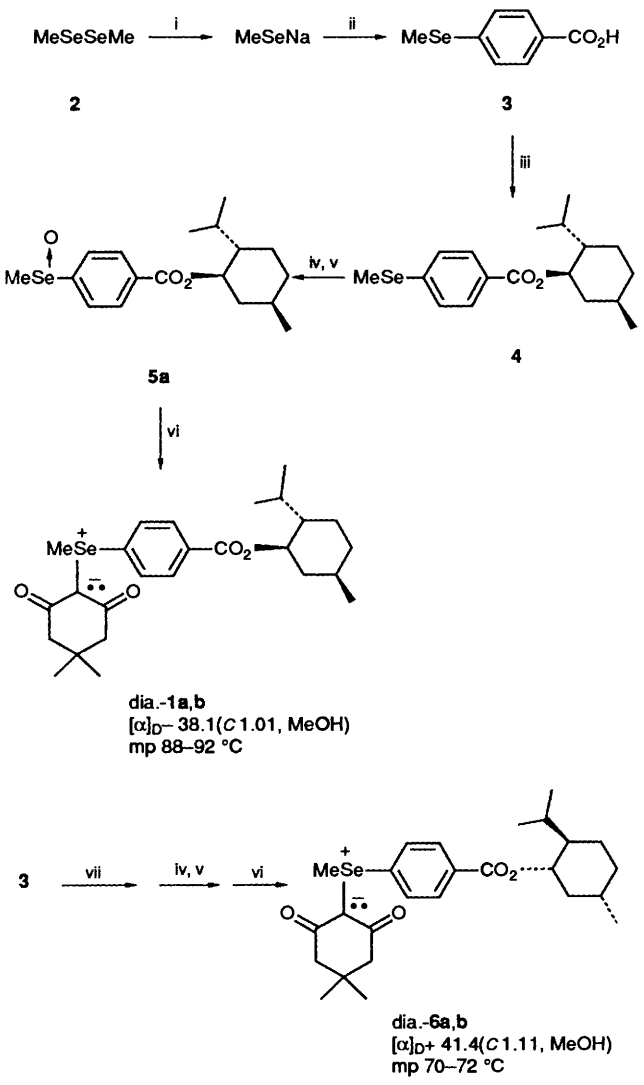
Results and Discussion

The first preparation of a selenonium ylide, dimethylselenonium fluorenylide, was reported by Hughes in 1935 but the ylide is unstable and gradually decomposes at room temperature.[20] Dimethylselenonium benzoylmethylide was isolated as a stable, crystalline solid; the presence of an electron-withdrawing substituent on the carbanionic centre results in stablization of the ylide.[21] To isolate an optically active selenonium ylide by fractional recrystallization, the ylide is required to be thermally stable and to possess a chiral source in the molecule. Therefore, we designed a selenonium ylide with an electron-withdrawing group on the selenium atom and possessing a (−)- or a (+)-menthyl group as a chiral source in the molecule in accordance with above requirement.

Syntheses of Diastereoisomeric Mixture of Selenonium Ylide.—Diastereoisomeric {4'-[(−)-menthyloxycarbonyl]phenyl}-(methyl)selenonium 4,4-dimethyl-2,6-dioxocyclohexylide (dia.-**1a**, **b**) was synthesized by the following procedure. Reaction of sodium methaneselenolate, prepared by the reduction of dimethyl selenide **2** with sodium borohydride, with 4-iodobenzoic acid in the presence of copper powder in aq. sodium hydroxide gave 4-(methylseleno)benzoic acid **3** in 63% yield after reflux for 1 day.[22] (−)-Menthyl-4-(methylseleno)benzoate **4a** was prepared in 75% yield by treatment of the acid **3** with (−)-menthol in the presence of dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) in dichloromethane for 24 h at room temperature.[23] Oxidation of selenide **4a** was achieved with *tert*-butyl hypochlorite in the presence of methanol and pyridine in dichloromethane[24] to give (−)-menthyl 4-methylseleninyl)benzoate **5a** in 92% yield. Reaction of compound **5a** with 5,5-dimethylcyclohexane-1,3-dione (dimedone) in the presence of magnesium sulfate in chloroform afforded a diastereoisomeric mixture of {4'-[(−)-menthyloxycarbonyl]phenyl}(methyl)selenonium 4,4-dimethyl-2,6-dioxocyclohexylide (dia.-**1a**, **b**) in 100% yield (Scheme 1).[25] The $[\alpha]_D$-value of the resulting ylide (dia.-**1a**, **b**) was −38.1† (*c* 1.01, MeOH) and the m.p. was 88–92 °C. Similarly, a diastereoisomeric mixture of {4'-[(+)- menthyloxycarbonyl]phenyl}(methyl)selenonium 4,4-dimethyl-2,6-dioxocyclohexylide (dia.-**6a**, **b**) was also synthesized, by treatment of compound **3** with (+)-menthol and subsequent reactions. The $[\alpha]_D$-value of the resulting ylide (dia-**6a**, **b**) was +41.4 (*c* 1.11, MeOH) and the m.p. was 70–72 °C. The ylides **1** and **6** were stable in the crystalline state and in chloroform solution at room temperature.

Optical Resolution of Diastereoisomers.—Diastereoisomeric isomers **1a**, **b** and **6a**, **b** were optically resolved by fractional recrystallization from hexane–diethyl ether. Optically pure (de 100%) selenonium ylide (+)-**1a** (2.0 g) was obtained after seven fractional recrystallizations from the diastereoisomeric mixture dia.-**1a**, **b** (13.5 g). The optical purity was determined by ^{1}H NMR spectroscopy (500 MHz). The specific rotation and m.p. of diastereoisomerically pure ylide **1a** were +22.6 (*c* 1.01, MeOH) and 135.5–136.5 °C, respectively. This is the first example of the isolation of an optically pure selenonium ylide

† IUPAC recommendation: units for $[\alpha]_D$ are now to be given as 10^{-1} deg cm^2 g^{-1}.



Scheme 1 i, $NaBH_4$, EtOH; ii, *p*-l-$C_6H_4CO_2H$, Cu, aq. KOH; iii, (–)-menthol, DCC, DMAP, CH_2Cl_2 room temp., 24 h; iv, ^tBuOCl, pyridine, MeOH, CH_2Cl_2, –20 °C; v, aq. NaOH; vi, dimedone, $MgSO_4$, $CHCl_3$, room temp., 12h; vii, (+)-menthol, DCC, DMAP, CH_2Cl_2 room temp., 24 h

as a stable crystalline solid. Another diastereoisomeric isomer (–)-**1b** (5.6 g) was obtained from the mother liquor, and showed $[\alpha]_D$ –54.1 (*c* 1.02, MeOH) and m.p. 102–104 °C. The diastereoisomeric purity of isomer (–)-**1b** was determined to be 27% de by ^1H NMR spectroscopy.

Similarly, the diastereoisomeric mixture of ylide **6a**, **b** was subjected to optical resolution by fractional recrystallization from hexane–diethyl ether. However, optically pure ylide could not be obtained by repeated fractional recrystallization, even of the crystalline fraction, and instead optically active (or diastereoisomerically excessive) isomers (+)-**6a**, showing $[\alpha]_D$ +35.9 (*c* 1.03, MeOH), m.p. 108–110 °C and (+)-**6b**, showing $[\alpha]_D$ +55.4 (*c* 1.03, MeOH), m.p. 105–107 °C, were obtained. Thus, we have succeeded in isolating one diastereoisomer as the optically pure form and three diastereoisomers in the diastereoisomeric excess form as stable crystals from two pairs of diastereoisomeric mixtures (dia.-**1a**, **b** and dia-**6a**, **b**) by fractional recrystallization. These results are summarized in Fig. 1.

Determination of the Absolute Configuration of Diastereoisomer (+)-**1a** *by X-Ray Diffraction.*—The absolute configuration of optically active selenonium ylides has not been determined, since optically pure selenonium ylides have not yet been synthesized in a stable form, in contrast to a number of optically active sulfonium ylides whose absolute configuration has been clarified.[26] As mentioned above, since we succeeded in synthesizing and isolating the optically active ylide as 100% pure crystals, the stereochemical structure of the optically pure selenonium ylide was studied by X-ray crystallographic analysis. The molecular structure of the optically pure diastereoisomer (+)-**1a** is shown in Fig. 2. Positional parameters are presented in Table 1. Bond distances and bond angles are given in Table 2. The configuration around the selenium atom in diastereoisomer **1a** was seen to be pyramidal and the lone-pair electron on the selenium atom was found to lie toward the rear side in space, and therefore the absolute configuration of the optically pure selenonium ylide (+)-**1a** was determined to be *R*. Accordingly, the configuration of the other diastereoisomer (–)-**1b** was *S*.

The bond length Se–C(2) (1.873 Å) in isomer **1a** is considerably shorter than the usual Se–C bond length (1.95–2.04 Å)[27] and slightly shorter than that in diphenylselenonium diacetylmethylide (1.906 Å).[28] This suggests that ylide **1a** has a large resonance contribution from an ylene structure or else some double-bond character in the Se–C(2) bond. The bond lengths C(2)–C(3) and C(2)–C(7) (1.41 Å) in isomer **1a** are also shorter than the usual C–C single-bond length. This implies that ylide **1a** is stabilized by the betaine resonance structure. The bond angles around selenium in compound **1a** are C(1)–Se–C(2) 103.8(4)°, C(1)–Se–C(10) 98.6(4)° and C(2)–Se–C(10) 102.1(4)°, which are significantly smaller than the values of 100.8, 105.0 and 107.5° found in diphenylselenonium diacetylmethylide or the corresponding bond angles 102, 103 and 107° found in dimethylsulfonium dicyanomethylide.[28] These results show that selenonium ylide **1a** has very sharp wedge structure, although a 'sharper' pyramidal structure has been reported in trimethylselenonium iodide whose C–Se–C bond angles are 98.0, 97.9 and 99.1°.[29]

Spectroscopic Studies of Optically Active Ylides **1a** *and* **1b**.—As we succeeded in isolating diastereoisomerically pure selenonium ylide **1a** and optically active selenonium ylide **1b**, spectroscopic studies of ylides **1a** and **1b** (^1H NMR and CD) were also carried out. The proton signal of MeSe was expected to be observed as a singlet at different chemical shifts with equal signal strength in the diastereoisomeric mixture of selenonium ylides dia.-**1a**, **b** and as only one singlet signal in optically pure selenonium ylide **1a**. However, only one singlet proton signal of MeSe was observed, at δ 3.22, not only in optically pure ylide (+)-**1a** but also in diasteroisomeric mixture of selenonium ylides dia.-**1a**, **b** when a 500 MHz NMR apparatus was used. The proton signal for the *ortho*-position of aromatic hydrogen from selenium in dia.-**1a**, **b** was observed as two kinds of AB quartet at δ 7.724 and 7.732, whereas that of diastereoisomerically pure selenonium ylide **1a** was observed as the usual AB quartet at δ 7.732 and 8.122 as shown in Fig. 3. In contrast to our expectations, the proton signal of MeSe in the two diastereoisomers appears at the same chemical shift. However, the AB quartet signal for the *ortho* proton of the aromatic ring in dia.-**1a**, **b** was found to appear at different chemical shifts.

Two singlet proton signals for MeSe were observed, at δ 4.01 and 4.16 with equal signal strength, for the diastereoisomeric mixture of selenonium ylides dia.-**1a**, **b** when the ^1H NMR spectrum was measured in the presence of shift reagent europium trisheptafluorobutyrylcamphorate [Eu(hfc)$_3$] (20 mmol%). On the other hand, only one singlet ^1H signal for MeSe was observed, at δ 4.53, for the diastereoisomeric pure selenonium ylide **1a**, and two singlet ^1H NMR signals for isomer **1b** were observed, at δ 4.25 and 4.33, with 5:4 signal-strength

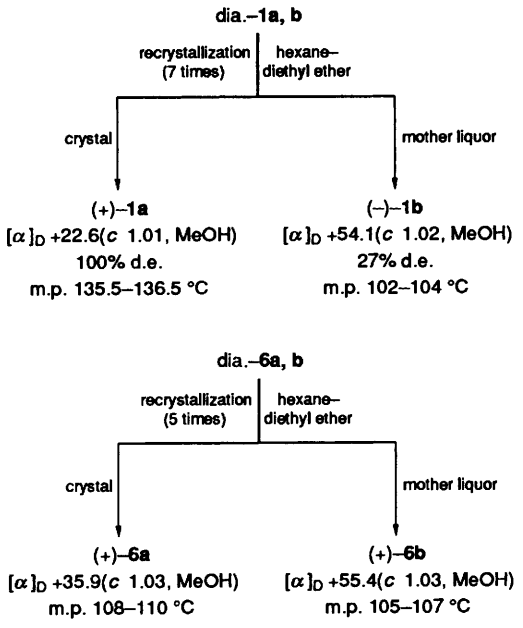


Fig. 1 Optical resolution of dia.-**1a**, **b** and dia.-**6a**, **b** by fractional recrystallization

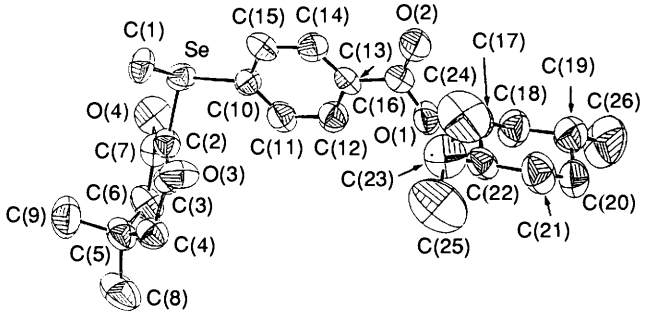


Fig. 2 ORTEP drawing of optically active selenonium ylide (+)-**1a**, showing the numbering scheme of the atoms

ratio under similar conditions. These results show that the proton signal of MeSe observed at higher magnetic field is assigned as that of (+)-**1a**, and that seen at lower magnetic field is assigned as that of (–)-**1b**. Hence, the optical purity of diastereoisomeric mixture of compound **1** can be determined from the integration ratio of their ^{1}H NMR signals at the *ortho*-position of the aromatic ring or at the MeSe proton signal using the shift reagent.

The CD spectrum of optically pure selenonium ylide (+)-**1a** showed positive Cotton effects at 266 and 234 nm and negative Cotton effects at 289 and 251 nm in methanol, and that of optically active ylide (–)-**1b** showed a negative Cotton effect at 266 nm and a positive Cotton effect at 251 nm as shown in Fig. 4. These results show that the Cotton effects at 266 and 251 nm reflect the chirality of the selenium atom in the ylide. Thus, it was clarified that the selenonium ylide **1** showing positive optical rotation, a positive Cotton effect at 266 nm, and a negative Cotton effect at 251 nm, has the *R* configuration, and consequently that the selenonium ylide **1** showing negative optical rotation, a negative Cotton effect at 266 nm, and a positive Cotton effect at 251 nm has the *S* configuration. The relationships between the absolute configuration, specific rotation and CD spectra of optically active selenonium ylide (+)-**1a** are summarized in Fig. 5.

Trial to Synthesize the Enantiomerically Pure Selenonium Ylide.—The optically active selenonium ylides thus obtained

Table 1 Positional parameters for compound (+)-**1a** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Se	−1.005 20(5)	−1.000 26(1)	−0.090 46(8)
O(1)	−1.354 5(4)	−0.543 1(6)	−0.187 0(8)
O(2)	−1.362 8(5)	−0.607(1)	0.035 6(9)
O(3)	−0.935 9(5)	−0.6821(8)	−0.158 8(7)
O(4)	−0.966 5(5)	−1.168(1)	−0.338 5(8)
C(1)	−0.932 3(6)	−0.924(1)	0.075 3(9)
C(2)	−0.953 3(6)	−0.926(1)	−0.244(1)
C(3)	−0.924 9(6)	−0.777(1)	−0.248(1)
C(4)	−0.878 3(6)	−0.731(1)	−0.376(1)
C(5)	−0.840 7(6)	−0.861(1)	−0.449 5(9)
C(6)	−0.907 5(6)	−0.982(2)	−0.482 3(9)
C(7)	−0.943 7(6)	−1.035(1)	−0.348(1)
C(8)	−0.815 3(7)	−0.797(2)	−0.598(1)
C(9)	−0.758 8(7)	−0.923(2)	−0.363(1)
C(10)	−1.101 3(5)	−0.864(1)	−0.085 2(9)
C(11)	−1.132 3(6)	−0.838(1)	0.044 1(9)
C(12)	−1.206 1(6)	−0.754(1)	0.045(1)
C(13)	−1.248 5(5)	−0.700(1)	−0.077(1)
C(14)	−1.217 3(6)	−0.727(1)	−0.209(1)
C(15)	−1.142 0(6)	−0.812(1)	−0.212(1)
C(16)	−1.327 3(6)	−0.614(1)	−0.069(1)
C(17)	−1.431 2(6)	−0.447(1)	−0.189(1)
C(18)	−1.491 9(6)	−0.504(2)	−0.315(1)
C(19)	−1.573 5(8)	−0.403(2)	−0.330(1)
C(20)	−1.547 7(8)	−0.246(2)	−0.356(2)
C(21)	−1.483 0(8)	−0.186(2)	−0.232(2)
C(22)	−1.404 6(6)	−0.288(1)	−0.206(1)
C(23)	−1.338 4(9)	−0.239(2)	−0.082(2)
C(24)	−1.378(1)	−0.214(2)	0.055(2)
C(25)	−1.294(1)	−0.092(2)	−0.122(2)
C(26)	−1.637(1)	−0.457(2)	−0.456(2)

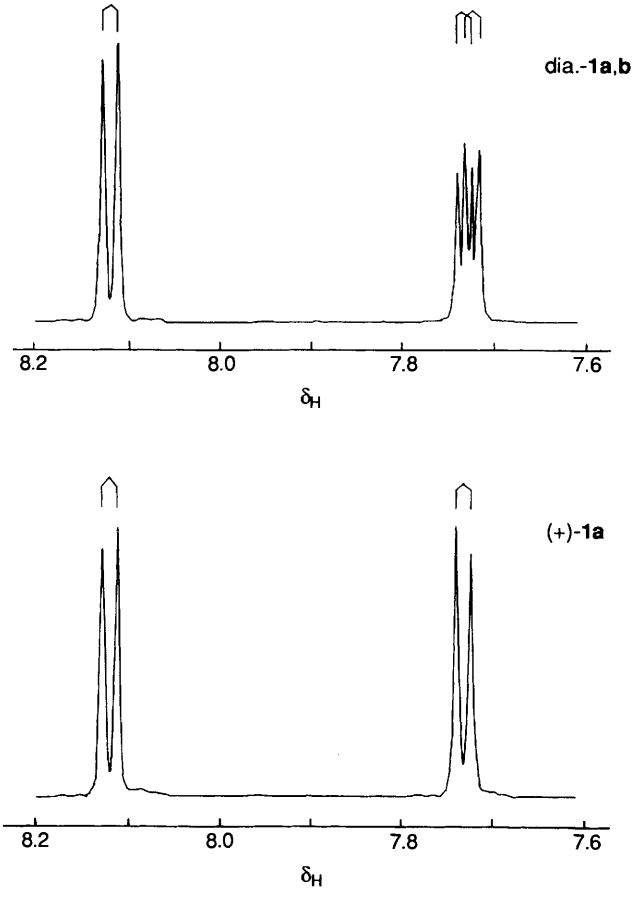


Fig. 3 1H NMR signals of aromatic hydrogens of dia.-**1a**, **b** and (+)-**1a**

Table 2 Bond distances (Å) and bond angles (degrees) with e.s.d.s in parentheses

(a) Bond distances

Se–C(1)	1.970(8)	C(10)–C(15)	1.39(1)
Se–C(2)	1.87(1)	C(11)–C(12)	1.38(1)
Se–C(10)	1.947(8)	C(12)–C(13)	1.37(1)
O(1)–C(16)	1.32(1)	C(13)–C(14)	1.42(1)
O(1)–C(17)	1.48(1)	C(13)–C(16)	1.47(1)
O(2)–C(16)	1.20(1)	C(14)–C(15)	1.41(1)
O(3)–C(3)	1.23(1)	C(17)–C(22)	1.50(1)
O(4)–C(7)	1.24(1)	C(17)–C(18)	1.53(1)
C(2)–C(3)	1.41(1)	C(18)–C(19)	1.56(2)
C(2)–C(7)	1.41(1)	C(19)–C(20)	1.49(2)
C(3)–C(4)	1.55(1)	C(19)–C(26)	1.55(2)
C(4)–C(5)	1.51(2)	C(20)–C(21)	1.56(2)
C(5)–C(6)	1.51(2)	C(21)–C(22)	1.53(2)
C(5)–C(8)	1.62(2)	C(22)–C(23)	1.56(2)
C(5)–C(9)	1.55(1)	C(23)–C(24)	1.52(2)
C(6)–C(7)	1.53(1)	C(23)–C(25)	1.55(3)
C(10)–C(11)	1.40(1)		

(b) Bond angles

C(2)–Se–C(10)	102.1(4)	C(2)–C(3)–C(4)	117.3(9)
C(2)–Se–C(1)	103.8(4)	O(4)–C(7)–C(2)	123(1)
C(10)–Se–C(1)	98.6(4)	O(4)–C(7)–C(6)	120(1)
C(16)–O(1)–C(17)	118.6(8)	C(2)–C(7)–C(6)	116.9(9)
C(15)–C(10)–C(11)	122.9(8)	C(5)–C(6)–C(7)	111.3(8)
C(15)–C(10)–Se	118.0(7)	C(4)–C(5)–C(6)	110.2(8)
C(11)–C(10)–Se	118.6(6)	C(4)–C(5)–C(9)	111.9(8)
C(12)–C(13)–C(14)	120.8(8)	C(4)–C(5)–C(8)	106(1)
C(12)–C(13)–C(16)	118.5(9)	C(6)–C(5)–C(9)	112(1)
C(14)–C(13)–C(16)	120.7(8)	C(6)–C(5)–C(8)	107.8(8)
O(2)–C(16)–O(1)	123(1)	C(9)–C(5)–C(8)	108.6(8)
O(2)–C(16)–C(13)	123(1)	C(5)–C(4)–C(3)	113.6(9)
O(1)–C(16)–C(13)	113.9(9)	C(17)–C(18)–C(19)	108(1)
C(12)–C(11)–C(10)	118.5(8)	C(20)–C(19)–C(26)	109(1)
O(1)–C(17)–C(22)	108.4(7)	C(20)–C(19)–C(18)	109(1)
O(1)–C(17)–C(18)	104.8(9)	C(26)–C(19)–C(18)	110(1)
C(22)–C(17)–C(18)	113(1)	C(22)–C(21)–C(20)	112(1)
C(15)–C(14)–C(13)	119.0(8)	C(19)–C(20)–C(21)	111(1)
C(3)–C(2)–C(7)	124.7(9)	C(17)–C(22)–C(21)	110.3(9)
C(3)–C(2)–Se	121.7(7)	C(17)–C(22)–C(23)	110.8(9)
C(7)–C(2)–Se	113.5(7)	C(21)–C(22)–C(23)	115(1)
C(13)–C(12)–C(11)	120.9(9)	C(24)–C(23)–C(25)	109(2)
C(10)–C(15)–C(14)	117.8(9)	C(24)–C(23)–C(22)	113(1)
O(3)–C(3)–C(2)	124.1(9)	C(25)–C(23)–C(22)	109(1)
O(3)–C(3)–C(4)	118.6(8)		

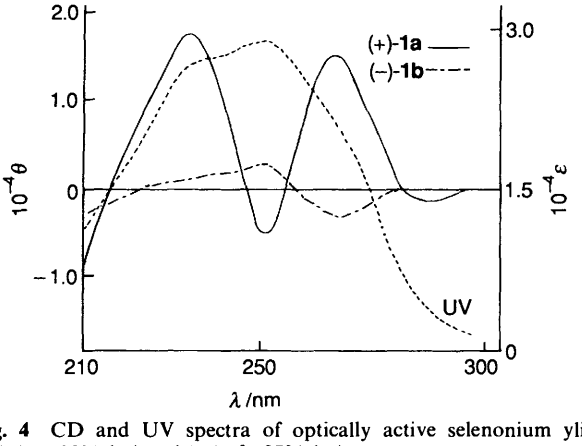


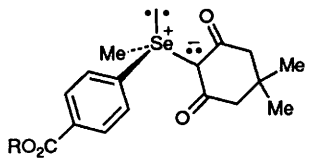
Fig. 4 CD and UV spectra of optically active selenonium ylides (+)-**1a** (100% d.e.) and (−)-**1b** (27% d.e.)

were diastereoisomerically active selenonium ylides containing two chiral moieties. We attempted their conversion into the enantiomeric selenonium ylides by removal of the menthyl moiety. The experimental conditions for the removal of a menthyl moiety are neutral or basic and as mild as possible since the selenonium ylide (+)-**1a** was found to be relatively stable under basic conditions and unstable under acidic conditions. Thus, the removal of the menthyl moiety from the selenonium ylide (+)-**1a** was carried out by the following three methods which are considered to use relatively mild conditions and to be generally excellent for ester exchange: (a) reduction of (+)-**1a** with lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at −78 °C and then by diisobutylaluminium hydride (DIBAL) at −78 °C,[30] (b) transesterification of (+)-**1a** with titanium tetraethoxide in an alcohol such as methanol, ethanol or benzyl alcohol under reflux for 6–24 h,[31] and (c) transesterification of (+)-**1a** with iodotrimethylsilane (TMSI) in chloroform at 50 °C for 3–9 days, tetrabutylammonium fluoride (TBAF) in THF for 30 min, and then iodomethane.[32] However, all such attempts to remove the menthyl moiety of compound (+)-**1a** failed, and accordingly we could not isolate the enantiomer of the selenonium ylide.

Epimerization of Optically Active Selenonium Ylide.—The rate of racemization of the optically active selenonium ylide was studied by heating of a solution of the diastereoisomeric excess selenonium ylide (−)-**1b** in methanol in a sealed tube. When the solution was heated at 80 °C for 2 days, no decrease of the specific rotation was observed and the ^{1}H NMR spectrum was the same as that of the starting compound (−)-**1b**. On the other hand, when the solution was heated at 100 °C for 2 h or at 110 °C for 1 h, the specific rotation was slightly changed to $[\alpha]_D$ −49.4 from $[\alpha]_D$ −50.2 but the colour of the solution was changed to yellow and the ^{1}H NMR spectrum had become complicated. This means that the selenonium ylide was not simply racemized thermally but also decomposed under these conditions. Although we could not determine the rate of racemization by pyramidal inversion, it is clear that the selenonium ylide is quite stable toward pyramidal inversion at temperatures lower than 80 °C and decomposes at temperatures higher than 100 °C. The rates of racemization of optically active sulfonium ylides by pyramidal inversion have previously been determined. For example the first-order rate constant (k_1) for the racemization of ethylmethylsulfonium acetyl(benzoyl)-methylide at 50 °C is 3.97×10^{-4} s^{-1} and the activation parameter is calculated as $\Delta H^{\ddagger}$ 23.6 kcal mol^{-1} * and $\Delta S^{\ddagger}$ −1.1 eu.[8] It was found that the selenonium ylide is extremely stable toward thermal inversion (racemization by pyramidal inversion) in comparison with similar sulfonium ylides. The reason why the selenonium ylide is much more stable than sulfonium ylides toward pyramidal inversion is not clear at the present time. We can only qualitatively interpret as follows. As was observed in the ORTEP drawing of optically pure selenonium ylide (+)-**1a** (Fig. 2), the pyramidal or wedge-shaped structure of selenonium ylide **1** is 'sharper' than that of sulfonium ylides probably because the valence shell electron-pair repulsion in the selenonium ylide is smaller than that in sulfonium ylides since the carbon–selenium bond length is longer than the carbon–sulfur bond and/or selenium is less electronegative than sulfur and that 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. Accordingly, an extremely high reaction temperature or an activation energy is required for pyramidal inversion of the selenonium ylide. Therefore, decomposition of the ylide structure itself occurs faster than does pyramidal inversion in such high temperatures.

In conclusion, an optically pure, stable selenonium ylide was isolated for the first time. The absolute configuration around the selenium atom of the optically pure selenonium ylide was also determined for the first time by X-ray diffraction.

* 1 cal = 4.184 J.



1a; R = (–)-menthyl

optical rotation: positive

cd spectrum: 266 nm (positive Cotton effect)
251 nm (negative Cotton effect)

absolute configuration: *R*-form

Fig. 5 The relationships between the absolute configuration, specific rotation and CD spectrum of optically active selenonium ylide (+)-**1a**

Experimental

M.p.s were determined on a Yamato MP-2 apparatus and are uncorrected. IR spectra were recorded on a Hitachi 260-10 spectrometer with samples as either neat liquids or KBr disks. UV spectra were measured on a Hitachi 220A spectrometer. ^{1}H NMR spectra with Me_4Si were determined on a JEOL JMN-PMX 60SI (60 MHz), a Bruker AM-500 FT NMR (500 MHz) or a JEOL EX400 FT NMR (400 MHz) spectrometer. ^{13}C NMR spectra were measured on a JEOL JNM FX 90Q FT NMR (22.5 MHz), a Bruker AM-500 FT NMR (125 MHz) or a JEOL EX400 FT NMR (100 MHz) spectrometer. ^{1}H–^{13}C COSY NMR spectra were determined on a Bruker AM-500 NMR spectrometer. ^{1}H and ^{13}C NMR signals were referenced to Me_4Si as internal standard, and *J*-values were given in Hz. Mass spectra were measured on a JEOL JMS DX-300 mass spectrometer with JEOL JMA 5000 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. TLC and preparative TLC (PLC) were performed with Merck Kieselgel $60F_{254}$ and Merck Aluminium-oxid $150F_{254}$ (Type T). Column chromatography was performed with Wako gel C-200 and Nakarai activated alumina 200. Medium-pressure prepack column chromatography was performed using a Kusano Micro Pump KPW-20 and C.I.G. column system I.D.-20 with Pre Packed Column Si-10 or Shodex RI SE-52. Gel-permeation chromatography (GPC) was performed using a JAI LC-08 liquid chromatograph with JAIGEL-1H column (20 mm × 600 mm × 2) and chloroform as eluent. X-Ray data collection was carried out on a Mac Science MXC18 fully automatic four-circle diffractometer and the computations were performed on an NS-SUN Work-Station System. All solvents were purified and dried by the usual procedures.

*Synthesis of Diastereoisomeric {4′-[(–)-Menthyloxycarbonyl]phenyl}(methyl)selenonium 4,4-Dimethyl-2,6-dioxocyclohexylide (dia.-***1a, b**).—Selenium powder (79 g, 1.0 mol) was added to a stirred solution of sodium hydroxide (60 g) in water (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 has 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 (1000 cm^3) and 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[33] **2** (61.8 g, 61%), ν_{max}(neat)/cm^{-1} 2890, 1405, 1255 and 885; δ_H($CDCl_3$) 2.55 (6 H, s, MeSe).

To a stirred solution of dimethyl diselenide (1.88 g, 10 mmol) in ethanol (100 cm^3) was slowly added sodium borohydride until the colour of the solution has been discharged at –10 °C. To this solution containing sodium methaneselenolate was added copper powder (0.50 g), *p*-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. 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 extracted with chloroform, and the extract was dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. Purification of the residue by silica gel chromatography with ethyl acetate as eluent to give 4-(methylseleno)benzoic acid **3**[22] (4.2 g, 63%), m.p. 162–163 °C; ν_{max}(KBr)/cm^{-1} 2950–2550, 1680, 1585, 1410, 1300, 1180, 1065, 1010, 835 and 750; δ_H($CDCl_3$) 2.39 (3 H, s, MeSe), 7.40 and 7.93 (4 H, ABq, *J* 8.0 Hz, ArH) and 9.23 (1 H, br, CO_2H).

A solution containing 4-(methylseleno)benzoic acid **3** (3.85 g, 17.5 mmol), DCC (3.97 g, 1.92 mmol), DMAP (0.214 g, 0.175 mmol), and (–)-menthol (3.01 g, 19.3 mmol) in dichloromethane (90 cm^3) was stirred at room temperature for 24 h.[23] 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 then dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure left a yellow residue, which was subjected to prepack column chromotography using a mixture of hexane and ethyl acetate (60:1) as eluent to give (–)-menthyl 4-(methylseleno)benzoate **4a** (4.63 g, 75%), m.p. 50–52 °C; ν_{max}(KBr)/cm^{-1} 2960–2870, 1710, 1595, 1460, 1395, 1280, 1110, 845 and 760; δ_H($CDCl_3$) 0.73–2.03 [18 H, m, (–)-methyl except *O*-methine], 2.33 (3 H, s, MeSe), 4.89 (1 H, td, *J* 10.0 and 3.8, *O*-methine) and 7.34 and 7.85 (4 H, ABq. *J* 8.2, ArH); *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-(methylseleno)-benzoate **4a**, (5.72 g, 16.3 mmol), pyridine (1.29 g) and methanol (2.61 g) 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.[24] 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 dichloromethane (30 cm^3 × 2), and the combined organic layers were dried over anhydrous magnesium sulfate. After removal of the solvent and pyridine under reduced pressure using a 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 **5a** (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, (–)-menthyl except *O*-methine], 2.63 (3 H, s, MeSe), 4.93 (1 H, td, *J* 10.0 and 3.8, *O*-methine) and 7.78 and 8.15 (4 H, ABq, *J* 8.4, ArH); *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.

To a solution containing (–)-menthyl 4-(methylselenininyl)-benzoate (2.22 g, 6.01 mmol) **5a** and dimedone (0.843 g, 6.01 mmol) in chloroform (150 cm^3) was added anhydrous magnesium sulfate (0.792 g, 6.61 mmol), and the mixture was stirred at room temperature for 12 h.[25] After confirmation that the starting selenoxide **5a** and dimedone had completely consumed (TLC and ^{1}H NMR), the magnesium sulfate was filtered off and the solvent was removed under reduced pressure to give a diastereoisomeric mixture (2.95 g, 100%) of {4′-[(–)-menthyloxycarbonyl]phenyl}(methyl)selenonium 4,4-

dimethyl-2,6-dioxocyclohexylide (dia.-**1a**, **b**), m.p. 88–92 °C; $[\alpha]_D$ −38.1 (*c* 1.01, MeOH); ν_{max}(KBr)/cm^{-1} 2950, 2920, 2820, 1715, 1550, 1450, 1390, 1340, 1270, 1110, 1050, 845 and 750; δ_H($CDCl_3$; 500 MHz) 0.780 (3 H, d, *J* 6.93, Me), 0.915 (3 H, d, *J* 7.00, Me), 0.933 (3 H, d, *J* 7.00, Me), 1.094 (6 H, s, Me_2C), 1.059–1.146 (2 H, m, CH_2), 1.519–1.566 (2 H, m, CH_2), 1.692–1.920 (2 H, m, CH × 2), 1.721–1.754 (2 H, m, CH_2), 2.099 (1 H, br d, *J* 11.9, CH), 2.350 and 2.390 [4 H, ABq, *J* 17.0, $(CH_2)_2CMe_2$], 3.22 (3 H, s, MeSe), 4.936 (1 H, td, *J* 10.9 and 4.39, OCH), 7.724 and 8.122 [2 H, ABq, *J* 8.41, ArH of (−)-isomer] and 7.732 and 8.122 [2 H, ABq, *J* 8.41, ArH of (+)-isomer]; δ_C($CDCl_3$) 16.44, 16.46, 20.68, 22.00, 23.55, 23.58, 26.49, 26.52, 28.53, 31.45, 31.77, 34.23, 40.85, 47.23, 51.58, 75.71, 92.17, 92.30, 128.92, 131.01, 133.57, 134.51, 164.63, 191.59 and 191.62; *m/z* 492 (M^+) (^{80}Se), 354, 352, 337, 335, 307, 291, 277, 261, 259, 233, 216, 214, 199, 197, 138, 123, 110 and 95 (Found: C, 63.8; H, 7.3. Calc. for $C_{26}H_{36}O_4Se$: C, 63.54; H, 7.38%). The ratio **1a**:**1b** was determined to be 1:1 by ^{1}H NMR spectroscopy (500 MHz).

Synthesis of Diastereoisomeric {4′-[(+)-Menthyloxycarbonyl]phenyl}(methyl)selenonium 4,4-Dimethyl-2,6-dioxocyclohexylide (dia.-**6a**, **b**).—A solution containing 4-(methylseleno)-benzoic acid **3** (3.85 g, 17.5 mmol), DCC (3.97 g, 19.3 mmol), DMAP (0.214 g, 1.75 mmol), (+)-menthol and (3.01 g, 19.3 mmol) in dichloromethane (90 cm^3) was stirred at room temperature for 24 h.[23] After the solid (dicyclohexylurea) was 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 then dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure left a yellow residue, which was subjected to silica gel chromatography with a mixture of hexane and ethyl acetate (15:1) as eluent and then prepack column chromotography with a mixture of hexane and ethyl acetate (60:1) as eluent to give (+)-menthyl 4-(methylseleno)benzoate **4b** (4.32 g, 70%); m.p. 49–51 °C; ν_{max}(neat)/cm^{-1} 2950, 2920, 2860, 1700, 1590, 1280, 1260, 1170, 1100, 1020, 835 and 750; δ_H($CDCl_3$) 0.74–2.05 [18 H, m, (+)-menthyl except *O*-methine], 2.33 (3 H, s, MeSe), 4.95 (1 H, td, *J* 10.0 and 3.8, *O*-methine) and 7.37 and 7.88 (4 H, ABq, *J* 7.8, ArH); *m/z* 354 (M^+) (^{80}Se), 216, 199, 184, 138, 123 and 95.

To a solution containing (+)-menthyl 4-(methylseleno)-benzoate **4b** (5.72 g, 16.3 mmol), pyridine (1.29 g, 16.3 mmol), and methanol (2.61 g) in dichloromethane (500 cm^3) cooled at −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.[24] 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 dichloromethane (30 cm^3 × 2), and the combined organic layers were dried over anhydrous magnesium sulfate. After the solvent and pyridine had been removed under reduced pressure (rotary evaporator and then 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 **5b** (5.44 g, 91%), m.p. 145–146 °C; ν_{max}(KBr)/cm^{-1} 2960, 2940, 2880, 1715, 1595, 1395, 1275, 1115, 1020, 810 and 755; δ_H($CDCl_3$) 0.75–2.05 [18 H, m, (+)-menthyl except *O*-methine], 2.63 (3 H, s, MeSe), 4.92 (1 H, td, *J* 10.0 and 3.8, *O*-methine) and 7.81 and 8.17 (4 H, ABq, *J* 8.4, ArH); *m/z* 371 (M^+) (^{80}Se), 369, 233, 232, 231, 216, 214, 199, 197, 184, 156, 138, 123, 109 and 95.

To a solution containing (+)-menthyl 4-(methylseleninyl)-benzoate **5b** (2.22 g, 6.01 mmol) and dimedone (0.843 g, 6.01 mmol) in chloroform (50 cm^3) was added anhydrous magnesium sulfate (0.792 g, 6.61 mmol), and the mixture was stirred at room temperature for 12 h.[25] After confirmation that the starting selenoxide **5b** and dimedone had been completely consumed (TLC and ^{1}H NMR), the magnesium sulfate was filtered off, and the solvent was removed under reduced pressure to give a diastereoisomeric mixture of {4′-[(+)-menthyloxycarbonyl]phenyl}(methyl)selenonium 4,4-dimethyl-2,6-dioxocyclohexylide dia.-**6a**, **b** (2.95 g, 100%), m.p. 70–72 °C; $[\alpha]_D$(41.4 (*c* 1.11, MeOH); ν_{max}(KBr)/cm^{-1} 2950, 2925, 2865, 2820, 1715, 1550, 1345, 1270, 1110, 950, 845 and 755; δ_H($CDCl_3$; 400 MHz) 0.778 (3 H, d, *J* 7.32, Me), 0.902 and 0.914 (6 H, d, *J* 7.32, Me_2C), 1.092 (6 H, s, Me_2C), 1.049–1.181 (2 H, m, CH_2), 1.505–1.561 (2 H, m, CH_2), 1.708–1.744 (3 H, m, CH_2 and CH), 1.889–1.936 (1 H, m, CH), 2.098 (1 H, br d, *J* 11.72, CH), 2.373 [4 H, s, $Me_2C(CH_2)_2$], 3.224 (3 H, s, MeSe), 4.935 (1 H, td, *J* 10.23 and 4.40, OCH) and 7.731 and 8.124 (4 H, ABq, *J* 8.30, ArH); *m/z* 492 (M^+, ^{80}Se) (Found: *m/z*, 492.1789 (^{80}Se). Calc. for $C_{26}H_{36}O_4{}^{80}Se$: *m/z*, 492.1779]. The ratio **6a**:**6b** was determined to be 1:1 by ^{1}H NMR spectroscopy (400 MHz).

Optical Resolution of Selenonium Ylides **1a**, **b** *and* **6a**, **b**.—A solution containing a diastereoisomeric mixture (13.5 g) of {4′-[(−)-menthyloxycarbonyl]phenyl}(methyl)selenonium 4,4-dimethyl-2,6-dioxocyclohexylide dia.-**1a**, **b** was optically resolved by fractional recrystallization from hexane–diethyl ether. The specific rotation of crystalline selenonium ylide (+)-**1a** became constant {$[\alpha]_D$ + 22.6 (*c* 1.01, MeOH)} after seven fractional recrystallizations (isolated 2.0 g), and the other diastereoisomer (−)-**1b** (5.6 g) was obtained from the mother liquor {$[\alpha]_D$ −54.1 (*c* 1.02, MeOH)}. The optical purity of (+)-**1a**, $[\alpha]_D$ +22.6, was determined to be 100% de whereas that of (−)-**1b**, $[\alpha]_D$ −54.1, was 27% de by ^{1}H NMR spectroscopy.

Similarly, a solution containing a diastereoisomeric mixture (12.8 g) of {4′-[(+)-menthyloxycarbonyl]phenyl}(methyl)-selenonium 4,4-dimethyl-2,6-dioxocyclohexylide dia.-**6a**, **b** was fractionally recrystallized from hexane–diethyl ether. However, in this case, all attempts to obtain optically pure (de 100%) selenonium ylide failed, and consequently the optically active compound (+)-**6a** (4.4 g) {$[\alpha]_D$ +35.9 (*c* 1.03, MeOH)}, was obtained by five recrystallizations from hexane–diethyl ether, and isomer (+)-**6b** (0.8 g) {$[\alpha]_D$ +55.4 (*c* 1.03, MeOH)}, was obtained from the mother liquor.

Compound (+)-**1a**: m.p. 135.5–136.5 °C; $[\alpha]_D^{25}$ +22.6 (*c* 1.01, MeOH); ν_{max}(KBr)/cm^{-1} 2950, 2930, 2870, 1715, 1550, 1340, 1270, 1105, 1010, 850 and 755; λ_{max}(MeOH)/nm 250.3 (ε 2.89 × 10^4); CD (MeOH)/nm 288 ([θ] −2.12 × 10^3), 266 ([θ] +1.48 × 10^4), 251 ([θ] −5.88 × 10^3) and 234 ([θ] +1.78 × 10^4); δ_H($CDCl_3$; 500 MHz) 0.781 (3 H, d, *J* 6.93, Me), 0.914 and 0.934 (6 H, d, *J* 7.00, Me_2CH), 1.092 (6 H, s, Me_2C), 1.047–1.147 (2 H, m, CH_2), 1.520–1.572 (2 H, m, CH_2), 1.721–1.748 (2 H, m, CH_2), 1.888–1.923 (2 H, m, CH × 2), 2.098 (1 H, br d, *J* 11.8, CH), 2.350 and 2.390 [4 H, ABq, *J* 17.0, $(CH_2)_2CMe_2$], 3.224 (3 H, s, MeSe), 4.937 (1 H, td, *J* 10.9 and 4.40, OCH) and 7.732 and 8.122 (4 H, ABq, *J* 8.41, ArH); δ_C($CDCl_3$) 16.46, 20.68, 22.00, 23.58, 26.52, 28.53, 31.45, 31.77, 34.23, 40.85, 47.23, 51.58, 75.71, 92.29, 128.92, 131.01, 133.57, 134.51, 164.63 and 191.59; *m/z* 492 (M^+, ^{80}Se) [Found: *m/z*, 492.1753 (^{80}Se). Calc. for $C_{26}H_{36}O_4{}^{80}Se$: *m/z*, 492.1779].

Compound (−)-**1b**: m.p. 102–104 °C; $[\alpha]_D$ −54.1 (*c* 1.02, MeOH); ν_{max}(KBr)/cm^{-1} 2950, 2925, 2870, 1715, 1550, 1340, 1265, 1100, 1010, 950, 840 and 755; CD (MeOH)/nm 266 ([θ] 3.56 × 10^3) and 251 ([θ] +3.05 × 10^3); δ_H($CDCl_3$; 400 MHz) 0.778 (3 H, d, *J* 6.84, Me), 0.901 and 0.915 (6 H, d, *J* 6.84, Me_2CH), 1.092 (6 H, s, Me_2C), 1.049–1.127 (2 H, m, CH_2), 1.515–1.569 (2 H, m, CH_2), 1.706–1.743 (3 H, m, CH_2 and CH), 1.889–1.908 (1 H, m, CH), 2.097 (1 H, br d, *J* 11.72, CH), 2.374 [4 H, s, $Me_2C(CH_2)_2$], 3.227 (3 H, s, MeSe), 4.935 (1 H, td, *J* 11.23 and 4.40, OCH) and 7.722 and 8.125 (4 H, ABq, *J* 8.30, ArH); *m/z* 492 (M^+, ^{80}Se) [Found: *m/z*, 492.1818 (^{80}Se). Calc. for $C_{26}H_{36}O_4{}^{80}Se$: *m/z*, 492.1779].

Compound (+)-**6a**: m.p. 108–110 °C; $[\alpha]_D^{27}$ +35.9 (*c* 1.01,

MeOH); ν_{max}(KBr)/cm^{-1} 2950, 2925, 2860, 1715, 1550, 1340, 1265, 1100, 1005, 845 and 755; δ_H($CDCl_3$; 400 MHz) 0.778 (3 H, d, *J* 6.83, Me), 0.912 and 0.931 (6 H, d, *J* 6.83, Me_2CH), 1.092 (6 H, s, Me_2C), 1.048–1.209 (2 H, m, CH_2), 1.539 (2 H, t, *J* 10.0, CH_2), 1.729 (2 H, d, *J* 11.7, CH_2), 1.825 (1 H, s, CH), 1.882–1.918 (1 H, m, CH), 2.080 (1 H, d, *J* 11.2 CH), 2.367 [4 H, s, $(CH_2)_2CMe_2$], 3.223 (3 H, s, MeSe), 4.935 (1 H, td, *J* 10.74 and 4.40, OCH) and 7.729 and 8.123 (4 H, ABq, *J* 8.79, ArH); δ_C($CDCl_3$; 100 Mz) 16.40, 20.61, 20.72, 21.98, 23.50, 26.44, 28.51, 31.42, 31.75, 34.18, 40.82, 47.17, 51.54, 51.59, 75.62, 75.69, 92.25, 128.84, 128.89, 131.03, 131.11, 133.50, 134.42, 164.59 and 191.57; *m/z* 492 (M^+, ^{80}Se) [Found: *m/z*, 492.1736 (^{80}Se). Calc. for $C_{26}H_{36}O_4{}^{80}Se$: *m/z*, 492.1779].

Compound (+)-**6b**: m.p. 105–107 °C; $[\alpha]_D{}^{27}$ +55.4 (*c* 1.03, MeOH); ν_{max}(KBr)/cm^{-1} 2950, 2930, 2870, 1715, 1560, 1345, 1270, 1110, 1010, 845 and 755; δ_H($CDCl_3$; 400 MHz) 0.777 (3 H, d, *J* 7.32, Me), 0.913 and 0.925 (6 H, d, *J* 7.32, Me_2CH), 1.092 (6 H, s, Me_2C), 1.048–1.136 (2 H, m, CH_2), 1.539 (2 H, t, *J* 10.74, CH_2), 1.730 (3 H, d, *J* 10.74, CH_2 and CH), 1.887–1.992 (1 H, m, CH), 2.096 (1 H, d, *J* 11.72, CH), 2.369 [4 H, s, $(CH_2)_2CMe_2$], 3.222 (3 H, s, MeSe), 4.933 (1 H, td, *J* 10.74 and 3.90, OCH) and 7.719 and 8.123 (4 H, ABq, *J* 8.79, ArH); δ_C($CDCl_3$; 100 MHz) 16.39, 20.73, 21.99, 23.53, 26.39, 26.45, 28.50, 31.41, 31.76, 34.13, 34.21, 40.75, 40.85, 47.19, 51.56, 75.59, 75.72, 128.81, 128.90, 131.02, 131.13, 133.51, 134.41, 164.60 and 191.61; *m/z* 492 (M^+, ^{80}Se) [Found: *m/z*, 492.1753 (^{80}Se). Calc. for $C_{26}H_{36}O_4{}^{80}Se$: *m/z*, 492.1779].

Crystal Data for Compound (+)-**1a**.—$C_{26}H_{36}O_4Se$, M = 492.60. Monoclinic, *a* = 15.765(7), *b* = 8.930(3), *c* = 9.546(5) Å, β = 96.42(4)°, *V* = 1336(1) Å^3, space group $P2_1$, *Z* = 2, D_x = 1.22 g cm^{-3}. Colourless rods. Crystal dimensions: 0.40 × 0.15 × 0.07 mm^3, μ(Mo-Kα) = 13.69 cm^{-1}. *F*(000) = 516. *T* = 295 K.

Data collection and processing. A Mac Science MXC18 four-circle diffractometer with graphite-monochromated Mo-Kα radiation (0.7107 Å) was used. The unit-cell parameters were determined from 25 reflections with $30° \leqslant 2\theta \leqslant 35°$. Intensity data with $2\theta \leqslant 55°$ ($0 \leqslant h \leqslant 20$, $0 \leqslant k \leqslant 11$, $-12 \leqslant l \leqslant 12$) were collected with the 2θ–ω-scan technique (scan speed 8° min^{-1}) at 3488 reflections. The deviation of three standard reflections measured every 100 reflections was less than 2.6% decay over the time of the entire data correction. The intensities were corrected for Lorentz and polarization factors, but not for absorption.

Structure analysis and refinement. The structure was solved by Monte-Carlo direct methods [34] by the use of the MULTAN-78 program.[35] The full-matrix least-squares refinement for non-H atoms was carried out for $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where the weight $w = 1.0/[\sigma^2(|F_o| + 0.001(|F_o|^2)]$, for 1810 independent reflections with $F_o > 3.0\sigma(F_o)$. The final discrepancy factors were $R = 0.062$ and $R_w = 0.072$ and $(\Delta/\sigma)_{max}$ in the final refinement cycle was 0.08. The scattering factors were taken from International Tables for X-Ray Crystallography, Vol. 4.[36] All the calculations were carried out on a Mac Science MXC18 SYSTEM, and ORTEP[37] was employed for drawing the molecular structure.*

Kinetic Studies on the Epimerization of Optically Active Selenonium Ylide (−)-**1b**.—A solution containing compound (−)-**1b** (1 g) ($[\alpha]_D$ −50.2; *c* 1.00, MeOH) in methanol (100 cm^3) was heated at either 80 or 100 °C. The same specific rotation and ^{1}H NMR spectrum were observed after heating at 80 °C for 2 days. The results means that compound **1b** does not epimerize by pyramidal inversion and also that the ylide structure is stable under the conditions used. The specific rotation was $[\alpha]_D$ −49.4 after heating at 100 °C for 2 h. However, the ^{1}H NMR spectrum was complicated and hence the ylide was decomposed at 100 °C. Hence, although the trial to determine the rate constants and to estimate the activation energy and entropy for the epimerization by pyramidal inversion of the selenonium ylide **1b** failed, these results suggest that selenonium ylides are very stable toward pyramidal inversion.

* Thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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