CHEMISTRY LETTERS, pp. 249-250, 1991.

Synthesis of Optically Active Selenonium Ylide

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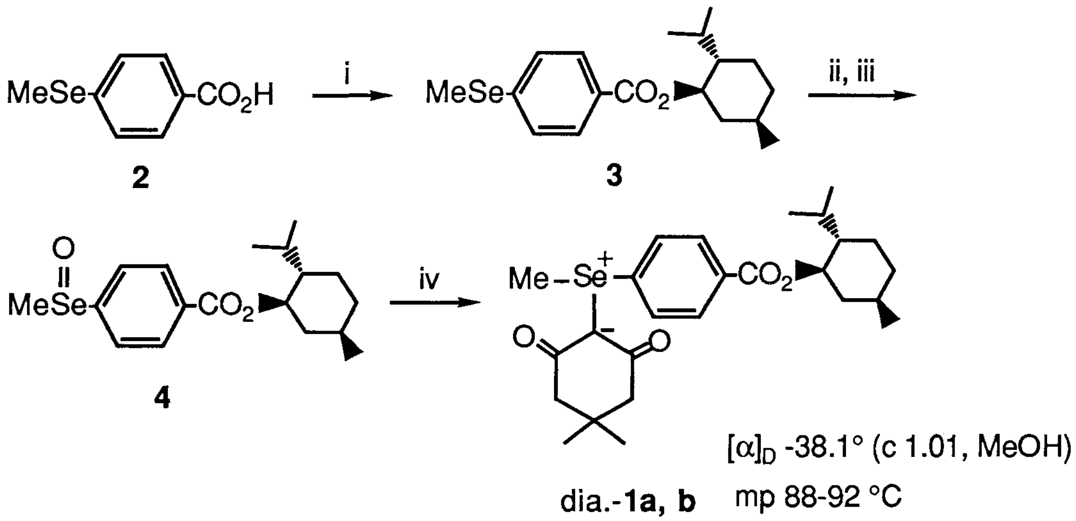
Fractional recrystallization of diastereomeric methyl[4'-(*l*-menthyloxycarbonyl)phenyl]selenonium 4,4-dimethyl-2,6-dioxocyclohexylide from hexane-ether gave optically pure (+)-selenonium ylide as a stable crystal.

Syntheses and stereochemistry of optically active sulfur compounds have been extensively investigated,1) and some of them are utilized for asymmetric syntheses.2) Meanwhile, there are a little studies on the corresponding optically active selenium compounds and the optical purity of these compounds were low.3) Recently, we have succeeded to resolve diastereomeric mixture of selenoxides by optical resolution and isolated optically pure selenoxides.4) We have extended this method to the preparation of optically active selenonium ylides, and the results will be described herein.

Diastereomeric methyl[4'-(*l*-menthyloxycarbonyl)phenyl]selenonium 4,4-dimethyl-2,6-dioxocyclohexylide (dia.-**1**) was prepared by the following Scheme.



[α]D -38.1° (c 1.01, MeOH)
mp 88-92 °C

i, *l*-menthol, DCC, DMAP, CH_2Cl_2, room temp , 24 h; ii, *t*-BuOCl, pyridine, MeOH, CH_2Cl_2, -20 °C; iii, aq. NaOH; iv, dimedone, $MgSO_4$, $CHCl_3$, room temp, 12 h.

Reaction of *p*-methylselenobenzoic acid (**2**) with *l*-menthol afforded *l*-menthyl *p*-methylselenobenzoate (**3**) in 75% yield. Oxidation of **3** with *t*-butyl hypochlorite$^{5)}$ gave the corresponding selenoxide **4** in 92% yield. Condensation of **4** with dimedone afforded a diastereomeric mixture of dia.-**1**, $[\alpha]_D$ -38.1° (c 1.01, MeOH) and mp 88-92 °C, in quantitative yield.$^{6)}$ The ylide was stable in crystalline state and even in chloroform solution at room temperature. Fractional recrystallization of dia.-**1ab** was repeated from hexane-ether. Optically pure diastereomeric selenonium ylide (+)-**1a** (2.0 g)$^{7)}$ was obtained after seven recrystallization from dia.-**1ab** (13.5 g). This is the first example of the isolation of optically pure selenonium ylide as a stable crystal. The optical purity was determined by ^{1}H NMR spectra (500 MHz), and the CD spectrum showed the positive Cotton effects at 266 and 234 nm and negative Cotton effects at 289 and 251 nm in methanol. (-)-**1b** (5.6 g) was obtained from mother liquid in 27% optical purity. The results are summarized in Table 1.

Table 1. Fractional recrystallization of dia.-**1**

	1a	**1b**
Optical purity	100%	27%
$[\alpha]_D$ (MeOH)	+22.6°	-54.1°
CD$[\theta]_{266}$ (MeOH)	$+1.48 \times 10^4$	-3.56×10^3
mp /°C	135.5-136.5	102-104

Thermal stabilities of optically active ylide (+)-**1a** toward racemization were preliminarily examined. No racemization was found at 80 °C in chloroform but decomposition was observed by heating to 100-120 °C.

Preparation of enantiomerically pure selenonium ylide on selenium atom by transesterification of (+)-**1a** and determination of the absolute configuration of (+)-**1** by X-ray diffraction are now in progress.

References

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7) ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 0.79$ (3H, d, $J = 7.0$ Hz), 0.90-0.96 (1H, m), 0.91 (3H, d, $J = 7.0$ Hz), 0.93 (3H, d, $J = 6.5$ Hz), 1.05-1.15 (1H, m), 1.09 (6H, s), 1.52-1.57 (2H, m), 1.72-1.75 (2H, m), 1.89-1.92 (2H, m), 2.09-2.11(1H, m), 2.37 (3H, s), 3.22 (4H, s), 4.91-4.95 (1H, m), and 7.73 and 8.12 (4H, ABq, $J = 8.5$ Hz).

(Received November 13, 1990)