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New Camphor-Derived Selenonium Ylides: Enantioselective Synthesis of Chiral Epoxides

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Optically pure selenonium salts **3** as the precursors of two new chiral selenonium ylides **4** can be synthesized stereoselectively from natural D-camphor in good yields. It is found that the reaction of the selenonium salt **3b**, an aldehyde, and potassium *tert*-butoxide can take place smoothly in 'one-pot' via the formation of selenonium ylide **4b**, to give chiral *trans*-diaryl epoxides **5** in good yields with good diastereoselectivities and enantioselectivities.

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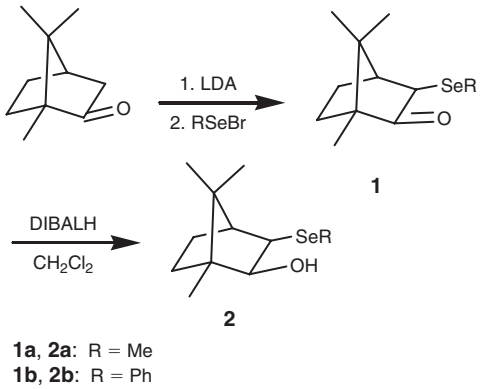
Introduction

Chiral epoxides are one of the most important synthetic intermediates[1] because of their significant biological activities[2] and versatile chemical transformations.[3] Nowadays, the development of new and efficient syntheses of chiral epoxides is still a challenging subject. Among various syntheses of chiral epoxides, the chiral ylide route is one of the most important methods. It centres around the tandem formation of carbon–carbon bonds and epoxidation.[4] Recently, camphor-derived sulfonium ylides have received much attention in the enantioselective synthesis of three-membered ring compounds.[5] Asymmetric syntheses of cyclopropanes and aziridines through the formation of camphor-derived semistabilized sulfonium ylides achieve excellent enantioselectivities (up to 99% e.e.),[5a,5b] however, the enantioselectivities for the asymmetric synthesis of epoxides derived from these ylides are only moderate (19–74% e.e.).[5c] The steric hindrance of a selenonium ylide is larger than that of the corresponding sulfonium ylide, and there are few reports concerned with chiral selenonium ylides.[6] As such, we synthesized camphor-derived selenonium ylides and employed them in an attempt to improve the enantioselectivity of the asymmetric synthesis of chiral epoxides.

Results and Discussion

We found that α-methylseleno camphor **1a** could be synthesized in good yield by the reaction of lithiated camphor with methylselenenyl bromide, which was prepared in situ (Scheme 1). α-Phenylseleno camphor **1b** was prepared according to the literature method.[7] Initially, it was found that almost equal amounts of *exo*- and *endo*-isomers of α-organoseleno camphor **1a** was produced at −40°C. After further investigation we found that the formation of the *exo*-isomer could be favoured by controlling the reaction conditions. A ratio of up to 10 : 1 of *exo*- to *endo*-isomer could be achieved using a low temperature, a short reaction time, and one equivalent of lithium diisopropylamide. The *exo*-isomer of α-organoseleno camphor **1a** could be isolated conveniently by chromatography. The optically pure *exo*-organoseleno camphor **1a** and **1b** were reduced by diisobutylaluminium hydride to give *exo*-α-methylseleno isoborneol **2a** and *exo*-α-phenylseleno isoborneol **2b** in 71 and 75% yield, respectively. No *endo*-hydroxy (borneol) isomer was observed, which might be due to the steric interaction of diisobutylaluminium hydride, as a nucleophile, with the methyl group in the 7-position.[8]



Scheme 1. Stereoselective synthesis of optically pure *exo*-α-organoseleno isoborneol **2**.

As expected, *exo*-α-methylseleno isoborneol **2a** was allowed to react with benzyl bromide at 0°C to afford the selenonium salt **3a** in 85% yield (Scheme 2). We then employed salt **3a** in the reaction with various aldehydes in the presence of potassium *tert*-butoxide. It was found that the one-pot reaction, in which the selenonium ylide **4a** was formed in situ, could take place smoothly at 0°C to give *trans*-(2*R*,3*R*)-diaryl epoxides **5** in good yield with good diastereoselectivity and moderate enantioselectivity

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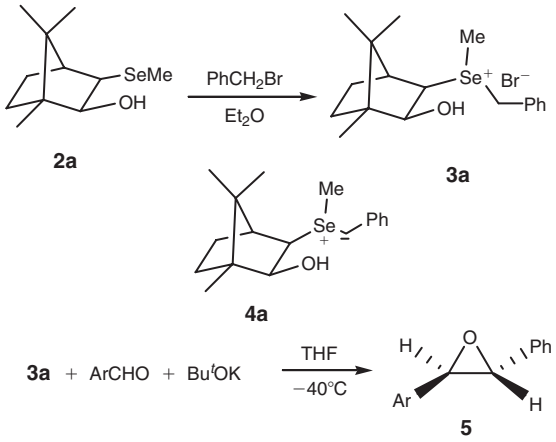
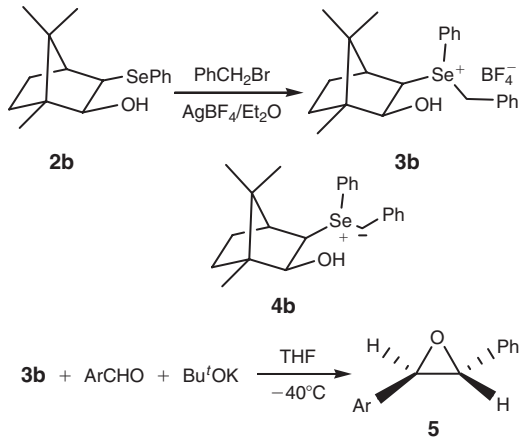


Scheme 2. Enantioselective synthesis of *trans*-(2*R*,3*R*)-diaryl epoxides via camphor-derived selenonium ylides **4a**.



Scheme 3. Enantioselective synthesis of *trans*-(2*R*,3*R*)-diaryl epoxides via camphor-derived selenonium ylides **4b**.

(Table 1). Using a different base, such as sodium hydroxide, sodium hydride, or sodium methoxide, did not improve the enantioselectivity. The absolute configuration of **5a**–**5f** was assigned by a comparison of the sign of their optical rotations with that of the known compounds.[9]

In order to increase the enantioselectivity of the epoxidation reaction from the selenonium ylide, we prepared the precursor **3b** of the sterically more encumbered phenylselenoniumylide **4b**. Selenonium salt **3b** could only be formed with the assistance of silver tetrafluoroborate and the reaction proceeded in good yield. Salt **3b** was then employed in the reaction with benzaldehyde in the presence of potassium *tert*-butoxide in tetrahydrofuran (THF) at 0°C. As expected, the one-pot reaction via the selenonium ylide **4b** took place smoothly to give *trans*-(2*R*,3*R*)-diphenyl epoxide **5a** in good yield (81%) with good diastereoselectivity (83%) and improved enantioselectivity (74%, entry 1 in Table 2; Scheme 3). Among various solvents, THF is the best for optimal yield, diastereoselectivity, and enantioselectivity of the reaction.

For further optimization, different bases were also used for the one-pot reaction of selenonium ylide **3b** with benzaldehyde in THF at 0°C. Experimental results showed that all the bases shown in Table 2 gave the *trans*-diphenyl epoxide **5a** with moderate to good yields and good diastereoselectivities. Interestingly, sodium hydroxide resulted in *trans*-diphenyl epoxide **5a** with a dominant (*S*,*S*)-configuration, which is contrary to that produced using other bases. In terms of the balance of yield, diastereoselectivity, and enantioselectivity, the best base is potassium *tert*-butoxide, and the most suitable mole ratio of selenonium salt **3b** to base is 1 : 4, to produce *trans*-diaryl epoxides in good yield with good diastereoselectivities and enantioselectivities.

Under optimal conditions, a variety of aromatic aldehydes were used in the reaction with selenonium salt **3b** in the presence of potassium *tert*-butoxide at −40°C. The experimental results revealed that the yields, the diastereoselectivities, and the enantioselectivities of *trans*-(2*R*,3*R*)-diaryl epoxides **5a**–**5f** are good under these conditions (Table 3).

Conclusions

Optically pure selenonium salts **3** as the precursors of two new chiral selenonium ylides **4** can be synthesized stereoselectively from natural D-camphor in good yields. The reaction of the selenonium salts **3**, an aldehyde, and potassium *tert*-butoxide can take place smoothly in a one-pot synthesis and form the selenonium ylides **4** in situ, to give chiral *trans*-diaryl epoxides **5** in good yields with good diastereoselectivities and low to good enantioselectivities. The enantioselectivity of the chiral epoxides achieved by the protocol reported here, which utilizes camphor-derived selenonium ylide **4b** in situ, is better than the literature method that employs the corresponding camphor-derived sulfonium ylides.[5c]

Experimental

All reactions were carried out under a nitrogen atmosphere. ^{1}H NMR spectra were determined in $CDCl_3$ on a Bruker ARX-300 (300 MHz) with tetramethylsilane as internal standard. Mass spectra (electron impact, EI) were obtained on a VG-ZAB-HS mass spectrometer. IR spectra were taken with a 5DX-FT-2 spectrometer. Melting points were uncorrected. Elemental analyses were determined on a Perkin–Elmer 240C analyzer.

exo-α-*Methylseleno Camphor* ***1a***

To a solution of diisopropylamine (3.68 mL, 24 mmol) in THF (80 mL) was added a solution of Bu^{n}Li (2.0 M, 12 mL) in hexane at −78°C. After stirring for 5 min, a solution of D-(+)-camphor (3.65 g, 24 mmol) in THF (8 mL) was added dropwise. The reaction mixture was stirred for 1 h at −78°C and then the solution of organoselenenyl bromide (4.2 g, 24 mmol) in THF (10 mL), prepared in situ,[10] was added rapidly. The reaction mixture was stirred for another 1 h at this temperature and then poured into an aqueous solution of HCl (0.5 N, 200 mL). After extraction with ether (100 mL × 2), the organic layer was washed with water, a saturated solution of sodium hydrogen carbonate, and a saturated solution of sodium chloride, and dried with anhydrous magnesium sulfate. After the solvent was removed by evaporation, the residue was separated by column chromatography (silica gel, petroleum ether–ether as eluent) to yield **1a** (75%) as a colorless oil. $[\alpha]_D^{20}$ +52.9° (*c* 1.0, EtOH). (Found: C 53.9, H 7.4%. $C_{11}H_{18}OSe$ requires C 53.9, H 7.4%.) δ_H 2.98 (1H, s, CH), 2.35 (3H, s, CH_3), 2.19 (1H d, *J* 4.1, CH), 2.06–1.07 (4H, m, $2CH_2$), 0.98 (3H, s, CH_3), 0.94 (3H, s, CH_3), 0.92 (3H, s, CH_3). *m/z* (EI) 246 (72.16%, M^+), 203 (11.27), 200 (2.45), 135 (85.50), 123 (100.00),

Table 1. Enantioselective synthesis of *trans*-diaryl epoxides via camphor-derived selenonium ylides 4a

Entry	Ar	Product	Yield[A] [%]	Diastereoselectivity[B] [%]	e.e.[C] [%]	Config.
1	C_6H_5	**5a**	78	86	58	*R*,*R*
2	4-FC_6H_4	**5b**	83	80	60	*R*,*R*
3	4-ClC_6H_4	**5c**	77	81	55	*R*,*R*
4	2-ClC_6H_4	**5d**	70	84	37	*R*,*R*
5	4-$CH_3C_6H_4$	**5e**	80	85	50	*R*,*R*
6	4-$CH_3OC_6H_4$	**5f**	71	78	48	*R*,*R*

[A] Isolated yields.
[B] Determined by ^{1}H NMR spectroscopy or gas chromatography.
[C] Determined by chiral HPLC on a Chiralcel OD-H column.

Table 2. Reaction of selenonium salt 3b with benzaldehyde in different bases

Entry[A]	Base	**3b**/Base	Yield[B] [%]	Diastereoselectivity[C] [%]	e.e.[D] [%]	Config.
1	Bu^{t}OK	1 : 2	81	83	74	*R*,*R*
2	—	1 : 4	83	86	78	*R*,*R*
3	NaH	1 : 2	65	76	70	*R*,*R*
4	—	1 : 4	71	78	66	*R*,*R*
5	$NaOCH_3$	1 : 2	63	86	57	*R*,*R*
6	—	1 : 4	80	85	60	*R*,*R*
7	NaOH	1 : 2	73	90	72	*S*,*S*
8	—	1 : 4	70	85	67	*S*,*S*

[A] THF was used as solvent and reaction time is 12 h.
[B] Isolated yields.
[C] Determined by ^{1}H NMR spectroscopy or gas chromatography.
[D] Determined by chiral HPLC on a Chiralcel OD-H column.

Table 3. Enantioselective synthesis of *trans*-diaryl epoxides via camphor-derived selenonium ylide 4b

Entry	Ar	Product	Temp. [°C]	Yield[A] [%]	Diastereoselectivity[B] [%]	e.e.[C] [%]	Config.
1	C_6H_5	**5a**	0	83	86	78	*R*,*R*
2	C_6H_5		−40	85	87	80	*R*,*R*
3	4-FC_6H_4	**5b**	0	85	86	73	*R*,*R*
4	4-FC_6H_4		−40	82	82	82	*R*,*R*
5	4-ClC_6H_4	**5c**	0	86	85	75	*R*,*R*
6	4-ClC_6H_4		−40	81	91	80	*R*,*R*
7	2-ClC_6H_4	**5d**	−40	72	85	70	*R*,*R*
8	4-$CH_3C_6H_4$	**5e**	0	87	81	77	*R*,*R*
9	4-$CH_3C_6H_4$		−40	86	86	81	*R*,*R*
10	4-$CH_3OC_6H_4$	**5f**	0	73	90	70	*R*,*R*
11	4-$CH_3OC_6H_4$		−40	70	93	72	*R*,*R*

[A] Isolated yields.
[B] Determined by ^{1}H NMR spectroscopy or gas chromatography.
[C] Determined by chiral HPLC on a Chiralcel OD-H column.

83 (84.50), 55 (75.51). ν_{max} (KBr)/cm^{-1} 2959, 2873, 1742, 1449, 1391, 1373, 1045, 1031.

exo-α-*Phenylseleno Camphor* ***1b***

This was synthesized by a similar method for **1a** to yield **1b** (81%) as colorless oil. $[\alpha]_D^{20}$ +75.9° (*c* 1.0, EtOH). δ_H 7.66–7.64 (2H, m, PhH), 7.28–7.24 (3H, m, PhH), 3.42 (1H, s, CH), 2.35 (1H d, *J* 3.9, CH), 2.08–1.31 (4H, m, 2CH_2), 0.95 (3H, s, CH_3), 0.89 (3H, s, CH_3), 0.81 (3H, s, CH_3). ν_{max} (KBr)/cm^{-1} 3056, 2959, 1746, 1757, 1477, 1026, 739, 692.

exo-α-*Methylseleno Isoborneol* ***2a***

To the solution of *exo*-α-methylseleno camphor **1** (3.43 g, 14.0 mmol) in dichloromethane (60 mL) was added a 25% solution of diisobutylaluminium hydride (12 mL, 21 mmol) in toluene, dropwise, at room temperature, and the reaction mixture was stirred for 0.5 h. The mixture was then poured into a saturated solution (180 mL) of ammonium chloride and extracted with petroleum ether (150 mL × 3). The organic layer was washed with a 2 M aqueous solution (100 mL × 3) of HCl and a saturated solution (100 mL × 3) of sodium hydrogen carbonate, and was then dried with anhydrous magnesium sulfate. After the solvent was evaporated, the residue was separated by column chromatography (silica gel, petroleum ether–ether as eluent) to yield **2a** (71%) as a colorless oil. $[\alpha]_D^{20}$ −17.2° (*c* 1.0, EtOH). (Found: C 53.5, H 8.2%. $C_{11}H_{20}OSe$ requires C 53.4, H 8.2%.) δ_H 3.58 (1H d, *J* 7.5, CH), 3.16 (1H, d, *J* 7.5, CH), 2.67 (1H, br, OH), 2.01 (3H, s, CH_3), 1.99 (1H, d, *J* 3.3, 1 of CH), 1.79–1.76 (1H, m, 1 of CH_2), 1.54–1.45 (1H, m, 1 of CH_2), 1.16–1.06 (2H, m, CH_2), 1.03 (3H, s, CH_3), 0.98 (3H, s, CH_3), 0.80 (3H, s, CH_3). *m*/*z* (EI) 248 (68%, M^+), 233 (6.60), 177 (1.68), 135 (54.94), 109 (89.81), 95 (96.84), 43 (100.00). ν_{max} (KBr)/cm^{-1} 3425, 2951, 1474, 1456, 1390, 1370, 1289, 1092.

exo-α-*Phenylseleno Isoborneol* ***2b***

This was synthesized by a similar method for **2a** to yield **2b** (75%) as a colorless oil. $[\alpha]_D^{20}$ −13.3° (*c* 1.0, EtOH). (Found: C 62.0, H 7.2%. $C_{16}H_{22}OSe$ requires C 62.1, H 7.2%.) δ_H 7.54–7.51 (2H, m, PhH), 7.30–7.26 (3H, m, PhH), 3.74 (1H, d, *J* 7.5, CH), 3.58 (1H, d, *J* 7.5, CH), 2.78 (1H, br, OH), 2.14 (1H, d, *J* 4.2, CH), 1.90–1.70 (1H, m, 1 of CH_2), 1.57–1.49 (1H, m, 1 of CH_2), 1.27–1.15 (2H, m, CH_2), 1.13 (3H, s, CH_3), 1.03 (3H, s, CH_3), 0.85 (3H, s, CH_3). *m/z* (EI) 310 (56.48%, M^+), 312 (9.75), 246 (3.25), 229 (6.82), 157 (45.21), 135 (52.41), 109 (77.00), 43 (100.00). ν_{max} (KBr)/cm^{-1} 3445, 3070, 3056, 2952, 2879, 1578, 1477, 1060, 732.

Selenonium Salt ***3a***

A solution of *exo*-α-methylseleno isoborneol **2a** (2.10 g, 8.5 mmol) and benzyl bromide (1.54 g, 9.0 mmol) in ether (10 mL) was stirred at 0°C for 24 h. The white solid formed was filtered off, washed with ether, and recrystallized from ethanol–ethyl acetate to yield **3a** (85%) as a white solid, mp 138°C. $[\alpha]_D^{20}$ +153.8° (*c* 1.0, EtOH). (Found: C 51.8, H 6.6%. $C_{18}H_{27}OSeBr$ requires C 51.7, H 6.5%.) δ_H 7.62–7.37 (5H, m, PhH), 6.51 (1H, br, OH), 5.56 (1H, d, *J* 11.1, 1 of CH_2Ph), 5.44 (1H, d, *J* 11.1, 1 of CH_2Ph), 4.16–4.13 (2H, m, 2CH), 2.55 (3H, s, CH_3), 1.84–1.78 (2H, m, CH + 1 of CH_2), 1.70–1.60 (1H, m, 1 of CH_2), 1.48–1.40 (1H, m, 1 of CH_2), 1.14 (3H, s, CH_3), 1.11–1.07 (1H, m, 1 of CH_2), 0.98 (3H, s, CH_3), 0.81 (3H, s, CH_3). *m/z* (EIS, positive mode) 339.0 [M − Br]. ν_{max} (KBr)/cm^{-1} 3200, 3039, 2990, 2944, 1456, 1070, 760, 700.

Selenonium Salt ***3b***

This was synthesized by a similar method for **3a** to yield **3b** (82%) as white solid, mp 137°C (dec.), $[\alpha]_D^{20}$ +142.8° (*c* 1.0, EtOH). (Found: C 56.8, H 6.1%. $C_{23}H_{29}BF_4OSe$ requires C 56.7, H 6.0%.) δ_H 7.67–7.54 (5H, m, PhH), 7.20–7.01 (6H, m, PhH + OH), 5.25 (1H, d, *J* 11.4, CH), 4.99 (1H, d, *J* 6.1, 1 of $PhCH_2$), 4.94 (1H, d, *J* 11.5, CH), 4.80 (1H, d, *J* 6.2, 1 of $PhCH_2$), 1.76–1.71 (1H, m, 1 of CH_2), 1.62–1.61 (1H, d, *J* 4.5, CH), 1.45–1.36 (2H, m, CH_2), 1.31 (3H, s, CH_3), 1.25–1.14 (1H, m, 1 of CH_2), 0.98 (3H, s, CH_3), 0.76 (3H, s, CH_3). *m/z* (EIS, positive mode) 401.0 [M − BF_4]. ν_{max} (KBr)/cm^{-1} 3464, 3134, 2953, 1477, 1455, 1062, 750, 696.

Asymmetric Synthesis of trans-*(2*R*,3*R*)-Diaryl Epoxides* ***5****; General Procedure*

To the solution of selenonium salt **3b** (1.0 mmol) and an aldehyde (0.49 g, 1.0 mmol) in THF (10 mL) was added Bu^{t}OK (0.44 g, 4.0 mmol) at −40°C. The reaction mixture was stirred for 12–18 h at this temperature. The mixture was then filtered through a short silica gel column. After evaporation of the solvent, the residue was separated by preparative thin-layer chromatography to give the *trans*-diaryl epoxides **5**.

trans-*(2*R*,3*R*)-2,3-Diphenyloxirane* ***5a***

White solid, mp 68–69°C (lit.[9a] 69°C). δ_H 7.43–7.28 (10H, m, ArH), 3.90 (2H, s, 2OCH). ν_{max} (KBr)/cm^{-1} 3060, 2987, 1452, 1071, 851, 748, 695, 611.

trans-*(2*R*,3*R*)-2-(4-Fluorophenyl)-3-phenyloxirane* ***5b***

White solid, mp 76–78°C (lit.[9e] 76–77°C). δ_H 7.41–7.09 (9H, m, ArH), 3.87 (1H, d, *J* 1.8, OCH), 3.85 (1H, d, *J* 1.8, OCH). ν_{max} (KBr)/cm^{-1} 3044, 2990, 1512, 1230, 1087, 831, 778, 697.

trans-*(2*R*,3*R*)-2-(4-Chlorophenyl)-3-phenyloxirane* ***5c***

White solid, mp 99–100°C (lit.[9a] 100°C). δ_H 7.39–7.15 (9H, m, ArH), 3.86 (1H, d, *J* 1.9, OCH), 3.84 (1H, d, *J* 1.9, OCH). ν_{max} (KBr)/cm^{-1} 3052, 1492, 1460, 1091, 819, 751, 700.

trans-*(2*R*,3*R*)-2-(2-Chlorophenyl)-3-phenyloxirane* ***5d***

Colorless oil.[9b] δ_H 7.42–7.28 (9H, m, ArH), 4.25 (1H, d, *J* 1.9, OCH), 3.79 (1H, d, *J* 1.9, OCH). ν_{max} (KBr)/cm^{-1} 3065, 2986, 1478, 1275, 1128, 750, 700, 612.

trans-*(2*R*,3*R*)-2-*p-*Tolyl-3-phenyloxirane* ***5e***

White solid, mp 60–61°C (lit.[9a] 62°C). δ_H 7.40–7.19 (9H, m, ArH), 3.87 (1H, d, *J* 1.8, OCH), 3.85 (1H, d, *J* 1.8, OCH), 2.38 (3H, s, CH_3). ν_{max} (KBr)/cm^{-1} 3052, 2916, 1406, 1111, 816, 738, 509.

trans-*(2*R*,3*R*)-2-(4-Methoxyphenyl)-3-phenyloxirane* ***5f***

White solid, mp 76–78°C (lit.[9d] 76–78°C). δ_H 7.40–6.91 (9H, m, ArH), 3.87 (1H, d, *J* 1.9, OCH), 3.84 (1H, d, *J* 1.9, OCH), 3.83 (d, *J* 1.9, 1H). ν_{max} (KBr)/cm^{-1} 3043, 2967, 1614, 1517, 1254, 1032, 826.

Acknowledgments

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