Isolation and Stereochemistry of Optically Active Selenoximines

Toshio Shimizu, Kazuhiko Mitsuya, Kazunori Hirabayashi, and Nobumasa Kamigata*

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Minami-ohsawa, Hachioji, Tokyo 192-0397

Received September 4, 2003; E-mail: kamigata-nobumasa@c.metro-u.ac.jp

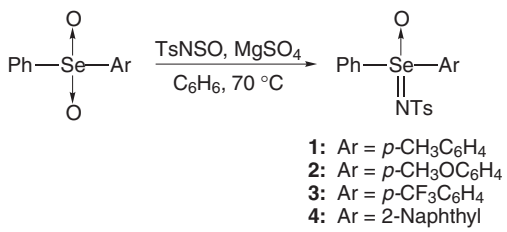
Asymmetric selenoximines were synthesized and their optical isomers were isolated for the first time by optical resolution using chromatography with a chiral column. The absolute configuration was determined by comparing their specific rotations and their circular dichroism spectra with those of a corresponding sulfur analogue with known absolute configuration. No racemization of the optically active selenoximines occurred under neutral, acidic, and basic conditions, and only decomposition was observed under aqueous acidic and basic conditions.

Recently, we have focused our interest on optically active tricoordinated chalcogen compounds,[1,2] and have reported the isolation and stereochemistry of such optically active selenium compounds[3] as selenoxide,[4,5] selenonium ylide,[6] selenonium imide,[7] selenonium salt,[8] and seleninic acid.[9] In sulfur chemistry, tetracoordinated chiral compounds have also been studied.[1] Sulfoximine is an example of tetracoordinated chiral compounds, and its optical isomers have been isolated; their stereochemistry was widely studied approximately 30 years ago.[10,11] On the other hand, a corresponding optically active selenium compound, selenoximine, has not yet been studied, and there are few reports on the synthesis of even symmetric achiral samples.[12] We have synthesized some asymmetric diaryl selenoximines, and optically resolved them into their enantiomers for the first time. We describe herein the isolation of optically active selenoximines, their optical properties, and their stereochemistry.

Results and Discussion

Asymmetric selenoximines **1**–**4** were synthesized by reacting the corresponding selenones with *N*-sulfinyl-*p*-toluenesulfonamide in the presence of anhydrous magnesium sulfate in 67, 61, 52, and 33% yields, respectively, whereas 1-naphthyl(phenyl)- and mesityl(phenyl)selenoximines could not be obtained in similar reactions, probably because of their bulkiness (Scheme 1).

When racemic *N*-tosyl(phenyl)-*p*-tolylselenoximine (*rac*-**1**) was subjected to an optically active column (4.6 × 250 mm) packed with cellulose carbamate derivative/silica gel using high-performance liquid chromatography on an analytical scale (hexane/2-propanol = 70/30), two peaks corresponding to each of the enantiomers of **1** were observed on the chromatogram. Using the same column, *N*-tosyl(*p*-methoxyphenyl)-phenylselenoximine (*rac*-**2**), *N*-tosyl(phenyl)(*p*-trifluoromethylphenyl)selenoximine (*rac*-**3**), and *N*-tosyl(2-naphthyl)phenylselenoximine (*rac*-**4**) were also resolved into two peaks corresponding to their optical isomers, respectively.



Scheme 1.

The optical resolution of the racemic selenoximines into their optical isomers on a preparative scale was achieved by using a larger column (10 × 250 mm) of the same type. In the case of optical resolution of *rac*-**1**, an enantiomer obtained from the first eluate had a positive specific rotation {$[\alpha]_D$ +11.3 (*c* 1.22, $CHCl_3$)}, whereas that obtained from the second eluate had a negative specific rotation {$[\alpha]_D$ −12.1 (*c* 1.05, $CHCl_3$)}. Both enantiomers (+)- and (−)-**1** were found to be optically pure by HPLC analysis. Similarly, the optical resolution of racemic selenoximines *rac*-**2**–**4** yielded their optically pure isomers, respectively. The enantiomers obtained from the first eluate also showed positive specific rotations in all cases, whereas the second-eluted enantiomers showed negative specific rotations, as listed in Table 1.

Optically active selenoximines with positive specific rotations (+)-**1**, (+)-**2**, and (+)-**4** showed positive Cotton effects at 241, 252, and 242 nm, respectively, and negative Cotton effects at 226, 229, and 225 nm on their circular dichroism spectra in acetonitrile, as shown in Fig. 1. In contrast, (−)-**1**, (−)-**2**, and (−)-**4** showed negative Cotton effects at 239–252 nm and

Table 1. Specific Rotations of Optically Active Selenoximines[a)]

Selenoximine	$[\alpha]_D^{25}$ ($CHCl_3$)	
	First enantiomer	Second enantiomer
1	+11.3 (*c* 1.22)	−12.1 (*c* 1.05)
2	+16.1 (*c* 1.09)	−15.5 (*c* 1.01)
3	+44.6 (*c* 1.01)	−42.4 (*c* 1.12)
4	+67.1 (*c* 1.09)	−65.0 (*c* 1.09)

a) Daicel Chiralcel OD was used as a chiral column, and hexane/2-propanol (70/30 for **1**, 50/50 for **2**–**4**) was used as the mobile phase.

Published on the web February 10, 2004; DOI 10.1246/bcsj.77.375

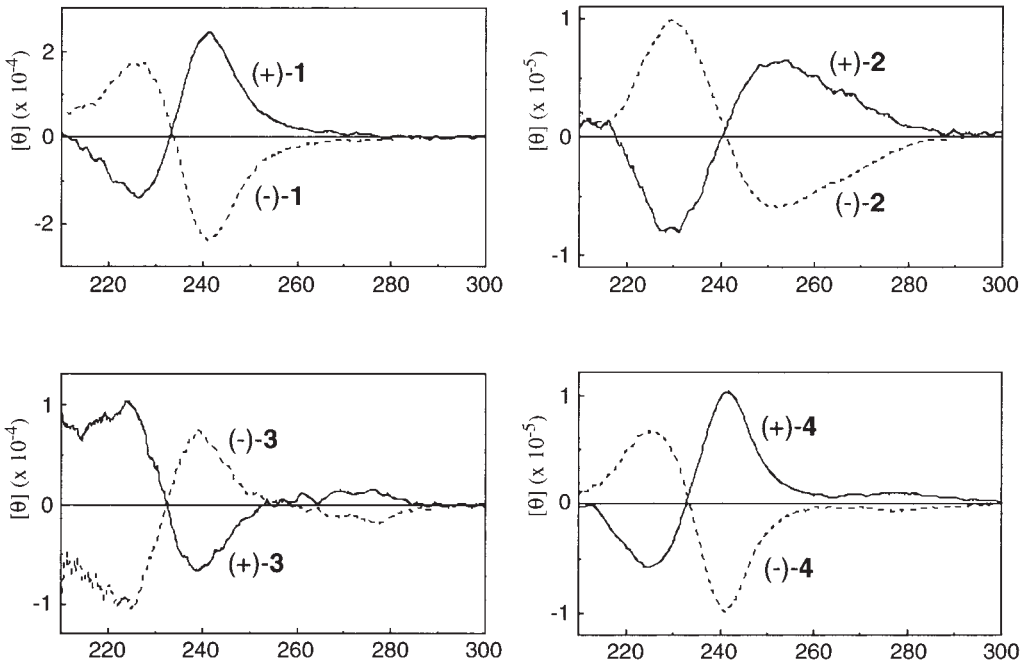
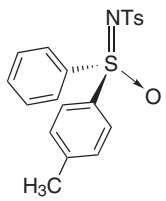


Fig. 1. Circular dichroism spectra of optically active selenoximines in acetonitrile.



(*S*)-(+)-**5**

Chart 1.

positive Cotton effects at 225–229 nm. However, (+)-**3**, which possesses a *p*-trifluoromethylphenyl substituent, showed a negative Cotton effect at 238 nm and a positive Cotton effect at 224 nm. To determine their absolute configuration, optically active *N*-tosyl(phenyl)-*p*-tolylsulfoximine (*S*)-(+)-**5** (Chart 1), of which the relationship between the absolute configuration and the specific rotation had been clarified, was synthesized.[13] Sulfoximine (*S*)-(+)-**5** {$[\alpha]_D$ +20.4 (*c* 0.71, $CHCl_3$)} showed a positive Cotton effect at 243 nm and a negative Cotton effect at 223 nm in acetonitrile, which corresponded well with those of the optically active selenoximines with positive specific rotations (+)-**1**, (+)-**2**, and (+)-**4**. Therefore, based on the similarity of the signs of their specific rotations and their circular dichroism spectra, the absolute configuration of selenoximines (+)-**1**, (+)-**2**, and (+)-**4** was assigned to be *S*-form, whereas that of (−)-**1**, (−)-**2**, and (−)-**4** was *R*.

Selenoximine (*S*)-(+)-**1** was stable under neutral conditions, and neither racemization nor decomposition was observed in acetonitrile containing water, even after 14 d. (*S*)-(+)-**1** was stable even in a refluxing acetonitrile solution containing water. Optically active selenoximines (+)-**2**–**4** were also stable at room temperature under neutral conditions. However, the decomposition of (*S*)-(+)-**1** occurred under both acidic and basic conditions. When an acetonitrile solution of (*S*)-(+)-**1** was stirred in the presence of hydrochloric acid for 24 h, 10% of (*S*)-(+)-**1** was hydrolyzed to give the corresponding selenone and *p*-toluenesulfonamide as sole products. (+)-**2**–**4** were also hydrolyzed under similar conditions to yield the respective selenones and *p*-toluenesulfonamide. Under basic conditions, 35% of (*S*)-(+)-**1** was consumed and the corresponding selenone and sulfonamide were formed after stirring for 24 h in acetonitrile in the presence of a sodium hydroxide solution. (+)-**2**–**4** also afforded hydrolyzed products under the same conditions. However, no racemization was observed in the recovered selenoximines (+)-**1**–**4** under both acidic and basic conditions, differing from many optically active tricoordinated selenium compounds.[3] This result means that the condensation reaction of selenone with *p*-toluenesulfonamide, formed by hydrolysis under these conditions, to give selenoximine did not proceed, since the reverse reaction should give racemic selenoximine.

In this study, optically active selenoximines could be isolated for the first time, and their absolute configurations were determined. The stability toward the hydrolysis of selenoximines and that toward racemization of their optical isomers were also clarified.

Experimental

Typical Procedure for Synthesis of Selenoximines. To a benzene solution (5 mL) of the corresponding selenone (1.0 mmol) and *N*-sulfinyl-*p*-toluenesulfonamide (1.2 mmol) was added anhydrous magnesium sulfate (300 mg) under nitrogen. The solution was heated at 70 °C for the desired period (**1**: 4 h, **2**: 13 h, **3**: 16 h, **4**: 5 h). Magnesium sulfate was filtered off, and the filtrate was concentrated. The product was purified by gel-permeation chromatography (chloroform) (**1**: 67%, **2**: 61%, **3**: 52%, **4**: 33%).

***N*-Tosyl(phenyl)-*p*-tolylselenoximine (1):** Mp 52.0–54.0 °C (colorless powder); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.44 (s, 3H), 7.23 (d, 2H, J = 8.2 Hz), 7.40 (d, 2H, J = 8.3 Hz), 7.60 (t, 2H, J = 8.0 Hz), 7.67 (t, 1H, J = 8.0 Hz), 7.90 (d, 2H, J = 8.2 Hz), 7.91 (d, 2H, J = 8.3 Hz), 8.02 (d, 2H, J = 8.0 Hz);

^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 21.6, 126.5, 127.1 (duplicate), 129.1, 130.4, 131.1, 134.3, 137.1, 140.7, 141.5, 142.1, 145.7; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 884; IR (KBr) ν_{max} 2924, 1598, 1447, 1300, 1144, 1088, 1059, 928 (N=Se=O), 858, 809, 745, 711, 668, 573, 550, 488, 463, 405 cm^{-1}; UV (MeCN) λ_{max} 232 (ε 2.52×10^4), 262 (sh, ε 2.70×10^3) nm; MS m/z 248 {M$^+$(^{80}Se)-$C_7H_7NO_3S$, 41%}, 246 {M$^+$(^{78}Se)-$C_7H_7NO_3S$, 21%}, 168 (100%), 107 (24%), 91 (93%), 65 (45%). Anal. Calcd for $C_{20}H_{19}NO_3SSe$: C, 55.56; H, 4.43; N, 3.24%. Found: C, 55.38; H, 4.49; N, 3.19%.

***N*-Tosyl(*p*-methoxyphenyl)phenylselenoximine (2):** Mp 54.0–56.0 °C (colorless amorphous); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.86 (s, 3H), 7.06 (d, 2H, J = 8.9 Hz), 7.22 (d, 2H, J = 8.2 Hz), 7.60 (t, 2H, J = 8.0 Hz), 7.66 (t, 1H, J = 8.0 Hz), 7.90 (d, 2H, J = 8.0 Hz), 7.95 (d, 2H, J = 8.9 Hz), 8.01 (d, 2H, J = 8.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 55.9, 115.8, 126.5, 127.1, 129.2, 129.3, 130.4, 130.6, 134.2, 141.1, 141.5, 142.1, 164.2; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 890; IR (KBr) ν_{max} 3061, 2943, 2579, 1585, 1491, 1446, 1411, 1301, 1285, 1264, 1173, 1143, 1087, 1061, 1020, 927 (N=Se=O), 831, 815, 745, 711, 682, 573, 549, 514, 463, 380 cm^{-1}; UV (MeCN) λ_{max} 227 (ε 5.01×10^4), 248 (ε 4.45×10^4) nm; MS m/z 264 {M$^+$(^{80}Se)-$C_7H_7NO_3S$, 66%}, 262 {M$^+$(^{78}Se)-$C_7H_7NO_3S$, 25%}, 184 (100%), 169 (25%), 155 (22%), 91 (66%), 77 (25%), 65 (27%). Anal. Calcd for $C_{20}H_{19}NO_4SSe$: C, 53.57; H, 4.27; N, 3.12%. Found: C, 53.09; H, 4.32; N, 3.04%.

***N*-Tosyl(phenyl)(*p*-trifluoromethylphenyl)selenoximine (3):** Mp 108.5–109.5 °C (decomp, colorless prisms from ethyl acetate–hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3H), 7.24 (d, 2H, J = 8.3 Hz), 7.64 (t, 2H, J = 8.0 Hz), 7.72 (t, 1H, J = 8.0 Hz), 7.87 (d, 2H, J = 8.6 Hz), 7.90 (d, 2H, J = 8.3 Hz), 8.06 (d, 2H, J = 8.0 Hz), 8.20 (d, 2H, J = 8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 122.7 (q, J = 273 Hz), 126.5, 127.2, 127.4 (q, J = 7.3 Hz), 127.9, 129.2, 130.7, 134.8, 135.9 (q, J = 33 Hz), 139.4, 141.1, 142.5, 144.4; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 887; IR (KBr) ν_{max} 3093, 1598, 1496, 1448, 1402, 1323, 1144, 1088, 1054, 1011, 997, 915 (N=Se=O), 839, 815, 745, 710, 692, 591, 573, 549, 498, 465, 392 cm^{-1}; UV (MeCN) λ_{max} 227 (ε 2.27×10^4), 264 (sh, ε 3.02×10^3) nm; MS m/z 300 {M$^+$(^{80}Se)-$C_7H_7NO_3S$, 62%}, 298 {M$^+$(^{78}Se)-$C_7H_7NO_3S$, 28%}, 221 (100%), 156 (22%), 91 (40%), 77 (45%), 65 (21%). Anal. Calcd for $C_{20}H_{16}F_3NO_3SSe$: C, 49.08; H, 3.91; N, 2.86%. Found: C, 49.46; H, 3.51; N, 2.91%.

***N*-Tosyl(2-naphthyl)phenylselenoximine (4):** Mp 114.0–116.0 °C (decomp, colorless powder from ethyl acetate–hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.36 (s, 3H), 7.21 (d, 2H, J = 8.3 Hz), 7.61 (t, 2H, J = 8.0 Hz), 7.65–7.71 (m, 4H), 7.91–7.95 (m, 3H), 8.00 (d, 1H, J = 8.0 Hz), 8.04 (d, 1H, J = 8.9 Hz), 8.09 (d, 2H, J = 8.3 Hz), 8.65 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 121.2, 126.5, 127.2, 128.1, 128.2, 129.0, 129.1, 129.2, 129.8, 130.5, 130.9, 132.5, 134.3, 135.4, 137.0, 140.6, 141.5, 142.2; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 891; IR (KBr) ν_{max} 3058, 2366, 1597, 1446, 1300, 1143, 1087, 911 (N=Se=O), 814, 744, 710, 682, 572, 549, 475, 462 cm^{-1}; UV (MeCN) λ_{max} 237 (ε 8.28×10^3), 270 (sh, ε 1.70×10^3) nm; MS m/z 284 {M$^+$(^{80}Se)-$C_7H_7NO_3S$, 35%}, 282 {M$^+$(^{78}Se)-$C_7H_7NO_3S$, 22%}, 204 (100%), 155 (16%), 126 (19%), 115 (42%), 91 (55%), 77 (25%), 65 (18%). Anal. Calcd for $C_{23}H_{19}NO_3SSe$: C, 58.97; H, 4.09; N, 2.99%. Found: C, 58.60; H, 4.13; N, 3.02%.

Optical Resolution of Racemic Selenoximines by Means of Medium-Pressure Column Chromatography Using an Optically Active Column. Typically, the racemic selenoximine (25 mg), dissolved in eluent (0.5 mL), was charged to an optically active column (Daicel Chiralcel OD: 250 × 10 mm) and eluted with hexane containing 30 (for **1**) and 50 (for **2**–**4**) vol % 2-propanol at a flow rate of 1.0 mL min^{-1}. Each ca. 8 mg of optically active selenoximine was collected from the first and second eluates, respectively.

(*S*)-(+)-*N*-Tosyl(phenyl)-*p*-tolylselenoximine {(*S*)-(+)-1}: Colorless oil; 100% ee; $[\alpha]_D$ +11.3 (*c* 1.22, $CHCl_3$); CD (MeCN) λ 226 ($[\theta]$ -1.44×10^4), 241 ($[\theta]$ 2.43×10^4), 273 ($[\theta]$ 7.85×10^2). ^{1}H and ^{13}C NMR were almost the same as those of the racemic one.

(*R*)-(−)-*N*-Tosyl(phenyl)-*p*-tolylselenoximine {(*R*)-(−)-1}: Colorless oil; 100% ee; $[\alpha]_D$ −12.1 (*c* 1.05, $CHCl_3$); CD (MeCN) λ 226 ($[\theta]$ 1.70×10^4), 241 ($[\theta]$ -2.38×10^4), 273 ($[\theta]$ -1.09×10^3). ^{1}H and ^{13}C NMR were almost the same as those of the racemic one.

(*S*)-(+)-*N*-Tosyl(*p*-methoxyphenyl)phenylselenoximine {(*S*)-(+)-2}: Colorless oil; 100% ee; $[\alpha]_D$ +16.1 (*c* 1.09, $CHCl_3$); CD (MeCN) λ 229 ($[\theta]$ -8.07×10^4), 252 ($[\theta]$ 6.27×10^4). ^{1}H and ^{13}C NMR were almost the same as those of the racemic one.

(*R*)-(−)-*N*-Tosyl(*p*-methoxyphenyl)phenylselenoximine {(*R*)-(−)-2}: Colorless oil; 100% ee; $[\alpha]_D$ −15.5 (*c* 1.01, $CHCl_3$); CD (MeCN) λ 229 ($[\theta]$ 9.84×10^4), 251 ($[\theta]$ -6.03×10^4). ^{1}H and ^{13}C NMR were almost the same as those of the racemic one.

(+)-*N*-Tosyl(phenyl)(*p*-trifluoromethylphenyl)selenoximine {(+)-3}: Mp 108.0–109.5 °C (decomp, colorless powder); 100% ee; $[\alpha]_D$ +44.6 (*c* 1.01, $CHCl_3$); CD (MeCN) λ 224 ($[\theta]$ 1.04×10^4), 238 ($[\theta]$ -6.76×10^3), 276 ($[\theta]$ 1.43×10^3). ^{1}H and ^{13}C NMR were almost the same as those of the racemic one.

(−)-*N*-Tosyl(phenyl)(*p*-trifluoromethylphenyl)selenoximine {(−)-3}: Mp 108.0–110.0 °C (decomp, colorless powder); 100% ee; $[\alpha]_D$ −42.4 (*c* 1.12, $CHCl_3$); CD (MeCN) λ 225 ($[\theta]$ -1.01×10^4), 239 ($[\theta]$ 7.26×10^3), 277 ($[\theta]$ -1.96×10^3). ^{1}H and ^{13}C NMR were almost the same as those of the racemic one.

(*S*)-(+)-*N*-Tosyl(2-naphthyl)phenylselenoximine {(*S*)-(+)-4}: Colorless oil; 100% ee; $[\alpha]_D$ +67.1 (*c* 1.09, $CHCl_3$); CD (MeCN) λ 225 ($[\theta]$ -5.87×10^4), 242 ($[\theta]$ 1.03×10^5), 277 ($[\theta]$ 9.16×10^4). ^{1}H and ^{13}C NMR were almost the same as those of the racemic one.

(*R*)-(−)-*N*-Tosyl(2-naphthyl)phenylselenoximine {(*R*)-(−)-4}: Colorless oil; 100% ee; $[\alpha]_D$ −65.0 (*c* 1.09, $CHCl_3$); CD (MeCN) λ 226 ($[\theta]$ 6.61×10^4), 241 ($[\theta]$ -9.90×10^4), 277 ($[\theta]$ -7.18×10^3). ^{1}H and ^{13}C NMR were almost the same as those of the racemic one.

(*S*)-(+)-*N*-Tosyl(phenyl)-*p*-tolylsulfoximine {(*S*)-(+)-5}:[13] Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.40 (s, 3H), 7.22 (d, 2H, J = 8.0 Hz), 7.30 (d, 2H, J = 8.3 Hz), 7.50 (t, 2H, J = 8.3 Hz), 7.57 (t, 1H, J = 8.3 Hz), 7.84 (d, 2H, J = 8.3 Hz), 7.87 (d, 2H, J = 8.3 Hz), 7.98 (d, 2H, J = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4, 21.5, 126.6, 127.5, 127.7, 129.1, 129.4, 130.1, 133.5, 136.6, 140.1, 140.9, 142.6, 145.0; 100% ee; $[\alpha]_D$ +20.4 (*c* 0.75, $CHCl_3$); CD (MeCN) λ 223 ($[\theta]$ -9.11×10^3), 243 ($[\theta]$ 1.41×10^4), 276 ($[\theta]$ 1.46×10^3).

Stability of Optically Active Selenoximines. To an acetonitrile solution (5 mL) of optically active selenoximine (2.3 μmol) was added water (0.5 mL), 1 M-HClaq (1 M = 1 mol dm^{-3}) (0.2 mL), or 1 M-NaOHaq (0.2 mL) and stirred at room temperature for 24 h. No racemization was observed in all of the selenoximines under all of the conditions. No decomposition was observed in the acetonitrile–water solution in all of the selenoximines. However, they were partly hydrolyzed to the corresponding selenones and *p*-toluenesulfonamide under both acidic and basic conditions, as

follows. Under acidic conditions: {decomposition: (+)-**1**: 10%, (+)-**2**: 4%, (+)-**3**: 23%, (+)-**4**: 10%}. Under basic conditions: {decomposition: (+)-**1**: 35%, (+)-**2**: 70%, (+)-**3**: 100%, (+)-**4**: 80%}.

This work was financially supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

References

1 For books, see: a) P. Metzner and A. Thuillier, "Sulfur Reagents in Organic Synthesis," Academic Press, London (1993). b) "The Chemistry of Sulphones and Sulphoxides," ed by S. Patai, Z. Rappoport, and C. J. M. Stirling, Wiley, New York (1988). c) "The Chemistry of the Sulphonium Group," ed by C. J. M. Stirling and S. Patai, Wiley, New York (1981). d) M. Mikolajczyk and J. Drabowicz, "Topics in Stereochemistry," ed by N. Allinger, E. L. Eliel, and S. H. Wilen, Wiley, New York (1982), Vol. 13, p. 333.

2 For books, see: a) "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai and Z. Rappoport, Wiley, New York (1987). b) "Organoselenium Chemistry," ed by D. Liotta, Wiley, New York (1987). c) C. Paulmier, "Selenium Reagents and Intermediates in Organic Synthesis," Pergamon Press, Oxford (1986). d) "Organic Selenium Compounds: Their Chemistry and Biology," ed by D. L. Klayman and W. H. H. Günther, Wiley, New York (1973).

3 For reviews, see: a) T. Shimizu and N. Kamigata, *Rev. Heteroat. Chem.*, **18**, 11 (1998). b) T. Shimizu and N. Kamigata, *Org. Prep. Proced. Int.*, **29**, 603 (1997).

4 For review, see: N. Kamigata and T. Shimizu, *Rev. Heteroat. Chem.*, **4**, 226 (1991), and references therein.

5 a) H. Taka, A. Matsumoto, T. Shimizu, and N. Kamigata, *Heteroat. Chem.*, **12**, 227 (2001). b) H. Taka, A. Matsumoto, T. Shimizu, and N. Kamigata, *Chem. Lett.*, **2000**, 726. c) T. Shimizu, M. Enomoto, H. Taka, and N. Kamigata, *J. Org. Chem.*, **64**, 8242 (1999). d) T. Shimizu, K. Kikuchi, Y. Ishikawa, I. Ikemoto, M. Kobayashi, and N. Kamigata, *J. Chem. Soc., Perkin Trans. 1*, **1989**, 597. e) T. Shimizu and M. Kobayashi, *J. Org. Chem.*, **52**, 3399 (1987).

6 a) T. Shimizu, A. Matsuhisa, N. Kamigata, and S. Ikuta, *J. Chem. Soc., Perkin Trans. 2*, **1995**, 1805. b) N. Kamigata, Y. Nakamura, K. Kikuchi, I. Ikemoto, T. Shimizu, and H. Matsuyama, *J. Chem. Soc., Perkin Trans. 1*, **1992**, 1721. c) N. Kamigata, Y. Nakamura, H. Matsuyama, and T. Shimizu, *Chem. Lett.*, **1991**, 249.

7 a) H. Taka, T. Shimizu, F. Iwasaki, M. Yasui, and N. Kamigata, *J. Org. Chem.*, **64**, 7433 (1999). b) T. Shimizu, N. Kamigata, and S. Ikuta, *J. Chem. Soc., Perkin Trans. 2*, **1999**, 1469. c) T. Shimizu, N. Seki, H. Taka, and N. Kamigata, *J. Org. Chem.*, **61**, 6013 (1996). d) N. Kamigata, H. Taka, A. Matsuhisa, H. Matsuyama, and T. Shimizu, *J. Chem. Soc., Perkin Trans. 1*, **1994**, 2257.

8 a) T. Shimizu, T. Urakubo, P. Jin, M. Kondo, S. Kitagawa, and N. Kamigata, *J. Organomet. Chem.*, **539**, 171 (1997). b) M. Kobayashi, K. Koyabu, T. Shimizu, K. Umemura, and H. Matsuyama, *Chem. Lett.*, **1986**, 2117.

9 a) T. Shimizu, Y. Nakashima, I. Watanabe, K. Hirabayashi, and N. Kamigata, *J. Chem. Soc., Perkin Trans. 1*, **2002**, 2151. b) T. Shimizu, I. Watanabe, and N. Kamigata, *Angew. Chem., Int. Ed.*, **40**, 2460 (2001).

10 For recent review, see: M. Reggelin and C. Zur, *Synthesis*, **2000**, 1.

11 a) G. Kresze and B. Wustrow, *Chem. Ber.*, **95**, 2652 (1962). b) R. Fusco and F. Tenconi, *Chem. Ind. (Milan)*, **47**, 61 (1965). c) D. R. Rayner, D. M. von Schriltz, J. Day, and D. J. Cram, *J. Am. Chem. Soc.*, **90**, 2721 (1968). d) M. A. Sabol, R. W. Davenport, and K. K. Andersen, *Tetrahedron Lett.*, **9**, 2159 (1968). e) B. W. Christensen, A. Kjaer, S. Neidle, and D. Rogers, *J. Chem. Soc. D*, **1969**, 169. f) B. W. Christensen and A. Kjaer, *J. Chem. Soc. D*, **1969**, 934. g) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schriltz, D. J. Duchamp, and D. C. Garwood, *J. Am. Chem. Soc.*, **92**, 7369 (1970). h) S. Neidle and D. Rogers, *J. Chem. Soc. B*, **1970**, 694. i) C. W. Schroeck and C. R. Johnson, *J. Am. Chem. Soc.*, **93**, 5305 (1971). j) E. U. Johnson and C. R. Johnson, *J. Am. Chem. Soc.*, **93**, 5308 (1971). k) T. R. Williams, A. Nudelman, R. E. Booms, and D. J. Cram, *J. Am. Chem. Soc.*, **94**, 4684 (1972). l) F. G. Yamagishi, D. R. Rayner, E. T. Zwicker, and D. J. Cram, *J. Am. Chem. Soc.*, **95**, 1916 (1973). m) C. R. Johnson and C. W. Schroeck, *J. Am. Chem. Soc.*, **95**, 7418 (1973). n) C. R. Johnson, C. W. Schroeck, and J. R. Shanklin, *J. Am. Chem. Soc.*, **95**, 7424 (1973). o) C. R. Johnson and E. R. Janiga, *J. Am. Chem. Soc.*, **95**, 7692 (1973). p) T. R. Williams and D. J. Cram, *J. Org. Chem.*, **38**, 20 (1973). q) S. Oae, Y. Tsuchida, and N. Furukawa, *Bull. Chem. Soc. Jpn.*, **46**, 648 (1973). r) C. R. Johnson, *Acc. Chem. Res.*, **6**, 341 (1973). s) C. R. Johnson, R. A. Kirchhoff, and H. G. Corkins, *J. Org. Chem.*, **39**, 2458 (1974). t) M. Moriyama, T. Yoshimura, N. Furukawa, T. Numata, and S. Oae, *Tetrahedron*, **32**, 3003 (1976). u) N. Furukawa, F. Takahashi, T. Yoshimura, and S. Oae, *Tetrahedron Lett.*, **18**, 3633 (1977). v) T. Akasaka, T. Yoshimura, N. Furukawa, and S. Oae, *Chem. Lett.*, **1978**, 417. w) H. Morita, H. Itoh, N. Furukawa, and S. Oae, *Chem. Lett.*, **1978**, 817. x) N. Furukawa, F. Takahashi, T. Yoshimura, and S. Oae, *Tetrahedron*, **35**, 317 (1979).

12 a) N. Ya. Derkach, T. V. Lyapina, and N. A. Pasmurtseva, *Zh. Org. Khim.*, **10**, 807 (1974). b) N. Ya. Derkach, G. G. Barashenkov, and E. I. Slyusarenko, *Zh. Org. Khim.*, **18**, 70 (1982).

13 M. Moriyama, T. Numata, and S. Oae, *Org. Prep. Proced. Int.*, **6**, 207 (1974).