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FREE RADICAL REACTIONS OF SODIUM SULFINATE WITH OLEFINS

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Abstract: A sulfonyl radical induced selenosulfonation and thiosulfonation with olefins by using sodium arylsulfinate as sulfonyl radical precursor is described. Phenyldiselenide and phenyldisulfide are used as free radical acceptors.

Recently there has been a growing interest in the application of free radical reaction in organic synthesis.[1] Free radical reactions mediated by sulfonyl radical have been reported by several groups.[2,3,4] The capture reaction of carbon radicals with aryldiselenide and aryldisulfide can proceed efficiently.[5] Sulfonyl radical can be generated from sodium arylsulfinate in aqueous acetic acid.[4,6] This led us to study the arylsulfonyl radical induced selenosulfonation and thiosulfonation of olefins by using sodium sulfinate as the sulfonyl radical precursor.

We began our studies by examining the reaction behavior of **1a**. Thus, treatment of **1a** with sodium *p*-

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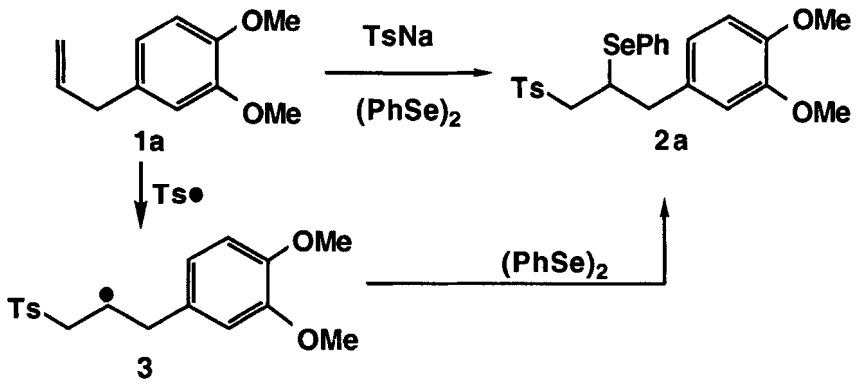
toluenesulfinate/phenyldiselenide in aqueous acetic acid, **2a** was obtained in 61% yield (Scheme I). The generality of this reaction was also examined by reacting the substrates **1b, 1c, 1d, 1e** under the condition used for **1a**. The results are shown in Table I. Each of these reactions gave the desired product in good yield and high regioselectivity. This reaction presumably proceeds via *p*-toluenesulfonyl radical addition to **1a**, followed by phenylseleno group abstraction from phenyldiselenide to give **2a**. Treatment of **1a** with sodium *p*-toluenesulfinate/*p*-tolyldisulfide under similar condition gave no desired thiosulfonation product. This result is presumably ascribed to the low reaction rate of *p*-toluenethio group abstraction by carbon radical.[7]

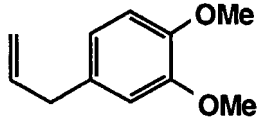
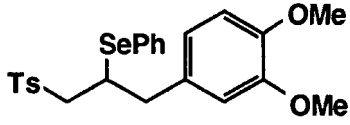
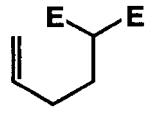
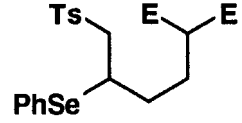
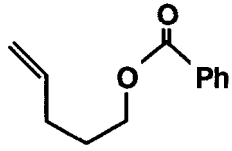
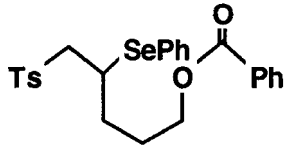
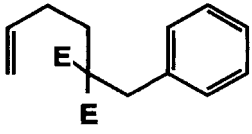
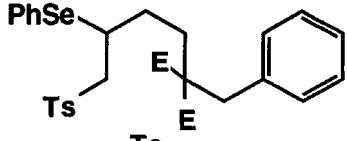
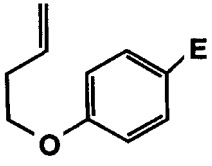
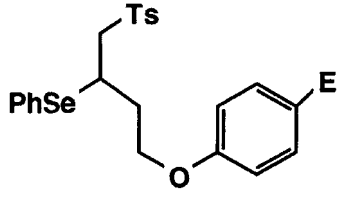
The free radical reaction of 1,6-dienes with a range of sulfonyl compounds have been reported by several groups.[3,4] Based on the results shown in Table I, we believed that the reaction of 1,6-dienes with sodium *p*-toluenesulfinate/phenyldiselenide can be effective. Reaction of diene **4a** with sodium *p*-toluenesulfinate/phenyldiselenide in aqueous acetic acid gave 93% of **5a** (Scheme II). The results of this addition-cyclization reaction are shown in Table II. In most cases, the cyclopentane products are obtained as a mixture of *cis*- and *trans*- stereoisomers in good yield and the *cis*- isomer predominates. This stereoselectivity is consistent with literature reports.[3,4e] With 1,6-hepatdiene, bisadduct **8** was also obtained in 18% yield. The yield of **5f** could be improved by decreasing the reaction concentration. The result was shown in Scheme III. A possible mechanism for this reaction is shown in Scheme II. Initiation occurs by *p*-toluenesulfonyl radical addition to diene **4a**, followed by 5-exo cyclization to cyclopentylmethyl radical and subsequent phenylseleno group abstraction from phenyldiselenide to give **5a**.

We also studied the *p*-toluenesulfonyl radical induced addition-cyclization reaction of 1,6-dienes with sodium *p*-toluenesulfinate/*p*-tolyldisulfide. When **4a** was treated with sodium *p*-toluenesulfinate and *p*-tolyldisulfide in aqueous acetic acid, an inseparable mixture of **9** and **10**

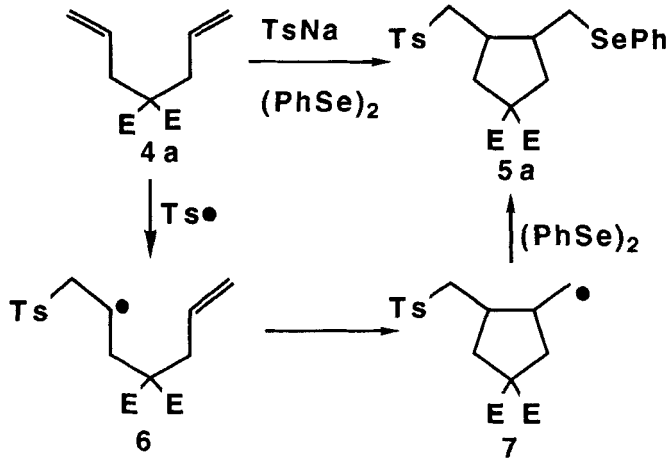


Scheme I

Table I: Free Radical Reaction of Olefins with $TsNa/(PhSe)_2$

Entry	Substrate 1	Product 2	Yield
a			61%
b			75%
c			72%
d			74%
e			77%

E: CO_2Me



Scheme II

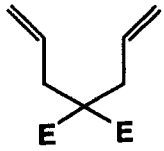
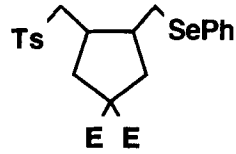
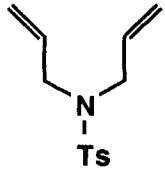
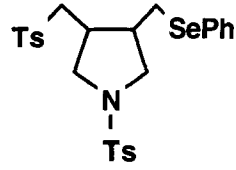
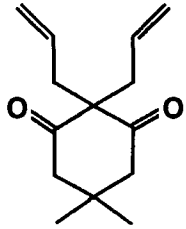
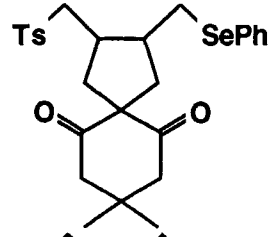
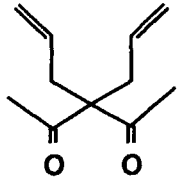
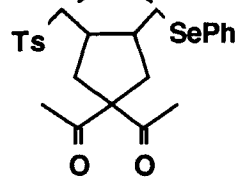
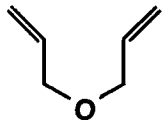
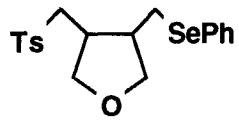
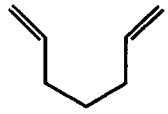
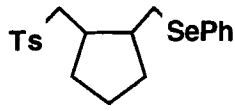
was obtained (Scheme IV). The formation of **10** was presumably mainly via the hydrogen atom abstraction from the *p*-tolyl groups. Based on this hypothesis, **4a** was treated with sodium benzenesulfinate/phenyldisulfide to give **11a** in 57% yield and only trace amount hydrogen atom abstraction product could be found. As shown in Table III, this addition reaction afforded the corresponding addition-cyclization product in a fair to good yield. This addition reaction occurs via a similar free radical mechanism shown in Scheme II.

In conclusion, sodium arylsulfinate is a potential sulfonyl radical precursor. By using readily available phenyldiselenide or phenyldisulfide as carbon radical acceptor, this radical addition reaction provides a potential method for selenosulfonation and thiosulfonation of olefins.

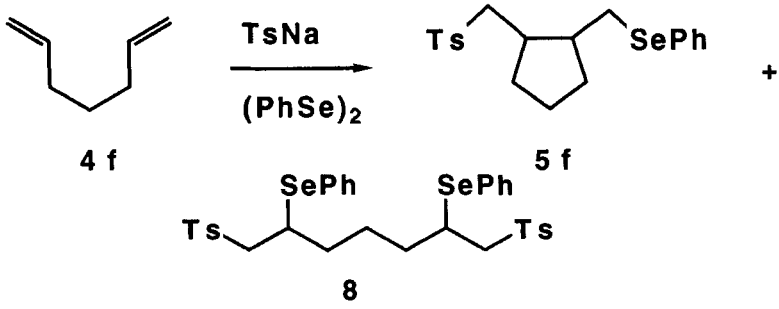
EXPERIMENTAL

General procedure: A solution of 103 mg (0.58 mmol) of **1a**, 1.03 g (5.80 mmol) of sodium *p*-toluenesulfinate and 194 mg (0.62 mmol) of phenyldiselenide in 5 ml of 80% aqueous

Table II: Free Radical Reaction of 1,6-Dienes with $TsNa/(PhSe)_2$

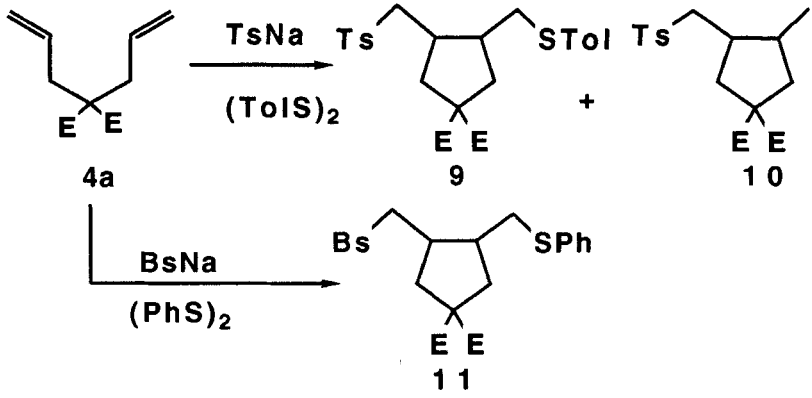
Entry	Substrate 4	Product 5	Yield (Ratio)[8]
a			93% (7.6:1)
b			76% (2.8:1)
c			84% (5.0:1)
d			89% (7.3:1)
e			71% (3.5:1)
f			38% (4.7:1)

E: CO_2Me



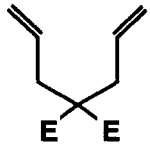
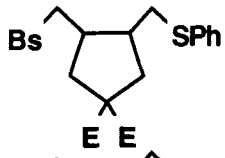
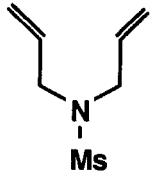
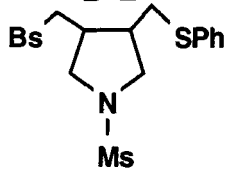
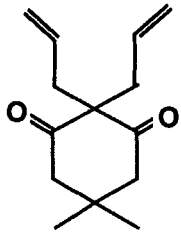
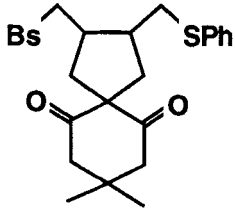
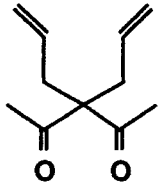
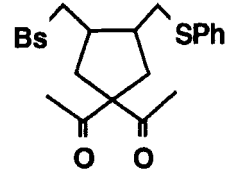
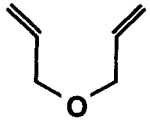
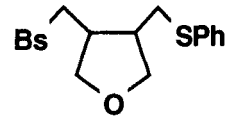
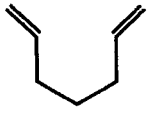
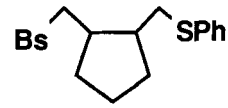
[4f]	Reaction Time	Yield	
		5 f	8
0.11M	24h	38%	18%
0.052M	24h	45%	12%
0.038M	48h	53%	9%

Scheme III



Scheme IV

Table III: Free Radical Reaction Of 1,6-Dienes With BsNs/$(PhS)_2$

Entry	Substrate 4	Product 11	Yield (Ratio)[8]
a			57% (7.5:1)
b			60% (2.8:1)
c			74% (4.5:1)
d			53% (6.5:1)
e			65% (2.9:1)
f			56% (4.4:1)

E: CO_2Me, Ms: CH_3SO_2, Bs: $PhSO_2$

acetic acid was heated at 80°C for 24 h. The reaction mixture was diluted with 50 ml of ethyl acetate, washed with three 25-mL portions of saturated aqueous sodium bicarbonate, three 25-mL portions of water, dried (Na_2SO_4) and concentrated in vacuo. The residue was chromatographed over 15 g silica gel (eluted with ethyl acetate-hexane,1:3.5) to give 194 mg (61%) of **2a**.

1,2-Dimethoxy-4-(2-phenylseleno-3-*p*-toluenesulfonyl-propyl)-benzene 2a: IR ($CHCl_3$) 3015, 1595, 1514, 1262, 1144 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.41 (s, 3H, CH_3), 3.08 (dd, J=7.6Hz, 15.2Hz, 1H, CH), 3.29-3.80 (m, 4H), 3.85 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 6.80 (s, 3H, ArH), 7.10-7.30 (m, 7H, ArH), 7.62 (d, J=8.2Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.2(q), 38.1(t), 39.0(d), 55.5(q), 59.6(t), 110.8(d), 112.4(d), 121.3(d), 127.4(d), 127.7(d), 128.9(d), 129.6(d), 129.9(s), 134.2(s), 135.7(s), 144.4(s), 147.6(s), 148.4(s); mass spectrum, m/e (relative intensity) 490(M^+, 17), 332(18), 177(100), 151(26); exact mass calcd for $C_{24}H_{26}O_4SSe$ m/e 490.0717, found m/e 490.0710.

Methyl 2-(3-Phenylseleno-4-*p*-toluenesulfonyl-butyl)-propanedioate 2b: IR ($CHCl_3$) 3020, 1732, 1438, 1318, 1148 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.55-1.84 (m, 1H, CH), 1.90-2.40 (m, 3H), 2.43 (s, 3H, CH_3), 3.24-3,55 (m, 4H), 3.74 (s, 3H, OCH_3), 3.75(s, 3H, OCH_3), 7.15-7.44 (m, 7H, ArH), 7.63 (d, J=8.0Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.3(q), 26.7(t), 30.7(t), 36.4(d), 50.8(d), 52.3(q), 61.2(q), 126.7(s), 127.6(d), 128.1(d), 129.1(d), 129.7(d), 134.9(d), 135.8(s), 144.6(s), 169.1(s), 169.2(s); mass spectrum, m/e (relative intensity) 498(M^+, 24), 467(6), 435(2), 343(22), 309(11), 277(12), 185(100); exact mass calcd for $C_{22}H_{26}O_6SSe$ m/e 498.0615, found m/e 498.0604.

4-Phenylseleno-5-*p*-toluenesulfonyl-pentyl Benzoate 2c: IR ($CHCl_3$) 3028, 1714, 1454, 1316, 1280, 1140 cm^{-1} ; ^1H NMR ($CDCl_3$) δ 1.72-1.86 (m, 1H, CH), 1.86-2.02 (m, 1H, CH), 2.02-2.17 (m, 1H, CH), 2.22-2.40 (m, 1H, CH), 2.36 (s, 3H, CH_3), 3.36 (dd, J=11.0Hz, 14.6Hz, 1H, CH),

3.43-3.53 (m, 2H, CH_2), 4.30 (t, J=6.2Hz, 2H, OCH_2), 7.11 (t, J=7.6Hz, 2H, ArH), 7.14-7.26 (m, 3H, ArH), 7.31 (dm, J=8.2Hz, 2H, ArH), 7.37 (t, J=8.2Hz, 2H, ArH), 7.49 (t, J=8.2Hz, 1H, ArH), 7.61 (d, J=8.2Hz, 2H, ArH), 8.00 (dm, J=8.2Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.4(q), 26.6(t), 30.0(t), 36.6(d), 61.5(t), 64.0(t), 126.8(s), 127.6(d), 128.1(d), 129.1(d), 129.4(d), 129.7(d), 130.0(d), 132.7(d), 134.9(d), 135.9(s), 144.6(s), 166.2(s); mass spectrum, m/e (relative intensity) 502(M^+, 45), 397(2), 347(41), 225(66), 189(55), 105(100); exact mass calcd for $C_{25}H_{26}O_4SSe$ m/e 502.0717, found m/e 502.0722.

Methyl 2-Benzyl-2-(3-phenylseleno-4-*p*-toluenesulfonyl-butyl)-propanedioate 2d: IR ($CHCl_3$) 3024, 1732, 1436, 1316, 1230, 1144 cm^{-1} ; ^1H NMR ($CDCl_3$) δ 1.52-2.05 (m, 2H, CH_2), 2.13-2.38 (m, 2H, CH_2), 2.41 (s, 3H, CH_3), 3.20-3.48 (m, 3H), 3.24 (s, 2H, CH_2), 3.71 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 7.11-7.39 (m, 12H, ArH), 7.59 (d, J=8.3Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.4(q), 28.2(t), 30.3(t), 36.9(d), 38.1(t), 52.3(q), 58.5(s), 61.1(t), 126.9(d), 127.2(s), 127.7(d), 128.0(d), 128.2(d), 129.1(d), 129.7(d), 129.8(d), 134.7(d), 135.6(s), 135.7(s), 144.6(s), 171.08(s), 171.13(s); mass spectrum, m/e (relative intensity) 588(M^+, 10), 431(6), 276(4), 91(100); exact mass calcd for $C_{29}H_{32}O_6SSe$ m/e 588.1085, found m/e 588.1088.

Methyl *p*-(3-Phenylseleno-4-*p*-toluenesulfonyl-butoxy)-benzoate 2e: IR ($CHCl_3$) 3016, 1714, 1608, 1438, 1286, 1252, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.92-2.15 (m, 1H, CH), 2.41 (s, 3H, CH_3), 2.62-2.87 (m, 1H, CH), 3.32-3.70 (m, 3H), 3.87 (s, 3H, OCH_3), 4.07-4.37 (m, 2H, OCH_2), 6.89 (d, J=8.6Hz, 2H, ArH), 7.02-7.30 (m, 7H, ArH), 7.65 (d, J=8.2Hz, ArH), 7.99 (d, J=8.6Hz, 2H, ArH); ^{13}C NMR (CDCl3) δ 21.6(q), 33.0(t), 34.0(d), 51.8(q), 61.8(t), 65.6(t), 114.1(d), 122.7(s), 127.2(s), 128.0(d), 128.3(d), 129.3(d), 129.9(d), 131.5(d), 135.0(d), 135.8(s), 144.8(s), 162.3(s), 166.8(s); mass spectrum, m/e (relative intensity) 518(M^+, 29), 487(2), 362(7), 331(34), 229(18), 205(100); exact mass calcd for $C_{25}H_{26}O_5SSe$ m/e 518.0666, found m/e 518.0662

Methyl 3-Phenylselenomethyl-4-*p*-toluenesulfonylmethyl-cyclopentane-1,1-dicarboxylate 5a: IR ($CHCl_3$) 2956, 1728, 1302, 1275 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0-3.4 (m, 10H), 2.44 (s, 3H, CH_3), 3.70 (s, 6H, OCH_3), 7.1-7.6 (m, 7H, ArH), 7.76 (d, J=8.2Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.3(q), 27.6(t), 36.6(d), 37.7(t), 38.6(t), 41.8(d), 52.7(q), 55.6(t), 57.9(s), 126.9(d), 127.7(d), 128.8(d), 129.2(s), 129.7(d), 132.7(d), 136.1(s), 144.6(s), 172.1(s), 172.4(s); mass spectrum, m/e (relative intensity) 524(M^+, 45), 493(8), 365(40), 367(40), 335(35), 275(36), 211(13), 151(100); exact mass calcd for $C_{24}H_{28}O_6SSe$ m/e 524.0772, found m/e 524.0818.

***N*-Methanesulfonyl-3-phenylselenmethyl-4-*p*-toluenesulfonylmethyl-pyrrolidine 5b:** IR ($CHCl_3$) 3032, 1336, 1152 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.43 (s, 3H, CH_3), 2.47-3.62 (m, 10H), 2.79 (s, 3H, CH_3), 7.17-7.47 (m, 7H, ArH), 7.74 (d, J=8.3Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.6(q), 25.7(t), 35.8(q), 36.4(d), 41.7(d), 50.5(t), 51.4(t), 54.4(t), 127.6(d), 127.9(d), 129.3(d), 130.1(d), 133.2(d), 136.2(s), 145.3(s); mass spectrum, m/e (relative intensity) 487(M^+, 81), 408(20), 332(50), 330(55), 253(14), 251(16), 174(59), 96(43), 94(95), 91(100); exact mass calcd for $C_{20}H_{25}O_4NS_2Se$ m/e 487.0390, found m/e 487.0387.

8,8-Dimethyl-2-phenylselenomethyl-3-*p*-toluenesulfonylmethyl-spiro[4,5]octa-6,10-dione 5c: IR ($CHCl_3$) 2962, 1728, 1692, 1320, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (s, 3H, CH_3), 0.95 (s, 3H, CH_3), 1.7-3.4 (m, 14H), 2.43 (s, 3H, CH_3), 7.1-7.6 (m, 7H, ArH), 7.75 (d, J=8.3Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.5(q), 27.5(t), 28.0(q), 28.3(q), 30.3(s), 35.7(t), 36.1(t), 37.5(d), 43.0(d), 51.1(t), 51.5(t), 55.1(t), 69.4(s), 127.1(d), 127.8(d), 129.0(d), 129.2(s), 129.8(d), 132.9(d), 136.4(s), 144.7(s), 206.8(s), 207.7(s); mass spectrum, m/e (relative intensity) 532(M^+, 51), 377(38), 375(42), 333(2), 219(100); exact mass calcd for $C_{27}H_{32}O_4SSe$ m/e 532.1186, found m/e 532.1190.

1,1-Diacetyl-3-phenylselenomethyl-4-*p*-toluenesulfonylmethyl-cyclopentane 5d: IR ($CHCl_3$) 3022, 1698, 1149 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.7-3.5 (m, 10H), 2.06 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 7.1-7.6 (m, 7H, ArH), 7.77 (d, J=8.2Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.4(q), 25.9(q), 26.5(q), 27.6(t), 33.9(t), 34.8(t), 36.6(d), 41.9(d), 55.6(t), 73.2(s), 127.0(d), 127.7(d), 129.0(d), 129.2(s), 129.8(d), 132.7(d), 136.2(s), 144.6(s), 203.5(s), 204.4(s); mass spectrum, m/e (relative intensity) 492(M^+, 65), 450(3), 337(40), 335(44), 294(15), 236(13), 137(100); exact mass calcd for $C_{24}H_{28}O_4SSe$ m/e 492.0874, found m/e 492.0903.

3-Phenylselenomethyl-4-*p*-toluenesulfonylmethyl-tetrahydrofuran 5e: IR ($CHCl_3$) 3010, 1731, 1149 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.1-3.4 (m, 6H), 2.44 (s, 3H, CH_3), 3.4-4.2 (m, 4H, OCH_2), 7.1-7.6 (m, 5H, ArH), 7.36 (d, J=8.2Hz, 2H, ArH), 7.77 (d, J=8.2Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.4(q), 25.9(t), 36.7(d), 41.6(d), 54.5(t), 71.7(t), 72.1(t), 127.1(d), 127.8(d), 129.0(d), 129.9(d), 132.7(d), 136.0(s), 144.8(s); mass spectrum, m/e (relative intensity), 410(M^+, 58), 255(41), 253(62), 97(74), 91(100); exact mass calcd for $C_{19}H_{22}O_3SSe$ m/e 410.0455, found m/e 410.0458.

1-Phenylselenomethyl-4-*p*-toluenesulfonylmethyl-cyclopentane 5f: IR ($CHCl_3$) 2964, 1478, 1314, 1302, 1148, 1088 cm^{-1} ; ^1H NMR ($CDCl_3$) δ 1.20-3.45 (m, 12H), 2,42 (s, 3H, CH_3), 7.15-7.50 (m, 7H, ArH), 7.77 (d, J=8.2Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.4(q), 22.0(t), 28.6(t), 29.8(t), 30.6(t), 37.3(d), 42.3(d), 56.6(t), 126.6(d), 127.8(d), 128.9(d), 129.7(d), 132.2(s), 132.4(d), 136.6(s), 144.4(s); mass spectrum, m/e (relative intensity) 408(M^+, 27), 253(16), 251(17), 95(100); exact mass calcd for $C_{20}H_{24}O_2SSe$ m/e 408.0662, found m/e 408.0660.

2,6-Bis(phenylseleno)-1,7-bis(*p*-toluenesulfonyl)-heptane 8: IR ($CHCl_3$) 3028, 1316, 1302, 1144, 1086 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50-2.25 (m, 6H), 2.41 (s, 6H,

CH_3), 3.25-3.65 (m, 6H, CHSe and CH_2S), 7.1-7.8 (m, 18H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.5(q), 25.3(t), 32.8(t), 36.9(d), 61.6(t), 127.2(s), 127.8(d), 128.1(d), 129.2(d), 129.9(d), 135.0(d), 136.2(s), 144.6(s); mass spectrum, m/e (relative intensity) 720(M^+, 0.9), 588(20), 563(1.3), 407(6), 183(62), 155(54), 91(100); exact mass calcd for $C_{33}H_{36}O_4S_2Se_2$ m/e 720.0385, found m/e 720.0387.

Methyl 3-Benzenesulfonylmethyl-4-phenylthiomethyl-cyclopentane-1,1-dicarboxylate 11a: IR ($CHCl_3$) 3024, 1730, 1438, 1272, 1152 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.90-3.52 (m, 10H), 3.66 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 7.06-7.40 (m, 5H, ArH), 7.40-7.70 (m, 3H, ArH), 7.87 (dm, J=7.3Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 34.0(t), 36.2(d), 38.0(t), 38.1(t), 41.1(d), 52.4(q), 52.9(q), 55.6(t), 58.1(s), 126.4(d), 127.9(d), 128.9(d), 129.3(d), 129.7(d), 133.7(d), 135.3(s), 139.3(s), 172.2(s), 172.6(s); mass spectrum, m/e (relative intensity) 462(M^+, 33), 431(4), 352(11), 321(36), 260(13), 213(64), 153(82), 93(100); exact mass calcd for $C_{23}H_{26}O_6S_2$ m/e 462.1171, found m/e 462.1174.

***N*-Methanesulfonyl-3-benzenesulfonylmethyl-4-phenylthiomethyl-pyrrolidine 11b:** IR ($CHCl_3$) 2962, 1731, 1695, 1449, 1308, 1248, 1149, 1086 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20-3.85 (m, 10H), 2.85 (s, 3H, CH_3), 7.17-7.35 (m, 5H, ArH), 7.55-7.78 (m, 3H, ArH), 7.91 (dm, J=6.8Hz); ^{13}C NMR ($CDCl_3$) δ 32.6(t), 35.9(d), 35.9(q), 40.8(d), 50.6(t), 50.7(t), 54.3(t), 127.0(d), 127.9(d), 129.2(d), 129.6(d), 130.2(d), 134.2(d), 134.5(s), 139.0(s); mass spectrum, m/e (relative intensity) 425(M^+, 58), 394(1), 346(35), 284(12), 236(66), 204(100); exact mass calcd for $C_{19}H_{23}NO_4S_3$ m/e 425.0789, found m/e 425.0787.

2-Benzenesulfonylmethyl-8,8-dimethyl-3-phenylthiomethyl-spiro[4,5]octa-6,10-dione 11c: IR ($CHCl_3$) 3034, 1731, 1338, 1152, 1086 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 1.76-3.43 (m, 14H), 7.07-7.40 (m, 5H, ArH), 7.46-7.70 (m, 3H, ArH), 7.84

(dm, J=6.6Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 28.0(q), 28.3(q), 30.2(s), 33.5(t), 35.0(t), 36.0(t), 36.9(d), 42.0(d), 51.1(t), 51.5(t), 54.8(t), 69.3(s), 126.0(d), 127.7(d), 128.9(d), 129.2(d), 129.5(d), 133.6(d), 135.5(s), 139.4(s), 206.7(s), 207.7(s); mass spectrum, m/e (relative intensity) 470(M^+, 100), 362(33), 329(66), 219(49); exact mass calcd for $C_{26}H_{30}O_4S_2$ m/e 470.1585, found m/e 470.1580.

1,1-Diacetyl-3-benzenesulfonylmethyl-4-phenylthiomethyl-cyclopentane 11d: IR ($CHCl_3$) 3016, 1701, 1308, 1149, 1086 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70-3.40 (m, 10H), 2.01 (s, 3H, CH_3), 2.05(s, 3H, CH_3), 7.06-7.30 (m, 5H, ArH), 7.44-7.69 (m, 3H, ArH), 7.87 (dm, J=7.7Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 25.9(d), 26.6(d), 33.8(t), 34.0(t), 34.1(t), 36.1(q), 41.1(q), 55.5(t), 73.3(s), 126.3(d), 127.8(d), 128.8(d), 129.2(d), 129.5(d), 133.7(d), 135.1(s), 139.1(s), 203.5(s), 204.4(s); mass spectrum, m/e (relative intensity) 430(M^+, 85), 388(3), 321(3), 289(45), 280(33), 179(109), 43(100); exact mass calcd for $C_{23}H_{26}O_4S_2$ m/e 430.1272, found m/e 430.1282.

3-Benzenesulfonylmethyl-4-phenylthiomethyl-tetrahydrofuran 11e: IR ($CHCl_3$) 3012, 1482, 1308, 1150, 1086 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.12-4.12 (m, 10H), 7.10-7.32 (m, 5H, ArH), 7.50-7.70 (m, 3H, ArH), 7.91 (dm, J=8.3Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 32.6(t), 36.2(d), 41.0(d), 54.5(t), 71.3(t), 71.6(t), 126.4(d), 127.9(d), 129.0(d), 129.4(d), 129.8(d), 133.9(s), 135.0(s), 139.1(s); mass spectrum, m/e (relative intensity) 348(M^+, 100), 239(7), 207(45), 96(60); exact mass calcd for $C_{18}H_{20}O_3S_2$ m/e 348.0854, found m/e 348.0845.

1-Benzenesulfonylmethyl-2-phenylthiomethyl-cyclopentane 11f: IR ($CHCl_3$) 2960, 1586, 1482, 1304, 1148, 1086 cm^{-1} ; ^1H NMR ($CDCl_3$) δ 1.2-3.5 (m, 12H), 7.10-7.40 (m, 5H, ArH), 7.91 (dm, J=8.2Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 22.0(t), 30.0(t), 30.0(t), 34.2(t), 36.7(d), 41.4(d), 56.4(t), 125.8(d), 127.8(d), 128.7(d), 129.0(d), 129.2(d), 133.5(d), 136.1(s), 139.5(s); mass spectrum, m/e

(relative intensity) 346(M^+, 82), 236(7), 205(92), 95(100); exact mass calcd for $C_{19}H_{22}O_2S_2$ m/e 346.1062, found m/e 346.1055.

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8. The ratio refers to *cis-* and *trans-* products.

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