Selective Epoxidation of 2-(Phenylsulfonyl) 1,3-Dienes. One-Pot Procedure for Regioselective Preparations of 2-(Phenylsulfonyl) 1,3-Diene Monoepoxides from 1,3-Dienes[1]

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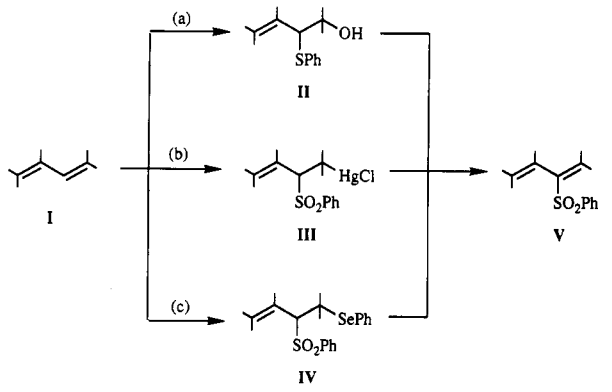
The epoxidation of 2-(phenylsulfonyl) 1,3-dienes with *m*-chloroperbenzoic acid or hydrogen peroxide under basic conditions affords regioselectively the corresponding 3,4- or 1,2-epoxy derivatives, respectively. The same type of products were prepared in a one-pot procedure involving a selenosulfonylation–oxidation of 1,3-dienes; in this case the second oxidation gave better yields using lithium *tert*-butyl peroxide instead of hydrogen peroxide/sodium hydroxide.

Introduction

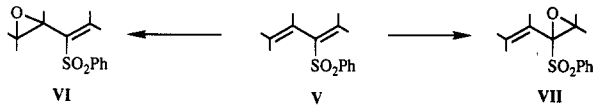
2-(Arylsulfonyl) 1,3-dienes of the type **V** have attracted a great deal of attention recently due to their versatility in organic synthesis, in particular in cycloaddition reactions.[2,3] Their preparation has been mainly carried out starting from 1,3-dienes **I**[4] and following three different routes: (a) via the hydroxy thioether **II** (five steps),[5] (b) through a tandem sulfonylmercuration–elimination sequence (two steps),[2,6] which involves the sulfonyl mercurial **III**, and (c) through a one-pot selenosulfonylation–oxidation process,[7] via the sulfonyl selenide **IV** (Scheme I).

In the present paper, we report the selective epoxidation of 2-(phenylsulfonyl) 1,3-dienes **V** to give both regioisomers **VI** and **VII** (Scheme II),[1] as well as a one-pot procedure, which starts from 1,3-dienes **I** and yields directly the corresponding epoxides **VI** or **VII**, via the *in situ* generated 2-(phenylsulfonyl)-1,3-dienes of the type **V**.

Scheme I



Scheme II



Results and Discussion

Regioselective epoxidation of 2-(phenylsulfonyl) 1,3-dienes **V** can be achieved taking advantage of the very different reactivity of the two double bonds toward oxidation reagents: whereas the (phenylsulfonyl)-substituted double bond is electron deficient and reacts with nucleophilic oxidants such as hydrogen peroxide under basic conditions, the other double bond is fairly electron-rich and undergoes epoxidation with *m*-chloroperbenzoic acid. Both types of epoxides have found synthetic applications in organic chemistry.[1,5]

The reaction of different cyclic and acyclic 2-sulfonyl 1,3-dienes **1–4** of type **V** with *m*-chloroperbenzoic acid in dichloromethane at room temperature gave the corresponding epoxides **5**, **7**, **9**, and **11**, respectively, of type **VI** (method A: Table I, entries 1, 3, 5, and 7, respectively). In all cases the selectivity for the epoxidation at the electron-rich double bond was >95% (determined on the crude product). When the epoxidation procedure was carried out by the use of hydrogen peroxide and sodium hydroxide[8,9] in acetone, methanol, or diethyl ether–acetone as solvents at room temperature, the corresponding epoxides **6**, **8**, **10**, and **12** of type **VII**, respectively, were formed, the regioselectivity being in all cases >99% (method B; Table I, entries 2, 4, 6, and 8, respectively).

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(8) Wasson, R. L.; House, H. O. *Org. Synth.* **1957**, *37*, 58. Wasson, R. L.; House, H. O. *Organic Synthesis*; Wiley: New York, 1963; Collect. Vol. IV, p 552.

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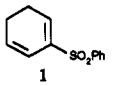
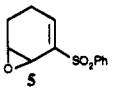
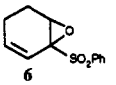
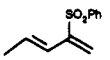
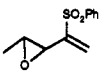
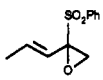
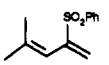
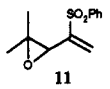
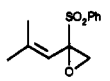
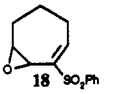
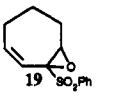
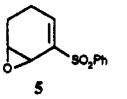
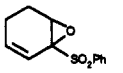
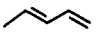
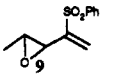
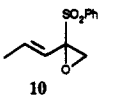
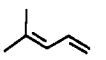
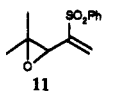
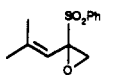
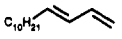
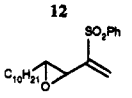
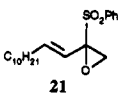
Table I. Selective Epoxidation of 2-(Phenylsulfonyl) 1,3-Dienes

entry	sulfonyl diene	condns[a]	product	yield,[b] %
1	 1	A (5 h)	 5	80
2	1	B (1 h)	 6	97[c]
3	 2	A (4 d)	 7	73
4	2	B (2 h)	 8	71
5	 3	A (4 d)	 9	76
6	3	B (3 h)	 10	80
7	 4	A (30 h)	 11	82
8	4	B (8 h)	 12	51

[a] Method A: *m*-chloroperbenzoic acid, CH_2Cl_2, 20 °C. Method B: H_2O_2/NaOH in methanol (entry 2), ether–acetone (entry 4) or acetone (entries 6 and 8), 20 °C. The reaction time is given in parentheses. [b] Isolated yield after chromatography (on silica except entry 7, where neutral alumina was used). [c] Chromatographic purification not needed.

The preparation of 2-(phenylsulfonyl) 1,3-dienes **V** via the selenosulfonylation route (path c, Scheme I) involves an oxidation of the selenosulfone **IV** by either peracid or peroxide in the last step. It therefore seemed possible to obtain a subsequent *in situ* epoxidation by employing an excess of the oxidant. In this way either epoxide of the sulfonyl diene (cf. Table I) would be available in one pot from the 1,3-diene by proper choice of the oxidant. We therefore studied the direct conversion of 1,3-dienes **I** into epoxides of type **VI** and **VII** employing a one-pot tandem selenosulfonylation–oxidation sequence. Thus, selenosulfonylation[7] of different cyclic and acyclic 1,3-dienes **13–17** with $PhSeSO_2Ph$[10] followed by *in situ* oxidation by *m*-chloroperbenzoic acid (*vide supra*) yielded the expected epoxides **18**, **5**, **9**, **11**, and **20**, respectively, of type **VI**, in a regioselective manner (method C; Table II, entries 1, 4, 7, 10 and 12, respectively); none of the other regioisomer could be detected in the crude reaction product. The other one-pot route to epoxides of type **VII** with alkaline hydrogen peroxide in methanol or acetone worked well only for the cyclic 1,3-dienes **13** and **14** (method E; Table II, entries 3 and 6); in the case of acyclic systems such as **15** (or **16**) the yields obtained were poor (Table II, entry 9). This problem was overcome by employing lithium *tert*-butyl peroxide (generated *in situ* by treatment of *tert*-butyl hydroperoxide with *n*-butyllithium) as oxidation reagent in the second step of the one-pot procedure.[11,12] Thus, 1,3-dienes **13–17** were selenosulfonylated (*vide supra*) and subsequently *in situ* oxidized with ^tBuOOLi in THF at temperatures ranging between −55 and 20 °C to yield directly and exclusively the expected epoxides **19**, **6**, **10**, **12**, and **21**, respectively (method D; Table II, entries 2, 5, 8, 11, and 13, respectively).

Table II. Selective One-Pot Synthesis of Epoxy(phenylsulfonyl)alkenes by Selenosulfonylation–Oxidation of 1,3-Dienes

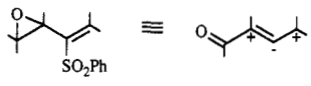
entry	diene	condns[a]	product	yield,[b] %
1	 13	C (4 h)	 18	65
2	13	D (1.5 h)	 19	81
3	13	E (18 h)	19	90[c]
4	 14	C (2 h)	 5	54
5	14	D (1.5 h)	 6	80
6	14	E (2 d)	6	83
7	 15	C (2 d)	 9	54
8	15	D (2.5 h)	 10	60
9	15	E (4 h)	10	23
10	 16	C (12 h)	 11	78
11	16	D (2 h)	 12	61
12	 17	C (2 d)	 20	61
13	17	D (2.5 h)	 21	67

[a] Corresponding to the oxidation step. Method C: *m*-chloroperbenzoic acid (in entries 1 and 4 diisopropylamine was also added), CH_2Cl_2, 20 °C. Method D: *tert*-butyl hydroperoxide/*n*-BuLi, THF, −55 °C (entries 8 and 13), −20 °C (entries 2 and 5), or 20 °C (entry 11). Method E: hydrogen peroxide/NaOH, MeOH (entries 3 and 6) or acetone (entry 9), 20 °C (entries 3 and 6) or 0 °C (entry 9). Oxidation reaction time is given in parentheses. [b] Isolated yield after flash chromatography (on silica gel except entry 10, where neutral alumina was used. [c] Chromatographic purification not needed.

In the case of 1,3-butadiene the one-pot procedure does not work following method C (an intractable mixture was

obtained), and with method E (5 h, 20 °C for the oxidation step) only ca. 10% yield of the corresponding epoxide 8 was isolated after workup. Also, method D led to an unsatisfactory result with this diene. For 1,3-butadiene the corresponding epoxides 7 and 8 were conveniently obtained via the isolated 2-(phenylsulfonyl)-1,3-butadiene (Table I, entries 3 and 4).

Epoxides of type VI and VII are useful building blocks in organic synthesis due to their high functionality. For instance, it has been demonstrated that epoxides of type VI can act as synthons of type VIII, and consequently, they are useful multicoupling reagents.[1,5]



VI VIII

Finally, we conclude that the procedures described here are convenient routes for preparing regioselectively epoxysulfonylalkenes of type VI and VII. Compared to the other methods previously reported[5] the present procedures are shorter, give higher overall yields, and in addition offer a useful regioselectivity.

Experimental Section

General Methods. Melting points were recorded on a Leitz Wetzlar melting point microscope and are uncorrected. NMR spectra were recorded either on a Varian XL-300 MHz or a Varian Unity 400 MHz spectrometer, ^1H at 300 MHz or 400 MHz and ^{13}C at 74.5 MHz or 100.6 MHz using $CDCl_3$ as solvent and tetramethylsilane (0.0 ppm, ^1H) and $CDCl_3$ (77.0 ppm, ^{13}C) as internal standard. IR spectra were recorded on either a Perkin-Elmer 1600 FT-IR or a Perkin-Elmer 177 spectrophotometer using a 0.1-mm KBr cell with $CDCl_3$ or CCl_4 as solvent. Only the strongest and structurally most important peaks (ν_{max}, cm^{-1}) are listed. Elemental analyses were performed by Analytische Laboratorien, Engelskirchen, Germany. Reaction solvents were dried and distilled under nitrogen using standard procedures. Merck silica gel 60 (230–400 mesh) was employed for flash chromatography. *m*-Chloroperbenzoic acid (*m*-CPBA) (either 85%, method A or 50–60%, method C) was purchased from Aldrich. 3.5 M *tert*-butyl hydroperoxide in toluene was made according to the procedure of Sharpless.[12] The sulfonyldienes 1–4 were prepared according to refs 2a and 6.

Method A. 3,4-Epoxy-2-(phenylsulfonyl)cyclohexene (5). To a solution of 2-(phenylsulfonyl)-1,3-cyclohexadiene (1) (1.20 g, 5.40 mmol) in CH_2Cl_2 (20.0 mL) was added *m*-CPBA (85%, 1.32 g, 6.50 mmol) in portions at room temperature, and the reaction mixture was allowed to stir for 5 h. The 3-chlorobenzoic acid formed was filtered off, and the filtrate was washed with aqueous solutions of Na_2SO_3 (3 × 5 mL), Na_2CO_3 (3 × 5 mL), and brine (3 × 5 mL) and finally dried (Na_2SO_4). The crude product was purified by flash chromatography on a silica gel (column: 1.5 × 7.0 cm; EtOAc/hexane = 10/90 and 20/80) affording 1.02 g (80%) of **5**: mp 96–97.5 °C; IR (KBr) 3050, 3000, 2935, 2920, 1630, 1445, 1315, 1300, 1285, 1150, 1085, 1035, 945, 870, 830, 760, 745, 715, 680 cm^{-1}; ^1H NMR δ 7.95–7.88 (m, 2H, ArH), 7.68–7.52 (m, 3H, ArH), 7.17 (dt, J = 7.0, 2.3 Hz, 1H, H-1), 3.68 (dd, J = 4.3, 2.3 Hz, 1H, H-3), 3.58 (m, 1H, H-4), 2.42–2.12 (m, 3 H, H-5, H-6 and H-6′), 1.66 (m, 1H, H-5); ^{13}C NMR δ 141.6, 139.6, 138.2, 133.5, 129.4, 127.7, 54.7, 45.4, 20.7, 19.5.

Anal. Calcd for $C_{12}H_{12}O_3S$: C, 61.00; H, 5.12. Found: C, 60.99; H, 5.20.

Method B. 3,4-Epoxy-3-(phenylsulfonyl)cyclohexene (6). To a solution of 2-(phenylsulfonyl)-1,3-cyclohexadiene (1) (4.43 g, 20.1 mmol) in MeOH (40 mL) were added H_2O_2 (~30%; 10.0 mL, ~100 mmol) and aqueous 2 M NaOH (1.00 mL, 2.00 mmol). After the reaction mixture was stirred at room temperature for 1 h an aqueous solution of Na_2SO_3 (5 mL), H_2O (50 mL), and CH_2Cl_2 (100 mL) was added. The layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with H_2O (50 mL), dried ($MgSO_4$), and concentrated in vacuo affording 4.63 g (97%) of **6** as white crystals: mp 80–82 °C; IR (KBr) 2940, 1445, 1315, 1310, 1165, 1135, 1085, 1040, 880, 720, 680 cm^{-1}; ^1H NMR δ 8.00–7.93 (m, 2H, ArH), 7.70 (m, 1H, ArH), 7.64–7.55 (m, 2H, ArH), 6.10–6.05 (m, 2H, H-1 and H-2), 4.30 (m, 1H, H-4), 2.35 (ddt, J = 14.7, 7.5, 2.0 Hz, 1H, H-5), 2.17–1.90 (m, 2H, H-6 and H-6′), 1.73 (dddd, J = 14.7, 11.6, 6.9, 0.7 Hz, 1H, H-5); ^{13}C NMR δ 136.4, 135.7, 134.3, 129.2, 129.1, 117.8, 67.8, 59.9, 20.2, 20.1.

Anal. Calcd for $C_{12}H_{12}O_3S$: C, 61.00; H, 5.12. Found: C, 60.82; H, 5.00.

3,4-Epoxy-2-(phenylsulfonyl)butene (7). Prepared according to method A from 2-(phenylsulfonyl)-1,3-butadiene (2) (160 mg, 0.82 mmol) and *m*-CPBA (85%, 2.00 g, 9.80 mmol) in CH_2Cl_2 (50 mL), room temperature, 4 days; yield 127 mg (73%) after flash chromatography (silica gel; EtOAc/hexane = 10/90); mp 44–46 °C; IR (KBr) 3060, 2990, 1445, 1315, 1305, 1180, 1145, 1080, 1020, 960, 915, 850, 800, 750, 685, 620 cm^{-1}; ^1H NMR δ 7.94–7.55 (m, 5H, ArH), 6.41 (s, 1H, H-1), 5.97 (d, J = 1.0 Hz, 1H, H-1), 3.62 (ddd, J = 4.0, 2.5, 1.0 Hz, 1H, H-3), 2.89 (dd, J = 5.8, 4.0 Hz, 1H, H-4), 2.40 (dd, J = 5.8, 2.5 Hz, 1H, H-4); ^{13}C NMR δ 148.3, 139.0, 133.9, 129.4, 128.1, 123.5, 50.2, 48.1.

Anal. Calcd for $C_{10}H_{10}O_3S$: C, 57.13; H, 4.79. Found: C, 57.18; H, 4.90.

3,4-Epoxy-3-(phenylsulfonyl)butene (8). Prepared according to method B from 2-(phenylsulfonyl)-1,3-butadiene (2) (225 mg, 1.15 mmol), H_2O_2 (~30%, 2.0 mL, ~20 mmol), and aqueous 2 M NaOH (1.00 mL, 2.00 mmol) in ether (75 mL) and acetone (30 mL), room temperature, 2 h. (Prior to extraction the ether and acetone were removed in vacuo and CH_2Cl_2 was added); yield 173 mg (71%) after flash chromatography (silica gel; EtOAc/hexane = 10/90): IR (neat) 3050, 2955, 1445, 1320, 1305, 1285, 1170, 1075, 1000, 950, 750, 715, 680, 650 cm^{-1}; ^1H NMR δ 7.92–7.54 (m, 5H, ArH), 6.36 (dd, J = 17.0, 11.0 Hz, 1H, H-2), 5.36 (d, J = 11.0 Hz, 1H, H-1), 5.35 (d, J = 17.0 Hz, 1H, H-1), 3.76 (d, J = 5.9 Hz, 1H, H-4), 2.95 (d, J = 5.9 Hz, 1H, H-4); ^{13}C NMR δ 135.6, 134.3, 129.4, 129.0, 126.4, 122.0, 71.7, 53.9.

Anal. Calcd for $C_{10}H_{10}O_3S$: C, 57.13; H, 4.79. Found: C, 56.91; H, 4.67.

Method C (Entries 1 and 4, Table II). 3,4-Epoxy-2-(phenylsulfonyl)cycloheptene (18). To a solution of $PhSeO_2$-Ph (633 mg, 2.12 mmol) and 1,3-cycloheptadiene (13) (200 mg, 2.12 mmol) in dry CH_2Cl_2 (2.1 mL) was added BF_3·OEt_2 (5.0 μL). The reaction mixture was stirred at 20 °C for 16 h. A solution of *m*-CPBA (50–60%, 1.46 g, 4.3 mmol) in CH_2Cl_2 (6.0 mL) was added, and after 15 min of stirring diisopropylamine (298 μl, 2.12 mmol) was added. After another 15 min a solution of *m*-CPBA (50–60%, 1.46 g, 4.3 mmol) in CH_2Cl_2 (2.0 mL) was added, and the reaction mixture was allowed to stir at 20 °C for 4 h. The reaction mixture was then washed with 1 M Na_2CO_3(aq) (10 mL), 50% Na_2SO_3(aq) (2 × 10 mL), 1 M Na_2CO_3(aq) (2 × 10 mL), and brine (10 mL) and finally dried ($MgSO_4$). The crude product was purified by flash chromatography on silica gel (EtOAc/hexane = 30/70) affording 345 mg (65%) of 18: mp 54–56 °C; IR (KBr) 3070, 2938, 2873, 1729, 1650, 1448, 1436, 1305, 1259, 1178, 1151, 1089, 9.71, 937 cm^{-1}; ^1H NMR δ 7.94–7.89 (m, 2H, ArH), 7.67–7.51 (m, 3H, ArH), 7.40 (ddd, J = 7.0, 4.0, 1.3 Hz, 1H, H-1), 3.70 (d, J = 4.0 Hz, 1H, H-3), 3.45 (m, 1H, H-4), 2.55 (m, 1H, H-7), 2.26 (m, 1H, H-7), 2.20–1.98 (m, 2H, H-5 and H-5′), 1.68–1.58 (m, 2H, H-6 and H-6′); ^{13}C NMR δ 146.7, 139.7, 138.6, 133.4, 129.2, 127.9, 59.5, 51.1, 30.6, 28.9, 20.9.

Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.28; H, 5.64. Found: C, 62.54; H, 5.78.

Method D (Entries 2 and 5, Table II). 3,4-Epoxy-3-(phenylsulfonyl)cycloheptene (19). To a solution of $PhSeSO_2$-Ph (317 mg, 1.06 mmol) and 1,3-cycloheptadiene (13) (100 mg, 1.06 mmol) in dry CH_2Cl_2 (1.5 mL) was added BF_3·OEt_2 (2.5 μL). The reaction was stirred at 20 °C for 16 h. The solvents were

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evaporated, and the resulting residue was dissolved in dry THF (1.5 mL). In another bottle *t*-BuOOH (1.37 mL, 4.77 mmol, 3.5 M) was dissolved in dry THF (9.0 mL). The solution was cooled to −78 °C by the use of a dry ice/acetone bath, and *n*-BuLi (2.19 mL, 3.50 mmol, 1.6 M) was added. The temperature was raised to −20 °C, and the first solution was added dropwise. The reaction mixture was stirred at −20 °C for 1.5 h. It was then poured into a mixture of CH_2Cl_2/50% Na_2SO_3 (1/1, 10 mL). The organic phase was collected, and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with 50% Na_2SO_3(aq) (20 mL), 1 M Na_2CO_3(aq) (2 × 20 mL), and brine (20 mL) and finally dried ($MgSO_4$). The crude product was purified by flash chromatography on silica gel (EtOAc/hexane = 20/80) affording 215 mg (81%) of **19**: mp 44–46 °C; IR (KBr) 3070, 3035, 2940, 2873, 1655, 1585, 1448, 1421, 1323, 1308, 1180, 1160, 1145, 1090 cm^{-1}; ^{1}H NMR δ 7.97–7.91 (m, 2H, ArH), 7.70 (m, 1H, ArH), 7.64–7.54 (m, 2H, ArH), 6.11 (m, 1H, H-1), 5.66 (dm, J = 11.5 Hz, 1H, H-2), 4.13 (m, 1H, H-4), 2.31–2.16 (m, 3H, H-7, H-7′ and H-5), 1.92 (m, 1H, H-5), 1.68–1.55 (m, 2H, H-6 and H-6′); ^{13}C NMR δ 141.2, 136.0, 134.2, 129.4, 129.1, 117.6, 73.0, 61.9, 29.3, 27.9, 20.3.

Method E. 3,4-Epoxy-3-(phenylsulfonyl)cycloheptene (19). To a solution of $PhSeSO_2Ph$ (0.15 mg, 0.50 mmol) and 1,3-cycloheptadiene (**13**) (0.64 mg, 0.65 mmol) in CH_2Cl_2 (10 mL) was added BF_3·OEt_2 (6.4 μL) and it was stirred at 20 °C for 16 h. The solvents were evaporated under reduced pressure, and the resulting residue was dissolved in MeOH (20 mL). To this solution was added H_2O_2 (~30%, 1.2 mL, 1.2 mmol) and NaOH (2 M, 1 mL, 2 mmol), and the reaction mixture was stirred for another 18 h at 20 °C. Then, the solvents were evaporated, and to the resulting residue a mixture of CH_2Cl_2/H_2O (1/1, 10 mL) was added. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with H_2O (10 mL) and dried ($MgSO_4$) and concentrated in vacuo affording 112 mg (90%) of pure compound **19**. Physical and spectral (IR, ^{1}H and ^{13}C NMR) data were identical as described above for **19**.

3,4-Epoxy-2-(phenylsulfonyl)cyclohexene (5). Prepared according to method C from 1,3-cyclohexadiene (**14**) (170 mg, 2.12 mmol). For the oxidation step the reaction mixture was stirred at 20 °C for 2 h. The crude product was purified by flash chromatography on silica gel (EtOAc/hexane = 30/70) affording 270 mg (54%) of **5**. Physical and spectral data (IR, mp, ^{1}H and ^{13}C NMR) were identical as described above for **5**.

3,4-Epoxy-3-(phenylsulfonyl)cyclohexene (6). Prepared according to method D from 1,3-cyclohexadiene (**14**) (85 mg, 1.06 mmol). For the oxidation step the reaction mixture was stirred at −20 °C for 1.5 h. The crude product was purified by flash chromatography on silica gel (EtOAc/hexane = 25/75) affording 200 mg (80%) of **6**. Physical and spectral data (IR, mp, ^{1}H and ^{13}C NMR) were identical as described above for **6**.

3,4-Epoxy-3-(phenylsulfonyl)cyclohexene (6). Prepared according to method E from 1,3-cyclohexadiene (**14**) (53.1 mg, 0.65 mmol). For the oxidation step the reaction mixture was stirred at 0 °C for 2 days. The crude product was purified by flash chromatography on silica gel (EtOAc/hexane = 25/75) affording 98 mg (83%) of **6**. Physical and spectral (IR, mp, ^{1}H and ^{13}C NMR) data were identical as described above for **6**.

3,4-Epoxy-2-(phenylsulfonyl)pentene (9). Method C was employed. To a solution of $PhSeSO_2Ph$ (633 mg, 2.12 mmol) and 1,3-pentadiene (**15**) (144 mg, 2.12 mmol) in dry CH_2Cl_2 (10.6 mL) was added BF_3·OEt_2 (30 μL). The reaction mixture was stirred at 20 °C for 16 h. A solution of *m*-CPBA (50–60%, 2.92 g, 8.5 mmol) in CH_2Cl_2 (11.5 mL) was added. The reaction mixture was stirred at 20 °C for 2 days. The reaction mixture was then washed with 1 M Na_2CO_3(aq) (15 mL), 50% Na_2SO_3(aq) (2 × 15 ml), 1 M Na_2CO_3(aq) (2 × 15 mL), and brine (15 mL) and finally dried ($MgSO_4$). The crude product was purified by flash chromatography on silica gel (EtOAc/hexane = 20/80) affording 268 mg (54%) of **9**: mp 57–59 °C; IR (neat) 3050, 2960, 2915, 1445, 1315, 1305, 1180, 1145, 1080, 1030, 850, 770, 750, 685 cm^{-1}; ^{1}H NMR δ 7.94–7.87 (m, 2H, ArH), 7.67 (m, 1H, ArH), 7.63–7.54 (m, 2H, ArH), 6.36 (s, 1H, H-1), 5.92 (d, J = 1.1 Hz, 1H, H-1), 3.34 (br. s, 1H, H-3), 2.53 (dq, J = 5.2, 2.0 Hz, 1H, H-4), 1.23 (d, J = 5.2 Hz, 3H, CH_3); ^{13}C NMR δ 148.3, 139.1, 133.9, 129.3, 128.1, 122.7, 58.7, 54.6, 17.3.

Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 58.74; H, 5.42.

4,5-Epoxy-4-(phenylsulfonyl)pent-2-ene (10). Method D was employed. To a solution of $PhSeSO_2Ph$ (316 mg, 1.06 mmol) and 1,3-pentadiene (**15**) (72 mg, 1.06 mmol) in dry CH_2Cl_2 (7.3 mL) was added BF_3·OEt_2 (15 μL). The reaction mixture was stirred at 20 °C for 16 h. The solvents were evaporated, and the resulting residue was dissolved in dry THF (7.3 mL). In another bottle *t*-BuOOH (1.36 mL, 4.77 mmol, 3.5 M) was dissolved in dry THF (9.0 mL). The solution was cooled to −78 °C by the use of a dry ice/acetone bath, and *n*-BuLi (2.19 mL, 3.50 mmol, 1.6 M) was added. The temperature was raised to −55 °C, and the first solution was added dropwise. The reaction mixture was stirred at −55 °C for 2.5 h. It was then poured into a mixture of CH_2Cl_2/50% Na_2SO_3(aq) (1/1, 10 mL). The organic phase was collected, and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were then washed with 50% Na_2SO_3(aq) (20 mL), 1 M Na_2CO_3(aq) (2 × 20 mL), and brine (20 mL) and finally dried ($MgSO_4$). The crude product was purified by flash chromatography on silica gel (EtOAc/hexane = 10/90) affording 143 mg (60%) of **10**: mp 59–60 °C; IR (neat) 3055, 2960, 2905, 1445, 1325, 1310, 1170, 1130, 1075, 965, 725, 685 cm^{-1}; ^{1}H NMR δ 7.90–7.83 (m, 2H, ArH), 7.68 (m, 1H, ArH), 7.60–7.51 (m, 2H, ArH), 5.93 (dq, J = 15.4, 1.5 Hz, 1H, H-3), 5.78 (dq, J = 15.4, 6.5 Hz, 1H, H-2), 3.66 (d, J = 5.8 Hz, 1H, H-5), 2.93 (d, J = 5.8 Hz, 1H, H-5), 1.66 (dd, J = 6.5, 1.5 Hz, 3H, CH_3); ^{13}C NMR δ 135.7, 134.8, 134.2, 129.4, 128.9, 118.9, 71.6, 53.1, 17.8.

Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39. Found: C, 58.75; H, 5.29.

4,5-Epoxy-4-(phenylsulfonyl)pent-2-ene (10). Prepared according to method E from 1,3-pentadiene (**15**) (46 mg, 0.65 mmol). For the oxidation step, the solvent was changed from MeOH to acetone, and the reaction mixture was stirred at 20 °C for 4 h. The crude product was purified by flash chromatography on silica gel (EtOAc/hexane = 20/80) affording 26 mg (23%) of **10**. Physical and spectral (IR, mp, ^{1}H and ^{13}C NMR) were identical as described above for **10**.

3,4-Epoxy-4-methyl-2-(phenylsulfonyl)pentene (11). Prepared according to method C (cf. **18**). To a solution of $PhSeSO_2$-Ph (633 mg, 2.12 mmol) and 4-methyl-1,3-pentadiene (**16**) (174 mg, 2.12 mmol) in dry CH_2Cl_2 (2.12 mL) was added BF_3·OEt_2 (30 μL). The reaction mixture was stirred at 20 °C for 16 h. A solution of *m*-CPBA (50–60%, 2.92 g, 8.5 mmol) in CH_2Cl_2 (6.0 mL) was added. The reaction mixture was stirred at 20 °C for 12 h. The reaction mixture was then washed with 1 M Na_2CO_3(aq) (10 mL), 50% Na_2SO_3(aq) (2 × 10 mL), 1 M Na_2CO_3(aq) (2 × 10 mL), and brine (10 mL) and finally dried ($MgSO_4$). The crude product was filtered through a plug of neutral alumina affording 385 mg (78%) of **11**: mp 73–75 °C; IR (KBr) 3100, 2995, 2960, 2920, 1580, 1445, 1390, 1380, 1320, 1305, 1255, 1185, 1140, 1080, 995, 970, 915, 805, 770, 760, 725, 695, 690, 620 cm^{-1}; ^{1}H NMR δ 7.93–7.87 (m, 2H, ArH), 7.68 (m, 1H, ArH), 7.62–7.54 (m, 2H, ArH), 6.48 (d, J = 0.56 Hz, 1H, H-1), 5.83 (d, J = 1.5 Hz, 1H, H-1), 3.58 (br.s, 1H, H-3), 1.25 (s, 3H, CH_3), 0.56 (s, 3H, CH_3); ^{13}C NMR δ 146.4, 138.6, 133.9, 129.2, 128.2, 123.9, 61.9, 60.0, 23.5, 16.4.

4,5-Epoxy-2-methyl-4-(phenylsulfonyl)pent-2-ene (12). Prepared according to method D (cf. **19**) from 4-methyl-1,3-pentadiene (**16**) (88 mg, 1.06 mmol). For the oxidation step the reaction mixture was stirred at 20 °C for 2 h. The crude product was purified by flash chromatography on silica gel (EtOAc/hexane = 10/90) affording 151 mg (61%) of **12**: IR (neat) 3055, 2965, 2905, 1445, 1315, 1305, 1165, 1155, 1125, 1080, 730, 685 cm^{-1}; ^{1}H NMR δ 7.92–7.85 (m, 2H, ArH), 7.69 (m, 1H, ArH), 7.61–7.57 (m, 2H, ArH), 5.37 (br s, 1H, H-3), 3.67 (d, J = 5.6 Hz, 1H, H-1), 2.98 (d, J = 5.6 Hz, 1H, H-1), 1.73 (d, J = 1.3 Hz, 3H, CH_3), 1.48 (d, J = 1.1 Hz, 3H, CH_3); ^{13}C NMR δ 147.5, 135.9, 134.1, 129.6, 128.9, 112.3, 70.3, 51.2, 25.7, 19.5.

Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.48, H; 5.92. Found: C, 60.02; H, 5.77.

3,4-Epoxy-2-(phenylsulfonyl)tetradecene (20). Prepared according to method C (cf. **9**) from 1,3-tetradecadiene (**17**) (2.12 mmol). For the oxidation step the reaction mixture was stirred at 20 °C for 2 days. The crude product was purified by flash chromatography on silica gel (EtOAc/hexane = 10/90) affording 455 mg (61%) of **20**: IR (KBr) 2928, 2856, 1600, 1467, 1448, 1318, 1308, 1184, 1142, 1082, 960 cm^{-1}; ^{1}H NMR δ 7.93–7.87 (m, 2H,

ArH), 7.66 (m, 1H, ArH), 7.61–7.55 (m, 2H, ArH), 6.36 (s, 1H, H-1), 5.93 (d, J = 1.0 Hz, 1H, H-1), 3.36 (m, 1H, H-3), 2.50 (dt, J = 5.0, 2.0 Hz, 1H, H-4), 1.49–1.39 (m, 2H, H-5 and H-5′), 1.33–1.17 (m, 16H, the remaining hydrogens), 0.89 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR δ 148.3, 139.2, 133.8, 129.3, 128.1, 122.8, 62.9, 53.7, 31.9, 31.7, 29.6, 29.5, 29.4, 29.3, 29.2, 25.4, 22.7, 14.1.

Anal. Calcd for $C_{20}H_{30}O_3S$: C, 68.53; H, 8.63. Found: C, 68.34; H, 8.47.

1,2-Epoxy-2-(phenylsulfonyl)tetradec-3-ene (21). Prepared according to method D (cf. 10) from 1,3-tetradecadiene (17) (1.06 mmol). For the oxidation step the reaction mixture was stirred at −55 °C for 5.5 h. The crude product was purified by flash chromatography on silica gel (EtOAc/hexane = 5/95) affording 249 mg (67%) of 21: IR (KBr) 2928, 2855, 1602, 1475, 1448, 1438, 1322, 1168, 1077, 1021, 970; ^1H NMR δ 7.90–7.84 (m, 2H, ArH), 7.66 (m, 1H, ArH), 7.58–7.50 (m, 2H, ArH), 5.91 (dt, J = 15.5, 1.2 Hz, 1H, H-3), 5.74 (dt, J = 15.5, 6.8 Hz, 1H, H-4), 3.69 (d, J = 6.0 Hz, 1H, H-1), 2.91 (d, J = 6.0 Hz, 1H, H-1), 2.03–1.93 (m, 2H, H-5 and H-5′), 1.35–1.07 (m, 16H, the remaining hydrogens), 0.88 (t, J = 7.0 Hz, 3H, H-14); ^{13}C NMR δ 139.7, 135.7, 134.0, 129.3, 128.7, 117.6, 71.5, 53.1, 31.9, 31.7, 29.5, 29.4, 29.2, 29.2, 28.8, 28.2, 22.6, 14.0.

Anal. Calcd for $C_{20}H_{30}O_3S$: C, 68.53; H, 8.63. Found: C, 68.60; H, 8.66.

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Supplementary Material Available: NMR spectra of 11 and 19 (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.