# Synthesis of α-Methylene-β-hydroperoxy Sulfoxides by Regioselective Photooxygenation (Schenck Reaction) of Racemic Vinyl Sulfoxides

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The β-hydroperoxy vinyl sulfoxides **3** were synthesized in good to excellent yields by regioselective photooxygenation of racemic vinyl sulfoxides **2**. Moderate diastereoselectivities were observed in the ene reaction of singlet oxygen (Schenck Reaction) with the *E*- or *Z*-vinyl sulfoxides **2e**. Titanium-catalyzed oxygen transfer reaction of these sulfoxy-functionalized racemic allylic hydroperoxides **3** resulted chemoselectively in the corresponding sulfones **5**.

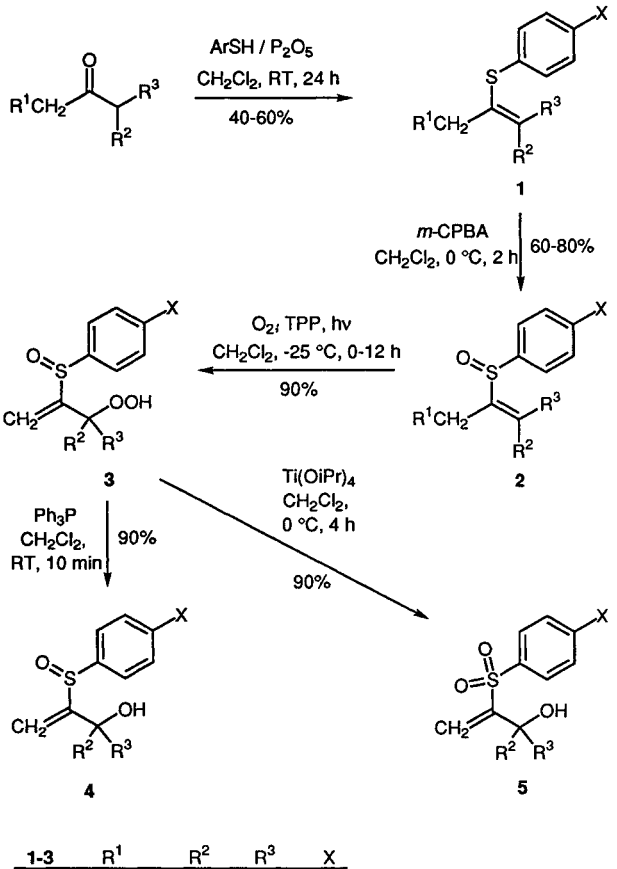
Hydroperoxides are versatile oxidants for the oxyfunctionalization of organic substrates.[1] Allylic hydroperoxides, which were employed successfully for the metal-catalyzed diastereo- and enantioselective hydroxy-epoxidations,[2] are readily available by the photooxygenation of alkenes.[3] Numerous functionalized allylic hydroperoxides are also accessible by this method.[4] However, apparently the sulfoxy-functionalized allylic hydroperoxides[5] are not known, which could serve as reactive intermediates in organic synthesis. These multifunctional hydroperoxides may be reduced to the corresponding alcohol, the latter have proved to be useful dienophiles in Diels–Alder reactions[6] and Michael-type additions.[7] Alternative approaches[8] to the synthesis of β-hydroxy vinyl sulfoxide involve the addition of the corresponding aldehydes to the α-anion derived from phenyl vinyl sulfoxides. The transition metal catalyzed chemoselective oxygen-transfer reaction of these hydroperoxides will lead to the corresponding α-methylene-β-hydroxy sulfones. The β-hydroxy sulfoxides and sulfones can be transformed to the corresponding dienes[9] for applications in Diels–Alder reactions.[10]

Here we report on the synthesis of α-methylene-β-hydroperoxy sulfoxides **3** by the regioselective photooxygenation of racemic vinyl sulfoxides **2** and their chemical transformations. The hitherto unknown hydroperoxy sulfoxides **3** were obtained in very good yield and were fully characterized.

Vinyl sulfides **1a–h** were prepared readily by the condensation of corresponding ketones with properly substituted thiophenols under acidic conditions[11] (Scheme). This convenient and general condensation yielded quantitatively the vinyl sulfides **1** when α-disubstituted ketones were used. However, diethyl ketone and cyclohexanone gave lower yields, for which thioketal formation was the major product. The vinyl sulfides **1** were oxidized selectively to the racemic sulfoxides **2** by *m*-chloroperoxybenzoic acid (Scheme).

The *E,Z*-diastereomers of the sulfoxide **2e** were separated by flash chromatography and the stereochemical assignment was made by NOE experiments (Scheme). Thus, the *Z*-isomer showed a NOE effect between the α- and β-methyl signals, while the *E*-isomer did not.

Photooxygenation of vinyl sulfoxides **2** was carried out in chloroform in the presence of tetraphenylporphine as sensitizer (Scheme). Rose Bengal was used as sensitizer




| 1-3 | $R^1$ | $R^2$ | $R^3$ | X |
|---|---|---|---|---|
| a | H | Me | Me | H |
| b | H | Me | Me | Me |
| c | H | Me | Me | $NO_2$ |
| d | H | Me | Me | F |
| e | H | Me | Et | H |
| f | Me | H | Me | H |
| g | -$(CH_2)_3$- | | H | H |
| h | -$(CH_2)_3$- | | Me | H |

**Scheme**

when the photooxygenation was carried out in methanol. The α-methylene-β-hydroperoxy sulfoxides **3** were obtained regioselectively as the only product from the sulfoxides **2a–e** (Table 1), while the derivatives **2f–h** were inert towards the ene reaction. For none of the substrates was any sulfone observed nor dioxetane products. The hydroperoxides **3a–e** were readily purified by low temperature (0 °C) silica gel chromatography. Although these hydroperoxides were fairly stable at room temperature, they slowly decomposed on prolonged standing, but could be stored in the refrigerator (ca. 5 °C).

The results in Table 1 (entries 1–6) reveal that the ene reactivity of vinyl sulfoxide **2** decreases with electron-withdrawing substituents on the phenyl ring in the order **2b** (Me) > **2a**(H) > )**2c** ($NO_2$) > **2d** (F), which is in ac-

**Table 1.** Product Studies of the Photooxygenation of the Vinyl Sulfoxides **2**

| Entry | Substrate **2** | Solvent | Sensitizer[a] | Time[b] (h) | Product **3** | Yield[c] (%) |
|---|---|---|---|---|---|---|
| 1 | **2a** | $CDCl_3$ | TPP | 4 | **3a** | 90 |
| 2 | **2a** | $CD_3OD$ | RB | 4 | **3a** | >95[d] |
| 3 | **2b** | $CDCl_3$ | TPP | 2 | **3b** | 92 |
| 4 | **2b** | $CD_3OD$ | RB | 2 | **3b** | >95[d] |
| 5 | **2c** | $CDCl_3$ | TPP | 12 | **3c** | 91 |
| 6 | **2d** | $CDCl_3$ | TPP | 20[e] | **3d** | 78 |
| 7 | (*Z*)-**2e** | $CDCl_3$ | TPP | 20[e] | **3e**[f] | 95[d] |
| 8 | (*E*)-**2e** | $CDCl_3$ | TPP | 20[e] | **3e**[g] | 95[d] |

[a] TPP = tetraphenylporphine, RB = Rose Bengal.
[b] conversion > 90%.
[c] Isolated material after silica gel chromatography.
[d] Determined by $^1H$ NMR analysis.
[e] Two 400-W sodium lamps were used.
[f] Diastereomeric ratio (d.r.) 70 : 30, determined by $^1H$ NMR analysis.
[g] Conversion 40%, d.r. 20 : 80.

cord with the usual electronic effects on singlet oxygen ene reaction, however, for all the cases the same regioselectivity applies. Furthermore, the regioselectivity of the vinyl sulfoxides **2a** and **2b** showed no solvent dependence since the same regioisomer was obtained irrespective of whether methanol or chloroform was used in the photooxygenation (Table 1, entries 2 and 4). This behavior of the vinyl sulfoxides is contrary to that of α,β-unsaturated esters, which show substantial dependence of their regioselectivity with respect to solvent polarity.[12]

To test the π-facial diastereoselectivity exercised by the racemic sulfoxide, the *Z,E*-**2e** isomers were photooxygenated. The pure (*Z*)-**2e** gave a 70:30 and the pure (*E*)-**2e** a 20:80 diastereomeric mixture of hydroperoxides **3e**. This moderate selectivity implies that irrespective of the (*E*)- or (*Z*)-**2e** sulfoxide configurations, the singlet oxygen preferentially approaches the double bond from the same side. The configuration of the diastereomer of hydroperoxide **3e** was assigned by comparing the NMR data of the corresponding alcohol **4e**, which was obtained by reduction of **3e** with triphenylphosphine, with that of the structurally similar literature-known 3-(phenylsulfinyl)but-3-en-2-ol.[13] Accordingly, the major diastereomer obtained from (*E*)-**2e** was assigned the (*R,R* – *S,S*)- and from (*Z*)-**2e** the (*R,S* – *S,R*)-configuration.

Also the titanium isopropoxide catalyzed oxygen-transfer reaction of the hydroperoxy sulfoxides **3b** and **3c** was investigated, whereby it was observed that the vinyl sulfone **4** was formed chemoselectively, irrespective of whether the phenyl ring is substituted with an electron-donating (**3b**, X = Me) or electron-accepting substituent (**3c**, X = $NO_2$). Instead of epoxidation, sulfur oxidation was observed exclusively in this metal-catalyzed oxygen-transfer reaction. Earlier we have shown that such oxygen transfer in silyl[14] or stannyl[15] containing hydroperoxides gave diastereoselectively the corresponding hydroxy epoxides.

In summary, we have shown that the α-methylene-β-hydroperoxy sulfoxides **3** can be obtained in good yields by regioselective photooxygenation of vinyl sulfoxides **2**. The high regioselectivities, irrespective of the substitution on the phenyl ring, are advantageous for synthetic purposes. It was also observed that the metal-catalyzed oxygen transfer with hydroperoxide **3** resulted exclusively in the sulfone **4** instead of the desired epoxy sulfoxide. The now readily accessible β-hydroxy vinyl sulfoxides or sulfones, which can be obtained by reduction or titanium-catalyzed oxygen-transfer reaction of hydroperoxide **3**, should serve as useful dienophiles in Diels–Alder reactions.

Melting points were determined on a Büchi 535 apparatus. Solvents were purified according to standard literature procedures. TLC was performed on Polygram Sil G UV (4080 mm), Macherey & Nagel. Silica gel (32–64 μm) from Woelm was used for flash chromatography. Elemental analyses were carried out by the Analytical Division of the Institute of Inorganic Chemistry, University of Würzburg. IR spectra were recorded on a Perkin-Elmer Model 1420 spectrometer and the $^1H$ and $^{13}C$ NMR spectra on a Bruker AC 200 or AC 250 spectrometer. Chemical shifts refer to $CDCl_3$. Petroleum ether used had bp 30–50 °C.

**Vinyl Sulfides 1; General Procedure:**
According to the literature procedure,[11] to a stirred solution of the ketone and equimolar amounts of thiophenol in $CH_2Cl_2$ (100 mL) was added solid $P_2O_5$ (2 equiv). The mixture was stirred at r.t. for 20 h, the organic phase decanted, the residue washed with $CH_2Cl_2$ (50 mL), and the combined organic layers were washed with aq NaOH (10%, 50 mL), followed by brine (50 mL). The organic layer was dried ($MgSO_4$), concentrated (50 °C/20 Torr) and the residue was purified by silica gel chromatography with petroleum ether as eluent to obtain the corresponding vinyl sulfides. The literature known 3-methyl-2-(phenylthio)but-2-ene[11] (**1a**) (yield, 42%), (*E,Z*)-3-(phenylthio)pent-2-ene[16] (**1f**) (yield, 20%), 1-(phenylthio)cyclohex-1-ene (**1g**) (yield, 40%) and 2-methyl-1-(phenylthio)cyclohexane[17] (**1h**) (yield, 70%) were also prepared by this procedure. The spectral data for all new compounds are presented in Table 2.

**Racemic Vinyl Sulfoxides 2; General Procedure:**
According to the literature procedure,[5] to a solution of the appropriate vinyl sulfide **1** (3–10 mmol) in $CH_2Cl_2$ (30 mL) was added dropwise *m*-chloroperbenzoic acid (*m*-CPBA, 3–10 mmol) in $CH_2Cl_2$ (10–20 mL) at 0 °C. After stirring at 0 °C for 30 min, the mixture was left stirring at r.t. for an additional hour and poured onto 10% aq $NaHCO_3$ (20 mL). The organic layer was washed with brine (20 mL) and dried ($MgSO_4$). The solvent was removed (50 °C/20 Torr) and the residue was purified by silica gel chromatography with 1:4 mixture of EtOAc and petroleum ether as eluent. The literature known (*R,S*)-3-methyl-2-(phenylsulfinyl)but-2-ene[5] (**2a**) (yield, 66%) and (*R,S*)-1-(phenylsulfinyl)cyclohex-1-ene[18] (**2g**) were also obtained by this procedure. Spectral data for the sulfoxides **2** are presented in Table 2.

**Photooxygenation of Racemic Vinyl Sulfoxides 2; General Procedure:**
A solution of the appropriate vinyl sulfoxide **2** and tetraphenylporphine (2 mg) in $CH_2Cl_2$ (5 mL) was photooxygenated by passing throug the solution cautiously a slow stream of dry oxygen gas at – 25 °C while irradiating externally with two OSRAM Violax NAV-E (150 W) sodium lamps. The reaction progress was monitored by $^1H$ NMR spectroscopy until complete conversion of the vinyl sulfoxide. The solvent was removed by rotoevaporation (0 °C at 20 Torr) and the remaining oily product was purified by silica gel chromatography at 0 °C with a 1:3 mixture of $Et_2O$ and petroleum ether as eluent. The spectral data of the β-hydroperoxy vinyl sulfoxides **3** are given in Table 2.

**(*R,R* – *S,S*) and (*R,S* – *S,R*)-3-Methyl-4-(phenylsulfinyl)pent-4-en-3-ol (4e):**
To the diastereomeric mixture (43:57) of hydroperoxide **3e** (20.0 mg, 0.083 mmol) in $CH_2Cl_2$ (2 mL) was added $Ph_3P$ (21.0 mg,

**Table 2.** Spectral Data for Compounds **1**–**3**[a]

| Product[b] | Yield (%) | mp[c] (°C) | IR (neat)[d] $\nu$ ($cm^{-1}$) | $^1H$ NMR ($CDCl_3$) $\delta$, $J$ (Hz) | $^{13}C$ NMR ($CDCl_3$) $\delta$ |
|---|---|---|---|---|---|
| **1b** | 60 | oil | 2980, 2935, 2860, 1465, 1420, 1350, 1100, 1060, 790 | 1.84 (s, 3H), 1.89 (s, 3H), 1.96 (s, 3H), 2.23 (s, 3H), 6.95–7.14 (m, 4H) | 20.7 (q), 21.2 (q), 21.6 (q), 23.3 (q), 121.4 (s), 129.2 (d), 129.8 (d), 133.3 (s), 135.5 (s), 138.2 (s) |
| **1c** | 60 | 72–74 | 2905, 1570, 1510, 1470, 1370, 1320, 1175, 1085, 955 | 1.91 (s, 3H), 1.96 (s, 3H), 2.04 (s, 3H), 7.24 (d, $J$ = 8.5, 2H), 8.19 (d, $J$ = 8.5, 2H) | 21.4 (q), 21.7 (q), 23.6 (q), 124.2 (d), 126.3 (d), 134.8 (s), 144.5 (s), 145.0 (s), 148.1 (s) |
| **1d** | 45 | oil | 2960, 2880, 2820, 1570, 1470, 1360, 1210, 1140, 1120, 1070, 1010, 810, 620 | 1.86 (s, 3H), 1.90 (s, 3H), 2.02 (s, 3H), 6.85–7.20 (m, 4H) | 20.6 (q), 21.5 (q), 23.3 (q), 115.8 (d), 116.2 (d), 130.9 (d), 131.0 (d), 131.9 (s), 138.7 (s), 159.6 (s), 163.5 (s) |
| **1e**[e] | 60 | oil | 3010, 2910, 2890, 2820, 1560, 1450, 1420, 1350, 1010, 730, 680 | minor isomer: 1.20 (t, $J$ = 6.5, 3H), 1.95 (s, 3H), 2.02 (s, 3H), 2.23 (q, $J$ = 6.5, 2H), 7.40–7.60 (m, 5H); major isomer: 1.02 (t, $J$ = 7.0, 3H), 1.80 (s, 3H), 1.93 (s, 3H), 2.48 (m, 2H), 7.40–7.60 (m, 5H) | 12.7 (q), 13.3 (q), 19.1 (q), 20.4 (q), 20.9 (q, 2C), 28.5 (t), 30.2 (t), 120.2 (s), 120.6 (s), 125.4 (d, 2C), 128.4 (d), 128.5 (d), 129.0 (d, 2C), 137.1 (s), 137.2 (s), 145.3 (s), 145.4 (s) |
| **2b** | 55 | 85–87 | 3010, 2960, 2900, 1610, 1470, 1440, 1350, 1060, 1015, 790 | 1.71 (br s, 3H), 1.92 (br s, 3H), 2.30 (br s, 3H), 2.47 (s, 3H), 7.33–7.48 (m, 4H) | 8.3 (q), 21.5 (q), 21.6 (q), 22.2 (q), 124.3 (d), 129.8 (d), 135.0 (s), 140.4 (s), 140.5 (s), 141.8 (s) |
| **2c** | 60 | 150–153 | 3080, 3020, 2880, 1620, 1580, 1550, 1500, 1330, 1090, 1060, 1030, 990 | 1.51 (s, 3H), 1.89 (s, 3H), 2.29 (s, 3H), 7.64 (d, $J$ = 8.5, 2H), 8.35 (d, $J$ = 8.5, 2H) | 8.6 (q), 22.0 (q), 22.4 (q), 124.2 (d), 125.6 (d), 134.2 (s), 144.2 (s), 149.2 (s), 151.8 (s) |
| **2d** | 50 | oil | 2980, 2900, 2840, 1590, 1500, 1370, 1240, 1150, 1090, 1060, 850 | 1.57 (br s, 3H), 1.86 (br s, 3H), 2.19 (br s, 3H), 7.11–7.45 (m, 4H) | 8.2 (q), 21.6 (q), 22.2 (q), 116.2 (d), 116.5 (d), 126.3 (d), 126.5 (d), 134.8 (s), 139.1 (s), 162.0 (s), 165.9 (s) |
| **2e** | 68 | oil | 3010, 2920, 2900, 2820, 1610, 1560, 1450, 1420, 1350, 1280, 1170, 1030 | *E*-isomer: 1.03 (t, $J$ = 7.5, 3H), 1.62 (s, 3H), 2.15 (q, $J$ = 7.5, 2H), 2.22 (s, 3H), 7.39–7.54 (m, 5H); *Z*-isomer: 1.22 (t, $J$ = 7.5, 3H), 1.62 (s, 3H), 1.84 (s, 3H), 2.67–2.74 (m, 2H), 7.39–7.54 (m, 5H) | *Z*-isomer: 8.6 (q), 13.6 (q), 19.5 (q), 28.1 (t), 28.9 (t), 124.4 (d), 129.0 (d), 130.1 (d), 134.2 (s), 143.5 (s), 148.2 (s); *E*-isomer: 7.7 (q), 11.7 (q), 19.2 (q), 28.9 (t), 124.2 (d), 129.0 (d), 130.1 (d), 134.6 (s), 143.7 (s), 147.2 (s) |
| **2f**[f] | 64 | oil | 3010, 2940, 2900, 2840, 1550, 1450, 1430, 1355, 1070, 1030, 830 | major isomer: 0.88 (t, $J$ = 7.4, 3H), 2.09 (m, 2H), 2.14 (dd, $J$ = 1.5 and 5.6, 3H), 6.03 (q, $J$ = 7.4, 1H), 7.44–7.58 (m, 5H); minor isomer: 0.65 (t, $J$ = 7.3, 3H), 1.89 (d, $J$ = 7.2, 3H), 2.40 (m, 2H), 6.51 (q, $J$ = 7.3, 1H), 7.44–7.58 (m, 5H) | 12.8 (q), 14.0 (q), 14.1 (q), 15.2 (q), 17.6 (t), 18.5 (t), 124.3 (d, 2C), 125.4 (d), 129.3 (d, 2C), 130.4 (d), 131.1 (d), 131.3 (d), 143.7 (s, 2C), 147.5 (s, 2C) |
| **2h** | 60 | oil | 3040, 2950, 2845, 1630, 1570, 1470, 1440, 1370, 1090, 1050 | 1.35–1.59 (m, 4H), 2.11 (m, 5H, $CH_3$ and $CH_2$), 2.37 (br d, 2H), 7.31–7.47 (m, 5H) | 18.5 (t), 20.6 (q), 22.2 (t), 22.4 (t), 33.2 (t), 124.3 (d, 2C), 129.0 (d), 129.3 (d), 130.0 (d), 136.8 (s), 143.4 (s), 144.0 (s) |
| **3a** | 90 | 83–84 | 3400–3040, 2965, 2800, 1430, 1150, 1065, 1025, 935 | 1.07 (s, 3H), 1.51 (s, 3H), 5.84 (d, $J$ = 1.5, 1H), 5.94 (d, $J$ = 1.5, 1H), 7.47–7.73 (m, 5H), 10.59 (s, 1H) | 26.5 (q), 26.7 (q), 84.8 (s), 123.9 (t), 125.6 (d), 129.0 (d), 131.5 (d), 140.0 (s), 160.3 (s) |
| **3b** | 92 | 90–92 | 3350–3000, 2945, 2895, 1430, 1150, 1070, 1020, 930 | 1.11 (s, 3H), 1.49 (s, 3H), 2.41 (s, 3H), 5.81 (d, $J$ = 1.5, 1H), 5.91 (d, $J$ = 1.5, 1H), 7.32 (d, $J$ = 8.2, 2H), 7.58 (d, $J$ = 8.2, 2H), 10.36 (s, 1H) | 26.5 (q), 26.8 (q), 30.2 (q), 84.9 (s), 123.6 (t), 124.0 (d), 130.0 (d), 136.6 (s), 142.1 (s), 160.4 (s) |
| **3c** | 91 | 109–110 | 3300–3000, 2945, 2895, 1520, 1325, 1150, 1065, 1030, 845 | 1.06 (s, 3H), 1.51 (s, 3H), 5.95 (d, $J$ = 1.5, 1H), 6.12 (d, $J$ = 1.5, 1H), 7.93 (d, $J$ = 8.5, 2H), 8.35 (d, $J$ = 8.5, 2H), 10.40 (s, 1H) | 26.8 (q), 27.2 (q), 85.2 (s), 124.1 (t), 125.4 (d), 125.5 (d), 126.8 (s), 159.8 (s) |
| **3d** | 78 | 91–92 | 3300–3000, 2960, 2895, 2805, 1570, 1470, 1215, 1140, 1070, 1020 | 1.10 (s, 3H), 1.42 (s, 3H), 5.85 (d, $J$ = 1.6, 1H), 6.00 (d, $J$ = 1.6, 1H), 7.16–7.73 (m, 4H), 10.71 (s, 1H) | 26.5 (q), 26.6 (q), 84.5 (s), 116.1 (d), 116.6 (d), 122.9 (t), 128.0 (d), 128.1 (d), 159.9 (s), 161.8 (s), 166.6 (s) |
| **3e** | 85 | oil | 3400–3040, 2920, 2905, 2860, 1430, 1145, 1100, 1075, 1030, 930 | (*R*,*R*-*S*,*S*)-isomer: 0.69 (t, $J$ = 7.4, 3H), 1.41 (s, 3H), 1.64 (m, 2H), 5.78 (d, $J$ = 1.4, 1H), 6.13 (d, $J$ = 1.4, 1H), 7.46–7.54 (m, 3H), 7.63–7.71 (m, 2H), 10.36 (s, 1H, OOH); (*R*,*S*-*S*,*R*)-isomer: 0.84 (t, $J$ = 7.4, 3H), 1.17 (s, 3H), 1.84 (m, 2H), 5.72 (t, $J$ = 1.5, 2H), 7.46–7.54 (m, 3H), 7.63–7.71 (m, 2H), 10.51 (s, 1H) | (*R*,*R*-*S*,*S*)-isomer: 8.0 (q), 23.2 (q), 30.4 (t), 87.9 (s), 125.1 (t), 125.7 (d), 128.9 (d), 131.4 (d), 140.0 (s), 158.4 (s); (*R*,*S*-*S*,*R*)-isomer: 7.4 (q), 22.2 (q), 30.3 (t), 87.5 (s), 123.4 (t), 125.4 (d), 129.0 (d), 131.4 (d), 139.8 (s), 160.0 (s) |

[a] The sulfoxides **2** and the $\beta$-hydroperoxy sulfoxides **3** are racemic.
[b] Satisfactory microanalyses were obtained for all new compounds. The deviation for C, H, N was in the range of $\pm$0.01 to 0.43.
[c] Compound **1c** was recrystallized from cyclohexane, **2b** and **2c** from MeOH and **3**–**5** from a 1 : 4 mixture of $CH_2Cl_2$ and petroleum ether.
[d] Solid samples were recorded in Nujol.
[e] *E*,*Z*-mixture (60 : 40).
[f] *E*,*Z*-mixture (65 : 35).

0.083 mmol) and stirred at r.t. for 10 min. The solvent was evaporated and the crude alcohol **4e** was purified by silica gel chromatography with a 4:1 mixture of petroleum ether and $Et_2O$ to afford a diastereomeric mixture (43:57) of hydroxy sulfoxide **4e** (17.0 mg, 90%) as a colorless oil.

IR (neat): $\nu$ = 3040–3600, 2940, 2890, 1430, 1360, 1250, 1060, 1010, 900 $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$) (*R,R–S,S*)-**4e**: $\delta$ = 0.79 (t, $J$ = 5.5 Hz, 3H), 1.30 (s, 3H), 1.50–1.80 (m, 2H), 2.70 (br s, 1H), 6.07 (d, $J$ = 1.4 Hz, 1H), 6.15 (d, $J$ = 1.4 Hz, 1H), 7.44–7.60 (m, 3H), 7.64–7.71 (m, 2H); (*R,S – S,R*)-**4e**: $\delta$ = 0.72 (t, $J$ = 5.5 Hz, 3H), 1.21 (s, 3H), 1.50–1.80 (m, 2H), 3.12 (br s, 1H), 5.68 (t, $J$ = 1.4 Hz, 2H), 7.44–7.60 (m, 3H), 7.64–7.71 (m, 2H).

$^{13}C$ NMR (50 MHz, $CDCl_3$) (*R,R – S,S*)-**4e**: $\delta$ = 7.7 (q), 29.1 (q), 35.3 (t), 77.2 (s), 116.0 (t), 125.9 (d), 128.9 (d), 131.0 (d), 144.3 (s), 159.9 (s); (*R,S – S,R*)-**4e**: $\delta$ = 7.7 (q), 29.3 (q), 35.9 (t), 76.5 (s), 115.5 (t), 125.9 (d), 128.9 (d), 131.0 (d), 143.7 (s), 159.9 (s).

| | | | |
|---|---|---|---|
| $C_{12}H_{16}O_2S$ | calc. | C 64.25 | H 7.19 |
| (224.3) | found | 64.04 | 7.15 |

**2-Methyl-3-(*p*-toluylsulfonyl)but-3-en-2-ol (5b):**

To the crude photooxygenate of **3b** (100 mg, 0.500 mmol) were added molecular sieves (1.00 g, 4 Å) and the mixture stirred at 0°C for 10 min. Subsequently, 50 mol% of $Ti(OPr\text{-}i)_4$ was administered and the mixture was stirred for 4 h. The molecular sieves were removed, washed with $Et_2O$ (20 mL), water (1 mL) was added, and stirred for 2 h at 20°C. The mixture was filtered over Celite, dried and concentrated (20°C/20 Torr). The residue was purified by silica gel chromatography with a 4:1 mixture of petroleum ether and $Et_2O$ as eluent to afford 105 mg (89%) of hydroxy sulfone **5b** as a colorless liquid.

IR (neat): $\nu$ = 3550–3100, 2940, 2890, 1580, 1440, 1280, 1140, 1060, 950 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ = 1.46 (s, 6H), 2.42 (s, 3H), 3.20 (br s, 1H), 6.00 (d, $J$ = 1.4 Hz, 1H), 6.28 (d, $J$ = 1.4 Hz, 1H), 7.29 (d, $J$ = 8.5 Hz, 2H), 7.76 (d, $J$ = 8.5 Hz, 2H).

$^{13}C$ NMR ($CDCl_3$, 50 MHz): $\delta$ = 21.8 (q), 30.9 (q), 72.5 (s), 124.7 (t), 128.1 (d), 129.9 (d), 138.3 (s), 144.5 (s), 157.6 (s).

| | | | |
|---|---|---|---|
| $C_{12}H_{16}O_3C$ | calc. | C 59.98 | H 6.71 |
| (240.3) | found | 59.83 | 7.03 |

**2-Methyl-3-(*p*-nitrophenylsulfonyl)but-3-en-2-ol (5c):**

According to the above procedure, from the crude photooxygenate of **3c** (100 mg, 0.400 mmol), 90.0 mg (83%) of hydroxy sulfone **5c** was obtained as yellow needles, mp 127–128°C (recrystallized from a 1:4 mixture of $CH_2Cl_2$ and petroleum ether).

IR ($CCl_4$): $\nu$ = 3600–3400, 2940, 2800, 2615, 1520, 1330, 1295, 1145, 1060, 950 $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 1.48 (s, 6H), 2.80 (br s, 1H), 6.13 (d, $J$ = 1.5 Hz, 1H), 6.52 (d, $J$ = 1.5 Hz, 1H), 8.50 (d, $J$ = 8.5 Hz, 2H), 8.33 (d, $J$ = 8.5 Hz, 2H).

$^{13}C$ NMR (63 MHz, $CDCl_3$): $\delta$ = 22.3 (q), 72.4 (s), 124.1 (t), 126.6 (d), 129.0 (d), 156.4 (s).

| | | | |
|---|---|---|---|
| $C_{11}H_{13}NO_5S$ | calc. | C 48.70 | H 4.83 |
| (271.2) | found | 48.60 | 4.75 |

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