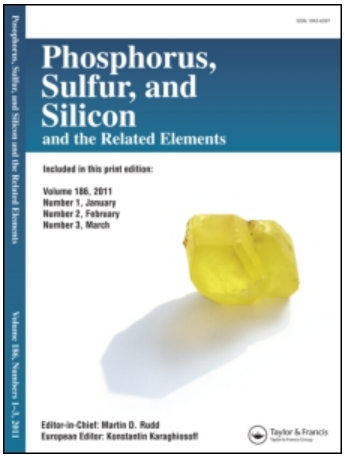

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α-Methylthiobenzylsulfones as Synthetic Intermediates Part VI. Syntheses of some Vinylic Sulfides and Sulfoxides

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α-METHYLTHIOBENZYLSULFONES AS SYNTHETIC INTERMEDIATES PART VI. SYNTHESES OF SOME VINYLIC SULFIDES AND SULFOXIDES

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The syntheses of some *p*-substituted isopropyl α-methylthiobenzylsulfones and their reaction with CCl_4-KOH-t-BuOH to give the corresponding vinyl sulfides, as well as their oxidation to the corresponding sulfoxides, are described. Some aspects of the reactivity of the α-sulfenyl, α-sulfonyl benzylic carbanions are discussed.

Key words: Sulfides, sulfoxides, benzyl sulfones, sulfenylation, rearrangement.

INTRODUCTION

In continuation to our previous studies of the sulfenylation of the ring substituted phenyl benzylsulfones, which showed to be useful intermediates for the synthesis of carbonyl compounds,[1–5] we undertook the sulfenylation studies of some *p*-substituted *i*-propyl benzylsulfones. (1). We expected to obtain the corresponding monosulfenylated derivatives (2) containing two α, α′-acidic hydrogens, which could undergo a modified Ramberg-Bäcklund rearrangement,[6,7] to give through intermediate chloro- and epi-sulfones, the corresponding vinyl sulfides (3), precursors of vinyl sulfoxides, potential dienophiles and Michael acceptors[8] (Scheme I).

It should be mentioned that although the vinyl sulfides have been mostly obtained by a Wittig type reaction[9] or by alkylation of sulfines through the dithioacetal monoxides formation,[10] no report on their obtention by the Ramberg-Bäcklund rearrangement has been found in the literature.

RESULTS AND DISCUSSION

Some *i*-propyl benzylsulfones (1a–f) were submitted to reaction with NaH, in excess, in dimethyl sulfoxide (DMSO), followed by reaction with dimethyl disulfide (Table I). In all cases, with exception of the *p*-methoxy substituted benzylic sulfone (1f), which did not undergo reaction, being the starting product recovered, the corresponding α-methylthiosulfones (2a–e) were obtained. Table I shows also that while for the sulfones (1a–c) the sulfenylation was over after 1 h, in the case of

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TABLE I

Reaction of *i*-propylbenzylsulfones 1 with NaH/DMSO[a] and some sulfenylating agents, at r.t.

p-$YC_6H_4CH_2SO_2CHMe_2$ 1	Sulf.agents	Reaction time (hs)	p-$YC_6H_4CH(SMe)SO_2CHMe_2$ 2 Yield %[c]
a Y = H	MeSSMe	1	62
b Y = Cl	MeSSMe	1	73
c Y = Me	MeSSMe	1	56
d Y = NO_2	MeSSMe	8	60
	$MeSO_2SMe$	1	51
e Y = CN	MeSSMe	30	66
	$MeSO_2SMe$	4	61
f Y = OMe	MeSSMe	1	-
	Phtal-N-SMe	1[b]	51

[a]1 h of formation of carbanion; [b]4 h of formation of carbanion; [c]Isolated products.

the nitro (1d) and cyano (1e) substituted sulfones it was completed only after 8 hs and 30 hs, respectively. We presumed that the slow reaction of the carbanions with dimethyl disulfide in the case of the nitro and cyano sulfones would be due to their large stability and, therefore, low reactivity. In fact, when a more powerful sulfenylating agent, such as S-methyl methanethiolsulfonate was employed, the time of reaction became reduced to 1 h for the sulfone (1d) and 4 hs for the sulfone (1e).

As for the methoxy substituted sulfone (1f), which should lead to the destabilized carbanion, the lack of reactivity can be attributed to the slow reaction with NaH. In fact, when the treatment with NaH was extended to 4 hs and, instead of dimethyl disulfide, N-methylthiophtalimide (1 mol eq.) was employed as sulfenylating agent, the *i*-propyl α-methylthio-*p*-methoxybenzylsulfone (2f) was obtained in 51% yield.

Isopropyl α-methylthiobenzylsulfones (2a–d,f) were submitted to reaction with powdered KOH, in CCl_4 and t-BuOH, at room temperature, for 1 h, following the procedure described by Meyers.[6] Table II shows that the unsubstituted α-methylthiosulfone (2a), the corresponding para-chloro (2b), methyl (2c) and methoxy (2f) substituted sulfones afforded the corresponding vinyl sulfides (3a–c,f) in ca 70% yield. However, no reaction, under the same conditions, occurred in the case

TABLE II

Reaction of *i*-propyl α-methylthiobenzylsulfones 2 with CCl_4-KOH-t-BuOH[a]

p-$YC_6H_4CH(SMe)SO_2CHMe_2$ 2	Styryl sulfides p-$YC_6H_4C(SMe)=CMe_2$ 3 Yield % Cromat. (isol. prod.)
a Y = H	68 (63)
b Y = Cl	68 (67)
c Y = Me	68 (63)
d Y = NO_2	– (22)[b]
f Y = OMe	70 (66)

[a]Conditions : r.t., 1h; [b]Conditions: 65°C, 60hs.

of the nitro substituted α-methylthiosulfone (2d) and only after 60 hs at 65°C, the corresponding vinyl sulfide (3d) was obtained in 22% yield.

The fact that in the case of the *i*-propyl α-methylthio-*p*-nitrobenzylsulfone (2d) the starting product is recovered unchanged indicates that the reaction is paralized at the chlorination step. It seems reasonable to admit that the lack of reactivity in the chlorination of the α-methylthio sulfone (2d) has similar origin as that in the sulfenylation of the nitro substituted sulfone (1d), i.e. the stabilization of the corresponding carbanion, being increased in the former by the presence of methylthio group.[11,12]

It is interesting to observe that the methoxy substituted α-methylthiosulfone (2f), contrary to the corresponding non-sulfenylated sulfone (1f), which did not give reaction with NaH and dimethyl disulfide, underwent chlorination as it yielded the corresponding vinyl sulfide (3f) in ca 70% yield. This seems to indicate that the stabilizing effect of the SMe group on the carbanion suppresses the destabilizing effect of the *p*-methoxy group.

It should be noted that in all cases no formation of dichlorocyclopropane, frequently formed as the side product in the Ramberg-Bäcklund rearrangement of sulfones,[6] was detected. Therefore, it recommends this process as a convenient "one flask" procedure for the obtention of the dimethyl styryl sulfides.

The confirmation for the viability of the transformation of the 1-dimethyl-2-methylthiostyrenes, Ramberg-Bäcklund rearrangement products, to the corresponding sulfoxides, was obtained when the sulfides (3a,b,f) were oxidized with sodium metaperiodate[13] and the corresponding vinyl sulfoxides (6a,b,f) were obtained in good yields (Table III).

In conclusion, we have developed an alternative method of obtention of some

TABLE III

Oxidation of some 1-dimethyl-2-methylthiostyrenes 3 with sodium metaperiodate

p-$YC_6H_4C(SMe)=CMe_2$ 3	p-$YC_6H_4C(SOMe)=CMe_2$ 4 Yield %[a]
a Y = H	62
b Y = Cl	72
f Y = OCH_3	64

[a]Isolated products.

p-substituted vinyl sulfides and the corresponding sulfoxides. We have also showed some aspects of the influence of the SMe group on the reactivity of the *p*-substituted benzylic carbanions, such as its decrease in the case of the electron withdrawing groups and increase for the electron repelling groups.

EXPERIMENTAL

Microanalyses were performed on a Perkin-Elmer 240B elemental analyser. M.p.s. are uncorrected and were determined on a Kofler hot-stage apparatus. ^1H NMR spectra were recorded on a Varian T-60 and a Bruker AC-200 spectrometers. Chemical shifts are expressed in ppm relative to $SiMe_4$ as internal standard and *J* values are in Hz. Mass spectra were measured at 70 eV with a Finnigan ITD-800 or an INCOS-50 instrument. IR spectra were obtained with a Perkin-Elmer FT 1750 or a Nicolet FT510 instruments. Gravity chromatography was performed on Merck Kieselgel 60 (70-230 mesh). *i*-Propyl benzylsulfides, precursors for sulfones (1a,b,d,e) were prepared, in analogy to the phenyl benzylsulfides,[14,15] however using stoichiometric amounts of reagents. *i*-Propyl 4-methyl and 4-methoxybenzylsulfides were prepared from the corresponding benzyl alcohols, applying the method described for the phenyl benzylsulfides.[16]

i-Propyl 4-chlorobenzylsulfide. (76% yield); b.p. 121–2°C/8 mmHg. (Found: C, 59.6; H, 6.6. $C_{10}H_{13}ClS$ requires C, 59.85; H, 6.5); δ_H (CCl_4) 1.22 (6H, d, *J*7, $\underline{CH_3}CH\underline{CH_3}$), 2.59–2.96 (1H, m), 3.67 (2H, s, $\underline{CH_2}C_6H_5$), 6.83–7.27 (4H, m, C_6H_4).

i-Propyl 4-nitrobenzylsulfide. (78% yield); b.p. 109–111°C/0.05–0.10 mmHg. (Found: C, 56.9; H, 6.1. $C_{10}H_{13}NO_2S$ requires C, 56.9; H, 6.2); δ_H (CCl_4) 1.21 (6H, d, *J*7, $\underline{CH_3}CH\underline{CH_3}$), 2.48–3.00 (1H, m, $\underline{CH}CH_3$), 3.69 (2H, s, $\underline{CH_2}C_6H_4$), 7.32 (2H, d, *J*9, C_6H_4), 7.97 (2H, d, *J*9, C_6H_4).

i-Propyl 4-cyanobenzylsulfide. (72% yield); b.p. 91–3°C/0.10 mmHg. (Found: C, 68.9; H, 5.9. $C_{11}H_{13}NS$ requires C, 69.1; H, 6.1); δ_H (CCl_4) 1.18 (6H, d, *J*7, $\underline{CH_3}CH$), 2.32–3.00 (1H, m, $\underline{CH}CH_3$), 3.60 (2H, s, $\underline{CH_2}C_6H_4$), 7.06–7.42 (4H, m, C_6H_4).

i-Propyl 4-methoxybenzylsulfide. (77% yield); b.p. 86–8°C/0.05 mmHg. (Found: C, 67.6; H, 8.1. $C_{11}H_{16}OS$ requires C, 67.3; H, 8.2); δ_H (CCl_4) 1.16 (6H, d, *J*7, $\underline{CH_3}CH$), 2.20–2.83 (1H, m, $\underline{CH}CH_3$), 3.50 (3H, s, $O\underline{CH_3}$), 3.61 (2H, m, $\underline{CH_2}C_6H_4$), 6.52 (2H, d, *J*8, C_6H_4), 6.95 (2H, d, *J*8, C_6H_4).

i-Proply benzylsulfones (1a–f) were prepared by oxidation of the corresponding sulfides with hydrogen peroxide in glacial acetic acid.[14]

i-Propyl 4-chlorobenzylsulfone 1b. Sulfone 1b was obtained in 79% yield as white crystals, m.p. 101–102°C (from ethylacetate-hexane). (Found: C, 51.5; H, 5.9. $C_{10}H_{13}ClO_2S$ requires C, 51.6; H, 5.6); δ_H ($CCl_4/CDCl_3$) 1.35 (6H, d, *J*7, $\underline{CH_3}CH$), 3.03 (1H, h, *J*7, $\underline{CH}CH_3$), 4.18 (2H, s, $\underline{CH_2}C_6H_4$), 7.33 (4H, s, C_6H_4), ν_{max} (KBr)/cm^{-1} 1127 and 1308 (SO_2).

i-Propyl 4-methylbenzylsulfone 1c. Sulfone 1c was obtained in 66% yield as white crystals, m.p. 54–57°C (from ethylacetate-hexane). (Found: C, 62.6; H, 7.5. $C_{11}H_{16}O_2S$ requires C, 63.3; H, 7.55); δ_H ($CCl_4/CDCl_3$) 1.30 (6H, d, *J*7, $\underline{CH_3}CH$), 2.40 (3H, s, $\underline{CH_3}C_6H_4$), 2.51–3.02 (1H, m, $\underline{CH}CH_3$), 4.02 (2H, s, $\underline{CH_2}C_6H_4$), 6.92–7.30 (4H, m, C_6H_4), ν_{max} (KBr)/cm^{-1} 1125 and 1310 (SO_2).

i-Propyl 4-nitrobenzylsulfone 1d. Sulfone 1d was obtained in 72% yield as yellow crystals, m.p. 140–142°C (from ethylacetate-carbon tetrachloride). (Found: C, 49.55; H, 5.3. $C_{10}H_{13}NO_4S$ requires C, 49.4; H, 5.35); δ_H ($CCl_4/CDCl_3$) 1.41 (6H, d, *J*7, $\underline{CH_3}CH$), 2.80–3.20 (1H, m, $\underline{CH}CH_3$), 4.21 (2H, s, $\underline{CH_2}C_6H_4$), 7.48 (2H, d, *J*9, C_6H_4), 8.16 (2H, d, *J*9, C_6H_4). ν_{max} (KBr)/cm^{-1} 1125 and 1310 (SO_2).

i-Propyl 4-cyanobenzylsulfone 1e. Sulfone 1e was obtained in 74% as white crystals, m.p. 100–101°C (from ethylacetate-hexane). (Found: C, 59.4; H, 5.9. $C_{11}H_{13}NO_2S$ requires C, 59.2; H, 5.8); δ_H ($CDCl_3$) 1.39 (6H, d, *J*7, $\underline{CH_3}CH$), 2.71–3.20 (1H, m, $\underline{CH}CH_3$), 4.16 (2H, s, $\underline{CH_2}C_6H_4$), 7.29–7.65 (4H, m, C_6H_4). ν_{max} (KBr)/cm^{-1} 1128 and 1307 (SO_2).

i-Propyl 4-methoxybenzylsulfones 1f. Sulfone 1f was obtained in 67% as light yellow crystals, m.p. 87–8°C (from ethylacetate-hexane). (Found: C, 57.6; H, 7.3. $C_{11}H_{16}O_3S$ requires C, 57.9; H, 7.0); δ_H ($CDCl_3$) 1.29 (6H, d, *J*7, $\underline{CH_3}CH$), 2.82–3.10 (1H, m, $\underline{CH}CH_3$), 3.74 (3H, s, $O\underline{CH_3}$), 4.03 (2H, s, $\underline{CH_2}C_6H_4$), 6.71 (2H, d, *J*8, C_6H_4), 7.13 (2H, d, *J*8, C_6H_4).

i-Propyl α-methylthiobenzylsulfones 2. *General Procedure.* The *i*-propyl benzylsulfone 1a–f (10 mmol) was added to a stirred suspension of sodium hydride (25 mmol; obtained from a 60% dispersion in mineral oil by washing with dry hexane) in dimethyl sulfoxide (20 mL) at r.t., and stirring was continued for 1–4 hs. Then, the sulfenylating agent (30 mmol) (see Table I) was added dropwise and stirring was continued by the times indicated in Table I. The mixture was poured into a saturated aqueous NaCl solution containing 1 g of NH_4Cl. The resulting mixture was extracted in dichloromethane (3 × 35 mL). The organic extract was washed with saturated aqueous solution of NaCl (35 mL) and twice with water (35 mL), and dried with $MgSO_4$. The solvent was removed and the crude product 2 purified by recrystallization.

i-Propyl α-methylthiobenzylsulfone 2a. Sulfone 2a was obtained with white crystals, m.p. 79–81°C (from chloroform-hexane). (Found: C, 54.4; H, 6.7. $C_{11}H_{16}O_2S_2$ requires C, 54.1; H, 6.6); δ_H ($CDCl_3$) 1.31 (3H, d, *J*7, $\underline{CH_3}CH$), 1.33 (3H, d, *J*7, $\underline{CH_3}CH$), 2.35 (3H, s, $S\underline{CH_3}$), 2.72–3.20 (1H, m, $\underline{CH}CH_3$), 4.97 (1H, s, $\underline{CH}C_6H_5$), 7.10–7.50 (5H, m, C_6H_5). ν_{max} (KBr)/cm^{-1} 1125 and 1305 (SO_2).

i-Propyl α-methylthio-4-chlorobenzylsulfone 2b. Sulfone 2b was obtained as white crystals, m.p. 91–3°C (from ethylacetate-hexane). (Found: C, 47.4; H, 5.4 $C_{11}H_{15}ClO_2S_2$ requires C, 47.4; H, 5.4); δ_H ($CDCl_3$) 1.30 (3H, d, *J*7, $\underline{CH_3}CH$), 1.34 (3H, d, *J*7, $\underline{CH_3}CH$), 2.33 (3H, s, $S\underline{CH_3}$), 3.26 (1H, h, *J*7, $\underline{CH}CH_3$), 5.05 (1H, s, $\underline{CH}C_6H_4$), 7.23–7.54 (4H, m, C_6H_4). ν_{max} (KBr)/cm^{-1} 1124 and 1300 (SO_2).

i-Propyl α-methylthio-4-methylbenzylsulfone 2c. Sulfone 2c was obtained as white crystals, m.p. 90–2°C (from chloroform-hexane). (Found: C, 56.2; H, 7.0. $C_{12}H_{18}O_2S_2$ requires C, 55.8; H, 7.0); δ_H ($CDCl_3$) 1.30 (3H, d, *J*7, $\underline{CH_3}CH$), 1.33 (3H, d, *J*7, $\underline{CH_3}CH$), 2.35 (3H, s, $S\underline{CH_3}$), 2.40 (3H, s, $\underline{CH_3}C_6H_4$), 3.07–3.21 (1H, m, $\underline{CH}CH_3$), 4.95 (1H, s, $\underline{CH}C_6H_4$), 7.18–7.42 (4H, m, C_6H_4). ν_{max} (KBr)/cm^{-1} 1125 and 1305 (SO_2).

i-Propyl α-methylthio-4-nitrobenzylsulfone 2d. Sulfone 2d was obtained as yellow crystals, m.p. 127°C (dec.). (Found: C, 45.5; H, 5.3. $C_{11}H_{15}NO_4S_2$ requires C, 45.2; H, 5.2); δ_H ($CDCl_3$) 1.32 (3H, d, *J*7, $\underline{CH_3}CH$), 1.36 (3H, d, *J*7, $\underline{CH_3}CH$), 2.27 (3H, s, $\underline{CH_3}S$), 3.11–3.62 (1H, m, $\underline{CH}CH_3$), 4.95 (1H, s, $\underline{CH}C_6H_4$), 7.70 (2H, d, *J*9, C_6H_4), 8.21 (2H, d, *J*9, C_6H_4). ν_{max} (KBr)/cm^{-1} 1120 and 1310 (SO_2).

i-Propyl α-methylthio-4-cyanobenzylsulfone 2e. Sulfone 2e was obtained as white crystals, m.p. 107–109°C (from ethylacetate-hexane). (Found: C, 53.4; H, 5.7. $C_{12}H_{15}NO_2S_2$ requires C, 53.5; H, 5.6); δ_H ($CDCl_3$) 1.30 (3H, d, *J*7, $CH\underline{CH_3}$), 1.36 (3H, d, *J*7, $CH\underline{CH_3}$), 2.30 (3H, s, $S\underline{CH_3}$), 3.08–3.60 (1H, m, $\underline{CH}CH_3$), 4.85 (1H, s, $\underline{CH}C_6H_4$), 7.50–7.75 (4H, m, C_6H_4). ν_{max} (KBr)/cm^{-1} 1125 and 1300 (SO_2).

i-Propyl α-Methylthio-4-methoxybenzylsulfone 2f. Sulfone 2f was obtained as white crystals, m.p. 64–5°C (from ethylacetate-hexane, after column chromatography on silica gel using chloroform as eluent). (Found: C, 52.9; H, 6.4. $C_{12}H_{18}O_3S_2$ requires C, 52.55, H, 6.6); δ_H ($CDCl_3$) 1.24 (3H, d, *J*7, $\underline{CH_3}CH$), 1.32 (3H, d, *J*7, $CH\underline{CH_3}$), 2.35 (3H, s, $\underline{CH_3}S$), 2.81–3.16 (1H, m, $\underline{CH}CH_3$), 3.77 (3H, s, $O\underline{CH_3}$), 4.87 (1H, s, $\underline{CH}C_6H_4$), 6.83 (2H, d, *J*8, $C_6\underline{H_4}$), 7.40 (2H, d, *J*8, C_6H_4). ν_{max} (KBr)/cm^{-1} 1125 and 1302 (SO_2).

Reaction of substituted α-methylthiosulfones (2a–d,f) *with carbon tetrachloride-sodium hydroxyde-t-butanol. General Procedure.* To a solution of 2 (7.3 mmol) in carbon tetrachloride (30 mL) -*t*-butanol (30 mL), 7.1 g of powdered KOH were added and the resulting mixture was vigorously stirred for 1 h. The reaction mixture was poured into a saturated aqueous solution of NaCl (50 mL) and extracted with dichloromethane (3 × 20 mL). The organic extract was washed with a saturated NaCl aqueous solution and dried over $MgSO_4$. After removal of solvent under reduced pressure, the crude oily product was subjected to silica gel column chromatography with hexane as eluent, to give methyl styryl sulfide 3.

1-Methylthio-2-methyl-1-(4-chlorophenyl)propene 3b. Styryl sulfide 3b was isolated as a light yellow oil. (Found: C, 62.15; H, 6.1. $C_{11}H_{13}ClS$ requires C, 62.1; H, 6.1); δ_H ($CDCl_3$) 1.63 (3H, s, $=\!\!\diagdown$), 1.80 (3H, s, $=\!\!\diagup$), 2.03 (3H, s, $\underline{CH_3}S$), 6.81–7.22 (4H, m, C_6H_4). ν_{max} (neat)/cm^{-1} 1602 (C=C).

1-Methylthio-2-methyl-1-(4-methylphenyl)propene 3c. Styryl sulfide 3c was isolated as a light yellow oil. (Found: C, 75.2; H, 8.5. $C_{12}H_{16}S$ requires C, 75.0; H, 8.3); δ_H ($CDCl_3$) 1.64 (3H, s, $=\!\!\diagdown$), 1.80 (3H, s, $=\!\!\diagup$), 2.02 (3H, s, $\underline{CH_3}S$), 2.34 (3H, s, $\underline{CH_3}C_6H_4$) 7.10 (4H, bs, C_6H_4). ν_{max} (neat)/cm^{-1} 1598 (C=C).

1-Methylthio-2-methyl-1-(4-nitrophenyl)propene 3d. Styryl sulfide 3d was isolated as a light yellow oil. (Found: C, 59.5; H, 6.0. $C_{11}H_{13}NO_2S$ requires C, 59.2; H, 5.8); δ_H ($CDCl_3$) 1.66 (3H, s, $=\!\!\diagdown$), 1.80 (3H, s, $=\!\!\diagup$), 2.05 (3H, s, $\underline{CH_3}S$), 7.22 (2H, d, *J*9, C_6H_4), 8.02 (2H, d, *J*9, C_6H_4). ν_{max} (neat)/cm^{-1} 1598 (C=C).

1-Methylthio-2-methyl-1-(4-methoxyphenyl)propene 3f. Styryl sulfide 3f was isolated as a light yellow oil, by column chromatography using hexane/acetone (with gradual increase of the proportion of the latter solvent in the eluent mixture). (Found: C, 69.2; H, 7.4. $C_{12}H_{16}OS$ requires C, 69.6; H, 7.25); δ_H ($CDCl_3$) 1.65 (3H, s, $=\!\!\diagdown$), 1.80 (3H, s, $=\!\!\diagup$), 2.03 (3H, s, $S\underline{CH_3}$), 3.81 (3H, s, $O\underline{CH_3}$), 6.86 (2H, d, *J*8, C_6H_4), 7.14 (2H, d, *J*8, C_6H_4). ν_{max} (neat)/cm^{-1} 1604 (C=C).

Oxidation of methyl vinyl sulfides (3a,b,f). *General Procedure.* To a methanolic solution of 3 (7.0 mmol) were added 23 mL of an aqueous solution of sodium metaperiodate (0.42 mol/L). The reaction mixture was stirred at 0–5°C for 4 h. After filtration, the solution was extracted with dichloromethane (3 × 10 mL). The organic extract was washed with a saturated NaCl aqueous solution and dried with $MgSO_4$. After removal of the solvent under reduced pressure, the oily crude product was purified by column chromatography on silica gel using hexane-acetone as eluent (the acetone content in the mixture was gradually increased during elution), to give methyl styryl sulfoxides (4a,b,f).

1-Methylsulfinyl-2-methyl-1-phenylpropene 4a. Compound 4a was obtained as white crystals, m.p. 70–2°C. (Found: C, 67.9; H, 7.2. $C_{11}H_{14}OS$ requires C, 68.0; H, 7.2); δ_H ($CDCl_3$) 1.66 (3H, s, $=\!\!\diagdown$), 2.20 (3H, s, $=\!\!\diagup$), 2.25 (3H, s, $\underline{CH_3}SO$), 6.97–7.36 (5H, m, C_6H_5). ν_{max} (neat)/cm^{-1} 1640 (C=C), 1045 (SO).

1-Methylsulfinyl-2-methyl-1-(4-chlorophenyl)propene 4b. Compound 4b was obtained as a colourless liquid. (Found: C, 57.7; H, 5.8. $C_{11}H_{13}ClOS$ requires C, 57.8; H, 5.7); δ_H ($CDCl_3$) 1.68 (3H, s, $=\!\!\diagdown$), 2.14 (3H, s, $=\!\!\diagup$), 2.21 (3H, s, $\underline{CH_3}SO$), 7.09 (2H, d, *J*9, C_6H_4), 7.37 (2H, d, *J*9, C_6H_4). ν_{max} (neat)/cm^{-1} 1641 (C=C), 1042 (SO).

1-Methylsulfinyl-2-methyl-1-(4-methoxyphenyl)propene 4f. Compound 4f was obtained as a colourless oil. (Found: C, 64.15; H, 7.0. $C_{12}H_{16}O_2S$ requires C, 64.6; H, 6.7); δ_H ($CDCl_3$) 1.86 (3H, s, $=\!\!\diagdown$), 2.18 (3H, s, $=\!\!\diagup$), 2.22 (2H, s, $\underline{CH_3}SO$), 3.82 (3H, s, $O\underline{CH_3}$), 6.94 (2H, d, *J*8, C_6H_4), 7.12 (2H, d, *J*8, C_6H_4). ν_{max} (neat)/cm^{-1} 1604 (C=C), 1034 (SO).

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