Stereoselective Synthesis of (*E*)-Vinyl Sulfoxides by the Horner−Wittig Reaction

Jan Hein van Steenis,[a] Joseph Johannes Gerardus Steven van Es,[a] and Arne van der Gen*[a]

Keywords: Aldehydes / Asymmetric synthesis / Horner−Wittig reaction / Oxides / Phosphanes / Sulfoxides

The Horner–Wittig reaction of sulfinylmethyl-substituted diphenylphosphane oxides **1**–**3** with aldehydes is reported. In a straightforward synthesis, (*E*)-vinyl sulfoxides **4** (R^1 = Ph), **5** (R^1 = Me) and **6** (R^1 = *p*Tol) were formed, mostly with high configurational selectivity and in high yields. In less selective cases, the (*E*)/(*Z*) ratio could be improved by slightly modifying the procedure. The use of (S_S)-(+)-diphenyl(*p*-tolylsulfinylmethyl)phosphane oxide (**3**) allowed the synthesis of enantiomerically pure (*E*)-vinyl sulfoxides.

Introduction

In the synthesis of stereochemically pure vinyl sulfoxides, use has often been made of stereochemistry already present in one of the starting compounds.[1] A different approach has stereoselective formation of the double bond as the keystep. 1-Alkynyl sulfoxides can be stereoselectively hydrogenated to yield both (*E*) and (*Z*) isomers.[2] One-carbon elongation of aldehydes usually proceeds in a nonstereoselective manner.[3] (*Z*)-Vinyl sulfoxides have been obtained by the Horner−Wadsworth−Emmons reaction of bis(2,2,2-trifluoroethyl)phosphono sulfoxides and aromatic aldehydes.[4] Recently, the stereoselective synthesis of (*E*)-vinyl sulfoxides by the Wittig reaction of (sulfinylmethyl)phosphonium ylides was reported.[5] Finally, it should be noted that (*E*)-vinyl sulfoxides containing fluorinated alkyl substituents have been reported to be formed almost exclusively by the demesylation of diastereomeric mixtures of β-mesylalkyl sulfoxides, although no (*E*)/(*Z*) ratios were presented.[6]

The Horner−Wittig reaction of methylphosphane oxides with electron-withdrawing α-substituents often shows more stereoselective double-bond formation than is found for the Horner−Wadsworth−Emmons reaction using the corresponding phosphonates. This has been demonstrated for α,β-unsaturated nitriles[7] and esters,[8] as well as for 1-chlorovinyl sulfoxides.[9] Sulfinyl-substituted methylphosphane oxides **1**−**3**, in which R^1 = Ph, CH_3, and *p*Tol, respectively, were reported in a preliminary investigation to yield vinyl sulfoxides **4**−**6** with excellent (*E*) selectivity, using either aromatic, aliphatic, or α,β-unsaturated aldehydes as substrates (Scheme 1).[10] Careful examination of the results revealed that revision of some of the reported figures was necessary. To obtain more insight into the factors determining the stereochemical outcome of the reaction, the reactivity of phosphane oxide **2** (R^1 = CH_3) was studied in greater detail, and additional substrates were tested with respect to the original report.[10] The possible occurrence of racemization when using enantiomerically pure **3** (R^1 = *p*Tol) was investigated. Finally, experiments were carried out to see whether changing the base or the solvent would lead to a better (*E*)/(*Z*) ratio in the less selective cases.

Results and Discussion

Phosphane oxides **1** and **2** were prepared using a modified literature procedure.[11] Enantiomerically pure (S_S)-(+)-diphenyl(*p*-tolylsulfinylmethyl)phosphane oxide (**3**) was synthesized using a known method.[12]

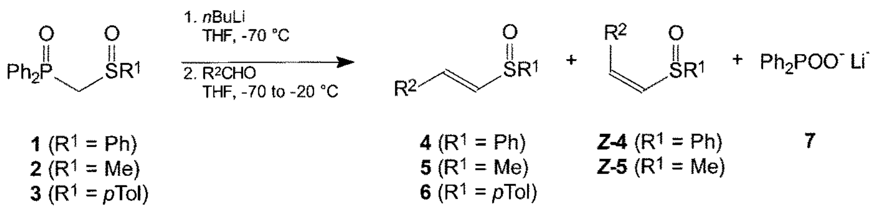
The general procedure for the Horner−Wittig reaction is outlined in the Experimental Section. Unless otherwise indicated, reactions were carried out on a 5-mmol scale. Phosphane oxides **1**−**3** were deprotonated with *n*BuLi at −70 °C. After addition of the appropriate aldehyde, the temperature was allowed to rise to −20 °C. Progress of the reaction was apparent from the precipitation of lithium diphenylphosphinate (**7**), which started at about −30 °C. Stirring was continued until the reaction had reached completion (TLC). After workup, the crude product was analyzed by ^{1}H NMR. Purification by column chromatography yielded pure (*E*)-vinyl sulfoxides **4a**−**p**, **5a**−**j**, and **6a**−**b**. In some cases, small amounts of the (*Z*) isomers ***Z*-4** and ***Z*-5** could be detected and isolated as well. This observation had not been made in our preliminary report,[10] except for the 2-chlorobenzaldehyde derivatives **4e** and **5e**. The threshold value for ^{1}H-NMR detection was found to be ≤ 2%. The results are listed in Table 1 and Table 2.

The results show that most aromatic and α,β-unsaturated aldehydes gave excellent (*E*) selectivity, usually with no (*Z*) isomer detectable in the crude product. Only for vinyl sulfoxides **4e**, **5e**, and **5f**, prepared from *ortho*-substituted benzaldehydes, were notable amounts of (*Z*) isomer found. Obviously, this lowering of selectivity is caused by steric rather than by electronic reasons. It should be noted that,

---

[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University,
P. O. Box 9502, 2300 RA Leiden, The Netherlands
Fax: (internat.) + 31-71/527-4537

1434−193X/00/0815−2787 $ 17.50+.50/0



Scheme 1

Table 1. Results for the Horner−Wittig synthesis of (*E*)-vinyl phenyl sulfoxides **4**

Sulfoxide	R^1	R^2	(*E*)/(*Z*) ratio[a]	Yield (*E*) isomer [%]
4a	Ph	Ph	> 98:2	88
4b	Ph	$4\text{-}O_2NC_6H_4$	> 98:2	83[b]
4c	Ph	$4\text{-}ClC_6H_4$	> 98:2	91
4d	Ph	$4\text{-}MeOC_6H_4$	> 98:2	88
4e	Ph	$2\text{-}ClC_6H_4$	93:7	82[c]
4f	Ph	$2\text{-}MeC_6H_4$	> 98:2	84
4g	Ph	Me	89:11	82
4h	Ph	Et	93:7[d]	72
4i	Ph	*i*Pr	97:3[d]	90
4j	Ph	*t*Bu	> 98:2	67
4k	Ph	*n*Bu	97:3[e]	78
4l	Ph	$PhCH_2CH_2$	88:12[f]	73
4m	Ph	$CH_2{=}CH$	> 98:2[g]	88
4n	Ph	$CH_2{=}C(Me)$	> 98:2	72
4o	Ph	(*E*)-$MeCH_2{=}CH$	> 98:2[g]	76
4p	Ph	(*E*)-$PhCH{=}CH$	> 98:2	81

[a] Determined from ^{1}H-NMR spectrum of the crude product. − [b] (*E*)/(*Z*) ratio 95:5 after column chromatography. − [c] Isomers not separated. − [d] (*Z*) isomer not isolated in pure form. − [e] (*Z*) isomer not isolated. − [f] Products separated in a 89:11 (*E*)/(*Z*) ratio. − [g] 1−2% of the (*Z*) isomer noted after column chromatography.[3g]

Table 2. Results for the Horner−Wittig synthesis of (*E*)-vinyl methyl sulfoxides **5**

Sulfoxide	R^1	R^2	(*E*)/(*Z*) ratio[a]	Yield (*E*) isomer [%]
5a	Me	Ph	> 98:2	82
5b	Me	$4\text{-}O_2NC_6H_4$	> 98:2	88
5c	Me	$4\text{-}ClC_6H_4$	> 98:2	70
5d	Me	$4\text{-}MeOC_6H_4$	> 98:2	85
5e	Me	$2\text{-}ClC_6H_4$	89:11	64
5f	Me	$2\text{-}MeC_6H_4$	95:5	71
5g	Me	*t*Bu	91:9[b]	55[c]
5h	Me	*n*Bu	97:3[b]	76
5i	Me	$PhCH_2CH_2$	77:23[d]	72
5j	Me	(*E*)-$PhCH{=}CH$	> 98:2	84

[a] Determined from ^{1}H-NMR spectrum of the crude product. − [b] (*Z*) isomer not isolated. − [c] Low yield possibly caused by evaporation of the product. − [d] Products separated in a 79:21 (*E*)/(*Z*) ratio.

after column chromatography, vinyl sulfoxide **4b** (R^1 = Ph, R^2 = $4\text{-}O_2NC_6H_4$) had undergone some silica-induced (*E*) → (*Z*) isomerization, a reaction observed earlier for a similar 4-nitrophenyl compound.[5] In the case of pentadienyl sulfoxide **4o**, in addition to pure (*E*) isomer, less than 2% of impure (*Z*) isomer was found after chromatography. For dienyl sulfoxide **4n**, where no (*Z*) isomer was observed, isomerization on the column has been reported, resulting in a higher (*E*)/(*Z*) ratio.[3g]

The selectivity was somewhat lower in the case of aliphatic aldehydes. 3-Phenylpropanal, especially, gave low (*E*)/(*Z*) ratios of sulfoxides **4l** and **5i**. In some cases, ratios were hard to determine because of overlap of the signals of the vinylic protons of the (*Z*) compound and the α-vinylic proton of the (*E*) isomer. However, in these cases it always proved possible to confirm the estimated values after column chromatography.

The reaction seems to be more selective for phenyl sulfoxides than for methyl sulfoxides. This is in agreement with the results found for the Horner−Wittig synthesis of 1-chlorovinyl sulfoxides.[9a][9b] Although comparison is not always straightforward, isolated yields tend to be equal to or higher than in the analogous Wittig reactions, which, however, were carried out on a smaller scale.[5]

Special attention was given to the synthesis of enantiomerically pure (*E*)-vinyl sulfoxides **6a** and **6b** (Table 3). In the Horner−Wadsworth−Emmons synthesis of **6b**, the enantiomeric excess (*ee*) was reported to be dependent on the type of base used, with *n*BuLi giving almost complete racemization.[13] In contrast, HPLC analysis of sulfoxides **6a** and **6b**[14] showed they were formed with complete retention of the configuration. The $[\alpha]_D^{20}$ values measured were in accordance with the values reported in literature.[3i,5,13] This showed that (S_S)-(+)-diphenyl(*p*-tolylsulfinylmethyl)phosphane oxide reacted in the Horner−Wittig reaction without loss of *ee*, even when *n*BuLi was used as the base. The yield of **6b** was somewhat disappointing. Earlier results, indicating a better yield, had to be withdrawn on the basis of the observed difference in melting points.[10]

Table 3. Results for the Horner−Wittig synthesis of (*S*)-(*E*)-vinyl tolyl sulfoxides **6**

Sulfoxide	R^1	R^2	(*E*)/(*Z*) ratio[a]	Yield (*E*) isomer [%]
6a	*p*-Tol	Ph	> 98:2	81[b]
6b	*p*-Tol	CO_2Me	> 98:2	41[c]

Determined from ^{1}H-NMR spectrum of the crude product. − [b] Reaction performed on a 1-mmol scale. − [c] Preliminary results with regard to the yield[10] could not be substantiated.

With the aim of increasing the stereoselectivity, the synthesis of vinyl sulfoxides **4e**, **5e**, and **4l** was further investigated. The results are listed in Table 4.

The use in the Horner−Wittig reaction of potassium instead of lithium as the counter-ion has been shown by Seyden-Penne et al. to enhance (*E*) selectivity in the formation of α,β-unsaturated nitriles and esters.[7,8] As shown in Table 4, the (*E*)/(*Z*) ratios of *ortho*-substituted compounds

Table 4. Strategies towards improving the (*E*) selectivity

Sulfoxide	Base	Solvent	(*E*)/(*Z*) ratio[a]	Yield (*E*) isomer [%]
4e−1	*n*BuLi	THF	93:7	82[b]
4e−2	*n*BuLi, KO*t*Bu	THF	> 98:2	70[c]
5e−1	*n*BuLi	THF	89:11	64
5e−2	*n*BuLi, KO*t*Bu	THF	97:3	78
4l−1	*n*BuLi	THF	89:11	73
4l−2	LDA	THF	89:11	85
4l−3	LTMP	THF	90:10	83
4l−4	KHMDS	THF	95:5	73[d]
4l−5	*n*BuLi	toluene/THF	95:5[e]	66[d]

[a] Determined from ^{1}H-NMR spectrum of the crude product. − [b] Isomers not separated. − [c] Conversion ≤ 75%. − [d] Conversion 90%. − [e] Products were separated in a 93.5:6.5 (*E*)/(*Z*) ratio.

4e and **5e** could be improved significantly by the addition of one equivalent of potassium *tert*-butoxide (KO*t*Bu) to the lithiated phosphane oxide. Similar results were found when 2,4-dichlorobenzaldehyde was used.[15] However, this procedure could not be applied successfully with the enolizable 3-phenylpropanal. The use of the non-nucleophilic bases lithium diisopropylamide (LDA) and 1-lithio-2,2,6,6-tetramethylpiperidide (LTMP) improved the yield somewhat, but hardly affected the stereoselectivity. Best results were obtained when using potassium bis(trimethylsilyl)amide (KHMDS), dissolved in THF. The use of a commercially available KHMDS solution in toluene only gave a low degree of conversion. It should be noted that, in the synthesis of related 1-chlorovinyl sulfoxides, the use of KHMDS completely failed to yield the desired products.[9b]

The use of apolar solvents has been reported to improve the (*E*) selectivity of the Wittig reaction.[5] Unfortunately, pure toluene could not be used as a solvent, because of the lack of solubility of the phosphane oxide. Use of a 2:1 mixture of toluene and THF as the solvent did improve the (*E*)/(*Z*) ratio, though the yield was only moderate.

Conclusions

The Horner−Wittig reaction with sulfinylmethyl-substituted phosphane oxides provides an excellent method for the conversion of aliphatic, aromatic and α,β-unsaturated aldehydes into the corresponding homologous (*E*)-vinyl sulfoxides. Methyl sulfoxides are somewhat less selective than phenyl sulfoxides. In some selected cases, the stereoselectivity can be improved by the use of a potassium base, although the yield may be affected adversely. The use of (S_S)-(+)-diphenyl(*p*-tolylsulfinylmethyl)phosphane oxide **3** permits the synthesis of enantiomerically pure (*E*)-vinyl sulfoxides, even when *n*-butyllithium is used as the base.

Experimental Section

General Procedures: Column chromatography was performed on Baker Silica Gel (0.063−0.200 mm). For TLC analyses, Schleicher and Schuell F1500/LS 254 silica plates were used, visualized with ultraviolet light, or with potassium permanganate in the case of vinyl sulfoxides **5g** and **5h**. − ^{1}H- (200 MHz), ^{13}C- (50 MHz), and ^{31}P-NMR (80 MHz) spectra were recorded with a Bruker AC-200 instrument, except in the cases indicated, for which a JEOL NM FX-200 instrument was used. Samples were measured in $CDCl_3$, with tetramethylsilane as an internal standard; δ in ppm, *J* in Hz. − Infrared spectra were obtained with a Pye Unicam SP3−200 spectrometer, except for compounds indicated, for which a Perkin−Elmer FT-IR Paragon 1000 spectrometer was used; ṽ given in cm^{-1}. − Melting points were determined with a Büchi melting point apparatus and are uncorrected. Enantiomeric purities of **6a** and **6b** were determined by HPLC using a Daicel Chiralcel OD column. As eluents, mixtures of *n*-hexane (H) and isopropyl alcohol (I), as specified in each case, were applied. − Optical rotations were measured with a Propol automatic polarimeter, at the sodium D line (λ = 589 nm). − Chemicals were obtained from Acros or Aldrich. Commercially available aldehydes were distilled or washed with base before use. Methyl glyoxylate was prepared using a known procedure.[16] Solvents were distilled before use, THF from $LiAlH_4$. Toluene was dried with molecular sieves (3 Å). Diisopropylamine and 2,2,6,6-tetramethylpiperidine were dried with KOH. Other compounds were used without purification. LDA and LTMP were freshly prepared by addition of *n*BuLi (1.6 M) to an ice-cooled solution of the appropriate amine in THF; KHMDS was dissolved in THF before use. Base concentrations were approximately 0.5 M.

Sulfinylmethyl-Substituted Phosphane Oxides: Racemic phosphane oxides **1** and **2** were synthesized using a modified literature procedure.[11] The corresponding sulfides[17] were mono-oxidized using 1.1 equivalents of *m*CPBA[10] as the oxidizing agent[3g] at −20 °C, leading to almost quantitative yields after workup (washing with thiosulfate, bicarbonate and saturated brine, followed by precipitation from ether). The products were sufficiently pure for use in the Horner−Wittig reaction. The possible contamination with the corresponding sulfones **8** and **9**[18,19] was not usually a problem, because these will not engage in a Horner−Wittig reaction at low temperatures.[10,20]

Diphenyl(phenylsulfinylmethyl)phosphane Oxide (1): An analytical sample was obtained by recrystallization from ethyl acetate. − Colorless crystals, m.p. 144−146 °C (ref.[11a] 151−152 °C, ref.[11c] 124−126 °C). − IR[21] (neat): ṽ (cm^{-1}) = 1435, 1179, 1114, 1052, 1023, 997, 801. − ^{13}C NMR: δ = 59.8 (CH_2), 124.1 (*C*H−SPh), 128.7 (d, J_{PC} = 12.2, *C*H−PPh), 128.8 (d, J_{PC} = 13.7, *C*H−PPh), 129.3 (*C*H−SPh), 130.7 (d, J_{PC} = 8.7, *C*H−PPh), 131.2 (d, J_{PC} = 9.2, *C*H−PPh), 131.4 (*C*H−SPh), 132.3 (*C*H−PPh), 132.5 (d, J_{PC} = 3.0, *C*H−PPh), 144.6 (S−C_{ipso}); P−C_{ipso} not elucidated. − ^{1}H- and ^{31}P-NMR data are in accordance with those reported by Drabowicz et al.[11c] − Published IR data agree quite well.[11a]

(Methylsulfinylmethyl)diphenylphosphane Oxide (2): An analytical sample was obtained by column chromatography (ethyl acetate/methanol = 10:1). − Colorless crystals, m.p. 136−137 °C (ref.[11c] 130−132 °C). − IR[21] (neat): ṽ (cm^{-1}) = 1438, 1183, 1123, 1052, 956. − ^{13}C NMR: δ 41.8 (CH_3), 55.2 (d, J_{PC} = 59.5, CH_2), 128.7 (d, J_{PC} = 10.7, *C*H−Ph), 130.2 (d, J_{PC} = 9.2, *C*H−Ph), 130.4 (d, J_{PC} = 8.7, *C*H−Ph), 132.3 (*C*H−Ph); C_{ipso} not determined. − ^{1}H- and ^{31}P-NMR data are in accordance with those reported.[11c]

(S_S)-(+)-Diphenyl(*p*-tolylsulfinylmethyl)phosphane Oxide (3): Prepared according to a known method.[12] − Colorless crystals, m.p. 104 °C (ref.[12] 134−135 °C). − IR[21] (neat): ṽ (cm^{-1}) = 1436, 1184, 1121, 1098, 1046, 1016, 814. − ^{13}C NMR: δ = 21.3 (CH_3), 59.8 (d, J_{PC} = 61.0, CH_2), 124.2 (*C*H-Tol), 128.6 (d, J_{PC} = 12.2, *C*H−Ph), 128.8 (d, J_{PC} = 14.2, *C*H−Ph), 129.9 (*C*H-Tol), 130.8

(d, J_{PC} = 9.2, *C*H−Ph), 131.2 (d, J_{PC} = 10.7, *C*H−Ph), 132.1 (d, J_{PC} = 3.0, *C*H−Ph), 132.5 (d, J_{PC} = 3.0, *C*H−Ph), 141.4 (*C*Me), 142.0 (S−C_{ipso}); P−C_{ipso} not identified. − $[\alpha]_D^{20}$ = +91 (*c* = 2.2, acetone) [ref.[12] +92 (*c* = 2.2, acetone)]. − ^{1}H- and ^{31}P-NMR data are in accordance with those reported.[12] − As a reference, the racemic compound was prepared by *m*CPBA oxidation of the corresponding sulfide as described above.

Preparation of Vinyl Phenyl Sulfoxides 4: Sulfinylmethyl-substituted phosphane oxide **1** (5 mmol) was dissolved in THF (100 mL) under nitrogen. *n*BuLi (5.5 mmol, 1.6 M in hexanes) was added at −70 °C. After stirring for 30 min at this temperature, the aldehyde (5.5 mmol) in THF (5 mL) was added. The temperature was allowed to rise to −20 °C, and stirring was continued until the reaction reached completion (TLC). This usually took 1−2 h, except for **4j**, which was stirred overnight at −20 °C. Saturated aqueous ammonium chloride solution (100 mL) was added and the layers were separated. The water layer was extracted with ether (3 × 30 mL). The combined organic layers were dried with magnesium sulfate. After filtration, the solvents were removed under reduced pressure. The crude product was analyzed by ^{1}H NMR. Column chromatography afforded the pure (*E*)-vinyl sulfoxides **4**, and in some cases also the corresponding (*Z*)-vinyl sulfoxides ***Z*-4**, as mentioned in Table 1. Eluents used were 25% ethyl acetate/petroleum ether (40:60) or 25% petroleum ether/ether, except in the case of 4-nitrobenzaldehyde derivative **4b**, for which dichloromethane was used. Compounds marked with an asterisk (*) have not been reported in the literature.

(*E*)-2-Phenyl-1-(phenylsulfinyl)ethene (4a): Colorless crystals, m.p.[10] 61−62 °C (ether/hexanes, ca. 1:1) (ref.[3i] 62−62.5 °C). − ^{13}C NMR:[22] δ = 124.3, 127.5, 128.6, 129.1, 129.5, 130.8 (each *C*H−Ph), 132.7 (*C*H), 133.3 (CHC_{ipso}), 135.9 (*C*H), 143.6 (S−C_{ipso}). − IR[3i] and ^{1}H-NMR[5] spectra are in accordance with those reported.

(*E*)-2-(4-Nitrophenyl)-1-(phenylsulfinyl)ethene (4b): Yellowish crystals, m.p.[10] 146−148 °C (ethyl acetate/hexanes, ca. 1:1). − IR (KBr): ṽ (cm^{-1}) = 1590, 1510, 1438, 1340, 1080, 1043, 952, 858. − ^{13}C NMR: δ = 124.0, 124.6, 128.3, 129.6 (*C*H-arom.), 131.5 (CH_{para}), 132.0 (S−*C*H), 137.6 (4-NO_2Ph*C*H), 142.8 (CHC_{ipso}), 146.2 (S−C_{ipso}), 147.9 (*C*−NO_2). − ^{1}H-NMR data are in accordance with those reported;[3i] IR data published refer to a mixture of isomers.[3i]

(*E*)-2-(4-Chlorophenyl)-1-(phenylsulfinyl)ethene (4c): Colorless crystals, m.p.[10] 94−95 °C (ether/hexanes, ca. 1:1) (ref.[3i] 97−98 °C). − ^{13}C NMR:[22] δ = 124.2 (*C*H−Ph), 128.5, 128.6, 129.0, 130.8 (each *C*H-arom.), 131.8 (CHC_{ipso}), 133.2, 133.9 (each *C*H), 135.0 (Cl−*C*), 143.2 (S−C_{ipso}). − IR and ^{1}H-NMR spectra are in accordance with those reported.[3i]

(*E*)-2-(4-Methoxyphenyl)-1-(phenylsulfinyl)ethene (4d): Colorless crystals, m.p.[10] 67−68 °C (ether/hexanes, ca. 1:1) (ref. 63−66,[3c] 64−65[3i]). − ^{13}C NMR:[22] δ = 55.2 (CH_3), 114.2, 124.5 (each *C*H), 126.2 (CHC_{ipso}), 129.3, 130.2, 136.7 (each *C*H), 144.1 (S−C_{ipso}), 160.9 (O−*C*). − IR and ^{1}H-NMR spectra are in accordance with those reported.[3i]

(*E*)-2-(2-Chlorophenyl)-1-(phenylsulfinyl)ethene* (4e): Colorless oil.[23] − IR[21] (neat): ṽ (cm^{-1}) = 1468, 1441, 1122, 1082, 1032, 958, 855, 806. − ^{1}H NMR: δ = 6.88 (d, 1 H, *J* = 15.4, α-C*H*), 7.19−7.33 (m, 2 H, H-arom.), 7.37−7.59 (m, 5 H, H-arom.), 7.66−7.73 (m, 2 H, H-arom.), 7.79 (d, 1 H, *J* = 15.4, β-C*H*). − ^{13}C NMR: 123.9 (*C*H−Ph), 127.0 (*C*H), 127.8 (*C*H), 129.4 (*C*H−Ph), 129.9 (*C*H), 130.5 (*C*H), 131.1 (*C*H), 131.7 (*C*H), 133.9 (Cl−*C*), 135.9 (*C*H), 143.7 (S−C_{ipso}), CHC_{ipso} not noted.

(*Z*)-2-(2-Chlorophenyl)-1-(phenylsulfinyl)ethene* (*Z*-4e): Colorless crystals, m.p. 75−77 °C (triturated; ether/petroleum ether, 40:60). − IR[21] (neat): ṽ (cm^{-1}) = 1464, 1436, 1277, 1077, 1030, 996, 872. − ^{1}H NMR: δ = 6.59 (d, 1 H, *J* = 10.2, α-C*H*), 7.29−7.73 (m, 10 H, β-C*H*, H-arom.). − ^{13}C NMR: δ 124.2 (*C*H−Ph), 126.8 (*C*H-arom.), 129.3 (*C*H−Ph), 129.6, 130.6, 130.9, 131.2 (*C*H-arom.), 132.3 (CHC_{ipso}), 133.8 (Cl−*C*), 136.4 (*C*H), 138.6 (*C*H), 144.1 (S−C_{ipso}).

(*E*)-2-(2-Methylphenyl)-1-(phenylsulfinyl)ethene* (4f): Colorless crystals, m.p. 43−45 °C (triturated; *n*-pentane). − IR[21] (neat): ṽ (cm^{-1}) = 1592, 1575, 1473, 1455, 1440, 1378, 1304, 1082, 1045, 961. − ^{1}H NMR: δ = 2.46 (s, 3 H, CH_3), 6.76 (d, 1 H, *J* = 15.4, α-C*H*), 7.12−7.23 (m, 4 H, H-arom.), 7.41 (d, 1 H, *J* = 7.3, H-arom.), 7.50−7.59 (m, 2 H, H-arom.), 7.56 (d, 1 H, *J* = 15.4, β-C*H*), 7.67−7.69 (m, 2 H, H-arom.). − ^{13}C NMR: 18.9 (CH_3), 123.8 (*C*H−Ph), 125.5, 125.7, 128.6 (*C*H−Ph), 128.7, 129.9 (each *C*H-arom.), 130.2 (CH_{para}), 131.8 (CH−C_{ipso}), 132.7 (*C*H), 133.3 (*C*H), 136.0 (CH_3−*C*), 143.2 (S−C_{ipso}).

(*E*)-1-(Phenylsulfinyl)prop-1-ene (4g): Colorless oil. − IR (neat): ṽ (cm^{-1}) = 3055, 3006, 2912, 1630, 1580, 1483, 1440, 1085, 1040, 1020, 949. − ^{13}C NMR:[22] δ = 17.3 (CH_3), 123.8 (*C*H−Ph), 128.8 (*C*H−Ph), 130.3 (CH_{para}), 135.8 (*C*H-2), 136.0 (*C*H-1), 143.7 (C_{ipso}). − ^{1}H-NMR data are in accordance with those reported;[3i] IR data published refer to a mixture of isomers.[3i]

(*Z*)-1-(Phenylsulfinyl)prop-1-ene (*Z*-4g): Colorless oil. − IR (neat): ṽ (cm^{-1}) = 3052, 2960, 2920, 2865, 1620, 1471, 1440, 1377, 1084, 1034. − ^{13}C NMR: δ = 15.1 (CH_3), 123.8 (*C*H−Ph), 129.1 (*C*H−Ph), 130.5 (CH_{para}), 137.1 (*C*H-2), 137.4 (*C*H-1), 144.2 (C_{ipso}). − ^{1}H-NMR data are in accordance with those reported;[3i] IR data published refer to a mixture of isomers.[3i]

(*E*)-1-(Phenylsulfinyl)but-1-ene (4h): Colorless oil. − ^{13}C NMR:[22] δ = 12.1 (CH_3), 25.1 (CH_2), 124.3 (*C*H−Ph), 129.1 (*C*H−Ph), 130.6 (CH_{para}), 134.1 (*C*H), 142.6 (*C*H), 144.1 (C_{ipso}). − IR and ^{1}H-NMR spectra are in accordance with those reported.[24]

(*Z*)-1-(Phenylsulfinyl)but-1-ene (*Z*-4h): Colorless oil. − ^{1}H NMR: δ = 1.15 (t, 3 H, *J* = 7.3, CH_3), 2.66 (dq, 2 H, *J* = 7.3, 3.6, CH_2), 6.21 (m, 2 H, C*H*=C*H*), 7.46−7.56 (m, 3 H, H-arom.), 7.59−7.64 (m, 2 H, H-arom.). − As the compound was not obtained in pure form, no other data were obtained.

(*E*)-3-Methyl-1-(phenylsulfinyl)but-1-ene (4i): Colorless oil. − IR (neat): ṽ (cm^{-1}) = 3050, 2958, 2866, 1618, 1580, 1460, 1442, 1080, 1045, 1022, 968. − ^{13}C NMR:[22] δ = 20.9 (CH*Me*$_2$), 30.5 (*C*HMe$_2$), 124.0 (*C*H−Ph), 128.9 (*C*H−Ph), 130.4 (CH_{para}), 132.3 (*C*H), 143.8 (C_{ipso}), 146.9 (*C*H). − ^{1}H-NMR data are in accordance with those reported;[3a,3g,3i] published IR data refer to a mixture of isomers.[3a,3i]

(*Z*)-3-Methyl-1-(phenylsulfinyl)but-1-ene (*Z*-4i): The identity of the product could only be assigned with the help of reference ^{1}H-NMR spectra.[3a,3g,3i]

(*E*)-3,3-Dimethyl-(phenylsulfinyl)but-1-ene (4j): Colorless oil. − ^{13}C NMR:[22] δ = 28.5 (C*Me*$_3$), 34.0 (*C*Me$_3$), 124.3 (*C*H−Ph), 129.1 (*C*H−Ph), 130.6 (CH_{para}), 130.8 (*C*H), 144.2 (C_{ipso}), 150.9 (*C*H). − IR and ^{1}H-NMR data are in accordance with those reported.[3i]

(*E*)-(Phenylsulfinyl)hex-1-ene (4k): Colorless oil. − IR (neat): ṽ (cm^{-1}) = 3050, 2950, 2920, 2860, 1622, 1569, 1473, 1465, 1433, 1301, 1082, 1043, 997, 963, 920. − ^{13}C NMR: δ = 13.1 (CH_3), 21.5 (*C*H-5), 29.6 (CH_2-4), 31.0 (CH_2-3), 123.8 (*C*H−Ph), 128.6 (*C*H−Ph), 130.1 (CH_{para}), 134.7 (*C*H-2), 140.2 (*C*H-1), 144.0 (C_{ipso}). − The ^{1}H-NMR spectrum is in accordance with the one reported.[25]

(*E*)-4-Phenyl-1-(phenylsulfinyl)but-1-ene[26] (4l): Colorless crystals, m.p. 43 °C (ether/hexanes, ca. 1:1). − IR[21] (neat): ṽ (cm^{-1}) = 2915, 2849, 1628, 1601, 1494, 1474, 1438, 1301, 1080, 1033, 1019, 995, 975, 932, 807. − ^{1}H NMR: δ = 2.51−2.62 (m, 2 H, CH_2Ph), 2.75−2.83 (m, 2 H, CH_2CH), 6.20 (d, 1 H, *J* = 15.4, α-C*H*), 6.63 (dt, 1 H, *J* = 15.4, 6.6, β-C*H*), 7.12−7.32 (m, 6 H, H-arom.), 7.45−7.54 (m, 4 H, H-arom.). − ^{13}C NMR: δ = 33.0 (CH_2), 33.8 (CH_2), 124.1, 125.9, 128.1, 128.9, 130.4 (each *C*H−Ph), 135.3 (*C*H), 139.0 (*C*H), 140.0 (CH_2C_{ipso}), 143.8 (S−C_{ipso}).

(*Z*)-4-Phenyl-1-(phenylsulfinyl)but-1-ene[26] (*Z*-4l): Colorless oil. − IR[21] (neat): ṽ (cm^{-1}) = 3055, 3020, 2920, 2854, 1617, 1602, 1492, 1450, 1440, 1082, 1047. − ^{1}H NMR: δ = 2.76−2.98 (m, 4H, CH_2CH_2), 6.22 (m, 2H, C*H*=C*H*), 7.20−7.37 (m, 6 H, H-arom.), 7.40−7.48 (m, 4 H, H-arom.). − ^{13}C NMR: δ = 30.97 (CH_2), 35.0 (CH_2), 123.9, 126.3, 128.5, 128.5, 128.9, 130.4 (each *C*H−Ph), 137.2 (*C*H), 140.1 (CHC_{ipso}), 141.0 (*C*H), 144.1 (S−C_{ipso}).

(*E*)-1-(Phenylsulfinyl)buta-1,3-diene (4m): Colorless oil. − IR (neat): ṽ (cm^{-1}) = 3055, 3000, 1625, 1580, 1473, 1442, 1080, 1045, 1020, 1000, 955, 920, 815. − ^{13}C NMR:[22] δ = 123.0 (CH=CH_2), 123.6, 128.5, 130.2, 132.5, 135.0, 135.8 (each *C*H), 143.1 (C_{ipso}). − ^{1}H-NMR data are in accordance with those reported.[3a,3g]

(*E*)-3-Methyl-1-(phenylsulfinyl)buta-1,3-diene (4n): Colorless crystals, m.p.[10] 50−51 °C (ref.[27] 51 °C). − ^{13}C NMR:[22] δ = 17.8 (CH_3), 122.6 (C=CH_2), 124.0, 128.9, 130.5, 132.8, 138.4 (each *C*H), 138.8 (*C*Me), 143.6 (C_{ipso}). − IR[27] and ^{1}H-NMR[3g] spectra are in accordance with those reported.

(1*E*,3*E*)-1-(Phenylsulfinyl)penta-1,3-diene (4o): Colorless oil. − IR (neat): ṽ (cm^{-1}) = 3010, 1640, 1580, 1472, 1441, 1080, 1040, 1020, 985, 928, 815. − ^{13}C NMR: δ = 18.0 (CH_3), 124.0 (*C*H−Ph), 128.0 (*C*H-diene), 128.8 (*C*H−Ph), 130.4 (CH_{para}), 132.6, 136.9, 137.4 (each *C*H-diene), 143.8 (C_{ipso}). − ^{1}H-NMR data are in accordance with those reported;[3g] IR data published refer to a mixture of isomers.[3i]

(1*Z*,3*E*)-1-(Phenylsulfinyl)penta-1,3-diene (*Z*-4o): The nature of the product could only be assigned with help of the reported ^{1}H-NMR spectra.[3g,3i]

(1*E*,3*E*)-4-Phenyl-1-(phenylsulfinyl)buta-1,3-diene (4p): Off-white crystals, m.p.[10] 85−86 °C (ether/hexanes, ca. 1:1) (ref.[3g] 83−85 °C). − IR (KBr): ṽ (cm^{-1}) = 1620, 1595, 1582, 1470, 1442, 1082, 1042, 1025, 988, 980. − ^{13}C NMR: δ = 123.7, 124.0, 126.3, 128.0, 128.1, 128.6, 130.2, 134.9 (each *C*H), 135.1 (CHC_{ipso}), 135.6, 138.1 (each *C*H), 143.4 (S−C_{ipso}). − ^{1}H-NMR[1c,3g] data are in accordance with those reported; published IR data refer to a mixture of isomers.[3a]

Preparation of Methyl Vinyl Sulfoxides 5: Methyl vinyl sulfoxides **5** were prepared from phosphane oxide **2**, following a procedure similar to that outlined for compounds **4**. For sulfoxide **5g**, overnight stirring at −20 °C was necessary. Pure (*E*)-vinyl sulfoxides **5**, and also in some cases the corresponding (*Z*)-vinyl sulfoxides ***Z*-5**, were obtained after column chromatography, as mentioned in Table 2. Methanol/diethyl ether (2%) was used as the eluent, except in the case of 4-nitrobenzaldehyde derivative **5b**, for which dichloromethane was used. Compounds marked with an asterisk (*) have not been reported in literature.

(*E*)-1-(Methylsulfinyl)-2-phenylethene (5a): Colorless crystals, m.p.[10] 64−65 °C (ether/hexanes, ca. 1:1) (ref.[28] 65 °C). − ^{13}C NMR: δ = 40.7 (CH_3), 127.4 (*C*H−Ph), 128.7 (*C*H−Ph), 129.5 (CH_{para}), 132.0 (*C*H), 133.5 (C_{ipso}), 136.1 (*C*H). − IR[1a] and ^{1}H-NMR[1a,5] spectra are in accordance with those reported.

(*E*)-1-(Methylsulfinyl)-2-(4-nitrophenyl)ethene[29] (5b): Yellowish crystals, m.p. 136−137 °C (ethyl acetate/petroleum ether, ca. 1:1). − IR[21] (neat): ṽ (cm^{-1}) = 2920, 2850, 1592, 1506, 1437, 1337, 1289, 1104, 1050, 947, 854, 798. − ^{1}H NMR: δ = 2.76 (s, 3 H, CH_3), 7.11 (d, 1 H, *J* = 15.4, α-C*H*), 7.35 (d, 1 H, *J* = 15.4, β-C*H*), 7.63 (d, 2 H, *J* = 8.8, H-arom.), 8.26 (d, 2 H, *J* = 9.5, H-arom.). − ^{13}C NMR: δ = 40.4 (CH_3), 124.1 (*C*H-arom.), 128.1 (*C*H-arom.), 132.8 (*C*H), 137.1 (*C*H), 139.7 (C_{ipso}), 147.8 (*C*-NO_2).

(*E*)-2-(4-Chlorophenyl)-1-(methylsulfinyl)ethene* (5c): Colorless crystals, m.p. 97−98 °C (ether/hexanes, ca. 1:1). − IR[21] (neat): ṽ (cm^{-1}) = 3027, 2997, 2914, 1489, 1403, 1286, 1172, 1088, 1042, 1014, 990, 954, 931, 840, 797. − ^{1}H NMR: δ = 2.71 (s, 3 H, CH_3), 6.88 (d, 1 H, *J* = 15.4, α-C*H*), 7.22 (d, 1 H, *J* = 15.4, β-C*H*), 7.36 (d, 2 H, *J* = 8.8, H-arom.), 7.42 (d, 2 H, *J* = 8.8, H-arom.). − ^{13}C NMR: δ = 40.2 (CH_3), 128.3 (*C*H-arom.), 128.5 (*C*H-arom.), 131.7 (C_{ipso}), 132.7 (*C*H), 133.8 (*C*H), 134.6 (Cl−*C*).

(*E*)-2-(4-Methoxyphenyl)-1-(methylsulfinyl)ethene (5d): Colorless crystals, m.p. 69.5−70.5 °C (ether/hexanes, ca. 1:1) (ref.[30] 67−68 °C). − IR[21] (neat): ṽ (cm^{-1}) = 2919, 2842, 1603, 1510, 1436, 1301, 1251, 1183, 1045, 1028, 967, 952, 940, 843, 795. − ^{1}H NMR: δ = 2.70 (s, 3 H, CH_3S), 3.84 (s, 3 H, CH_3O), 6.76 (d, 1 H, *J* = 15.4, α-C*H*), 6.91 (d, 2 H, *J* = 8.8, H-arom.), 7.20 (d, 1 H, *J* = 15.4, β-C*H*), 7.43 (d, 2 H, *J* = 8.8, H-arom.), ^{13}C NMR: δ = 40.6 (CH_3S), 54.9 (CH_3O), 113.9 (*C*H-arom.), 126.0 (C_{ipso}), 128.8 (*C*H-arom.), 129.5 (*C*H), 135.8 (*C*H), 160.5 (O−*C*).

(*E*)-2-(2-Chlorophenyl)-1-(methylsulfinyl)ethene* (5e): Colorless crystals, m.p. 33.5−34 °C (ether/hexanes, ca. 1:1). − IR[21] (neat): ṽ (cm^{-1}) = 1589, 1469, 1436, 1418, 1289, 1183, 1121, 1031, 955, 803. − ^{1}H NMR: δ = 2.74 (s, 3 H, CH_3), 6.97 (d, 1 H, *J* = 15.4, α-C*H*), 7.29−7.34 (m, 2 H, H-arom.), 7.41−7.45 (m, 1 H, H-arom.), 7.54−7.59 (m, 1 H, H-arom.), 7.65 (d, 1 H, *J* = 15.4, β-C*H*). − ^{13}C NMR: δ = 40.3 (CH_3), 126.7, 127.5, 129.6, 130.1 (*C*H-arom.), 131.3 (C_{ipso}), 131.5 (*C*H), 133.5 (Cl−*C*), 135.2 (*C*H).

(*Z*)-2-(2-Chlorophenyl)-1-(methylsulfinyl)ethene* (*Z*-5e): Obtained as a mixture with sulfone **9** after column chromatography. A pure sample of (*Z*)-vinyl sulfoxide ***Z*-5e** was obtained after removing the phosphane oxide contaminant by precipitation from ether: colorless crystals, m.p. 108−109.5 °C (triturated; petroleum ether, 40:60). − IR[21] (neat): ṽ (cm^{-1}) = 1714, 1588, 1467, 1436, 1418, 1288, 1128, 1016, 960. − ^{1}H NMR: δ = 2.71 (s, 3 H, CH_3), 6.64 (d, 1 H, *J* = 11.0, α-C*H*), 7.31 (d, 1 H, *J* = 11.0, β-C*H*), 7.30−7.36 (m, 2 H, H-arom.), 7.37−7.48 (m, 2 H, H-arom). − ^{13}C NMR: δ 40.3 (CH_3), 126.7, 129.5, 130.4, 130.9 (each *C*H-arom.), 132.2 (C_{ipso}), 133.5 (Cl−*C*), 136.1 (*C*H), 138.5 (*C*H).

(*E*)-2-(2-Methylphenyl)-1-(methylsulfinyl)ethene* (5f): Colorless crystals, m.p. 35−37 °C (triturated, *n*-pentane). − IR[21] (neat): ṽ (cm^{-1}) = 1608, 1594, 1480, 1455, 1412, 1377, 1291, 1050, 960. − ^{1}H NMR: δ = 2.43 (s, 3 H, CH_3Ph), 2.72 (s, 3 H, CH_3S), 6.82 (d, 1 H, *J* = 15.3, α-C*H*), 7.22−7.25 (m, 3 H, H-arom.), 7.47−7.50 (m, 1 H, H-arom.), 7.52 (d, 1 H, *J* = 15.3, β-C*H*) . − ^{13}C NMR: δ = 18.9 (CH_3Ph), 40.0 (CH_3S), 125.6, 125.7, 128.6, 130.0 (each *C*H-arom.), 131.8 (C_{ipso}), 132.7 (*C*H), 132.8 (*C*H), 135.9 (CH_3−*C*).

(*Z*)-2-(2-Methylphenyl)-1-(methylsulfinyl)ethene* (*Z*-5f): Obtained as a mixture with sulfone **9** after column chromatography. A pure sample of (*Z*)-vinyl sulfoxide ***Z*-5f** was obtained after removing the phosphane oxide contaminant by precipitation from ether: colorless crystals, m.p. 73−75 °C (triturated; hexanes). − IR (KBr): ṽ (cm^{-1}) = 1595, 1475, 1456, 1394, 1030, 968. − ^{1}H NMR: δ = 2.32 (s, 3 H, CH_3Ph), 2.70 (s, 3 H, CH_3Ph), 6.56 (d, 1 H, *J* = 11.0, α-C*H*), 7.21−7.28 (m, 5 H, H-arom., β-C*H*). − ^{13}C NMR: δ 19.8 (CH_3Ph), 40.4 (CH_3S), 125.8, 129.4, 129.6, 130.2 (each *C*H-arom.), 130.8 (C_{ipso}), 136.4 (CH_3−*C*), 137.6 (*C*H), 138.1 (*C*H).

(*E*)-3,3-Dimethyl(methylsulfinyl)but-1-ene*[31] (5g): Colorless oil, − IR (neat): ṽ (cm^{-1}) = 2950, 2865, 1623, 1472, 1463, 1415, 1361, 1291, 1257, 1232, 1053, 967. − ^{1}H NMR: δ = 1.10 (s, 9 H, CCH_3), 2.61 (s, 3 H, CH_3S), 6.17 (d, 1 H, *J* = 15.4, α-C*H*), 6.48 (d, 1 H, *J* = 15.4, β-C*H*). − ^{13}C NMR: δ = 27.9 (CMe_3), 32.9, (CMe_3), 39.7 (S*Me*), 129.1 (*C*H), 148.4 (*C*H).

(*E*)-(Methylsulfinyl)hex-1-ene[32] (5h): Colorless oil. − IR (neat): ṽ (cm^{-1}) = 2950, 2920, 2853, 1630, 1465, 1420, 1397, 1296, 1050, 964, 924. − ^{1}H NMR: δ = 0.92 (t, 3 H, *J* = 7.3, CH_2CH_3), 1.29−1.50 (m, 4 H, CH_2-4, CH_2-5), 2.25 (dt, 2 H, *J* = 6.6, CH_2-3), 2.60 (s, 3 H, CH_3S), 6.27 (d, 1 H, *J* = 15.4, α-C*H*), 6.49 (dt, 1 H, *J* = 15.4, 6.6, β-C*H*). − ^{13}C NMR: δ = 13.4 (CH_2CH_3), 21.8 (CH_2-5), 30.0 (CH_2-4), 31.3 (CH_2-3), 40.6 (CH_3S), 133.9 (*C*H-2), 140.3 (*C*H-1).

(*E*)-1-(Methylsulfinyl)-4-phenylbut-1-ene (5i): Colorless crystals, m.p. 25.5 °C (ether/hexanes, ca. 1:1, −18 °C). − ^{13}C NMR: δ = 32.8 (CH_2), 33.8 (CH_2), 40.0 (CH_3), 125.6 (*C*H−Ph), 127.8 (*C*H−Ph), 134.3 (*C*H), 138.0 (*C*H), 139.9 (C_{ipso}). − IR[21] and ^{1}H-NMR spectra are in accordance with those reported.[1f]

(*Z*)-1-(Methylsulfinyl)-4-phenylbut-1-ene* (*Z*-5i): Colorless oil. − IR[21] (neat): ṽ (cm^{-1}) = 3052, 3020, 3000, 2919, 2855, 1620, 1603, 1496, 1452, 1437, 1295, 1189, 1120, 1040. − ^{1}H NMR: δ = 2.26 (s, 3 H, CH_3), 2.54−2.89 (m, 4 H, CH_2CH_2), 6.14 (dt, 1 H, *J* = 10.2, 6.6, C*H*=CHS), 6.24 (d, 1 H, *J* = 10.2, α-C*H*), 7.12−7.30 (m, 5 H, H-arom.). − ^{13}C NMR: δ = 30.6 (CH_2), 34.3 (CH_2), 125.8 (*C*H−Ph), 128.0 (*C*H−Ph), 128.2 (*C*H−Ph), 136.6 (*C*H), 139.6 (C_{ipso}), 140.0 (*C*H).

(1*E*,3*E*)-1-(Methylsulfinyl)-4-phenylbuta-1,3-diene* (5j): Colorless crystals, m.p. 89−90 °C (ether/hexanes, ca. 1:1). − IR[21] (neat): ṽ (cm^{-1}) = 3028, 3005, 1622, 1597, 1490, 1452, 1274, 1048, 1005, 951, 929, 877, 785, 757. − ^{1}H NMR:[22] δ = 2.67 (s, 3 H, CH_3), 6.51 (d, 1 H, *J* = 14.4, α-C*H*), 6.78−6.93 (m, 2 H, C*H*=C*H*Me), 7.06 (ddd, *J* = 14.4, 7.2, 3.1, β-C*H*), 7.29−7.47 (m, 5 H, H-arom.). − ^{13}C NMR: δ = 40.7 (CH_3), 124.5, 126.8, 128.6, 128.7, 134.6 (each *C*H), 135.7 (C_{ipso}), 136.3, 138.4 (each *C*H).

Preparation of Enantiomerically Pure Tolyl Vinyl Sulfoxides 6: Tolyl vinyl sulfoxides **6** were prepared from phosphane oxide **3** following a procedure similar to that outlined for compounds **4**. Pure (*E*)-vinyl sulfoxides **6** were obtained after column chromatography, as mentioned in Table 3. Eluents used were 25% ethyl acetate/petroleum ether, 40:60 or 25% petroleum ether/ether. The purified compounds were analyzed using chiral HPLC.

(*R*)$_S$-(*E*)-2-Phenyl-1-(*p*-tolylsulfinyl)ethene (6a): Colorless crystals, m.p.[10] 82 °C (ether/hexanes, ca. 1:1); m.p. 81 °C (dichloromethane/hexanes, ca. 1:1) (ref.[3i] 82−83 °C). − ^{13}C NMR: δ = 21.3 (CH_3), 124.8 (*C*H-Tol), 127.6 (*C*H−Ph), 128.8 (*C*H−Ph), 129.6 (CH_{para}), 130.0 (*C*H-Tol), 133.0 (*C*H), 133.7 (CHC_{ipso}), 135.8 (*C*H), 140.6 (*C*Me), 141.6 (S−C_{ipso}). − $[\alpha]_D^{20}$ = +158 (*c* = 1.0, $CHCl_3$) [ref. +166.0 (*c* = 1.14, $CHCl_3$),[5] +160.2 (*c* = 1.35, $CHCl_3$)[3i]]; *ee* > 99% (HPLC eluent H/I = 90:10). − IR[3i,21] and ^{1}H-NMR[3i,5] spectra are in accordance with those reported.

Methyl (*E*)-(R_S)-3-(*p*-Tolylsulfinyl)prop-1-enoate (6b): Colorless crystals, m.p. 91.5 °C (ether/hexanes, ca. 1:1) (ref.[13] 91−92 °C). − $[\alpha]_D^{20}$ = +441 (*c* = 0.7, acetone) [ref.[13] +421 (*c* = 1, acetone)]; *ee* > 99% (HPLC eluent H/I = 95:5[14]). − Spectral data are in accordance with those reported.[3h] − Preliminary results with regard to the yield[10] could not be substantiated.

Strategies Towards Improving the Stereoselectivity: The reactions were basically carried out according to the general procedure. In the synthesis of **4e**−2 and **4e**−2, KO*t*Bu was added to the lithiated phosphane oxide, and stirring was continued for 30 min before the aldehyde was added. For **4l**−2/3/4, LDA, LTMP, or KHMDS were added at −70 °C as a THF solution. In the case of **4l**−5, the phosphane oxide was dissolved in toluene with as little THF as possible. Upon cooling, the phosphane oxide precipitated, and THF was added until the phosphane oxide stayed in solution. The general procedure was followed from this point on.

---

[1] By oxidation of vinyl sulfides: [1a] M. Mikołajczyk, S. Grzejszczak, A. Zatorski, *J. Org. Chem.* **1975**, *40*, 1979−1984. − [1b] C. Rossi, A. Fauve, M. Madesclaire, D. Roche, F. A. Davis, R. T. Reddy, *Tetrahedron: Asymmetry* **1992**, *3*, 629−636. − By reaction of sulfinate esters with Grignard reagents: [1c] D. J. Abbott, S. Colonna, C. J. M. Stirling, *J. Chem. Soc., Perkin Trans. 1* **1976**, 492−498. − [1d] G. H. Posner, P.-W. Tang, *J. Org. Chem.* **1978**, *43*, 4131−4136. − From *anti*-alkylthiirane *S*-oxides: [1e] M. D. Refvik, R. D .J. Froese, J. D. Goddard, H. H. Pham, M. F. Pippert, A. L. Schwan, *J. Am. Chem. Soc.* **1995**, *117*, 184−192. − [1f] A. L. Schwan, M. R. Roche, J. F. Gallagher, G. Ferguson, *Can. J. Chem.* **1994**, *72*, 312−324. − From 2-hydroxyalkyl sulfoxides: [1g] E. Arce, M. Carmen Carreño, M. Belén Cid, J. L. García Ruano, *Tetrahedron: Asymmetry* **1995**, *6*, 1757−1764.

[2] H. Kosugi, M. Kitaoka, K. Tagami, A. Takahashi, H. Uda, *J. Org. Chem.* **1987**, *52*, 1078−1082.

[3] For non-stereoselective examples: Peterson olefination: [3a] F. A. Carey, O. Hernandez, *J. Org. Chem.* **1973**, *38*, 2670−2675. − [3b] M. Cinquini, F. Cozzi, L. Raimondi, *Gazz. Chim. Ital.* **1986**, *116*, 185−187. − Horner−Wadsworth−Emmons reaction: [3c] M. Mikołajczyk, S. Grzejszczak, W. Midura, A. Zatorski, *Synthesis* **1975**, 278−280. − [3d] R.W. Hoffmann, N. Maak, *Tetrahedron Lett.* **1976**, 2237−2240. − [3e] M. Mikołajczyk, S. Grzejszczak, W. Midura, A. Zatorski, *Synthesis* **1976**, 396−398. − [3f] M. Mikołajczyk, W. Midura, S. Grzejszczak, A. Zatorski, A. Chefczyńska, *J. Org. Chem.* **1978**, *43*, 473−478. − [3g] B. E. de Jong, H. de Koning, H. O. Huisman, *Recl. Trav. Chim. Pays-Bas* **1981**, *10*, 410−414. − [3h] A. Guessous, F. Rouessac, C. Maignan, *Bull. Soc. Chim. Fr.* **1986**, 837−843. − One-pot Horner−Wadsworth−Emmons procedure: [3i] D. Craig, K. Daniels, A. R. McKenzie, *Tetrahedron* **1993**, *49*, 11263−11304. − [3j] From phosphonamidates: T. Koizumi, M. Iwata, N. Tanaka, E. Yoshii, *Chem. Pharm. Bull.* **1983**, *31*, 4198−4201.

[4] K. Kokin, S. Tsuboi, J. Motoyoshiya, S. Hayashi, *Synthesis* **1996**, 637−640.

[5] M. Mikołajczyk, W. Perlikowska, J. Omelańczuk, H. J. Cristau, A. Perraud-Darcy, *J. Org. Chem.* **1998**, *63*, 9716−9722.

[6] P. Bravo, A. Arnone, P. Bandiera, L. Bruché, Y. Ohashi, T. Ono, A. Sekine, M. Zanda, *Eur. J. Org. Chem.* **1999**, 111−115.

[7] [7a]A. Loupy, K. Sogadji, J. Seyden-Penne, *Synthesis* **1977**, 126−127. − [7b]G. Etemad-Moghadam, J. Seyden-Penne, *Synth. Commun.* **1984**, *14*, 565−573.

[8] [8a] T. Bottin-Strzalko, G. Etemad-Moghadam, J. Seyden-Penne, M.-J. Pouet, M.-P. Simonnin, *Nouv. J. Chim.* **1982**, *7*, 155−160. − [8b] G. Etemad-Moghadam, J. Seyden-Penne, *Tetrahedron* **1984**, *40*, 5153−5166.

[9] From phosphane oxides: [9a] P. A Otten, H. M. Davies, A. van der Gen, *Tetrahedron Lett.* **1995**, *36*, 781−784. − [9b] P. A. Otten, H. M. Davies, J. H. van Steenis, S. Gorter, A. van der Gen, *Tetrahedron* **1997**, *53*, 10527−10544. − From phosphonates: [9c] M. Mikołajczyk, J. A. Krysiak, W. H. Midura, M. W. Wieczorek, J. Błaszczyk, *Tetrahedron: Asymmetry* **1996**, *7*, 3513−3520. − [9d] T. H. Kim, E. J. Lee, D. Y. Oh, *Bull. Korean Chem. Soc.* **1996**, *17*, 4−5.

[10] J. J. G. S. van Es, Ph. D. Dissertation, Leiden University, **1992**.

[11] For **1**: [11a] N. W. Alcock, J. M. Brown, P. L. Evans, *J. Organomet. Chem.* **1988**, *356*, 233−247. − For **1** and **2**: [11b] M. I. Kabachnik, M. Mikołajczyk, M. Popielarczyk, F. I. Bel′skii, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1989**, 2033−2036. − [11c] J. Drabowicz, P. Łyżwa, M. Popielarczyk, M. Mikołajczyk, *Synthesis* **1990**, 937−938.

[12] M. Mikołajczyk, W. Midura, M. Kajtár, *Phosphorus Sulphur* **1988**, *36*, 79−84.

[13] C. Cardellicchio, A. Iacuone, F. Naso, *Tetrahedron Lett.* **1995**, *36*, 6563−6566.

[14] C. Cardellicchio, F. Naso, A. Scilimati, *Tetrahedron Lett.* **1994**, *36*, 4635−4638.

[15] J. J. G. S. van Es, unpublished results.

[16] T. R. Kelly, T. E. Schmidt, J. G. Haggerty, *Synthesis* **1972**, 544−545.

[17] J. I. Grayson, S. Warren, *J. Chem. Soc., Perkin Trans. 1* **1977**, 2263−2272.

[18] For **8** and **9**: [18a] H. Hellmann, J. Bader, *Tetrahedron Lett.* **1961**, 724−729. For **9**: [18b] G. Ya. Legin, *J. Gen. Chem. USSR* **1976**, *46*, 540−543.

[19] The sulfones were detectable by NMR on the basis of the δ value of their aliphatic protons: **5a** (R^1 = Ph): ^1H NMR: δ = 4.28 (d, J_{PH} = 10.2, CH_2). − **5b** (R^1 = Me): ^1H NMR: δ = 3.31 (s, 3 H, CH_3), 4.04 (d, 2 H, J_{PH} = 10.2, CH_2).

[20] Compounds ***Z*-5e** and ***Z*-5f** were obtained as mixtures with sulfone **9** after column chromatography.

[21] Recorded with a Perkin−Elmer FT-IR Paragon 1000 spectrometer.

[22] Recorded with a JEOL NM FX-200 instrument.

[23] The melting point mentioned in the preliminary report was probably in error.

[24] H. Watanabe, H. Shimizu, K. Mori, *Synthesis* **1994**, 1249−1254.

[25] [25a] K. Takaki, T. Maeda, M. Ishikawa, *J. Org. Chem.* **1989**, *54*, 58−62. − [25b] The (*Z*) isomer, which in our case was not isolated, has also been reported: C. Cardellicchio, V. Fiandanese, F. Naso, *J. Org. Chem.* **1992**, *57*, 1718−1722).

[26] The shift of the β-vinylic proton signal (in CCl_4) has been reported: H. Okamura, Y. Mitsuhira, H. Takei, *Chem. Lett.* **1978**, 517−520.

[27] E. Guittet, S. Julia, *Synth. Commun.* **1981**, *11*, 697−708.

[28] H. Langhals, M. Julia, D. Uguen, *Liebigs Ann. Chem.* **1982**, 2216−2222.

[29] This compound has been reported, but no physical data were published: see ref.[4]

[30] G. A. Russell, E. G. Janzen, H.-D. Becker, F. J. Smentowski, *J. Am. Chem. Soc.* **1962**, *84*, 2652−2653.

[31] The ^1H- and ^{13}C-NMR spectra of the (*Z*) isomer have been reported, without assignment of stereochemistry: T. Arenz, H. Frauenrath, G. Raabe, M. Zorn, *Liebigs Ann. Chem.* **1994**, 931−942.

[32] This compound has been reported (probably as a mixture of isomers): D. E. O'Connor, W. I. Lyness, *J. Am. Chem. Soc.* **1964**, *86*, 3840−3846.

Received February 23, 2000
[O00085]