Stereoselective Synthesis of Racemic and Optically Active *E*-Vinyl and *E*-Dienyl Sulfoxides via Wittig Reaction of α-Sulfinyl Phosphonium Ylides

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Received June 9, 1998

A series of α-sulfinyl phosphonium ylides have been obtained in the reaction of phosphonium mono- and diylides with sulfinic acid esters. The use of (−)-(*S*)-menthyl *p*-toluenesulfinate in this reaction afforded the corresponding (*S*)-((*p*-tolylsulfinyl)methyl)triphenylphosphonium ylide. The Wittig reaction of these ylides with saturated and unsaturated aldehydes resulted in the formation of racemic and optically active (+)-(*R*)-vinyl and dienyl sulfoxides with the E-geometry. The synthesis of (+)-(*R*)-((*p*-tolylsulfinyl)methyl)triphenylphosphonium iodide as a precursor of the optically active ylide has also been described.

Introduction

α,*β*-Unsaturated sulfoxides are valuable intermediates in a variety of synthetic transformations and useful building blocks in the synthesis of biologically active compounds.[1] Vinyl sulfoxides display three main types of reactivity. Thus, they undergo electrophilic addition to the carbon−carbon double bond, are Michael acceptors in addition of carbon and heteroatom nucleophiles, and serve as dienophiles in the Diels−Alder reaction. Moreover, it is also possible to generate α-lithiated vinyl sulfoxides and use them as nucleophilic reagents. Recently, the use of chiral, enantiomerically pure vinyl sulfoxides in asymmetric synthesis has received increasing attention.[2,3]

The general methods of the synthesis of optically active α,*β*-unsaturated sulfoxides are based on the Andersen reaction of (−)-(*S*)-menthyl *p*-toluenesulfinate with vinylic Grignard reagents[4] and the Horner−Wittig reaction of (+)-(*S*)-dimethoxyphosphorylmethyl *p*-tolyl sulfoxide with carbonyl compounds developed in our laboratory.[5] However, the efficient, stereoselective synthesis of arbitrarily substituted vinyl sulfoxides with defined *E*- or *Z*-geometry is still faced with difficulties. The first method requires the synthesis of vinylic organometallic reagents of desired geometry while the Horner−Wittig reaction is nonstereoselective and usually affords mixtures of *E*- and *Z*-isomeric vinyl sulfoxides (Scheme 1).[6,7]

Optically pure *E*- and *Z*-α,*β*-unsaturated sulfoxides can be prepared by stereoselective reduction of chiral 1-alkynyl sulfoxides, which, in turn, are synthesized from (−)-(*S*)-menthyl *p*-toluenesulfinate and alkynylmagnesium bromides (Scheme 2).[8,9]

In the hope that the Wittig reaction will occur in a stereoselective way, we turned our attention to α-sulfinyl phosphorus ylides. Surprisingly, before our studies this class of compounds was practically unknown and their reactivity unexplored. In 1968 Hamid and Trippett[10] isolated α-sulfinyl ylide **1a** from the reaction between phenyl sulfine and the corresponding phosphorus ylide. In the American patent[11] from 1972 three other α-sulfinyl phosphorus ylides **1b**−**d** stabilized by an ester or cyano group were reported. They were prepared by condensation of phosphorus ylides with sulfinyl chlorides in the presence of triethylamine. More recently, Aitken et al.[12] used the latter method to obtain a series of α-sulfinyl α-phenyl triphenylphosphonium ylides for their vacuum pyrolysis studies. However, both reactions shown in Scheme 3 do not allow the synthesis of optically active (at sulfur) α-sulfinyl ylides **1**.

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(2) (a) Carreño, M. C. *Chem. Rev.* **1995**, *95*, 1717−1760. (b) Aversa, M. C.; Barattucci, A.; Bonaccorsi, P.; Giannetto, P. *Tetrahedron: Asymmetry*, **1997**, *8*, 1339−1367.

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(6) For a recent review on α-phosphoryl sulfoxides see: Mikołajczyk, M.; Bałczewski, P. In *Advances in Sulfur Chemistry*; Block, E., Ed.; JAI Press Inc.: Greenwich, CT, 1994; Vol. 1, pp 41−96.

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(8) Kosugi, H.; Kitaoka, M.; Tagami, K.; Takahashi, A.; Uda, H. *J. Org. Chem.* **1987**, *58*, 1078−1082.

(9) Interestingly, *Z*-vinyl sulfoxides can be transformed into their *E*-isomers without racemization at sulfur via lithiation and protonation: Fawcett, J.; House, S.; Jenkins, P. R.; Lawrance, N. J.; Russell, D. R. *J. Chem. Soc., Perkin Trans. 1* **1993**, 67−73.

(10) Hamid, A. M.; Trippett, S. *J. Chem. Soc. C* **1968**, 1612−1615.

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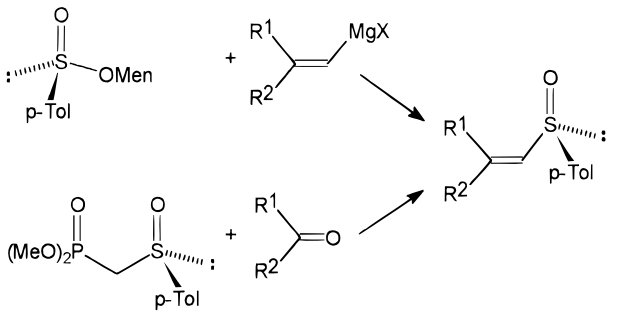
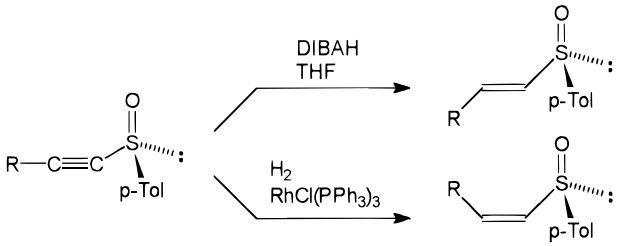
10.1021/jo981100e CCC: $15.00
Published on Web 12/01/1998

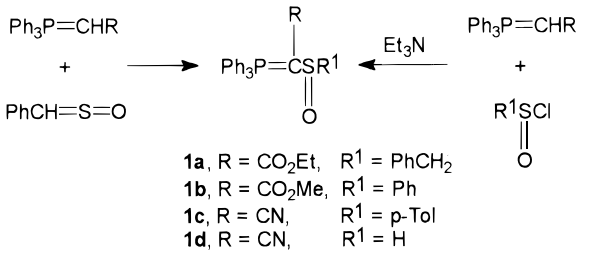
Scheme 1



Scheme 2



Scheme 3



In this paper we wish to report a new general synthesis of racemic and enantiopure α-sulfinyl phosphorus ylides and their stereoselective reaction with carbonyl compounds leading to vinyl and dienyl sulfoxides of *E*-geometry.

Results and Discussion

One-Pot Synthesis of Racemic *E*-Vinyl and *E*-Dienyl Sulfoxides from α-Sulfinyl Phosphonium Ylides. To establish the stereochemistry of the Wittig reaction of α-sulfinyl phosphonium ylides and to develop a new synthesis of the latter, in the first part of this work the desired α-sulfinyl phosphonium ylide **6a** was obtained by treatment of methyltriphenylphosphonium ylide (**3**) (generated from methyltriphenylphosphonium iodide (**2**) and *n*-BuLi) with racemic methyl *p*-toluenesulfinate (**4a**) in a benzene solution.

Due to a fast proton transfer from the primarily formed α-sulfinyl methyltriphenylphosphonium salt **5a** to the ylide **3** regenerating the starting phosphonium salt **2**, the reaction was carried out using a 0.5 equiv amount of the sulfinate **4a** with respect to **3**. The ylide **6a** so generated (Scheme 4) was then treated with aldehydes **7a**−**h** at room temperature, and the reaction mixture was refluxed for ca. 10 h in benzene or THF. The usual workup gave the crude sulfoxides **8a**−**h** which, after determination of the *E*/*Z* ratio by ^{1}H NMR spectroscopy, were purified by column chromatography. The yields and *E*:*Z* ratios of the sulfoxides **8** are listed in Table 1.

It was gratifying to find that the synthesis of vinyl and dienyl sulfoxides **8** via the Wittig reaction is very efficient

Scheme 4

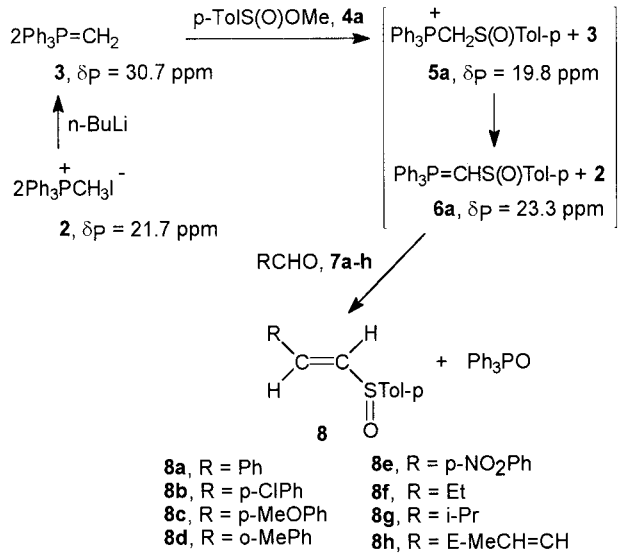
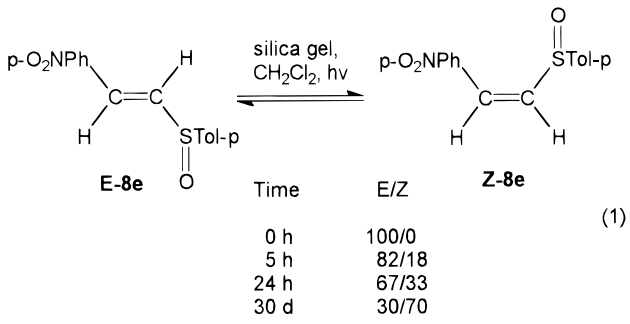


Table 1. Racemic α,β-Unsaturated Sulfoxides 8, $R^1S(O)CH{=}CHR^2$, Prepared by Wittig Reaction with α-Sulfinyl Phosphonium Ylide 6a

no.	R^1	R^2	solvent	*E*/*Z* (%)[a]	yield (%)[b,c]
8a	*p*-Tol	Ph	THF	68/32	84
			C_6H_6	97/3	88
8b	*p*-Tol	*p*-ClPh	C_6H_6	99/1	78
8c	*p*-Tol	p-MeOPh	C_6H_6	100/0	85
8d	*p*-Tol	*o*-MePh	C_6H_6	96/4	70
8e	*p*-Tol	*p*-NO_2Ph	C_6H_6	100/0	50
8f	*p*-Tol	Et	C_6H_6	100/0	62
8g	*p*-Tol	*i*-Pr	C_6H_6	100/0	65
8h	*p*-Tol	*E*-MeCH=CH	C_6H_6	100/0	66

[a] Determined by ^{1}H NMR analysis of the crude reaction mixture. [b] After column chromatography. [c] Calculated on 0.5 equiv of the phosphonium iodide **2**.

and fully or almost fully *E*-stereoselective, especially when benzene is used as a solvent. The *E*-geometry of the double bond in **8** was unambiguously confirmed by observing characteristic coupling patterns of the α-olefinic proton signals (doublets) and *J* values (ca. 15.5 Hz) (eq 1).



Time	E/Z
0 h	100/0
5 h	82/18
24 h	67/33
30 d	30/70

(1)

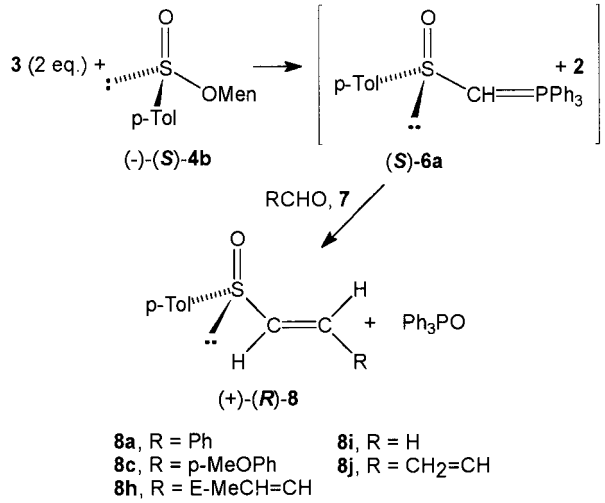
Interestingly, 1-(p-tolylsulfinyl)-2-(*p*-nitrophenyl)ethene (**8e**) obtained according to the procedure described above as the *E*-isomer turned out to be configurationaly unstable. Its purification by column chromatography on silica gel with CH_2Cl_2 as eluent was accompanied by isomerization affording a mixture of ***E*-8e** and ***Z*-8e** in a 82:18 ratio. This ratio was unchanged when the pure, solid sulfoxide **8e** was stored in the dark. When, however, the sulfoxide **8e** was kept in a CH_2Cl_2 solution in the presence of silica gel for a longer time, the isomerization

Table 2. Optically Active Sulfoxides *E*-(*R*)-8, TolS(O)CH=CHR, Prepared by Wittig Reaction with (*S*)-α-Sulfinyl Phosphonium Ylide 6a

		$[\alpha]_D$ (solvent)			
no.	R	present work	lit. data	ee (%)	yield (%)
8a	Ph	+159.5 ($CHCl_3$)	+166.0 ($CHCl_3$)[5]	100[a]	87
8c	*p*-MeOPh	+100.0 ($CHCl_3$)		96	82
8h	*E*-MeCH=CH	+287.5 (acetone) +158.5 ($CHCl_3$)	+224.5 (Acetone)[17]	100	61
8i	H	+389.7 (EtOH)	+413 (EtOH)[8]	94	40
8j	CH_2=CH	+283.4 ($CHCl_3$)	+283.8 ($CHCl_3$)[18]	100	20

[a] Contains 1.4% of *Z*-isomer. This value was calculated based on the known rotations values of *E*- and *Z*-isomers of **8a** equal to $[\alpha]_D$ = +172.92 ($CHCl_3$) and $[\alpha]_D$ = −766.67 ($CHCl_3$), respectively.

Scheme 5



was slowly occurring and resulting after 30 days in the formation of a mixture of ***E*-8e** and ***Z*-8e** in a 30:70 ratio.

Synthesis of Optically Active *E*-Vinyl and *E*-Dienyl Sulfoxides from (*S*)-((p-Tolylsulfinyl)methyl)triphenylphosphonium Ylide. In contrast to sulfinyl chlorides and achiral sulfines, sulfinic esters are optically stable compounds and easily available as pure enantiomers or diastereomers.[13] Therefore, the present approach to the synthesis of α-sulfinyl phosphorus ylides **1** makes it possible to prepare them in an enantioselective way from optically active sulfinates. As in the case of (+)-(*S*)-dimethoxyphosphorylmethyl *p*-tolyl sulfoxide,[5] the optically active title ylide **6a** was prepared from (−)-(*S*)-menthyl *p*-toluenesulfinate (**4b**)[14]—a common substrate in the synthesis of optically active sulfinyl derivatives—upon treatment with the ylide **3** (Scheme 5). Then, the ylide **6a** was reacted in situ with saturated and unsaturated aldehydes **7** to afford optically active sulfoxides ***E*-8**. For the synthesis of the sulfoxide **8i** trimer of formaldehyde was used. The results of this one-pot, enantioselective synthesis of **8** are summarized in Table 2.

It deserves to be noted that in all cases the ^{1}H NMR spectra of the crude, optically active sulfoxides **8** did not reveal the presence of the corresponding *Z*-isomers. Since vinyl and dienyl sulfoxides ***E*-8** formed were dextrorotatory, the *R*-chirality at sulfur was assigned to all of them.[15] Moreover, taking into account the fact that the Wittig reaction does not disturb configuration at sulfur, the *S*-configuration was assigned to the ylide **6a**. Consequently, the reaction of (−)-(*S*)-menthyl sulfinate **4b** with the ylide **3** should occur with inversion of configuration at sulfur, as depicted in Scheme 5.

A comparison of the optical rotation values of the sulfoxides ***E*-(+)-(*R*)-8** obtained in the present work with those reported in the literature and claimed to correspond to enantiopure forms (see Table 2) showed that only in the case of **8j** optical rotations were the same. A big difference in rotation values was noted for the sulfoxide **8h**, our value being much higher. Therefore, it was prudent to determine enantiomeric purity of **8** by an independent and accurate method. We decided to apply the NMR method and use (−)-(*S*)-*tert*-butylphenylphosphinothioic acid (**9**), t-BuPhP(S)OH, as an excellent chiral solvating agent,[16] especially for sulfoxides.[16a] In the case of the racemic sulfoxide (±)-***E*-8a**, the ^{1}H NMR spectrum of the diastereomeric solvates formed with (−)-(***S*)-9** exhibited clearly resolvable α-vinyl proton doublets at δ = 6.91 and δ = 6.89 ppm ($\Delta\delta$ = 4.9 Hz), while the spectrum of the sample of **E-8a**, $[\alpha]_D$ = +159.5, in the presence of this acid exhibited only one doublet at δ = 6.89 ppm. This indicated that our reaction product was enantiomerically pure. Its smaller rotation value than that reported by us earlier[5] is most probably due to minute amounts (1.4%) of the *Z*-isomer of **8a** which has much larger rotation value and opposite in sign (***Z*-8a**, $[\alpha]_D$ = −766.7[5]). In a similar way, the enantiomeric purity of the unknown sulfoxide ***E*-8c** was determined as 96% [$(\Delta\delta_{H(C1)}$ = 4.9 Hz for a mixture of (±)-***E*-8c** and (−)-(***S*)-9**]. The racemic sulfoxide ***E*-8i**, when mixed with (−)-(***S*)-9**, formed diastereomeric solvates which showed in the ^{1}H NMR spectrum different chemical shifts for each vinylic proton (three double doublets). Interestingly, the $\Delta\delta$ value for cis- and trans-protons at C2 was also different and equal to 2.5 and 5.1 Hz, respectively. The ^{1}H NMR spectrum of a mixture of the sulfoxide ***E*-8i**, $[\alpha]_D$ = +389.7, and (−)-(***S*)-9** allowed one to determine its enantiomeric purity as 94% and to confirm that the sulfoxide ***E*-8b**, $[\alpha]_D$ = +413, obtained by Kosugi et al.[8] was enantiopure. Finally, the ^{1}H NMR spectra of the racemic and enantiopure sulfoxide ***E*-8h** in the presence of (−)-(***S*)-9** (see Figure 1) showing well-resolved doublets of the α-vinyl proton ($\Delta\delta$ = 3.2 Hz) confirmed a full enantiomeric purity of the dienyl sulfoxide ***E*-8h** prepared herein by the Wittig reaction.

(13) Mikołajczyk, M.; Drabowicz, J. *Top. Stereochem.* **1982**, *13*, 333−468.

(14) Solladie, G. *Synthesis* **1981**, 185−196. (−)-(*S*)-menthyl *p*-toluenesulfinate (**4b**) was obtained from (−)-(1*R*,2*S*,5*R*)-menthol.

(15) For a relationship between the chirality at sulfur, *E*,*Z*-geometry, and sign of optical rotation in α,β-unsaturated sulfoxides, see: Mikołajczyk, M.; Midura, W. H.; Wladislaw, B.; Biaggio, F. C.; Marzorati, L. *Tetrahedron* **1997**, *53*, 2959−2972.

(16) (a) Drabowicz, J.; Dudziński, B.; Mikołajczyk, M.; *Tetrahedron: Asymmetry* **1992**, *3*, 1231−1232. (b) Omelańczuk, J.; Mikołajczyk, M.; *Tetrahedron: Asymmetry* **1996**, *7*, 2687−2694. (c) Drabowicz, J.; Dudziński, B.; Mikołajczyk, M.; Colonna, S.; Gaggero, N. *Tetrahedron: Asymmetry* **1997**, *8*, 2267−2270.

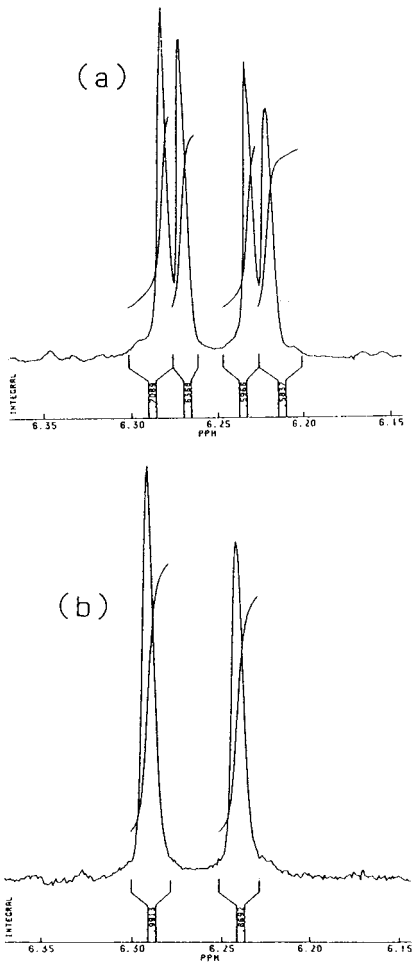
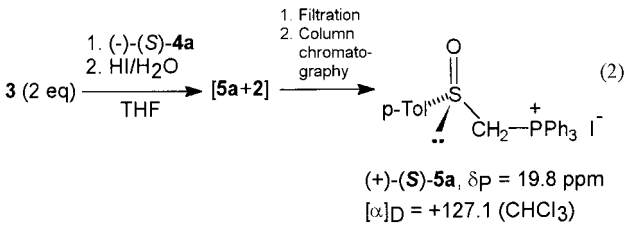


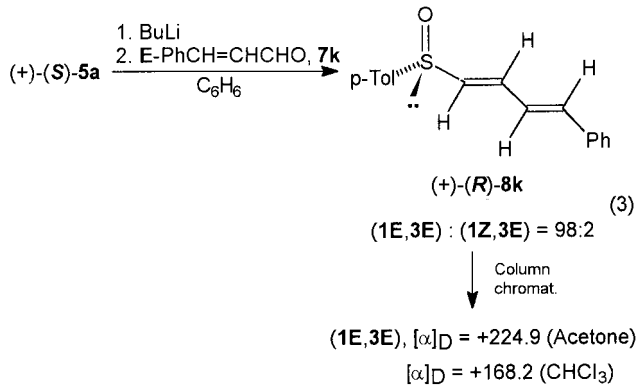
Figure 1. ^{1}H NMR (300 MHz) spectra (α-dienyl proton region) of the racemic (a) and enantiopure (b) sulfoxide ***E*-8h** in the presence of (−)-(S)-*tert*-butylphenylphosphinothioic acid (**9**).

Having established the *E*-stereochemistry and enantioselectivity of the Wittig reaction of the optically active, α-sulfinyl ylide **6a**, we next focused our attention on isolation and characterization of the α-sulfinyl phosphonium salt **5a** in the hope that it may be the best starting reagent for the synthesis of optically active α,*β*-unsaturated sulfoxides. It was found that, when the reaction of the ylide **3** with the sulfinate (−)-(***S*)-4b** was carried out in THF and the reaction mixture neutralized with hydroiodic acid, two phosphonium iodides **5a** and **2** were formed (eq 2). Fortunately, the latter turned out to be

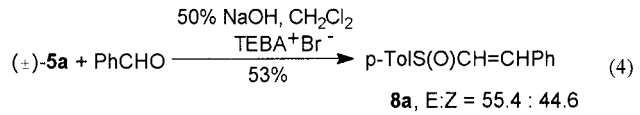


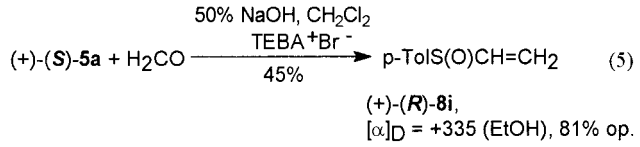
insoluble in THF and was removed simply by filtration. Evaporation of the solvent and column chromatography afforded the desired, analytically pure α-sulfinyl phosphonium salt (+)-**5a** in 70% yield.

When the salt (+)-(***S*)-5a** was used for the Wittig reaction with *trans*-cinnamaldehyde (**7k**), the corresponding dienyl sulfoxide **8k** was formed as a mixture of two geometrical isomers **1*E***, **3*E*** and **1*Z***, **3*E*** in a 98:2 ratio as revealed by the ^{1}H NMR spectra (α-vinyl protons appeared at $\delta = 6.43$ and 6.21 ppm with $^3J = 14.7$ and 9.7 Hz, respectively). Column chromatography afforded the enantiomerically pure sulfoxide (**1*E*,3*E***)−(+)-(***R*)-8k** with the same rotation values as the literature ones ($[\alpha]_D = +225.1$ (acetone);[17] $[\alpha]_D = +168.9$ ($CHCl_3$)[18]) (eq 3).



However, the Wittig reaction with the racemic or optically acitve salt **5a** carried out under phase-transfer catalytic conditions gave less satisfactory results in terms of *E*-stereoselectivity and optical purity. Thus, treatment of (±)-**5a** with benzaldehyde under classical PTC conditions (see eq 4) resulted in the formation of **8a** as a





mixture of *E* and *Z* isomers in comparable amounts. On the other hand, the sulfoxide (+)-(***R*)-8i** obtained from the reaction of (+)-(***S*)-5a** with formaldehyde (40% water solution) was only 81% optically pure (eq 5).

Synthesis of Racemic and Optically Active α,*β*-Unsaturated Sulfoxides from Sulfinates and Lithium Dimethyldiphenylphosphonium Diylide.[19] Although the synthesis of the α-sulfinyl phosphonium ylide **6a** and α-sulfinyl phosphonium iodide **5a** has been accomplished as shown in Scheme 4 and eq 2, this method has one drawback connected with the formation of the ylide **6a** together with the starting phosphonium salt **2**. This is due to intermolecular proton transfer from **5a** to **3**. To overcome this problem, it is advantageous to use instead of the monoylide **3** dimethyldiphenylphosphonium diylide (**11**),[20] which may be easily generated from the corresponding phosphonium salt **10** and 2 equiv of BuLi. As

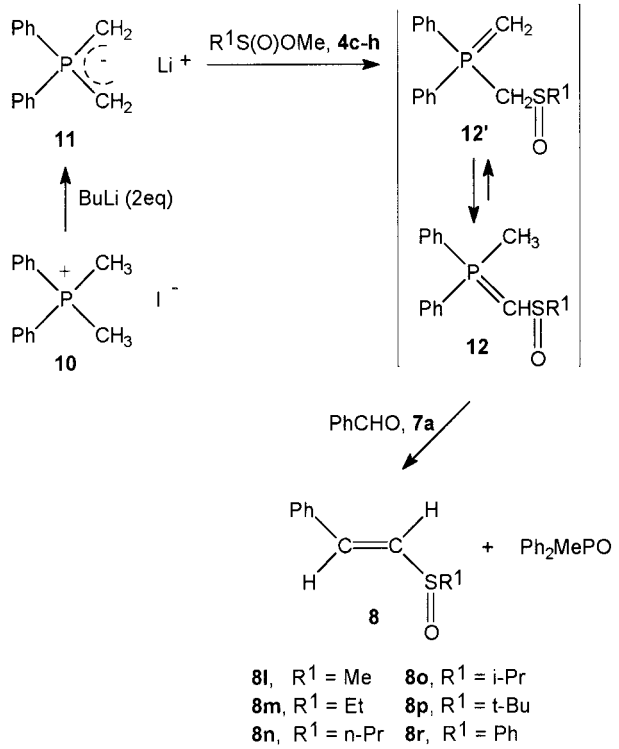
(17) Solladie, G.; Ruiz, P.; Colobert, F.; Carreño, M. C.; Garcia-Ruano, J. L. *Synthesis* **1991**, 1011−1012.

(18) (a) Paley, R. S.; de Dios, A.; Fernandez de la Pradilla, R. F. *Tetrahedron Lett.* **1993**, *34*, 2429−2432. (b) Paley, R. S.; de Dios, A.; Estroff, L. A.; Lafontaine, J. A.; Montero, C.; McCullcy, D. J.; Rubio, M. B.; Ventura, M. P.; Weers, H. L.; Fernandez de la Pradilla, R. F.; Castro, S.; Dorado, R.; Morente, M. *J. Org. Chem.* **1997**, *62*, 6326−6343.

(19) A part of this work has been published in a preliminary form: Mikołajczyk, M.; Perlikowska, W.; Omelańczuk, J.; Cristau, H.-J.; Perraud-Dercy, A. *Synlett* **1991**, 913−915.

(20) Cristau, H.-J. *Chem. Rev.* **1994**, *94*, 1299−1313.

Scheme 6



8l, R^1 = Me **8o**, R^1 = i-Pr
8m, R^1 = Et **8p**, R^1 = t-Bu
8n, R^1 = n-Pr **8r**, R^1 = Ph

Table 3. Racemic α,β-Unsaturated Sulfoxides 8, $R^1S(O)CH{=}CHR^2$, Prepared by Wittig Reaction with α-Sulfinyl Phosphonium Ylides 12

no.	R^1	R^2	solvent	*E*/*Z* (%)[a]	yield (%)[b]
8l	Me	Ph	THF	91/9	78
8m	Et	Ph	THF	100/0	70
8n	*n*-Pr	Ph	THF	100/0	71
8o	*i*-Pr	Ph	THF	100/0	75
8p	*t*-Bu	Ph	THF	100/0	48
8r	Ph	Ph	THF	96/4	69

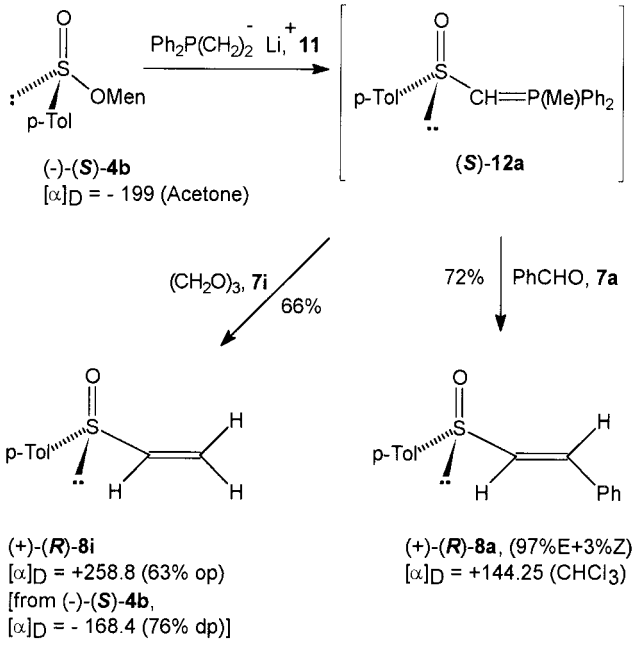
[a] Determined by ^{1}H NMR analysis of the crude reaction mixture. [b] After column chromatography.

expected, the diylide **11** reacted with methyl sulfinates **4c**−**h** used in equimolar amounts to give (α-sulfinylmethyl)diphenylmethylphosphonium ylides **12** as the only reaction products. In this case, the primarily formed ylides **12′** were transformed into more stable ylides **12** via intramolecular proton migration. Subsequent reaction of the latter with benzaldehyde **7a** resulted in the formation of vinyl sulfoxides **8l**−**r** in high yields (over 70%) and with full or almost full *E*-stereoselectivity (Scheme 6, Table 3). A lower yield (48%) was only noted for *tert*-butyl styryl sulfoxide (**8p**), which under the reaction conditions (reflux in THF for 20h) underwent partial decomposition.

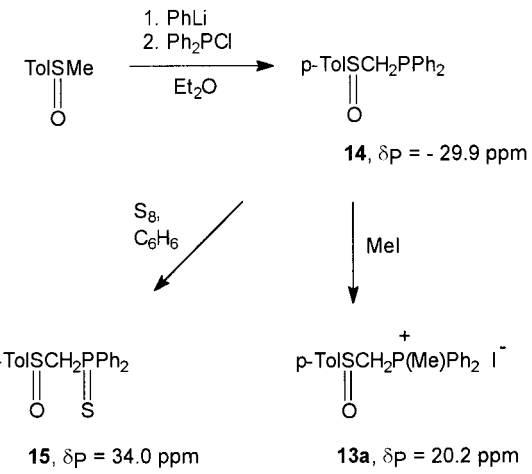
When (−)-(*S*)-menthyl sulfinate **4b** was reacted with the diylide **11**, the corresponding optically active α-sulfinyl ylide **12a** was generated with inversion of configuration at the sulfur atom. The in situ reaction of this ylide with carbonyl compounds produced optically active vinyl sulfoxides. The results with benzaldehyde **7a** and formaldehyde **7i** are shown in Scheme 7.

It was also of interest to prepare (α-sulfinylmethyl)-diphenylmethylphosphonium iodide (**13a**), which could serve as a substrate for the Wittig reaction under different experimental conditions. Unfortunately, our attempt to quench the ylide **12a** with hydroiodic acid and isolate the salt **13a** was unsuccessful. Therefore, another strategy was applied. On the basis of the literature data[21,22] we were able to obtain in 53% yield diphenylphosphinylmethyl *p*-tolyl sulfoxide (**14**) from the reaction of the methyl *p*-tolyl sulfoxide carbanion with diphenylchlorophosphine. It should be noted that we used phenyllithium and not LDA for deprotonation of sulfoxide which resulted in a more efficient and cleaner condensation. For characterization purposes, **14** was converted into the corresponding phosphine sulfide **15** by addition of elemental sulfur. Methylation of **14** with freshly distilled methyl iodide afforded the desired phosphonium salt **13a** as a crystalline substance, mp 104−106 °C. Its Wittig reaction with benzaldehyde **7a** gave the sulfoxide **8a** which was a 95:5 mixture of *E*- and *Z*-isomers, respectively (Scheme 8).

Scheme 7



Scheme 8



Conclusions

In summary, a new method for the synthesis of *E*-vinyl and *E*-dienyl sulfoxides has been developed which is

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based on the Wittig reaction of α-sulfinyl phosphonium ylides. The latter, practically unknown class of phosphonium ylides, have been obtained from phosphonium monoylides or diylides upon treatment with sulfinic acid esters. This approach is particularly attractive as the use of (−)-(*S*)-menthyl *p*-toluenesulfinate allowed one to synthesize in an enantioselective way optically active (*S*)-α-sulfinyl phosphonium ylides and use them for the preparation of (+)-(*R*)-vinyl and -dienyl sulfoxides of *E*-geometry. In addition, (+)-(*R*)-((*p*-tolylsulfinyl)methyl)-triphenylphosphonium iodide as a suitable precursor of the corresponding ylide has been obtained and characterized. This study has also demonstrated that enantiomeric *tert*-butylphenylphosphinothioic acids may be used as efficient chiral solvating agents for determination of enantiomeric excesses of vinyl and dienyl sulfoxides.

Experimental Section

All melting and boiling points were uncorrected. ^{1}H NMR spectra were recorded at 200.13 MHz. The ^{31}P NMR spectra were measured at 81.0 and 121.49 MHz. Optical rotation measurements were made with automatic photopolarimeter (sensitivity ± 0.002°). TLC was done on silica gel (Merck Silica 60 F_{254}) and column chromatography on Merck Silica gel 230−400 mesh. Solvents and commercial reagents were distilled and dried by conventional methods before use. All moisture sensitive reactions were carried out in a dry argon atmosphere.

Starting methyltriphenylphosphonium iodide (**1**) was prepared by quaternization of triphenylphosphine with methyl iodide by standard method, and dimethyldiphenylphosphonium iodide was prepared according to the reported procedure.[23a,b] Methyl *p*-toluenesulfinate (**4a**) and (−)-(*S*)-menthyl *p*-toluenesulfinate (**4b**) were prepared according to the method described by Solladie.[14] Starting methyl sulfinates **4c**−**h** were obtained from the corresponding sulfinyl chlorides and methanol in the presence of triethylamine according to the method described by Douglas[24] and Brownbridge.[25]

Synthesis of Racemic and Optically Active α,β-Unsaturated Sulfoxides 8a−h. General Procedure. To a solution of methyltriphenylphosphonium iodide (**2**) (0.81 g, 2 mmol) in dry C_6H_6 (50 mL) at room-temperature *n*-BuLi (1.4 mL of 1.5 M solution in hexanes, 2.1 mmol) was added, and the mixture was stirred for 1 h. After this time, methyl or menthyl *p*-toluenesulfinate (**4a**,**b**) (1 mmol) was added and the mixture was stirred for 1 h. Then, freshly distilled aldehydes **7a**−**h** (1.5 mmol) were added and the mixture was refluxed for 10 h. After this period, the mixture was cooled to room temperature and quenched by the addition of 0.2 N HCl to the pH ∼ 3−4. Next, water (10 mL) was added and the layers were separated. The water layer was extracted with $CHCl_3$ (2 × 15 mL), and combined organic layers were dried over Na_2SO_4. Then, the solvents were evaporated and the crude vinyl sulfoxides were analyzed by ^{1}H NMR and purified by column chromatography on silica gel using hexane−dichloromethane as the eluent.

Racemic α,β-Unsaturated Sulfoxides 8a−h. 1-(*p*-Tolylsulfinyl)-2-phenylethene (8a): ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H), 6.43 and 6.80 [2d, J_{AB} = 10.6 Hz (*Z*), J_{AB} = 15.5 Hz (*E*), 1H], 7.09 and 7.21−7.61 [d, J_{AB} = 10.6 Hz (*Z*) and m, 10H].[5]

1-(*p*-Tolylsulfinyl)-2-(*p*-chlorophenyl)ethene (8b): Mp 95−97 °C; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H), 6.79 [d, J_{AB} = 15.5 Hz (*E*), 1H], 7.22−7.64 (m, 9H).[26]

1-(*p*-Tolylsulfinyl)-2-(p-methoxyphenyl)ethene (8c): Mp 81−82 °C; ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3H), 3.80 (s, 3H), 6.67 [d, J_{AB} = 15.5 Hz (*E*)], 6.87−7.67 (m, 9H). Anal. Calcd for $C_{16}H_{16}O_2S$; C, 70.56; H, 5.92; S, 11.77. Found: C, 70.32; H, 6.00; S, 11.64.

1-(*p*-Tolylsulfinyl)-2-(*o*-methylphenyl)ethene (8d): Colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3H), 2.45 (s, 3H), 6.52 and 6.73 [2d, J_{AB} = 10.3 Hz (*Z*), J_{AB} = 15.4 Hz (*E*), 1H], 7.14−7.66 (m, 9H). Anal. Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29; S, 12.51. Found: C, 75.08; H, 6.26; S, 12.42.

1-(*p*-Tolylsulfinyl)-2-(*p*-nitrophenyl)ethene (8e) (*E*:*Z*/82:18): Mp 141−143 °C; ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3H), 6.64 and 6.99 [2d, J_{AB} = 10.7 Hz (*Z*), J_{AB} = 15.4 Hz (*E*), 1H], 7.12 and 7.21−8.22 [d, J_{AB} = 10.7 Hz (*Z*), and m, 9H]. Anal. Calcd for $C_{15}H_{13}O_3SN$: C, 62.70; H, 4.56; S, 11.16. Found: C, 62.52; H, 4.68; S, 11.02.

1-(*p*-Tolylsulfinyl)-1-butene (8f): Colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.03 (t, 3H, *J* = 7.4 Hz), 2.19−2.23 (m, 2H), 2.37 (s, 3H); 6.18 (dt, J_{AB} = 15.2 Hz, J_{AB} = 1.6 Hz, 1H), 6.61 (dt, J_{AB} = 15.2 Hz, *J* = 6.2 Hz, 1H), 7.28−7.50 (m, 4H). Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26; S, 16.50. Found: C, 68.20; H, 7.10; S, 16.40.

1-(*p*-Tolylsulfinyl)-4-methyl-1-butene (8g): Colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.05 (d, 6H, *J* = 6.8 Hz), 2.39 (s, 3H) 2.42−2.54 (m, 1H), 6.14 (dd, J_{AB} = 15.3 Hz *J* = 1.4 Hz, 1H), 6.55 (dd, J_{AB} = 15.3 Hz, *J* = 6.3 Hz, 1H), 7.25−7.52 (m, 4H).[8]

(1*E*,3*E*)-1-(*p*-Tolylsulfinyl)-1,3-pentadiene (8h): Mp 59−60 °C; ^{1}H NMR ($CDCl_3$) (300 MHz) δ 1.80 (d, 3H, *J* = 5.3 Hz), 2.37 (s, 3H) 6.06−6.10 (m, 2H), 6.18 (d, 1H, *J* = 15.1 Hz), 6.88−6.96 (m, 1H), 7.26−7.51 (m, 4H). (Lit. 17).

Optically Active α,β-Unsaturated Sulfoxides 8a,c,h−k. (*E*)-(+)-(*R*)-1-(*p*-Tolylsulfinyl)-2-phenylethene (8a): Mp 82 °C, $[\alpha]_D$ = +159.5° (*c*, 2.11, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3H), 6.81 (d, 1H, J_{AB} = 15.5 Hz) 7.30−7.60 (m, 10H).[5]

(*E*)-(+)-(*R*)-1-(*p*-Tolylsulfinyl)-2-(p-methoxyphenyl)-ethene (8c): Mp 94−95 °C, $[\alpha]_D$ = +100° (*c*, 2.68, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3H), 3.80 (s, 3H), 6.67 (d, 1H, J_{AB} = 15.5 Hz), 6.87−7.67 (m, 9H).

(1*E*,3*E*)-(+)-(*R*)-1-(*p*-Tolylsulfinyl)-1,3-pentadiene (8h): Mp 72−73 °C, $[\alpha]_D$ = +287.6 (*c*, 0.94, acetone), $[\alpha]_D$ = +158.8 (*c*, 0.9, $CHCl_3$).[17]

(+)-(*R*)-1-(*p*-Tolylsulfinyl)ethene (8i): Colorless oil; $[\alpha]_D$ = +389.7 (*c*, 0.76, EtOH); ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H), 5.88 (d, 1H, *J* = 9.5 Hz) 6.18 (d, 1H, *J* = 16.5 Hz), 6.55 (dd, 1H, *J* = 16.5 Hz, *J* = 9.5 Hz), 7.28−7.53 (m, 4H).[4a,5,8]

(*E*)-(+)-(*R*)-1-(*p*-Tolylsulfinyl)-1,3-butadiene (8j): Colorless oil; $[\alpha]_D$ = +283.3 (*c*, 0.56, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3H), 5.40 (d, 1H, *J* = 10.8 Hz) 5.54 (d, 1H, *J* = 17.0 Hz), 6.38 (d, 1H, *J* = 15.2 Hz) 6.39 (dt, 1H, *J* = 10.5 Hz, *J* = 17.0 Hz), 6.99 (dd, 1H, *J* = 15.2 Hz, *J* = 10.3 Hz) 7.27−7.53 (m, 4H).[18a]

(1*E*,3*E*)-(+)-(*R*)-1-(*p*-Tolylsulfinyl)-4-phenyl-1,3-butadiene (8k): Mp = 102.5 °C, $[\alpha]_D$ = +224.9 (*c*, 0.55, acetone), $[\alpha]_D$ = +168.2 (*c*, 0.82, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3H), 6.43 (d, 1H, *J* = 14.7 Hz), 6.80−6.84 (m,2H), 7.14 (ddd, 1H, *J* = 14.7 Hz, *J* = 8.3 Hz, *J* = 1.9 Hz), 7.29−7.58 (M, 9H).[17,18a]

Optically Active (+)-(*S*)-(α-Sulfinylmethyl)triphenylphosphonium Iodide (5a). To a solution of methyltriphenylphosphonium iodide (**2**) (1.21 g, 3 mmol) in dry THF (35 mL) at −20 °C was added *n*-BuLi (2.1 mL of 1.55 M solution in hexanes, 3.2 mmol). The solution was stirred at −20 °C for a further 5 min and then for 1 h at room temperature. After this time, the mixture was cooled to −20 °C and (−)-(*S*)-menthyl *p*-toluenesulfinate (**4b**) (0.471 g, 1.6 mmol) was added. After 10 min stirring at −20 °C and 1 h at room temperature the mixture was quenched by the addition of 50% aqueous solution of HI (0.25 mL, 1.5 mmol). Methyltriphenylphosphonium iodide (**2**), insoluble in THF, was filtered off, and the THF was evaporated to give the crude product **5a**. To the product water (10 mL) was added, and the mixture was extracted with $CHCl_3$ (3 × 15 mL). The organic layer was washed with a water solution of $Na_2S_2O_3$ and dried over Na_2SO_4. The solvent was evaporated, and the crude product was chromatographed on silica gel using dichloromethane−methanol (2%) as the eluent. Yield: 0.57 g (70%), mp 86−88 °C,

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$[\alpha]_D$ = +127.1° (*c*, 1.62, $CHCl_3$); ^{31}P NMR ($CDCl_3$) δ_P +19.8 ppm; ^1H NMR ($CDCl_3$) δ 2.38 (s, 3H), 4.44 (dd, 1H, J_{H-H} = 14.3 Hz, J_{P-H} = 7.8 Hz), 6.70 (dd, 1H, J_{H-H} = 14.3 Hz, J_{P-H} = 13.5 Hz) 7.35 (d, 2H, J_{H-H} = 8.2 Hz) 7.50−8.16 (m, 17H). Anal. Calcd for $C_{26}H_{24}PSOI$; C, 57.57; H, 4.46; P, 5.71; S, 5.91. Found: C, 57.32; H, 4.30; P, 5.67; S, 5.98.

Racemic (α-sulfinylmethyl)triphenylphosphonium iodide (**5a**), mp 177−179 °C, was obtained in the same way using methyl *p*-toluenesulfinate (**4a**).

Synthesis of Racemic and Optically Active α,β-Unsaturated Sulfoxides via the Wittig Reaction under Two-Phase System Catalyzed by (TEBA)Br. α,β-Unsaturated sulfoxides **8a** and (+)-(***R***)-**8i** were obtained from the racemic (±)-**5a** and optically active (+)-(***S***)-**5a** and benzaldehyde **7a** and 40% aqueous formaldehyde, respectively, according to the procedure described by Mikołajczyk.[26]

Synthesis of Racemic 8l−r and Optically Active α,β-Unsaturated Sulfoxides 8a,i. General Procedure. To a stirred solution of dimethyldiphenylphosphonium iodide (0.684 g, 2 mmol) in dry THF (30 mL) at −50 °C was added *n*-BuLi (2.7 mL of 1.55 M solution in hexanes, 4.2 mmol) via a dropping funnel. The colorless diylide solution was stirred at −50 °C for a further 5 min and 1 h at room temperature. After this time, the mixture was cooled to −20 °C and methyl or menthyl sulfinate **4b**−**h** (2 mmol) was added. The mixture was stirred for 10 min at −20 °C and 1 h at room temperature; then freshly distilled benzaldehyde (0.23 g, 2.2 mmol) was added, and the mixture was refluxed with stirring for 8 h. After this period, the mixture was cooled to room temperature and quenched by addition of 0.4 N HCl to the pH 3−4. The solvent was evaporated, and water (10 mL) was added. The water solution was extracted with dichloromethane (3 × 15 mL), and the organic layer was dried (Na_2SO_4) and concentrated under reduced pressure to give the crude vinyl sulfoxide which was analyzed by ^1H NMR. The resulting products were purified by chromatography on silica gel using hexane−dichloromethane as the eluent.

Racemic α,β-Unsaturated Sulfoxides 8l−r. 1-(Methylsulfinyl)-2-phenylethene (8l): ^1H NMR ($CDCl_3$) δ 2.70 (s, 3H) 6.45 and 6.90 [2d, 1H, J_{AB} = 10.6 Hz (*Z*), J_{AB} = 15.4 Hz (*E*)], 7.05 and 7.22 [2d, 1H, J_{AB} = 10.6 Hz (*Z*), J_{AB} = 15.4 Hz (*E*)], 7.37−7.52 (m, 5H).[27,28]

1-(Ethylsulfinyl)-2-phenylethene (8m): Mp 55−57 °C; ^1H NMR ($CDCl_3$) δ 1.27 (t, 3H, *J* = 7.4 Hz), 2.68−2.91 (m, 2H), 6.78 and 7.19 (2d, 2H, J_{AB} = 15.5 Hz), 7.29−7.44 (m, 5H); MS *m/e* (%) 180 (34), 91 (100). Anal. Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71; S, 17.79. Found: C, 66.60; H, 6.75; S, 17.83.

1-(*n*-Propylsulfinyl)-2-phenylethene (8n): Mp 56−58 °C; ^1H NMR ($CDCl_3$) δ 1.06 (t, 3H, *J* = 7.4 Hz), 1.69−1.96 (m, 2H), 2.76 (t, 2H, *J* = 7.5 Hz), 6.81 (d, 1H, J_{AB} = 15.5 Hz), 7.17−7.67 (m, 6H); MS *m/e* (%) 194 (17), 135 (100). Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26; S, 16.50. Found: C, 67.99; H, 7.19; S, 16.56.

1-(Isopropylsulfinyl)-2-phenylethene (8o): Mp 49−51 °C; ^1H NMR ($CDCl_3$) δ 1.21 (d, 3H, *J* = 7.0 Hz), 1.25 (d, 3H, *J* = 7.0 Hz), 2.73−2.98 (m, 1H), 6.73 (d, 1H, J_{AB} = 15.5 Hz) 7.11−7.43 (m, 6H); MS *m/e* (%) 194 (2), 152 (100). Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26; S, 16.50. Found: C, 67.98; H, 7.20; S, 16.52.

1-(*tert*-Butylsulfinyl)-2-phenylethene (8p): Mp 69−71 °C; ^1H NMR ($CDCl_3$) δ 1.29 (s, 9H), 6.79 (d, 1H, J_{AB} = 15.5 Hz) 7.20−7.49 (m, 6H); MS *m/e* (%) 152 (100). Anal. Calcd for $C_{12}H_{16}OS$: C, 69.19; H, 7.74; S, 15.39. Found: C, 69.25; H, 7.70; S, 15.45.

1-(Phenylsulfinyl)-2-phenylethene (8r): ^1H NMR ($CDCl_3$) δ 6.48 and 6.83 [2d, 1H, J_{AB} = 10.5 Hz (*Z*), J_{AB} = 15.6 Hz (*E*)], 7.29−7.72 (m, 11H).[26]

Optically Active α,β-Unsaturated Sulfoxides 8a,i. (+)-(*R*)-1-(*p*-Tolylsulfinyl)-2-phenylethene (8a) (*E*:*Z*/97:3): $[\alpha]_D$ = +144.3° (*c*, 2.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.40 (s, 3H), 6.43 and 6.86 [2d, J_{AB} = 10.6 Hz (*Z*), J_{AB} = 15.5 Hz (*E*), 1H], 7.09 and 7.21−7.61 [d, J_{AB} = 10.6 (*Z*) and m, 10H].[5]

(+)-(*R*)-1-(*p*-Tolylsulfinyl)ethene (8i): $[\alpha]_D$ = +258.8° (*c*, 2.25, EtOH); ^1H NMR ($CDCl_3$) δ 2.40 (s, 3H), 5.88 (d, *J* = 9.5 Hz, 1H), 6.18 (d, *J* = 16.5 Hz, 1H), 6.55 (dd, *J* = 16.5 Hz, *J* = 9.5 Hz, 1H), 7.28−7.53 (m, 4H).[5]

((*p*-Tolylsulfinyl)methyl)diphenylphosphine (14). To a solution of methyl *p*-tolyl sulfoxide (0.77 g, 5 mmol) in dry Et_2O (15 mL) at −10 °C PhLi [prepared from 5.5 mmol of *n*-BuLi and PhBr (0.86 g 5.5 mmol)] in hexane was added dropwise, and the mixture was stirred at this temperature for 0.5 h. Then, the solution was cooled to −78 °C and Ph_2PCl (1.2 g, 5.5 mmol) was added. After 5 min, the mixture was warmed to room temperature, washed with water (2 mL), and dried over $MgSO_4$. Ether was evaporated, and the crude product was purified by rapid column chromatography under argon using dry ether as the eluent. Yield: 0.89 g (53%), oil after chromatography. ^{31}P NMR: δ_P − 29.9 ppm ($CDCl_3$). ^1H NMR ($CDCl_3$): δ 2.37 (s, 3H), 3.64 (dd, 1H, J_{H-H} = 13.15 Hz, J_{P-H} = 1.58 Hz), 3.75 (dd, 1H, J_{H-H} = 13.15, J_{P-H} = 1.16 Hz), 7.17−7.57 (m, 14H).[22]

((*p*-Tolylsulfinyl)methyl)diphenylphosphine Sulfide (15). To a solution of (α-sulfinylmethyl)diphenylphosphine **14**) (0.25 g, 0.74 mmol) in dry benzene (10 mL) was added elemental sulfur (0.04 g, 1.2 mmol), at room temperature, and the mixture was stirred at this temperature for 2 h. After evaporation of benzene, MeOH (5 mL) was added and the excess of sulfur was filtered off. The crude sulfide **15** was chromatographed (10:1 benzene−acetone): Yield 0.2 g (75%); ^{31}P NMR ($CDCl_3$) δ_P 34.0 ppm; ^1H NMR ($CDCl_3$) δ 2.34 (s, 3H), 3.76 (dd, 1H, J_{H-H} = 13.97 Hz, J_{P-H} = 10.22 Hz), 4.18 (dd, 1H, J_{H-H} = 13.97 Hz, J_{P-H} = 8.28 Hz), 7.15−8.00 (m, 14H); MS *m/e* (%) 370 (43) M^+; 231 (61), 185 (100). Anal. Calcd for $C_{20}H_{19}PS_2O$: C, 64.84; H, 5.17; P, 8.36; S, 17.31. Found: C, 64.98; H, 5.00; P, 8.18; S, 17.50.

((*p*-Tolylsulfinyl)methyl)diphenylmethylphosphonium Iodide (13a). To a solution of (α-sulfinylmethyl)diphenylphosphine **14** (0.57 g, 1.7 mmol) in dry Et_2O (5 mL) was added methyl iodide (0.5 mL) at room temperature, and the mixture was stirred overnight. The crystalline, Et_2O-insoluble, crude product was filtered off and purified by column chromatography (10:1 benzene−methanol): Yield 0.45 g (55%); mp 104−106 °C; ^{31}P NMR ($CDCl_3$) δ 20.2 ppm; ^1H NMR ($CDCl_3$) δ 2.33 (s, 3H), 2.97 (d, 3H, J_{P-H} = 13.92 Hz), 4.47 (dd, 1H, J_{H-H} = 14.43 Hz, J_{P-H} = 8.40 Hz), 5.84 (dd, 1H, J_{H-H} = 14.4 Hz, J_{P-H} = 12.76 Hz), 7.29−8.20 (m, 14H); MS *m/e* (%) 215 (11), 200 (100), 185 (50). Anal. Calcd for $C_{21}H_{22}PSOI$: C, 52.51; H, 4.62; P, 6.45; S, 6.68. Found: C, 52.34; H, 4.55; P, 6.48; S, 6.47.

1-(*p*-Tolylsulfinyl)-2-phenylethene (8a). To a stirred solution of ((*p*-tolylsulfinyl)methyl)diphenylmethylphosphonium iodide (**13a**) (0.96 g, 2 mmol) in dry THF (25 mL) at − 50 °C was added *n*-BuLi (1.35 mL of a 1.55 M solution in hexanes, 2.1 mmol) via dropping funnel. The colorless solution was stirred for 1 h. Then, benzaldehyde (0.23 g, 2.2 mmol) was added and the mixture was refluxed for 10 h and worked up as described above. The ratio *E*/*Z* of was determined by ^1H NMR spectroscopy (see Scheme 7).

Acknowledgment. One of us (M.M.) gratefully acknowledges an award from the Alexander von Humboldt Foundation that facilitated the preparation of the final form of this paper.

Supporting Information Available: ^1H NMR spectra for compounds **8c**−**f**,**m**−**p**, **5a**, **13a**, and **15** (12 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.

JO981100E

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