Synthesis and Reactions of Phosphoryl-Substituted Sulfines

Pascal A. T. W. Porskamp, Ben H. M. Lammerink, and Binne Zwanenburg*

Department of Organic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Received August 1, 1983

The synthesis of a variety of phosphoryl-substituted sulfines **5** by the reaction of α-silyl carbanions with sulfur dioxide is described. For characterization purposes the prepared sulfines were converted into their cycloadducts **6** with 2,3-dimethyl-1,3-butadiene. (Diethoxyphosphoryl)phenylsulfine **5a** was reacted with alkyllithium to give α-phosphoryl carbanions, which on treatment with aromatic aldehydes gave α,β-unsaturated sulfoxides **9**. Alkylation of the α-phosphoryl carbanion obtained from **5a** and methyllithium and subsequent thermal elimination of sulfenic acid gave α,β-unsaturated phosphonates **11**. Sulfines **5l,m,s** were subjected to electrophilic alkylation, producing the α,β-unsaturated sulfoxides **12** and α,β-unsaturated sulfides **13**.

Sulfines (thione *S*-oxides) are sulfur-centered heterocumulenes that were mentioned in the chemical literature as early as 1923. However, the sulfine structure as advanced by Wedekind et al.[1] was confirmed about 40 years thereafter by spectroscopic methods.[2] After this renewal of interest in sulfines, soon new synthetic methods for these heterocumulenes were developed.[3] The most important routes to sulfines are 1,2-dehydrochlorination of appropriate sulfinyl chlorides[3] and the oxidation of thiocarbonyl compounds, such as aromatic thiones,[4] thioacyl chlorides,[5] dithiocarboxylic esters,[6] thioamides,[7] thioketenes,[8] and non-enethiolizable aliphatic thiones.[9] Although a wide variety of sulfines has been prepared by the oxidation method a serious drawback is that it is limited to non-enethiolizable thiocarbonyl compounds.[10]

A new approach which was recently developed in our laboratory, involves the formation of the C=S bond by a Wittig-type reaction of phosphonium ylids with sulfur dioxide.[11] An attractive extension of the alkylidenation of sulfur dioxide is the use of α-silyl carbanions as nucleophilic reagents.[12] The sequence of events in this sulfine synthesis, in fact a modification of the Peterson olefination, is shown in Scheme I. The initially formed adduct from the α-silyl carbanion and sulfur dioxide in most cases spontaneously eliminates trimethylsilanolate to give sulfines in good yields.

The aim of the present investigation is to prepare phosphoryl-substituted sulfines using the concept of alkylidenation of sulfur dioxide. Such type of sulfines cannot be obtained by other methods. These phosphoryl sulfines are of interest as they enable us to prepare α,β-unsaturated sulfoxides and α,β-unsaturated phosphonates as will be demonstrated below.

Synthesis of Phosphoryl-Substituted Sulfines. For the preparation of the required starting trimethylsilyl compounds **3** two strategies can be envisaged (Scheme II). In route A active methylene compounds **1** are silylated by means of base and trimethylsilyl chloride. According to route B alkylation of either diethyl ((trimethylsilyl)-methyl)phosphonate **2a** or diphenyl ((trimethylsilyl)-methyl)phosphine oxide **2b** is accomplished. The silyl compounds **3** are converted into sulfines by deprotonation with *n*-butyllithium and subsequent treatment with an excess of sulfur dioxide. The results are compiled in Table I.

An interesting conclusion is that the primary intermediate **4** arising from the α-silyl carbanion and sulfur dioxide eliminates trimethylsilanolate rather than lithium diethyl phosphate. This is in accordance with the earlier observed preference of a Peterson reaction over a Wittig–Horner–Wadsworth–Emmons olefination using α-phosphoryl-substituted alkylsilanes.[13]

It is not always necessary to isolate the silyl compounds **3**. The sulfines **5a–f** also have been synthesized without the isolation of **3**, using a one-pot procedure starting from the corresponding active methylene compounds **1**. In some cases, however, it was found to be essential to perform the sulfine synthesis with isolated silyl compounds **3**, viz, for **5g–i**. The preparation of the silyl compounds **3g–i** requires special attention as silylation of the anions of **1g–i** is a relatively slow process with the consequence that deprotonation of **3** by the anion of **1** may occur, which then leads to disilylation. To avoid this complication the anion of **1** must be added to an excess of trimethylsilyl chloride.

For the synthesis of sulfines by treatment of the anions of **3** with sulfur dioxide, it is crucial that the reaction is performed at −78 °C and also that the anion is added to an excess of sulfur dioxide. In this manner side reactions, e.g., the disturbing formation of an olefin,[14] can be circumvented.

The sulfines **5a-i,k–n,r,s** were all prepared by the modified Peterson reaction. When the isolation of the sulfines could not be accomplished by crystallization, we resorted to chromatography on silica gel in spite of the considerable loss of material. Difficulties were encountered with **5j** as this sulfine is very sensitive toward hydrolysis. Therefore, crude **5j** was treated with 2,3-dimethyl-1,3-butadiene in order to convert the sulfine to Diels–Alder adduct **6j**. Attempts to convert the silyl compounds **3o–q** into the corresponding sulfines met with no sucess, neither could the sulfines be isolated nor could they be trapped as cycloadducts with dimethylbutadiene.

It is of interest to note that with the method presented above sulfines can be obtained having hydrogen atoms at the α-carbon atom, viz, **5k–n,rs**. So far, only a few representatives of this type of sulfines have previously been

(1) E. Wedekind, D. Schenk, and R. Stüsser, *Ber. Dtsch. Chem. Ges.*, **56**, 633 (1923).
(2) J. F. King and T. Durst, *Tetrahedron Lett.*, 585 (1963); *J. Am. Chem. Soc.*, **85**, 2676 (1963); *Can. J. Chem.*, **44**, 819 (1966).
(3) B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **101**, 1 (1982).
(4) B. Zwanenburg, L. Thijs, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **86**, 577 (1967).
(5) G. E. Veenstra, N. M. Bronold, J. F. M. Smits, A. Tangerman, and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **96**, 139 (1977).
(6) G. E. Veenstra and B. Zwanenburg, *Tetrahedron*, **34**, 1585 (1978).
(7) (a) W. Walter in "Organosufur Chemistry", M. J. Janssen, Ed., Interscience, New York, 1970. (b) W. Walter and J. Vosz in "The Chemistry of Amides", J. Zabicky, Ed., Interscience, New York, 1970.
(8) E. Schaumann and W. Walter, *Chem. Ber.*, **107**, 3562 (1974).
(9) G. E. Veenstra and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **95**, 37 (1976).
(10) R. Mayer, J. Morgenstern, and J. Fabian, *Angew. Chem.*, **76**, 157 (1964); L. Carlsen and F. Duus, *Synthesis*, 252 (1977).
(11) B. Zwanenburg, C. G. Venier, P. A. T. W. Porskamp, and M. van der Leij, *Tetrahedron Lett.*, 807 (1978).
(12) M. van der Leij, P. A. T. W. Porskamp, B. H. M. Lammerink, and B. Zwanenburg, *Tetrahedron Lett.*, 811 (1978).
(13) F. A. Carey and A. S. Court, *J. Org. Chem.*, **37**, 939 (1972).
(14) P. A. T. W. Porskamp, M. van der Leij, B. H. M. Lammerink, and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **102**, 400 (1983).

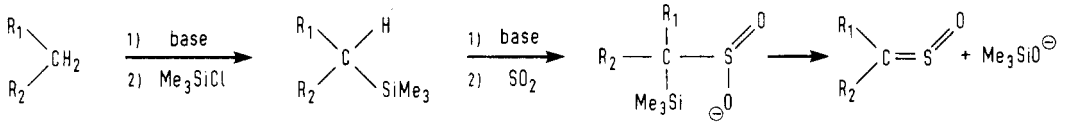
0022-3263/84/1949-0263$01.50/0

Table I. Synthesis of Compounds 3, 5, and 6 according to Scheme II

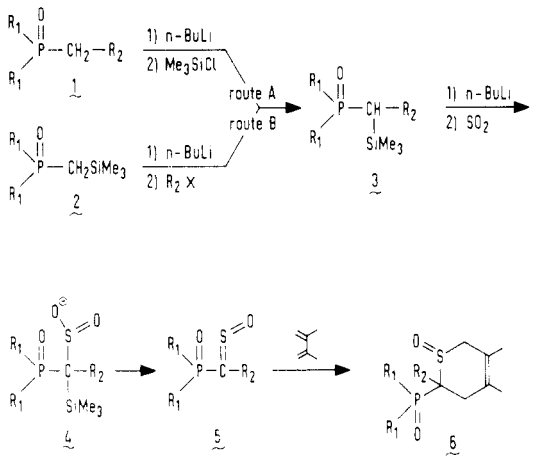
	silyl compound 3				sulfine 5		cycloadduct 6	
	R_1	R_2	yield, %	route		yield, %		yield, %
3a	EtO	Ph-	80	A	5a	70 (65)[a]	6a	80
3b	EtO	β-naphthyl-	78	A	5b	75 (70)[a]	6b	23
3c	EtO	2,5-$Me_2C_6H_3$-	73	A	5c	72 (61)[a]	6c	
3d	EtO	3-MeC_6H_4-		A	5d	(72)[a]	6d	86
3e	EtO	PhS-		A	5e	(41)[a]	6e	76
3f	EtO	CH_3S-		A	5f	(72)[a]	6f	72
3g	Ph	CH_3S-	70	A	5g	53	6g	78
3h	Ph	Ph-	80	A	5h	83	6h	82
3i	Ph	PhS-	70	A	5i	60	6i	71
3j	EtO	Cl-	89	A	5j	*b*	6j	37
3k	EtO	H_3C-	82	B	5k	45	6k	91
3l	EtO	$PhCH_2$-	80	B	5l	60	6l	95
3m	EtO	2,4,6-$Me_3C_6H_2$-CH_2-	70	B	5m	24	6m	
3n	EtO	$CH_3SCH_2CH_2$-	60	B	5n	32	6n	93
3o	EtO	Me_3Si-	85	B	5o		6o	
3p	EtO	Me_3SiCH_2-	76	B	5p		6p	
3q	EtO	(OEt)C(=O)CH_2-	70	B	5q		6q	
3r	Ph	H_3C-	76	B	5r	71	6r	80
3s	Ph	$PhCH_2$-	80	B	5s	30	6s	79

[a] Yield without isolation of silyl compound 3 is given in parenthesis. [b] Sulfine trapped by cycloaddition with dimethylbutadiene.

Scheme I



Scheme II



Scheme III

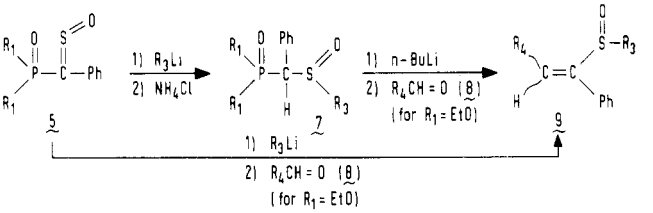


Table II. Synthesis of α-Phosphoryl Sulfoxides 7 according to Scheme III

starting sulfine, R_1	nucleophile, R_3	addition product 7, yield, %
5a, EtO	Me	7a, 92
5a, EtO	*n*-Bu	7b, 72
5a, EtO	*sec*-Bu	7c, 59
5a, EtO	*t*-Bu	7d,
5h, Ph	Me	7e, 82
5h, Ph	*n*-Bu	7f, 82

prepared.[3] In most cases they are rather unstable. Apparently, a stabilizing effect is exerted by the phosphoryl group.

The geometrical configuration of sulfines **5a** and **5d** could be derived from their ^1H NMR spectra. The low field absorption of aromatic protons of R_2 point to a deshielding effect of the S=O moiety, positioned syn with respect to these protons. Although the geometry of the other sulfines cannot be established by ^1H NMR we believe that the S=O function is also pointing away from the bulky phosphoryl substituent (cf. ref 14).

The sulfines were all converted into [4 + 2] cycloadducts **6** by reaction with dimethylbutadiene (Table I, Scheme II). An exception is **5c** which failed to react, probably owing to steric hindrance.

Synthesis of α,β-Unsaturated Sulfoxides. Two modes of reactions of sulfines with nucleophiles can be envisaged, viz, a thiophilic and a carbophilic reaction.[3] Nucleophilic reactions at the sulfine sulfur atom are most common; carbophilic reactions are less frequently encountered and, in fact, only when the sulfine carbon atom bears a good leaving group as a substituent. As the nucleofugality of phosphoryl groups is rather low, reaction of a nucleophile with sulfines **5** is expected to occur at sulfur, leading to α-phosphoryl sulfoxides (Scheme III). Indeed, reaction of sulfines **5a** and **5h** with alkyllithiums and subsequent quenching with aqueous ammonium chloride produced the sulfoxides[15] **7a–f** in good yields (Scheme III, Table II).

In the preparation of the compounds **7** according to Scheme III two chiral centers are introduced. The ratio

(15) α-Phosphoryl sulfoxides have previously been prepared by Mikolajczyk et al. by selective oxidation of the corresponding sulfides with sodium metaperiodate,[16] by reaction of phosphonate carbanions with sulfinic esters,[17] and by reaction of dialkyl phosphite anions with α-halo sulfoxides.[17]

(16) M. Mikolajczyk and A. Zatorski, *Synthesis*, 669 (1973).

(17) M. Mikolajczyk, S. Grzejszczak, and A. Zatorski, Abstracts, *Int. Symp. Org. Sulfur Chem.*, 6th, abstr. No. R C5.

Table III. Synthesis of α,β-Unsaturated Sulfoxides 9 according to Scheme III

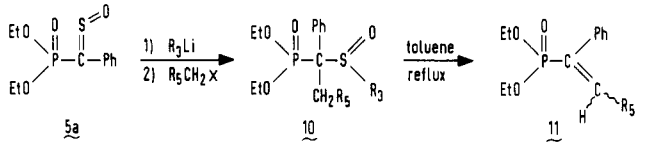
starting materials			product (E + Z)		
R_3	R_4			yield, %[a]	yield, %[b]
Me	8a	Ph	9a	91	88
n-Bu	8a	Ph	9f		55
sec-Bu	8a	Ph	9g		52
Me	8b	p-Tol	9b	95	64
Me	8c	p-Me_2N-C_6H_4	9c	59	47
Me	8d	p-MeO-C_6H_4	9d	82	70
Me	8e	2,4,6-Me_3-C_6H_2	9e	31	14

[a] 5a as starting material. [b] 7 as starting material: R_1 = EtO; R_3 see first column.

Table IV. Synthesis of α,β-Unsaturated Phosphoryl Compounds 11 according to Scheme IV

starting materials				product	
	R_3	R_5	X		yield, %
5a	Me	H	I	11a	24
5a	n-Bu	H	I	11a	47
5a	n-Bu	Ph	Br	11b	18

Scheme IV



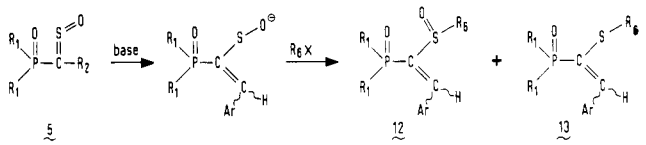
5a 10 11

of diastereomers appeared to be dependent on the reaction conditions (temperature, concentration of reagents, etc.).

The α-phosphoryl sulfoxides **7** can serve as substrates in Wittig–Horner olefination reactions to give α,β-unsaturated sulfoxides (Scheme III). Deprotonation of **7** (R_1 = EtO) with n-butyllithium and subsequent treatment with the aromatic aldehydes **8** produced the α,β-unsaturated sulfoxides **9a–e** (Table III). These sulfoxides can also be prepared directly from (diethoxyphosphoryl)-sulfines without isolating the phosphoryl sulfoxides **7**. The results are also listed in Table III. The sulfoxides **9** were obtained as *E*/*Z* mixtures, the isomer ratio appeared to be dependent on the experimental conditions. In some cases pure single isomers could be obtained by fractional crystallization (**9b–e**). This synthesis of α,β-unsaturated sulfoxides is sensitive to steric hindrance as is apparent from the low yield obtained from mesitylaldehyde and the failure of benzophenone to react.

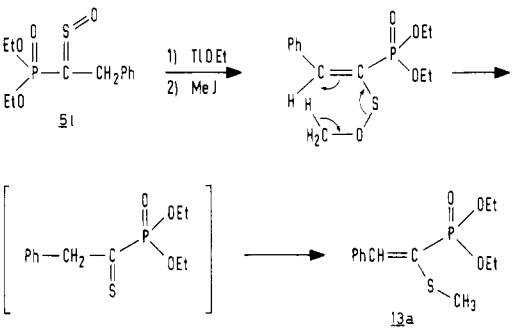
The commonly used method of preparation of unsaturated sulfoxides involves the oxidation of vinyl sulfides with various oxidizing agents.[18,19]

Scheme V



5 12 13

Scheme VI



51 13a

Synthesis of α,β-Unsaturated Phosphonates. It has been shown by Koizumi et al.[25] that α-sulfinyl-substituted alkylphosphonates undergo thermal elimination of sulfenic acid to give alkenephosphonates. This reaction leads to the proposal that sulfines of the type **5** can also be used to prepare unsaturated phosphonates. As shown in Scheme IV thiophilic addition of alkyllithium to sulfine **5a** followed by an alkylation of the α-sulfinyl carbanion leads to sulfinyl phosphonates **10**, which on heating in refluxing toluene indeed produce α,β-unsaturated phosphonates **11** (Table IV).

Electrophilic Alkylation of Phosphorylsulfines. Sulfines bearing a hydrogen atom on the α-carbon atom are of special interest as deprotonation leads to anions which in fact are vinylsulfenates. As we showed previously for thiocamphor *S*-oxide[26] and methylthio((phenylsulfonyl)methyl)sulfine,[27] both having an α-hydrogen atom, the intermediate vinylsulfenates can be electrophillically alkylated at sulfur to give α,β-unsaturated sulfoxides. It was also found that the choice of the base for the deprotonation is of great importance. By far the best results were obtained with thallium(I) ethoxide as the base.[26,27]

The phosphorylsulfines **51,m,s** are also suited to be used in a deprotonation alkylation sequence (Scheme V). Two bases were used, namely sodium hydride and thallium(I) ethoxide. With the former a complicated mixture of products was obtained after alkylation with methyl iodide. Two products were isolated and identified as the unsaturated sulfoxide **12** and sulfide **13** (Table V). By using thallium(I) ethoxide in benzene alkylation gave unsaturated sulfoxides **12** as the predominant products, the corresponding sulfides **13** being a byproduct in some cases. The explanation for the formation of the sulfide byproducts is depicted in Scheme VI for sulfine **51**. In analogy with previous work[28] it is assumed that alkylation can take place at sulfur (as expected on the basis of the theory of hard acids and soft bases) as well as at oxygen (anomalous product). In the latter case sulfenic esters are obtained that in a kind of ene reaction rearrange to formaldehyde and α-thioxo phosphonates. *S*-Alkylation then leads to

(18) G. Barbieri, M. Cinguini, S. Collonna, and F. Montanari, *J. Chem. Soc. C*, 659 (1968); A. V. Sviridova, V. J. Laba, and E. N. Prilizezhaeva, *Zh. Org. Khim.* **7**, 2480 (1971); D. A. Evans, C. A. Bryan, and C. L. Sims, *J. Am. Chem. Soc.*, **94**, 2891 (1972).

(19) Other methods are the reaction of vinyl Grignard reagents with sulfinic esters,[20] the addition of sulfenic acid to alkynes,[21] and the Peterson olefination using α-silyl sulfoxides.[22,23] Mikolajczyk et al.[24] also used the Wittig–Horner reaction of (diethoxyphosphoryl)methyl methyl sulfoxide [$(EtO)_2P(O)CH_2S(O)CH_3$] with carbonyl compounds.

(20) E. J. Mulvaney and R. A. Ottaviani, *J. Polym. Sci., Part A*, **1**, 2293 (1970); D. J. Abbott, S. Collonna, and C. J. M. Stirling, *Chem. Commun.*, 471 (1971).

(21) E. Block and J. O'Connor, *J. Am. Chem. Soc.*, **96**, 3929 (1974); I. R. Shelton and K. E. Davis, *Int. J. Sulfur Chem.*, **8**, 197, 205, (1973); D. H. R. Barton, J. H. Coates, and P. G. Sammes, *J. Chem. Soc., Perkin Trans. 1*, 1459 (1974).

(22) A limitation of this method is the relatively low thermal stability of the starting α-silyl substituted sulfoxides.[14]

(23) F. A. Carey and O. Hernandez, *J. Org. Chem.*, **38**, 2670 (1973).

(24) M. Mikolajczyk, S. Grzejsczak, and A. Zatorski, *J. Org. Chem.*, **40**, 1979 (1975).

(25) T. Koizumi, N. Tanaka, M. Iwata, and E. Yoshi, *Synthesis*, 917 (1982).

(26) G. E. Veenstra and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **95**, 37 (1976).

(27) G. E. Veenstra and B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **95**, 202 (1976).

(28) G. E. Veenstra, Thesis, University of Nijmegen, 1976.

Table V. Synthesis of α,β-Unsaturated Sulfoxides 12 according to Scheme V

starting materials						products			
	R_1	R_2	R_6X	base	solvent		yield, %		yield, %
5l	EtO	$PhCH_2$	MeI	NaH	DME	12a	30	13a	30
5l	EtO	$PhCH_2$	MeI	TlOEt	benzene	12a	61	13a	18
5l	EtO	$PhCH_2$	MeI	TlOEt	THF	12a	54	13a	28
5l	EtO	$PhCH_2$	EtI	TlOEt	benzene	12b	37	13b	45
5m	EtO	$2,4,6\text{-}Me_3C_6H_2\text{-}CH_2$	MeI	TlOEt	benzene	12c	39		
5s	Ph	$PhCH_2$	MeI	TlOEt	benzene	12d	60		

the isolated alkene sulfides 13 (the deoxygenated products).

Experimental Section

Melting points were determined on a Reichert hot stage microscope and are uncorrected. ^1H NMR spectra were recorded on a Varian E390 spectrometer using Me_4Si as internal standard. IR spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer. Mass spectra were obtained with a Varian MAT SM2B mass spectrometer. Elemental analyses were performed by J. Diersmann (Micro Analytical Department of our University). THF was distilled twice over CaH_2. The *n*-BuLi used was a stock solution of 1.6 M in hexane.

Diethyl (Phenyl(trimethylsilyl)methyl)phosphonate (3a). To a solution of diethyl benzylphosphonate[29] **1a** (10.0 g, 44 mmol) in dry THF (150 mL) was added 1.10 equiv of *n*-BuLi at −78 °C under nitrogen. After stirring for 15 min at room temperature, the solution of the anion was added at −78 °C to a solution of an excess trimethylsilyl chloride (66 mmol) in THF (5 mL). After again stirring for 15 min at room temperature the reaction mixture was poured into a saturated aqueous solution of NH_4Cl. The organic layer was dried with $MgSO_4$ and concentrated. Crude **3a** was purified by distillation under reduced pressure: bp 110 °C (0.3 mm); yield, 80%; IR (NaCl) 850, 1246 ($SiMe_3$), 1030, 1246 cm^{-1} $[P(O)(OEt)_2]$; ^1H NMR ($CDCl_3$) δ 0.17 (s, 9 H, $SiMe_3$), 1.17 (t, 3 H, J = 7.5 Hz, OCH_2CH_3), 1.30 (t, 3 H, J = 7.5 Hz, OCH_2CH_3), 2.72 (d, 1 H, J = 24.5 Hz, CH), 3.63–4.37 (m, 4 H, OCH_2CH_3), 7.30 (br s, 5 H, aromatic); MS, m/e 300.1334 (M^+); calcd for $C_{14}H_{25}O_3PSi$, 300.1311.

The silyl compounds **3b** and **3c** were prepared following the same procedure (for yields see Table I). The required starting diethyl phosphonates were all obtained by the Arbusov reaction.[22] See the paragraph at the end of the paper about supplementary material concerning the spectroscopic characteristics of the above-mentioned silyl compounds **3b** and **3c**.

Diphenyl((methylthio)(trimethylsilyl)methyl)phosphine Oxide (3g). To a solution of phosphonate **1g** (5.24 g, 20 mmol) and 20 mmol of TMEDA in dry THF (100 mL) was added 1.10 equiv of *n*-BuLi at −78 °C under nitrogen. After stirring for 15 min at room temperature the solution of the anion was added at −78 °C to a solution of an excess trimethylsilyl chloride (40 mmol) in THF (5 mL). After again stirring for 15 min at room temperature the reaction mixture was poured into a saturated aqueous solution of NH_4Cl. The organic layer was dried with $MgSO_4$ and concentrated. Chromatography (silica gel, $CHCl_3$/MeOH/diisopropyl ether) and crystallization from ether/$CHCl_3$ gave pure product.

The silyl compounds **3h** and **3i** were prepared following the same procedure. See the paragraph at the end of the paper about supplementary material concerning the spectroscopic characteristics of the compounds **3g–i**.

Diethyl (Chloro(trimethylsilyl)methyl)phosphonate (3j). To a solution of LiCl (0.85 g, 20 mmol) in dry THF (40 mL) was added 1.1 equiv of *n*-BuLi at room temperature under nitrogen. At −78 °C diethyl (chloromethyl)phosphonate[30] (3.73 g, 20 mmol) dissolved in dry THF (10 mL) was gradually added. After the mixture had stirred for 10 min at −78 °C 1.1 equiv of trimethylsilyl chloride was added. The reaction mixture was stirred for 1.5 h at room temperature and then poured into a saturated aqueous solution of NH_4Cl. The organic layer was dried over $MgSO_4$ and concentrated. Crude **3j** was distilled under reduced pressure: bp 98–99 °C (2 mm); yield, 89%; IR (NaCl) 850, 1250 ($SiMe_3$), 1022, 1250 cm^{-1} $[P(O)(OEt)_2]$; ^1H NMR ($CDCl_3$) δ 0.22 (s, 9 H, $SiMe_3$), 1.33 (t, 3 H, OCH_2CH_3), 3.17 (d, 1 H, J = 16.8 Hz, CHP), 3.90–4.47 (m, 4 H, OCH_2CH_3).

Diethyl (1-(Trimethylsilyl)ethyl)phosphonate (3k).[13] To a solution of diethyl ((trimethylsilyl)methyl)phosphonate (4.0 g, 18 mmol) in dry THF (70 mL) was added 1.1 equiv of *n*-BuLi at −78 °C under nitrogen. After stirring for 1 h at room temperature an excess of MeI (1.5 equiv) was added at −78 °C. The reaction mixture was warmed to room temperature and then poured into a saturated aqueous solution of NH_4Cl. The organic layer was dried over $MgSO_4$ and concentrated. Distillation under reduced pressure (bp 64 °C (0.7 mm)) gave 3.5 g of **3k** (82%): IR (NaCl) 840, 1245 ($SiMe_3$), 1025, 1245 cm^{-1} $[P(O)(OEt)_2]$; ^1H NMR ($CDCl_3$) δ 0.03 (s, 9 H, $SiMe_3$), 1.07 (d, 1 H, J = 13.5 Hz, CHSi), 1.17 (t, 6 H, J = 7 Hz, OCH_2CH_3), 3.73–4.13 (m, 4 H, OCH_2CH_3); MS, m/e 223.0917 ($M^+ - CH_3$); calcd for $C_9H_{23}O_3PSi$, 223.1119.

The silyl compounds **3l–s** were prepared following the procedure as given for **3k**. See the paragraph at the end of the paper about supplementary material concerning the characteristics of the compounds **3l–s**.

(Diethoxyphosphoryl)phenylsulfine (5a). To a solution of diethyl benzylphosphonate (6.8 g, 0.03 mol) in THF (200 mL) was added 1.1 equiv of *n*-BuLi at −78 °C under nitrogen. After the mixture stirred for 15 min at room temperature 1.1 equiv of trimethylsilyl chloride (3.3 g) was added at −78 °C. After the mixture stirred for 0.5 h at room temperature again 1.1 equiv of *n*-BuLi was added at −78 °C. The thus-obtained solution of the α-silyl carbanion was added to an excess of SO_2 dissolved in THF (10 mL) at −78 °C. After stirring at room temperature for 1 h the reaction mixture was poured into a saturated aqueous NH_4Cl solution. The organic layer was separated, dried over $MgSO_4$, and concentrated. The crude sulfine **5a** was purified by chromatography (silica gel, ether): yield, 65%. When the reaction was started with the isolated **3a** the yield of sulfine **5a** was 70%: IR (NaCl) 1015, 1250 $[P(O)(OEt)_2]$, 1130 cm^- (C=S=O); ^1H NMR ($CDCl_3$) δ 1.31 (t, 6 H, J = 7.5 Hz, OCH_2CH_3), 3.95–4.35 (m, 4 H, OCH_2CH_3), 7.28–7.45 (m, 3 H, aromatic), 7.87–8.00 (m, 2 H, aromatic); MS, m/e 274.0436 (M^+); calcd for $C_{11}H_{15}SO_4P$, 274.0431.

(Diethoxyphosphoryl)(β-naphthyl)sulfine (5b). The procedure as given for **5a** was followed: yield, 70%. When isolated **3b** was used as starting material the yield of **5b** was 75%: IR (KBr) 1015, 1257 $[P(O)(OEt)_2]$, 1145 cm^{-1} (C=S=O); ^1H NMR ($CDCl_3$) δ 1.17 (t, 6 H, J = 7 Hz, OCH_2CH_3), 3.83–4.23 (m, 4 H, OCH_2CH_3), 7.20–7.90 (m, 7 H, aromatic. Anal. Calcd for $C_{15}H_{17}O_4SP$ (324.335): C, 55.55; H, 5.28. Found: C, 55.77, 55.47; H, 5.29, 5.05. MS, m/e 324.0602 (M^+); calcd for $C_{15}H_{17}O_4SP$, 324.0595.

The sulfines **5c–f** and **5k–n** were prepared following the procedure as given for **5a**. See the paragraph at the end of the paper about supplementary material concerning the characteristics of the compounds **5c–f** and **5k–n**.

(Diphenylphosphoryl)(methylthio)sulfine (5g). The procedure as given for **5a** was followed. Crystallization from a chloroform/ether/*n*-hexane mixture yielded (starting from **3g**) **5g** (53%): mp 119–120 °C; IR (KBr) 1090 (C=S=O), 1192 cm^- (P=O); ^1H NMR ($CDCl_3$) δ 2.62 (s, 3 H, SCH_3), 7.30–8.00 (m, 10 H, aromatic); MS, m/e 308 (M^+). Anal. Calcd for $C_{14}H_{13}S_2O_2P$: C, 54.53; H, 4.25. Found: C, 54.50, 54.31; H, 4.34, 4.30.

The sulfines **5h,i,r,s** were prepared following the procedure as given for **5a**. See the paragraph at the end of the paper about supplementary material concerning the characteristics of the compounds **5h,i,r,s**.

(29) F. Kagan, R. D. Birkenmeyer, and R. E. Strube, *J. Am. Chem. Soc.*, **81**, 3026 (1959).
(30) *Chem. Abstr.*, **47**, 9254 (1955).

2-(Diethoxyphosphoryl)-3,6-dihydro-4,5-dimethyl-2-phenyl-2*H*-thiopyran 1-Oxide (6a). A solution of sulfine **5a** (2.0 g, 7.3 mmol) and 2,3-dimethyl-1,3-butadiene (4 mL) in $CHCl_3$ (5 mL) was stirred at room temperature during one week in the dark. After evaporation of excess of dimethylbutadiene and purification by chromatography (silica gel, methanol/chloroform/diisopropyl ether) **6a** was obtained (2.1 g, 80%). Crystallization from ether gave pure product: mp 55–57 °C; IR (KBr) 1015, 1250 [P(O)(OEt)$_2$], 1068 cm^{-1} (S=O); ^{1}H NMR ($CDCl_3$) δ 1.24 (t, 6 H, J = 7.0 Hz, OCH_2CH_3), 1.38 (br s, 3 H, CH_3), 1.78 (br s, 3 H, CH_3), 3.80–4.33 (m, 4 H, OCH_2CH_3), 7.20–7.70 (m, 5 H, aromatic), 2.43–3.40 (m, 4 H, remaining protons); MS, m/e 356.1236 (M$^+$); calcd for $C_{17}H_{25}SO_4P$: 356.1211. Anal. Calcd for $C_{17}H_{25}SO_4P$ (356.421): C, 57.29; H, 7.07. Found: C, 57.35, 57.43; H, 6.97, 7.00.

2-(Diethoxyphosphoryl)-3,6-dihydro-4,5-dimethyl-2-(β-naphthyl)-2*H*-thiopyran 1-Oxide (6b). A solution of sulfine **5b** (1.0 g, 3.1 mmol) and 2,3-dimethyl-1,3-butadiene (4 mL) in $CHCl_3$ (5 mL) was stirred at 70 °C during one week in the dark. Evaporation of volatiles and chromatography (silica gel, ethyl acetate/ether) gave **6b**: yield, 0.3 g (23%). Crystallization from chloroform/ether gave pure **6b**: mp 154.5–155.5 °C; IR (KBr) 1020, 1240 [P(O)(OEt)$_2$], 1050 cm^{-1} (S=O); ^{1}H NMR ($CDCl_3$) δ 0.60 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 1.15 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 1.73 (br s, 3 H, CH_3), 1.87 (br s, 3 H, CH_3), 7.20–7.80 (m, 6 H, aromatic), 8.70–8.90 (m, 1 H, aromatic), 2.66–4.40 (m, 8 H, remaining protons). Anal. Calcd for $C_{21}H_{27}O_4SP$ (426): C, 62.05; H, 6.70. Found: C, 62.12, 61.89; H, 6.83, 6.72.

The thiopyran *S*-oxides **6d-i,k,l,n,r,s** were prepared following the procedure as given for **6a**. See the paragraph at the end of the paper about supplementary material concerning the characteristics of the compounds **6d–i,k,l,n,r,s**.

2-Chloro-2-(diethoxyphosphoryl)-3,6-dihydro-4,5-dimethyl-2*H*-thiopyran 1-Oxide (6j). To a solution of **3j** (2.0 g, 7.7 mmol) and LiCl (2.0 g) in THF (50 mL) was added 1.1 equiv of *n*-BuLi under nitrogen. After stirring for 1 h at −78 °C this reaction mixture was added to an excess of sulfur dioxide in THF (10 mL). At room temperature an excess of 2,3-dimethyl-1,3-butadiene was added and then the mixture was stirred overnight. The solution was poured into a saturated aqueous NH_4Cl solution, and the organic layer was separated, dried over $MgSO_4$, and concentrated. The crude product was purified by chromatrography (silica gel, ethyl acetate/ether) and crystallized from ether/hexane: yield, 0.9 g (37%); mp 91–93 °C; IR (KBr) 1010, 1260 [P(O)(OEt)$_2$], 1080 cm^{-1} (S=O); ^{1}H NMR ($CDCl_3$) δ 1.40 (t, 6 H, J = 7.5 Hz, OCH_2CH_3), 1.70 (br s, 3 H, CH_3), 1.73 (br s, 3 H, CH_3), 4.10–4.57 (m, 4 H, OCH_2CH_3) 2.77–3.20 and 3.43–3.63 (m, 4 H, remaining protons). Anal. Calcd for $C_{11}H_{20}O_4SClP$ (314.5): C, 41.97; H, 6.40; S, 10.19. Found: C, 41.87, 42.02; H, 6.44, 6.45; S, 10.15, 10.33.

(Diethoxyphosphoryl)phenylmethyl Methyl Sulfoxide (7a). To a solution of (diethoxyphosphoryl)phenylsulfine **5a** (6.1 g, 22.3 mmol) in THF (75 mL) was added 1.1 equiv of MeLi at −78 °C. After stirring for 1 h at −78 °C the reaction mixture was poured into a saturated aqueous NH_4Cl solution. The organic layer was separated, dried over $MgSO_4$, and concentrated. Crystallization from ether/pentane gave **7a** (6.0 g, 92%) as a mixture of diastereomers: mp 85–98 °C; IR (KBr) 1025, 1250 [P(O)(OEt)$_2$], 1050 cm^{-1} (S=O); ^{1}H NMR ($CDCl_3$) δ 1.05–1.50 (m, 6 H, OCH_2CH_3), 2.38 and 2.58 [s, CH_3, $CH_3S(O)$], 3.80–4.50 (m, 5 H, OCH_2CH_3 and CHP), 7.38 (br s, 5 H, aromatic). Anal. Calcd for $C_{12}H_{19}SO_4P$ (290.318): C, 49.65; H, 6.60. Found: C, 49.77, 49.78; H, 6.62, 6.67.

The sulfoxides **7b,c,e** were prepared following the procedure as given for **7a**. See the paragraph at the end of the paper about supplementary material concerning the characteristics of the compounds **7b,c,e**.

***n*-Butyl (Diphenylphosphoryl)phenylmethyl Sulfoxide (7f).** The procedure as given for **7a** was followed. By chromatography (silica gel, ethyl acetate) the two diastereomers could be isolated separately. After crystallization from ether/chloroform both isomers were obtained analytically pure (total yield, 82%).

Diastereomer a: mp 175–176 °C; IR (KBr) 1070 (S=O), 1190 cm^{-1} (P=O); ^{1}H NMR ($CDCl_3$) δ 0.83 (t, 3 H, J = 7.0 Hz, $C_3H_6CH_3$), 1.10–3.20 (m, 6 H, $C_3H_6CH_3$), 4.93 (d, 1 H, J = 7.0 Hz, CHP), 7.00–8.10 (m, 15 H, aromatic). Anal. Calcd for $C_{23}H_{25}PSO_2$ (396.489): C, 69.67; H, 6.36. Found: C, 69.57, 69.75; H, 6.46, 6.46. Diastereomer b: mp 186–188 °C; IR (KBr) 1045 (S=O), 1190 cm^{-1} (P=O); ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 3 H, J = 7.0 Hz, $C_3H_6CH_3$), 1.10–2.73 (m, 6 H, $C_3H_6CH_3$), 4.43 (d, 1 H, J = 10 Hz, CHP), 7.10–8.00 (m, 15 H, aromatic). Anal. Calcd for $C_{23}H_{25}SPO_2$ (396.489): C, 69.67; H, 6.36. Found: C, 69.39; H, 6.34.

Synthesis of α,β-Unsaturated Sulfoxides (9a–e). General Procedure A. To a solution of (diethoxyphosphoryl)(phenyl)-methyl methyl sulfoxide **7a** (2.5 g, 8.6 mmol) in THF (100 mL) was added *n*-BuLi (1.05 equiv) at −78 °C. After the mixture stirred for 1 h at −78 °C a solution of the carbonyl compound (10 mmol) in THF (20 mL) was added at −78 °C and the reaction mixture was stirred for 15 min at this temperature. The mixture was warmed to room temperature, stirred overnight, and then poured into a saturated aqueous NH_4Cl solution. The organic layer was dried ($MgSO_4$) and concentrated in vacuo to afford the crude sulfoxide **9**.

Synthesis of α,β-Unsaturated Sulfoxide (9a–g). General Procedure B. To a solution of (diethoxyphosphoryl)phenylsulfine **5a** (3.0 g, 10.9 mmol) in THF (100 mL) was added alkyllithium (1.05 equiv) at −78 °C. Then Procedure A was followed to give sulfoxides **9**.

1-(Methylsulfinyl)-1,2-diphenylethene (9a). The crude product, which was obtained as a mixture of *E* and *Z* isomers, was purified by chromatography (silica gel, benzene/acetone/ethyl acetate) and crystallization (ether/hexane): mp 52.5–55 °C; IR (KBr) 1066 cm^{-1} (S=O); ^{1}H NMR ($CDCl_3$) δ 2.35 (br s, 3 H, CH_3SO), 7.00–7.50 (m, 11 H, aromatic, olefin); MS, m/e calcd for $C_{15}H_{14}SO$, 242.0765; Found, m/e 242.0759 (M$^+$). Anal. Calcd for $C_{15}H_{14}SO$: C, 74.34; H, 5.82. Found: C, 74.26; H, 5.79.

The sulfoxides **9b–g** were prepared as described above. See the paragraph at the end of the paper about supplementary material concerning the characteristics of the compounds **9b–g**.

1-(Diethoxyphosphoryl)-1-phenylethene (11a). To a stirred solution of sulfine **5a** (0.93 g, 3.4 mmol) in tetrahydrofuran (30 mL) was added 1.1 equiv of MeLi at −78 °C. After the solution stirred for 10 min at −78 °C methyl iodide (1.2 equiv) was added. At room temperature the reaction mixture was stirred for 1 h after which the solution was poured into a saturated aqueous NH_4Cl solution. The organic layer was dried ($MgSO_4$) and concentrated in vacuo to afford the crude product **10a**. It was dissolved in toluene (30 mL) and refluxed overnight. The solvent was evaporated in vacuo and the resulting oil chromatographed (silica gel, methanol/diisopropyl ether) giving vinyl phosphonate **11a** (yield, 0.2 g, 24%): IR (NaCl) 1025, 1250 cm^{-1} [P(O)(OEt)$_2$]; ^{1}H NMR ($CDCl_3$) δ 1.27 (t, 6 H, J = 7.0 Hz, OCH_2CH_3), 3.85–4.25 (m, 4 H, OCH_2CH_3), 6.08 (d, 1 H, J = 22 Hz), 6.27 (d, 1 H, J = 4.5 Hz), 7.00–7.60 (m, 5 H, aromatic); MS; m/e 240 (M$^+$). The same procedure was followed with *n*-BuLi as the nucleophile (yield, 47%) of the product **11a**.

1-(Diethoxyphosphoryl)-1,2-diphenylethene (11b). The procedure as given for **11a** was followed. Instead of methyl iodide now benzyl bromide (1.2 equiv) was used. After chromatography (silica gel, methanol/diisopropyl ether) **11b** was obtained as an oil (yield, 18%): IR (NaCl) 1020, 1200 cm^{-1} [P(O)(OEt)$_2$]; ^{1}H NMR ($CDCl_3$) δ 1.27 (t, 6 H, J = 7.0 Hz, OCH_2CH_3), 3.87–4.27 (m, 4 H, OCH_2CH_3), 6.95–7.80 (m, 1 H, aromatic); MS, m/e 316 (M$^+$).

1-(Methylsulfinyl)-1-(diethoxyphosphoryl)-2-phenylethene (12a) and 1-(Methylthio)-1-(diethoxyphosphoryl)-2-phenylethene (13a). Procedure A. To a solution of sulfine **5l** (0.47 g, 1.6 mmol) in dimethoxyethane (40 mL) was added sodium hydride (2 equiv) at −40 °C. After stirring for 15 min at room temperature an excess of methyl iodide was added and again stirred for 1 h. The reaction mixture was extracted with water (50 mL) and then dried ($MgSO_4$). After concentration in vacuo the residue was chromatographed (silica gel, benzene/methanol/acetone). Both **12a** (30%) and **13a** (30%) were isolated as an oil.

12a: IR (NaCl) 1015, 1245 [P(O)(OEt)$_2$], 1050 cm^{-1} (S=O); ^{1}H NMR ($CDCl_3$) δ 1.18, 1.23 (t, 6 H, J = 7.0 Hz, OCH_2CH_3), 2.85 (s, 3 H, CH_3SO), 3.83–4.25 (m, 4 H, OCH_2CH_3), 7.23–7.48 (m, 3 H, aromatic), 7.67–7.87 (m, 2 H, aromatic), 7.83 (d, 1 H, J = 39 Hz, olefin); MS, m/e 302 (M$^+$).

13a: IR (NaCl) 1025, 1250 cm^{-1} [P(O)(OEt)$_2$]; ^{1}H NMR ($CDCl_3$) δ 1.38 (t, 6 H, J = 7.0 Hz, OCH_2CH_3), 2.38 (s, 3 H, CH_3S), 3.75–4.38

(m, 4 H, OCH_2CH_3), 7.10–7.90 (m, 6 H, aromatic, olefin; MS, *m/e* 286 (M^+).

Procedure B. To a solution of sulfine **5l** (1.0 g, 3.5 mmol) in dry benzene (50 mL) was added thallous ethoxide (0.875 g, 3.5 mmol) in benzene (5 mL) at room temperature. After the mixture stirred for 1.5 h at room temperature an excess of methyl iodide was added. After stirring at room temperature again for 1 h the reaction mixture was filtered over Celite and the filtrate concentrated. The residue was chromatographed (silica gel, methanol/chloroform/diisopropyl ether) giving **12a** (61%) and **13a** (18%). The spectroscopic data of **12a** were as those reported above. For **13a** both geometrical isomers were obtained as was concluded from the ^1H NMR spectrum: δ 1.15, 1.38 (t, 6 H, J = 7.0 Hz, OCH_2CH_3), 2.38, 2.39 (s, 3 H, CH_3S), 3.75–4.40 (m, 4 H, OCH_2CH_3), 7.05–7.90 (m, 6 H, aromatic, olefin).

The procedure as given above was also followed for thallous ethoxide as base in tetrahydrofuran as the solvent. After purification (as described above) **12a** (54%) and **13a** (28%) were obtained both as a mixture of isomers.

1-(Ethylsulfinyl)-1-(diethoxyphosphoryl)-2-phenylethene (12b) and 1-(Ethylthio)-1-(diethoxyphosphoryl)-2-phenylethene (13b). The procedure as described for **12a** and **13a** (Procedure B) was followed. After chromatography (silica gel, benzene/methanol/acetone) **12b** (37%) and a mixture of geometrical isomers of **13b** (45%) was obtained.

12b: IR (NaCl) 1015, 1244 [$P(O)(OEt)_2$], 1040 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 1.05–1.45 (m, 9 H, CH_2CH_3), 2.67–3.40 (m, 2 H, CH_2CH_2SO), 3.78–4.18 (m, 4 H, OCH_2CH_3), 7.17–7.50 (m, 3 H, aromatic), 7.75 (d, 1 H, J = 5.2 Hz, olefin), 7.70–7.87 (m, 2 H, aromatic); MS, *m/e* calcd for $C_{14}H_{21}SO_3P$, 300.0949; found, 300.0931 ($M^+ - O$); MS, *m/e* 316 (M^+), 239 ($M^+ - CH_3CH_2SO$).

13b: IR (NaCl) 1020, 1250 cm^{-1} [$P(O)(OEt)_2$]; ^1H NMR ($CDCl_3$) δ 1.00–1.60 (m, 9 H, CH_2CH_3), 2.7–3.7 (m, 2 H, CH_3CH_2SO), 3.80–4.40 (m, 4 H, OCH_2CH_3), 7.20–8.00 (m, 6 H, aromatic, olefin).

1-(Methylsulfinyl)-1-(diethoxyphosphoryl)-2-(2,4,6-trimethylphenyl)ethene (12c). The procedure as given for **12a** (Procedure B) was followed. Crude **12c** was chromatographed (silica gel, benzene/methanol/acetone) giving an oil which crystallized on standing. Careful washing with hexane gave analytically pure **12c**: mp 66.5–68 °C; IR (KBr) 1020, 1234 [$P(O)(OEt)_2$], 1044 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 1.06, 1.22 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 2.17 (s, 6 H, *o*-CH_3), 2.24 (s, 3 H, *p*-CH_3), 2.88 (s, 3 H, CH_3SO), 3.38–4.10 (m, 4 H, OCH_2CH_3), 6.85 (br s, 2 H, aromatic), 7.90 (d, 1 H, J = 42 Hz, olefin); Anal. Calcd for $C_{16}H_{25}O_4SP$: C, 55.80; H, 7.32. Found: C, 55.82; H, 7.29.

1-(Methylsulfinyl)-1-(diphenylphosphoryl)-2-phenylethene (12d). The procedure as given for **12a** (Procedure B) was followed. Crude **12d** was chromatographed (silica gel, methanol/chloroform/diisopropyl ether) giving an oil which crystallized on standing: mp 160–168 °C; IR (KBr) 1061 (S=O), 1180 cm^{-1} (P=O); ^1H NMR ($CDCl_3$) δ 2.63 (s, 3 H, CH_3SO), 6.97–7.88 (m, 15 H, aromatic), 8.20 (d, 1 H, J = 32 Hz); MS, *m/e* 366 (M^+).

Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. **1a**, 1080-32-6; **1b**, 57277-25-5; **1c**, 63909-51-3; **1d**, 63909-50-2; **1e**, 38066-16-9; **1f**, 28460-01-7; **1g**, 13119-15-8; **1h**, 2959-74-2; **1i**, 31238-57-0; **1j**, 3167-63-3; **2** (R_1 = EtO), 14467-94-8; **2** (R_1 = Ph), 4920-02-9; **3a**, 37628-27-6; **3b**, 87762-53-6; **3c**, 87762-54-7; **3d**, 87762-55-8; **3e**, 87762-56-9; **3f**, 87762-57-0; **3g**, 87762-58-1; **3h**, 87762-59-2; **3i**, 87762-60-5; **3j**, 87781-74-6; **3k**, 33521-86-7; **3l**, 87762-61-6; **3m**, 87762-62-7; **3n**, 87762-63-8; **3o**, 87762-64-9; **3p**, 87762-65-0; **3q**, 87762-66-1; **3r**, 23176-47-8; **3s**, 87762-67-2; **5a**, 87762-68-3; **5b**, 87762-69-4; **5c**, 87762-70-7; **5d**, 87762-71-8; **5e**, 87762-72-9; **5f**, 87762-73-0; **5g**, 87762-74-1; **5h**, 87762-75-2; **5i**, 87762-76-3; **5j**, 87762-77-4; **5k**, 87762-78-5; **5l**, 87762-79-6; **5m**, 87762-80-9; **5n**, 87762-81-0; **5r**, 87762-82-1; **5s**, 87762-83-2; **6a**, 87762-84-3; **6b**, 87762-85-4; **6d**, 87762-86-5; **6e**, 87762-87-6; **6f**, 87762-88-7; **6g**, 87762-89-8; **6h**, 87762-90-1; **6i**, 87762-91-2; **6j**, 87762-92-3; **6k**, 87762-93-4; **6l**, 87762-94-5; **6n**, 87762-95-6; **6r**, 87762-96-7; **6s**, 87762-97-8; **7a**, 87762-98-9; **7b**, 87762-99-0; **7c**, 87763-00-6; **7e**, 87763-01-7; **7f** (isomer 1), 87763-02-8; **7f** (isomer 2), 87763-03-9; **8a**, 100-52-7; **8b**, 104-87-0; **8c**, 100-10-7; **8d**, 123-11-5; **8e**, 487-68-3; (*E*)-**9a**, 73774-46-6; (*Z*)-**9a**, 73774-47-7; (*E*)-**9b**, 87763-04-0; (*Z*)-**9b**, 87763-05-1; (*E*)-**9c**, 87763-06-2; (*Z*)-**9c**, 87763-07-3; (*E*)-**9d**, 87763-08-4; (*Z*)-**9d**, 87763-09-5; (*E*)-**9e**, 87763-10-8; (*Z*)-**9e**, 87763-11-9; (*E*)-**9f**, 87763-12-0; (*Z*)-**9f**, 87763-13-1; (*E*)-**9g**, 87763-14-2; (*Z*)-**9g**, 87763-15-3; **10a** (R_3 = Me), 87763-16-4; **10a** (R_3 = *n*-Bu), 87763-28-8; **10b**, 87763-17-5; **11a**, 25944-64-3; **11b**, 87763-18-6; (*Z*)-**12a**, 87763-19-7; (*E*)-**12a**, 87763-20-0; **12b**, 87763-21-1; **12c**, 87763-22-2; **12d**, 87763-23-3; (*Z*)-**13a**, 87763-24-4; (*E*)-**13a**, 87763-25-5; (*Z*)-**13b**, 87763-26-6; (*E*)-**13b**, 87763-27-7.

Supplementary Material Available: Characteristics of compounds **3**, **5**, **6**, **7**, and **9** not described in the Experimental Section (14 pages). Ordering information is given on any current masthead page.