Notes

Fluoride Ion Induced Thiophilic Reactivity of Organosilanes with Sulfines: Regiospecific Access to Allyl and Benzyl Sulfoxides

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Studies[1] of the chemistry of sulfines **1** (thione *S*-oxides) have shown that these heterocumulenes are versatile intermediates in organic synthesis. They undergo a variety of cycloaddition reactions with dienes[2] and 1,3-dipoles,[3] and recently a complete asymmetric induction with chiral sulfines was reported.[4] Attention has also been focused on their reactivity toward nucleophilic species:[5] the carbophilic or thiophilic course of this reaction was found to be dependent on the nature of the reagent (lithium,[5b,d−g] sodium,[5b] or Grignard reagents[5c]) and on the substituents attached to the sulfine carbon atom. Thiophilic attack is more frequently observed,[5b,d−f] but some cases of carbophilic substitution on the sulfinyl carbon have been reported.[5a,b,f]

Our long interest in the chemistry of sulfurated molecules,[6] joined with our recent interest in their reactivity toward organosilicon compounds, led us recently to disclose a novel fluoride ion induced addition of allylsilanes and benzylsilane with thiocarbonyl molecules such as thioketones[7] and dithioesters.[7a,8] This reaction occurs under mild conditions and exclusively affords the corresponding allyl and benzyl sulfides, arising from thiophilic addition. It demonstrates a silicon-mediated inversion of the regiochemistry previously reported for the reaction of allyllithium or magnesium species with the same thiocarbonyl compounds.[9]

We were then interested in evaluating the behavior of somewhat related molecules, sulfines **1**. A thiophilic addition may be predicted, due to the electron-poor character of the sulfur center relative to carbon, but the behavior of known nucleophiles does not yet allow correlation of S *versus* C addition in terms of the hard or soft nature of the reagent. In contrast to literature expectations, we have shown that aliphatic sulfines of enethiolizable dithioesters are readily available by direct oxidation with mCPBA under strictly controlled conditions.[10] This and the former availability of aromatic sulfines[11] prompted us to investigate the reactivity of various sulfines toward silylated nucleophiles with the aim of getting information about the competition between a nucleophilic attack at the sulfur and the carbon atom of the sulfinyl moiety.

Results

The reaction of aromatic sulfines **1a-c** with allylsilane **2a** was performed, in the presence of anhydrous TBAF in DMF at room temperature for some hours (Scheme 1). Allylic sulfoxides **3aa**−**ca** were isolated (Table 1, entries 1−3). Thiophilic addition is thus demonstrated. The fluoride ion induced reactivity of allylsilanes, due to its inherent mildness, allows a smooth transformation of this class of very reactive sulfur compounds.

No product from carbophilic addition was detected in the crude materials. It must be noted that, for the unsubstituted allylsilane **2a**, minor amounts of α,β-unsaturated sulfoxides (<10%) have been detected, thus showing that, under these conditions, some isomerization of the double bond occurs.[12]

Next we examined the reactivity of substituted allylsilanes. The reaction occurs smoothly when using (phenylallyl)silane **2b** (entries 4, 5), affording 3-phenylallyl sulfoxides **3ab** and **3bb**. Inversion of the allyl moiety has not been observed. The stereochemistry of the double bond of the starting allylsilane was always retained in the final allyl sulfoxides.

Other sulfines, **1d**−**f**, deriving from aromatic or aliphatic dithioesters (entries 6−9), also undergo a smooth thiophilic attack in the presence of TBAF. Products **3da**, **3ea**, **3fa**, and **3eb** are dithioacetal monoxides, derivatives that have been reported as useful intermediates, synthetically equivalent to acylcarbanions.[5e,13] In the cases of compounds **3ea**, **3fa**, and **3eb**, the isolated yields are generally lower, this due to partial decomposition of the

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(1) (a) Zwanenburg, B. *Phosphorus, Sulfur Silicon, Relat. Elem.* **1989**, *43*, 1. Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 1. (b) Metzner, P. *Phosphorus, Sulfur Silicon, Relat. Elem.* **1991**, *59*, 1 and refs. cited therein.

(2) Zwanenburg, B.; Thijs, L.; Broens, J. B.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 443.

(3) Zwanenburg, B.; Wagenar, A.; Thijs, L.; Strating, J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 73. Bonini, B. F.; Maccagnani, G.; Wagenar, A.; Thijs, L.; Zwanenburg, B.; *J. Chem. Soc., Perkin Trans. 1* **1971**, 2490.

(4) Porskamp, P. A. T. W.; Haltiwanger, R. C.; Zwanenburg, B. *Tetrahedron Lett.* **1983**, *24*, 2035.

(5) (a) Cerreta, F.; Leriverend, C.; Metzner, P. *Tetrahedron Lett.* **1993**, *34*, 6741. (b) Loontjes, J. A.; Van Der Leji, M.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 39. (c) Ohno, A.; Uohama, M.; Nakamura, K.; Oka, S. *J. Org. Chem.* **1979**, *44*, 2244. (d) Zwanenburg, B.; Kielbasinski, P. *Tetrahedron* **1979**, *38*, 169. (e) Veenstra, G. B.; Zwanenburg, B. *Tetrahedron* **1978**, *34*, 1585. (f) Veenstra, G. B.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 28. (g) Scholtz, A. G.; Schlessinger, R. H. *J. Chem. Soc. C* **1970**, 747 and 748.

(6) (a) Le Nocher, A.-M.; Metzner, P. *Tetrahedron Lett.* **1992**, *33*, 6151. (b) Désert, S.; Metzner, P. *Tetrahedron* **1992**, *48*, 10327. (c) Degl'Innocenti, A.; Capperucci, A.; Mordini, A.; Reginato, G.; Ricci, A.; Cerreta, F. *Tetrahedron Lett.* **1993**, *34*, 873. (d) Capperucci, A.; Degl'Innocenti, A.; Ricci, A.; Mordini, A.; Reginato, G. *J. Org. Chem.* **1991**, *56*, 7326. (e) Bellucci, G.; Capperucci, A.; Degl'Innocenti, A.; Ricci, A.; Mordini, A.; Reginato, G. *Phosphorus, Sulfur Silicon, Relat. Elem.* **1991**, *59*, 117. (f) Ricci, A.; Degl'Innocenti, A.; Capperucci, A.; Reginato, G. *J. Org. Chem.* **1989**, *54*, 19.

(7) (a) Degl'Innocenti, A.; Bonini, B. F.; Mazzanti, G.; Capperucci, A.; Ferrara, M. C.; Ricci, A.; Zani, P. *Phosphorus, Sulfur Silicon, Relat. Elem.* **1993**, *74*, 365. (b) Capperucci, A.; Ferrara, M. C.; Degl'Innocenti, A.; Bonini, B. F.; Mazzanti, G.; Ricci, A.; Zani, P. *Synlett* **1992**, 880.

(8) Capperucci, A.; Degl'Innocenti, A.; Ferrara, M. C.; Bonini, B. F.; Mazzanti, G.; Ricci, A.; Zani, P. *Tetrahedron Lett.* **1994**, *35*, 161.

(9) (a) Metzner, P. *Synthesis* **1992**, 1185. (b) Metzner, P.; Thuillier, A. *Sulfur Reagents in Organic Synthesis*; Academic Press: London; 1994.

(10) Cerreta, F.; Le Nocher, A.-M.; Leriverend, C.; Metzner, P.; Pham, T. N. *Bull. Soc. Chim. Fr.* **1995**, *132*, 67.

(11) (a) Zwanenburg, B.; Thijs, L.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 577. (b) Zwanenburg, B.; Thijs, L.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 614.

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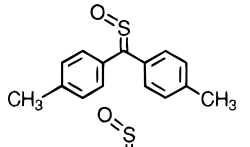
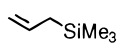
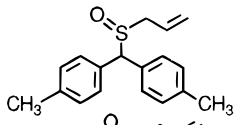
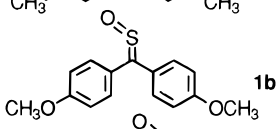
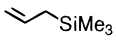
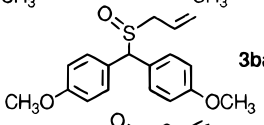
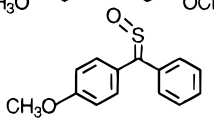
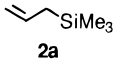
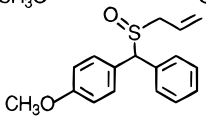
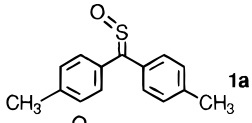
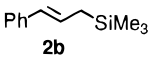
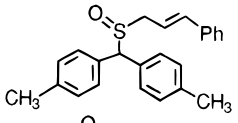
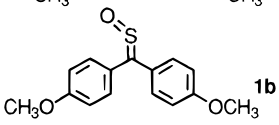
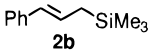
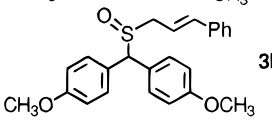
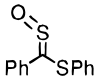
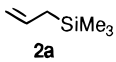
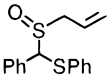
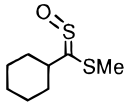
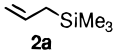
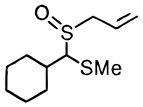
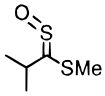
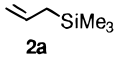
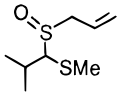
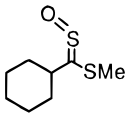
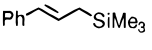
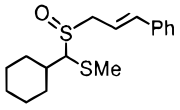
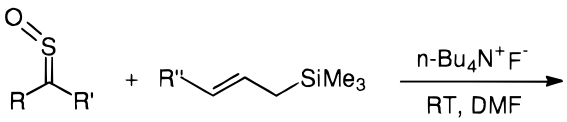
Table 1. Synthesis of Allyl Sulfoxides

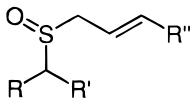
entry	sulfine	allylsilane	product	yield (%)[a]
1	 **1a**	 **2a**	 **3aa**	68
2	 **1b**	 **2a**	 **3ba**	76
3	 **1c**	 **2a**	 **3ca**	45[b]
4	 **1a**	 **2b**	 **3ab**	57
5	 **1b**	 **2b**	 **3bb**	55
6	 **1d**	 **2a**	 **3da**	61[b]
7	 **1e**	 **2a**	 **3ea**	32[b]
8	 **1f**	 **2a**	 **3fa**	30[b]
9	 **1e**	 **2b**	 **3eb**	31[b]

[a] Yields of isolated products. [b] Mixture of diastereoisomers.

Scheme 1



1a-g **2a-b**



3aa-fa
3ab-fb

starting dithioester into the carbonyl analogue, together with somewhat larger amounts of undetermined byproducts.

Worthwhile noting is the fact that even the more unstable sulfines **3e** and **3f** of enethiolizable aliphatic dithioesters afford the corresponding allyl sulfoxides in reasonable yields (entries 7 and 8).

Moreover, in these cases, we have never observed products from a nucleophilic substitution of the SR group at the C-atom, in contrast to other published works with different nucleophiles.[5a,b,14] This highlights the influence of the metal atom and the reaction conditions.

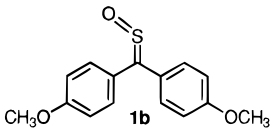
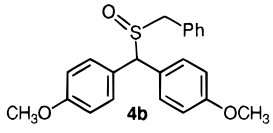
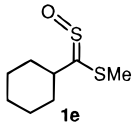
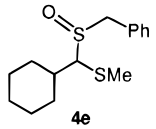
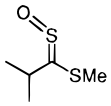
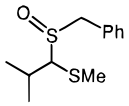
When using unsymmetrical sulfines (Table 1, entries 6, 7, 8, 9) we have used an *E* and *Z* mixture of geometrical isomers, usually in the range 90:10 or better, as determined by NMR just before the reaction with the allylsilane. Irrespective of the *E:Z* ratio, the products **3** have always been obtained as almost equimolar mixtures of diastereomeric allyl sulfoxides **3da**, **3ea**, **3fa**, and **3eb**. No diastereoselectivity could be obtained.

The reaction between sulfines and silylated nucleophiles is not restricted to allylsilanes, but can be conveniently extended to other silylated nucleophiles, such as benzylsilane. Under the same conditions, a smooth regiospecific transformation was achieved to the corresponding benzyl sulfoxides **4b**, **4e**, and **4f** (Table 2).

Conclusion

The reactivity of organosilanes with a wide range of thione *S*-oxides outlines the development of a novel, mild methodology of selective sulfine functionalization, which allows, through a thiophilic reaction, a regiospecific access to allyl- and benzylsulfoxides, useful starting materials in synthetic organic chemistry[15] and asymmetric synthesis.[16]

Table 2. Synthesis of Benzyl Sulfoxides

entry	sulfine	nucleophile	product	yield (%)[a]
1	 **1b**	$PhCH_2SiMe_3$	 **4b**	71
2	 **1e**	$PhCH_2SiMe_3$	 **4e**	36[b]
3	 **1f**	$PhCH_2SiMe_3$	 **4f**	33[b]

[a] Yields of isolated products. [b] Mixture of diastereoisomers.

Experimental Section

General. All reactions were performed in oven-dried glassware equipped with a magnetic stirring bar under a positive pressure of dry argon using standard syringe techniques.

N,*N*-dimethylformamide (DMF) was distilled from CaH_2 and stored over molecular sieves. TLC was performed on precoated silica gel 60 F_{254} plates.

NMR spectra were recorded on spectrometers operating at 200 and 300 MHz (^{1}H) and at 50 and 75 MHz (^{13}C) in deuteriochloroform ($CDCl_3$), with chloroform as an internal reference (7.26 ppm for ^{1}H, 77.0 ppm for ^{13}C). Composition of stereogenic mixtures was determined by NMR analysis on crude products before any purification. An italic a with the NMR data designates the presence of a stereogenic center and therefore inequivalent aromatic rings.

Preparation of thiocarbonyl compounds was accomplished by standard procedures (thioketones,[6d,17] dithioesters[10]). Sulfines **1a**−**c**,[11a] **1d**,[11b] and **1e**,**f**[10] were synthesized by the oxidation reaction of thiocarbonyl compounds with one equivalent of *m*-chloroperoxybenzoic acid in dichloromethane according to our procedure.[10] For dithioester sulfines **1e** and **1f**, freshly prepared materials have to be used (*E*:*Z* ratio > 90:10).

Reaction of Sulfines with Allylsilanes. General Procedure. To a solution of anhydrous TBAF,[18] prepared from TBAF·$3H_2O$ (0.27 mmol) in dry DMF (2.6 mL) containing activated[19] 4 Å molecular sieves (300 mg), was added, under inert atmosphere, a solution of the appropriate sulfine (0.21 mmol) and the allylsilane (0.27 mmol) in dry DMF (2.6 mL). The mixture was stirred at room temperature and progression of the reaction was monitored by TLC. After quenching with saturated NH_4Cl, the product was extracted with diethyl ether and dried over Na_2SO_4. Evaporation of the solvent afforded the crude material, which was purified on silica gel (elution with hexanes/EtOAc).

3-{[Bis(4-methylphenyl)methyl]sulfinyl}-1-propene (3aa). From 65 mg (0.27 mmol) of **1a**, after a 3 h reaction time, there was obtained 51 mg of **3aa** (68%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ^a 2.33 (s, 3H), 2.35 (s, 3H), 3.07−3.18 (dd, 1H, J = 7.3 and 12.7 Hz), 3.32−3.45 (dd, 1H, J = 6.5 and 12.8 Hz), 4.84 (s, 1H), 5.22−5.46 (m, 2H), 5.82−6.07 (m, 1H), 7.23−7.41 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ^a 21.1, 53.9, 69.7, 123.3, 126.0, 128.5, 129.2, 129.4, 129.9, 131.9, 132.8, 138.0, 138.1. Anal. Calcd for $C_{18}H_{20}$OS: C, 76.01; H, 7.09. Found: C, 75.77; H, 7.32.

3-{[Bis(4-methoxylphenyl)methyl]sulfinyl}-1-propene (3ba). From 80 mg (0.29 mmol) of **1b,** after a 3 h reaction time, there was obtained 70 mg of **3ba** (76%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ^a 3.04−3.16 (dd, 1H, J = 7.8 and 12.9 Hz), 3.31−3.42 (dd, 1H, J = 7.1 and 12.9 Hz), 3.79 (s, 3H), 3.81 (s, 3H), 4.82 (s, 1H), 5.21−5.46 (m, 2H), 5.80−6.03 (m, 1H), 6.87−6.96 (m, 4H), 7.28−7.42 (m, 4H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ^a 53.5, 55.2, 68.7, 114.1, 114.6, 123.2, 126.9, 127.7, 128.3, 129.8, 130.5, 159.4, 159.6. Anal. Calcd for $C_{18}H_{20}O_3S$: C, 68.32; H, 6.37. Found: C, 68.60; H, 6.25.

3-{[(4-Methoxyphenyl)phenylmethyl]sulfinyl}-1-propene (3ca). From 50 mg (0.20 mmol) of **1c**, after a 3 h reaction time, there was obtained 26 mg of **3ca** (45%). Diastereomeric ratio = 55:45.

Diastereomer A: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.04−3.18 (dd, 1H, J = 6.4 and 12.2 Hz), 3.32−3.45 (dd, 1H, J = 6.0 and 12.3 Hz), 3.79 (s, 3H), 4.85 (s, 1H), 5.18−5.49 (m, 2H), 5.81−6.04 (m, 1H), 6.78−6.93 (m, 2H), 7.30−7.51 (m, 7H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 53.05, 55.3, 69.4, 114.1, 114.6, 123.3, 125.9, 127.4, 128.6, 129.2, 129.8, 135.9, 159.9. Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.29; H, 6.33. Found: C, 71.00; H, 6.39.

Diastereomer B: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.06−3.18 (dd, 1H, 6.9 and 12.5 Hz), 3.31−3.43 (dd, 1H, J = 6.0 and 12.6 Hz), 3.81 (s, 3H), 4.87 (s, 1H), 5.19−5.48 (m, 2H), 5.81−6.03 (m, 1H), 6.88−6.97 (m, 2H), 7.31−7.49 (m, 7H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 53.6, 55.3, 69.5, 114.0, 114.3, 123.3, 125.9, 127.4, 128.7, 129.3, 130.6, 135.9, 159.8.

***(E)*-3-{[Bis(4-methylphenyl)methyl]sulfinyl}-1-phenyl-1-propene (3ab).** From 65 mg (0.27 mmol) of **1a**, after an 8 h reaction time, there was obtained 55 mg of **3ab** (57%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ^a 2.23 (s, 3H), 2.26 (s, 3H), 3.17−3.24 (dd, 1H, J = 7.7 and 13.2 Hz), 3.44−3.51 (dd, 1H, J = 6.7 and 13.3 Hz), 4.78 (s, 1H), 6.08−6.19 (m, 1H), 6.39 (bd, 1H, J = 16 Hz), 7.15−7.43 (m, 13H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ^a 21.1, 53.8, 70.2, 116.9, 126.5, 128.1, 128.5, 128.6, 129.2, 129.4, 129.9, 132.1, 132.7, 136.2, 137.6, 138.1, 138.2. Anal. Calcd for $C_{24}H_{24}$OS: C, 79.96; H, 6.71. Found: C, 79.60; H, 6.94.

(*E*)-3-{[Bis(4-methoxylphenyl)methyl]sulfinyl}-1-phenyl-1-propene (3bb). From 80 mg (0.29 mmol) of **1b**, after a 8 h reaction time, there was obtained 63 mg of **3bb** (55%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ^a 3.22−3.45 (dd, 1H, J = 7.9 and 13.2 Hz), 3.51−3.62 (dd, 1H, J = 7.0 and 13.3 Hz), 3.79 (s, 3H), 3.81 (s, 3H), 4.84 (s, 1H), 6.16−6.31 (m, 1H), 6.48 (bd, 1H, J = 15.8 Hz), 6.87−6.98 (m, 4H), 7.28−7.45 (m, 9H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ^a 53.7, 55.3, 69.1, 114.1, 114.6, 116.9, 126.5, 127.0,

(12) Base-catalyzed isomerization of allylic sulfoxides has been reported: (a) Svata, V.; Prochazka, V.; Bakos, V. *Coll. Czech. Chem. Commun.* **1978**, *43*, 2619. (b) O'Connor, D. E.; Broaddus, C. D. *J. Am. Chem. Soc.* **1964**, *86*, 2267. (c) O'Connor, D. E.; Lyness, W. J. *J. Am. Chem. Soc.* **1963**, *85*, 3044.

(13) Ogura, K.; Tsuchihashi, G.-i. *Tetrahedron Lett.* **1971**, 3151. Ogura, K. *Pure Appl. Chem.* **1987**, *59*, 1033. Richman, J. E.; Herrmann, J. L.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 3267.

(14) Veenstra, G. E.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 195.

(15) (a) Haynes, R. K.; Katsitis, A. G. *Aust. J. Chem.* **1989**, *42*, 1455. (b) Hartke, K.; Teuber, D. *Liebigs Ann. Chem.* **1988,** 225. (c) Hasaki, Y.; Sakuma, K.; Kaji, K. *J. Chem. Soc. Chem. Commun.* **1980**, 434. (d) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.

(16) Goodridge, R. J.; Hambley, T. W.; Haynes, K.; Ridley, D. D. *J. Org. Chem.* **1988**, *53*, 2881, and refs. cited therein.

(17) Cava, M. P.; Levinson, M. I. *Tetrahedron,* **1985**, *41*, 5087.

(18) Majetich, G.; Casares, A.; Chapman, D.; Behnke, M. *J. Org. Chem.* **1986**, *51*, 1745.

(19) Activated molecular sieves have been proved to be inert in the fluoride ion induced reactions of allylsilanes (see ref 18).

127.7, 128.1, 128.6, 129.9, 130.4, 136.1, 137.5, 159.4, 159.6. Anal. Calcd for $C_{24}H_{24}O_3S$: C, 73.44; H, 6.16. Found: C, 73.02; H, 6.42.

3-{[Phenyl(phenylthio)methyl]sulfinyl}-1-propene (3da). From 50 mg (0.20 mmol) of **1d**, after a 6 h reaction time, there was obtained 36 mg of **3da** (61%). Diastereomeric ratio = 61:39.

Diastereomer A: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.31−3.51 (m, 2H), 4.94 (s, 1H), 5.09−5.35 (m, 2H), 5.66−5.85 (m, 1H), 7.18−7.46 (m, 10H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 52.6, 70.6, 123.4, 125.9, 128.3, 128.6, 128.8, 129.1, 129.3, 132.5, 132.7, 133.5. Anal. Calcd for $C_{16}H_{16}OS_2$: C, 66.63; H, 5.59. Found: C, 66.37; H, 6.00.

Diastereomer B: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.32−3.53 (m, 2H), 5.01 (s, 1H), 5.09−5.36 (m, 2H), 5.66−5.85 (m, 1H), 7.18−7.46 (m, 10H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 53.4, 72.0, 123.6, 126.3, 128.7, 128.8, 129.0, 129.2, 129.4, 132.6, 132.8, 133.6.

3-{[Cyclohexyl(methylthio)methyl]sulfinyl}-1-propene (3ea). From 60 mg (0.31 mmol) of **1e**, after a 3 h reaction time, there was obtained 23 mg of **3ea** (32%). Diastereomeric ratio = 56:44.

Diastereomer A: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.21−1.40 (m, 6H), 1.62−1.78 (m, 2H), 1.93−2.12 (m, 3H), 2.31 (s, 3H), 3.19 (d, 1H, J = 6.5 Hz), 3.56−3.67 (dd, 1H, J = 8.0 and 15.2 Hz), 3.75−3.86 (dd, 1H, J = 8.1 and 14.8 Hz), 5.34−5.42 (m, 2H), 5.72−5.95 (m, ^{1}H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.5, 25.9, 26.0, 26.1, 31.0, 31.6, 37.7, 54.0, 70.9, 123.3, 126.5. Anal. Calcd for $C_{11}H_{20}OS_2$: C, 56.85; H, 8.67. Found: C, 57.00; H, 8.70.

Diastereomer B: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.21−1.37 (m, 6H), 1.55−1.78 (m, 5H), 2.22 (s, 3H), 3.41 (d, 1H, J = 4.8 Hz), 3.61−3.68 (m, 1H), 3.82−3.91 (m, 1H), 5.37−5.52 (m, 2H), 5.95−6.13 (m, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 18.0, 25.8, 26.0, 26.1, 29.6, 31.8, 37.2, 56.2, 70.7, 131.3, 137.4.

3-{[(2-Methylpropyl)(methylthio)methyl]sulfinyl}-1-propene (3fa). From 40 mg (0.27 mmol) of **1f,** after a 3 h reaction time, there was obtained 15 mg of **3fa** (30%). The presence of two isomers was observed on NMR spectra (isomer A:isomer B, 80:20). The NMR data refer to the major isomer: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.15 (d, 3H, J = 6.7 Hz), 1.24 (d, 3H, J = 6.6 Hz), 2.33 (s, 3H), 2.32−2.49 (m, partially overlapped with the peak at 2.33 ppm, 1H), 3.19 (d, 1H, J = 6.8 Hz), 3.55−3.67 (dd, 1H, J = 6.3 and 12.6 Hz), 3.73−3.82 (dd, 1H, J = 6.7 and 12.4 Hz), 5.36−5.52 (m, 2H), 5.75−6.10 (m, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.7, 20.3, 21.3, 28.7, 54.2, 72.4, 123.3, 126.4. Anal. Calcd for $C_8H_{16}OS_2$: C, 49.95; H, 8.38. Found: C, 50.29; H, 8.43.

Minor isomer (not isolated, characteristic data): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.36 (s, 3H), 3.42 (d, 1H, J = 4.2 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 16.8, 27.2, 52.5, 73.8, 123.4.

***(E)*-3-{[Cyclohexyl(methylthio)methyl]sulfinyl}-1-phenyl-1-propene (3eb).** From 60 mg (0.31 mmol) of **1e**, after a 6 h reaction time, there was obtained 30 mg of **3eb (**31%). Diastereomeric ratio = 53:47.

Diastereomer A: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.19−1.38 (m, 6H), 1.58−1.81 (m, 2H), 1.94−2.18 (m, 3H), 2.32 (s, 3H), 3.23 (d, 1H, J = 6.3 Hz), 3.63−3.74 (dd, 1H, J = 6.7 and 13.6 Hz), 3.98−4.08 (dd, 1H, J = 8.2 and 13.2 Hz), 6.10−6.27 (m, 1H), 6.42−6.76 (m, 1H), 7.24−7.43 (m, 5H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.5, 25.6, 25.9, 26.1, 28.8, 31.0, 36.9, 52.5, 71.0, 117.2, 126.5, 128.2, 128.6, 136.0, 137.8. Anal. Calcd for $C_{17}H_{24}OS_2$: C, 66.18; H, 7.84. Found: C, 65.87; H, 8.00.

Diastereomer B: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.18−1.37 (m, 6H), 1.56−2.01 (m, 5H), 2.38 (s, 3H), 3.46 (d, 1H, J = 3.9 Hz), 3.74−3.85 (dd, 1H, J = 7.4 and 13.8 Hz), 3.94−4.04 (dd, 1H, J = 8.0 and 13.2 Hz), 6.31−6.46 (m, 1H), 6.50−6.74 (m, 1H), 7.22−7.43 (m, 5H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 18.0, 25.7, 26.0, 27.5, 30.6, 31.6, 37.7, 53.8, 73.1, 117.5, 126.6, 128.3, 128.7, 136.1, 137.9.

Reaction of Sulfines with Benzylsilane. General Procedure. Following the preceding procedure, the sulfine (0.21 mmol) and benzyltrimethylsilane (0.27 mmol), dissolved in dry DMF (2.6 mL), were added, under inert atmosphere, to a solution of anhydrous[18] TBAF (0.27 mmol) in dry DMF (2.6 mL), at room temperature. Progression of the reaction was monitored by TLC. The mixture was then extracted with diethyl ether, after quenching with saturated NH_4Cl, and dried over Na_2SO_4, and the desired benzyl sulfoxides were purified on silica gel (elution with hexanes/EtOAc).

Bis(4-methoxyphenyl)[(phenylmethyl)sulfinyl]-methane (4b). From 70 mg (0.26 mmol) of **1b**, after a 4 h reaction time, there was obtained 66 mg of **4b** (71%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ^a 3.68 (d, 1H, J = 13.2 Hz), 3.79 (s, 3H), 3.82 (s, 3H), 3.86 (d, 1H, J = 13.2 Hz), 4.63 (s, 1H), 6.87−6.96 (m, 4H), 7.18−7.48 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ^a 55.3, 56.2, 68.6, 114.0, 114.6, 126.8, 128.0, 128.1, 128.6, 129.8, 130.1, 130.5, 130.7, 159.4, 159.5. Anal. Calcd for $C_{22}H_{22}O_3S$: C, 72.10; H, 6.05. Found: C, 71.87; H, 6.36.

Cyclohexyl(methylthio)[(phenylmethyl)sulfinyl]-methane (4e). From 60 mg (0.31 mmol) of **1e,** after a 4 h reaction time, there was obtained 32 mg of **4e** (36%). Diastereomeric ratio = 55:45.

Diastereomer A: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.05−1.96 (m, 10H), 1.92−2.15 (m, 1H), 2.29 (s, 3H), 3.34 (d, 1H, J = 3.8 Hz), 3.89 (d, 1H, J = 12.8 Hz), 4.41 (d, 1H, J = 12.8 Hz), 7.31−7.37 (m, 5H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 18.1, 25.6, 25.8, 26.0, 30.8, 31.4, 37.4, 56.0, 74.1, 128.2, 129.0, 129.1, 131.0. Anal. Calcd for $C_{15}H_{22}OS_2$: C, 63.78; H, 7.85. Found: C, 64.29; H, 7.73.

Diastereomer B: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.05−1.96 (m, 10H), 1.92−2.15 (m, 1H), 2.27 (s, 3H), 2.99 (d, 1H, J = 7.4 Hz), 4.16 (d, 1H, J = 12.8 Hz), 4.36 (d, 1H, J = 12.8 Hz), 7.31−7.37 (m, 5H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.0, 25.6, 25.9, 26.0, 27.8, 31.1, 37.2, 55.8, 69.7, 128.2, 128.7, 129.9, 130.4.

2-Methyl-1-(methylthio)-1-[(phenylmethyl)sulfinyl]propane (4f). From 40 mg (0.27 mmol) of **1f**, after a 6 h reaction time, there was obtained 21 mg of **4f** (33%). Diastereomeric ratio = 57:43.

Diastereomer A: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.04 (d, 3H, J = 6.6 Hz), 1.15 (d, 3H, J = 7 Hz), 2.28 (s, 3H), 2.54−2.69 (m, 1H), 3.36 (d, 1H, J = 3.2 Hz), 3.87 (d, 1H, J = 12.8 Hz), 4.45 (d, 1H, J = 12.8 Hz), 7.36−7.40 (m, 5H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 17.2, 18.1, 20.5, 27.6, 56.0, 75.0, 128.2, 128.8, 130.3, 131.2. Anal. Calcd for $C_{12}H_{18}OS_2$: C, 59.46; H, 7.48. Found: C, 59.11; H, 7.62.

Diastereomer B: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.13 (ap t, 6H, J = 7 Hz), 2.30 (s, 3H), 2.30−2.46 (m, partially overlapped with the peak at 2.30 ppm, 1H), 2.97 (d, 1H, J = 7.4 Hz), 4.14 (d, 1H, J = 12.8 Hz), 4.32 (d, 1H, J = 12.8 Hz), 7.32−7.34 (m, 5H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.1, 20.6, 21.1, 28.6, 56.1, 71.2, 128.2, 129.0, 129.9, 130.4.

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