JOC Article

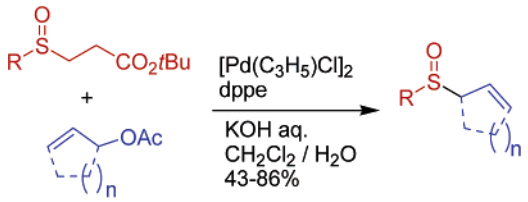
Preparation of Allyl Sulfoxides by Palladium-Catalyzed Allylic Alkylation of Sulfenate Anions

Guillaume Maitro, Guillaume Prestat, David Madec,* and Giovanni Poli*

Laboratoire de Chimie organique (UMR CNRS 7611), Institut de Chimie Moléculaire (FR 2769), Université Pierre et Marie Curie-Paris 6, Case 183, 4 Place Jussieu, F-75252, Paris Cedex 05, France

giovanni.poli@upmc.fr; david.madec@upmc.fr

Received June 30, 2006

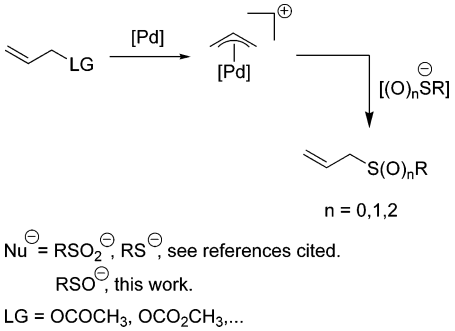


Palladium-catalyzed allylic alkylation of sulfenate anions, generated from β-sulfinylesters by retro-Michael reaction, can take place under biphasic conditions. This new reaction provides a simple, mild, and efficient route to allyl sulfoxides in good yields.

Introduction

Palladium-catalyzed allylic alkylation represents a primary synthetic tool to generate carbon−carbon and carbon−heteroatom bonds.[1] In particular, the use of sulfur-based nucleophiles[2] such as sulfinates[3] and thiolates[4] allows the easy generation of allyl sulfones and allyl ethers (Scheme 1). On the other hand, no related methods allowing the generation of allyl sulfoxides via allylation of a sulfenate anion has, to our knowledge, so far been reported, probably because of the nonstraightforward preparation of this nucleophile.[5] Such a transformation is expected to be of interest in light of the stereogenic nature of the newly generated sulfoxide sulfur atom, as well as of the sulfoxide−sulfenate rearrangement,[6] potentially associated to the resulting products.

SCHEME 1. Palladium-Catalyzed Allylic Alkylation of Sulfur Nucleophiles



Results and Discussion

We recently described the Pd-catalyzed allylation of EWG-stabilized α-sulfinyl carbanions,[7] a delicate transformation that could be successfully achieved by the use of specifically developed biphasic conditions.[8] In the course of this study we

(1) For reviews, see: (a) Tsuji, J. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-I., Ed.; John Wiley & Sons: New York, 2002; Vol.1, pp 1669−1844. (b) Trost, B. M.; Vranken, D. L. V. *Chem. Rev.* **1996**, *96*, 395−422. (c) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Book; Mill Valley, 1994.

(2) Kondo, T.; Mitsudo, T.-A. *Chem. Rev.* **2000**, *100*, 3205−3220.

(3) For palladium-catalyzed allylic alkylation of sulfinates, see: Inomata, K.; Yamamoto, T.; Kotake, H. *Chem. Lett.* **1981**, 1357−1360.

(4) For palladium-catalyzed allylic alkylation of thiolates, see: Goux, C.; Lhoste, P.; Sinou, D. *Tetrahedron Lett.* **1992**, *33*, 8099−8102. (b) Genêt, J. P.; Blart, E.; Savignac, M.; Lemeune, S.; Lemaire-Audoire, S.; Bernard, J. M. *Synlett* **1993**, 680−682. (c) Goux, C.; Lhoste, P.; Sinou, D. *Tetrahedron* **1994**, *50*, 10321−10330. (d) Kang, S.-K.; Park, D.-C.; Jeon, J.-H.; Rho, H.-S.; Yu, C.-M. *Tetrahedron Lett.* **1994**, *35*, 2357−2360.

(5) (a) Hogg, D. R. *Chemistry of Sulfenic Acids and Esters. The Chemistry of Sulfenic Acids and their Derivatives*; Wiley-Interscience: Toronto, 1990; pp 361−402. (b) Drabowicz, J.; Kielbasinski, P.; Mikolajczyk, M. *The Chemistry of Sulfenic Acids, Esters and their Derivatives*; Patai, S. Ed.; John Wiley & Sons: New York, 1990; pp 351−429. (c) O'Donnell, J. S.; Schwan, A. L. *Sulfur Lett.* **2004**, 25, 183-211.

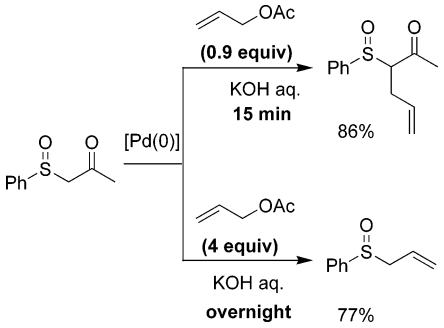
(6) (a) Bikart, P.; Carson, F. W.; Jacobus, J.; Miller, E. G.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4869−4876. (b) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147−155.

(7) Maitro, G.; Prestat, G.; Madec, D.; Poli, G. *Synlett* **2006**, 1055−1058.

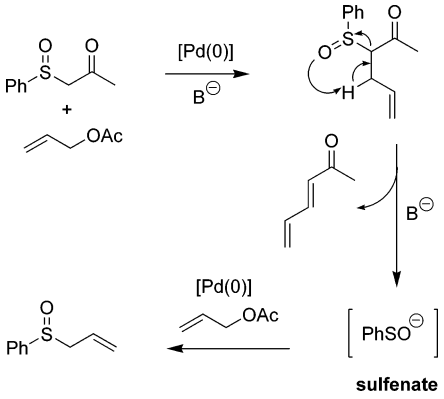
(8) Madec, D.; Prestat, G.; Martini, E.; Fristrup, P.; Poli, G.; Norrby, P.-O. *Org. Lett.* **2005**, *7*, 995−998.

10.1021/jo061359u CCC: $33.50
Published on Web 08/17/2006

SCHEME 2



SCHEME 3



serendipitously observed that, under prolonged reaction time and in the presence of an excess amount of the allylating agent, reaction of acetylmethyl phenyl sulfoxide with allyl acetate gave rise to allyl phenyl sulfoxide, instead of the expected allylated ketone (Scheme 2).

We interpreted such a result on the basis of a sulfenic acid elimination[9] of the allylated sulfoxide, followed by addition of potassium sulfenate to the transiently generated η^3-allyl palladium complex (Scheme 3).

The latter step of the above sequence would represent an unprecedented Pd-catalyzed allylation of sulfenate anions. With the aim of confirming the envisaged mechanism and, if positive, of studying the scope of the new transformation, we thus focused our attention on this transformation.

To turn this observation into a general reaction, we decided to distinguish the generation of the sulfenate anion from the allylation step. Sulfenate anions are rather unstable species and are usually generated in situ. Among the several options reported in the literature[10] our choice went to the base-promoted elimination of β-sulfinylesters, recently described by Perrio and Metzner.[11] Accordingly, the three sulfenate precursors **2a**−**c** have been prepared by addition of *p*-thiocresol, 2-thionaphthol, or 2-propanethiol to *tert*-butyl acrylate followed by Oxone-promoted thioether-to-sulfoxide oxidation of the resulting thioethers **1a**−**c** in the presence of wet alumina (Scheme 4).[12]

The Pd-catalyzed allylation between the in situ generated *p*-tolyl sulfenate anion and allyl acetate was chosen as the model reaction (Table 1). Much to our satisfaction, treatment of the two substrates with $[Pd(C_3H_5)Cl]_2$ (2 mol %), dppe (5 mol %), *n*Bu_4NBr (10 mol %), and KOH (2.0 equiv) in 1:1 CH_2Cl_2/H_2O gave, after 16 h at room temperature, the expected allyl *p*-tolyl sulfoxide in 50% yield (entry 1). An increase of the amount of KOH to 10 and 20 equiv, under otherwise identical conditions, raised the yield to 70% and 88%, respectively (entries 2 and 3). Interestingly, the presence of the phase transfer agent turned out to be unnecessary for the reaction (entry 4). Finally, an experiment performed in the absence of the palladium catalyst gave only partial degradation of the starting sulfinylester, thereby confirming the compulsory involvement of a η^3-allylpalladium intermediate (entry 5).

With the optimized reaction conditions in hand, scope and limitations of the transformation were then evaluated (Table 2). Reaction between the *p*-tolyl sulfenate precursor **2a** and cinnamyl acetate gave the corresponding cinnamyl sulfoxide **4a** in 82% yield (entry 2). The same product was also obtained,

SCHEME 4. Preparation of β-Sulfinylesters

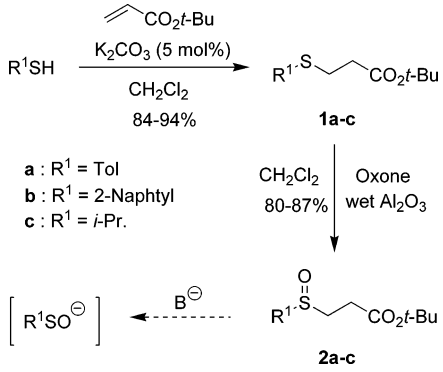
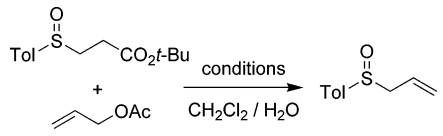


TABLE 1. Optimization of Reaction Conditions[a]



entry	catalytic system.	phase transfer agent	KOH (equiv)	yield (%)[b]
1	$[Pd(C_3H_5)Cl]_2$/dppe	*n*-Bu_4NBr	2	50
2	$[Pd(C_3H_5)Cl]_2$/dppe	*n*-Bu_4NBr	10	70
3	$[Pd(C_3H_5)Cl]_2$/dppe	*n*-Bu_4NBr	20	88
4	$[Pd(C_3H_5)Cl]_2$/dppe		20	86
5			20	0

[a] Reagents and reaction conditions: allyl acetate (2 equiv), β-sulfinylester, *n*-Bu_4NBr (10 mol % if used), $[Pd(C_3H_5)Cl]_2$ (2 mol %), dppe (5 mol %), KOH (50% aqueous solution, 2−20 equiv) in 1:1 CH_2Cl_2/H_2O mixture. [b] Yields are given for isolated products.

(9) (a) Trost, B.; Weber, L.; Strege, P.; Fullerton, T.; Dietsche, T. *J. Am. Chem. Soc.* **1978**, *100*, 3426−3435. (b) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887−4902.

(10) (a) Katritzky, A. R.; Takahashi, I.; Marson, C. M. *J. Org. Chem.* **1986**, *51*, 4914−4920. (b) O'Donnell, J. S.; Schwan, A. L. *Tetrahedron Lett.* **2003**, *44*, 6293−6296. (c) Maezaki, N.; Yoshigami, R.; Maeda, J.; Tanaka, T. *Org. Lett.* **2001**, *3*, 3627−3629. (d) Maezaki, N.; Yagi, S.; Ohsawa, S.; Ohishi, H.; Tanaka, T. *Tetrahedron* **2003**, *59*, 9895−9906. (e) Maezaki, N.; Yagi, S.; Yoshigami, R.; Maeda, J.; Suzuki, T.; Ohsawa, S.; Tsukamoto, K.; Tanaka, T. *J. Org. Chem.* **2003**, *68*, 5550−5558. (f) Maezaki, N.; Yagi, S.; Maeda, J.; Yoshigami, R.; Tanaka, T. *Heterocycles* **2004**, *62*, 263−277. (g) Sandrinelli, F.; Perrio, S.; Beslin, P. *J. Org. Chem.* **1997**, *62*, 8626−8627. (h) Sandrinelli, F.; Perrio, S.; Beslin, P. *Org. Lett.* **1999**, *1*, 1177−1180. (i) Sandrinelli, F.; Perrio, S.; Averbuch-Pouchot, M.-T. *Org. Lett.* **2002**, *4*, 3619−3622. (j) Sandrinelli, F.; Fontaine, G.; Perrio, S.; Beslin, P. *J. Org. Chem.* **2004**, *69*, 6916−6919. (k) Aversa, M. C.; Bonaccorsi, P.; Faggi, C.; Lamanna, G.; Menichetti, S. *Tetrahedron* **2005**, *61*, 11902−11909. (l) Martin, C.; Sandrinelli, F.; Perrio, C.; Perrio, S.; Lasne, M.-C. *J. Org. Chem.* **2006**, *71*, 210−214.

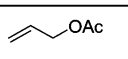
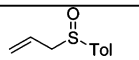
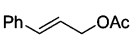
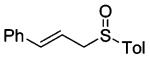
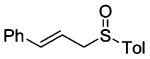
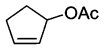
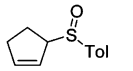
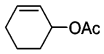
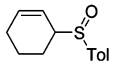
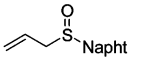
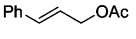
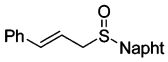
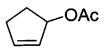
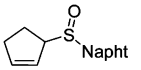
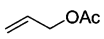
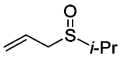
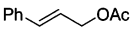
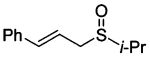
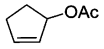
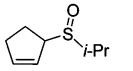
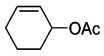
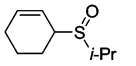
(11) Caupène, C.; Boudou, C.; Perrio, S.; Metzner, P. *J. Org. Chem.* **2005**, *70*, 2812−2815.

(12) Greenhalgh, R. P. *Synlett* **1992**, 235−236.

TABLE 2. Scope of the Reaction[a]

2a-c **a** : R^1 = Tol
b : R^1 = 2-Naphtyl
c : R^1 = *i*-Pr.

3-6a-c

Entry	Substrate	Allyl Acetate	Product		Yield (%)[b] (dr)[c]
1	**2a**			**3a**	86
2	"			**4a**	82
3	"			**4a**	75
4	"			**5a**	65 (50/50)
5	"			**6a**	14 (86/14)
6	**2b**			**3b**	63
7	"			**4b**	63
8	"			**5b**	54[d] (70/30)
9	**2c**			**3c**	83
10	"			**4c**	59
11	"			**5c**	43 (55/45)
12	"			**6c**	57 (55/45)

[a] Reagents and reaction conditions: allyl acetate (2 equiv), β-sulfinylesters, $[Pd(C_3H_5)Cl]_2$ (2 mol %), dppe (5 mol %), KOH (50% aqueous solution, 20 equiv) in 1:1 CH_2Cl_2/H_2O mixture. [b] Yields are given for isolated products. [c] Diastereomeric ratios determined by ^1H NMR. [d] Use of cyclohex-2-enyl acetate in place of cyclopent-2-enyl acetate did not allow generation of the corresponding sulfoxide.

albeit in a slightly lower yield, starting from the corresponding branched isomer (entry 3). Cyclic allylic acetates were then tested. In the event, cyclopent-2-enyl acetate gave cyclopent-2-enyl *p*-tolyl sulfoxide **5a** in 65% yield as an equimolar diastereomeric mixture (entry 4). More disappointingly, cyclohex-2-enyl acetate afforded the corresponding sulfoxide **6a** in a limited 14% yield as a 86:14 (*R**,*S**/*R**,*R**) ratio (entry 5).[13,14]

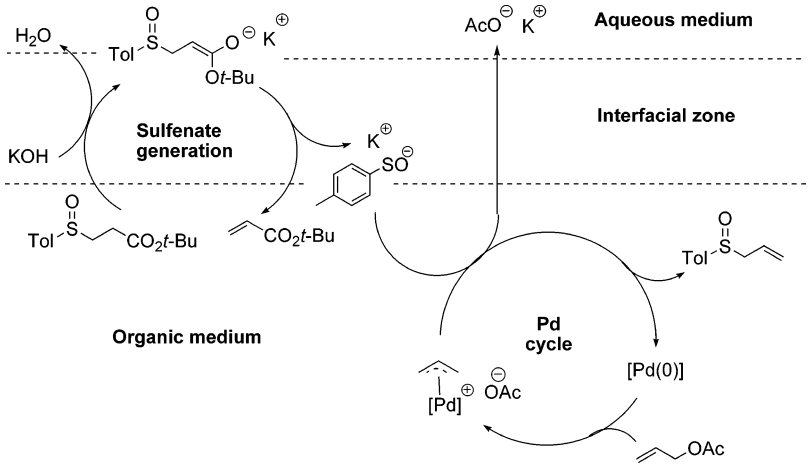
Reaction between the 2-naphthyl sulfenate precursor **2b** and allyl or cinnamyl acetate afforded the corresponding 2-naphthyl sulfoxides **3b** and **4b** in 63% yield (entries 6 and 7). Cyclic allylic acetates gave variable results. Indeed, whereas cyclopent-2-enyl acetate gave the corresponding sulfoxide **5b** in 54% yield (entry 8), cyclohex-2-enyl acetate did not allow generation of the expected homologous product. Alkyl sulfenates could also be satisfactorily entered. Thus, starting from 3-isopropylsulfinyl *tert*-butyl ester **2c** (R^1 = *i*-Pr), reaction with allyl or cinnamyl acetate afforded the corresponding isopropyl sulfoxides **3c** or **4c** in 83% and 59% yield, respectively (entries 9 and 10). Interestingly, with this alkyl sulfenate both the cyclic acetates cyclopent-2-enyl acetate and cyclohex-2-enyl acetate gave the expected corresponding sulfoxides **5c** and **6c** in 43% and 57% yield (entries 11 and 12).

We propose for this new allylation reaction the following mechanism (Scheme 5). KOH-mediated deprotonation of the β-sulfinylester, which likely takes place in the interfacial zone,[15] first gives the corresponding potassium ester enolate.[11] The following retro-Michael reaction generates a lypophilic acrylate ester and a sulfenate anion. Finally, interaction of the latter

(13) (a) Alajarín, M.; Pastor, A.; Cabrera, J. *Synlett* **2004**, 995−998. (b) Knight, D. J.; Lin, P.; Russell, S. T.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2701−2705.

(14) The major diastereoisomer of this reaction corresponds to the minor one obtained from sulfoxide−sulfenate rearrangement, ref 13.

SCHEME 5



species with a transiently generated η^3-allyl palladium complex, in turn derived from the allylic derivative, gives the allyl sulfoxide and regenerates the Pd(0) catalyst.

Conclusion

We have reported the first palladium-catalyzed allylation of sulfenate anions. This new, smooth, and operationally very simple method further extends the set of sulfur-based nucleophiles that can be successfully allylated under palladium catalysis. The stereogenic nature of the sulfur atom in the generated allyl sulfoxides, and the potential sulfoxide-sulfenate rearrangement associated to these compounds are expected to make of this reaction a synthetically interesting transformation.

Further Pd-catalyzed C−S bond formations involving sulfenate anions as nucleophilic partners are presently under investigation and will be reported in due course.

Experimental Section

Experimental Procedure and Characterization Data for β-Sulfanyl Esters. To a solution of thiol (20 mmol) and potassium carbonate (5 mol %) in dichloromethane (5 mL) was added rapidly *tert*-butyl acrylate (3.2 mL, 22 mmol). After 20 h of stirring, water was added to the mixture and the organic layer was successively washed with water (twice) and brine, then dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The resulting crude product was purified by flash chromatography.

3-*p*-Tolylsulfanyl-propionic Acid *tert*-Butyl Ester (1a). Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 95:5) afforded the product as a colorless oil (89% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 3.10 (t, J = 7.6 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H), 2.34 (s, 3H), 1.47 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.2, 136.8, 131.7, 131.0, 129.9, 80.9, 35.7, 30.0, 28.2, 21.1. IR (powder): 2977, 1726, 1492, 1392, 1248, 1144, 803 cm^{-1}. MS (CI/NH_3): *m*/*z* 270 (MNH_4^+), 253 (MH^+), 214, 197. HRMS calcd for $C_{14}H_{20}O_2S$ (M^+) 252.1184, found 252.1206.

3-(Naphthalen-2-ylsulfanyl)-propionic Acid *tert*-Butyl Ester (1b). Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 95:5) followed by recrystallization from ethanol/dichloromethane (95:5) mixture gave a white solid (84% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83−7.78 (m, 4H), 7.53−7.45 (m, 3H), 3.27 (t, J = 7.3 Hz, 2H), 2.63 (t, J = 7.3 Hz, 2H), 1.50 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.1, 133.8, 133.1, 132.0, 128.6, 127.9, 127.8, 127.2, 126.6, 125.9, 81.0, 35.5, 29.0, 28.1. IR (powder): 2989, 1737, 1362, 1223, 1168, 822, 750 cm^{-1}. MS (CI/NH_3): *m*/*z* 306 (MNH_4^+), 289 (MH^+), 250, 233. Anal. Calcd for $C_{17}H_{20}O_2S$: C, 70.80; H, 6.99; S, 11.12. Found: C, 70.73; H, 6.91; S, 10.89. Mp 62−64 °C.

3-Isopropylsulfanyl-propionic Acid *tert*-Butyl Ester (1c). The reaction was performed with a stoechiometric amount of K_2CO_3 for 36 h to give a colorless oil (94% yield), which was used without further purification. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.93 (h, J = 6.6 Hz, 1H), 2.74 (t, J = 7.6 Hz, 2H), 2.49 (t, J = 7.6 Hz, 2H), 1.45 (s, 9H), 2.51 (d, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.4, 80.7, 36.2, 34.9, 28.1, 25.6, 23.4. IR (neat): 2950, 1729, 1456, 1366, 1249, 1142, 845 cm^{-1}. MS (CI/NH_3): *m*/*z* 222 (MNH_4^+), 205 (MH^+), 149. HRMS calcd for $C_{10}H_{20}O_2S$ (M^+) 204.1184, found 204.1177.

Experimental Procedure and Characterization Data for β-Sulfinyl Esters. A dry dichloromethane solution (25 mL) of thioether (10 mmol) was added to a suspension of wet neutral alumine oxide (10 g, ratio alumina oxide/water = 5 g for 1 mL) and Oxone in dry dichloromethane (25 mL) at room temperature. The reaction mixture was refluxed for 3 h, then cooled to room temperature, filtered, and evaporated under reduced pressure. The crude residue was then purified by flash chromatography.

3-(*p*-Toluenesulfinyl)-propionic Acid *tert*-Butyl Ester (2a). Purification by silica gel flash chromatography (ethyl acetate/cyclohexane, 3:2 → 7:3) followed by recrystallization from *n*-hexane afforded the product as colorless crystals (87% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 3.16 (ddd, J = 15.4, 8.6, 6.6 Hz, 1H), 2.94 (ddd, J = 15.4, 8.6, 5.6 Hz, 1H), 2.75 (ddd, J = 17.2, 8.6, 6.8 Hz, 1H), 2.46 (ddd, J = 17.2, 8.6, 5.6 Hz, 1H), 2.45 (s, 3H), 1.44 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.5, 141.6, 139.9, 130.1, 124.1, 81.5, 51.6, 28.1, 27.4, 21.5. IR (powder): 2977, 1727, 1424, 1349, 1244, 1153, 1037, 812 cm^{-1}. MS (CI/NH_3): *m*/*z* 269 (MH^+), 230, 213. Anal. Calcd for $C_{14}H_{20}O_3S$: C, 62.66; H, 7.51; S, 11.95. Found: C, 62.53; H, 7.73; S, 12.11. Mp 61−62 °C.

3-(Naphthalene-2-sulfinyl)-propionic Acid *tert*-Butyl Ester (2b). Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 3:2 → 1:1) gave the pure product as a white solid (85% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 (d, J = 1.5 Hz, 1H), 7.97−7.88 (m, 3H), 7.60−7.55 (m, 3H), 3.27 (ddd, J = 15.2, 8.3, 6.7 Hz, 1H), 3.00 (ddd, J = 15.2, 8.3, 5.8 Hz, 1H), 2.78 (ddd, J = 17.2, 8.3, 6.8 Hz, 1H), 2.45 (ddd, J = 17.2, 8.6, 5.8 Hz, 1H), 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4, 140.1, 134.5, 132.9, 129.5, 128.5, 128.1, 127.8, 127.4, 124.8, 119.8, 81.5, 51.0, 28.0, 27.2. IR (powder): 2970, 1721, 1351, 1247, 1147, 1074, 1043,

(15) (a) Makosza, M.; Krylowaa, I. *Tetrahedron* **1999**, *55*, 6395−6402. (b) Mason, D.; Magdassi, S.; Sasson, Y. *J. Org. Chem.* **1990**, *55*, 2714−2717. (c) Gobbi, A.; Landini, D.; Maia, A.; Petricci, S. *J. Org. Chem.* **1998**, *63*, 5356−5361. (d) Lygo, B.; Andrews, B. *Acc. Chem. Res.* **2004**, *37*, 518−525.

820, 752 cm^{-1}. MS (CI/NH_3): *m/z* 610, 305 (MH^+), 266, 249. Anal. Calcd for $C_{17}H_{20}O_3S$: C, 67.08; H, 6.62; S, 10.53. Found: C, 66.68; H, 6.77; S, 10.53. Mp 93−95 °C.

3-(Propane-2-sulfinyl)-propionic Acid *tert*-Butyl Ester (2c). Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 1:1 → 0:10) afforded the pure product as a colorless oil (80% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.93−2.84 (m, 1H), 2.78−2.66 (m, 4H), 1.41 (s, 9H), 1.28 (d, J = 6.8 Hz, 3H), 1.23 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.7, 81.5, 50.7, 43.7, 28.5, 28.0, 15.8, 14.8. IR (neat): 2975, 1726, 1366, 1245, 1153, 1020, 842 cm^{-1}. MS (CI/NH_3): *m/z* 441, 238 (MNH_4^+), 221 (MH^+), 165. HRMS calcd for $C_7H_{14}O_3S$ ($M - C_3H_6^+$) 178.0664, found: 178.0650.

General Procedure for Palladium-Catalyzed Allylic Alkylation of Sulfenate Ions under Biphasic Conditions and Characterization Data for Allylic Sulfoxides. To a solution of allylpalladium chloride dimer (2 mol %) in dichloromethane (500 μL) was added dppe (5 mol %). The solution was stirred at room temperature for 5 min. Then, a solution of the acetate substrate (0.6 mmol in 1.5 mL of dichloromethane), β-sulfinylester (0.3 mmol in 1.5 mL of dichloromethane), 3.5 mL of distilled water, and 50% aqueous KOH solution (6 mmol) were successively added. The resulting biphasic system was stirred vigorously at room temperature for 1 h. Then, the aqueous phase was extracted twice with dichloromethane, the collected organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography.

Allyl-*p*-tolyl Sulfoxide (3a). Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 3:2) afforded the product as a pale yellow oil (86% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 5.68−5.57 (m, 1H), 5.31 (d, J = 10.1 Hz, 1H), 5.18 (dd, J = 17.2, 1.3 Hz, 1H), 3.54 (dd, J = 12.6, 7.3 Hz, 1H), 3.48 (dd, J = 12.6, 7.6 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.6, 139.7, 129.8, 125.4, 124.4, 123.8, 61.0, 21.5. Spectral data were in agreement with those previously reported.[16]

Cinnamyl-*p*-tolyl Sulfoxide (4a). Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 3:2) afforded a pale yellow solid (82% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (d, J = 8.3 Hz, 2H), 7.33−7.27 (m, 7H), 6.45 (d, J = 15.9 Hz, 1H), 5.99 (dt, J = 15.9, 7.6 Hz, 1H), 3.74−3.66 (m, 2H), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.7, 139.8, 138.4, 136.3, 129.9, 128.7, 128.3, 126.6, 124.5, 116.4, 61.0, 21.6. Spectral data were in agreement with those previously reported.[17]

(Cyclopent-2-enyl)-*p*-tolyl Sulfoxide (5a). Purification by silica gel flash chromatography (cyclohexane/ethyl acetate 3:2) gave the product as a mixture of two diastereoisomers (A and B) in a 1:1 ratio and as a pale yellow oil (65% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47−42 (m, $4H_{(A+B)}$), 7.27−7.24 (m, $4H_{(A+B)}$), 6.10−6.06 (m, $2H_{(A+B)}$), 5.52−5.49 (m, $1H_{(A)}$), 5.43−5.41 (m, $1H_{(B)}$), 3.93−3.89 (m, $1H_{(A)}$), 3.84−3.80 (m, $1H_{(B)}$), 2.37 (s, $6H_{(A+B)}$), 2.34−1.93 (m, $8H_{(A+B)}$). Spectral data were in agreement with those previously reported.[18]

(Cyclohex-2-enyl)-*p*-tolyl Sulfoxide (6a). Purification by silica gel flash chromatography (cyclohexane/ethyl acetate 3:2) afforded the product as a mixture of two diastereoisomers in a 86:14 ratio and as a yellow oil (14% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61−7.51 (m, $4H_{(A+B)}$), 7.38−7.31 (m, $4H_{(A+B)}$), 6.15−6.12 (m, $1H_{(A)}$), 6.02−5.99 (m, $1H_{(B)}$), 5.69−5.67 (m, $1H_{(A)}$), 5.16−5.13 (m, $1H_{(B)}$), 3.36−3.28 (m, $2H_{(A+B)}$), 2.44 (s, $3H_{(A)}$), 2.42 (s, $3H_{(B)}$), 2.37−2.31 (m, $2H_{(A+B)}$), 2.10−2.04 (m, $4H_{(A+B)}$), 1.96−1.80 (m, $4H_{(A+B)}$), 1.74−1.68 (m, $2H_{(A+B)}$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ $141.8_{(A+B)}$, $139.0_{(A+B)}$, $135.2_{(A+B)}$, 130.1 and 129.8, 125.5 and 125.0, 120.3 and 119.9, 63.1 and 61.6, 25.1 and 24.8, 23.4 and 21.7, 20.2 and 19.1. Spectral data were in agreement with those previously reported.[19]

Allyl-2-naphthyl Sulfoxide (3b). Purification by silica gel flash chromatography (cyclohexane/ethyl acetate, 95:5 → 7:3) afforded the product as a pale yellow solid (63% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.17 (s, 1H), 8.0−7.91 (m, 3H), 7.62−7.58 (m, 3H), 5.72−5.62 (m, 1H), 5.35−5.32 (m, 1H), 5.23 (dd, J = 16.9, 1.3 Hz, 1H), 3.68 (dd, J = 12.9, 7.8 Hz, 1H), 3.59 (dd, J = 12.9, 7.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.1, 134.6, 132.8, 129.3, 128.6, 128.2, 127.9, 127.4, 125.3, 125.2, 124.1, 120.2, 60.6. Spectral data were in agreement with those previously reported.[20]

Cinnamyl-2-naphthyl Sulfoxide (4b). Purification by silica gel chromatography (cyclohexane/ethyl acetate, 94:6 → 8:2) afforded the product as a pale yellow solid (63% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 (s, 1H), 7.99 (d, J = 8.6 Hz, 1H), 7.93−7.91 (m, 2H), 7.64−7.57 (m, 3H), 7.31−7.23 (m, 5H), 6.48 (d, J = 15.7 Hz, 1H), 6.02 (ddd, J = 15.7, 7.8, 7.6 Hz, 1H), 3.84−3.74 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.2, 138.6, 136.1, 134.6, 132.8, 129.3, 128.7, 128.6, 128.3, 128.1, 127.9, 127.4, 126.6, 125.2, 120.3, 116.2, 60.7. IR (powder): 3045, 1036, 966, 818, 742 cm^{-1}. MS (CI/NH_3): *m/z* 585, 310 (MNH_4^+), 293 (MH^+), 117. HRMS calcd for $C_{10}H_7OS$ ($M - C_9H_9^+$) 175.0218, found: 175.0206. Mp 133−135 °C.

(Cyclopent-2-enyl)-2-naphthalene Sulfoxide (5b): Purification by silica gel chromatography (cyclohexane/ethyl acetate, 9:1 → 8:2) gave a mixture of two diastereoisomers (A and B) in a 70:30 ratio and as a yellow oil (54% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.19−8.17 (m, $2H_{(A+B)}$), 7.99−7.91 (m, $6H_{(A+B)}$), 7.64−7.58 (m, $6H_{(A+B)}$), 6.19−6.15 (m, $2H_{(A+B)}$), 5.56−5.52 (m, $2H_{(A+B)}$), 4.10−4.08 (m, $1H_{(A)}$), 4.02−3.99 (m, $1H_{(B)}$), 2.54−2.16 (m, $6H_{(A+B)}$), 2.05−1.97 (m, $2H_{(A)}$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.2 and 139.4, 140.1 and 139.6, 134.6 and 134.5, 132.9 and 132.8, 129.2 and 128.9, $128.7_{(A+B)}$, $128.2_{(A+B)}$, 127.8 and 127.7, $127.3_{(A+B)}$, 125.5 and 125.4, 125.1 and 123.5, $120.8_{(A+B)}$, 73.4 and 71.8, 32.6 and 32.1, 24.5 and 22.9. IR (neat): 2912, 1067, 1041, 814, 732, 654 cm^{-1}. MS (CI/NH_3): *m/z* 351, 260 (MNH_4^+), 243 (MH^+), 225, 176. HRMS calcd for $C_{20}H_{14}O_2S_2$ ($M - C_5H_8^+$)$_2$ 350.0435, found 350.0402.

Allyl-isopropyl Sulfoxide (3c). Purification by silica gel flash chromatography (ethyl acetate/cyclohexane, 8:2) afforded a pale yellow oil (83% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.89 (dddd, J = 17.7, 10.1, 7.6, 7.3 Hz, 1H), 5.39 (dd, J = 10.1, 1.3 Hz, 1H), 5.35 (dd, J = 17.7, 1.3 Hz, 1H), 3.42 (dd, J = 13.1, 7.3 Hz, 1H), 3.33 (dd, J = 13.1, 7.6 Hz, 1H), 2.81 (h, J = 6.9 Hz, 1H), 1.29 (d, J = 6.9 Hz, 3H), 1.23 (d, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 126.3, 123.0, 52.6, 48.7, 16.3, 14.3. IR (neat): 2966, 1462, 1017, 926 cm^{-1}. MS (CI/NH_3): *m/z* 150 (MNH_4^+), 133 (MH^+). HRMS calcd for $C_6H_{12}OS$ (M^+) 132.0609, found 132.0596.

Cinnamyl-isopropyl Sulfoxide (4c). Purification by silica gel flash chromatography (ethyl acetate/cyclohexane, 75:25) afforded a pale yellow solid (59% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42−7.41 (m, 2H), 7.39−7.28 (m, 2H), 7.27−7.25 (m, 1H), 6.68 (d, J = 15.9 Hz, 1H), 6.29 (ddd, J = 15.7, 7.8, 7.8 Hz, 1H), 3.62 (dd, J = 13.1, 7.8 Hz, 1H), 3.53 (dd, J = 13.1, 7.8 Hz, 1H), 2.88 (h, J = 6.8 Hz, 1H), 1.35 (d, J = 6.8 Hz, 3H), 1.29 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.4, 136.1, 128.7, 128.3, 126.6, 117.2, 52.5, 48.7, 16.4, 14.3. IR (neat): 2967, 1494, 1398, 1032, 972, 754, 697, 640 cm^{-1}. MS (CI/NH_3): *m/z* 417, 226 (MNH_4^+), 209 (MH^+). HRMS calcd for C_9H_7 ($M - C_3H_7OS^+$) 115.0548, found 115.0559. Mp 54−55 °C.

(Cyclopent-2-enyl)-isopropyl Sulfoxide (5c). Purification by silica gel flash chromatography (ethyl acetate/cyclohexane, 75:25

(16) Antonjuk, D. J.; Ridley, D. D.; Smal, M. A. *Aust. J. Chem.* **1980**, *33*, 2635−2651.

(17) Goldmann, S.; Hoffmann, R. W.; Maak, N.; Geueke, K. J. *Chem. Ber.* **1980**, *113*, 831−844.

(18) Snider, B. B. *J. Org. Chem.* **1981**, *46*, 3155−3157.

(19) D. J.; Lin, P.; Russel, S. T.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1987**, *12*, 2701−2705. In our work, the major diastereomer is (*R**,*S**).

(20) Yadav, J. S.; Subba Reddy, B. V.; Srinivas, C.; Srihari, P. *Synlett* **2001**, 854−856.

→ 9:1) afforded a mixture of two diastereoisomers (A and B) in a 55:45 ratio and as a pale yellow oil (43% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.24−6.21 (m, $1H_{(A)}$), 6.15−6.13 (m, $1H_{(B)}$), 5.85−5.82 (m, $1H_{(A)}$), 5.61 (m, $1H_{(B)}$), 3.92−3.89 (m, $1H_{(A)}$), 3.83−3.80 (m, $1H_{(B)}$), 2.84−2.71 (m, $2H_{(A+B)}$), 2.55−1.99 (m, $4H_{(A+B)}$), 1.32 (d, J = 6.56 Hz, $6H_{(B)}$), 1.29 (d, J = 6.95 Hz, $6H_{(A)}$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.0 and 138.9, 124.9 and 124.2, 65.2 and 63.7, 48.2 and 47.8, 32.7 and 32.0, 25.0 and 22.8, 17.6 and 17.2, 14.7 and 14.0. IR (neat): 2929, 1728, 1459, 1156, 1011, 736 cm^{-1}. MS (CI/NH_3): m/z 317, 176 (MNH_4^+), 165, 159 (MH^+).

(Cyclohex-2-enyl)-isopropyl Sulfoxide (6c). Purification by silica gel flash chromatography (ethyl acetate/cyclohexane, 75:25 → 9:1) gave a mixture of two diastereoisomers (A and B) in a 55:45 ratio and as a pale yellow oil (57% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.17−6.13 (m, $1H_{(A)}$), 6.08−6.03 (m, $1H_{(B)}$), 5.83−5.80 (m, $1H_{(A)}$), 5.49−5.45 (m, $1H_{(B)}$), 3.33−3.32 (m, $1H_{(A)}$), 3.24−3.23 (m, $1H_{(B)}$), 2.92−2.78 (m, $1H_{(A+B)}$), 2.37−1.52 (m, $6H_{(A+B)}$), 1.36−1.27 (m, $6H_{(A+B)}$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.6 and 134.6, 120.1 and 119.7, 55.1 and 53.2, 47.0 and 45.2, 25.0 and 24.7, 24.0 and 21.4, 20.2 and 18.7, 18.4 and 17.5, 13.8 and 12.3. IR (neat): 2928, 1446, 1050, 1013, 726, 637 cm^{-1}. MS (CI/NH_3): m/z 345, 190 (MNH_4^+), 173 (MH^+). HRMS calcd for $C_9H_{16}OS$ (MH^+) 172.0922, found: 172.0917.

Acknowledgment. The support and sponsorship by CNRS and COST Action D24 "Sustainable Chemical Processes: Stereoselective Transition Metal-Catalysed Reactions" are kindly acknowledged.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO061359U