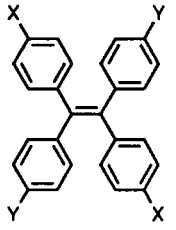
(R^2 = 0.85) was found with $\sum\sigma$. This is as expected, since the reduction builds up negative charge at sites directly in resonance with the ring substituents. This plot also accommodates, with high correlation coefficients, the reduction potentials for 1 (X = CN) and merostabilized tetraphenylethylenes 2 (X = H, Y = Me; X = H, Y = OMe; X = H, Y = CN; and X = OMe, Y = CN) and their geometric isomers in acetonitrile which were previously reported by Leigh and Arnold.[27]



2

The observed anion radical disproportionation equilibrium constants for 1 (Table II), however, are much less sensitive to the substituent, with an anomalously large difference being observed for only 1, X = F. The near invariability of the equilibrium constants for most members of this series indicates that although the electronic effect of the substituents greatly perturbs the reduction potentials, their effect on the disproportionation of the electrogenerated anion is negligible. This suggests that the substituents studied here have minor effects on ion pairing relative to the effects of solvent and counterion.

The cation disproportionation constants determined here (Table II), like the anion dismutations, fail to show strong substituent dependence, but rather exhibit appreciable solvent sensitivity. Thus, the strong solvent and ion-pairing effects observed in the disproportionation of radical anions seem to affect the radical cations similarly.

The oxidation and reduction potentials for pairs of electron-rich and -poor 1, Tables I and II, indicate that complete ground-state equilibration to form a dication–dianion pair would be endothermic, as is consistent with the absence of CT bands. Although this contrasting behavior is at least partially thermodynamic, it may also in fact derive from the kinetic retardation for electron transfer in these systems imposed by a requisite geometry change[18,28] encountered in either the two-electron oxidation or reduction or the difficulty of permitting strong electronic interaction between two substrates twisted from planarity in their ionic states. No evidence for ground-state charge-transfer complexation between electron-rich and -poor members of the series could be detected.

Experimental Section

Instrumentation. Absorption spectra were obtained on a Hewlett-Packard 8451A diode-array spectrophotometer. The cyclic voltammetric and differential pulse voltammetric experiments were performed on a Bioanalytical Systems BAS-100 electrochemical analyzer. The solvent (ca. 3 mL) was cryostatically distilled into the electrochemical cell, which had been held under vacuum for at least 1 h. The cell, which had a silver wire quasi-reference electrode (−0.38 V with respect to SCE) in a compartment separated by a pin hole, contained flame-dried basic alumina and approximately 300 mg of tetrabutylammonium perchlorate (TBAP), producing a final electrolyte concentration of approximately 0.3 M. The working electrode was a Pt disk electrode, and a Pt foil served as the counter electrode. Ferrocene was added to the solution after the measurements as an internal potential calibration. The substituted tetraphenylethylene was added as a solid via a side arm after checking the electroactivity of the background. Coulometry was conducted on a Princeton Applied Research (PAR) electrochemical apparatus (Model 173 potentiostat, Model 176 universal programmer, Model 179 coulometer, and Houston Instruments Model 2000 x-y-t recorder).

Materials. Tetrahydrofuran was distilled from sodium before being stored over $LiAlH_4$ under vacuum until use. Tetrabutylammonium perchlorate (TBAP, Aldrich) was recrystallized from acetone–ether and dried under vacuum before use.

Tetraphenylethylene (Aldrich) was used as received, and the substituted 1 were prepared by literature methods, often by titanium-induced reductive coupling of the substituted benzophenones as the key step:[29] tetra-4-biphenylylethylene (1, X = Ph),[29] tetra-4-tolylethylene (1, X = CH_3),[30] tetrakis(4-*tert*-butylphenyl)ethylene (1, X = *t*-Bu),[31] tetrakis(4-nitrophenyl)ethylene (1, X = NO_2),[32] tetrakis(4-fluorophenyl)ethylene (1, X = F),[33] tetrakis(4-bromophenyl)ethylene (1, X = Br),[34] tetrakis(4-chlorophenyl)ethylene (1, X = Cl),[29] tetrakis[4-(trifluoromethyl)phenyl]ethylene (1, X = CF_3),[35] tetrakis(4-anisylphenyl)ethylene (1, X = OMe),[29,36] tetrakis(4-aminophenyl)-ethylene (1, X = NH_2),[32] and tetrakis[4-(*N*,*N*,-dimethylamino)-phenyl]ethylene (1, X = NMe_2).[37]

Acknowledgment. We acknowledge the financial support of the U.S. Department of Energy, Office of Basic Energy Sciences. We are grateful to Dr. David Shultz for providing samples of several 1 and Dr. Changjin Lee for making the coulometry measurements described herein.

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Improved Method for the Preparation of Enantiomerically Pure Sulfinate Esters

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Applications of chiral sulfoxides[1] have been examined extensively since the pioneering studies of Phillips[2] and Gilman[3] that provided access to these materials in enantiomerically pure form. Their method, based on the separation of diastereomeric sulfinate esters of menthol and subsequent reaction with Grignard reagents, has remained, with some improvements,[4] the most practical technique for the preparation of enantiomerically pure sulfoxides.[5] The technique provides ready access to only one enantiomeric series because only one of the diastereomers of the intermediate menthol sulfinate esters is generally crystalline.[6]

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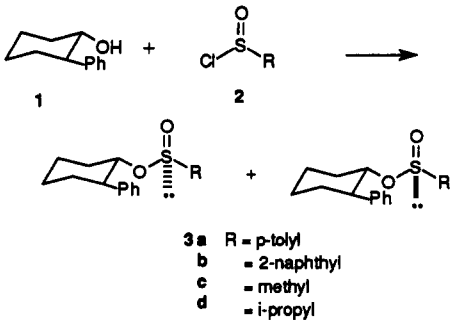

Figure 1.

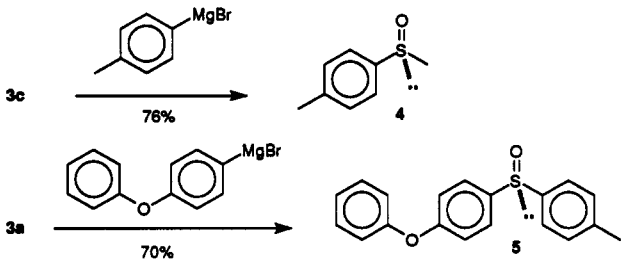

Figure 2.

As part of a broad program examining the utility of the chiral auxiliary *trans*-2-phenylcyclohexanol (1) introduced by us in 1986,[7] we have investigated the use of this alcohol for the production of enantiomerically enriched sulfinate esters. Indeed, reaction of 1 with an excess of alkane- and arenesulfinyl chlorides 2 affords sulfinate esters 3 (Figure 1) in good yield with considerably better [(4–10):1] kinetic selectivity than observed with menthol [(2–3):1].[8] It is important, however, to ensure that sufficient solvent is used so that all materials are in solution at the start of the reaction in order to ensure maximum selectivity. The diastereomers can be readily separated by chromatography (α 1.13–1.54), and in all four examples the major diastereomer is crystalline. Thus, separation is also possible by recrystallization, as, for example, the major diastereomer of **3a** was obtained in 98% de after two crystallizations with a recovery of 62%.

These sulfinate esters undergo typical reaction with Grignard reagents to provide sulfoxides in good yield with clean inversion of stereochemistry at sulfur. For example, the major diastereomer of the methanesulfinate ester **3c** was reacted with *p*-tolylmagnesium bromide to afford methyl *p*-tolyl sulfoxide in 76% yield and with 98% optical purity. In a similar fashion, the major diastereomer of the *p*-tolyl ester **3a** was reacted with (*p*-phenoxyphenyl)magnesium bromide to afford the derived sulfoxide in 70% yield (Figure 2).

Both enantiomers of our auxiliary are readily available,[9] and thus this selectivity can be used to advantage to provide ready and equal access to sulfinate esters and derived sulfoxides of either absolute configuration at sulfur.

In conclusion, we have demonstrated a new and practical method for the preparation of enantiomerically pure alkane- and arenesulfinate esters. Further transformation with Grignard reagents provides access to alkyl alkyl, alkyl aryl, and aryl aryl sulfoxides of high stereochemical purity in either absolute configuration.

Experimental Section

Materials. Skelly B was stirred first with concentrated sulfuric acid and then with solid sodium carbonate, filtered through alumina, and distilled before use. All other solvents and reagents were used as obtained from commercial sources unless stated otherwise.

Procedures. Reactions were routinely carried out under dry nitrogen or argon atmospheres with magnetic stirring. Preparative chromatography was carried out with a Waters 6000 A HPLC instrument with two 7.8 mm × 60 cm Porasil A silica gel semipreparative columns and with a refractive index detector. Analytical HPLC was performed with a Waters 6000A HPLC pump with two 30-cm Porasil A silica gel analytical columns with a Waters 440 UV detector.

(+)-*trans*-2-Phenylcyclohexyl *p*-Toluenesulfinates (3a). To a suspension of 5.84 g (32.8 mmol) of sodium *p*-toluenesulfinate (dried in an oven at 120 °C under vacuum overnight) in 30 mL of ether was added 2.4 mL (33 mmol) of distilled $SOCl_2$ at 0 °C over 0.5 h. After 2 h at rt, the reaction mixture was filtered and the solvent was removed in vacuo, affording 3.59 g of residue. To 0.37 g of this residue in 15 mL of ether was added dropwise a solution of 0.1 g (0.6 mmol) of (+)-*trans*-2-phenylcyclohexanol and 0.18 mL (2.3 mmol) of pyridine in 20 mL of ether at −78 °C over 0.5 h. After 3 h at −78 °C, the reaction mixture was quenched with H_2O and washed with dilute Na_2CO_3 solution, followed by dilute HCl and saturated NaCl solution, and dried over Na_2SO_4. The crude product was filtered through a silica gel column with 4:1 Skelly B/EtOAc to afford 0.17 g (92%) of a white solid. Analytical HPLC analysis both before and after this treatment showed a 10:1 *S*:*R* diastereomeric ratio of sulfinates (α 1.54, 4:1 Skelly B/EtOAc). The individual diastereomers were then obtained in stereochemically homogeneous form by semipreparative HPLC. Alternatively, separation could be accomplished by fractional crystallization. For example, a 1.49-g sample with a 7:3 ratio of diastereomers was crystallized from ethyl acetate/Skelly B. Two further fractions were obtained from the supernatant, and all three batches were combined and recrystallized from the same solvent, affording 0.65 g (62% recovery) of the major, *S* diastereomer that had 98% de (by analytical HPLC) with mp 139–140 °C.

For the major diastereomer: $[\alpha]^{25}_D$ +82° (*c* 2.0, acetone); ^{13}C NMR (75 MHz) δ 143.1 (s), 142.7 (s), 141.9 (s), 129.1 (d), 128.5 (d), 128.0 (d), 126.7 (d), 124.5 (d), 85.6 (d), 51.4 (d), 35.5 (t), 34.1 (t), 25.4 (t), 25.0 (t), 21.3 (q); ^1H NMR (300 MHz) δ 7.39–7.27 (m, 5 H), 7.07 (d, J = 8.1 Hz, 2 H), 6.79 (d, J = 8.1 Hz, 2 H), 4.55–4.47 (m, 1 H), 2.71–2.62 (m, 1 H), 2.34–2.32 (m, 1 H), 2.32 (s, 3 H), 2.00–1.20 (br m, 7 H); IR 3020, 3005, 1430, 1270 cm^{-1}; MS-CI m/z 315.4 (M^+ + H), 159.3; HRMS-CI m/z calcd for $C_{19}H_{22}O_2S$ 314.1341, found 314.1288. Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.58; H, 7.05; S, 10.20. Found: C, 72.56, H, 7.13; S, 10.14.

A sample of the minor diastereomer was recrystallized for analysis from acetone, mp 114–115 °C: $[\alpha]^{25}_D$ +176.5° (*c* 2.0, acetone); ^{13}C NMR (75 MHz) δ 142.7 (s), 142.0 (s), 142.0 (s), 129.4 (d), 128.2 (d), 127.8 (d), 126.3 (d), 125.0 (d), 81.1 (d), 50.3 (d), 35.1 (t), 34.1 (t), 25.6 (t), 25.0 (t), 21.5 (q); ^1H NMR (300 MHz) δ 7.26–7.22 (m, 3 H), 7.13–7.00 (m, 6 H), 4.30–4.23 (m, 1 H), 2.77–2.69 (m, 1 H), 2.48–2.43 (m, 1 H), 2.37 (s, 1 H), 1.95–1.34 (m, 7 H); IR 3010, 2850, 1105 cm^{-1}; MS-CI m/z 315.5 (M + H), 159.3, 157.3; HRMS-CI m/z calcd for $C_{19}H_{23}O_2S$ (M^+ + H) 315.1419, found 315.1427. Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.58; H, 7.05; S, 10.20. Found: C, 72.88; H, 7.07; S, 9.95.

(+)-*trans*-2-Phenylcyclohexyl 2-Naphthalenesulfinates (3b). The procedure above was followed with 207 mg (0.98 mmol) of 2-naphthalenesulfinyl chloride (prepared from the reduction of 2-naphthalenesulfonyl chloride),[10] 0.076 mL (0.98 mmol) of pyridine, and 40 mg (0.23 mmol) of (+)-*trans*-2-phenylcyclohexanol and a 4-h reaction time. Isolation as described above for **3a** afforded 67 mg (84%) as a 6.5:1 diastereomeric mixture (α 1.39, 4:1 Skelly B/EtOAc). The major diastereomer was ob-

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tained in 98% de by one crystallization from EtOAc/Skelly B (mp 138–139 °C). Pure samples of each diastereomer were obtained by semipreparative HPLC.

For the major diastereomer: mp 142.5–143 °C; $[\alpha]^{25}_D$ +104.2° (*c* 1.0, acetone); ^{13}C NMR (75 MHz) δ 143.2 (s), 142.3 (s), 134.7 (s), 132.3 (s), 128.9 (d), 128.7 (d), 128.6 (d), 128.2 (d), 127.8 (d), 127.8 (d), 126.8 (d), 125.3 (d), 120.5 (d) 86.1 (d), 51.5 (d), 35.3 (t), 34.2 (t), 25.5 (t), 25.1 (t); ^{1}H NMR (300 MHz) δ 7.79–7.75 (m, 2 H), 7.69 (d, *J* = 8.7 Hz, 1 H), 7.52–7.46 (m, 3 H), 7.40–7.38 (m, 3 H), 7.27–7.25 (m, 2 H), 6.84 (d, *J* = 8.4 Hz, 1 H), 4.62–4.55 (m, 1 H), 2.72–2.63 (m, 1 H), 2.42–2.38 (m, 1 H), 1.99–1.30 (br m, 7 H); IR 3020, 2920, 1850, 1470, 1440, 1340, 1130 cm^{-1}; MS-CI *m/z* 351 (M + H), 221, 193, 159; HRMS-CI *m/z* calcd for $C_{22}H_{23}O_2S$ (M^+ + H) 351.1419, found 351.1396.

For the minor diastereomer: mp 113–114 °C; $[\alpha]^{25}_D$ +124.5° (*c* 1.0, acetone); ^{13}C NMR (75 MHz) δ 142.6 (s), 142.1 (s), 134.8 (s), 132.4 (s), 129.1 (d), 128.9 (d), 128.2 (d), 128.0 (d), 127.8 (d), 126.8 (d), 126.5 (d), 126.1 (d), 120.8 (d), 81.6 (d), 50.4 (d), 35.2 (t), 34.1 (t), 25.6 (t), 25.1 (t); ^{1}H NMR (300 MHz) δ 7.86–7.81 (m, 3 H), 7.74–7.71 (dd, 1 H), 7.59–7.54 (m, 2 H), 7.27–7.11 (m, 4 H), 7.10–7.00 (m, 2 H), 4.35–4.20 (m, 1 H), 2.82–2.72 (m, 1 H), 2.54–2.49 (m, 1 H), 1.92–1.72 (m, 4 H), 1.50–1.26 (m, 3 H); IR 3020, 2920, 1590, 1470, 1440, 1340, 1130 cm^{-1}; MS-CI *m/z* 351 (M + H), 175, 159, 133; HRMS-CI *m/z* calcd for $C_{22}H_{23}O_2S$ (M^+ + H) 351.1419, found 351.1395.

(+)-*trans*-2-Phenylcyclohexyl Methanesulfinates (3c). The procedure above was followed except with 2.25 g (22.8 mmol) of methanesulfinyl chloride (prepared from dimethyl disulfide),[11] 1.85 mL (22.8 mmol) of pyridine, and 1.0 g (5.7 mmol) of (+)-*trans*-2-phenylcyclohexanol. Isolation as above afforded 1.08 g (80%) as a 9:2 mixture of diastereomers (α 1.20, 4:1 Skelly B/EtOAc). Pure samples of each diastereomer was obtained by semipreparative HPLC. The major diastereomer was assigned the *S* configuration at sulfur based on its conversion to (*S*)-methyl *p*-tolyl sulfoxide (see below). In this case, the minor diastereomer was less soluble and it was not possible to purify the major isomer by recrystallization. Conversly, the *R* isomer could be obtained in 98% de and 62% recovery by two crystallizations of a 1.49-g sample of a 3:7 mixture of major to minor diastereomer.

For the major diastereomer, (+)-(1*S*,2*R*)-*trans*-2-phenylcyclohexyl (*S*)-methanesulfinate: mp 36–38 °C; $[\alpha]^{25}_D$ +25° (*c* 2.0, acetone); ^{13}C NMR (75 MHz) δ 142.8 (s), 128.3 (d), 127.9 (d), 126.8 (d), 85.7 (d), 51.3 (d), 44.0 (q), 34.9 (t), 33.2 (t), 25.4 (t), 25.0 (t); ^{1}H NMR (300 MHz) δ 7.34–7.17 (m, 5 H), 4.23–4.14 (m, 1 H), 2.66–2.56 (m, 1 H), 2.30–2.23 (m, 1 H), 2.08 (s, 3 H), 1.98–1.25 (br m, 7 H); IR 3010, 2850, 1065, 1050 cm^{-1}; MS-CI *m/z* 239.3 (M + H), 159.2; HRMS-CI *m/z* calcd for $C_{13}H_{19}O_2S$ (M + H) 239.1106, found 239.1074.

The minor diastereomer, (+)-(1*S*,2*R*)-*trans*-2-phenylcyclohexyl (*R*)-methanesulfinate, could be obtained in diastereomerically pure form (analytical HPLC) by fractional crystallization from Skelly B: mp 56–56.5 °C; $[\alpha]^{25}_D$ +157° (*c* 2.0, acetone); ^{13}C NMR (75 MHz) δ 142.7 (s), 128.5 (d), 127.7 (d), 126.5 (d), 79.7 (d), 50.2 (d), 43.7 (q), 34.1 (t), 33.9 (t), 25.5 (t), 24.8 (t); ^{1}H NMR (250 MHz) δ 7.34–7.17 (m, 5 H), 4.36–4.26 (m, 1 H), 2.77–2.67 (m, 1 H), 2.31–2.26 (m, 1 H), 2.20 (s, 3 H), 2.00–1.25 (m, 7 H); IR 3015, 2980, 2850, 1450, 1250, 1065, 1050 cm^{-1}; MS-CI *m/z* 239.3 (M + H), 159.2; HRMS-CI *m/z* calcd for $C_{13}H_{19}O_2S$ (M + H) 239.1106, found 239.1053.

(+)-*trans*-2-Phenylcyclohexyl 2-Propanesulfinates (3d). The procedure above was followed with 3.5 g (27.6 mmol) of 2-propanesulfinyl chloride (prepared from diisopropyl disulfide),[11] 2.2 mL (27.6 mmol) of pyridine, and 1.22 g (6.9 mmol) of (+)-*trans*-2-phenylcyclohexanol and a 4-h reaction time. Isolation as described above afforded a quantitative yield of a 9:2 mixture of diastereomers (α 1.13, 4:1 Skelly B/EtOAc). Pure samples of each diastereomer were obtained by preparative and semipreparative HPLC.

For the major diastereomer, (+)-(1*S*,2*R*)-*trans*-2-phenylcyclohexyl 2-propanesulfinate: mp 32.5–33 °C; $[\alpha]^{25}_D$ +51.7° (*c* 1.0, acetone); ^{13}C NMR (75 MHz) δ 143.0 (s), 128.3 (d), 127.8 (d), 126.6 (d), 84.9 (d), 51.3 (d), 35.0 (t), 34.0 (t), 25.5 (t), 25.0 (t), 13.4 (q), 13.3 (q); ^{1}H NMR (300 MHz) δ 7.30–7.15 (m, 5 H), 4.26–4.19 (m, 1 H), 2.64–2.60 (m, 1 H), 2.37–2.21 (m, 1 H), 1.94–1.30 (br m, 7 H), 0.80 (d, *J* = 7.2 Hz, 3 H), 0.76 (d, *J* = 7.2 Hz, 3 H); IR 3020, 2920, 2850, 1440, 1250, 1110 cm^{-1}; MS-CI *m/z* 267 (M + H), 159, 109; HRMS-CI *m/z* calcd for $C_{15}H_{23}O_2S$ (M + H) 267.1419, found 267.1396.

For the minor diastereomer, (+)-(1*S*,2*R*)-*trans*-2-phenylcyclohexyl 2-propanesulfinate: $[\alpha]^{25}_D$ +196.6° (*c* 0.77, acetone); ^{13}C NMR (75 MHz) δ 142.8 (s), 128.2 (d), 127.8 (d), 126.5 (d), 79.7 (d), 54.8 (d), 50.6 (d), 34.6 (t), 33.3 (t), 25.7 (t), 24.9 (t), 13.6 (q), 13.4 (q); ^{1}H NMR (300 MHz) δ 7.31–7.16 (m, 5 H), 4.33–4.26 (m, 1 H), 2.75–2.67 (m, 1 H), 2.49–2.31 (m, 2 H), 1.98–1.87 (m, 2 H), 1.79–1.74 (m, 1 H), 1.62–1.37 (m, 4 H), 0.96 (d, *J* = 2.4 Hz, 3 H), 0.94 (d, *J* = 2.4 Hz, 3 H); IR 3020, 2930, 2850, 1440, 1110 cm^{-1}; MS-CI *m/z* 267 (M + H), 159, 109; HRMS-CI *m/z* calcd for $C_{15}H_{23}O_2S$ (M + H) 267.1419, found 267.1423.

(*S*)-Methyl *p*-Tolyl Sulfoxide. To a solution of 400 mg (1.68 mmol) of (+)-(1*S*,2*R*)-*trans*-2-phenylcyclohexyl (*S*)-methanesulfinate in 5 mL ether at 0 °C was added a solution of *p*-tolylmagnesium bromide, prepared from 0.41 mL (3.36 mmol) of 4-bromotoluene and 200 mg (8.40 mmol) of magnesium turnings, over 10 min. The reaction mixture was stirred for 1 h at rt after completed addition. The mixture was quenched with saturated NH_4Cl solution, extracted with ether twice, washed with saturated NaCl solution, and then dried over $MgSO_4$. The crude sulfoxide was purified by silica gel chromatography with 7:3 Skelly B/EtOAc, affording 200 mg (76%) of a white solid, mp 73.5–74 °C (lit.[8] for *R* enantiomer, mp 73–74.5 °C): $[\alpha]^{25}_D$ −143° (*c* 2, acetone) [lit.[8] for *R* enantiomer, $[\alpha]^{20}_D$ +145.5° (acetone)]; ^{13}C NMR (75 MHz) δ 142.6 (s), 141.5 (s), 130.0 (d), 123.5 (d), 44.0 (q), 21.4 (q); ^{1}H NMR (300 MHz) δ 7.54 (d, *J* = 8.1 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 2.70 (s, 3 H), 2.41 (s, 3 H).

(*S*)-*p*-Phenoxyphenyl *p*-Tolyl Sulfoxide. To a solution of 150 mg (48 mmol) of (+)-(1*S*,2*R*)-*trans*-2-phenylcyclohexyl (*S*)-*p*-toluenesulfinate in 5 mL ether at 0 °C was added over 10 min a solution of (*p*-phenoxyphenyl)magnesium bromide [prepared from 0.17 mL (96 mmol) of 4-bromophenyl phenyl ether and 62 mg (240 mmol) of magnesium turnings]. The reaction mixture was stirred for 1 h at rt and then quenched by the addition of a saturated NH_4Cl solution. The mixture was extracted with ether twice, and the combined organic layers were washed with saturated NaCl solution and then dried over $MgSO_4$. The crude sulfoxide was purified by silica gel chromatography with 7:3 Skelly B/EtOAc, affording 103 mg (70%) of a white solid: mp 116–116.5 °C; $[\alpha]^{25}_D$ −2.0° (*c* 2, acetone); ^{13}C NMR (75 MHz) δ 160.1 (s), 155.6 (s), 142.4 (s), 141.4 (s), 139.3 (s), 129.9 (d), 126.9 (d), 124.7 (d), 124.4 (d), 119.8 (d), 118.5 (d), 21.3 (q); ^{1}H NMR (300 MHz) δ 7.56 (d, *J* = 8.7 Hz, 2 H), 7.52 (d, *J* = 8.1 Hz, 2 H), 7.35–7.30 (m, 2 H), 7.41 (d, *J* = 8.7 Hz, 2 H), 7.16–7.11 (m, 2 H), 7.00 (d, *J* = 8.7 Hz, 2 H), 6.98 (d, *J* = 8.1 Hz, 2 H); IR 3020, 1575, 1480, 1220, 1040 cm^{-1}; MS-EI *m/z* 308 (M), 260, 201, 185, 91, 77; HRMS-EI *m/z* calcd for $C_{19}H_{16}O_2S$ 308.0871, found 308.0865.

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[1,3]-Hydrogen Sigmatropic Rearrangements in Alkyl-Substituted Allenes

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The suprafacial [1,3]-hydrogen sigmatropic rearrangement in alkenes is forbidden by orbital symmetry. The antarafacial [1,3]-hydrogen sigmatropic rearrangement in

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