IR (neat, major peaks) 1676, 1655, 1625 (w), 1350, 1021, 905, 733, 695 cm^{-1}; UV (methanol) λ_{max} 327 nm (ϵ 4010). Anal. Calcd for $C_{21}H_{24}OBr_2$: C, 55.76; H, 5.35; Br, 35.33. Found: C, 55.42; H, 5.36; Br, 35.53.

2-Benzyl-2-*tert*-butyl-1-naphthalenone (7). A solution of ketone **5** (0.34 g, 0.75 mmol) in 10 mL of dry carbon tetrachloride was cooled to 0 °C and stirred while 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.30 g, 1.97 mmol) was added rapidly. The deep yellow solution was stirred at 0 °C for 5 h and then allowed to warm to room temperature while stirring was continued for an additional 13 h. Dichloromethane (25 mL) was added to the resulting mixture, which was cooled in ice, washed with water, with a mixture of 0.01 M hydrochloric acid and ice, and again with water, and dried over magnesium sulfate. The solvent was evaporated under vacuum to give 0.26 g of a brown oil, which was chromatographed on silica gel, eluting with 5% dichloromethane in petroleum ether. Ketone **7** (0.15 g, 0.53 mmol, 70%) was obtained as a pale yellow oil: ^1H NMR ($CDCl_3$) δ 1.01 (s, 9 H), 2.80 (d, J = 13.0 Hz, 1 H), 3.73 (d, J = 13.0 Hz, 1 H), 6.21 (d, J = 10.5 Hz, 1 H), 6.50 (d, J = 10.5 Hz, 1 H), 7.0–7.2 (m, 3 H), 7.95 (dd, J = 7.5, 1.5 Hz, 1 H). IR (neat) 1685, 1676, 1601, 1463, 1385, 1298, 1196, 693 cm^{-1}; UV (methanol) λ 239 (ϵ 35 147), 274 (6759), 336 (3714) nm. Anal. Calcd for $C_{21}H_{22}O$: C, 86.84; H, 7.64. Found: C, 86.81; H, 7.80.

Reaction of 7 with Acid. Concentrated sulfuric acid (one drop) was added to a solution of ketone **7** (0.048 g, 0.166 mmol) in 2 mL of glacial acetic acid. The solution was allowed to stand at room temperature for 5 min and then poured into a mixture of water (50 mL) and dichloromethane (25 mL). The organic layer was separated, washed with water and with sodium bicarbonate solution, and dried over magnesium sulfate. Evaporation of the solvent left 0.4 g of dark brown oil, which crystallized on seeding with a sample of 2-benzyl-1-naphthol which had been prepared by Claisen alkylation of 1-naphthol. Recrystallization from petroleum ether yielded 0.024 g (0.01 mmol, 62%) of 2-benzyl-1-naphthol, mp 72–73 °C (lit.[14] mp 73–74 °C).

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Registry No. **4**, 103768-73-6; **5**, 103768-74-7; **7**, 103768-75-8; 2-*tert*-butyl-1-naphthalenol, 27286-81-3; 2-*tert*-butyl-5,8-dihydro-1-naphthalenol, 103768-72-5; 4-bromo-2-*tert*-butyl-1-naphthalenol, 108744-28-1; 2-benzyl-1-naphthalenol, 36441-32-4.

(14) Hassner, A.; Cromwell, N. H.; Davis, S. J. *J. Am. Chem. Soc.* **1957**, *79*, 230.

4-Bromo-2-sulfolenes. Butadienyl Cation Equivalents

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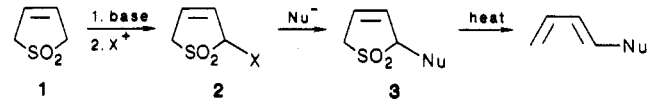
4-Bromo-2-sulfolene and 4-bromo-3-methyl-2-sulfolene react with alkylcuprates to give direct substitution products, with vinyl- or phenylcuprates or sulfur-containing nucleophiles to give allylic substitution products, and with strongly basic nucleophiles to give elimination products. The allylic substitution products and the isomerized direct substitution products are precursors for substituted 1,3-butadienes. Thus, these 4-bromo-2-sulfolenes serve as butadienyl cation equivalents.

1,3-Butadiene is a commonly occurring functionality in natural products. The use of substituted 1,3-butadienes in Diels–Alder reactions is a major route toward the formation of complex cyclic molecules. Therefore, the preparation of functionalized 1,3-butadienes is an important task in organic synthesis. Recently,[1] there has been an increasing interest in studying the deprotonation/substitution reactions of 3-sulfolenes for the preparation of the stable precursors for alkylated,[1a,b] acylated,[1c] and silylated[1d] 1,3-butadienes and their application in the synthesis of natural products.[1e,f] The advantages of this strategy include the preparation reaction being essentially one step, the moderately unstable dienes being produced in their protected forms, the substitution step being regioselective, and the SO_2 extrusion reaction step being stereospecific. However, since this approach is limited to attaching electrophiles to the 1- or 4-positions of conjugated dienes, it is desirable to have butadienyl cation equivalents where nucleophiles can be introduced so that more differently functionalized 1,3-butadienes can be synthesized.

(1) (a) Chou, T. S.; Tso, H. H.; Chang, L. J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 515. (b) Chou, T. S.; Chang, L. J.; Tso, H. H. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1039. (c) Chou, T. S.; Tso, H. H.; Lin, L. C. *J. Org. Chem.* **1986**, *51*, 1000. (d) Chou, T. S.; Tso, H. H.; Tao, Y. T.; Lin, L. C. *J. Org. Chem.* **1987**, *52*, 244. (e) Chou, T. S.; Tso, H. H.; Chang, L. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1323. (f) Nomoto, T.; Takayama, H. *Heterocycles* **1985**, *23*, 2913. (g) Tao, Y. T.; Liu, C. L.; Lee, S. J.; Chou, S. S. P. *J. Org. Chem.* **1986**, *51*, 4718.

Scheme I[a]



It was considered that the introduction of a potential leaving group such as a halide or a sulfide at the α-position of 3-sulfolene (**1**) would yield an electrophilic sulfolene **2** that, upon treatment with a nucleophile, should give the α-substituted product **3**. However, attempts at the preparation of **2** were unsuccessful. The reactions of 3-sulfolene anion with *N*-bromosuccinimide, *N*-chlorosuccinimide, 1-chlorobenzotriazole, and diphenyl disulfide resulted in no reaction, while reactions with iodine, bromine, iodine chloride, and dimethyl disulfide gave complex mixtures. In no case were we able to identify the formation of the desired product **2** (Scheme I, X = halogen or sulfide).

We later found that 4-bromo-2-sulfolene (**4**),[2] available from 3-sulfolene (**1**) by a reaction sequence of bromine addition and partial dehydrobromination, could react with a variety of nucleophiles via different routes (Scheme II). The reaction of **4** with methylcuprate (from methyllithium and CuI) or *n*-butylcuprate (from butyllithium and CuI) proceeded in an allylic substitution reaction mode, giving 2-alkylated 3-sulfolenes **5** and **6**, respectively. The reaction

(2) Bailey, W. J.; Cummins, E. W. *J. Am. Chem. Soc.* **1954**, *76*, 1932.

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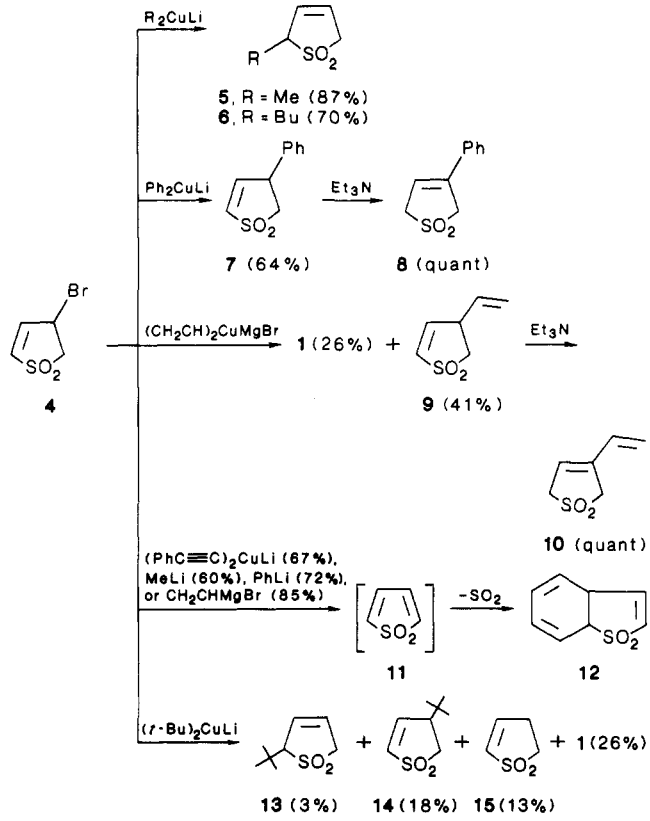
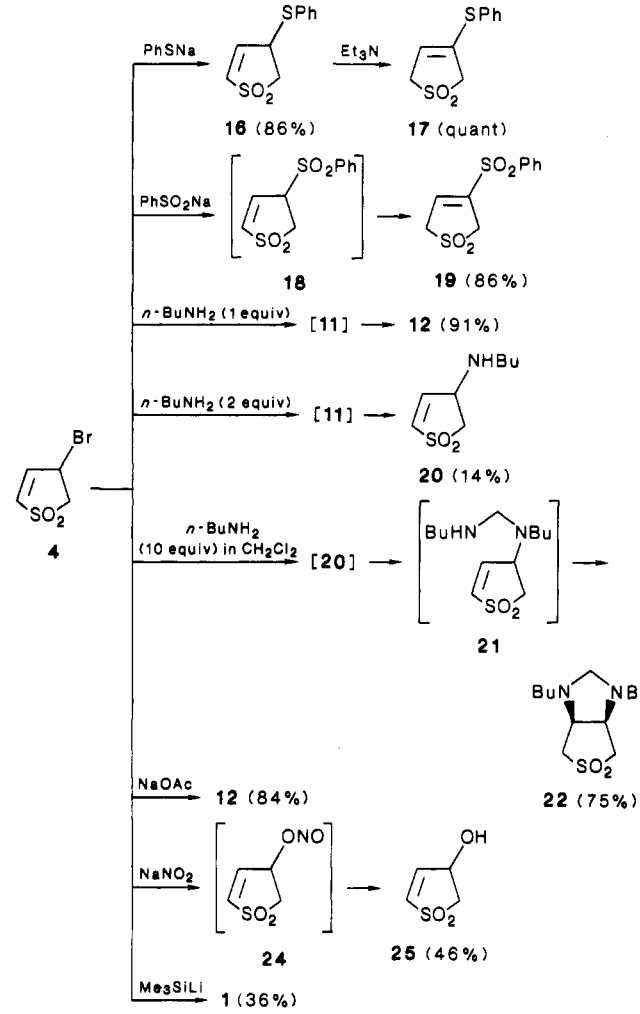
Scheme II



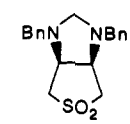
of **4** with phenylcuprate (from phenyllithium and CuI) or vinylcuprate (from vinylmagnesium bromide and CuI) proceeded in a direct substitution reaction mode to produce 4-substituted 2-sulfolenes **7** and **9**, respectively. Some debrominated product **1** accompanied **9** as a minor component. Compounds **7** or **9** easily isomerized with Et_3N to their double-bond isomers **8** and **10**, which perhaps are synthetically more useful. The use of cuprate reagents is essential in these C–C bond formation reactions because treatment of **4** with methyllithium, phenyllithium, or vinylmagnesium bromide results only in elimination reactions to give, after the dimerization of the unstable intermediate **11**, the bicyclic sulfone **12**.[3] The attempts at introducing an acetylene group to the sulfolene skeleton by the same strategy were unsuccessful. The reaction of **4** with (phenylacetylene)cuprate (from lithium phenylacetylide and CuI) gave only the elimination product **12**. The reaction of **4** with *tert*-butylcuprate (from *tert*-butyllithium and CuI) gave a mixture consisting mainly of the debrominated products **1** and **15**, some direct substitution product **14**, and a trace of the allylic substitution product **13**.

The reactions of **4** with some heteroatom nucleophiles have also been studied[4] (Scheme III). Reaction of **4** with thiophenoxide proceeded in a direct-substitution reaction mode to give product **16**, which was then isomerized with Et_3N to 3-(phenylthio)-3-sulfolene (**17**). Reaction with phenylsulfinate anion also resulted in a direct substitution reaction giving product **19**. It is assumed that the intermediate **18** isomerized to **19** very rapidly under the reaction

Scheme III



conditions. It has been reported that **18** could be obtained without rearrangement; however, the experimental details are not accessible.[5] When **4** was treated with 1 equiv of *n*-butylamine in CH_2Cl_2, the product isolated was **12**. Apparently, the elimination of HBr took place. If 2 equiv of $BuNH_2$ was used in this reaction, 4-(butylamino)-2-sulfolene (**20**) was obtainable. Although it looked as if a substitution reaction had occurred, the product **20** must have been generated by the Michael addition of a second equivalent of amine on **12**. When a large excess (10 equiv) of butylamine was used, another Michael addition took place to give **22**. The methylene bridge is speculated to come from the solvent CH_2Cl_2 and should have been formed before the second Michael addition reaction occurred (as shown in structure **21**). This is based on the ring junction of **22** being cis-fused, which is so assigned because of the similarity of its NMR spectral data to those of the dibenzyl analogue **23**.[6] The formation of the trans-fused product is expected to be more favored[6] should the methylene bridge form after the second Michael addition.



23

(3) Bailey, W. J.; Cummins, E. W. *J. Am. Chem. Soc.* **1954**, *76*, 1936.
(4) The substitution reactions of **4** with some other heteroatom nucleophiles have been reported: (a) Krug, R. C.; Tichelaar, G. R.; Didot, F. E. *J. Org. Chem.* **1958**, *23*, 212. (b) Backer, H. J.; Blass, Th. A. H. *Recl. Trav. Chim. Pays-Bas* **1942**, *61*, 785. (c) Prochazka, M.; Palecek, M. *Collect. Czech. Chem. Commun.* **1966**, *31*, 3744. (d) Inomata, K.; Kinoshita, H.; Takemoto, H.; Murata, Y.; Kotake, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3341.
(5) Bezmenova, T. E.; Varshavets, T. N.; Bezmenov, A. Ya. *Khim. Geterotsikl. Soedin.* **1974**, 468; *Chem. Abstr.* **1974**, *81*, 63422g.
(6) Bates, H. A.; Smilowitz, L.; Lin, J. *J. Org. Chem.* **1985**, *50*, 899.

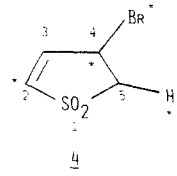


Figure 1. Reaction sites of compound 4.

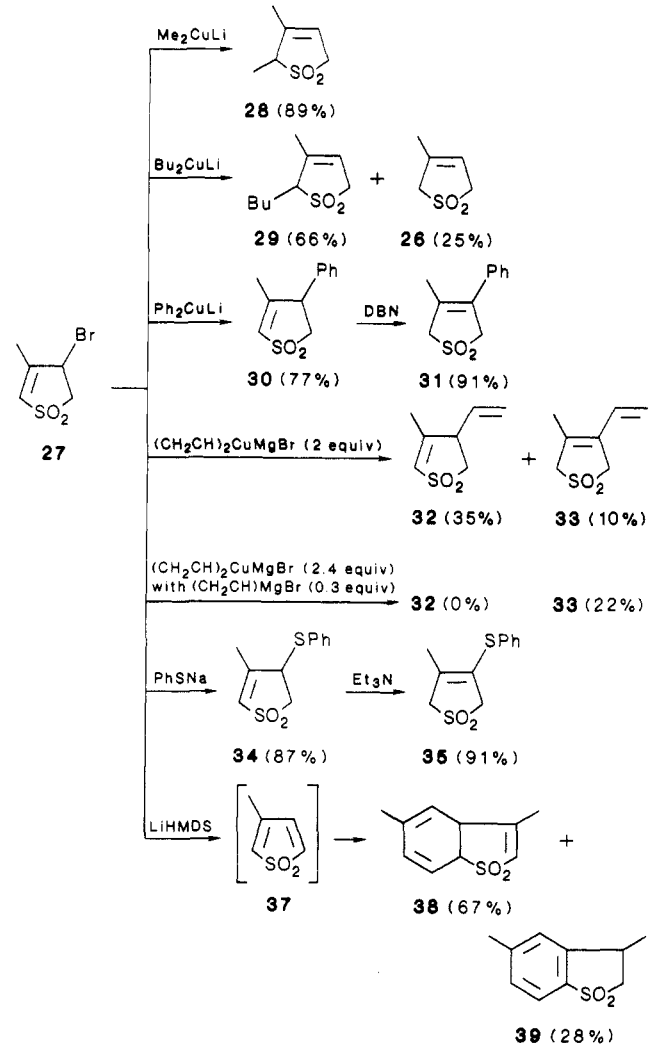
The reaction of **4** with sodium acetate resulted in the elimination of HBr, giving product **12** without formation of any substitution product. The reaction with sodium nitrite proceeded in a direct-substitution reaction mode, giving 4-hydroxy-2-sulfolene (**25**), a hydrolyzed product from the corresponding nitrite **24**. The reaction with (trimethylsilyl)lithium gave **1** as the only product where a bromine exchange reaction took place.

Although the nucleophiles behaved differently on **4**, they showed very high selectivity, and except for a very few cases, essentially one single product was obtained in each of the reactions. In principle, there are four possible reaction sites on **4**, which are C-2, C-4, the proton on C-5, and the bromine on C-4 (Figure 1).[7] The nucleophiles used in this study and their modes of reaction with **4** can be roughly grouped into four categories. An alkylcuprate reacts at C-2 giving the allylic substitution product. A strongly basic nucleophile such as an organolithium salt, a Grignard reagent, an amine, a metal acetylide, or sodium acetate abstracts the C-5 hydrogen causing the deprotonation/elimination reaction to occur. A vinyl- or phenylcuprate or a sulfur-containing nucleophile appears to react at C-4, giving mainly the direct substitution product. The bulky (trimethylsilyl)lithium or *tert*-butylcuprate reacts with **4** mainly by attacking the bromine to give little or no substitution products probably due to both steric and electronic reasons.

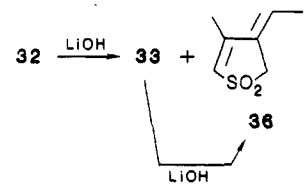
Similar selectivities were also observed when 4-bromo-3-methyl-2-sulfolene (**27**),[8] readily available from isoprene sulfone (**26**) by a reaction sequence of bromine addition and partial dehydrobromination, was treated with different nucleophiles (Scheme IV). 2-Alkylated 3-methyl-3-sulfolenes **28** and **29** were prepared by the allylic substitution reaction of **27** with alkylcuprates, although compound **26** was a minor product when *n*-butylcuprate was used. Compounds **30**, **32**, and **34** were prepared by the direct substitution reaction of **27** with phenylcuprate, vinylcuprate, and thiophenoxide, respectively. It was found that the preparation of **32** invariably was accompanied by some **33**, whereas by a slight modification of the procedure compound **33** could be prepared directly from **27** with no **32** present in the product mixture. The base-induced double-bond isomerization reactions of **30**, **32**, and **34** appeared somewhat more difficult than those of **7**, **9**, and **16**. The isomerization of **34** to **35** with Et_3N required much longer reaction time (27 h) than that of **16** to **17** (5 h). Compound **30** was found to be unreactive with Et_3N, and its isomerization to **31** was achieved by treatment with DBN in refluxing THF. Compound **32** was unaffected by DBN in refluxing THF. On the other hand, a brief treatment of **32** with LiOH in MeOH at room temperature resulted in the isomerization of the double bond, giving, however, a mixture of isomers **33** and **36**. Prolonged stirring of either **32** or **33** with LiOH eventually gave **36** as the sole product (Scheme V). This result suggests that **36** is thermodynamically more stable than the other isomers **32** and **33**. The difficulty encountered in the isomerization of **30**, **32**, and **34** is not too surprising. A methyl group on C-3 would kinetically disfavor the formation of the 3-sulfolenes **31**, **33**, and **35**, since a double bond at the 3-position would cause an unfavorable repulsion between the substituents on C-3 and C-4. Such a repulsion does not exist in **8**, **10**, and **17**. Elimination of HBr from **27** could be achieved by treatment with lithium hexamethyldisilazide (LiHMDS), a hard base, giving the unstable 3-methylthiophene dioxide (**37**), which readily dimerized to give **38** and its isomer **39**.[9]

Since it has been well established that substituted 3-sulfolenes extrude SO_2 to give stereospecifically the corresponding dienes upon thermolysis at 110–130 °C[1,10] or

Scheme IV



Scheme V



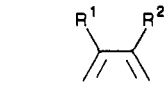
(7) In fact, a fifth electrophilic reaction site possible on **4** is at C-3, a Michael acceptor. However, we have not observed any reaction taking place at this position.

(8) Krug, R. C.; Yen, T. F. *J. Org. Chem.* **1956**, *21*, 1441.

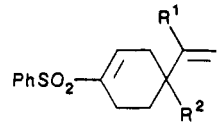
(9) A similar isomerization of the phenyl analogue of **37** to its aromatic isomer has been reported: Melles, J. L.; Backer, H. J. *Recl. Trav. Chim. Pays-Bas* **1953**, *72*, 491.

(10) (a) Mock, W. L. *J. Am. Chem. Soc.* **1975**, *97*, 3666. (b) Kellogg, R. M.; Prins, W. L. *J. Org. Chem.* **1974**, *39*, 2366. (c) McGregor, S. D.; Lemal, D. M. *J. Am. Chem. Soc.* **1966**, *88*, 2858. (d) Cava, M. P.; Deana, A. A. *J. Am. Chem. Soc.* **1959**, *81*, 4266. (e) Isaacs, N. S.; Laila, A. A. R. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1470.

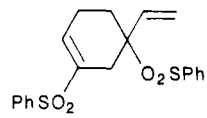
by treatment with $LiAlH_4$[11] or ultrasonically dispersed potassium,[12] the sulfolenes **5**, **6**, **8**, **10**, **17**, **19**, **28**, **29**, **31**, **33**, and **35** prepared from **4** and **27** by treatment with the proper nucleophiles with or without a subsequent double-bond isomerization reaction should be useful in the syntheses of a variety of substituted butadienes. For example, the thermolysis of **8** or **31** gave the corresponding diene **40** or **41** as the sole product. The thermolysis of **19**



40: R^1 = H, R^2 = Ph
41: R^1 = Me, R^2 = Ph
42: R^1 = H, R^2 = $PhSO_2$



43: R^1 = H, R^2 = $PhSO_2$
44: R^1 = $PhSO_2$, R^2 = H



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in refluxing xylene did not give the diene **42** but its dimers **43**–**45** (quantitative yield) in 6:2:1 ratio. The regioselectivity of the dimerization of **42** is considerably different from that of the dimerization of its tolylsulfonyl analogue, where only one dimer was obtained under identical conditions.[6d] In addition, **5**,[10e] **17**,[13] and **35**[14] have been reported to yield their corresponding dienes upon thermolysis. Accordingly, compounds **4** and **27** are regarded as valuable butadienyl cation equivalents. This method complements the ones that we described earlier,[1] where 3-sulfolenes serve as butadienyl anion equivalents.

Experimental Section

General Methods. NMR spectra were routinely determined on a Bruker AW-80 spectrometer and, in a few cases as noted, on a Bruker MSL-200 spectrometer as solutions in $CDCl_3$. IR spectra were determined on a Perkin-Elmer 290 IR spectrophotometer. Mass spectra were recorded on a Hewlett-Packard 5995B mass spectrometer. Elemental analyses were performed at the microanalysis laboratory of National Taiwan University. All reactions were carried out under an atmosphere of dry nitrogen. All anhydrous solvents were freshly distilled before use.

Reactions of Organocuprates with the Bromosulfolenes 4 and 27. To a solution of 4-bromo-2-sulfolene (2.1 mmol) in THF (40 mL) was added dropwise the solution of a cuprate (2.0 mmol) prepared as described below at −78 °C, and the resulting mixture was stirred at −78 °C for 2 h. Saturated NH_4Cl (15 mL) was added at once, and the reaction mixture was allowed to warm to room temperature gradually with vigorous stirring. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (4 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude oil was then purified by HPLC (LiChrosorb column; hexane/EtOAc, 3:2) to give the pure product.

2-Methyl-3-sulfolene (5). This was obtained by the reaction of Me_2CuLi [prepared from MeLi (2 equiv) and CuI (1 equiv) in THF at 0 °C for 30 min] with **4** in 87% yield. The spectral data are identical with those reported in literature.[1a]

2-*n*-Butyl-3-sulfolene (6). This was obtained by the reaction of *n*-Bu_2CuLi [prepared from *n*-BuLi (2 equiv) and CuI (1 equiv) in THF at −70 °C for 1.5 h] with **4** in 70% yield. The spectral data are identical with those reported in literature.[1a]

4-Phenyl-2-sulfolene (7). This was obtained by the reaction of Ph_2CuLi [prepared from PhLi (2 equiv) and CuI (1 equiv) in THF at −78 °C for 1.5 h] with **4** in 64% yield as a white solid: mp 75–77 °C; IR (KBr) 1600, 1305, 1230, 1145, 1100 cm^{-1}; ^1H NMR δ 3.13 (dd, 1 H, J = 5, 14 Hz), 3.69 (dd, 1 H, J = 9, 14 Hz), 4.34 (dd, 1 H, J = 5, 9 Hz), 6.71 (s, 2 H), 7.10–7.50 (m, 5 H); MS, m/z 194 (M^+), 83 (100%). Anal. Calcd for $C_{10}H_{10}O_2S$: C, 61.8; H, 5.2. Found: C, 61.8; H, 5.2.

4-Vinyl-2-sulfolene (9). This was obtained by the reaction of $(CH_2{=}CH)_2CuMgBr$ [prepared from $CH_2{=}CHMgBr$ (2 equiv) and CuI (1 equiv) in THF at −60 °C for 2 h] with **4**. Compounds **9** (41%) and **1** (26%) were isolated from the product mixture. Compound **9**: colorless oil; IR (neat) 1610, 1310, 1250, 1140 cm^{-1}; ^1H NMR δ 3.00 (dd, 1 H, J = 6, 13 Hz), 3.50 (dd, 1 H, J = 10, 13 Hz), 3.60–4.00 (m, 1 H), 5.21 (d, 1 H, J = 16.5 Hz), 5.24 (d, 1 H, J = 10 Hz), 5.55–5.95 (m, 1 H), 6.62 (s, 2 H); MS, m/z 144 (M^+), 113, 79 (100%). Anal. Calcd for $C_6H_8O_2S$: C, 50.0; H, 5.6. Found: C, 50.0; H, 5.6.

2-*tert*-Butyl-3-sulfolene (13) and 4-*tert*-Butyl-2-sulfolene (14). These were obtained by the reaction of *t*-Bu_2CuLi [prepared from *t*-BuLi (2 equiv) and CuI (1 equiv) at −78 °C in THF for 1 h] with **4**. Compound **13** (4%), compound **14** (18%), compound **1** (26%), and 2-sulfolene (**15**; 13%) were isolated from the product mixture.

Compound 13: colorless oil; IR (neat) 1310, 1260, 1120 cm^{-1}; ^1H NMR δ 1.17 (s, 9 H), 3.53 (s, 1 H), 3.67 (s, 2 H), 6.11 (s, 2 H); MS, m/z 174 (M^+), 110, 95 (100%). Anal. Calcd for $C_8H_{14}O_2S$: C, 55.15; H, 8.1. Found: C, 55.1; H, 7.9.

Compound 14: white solid, mp 54–55 °C; IR (KBr) 1608, 1295, 1220, 1130, 1100 cm^{-1}; ^1H NMR δ 0.94 (s, 9 H), 2.91–3.33 (m, 3 H), 6.67 (s, 2 H); MS, m/z 159 ($M^+ - CH_3$), 118, 57 (100%). Anal. Calcd for $C_8H_{14}O_2S$: C, 55.15; H, 8.1. Found: C, 55.2; H, 8.1.

2,3-Dimethyl-3-sulfolene (28). This was obtained by the reaction of Me_2CuLi with **27** in 89% yield. The spectral data are identical with those reported in literature.[15]

2-*n*-Butyl-3-methyl-3-sulfolene (29). This was obtained by the reaction of *n*-Bu_2CuLi with **27**. Compounds **29** (66%) and **26** (25%) were isolated from the product mixture. Compound **29**: colorless oil; IR (neat) 1315, 1250, 1225, 1125 cm^{-1}; ^1H NMR δ 0.91 (t, 3 H, J = 7 Hz), 1.10–1.70 (m, 6 H), 1.83 (s, 3 H), 3.30–3.60 (m, 1 H), 3.67 (s, 2 H), 5.68 (br s, 1 H); MS, m/z 124 ($M^+ - SO_2$), 93, 81, 80 (100%), 68, 67. Anal. Calcd for $C_9H_{16}O_2S$: C, 57.4; H, 8.55. Found: C, 57.4; H, 8.6.

3-Methyl-4-phenyl-2-sulfolene (30). This was obtained by the reaction of Ph_2CuLi with **27** in 77% yield as a white solid: mp 106–108 °C; IR (KBr) 1640, 1610, 1285, 1270, 1145, 1095 cm^{-1}; ^1H NMR δ 1.72 (s, 3 H), 3.27 (dd, 1 H, J = 5, 14 Hz), 3.75 (dd, 1 H, J = 7, 14 Hz), 3.91–4.20 (m, 1 H), 6.44 (s, 1 H), 7.29 (s, 5 H); MS, m/z 208 (M^+, 100%), 115, 104, 91. Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.4; H, 5.8. Found: C, 63.4; H, 5.8.

3-Methyl-4-vinyl-2-sulfolene (32). This was obtained by the reaction of $(CH_2{=}CH)_2CuMgBr$ (2 equiv) with **27** in 35% yield. A small amount (<10%) of **33** was also present in the product mixture. Compound **32**: colorless oil; IR (neat) 1645, 1305, 1230, 1150, 1105 cm^{-1}; ^1H NMR δ 1.92 (s, 3 H), 2.90–3.90 (m, 3 H), 5.25 (d, 1 H, J = 17.5 Hz), 5.28 (d, 1 H, J = 10 Hz), 5.50–5.95 (m, 1 H), 6.35 (s, 1 H); MS, m/z 158 (M^+), 129, 110, 109, 94, 91, 79, 53 (100%). Anal. Calcd for $C_7H_{10}O_2S$: C, 53.15; H, 6.4. Found: C, 53.0; H, 6.3.

3-Methyl-4-vinyl-3-sulfolene (33). This was obtained by the reaction of **27** with $(CH_2{=}CH)_2CuMgBr$ (2.4 equiv) in the presence of an excess of vinylmagnesium bromide (0.3 equiv) in 22% yield. 3-Methyl-3-sulfolene (**26**) was also formed in 19% yield. Compound **33**: white solid; mp 75–76 °C; IR (neat) 1645, 1300, 1260, 1180, 1110 cm^{-1}; ^1H NMR (200 MHz) δ 1.91 (s, 3 H), 3.86 (s, 4 H), 5.06 (d, 1 H, J = 17.5 Hz), 5.30 (d, 1 H, J = 10 Hz), 6.66 (dd, 1 H, J = 10, 17.5 Hz); MS, m/z 158 (M^+), 94, 79 (100%). Anal. Calcd for $C_7H_{10}O_2S$: C, 53.15; H, 6.4. Found: C, 52.9; H, 6.4.

4-(Phenylthio)-2-sulfolene (16). To a solution of NaOMe (64 mg, 1.2 mmol) in MeOH (20 mL) at 0 °C was added dropwise thiophenol (172 mg, 1.6 mmol), and the reaction mixture was stirred at 0 °C for 10 min. To this thiophenoxide solution was

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then added dropwise a solution of **4** (260 mg, 1.3 mmol) in MeOH (10 mL), and the resulting mixture was stirred at room temperature for 20 h. The solvent was removed under reduced pressure, and saturated NH_4Cl (5 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude yellow oil was purified by HPLC (LiChrosorb column, hexane/EtOAc, 3:2) to give **16** in 86% yield as a white solid: mp 57–58.5 °C; IR (KBr) 1600, 1305, 1150, 1100 cm^{-1}; ^1H NMR δ 3.15 (dd, 1 H, J = 5, 14 Hz), 3.60 (dd, 1 H, J = 7.5, 14 Hz), 4.44 (dd, 1 H, J = 5, 7.5 Hz), 6.63 (s, 2 H), 7.36 (s, 5 H); MS, m/z 226 (M^+), 162, 161, 109 (100%). Anal. Calcd for $C_{10}H_{10}O_2S_2$: C, 53.1; H, 4.4. Found: C, 53.1; H, 4.45.

3-Methyl-4-(phenylthio)-2-sulfolene (34). This was obtained by the same procedure as described for **16** from thiophenoxide and **27** in 87% yield as a white solid; mp 100–102 °C; IR (KBr) 1630, 1280, 1150, 1100 cm^{-1}; ^1H NMR δ 2.14 (s, 3 H), 3.35 (dd, 1 H, J = 4, 14 Hz), 3.66 (dd, 1 H, J = 9, 14 Hz), 4.10–4.40 (m, 1 H), 6.37 (s, 1 H), 7.36 (s, 5 H); MS, m/z 240 (M^+), 161, 109, 65 (100%). Anal. Calcd for $C_{11}H_{12}O_2S_2$: C, 55.0; H, 5.0. Found: C, 55.2; H, 5.0.

Isomerization of the 4-Substituted 2-Sulfolenes 7, 9, 16, 30, and 34 to the Corresponding 3-Sulfolenes 8, 10, 17, 31, and 35. A solution of a substituted 2-sulfolene (1 mmol) and an amine base (8 mmol) in CH_2Cl_2 or THF (15 mL) was either stirred at room temperature or heated under reflux until the reaction was complete as indicated by TLC analysis [using silica gel 60 plate (Merck Art. 5735) eluted with EtOAc/hexane]. The excess of solvent was removed under reduced pressure, and the amine base was removed by elution through a silica gel column with EtOAc to give the essentially pure product. The analytical sample was obtained by HPLC (LiChrosorb column, hexane/EtOAc).

3-Phenyl-3-sulfolene (8). This was obtained by the isomerization of **7** with Et_3N in CH_2Cl_2 (reflux for 6 h) as a white solid in quantitative yield: mp 130–131 °C (lit.[16] mp 131.3–131.8 °C); ^1H NMR δ 4.01 (s, 2 H), 4.11 (s, 2 H), 6.31 (s, 1 H), 7.36 (s, 5 H). The data are identical with those of the product prepared from the cheletropic cycloaddition reaction of 2-phenyl-1,3-butadiene with SO_2 by a known procedure.[16] Anal. Calcd for $C_{10}H_{10}O_2S$: C, 61.8; H, 5.2. Found: C, 61.8; H, 5.2.

3-Vinyl-3-sulfolene (10). This was obtained by the isomerization of **9** with Et_3N in CH_2Cl_2 (room temperature for 14 h) as a white solid in quantitative yield: mp 89–91 °C; IR (KBr) 1645, 1600, 1300, 1130 cm^{-1}; ^1H NMR (200 MHz) δ 3.85 (s, 4 H), 5.12 (d, 1 H, J = 16 Hz), 5.30 (d, 1 H, J = 11 Hz), 5.94 (br s, 1 H), 6.43 (dd, 1 H, J = 11, 16 Hz); MS, m/z 144 (M^+), 80, 79 (100%). Anal. Calcd for $C_6H_8O_2S$: C, 50.0; H, 5.6. Found: C, 50.0; H, 5.6.

3-(Phenylthio)-3-sulfolene (17). This was obtained by the isomerization of **16** with Et_3N in CH_2Cl_2 (room temperature for 5 h) in quantitative yield. The spectral data are identical with those reported in literature.[17]

3-Methyl-4-phenyl-3-sulfolene (31). This was obtained by the isomerization of **30** with DBN in THF (reflux for 48 h) in 91% yield as a white solid: mp 84–85 °C (lit.[18] mp 85 °C); IR (KBr) 1295, 1260, 1120 cm^{-1}; ^1H NMR δ 1.85 (s, 3 H), 3.91 (s, 2 H), 4.08 (s, 2 H), 7.05–7.53 (m, 5 H); MS, m/z 208 (M^+), 144, 129 (100%), 91, 77.

3-Methyl-4-(phenylthio)-3-sulfolene (35). This was obtained by the isomerization of **34** with Et_3N in CH_2Cl_2 (room temperature for 27 h) in 91% yield as a white solid: mp 86–88 °C (lit.[14] pale yellow solid, mp 87–88 °C). The spectral data are identical with those reported in literature.[14]

3-Methyl-4-ethylidenyl-2-sulfolene (36). A solution of either **32** or **33** (96 mg, 0.6 mmol) and LiOH (73 mg, 3 mmol) in MeOH (8 mL) was stirred at room temperature for 15 h. After the solvent was removed under vacuum, saturated brine (10 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give the essentially pure **36** as a white solid in 83% yield. An analytical sample was obtained by HPLC (LiChrosorb column, hexane/EtOAc, 1:1): white solid; mp 125–126 °C; IR (KBr) 1655, 1390, 1290, 1180, 1135, 1105 cm^{-1}; ^1H NMR (200 MHz) δ 1.79 (d, 3 H, J = 6.5 Hz), 2.01 (s, 3 H), 3.84 (s, 2 H), 6.00 (q, 1 H, J = 6.5 Hz), 6.34 (s, 1 H); MS, m/z 158 (M^+), 129, 110, 91, 77 (100%). Anal. Calcd for $C_7H_{10}O_2S$: C, 53.15; H, 6.4. Found: C, 53.3; H, 6.4.

3-(Phenylsulfonyl)-3-sulfolene (19). An orange solution of sodium phenylsulfinate dihydrate (930 mg, 4.6 mmol) and **4** (830 mg, 4.2 mmol) in DMF (30 mL) was allowed to stir at room temperature for 24 h. After the removal of the solvent under vacuum, saturated brine (10 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude oil was then purified with a silica column (hexane/EtOAc, 1:1) to give **19** in 86% yield as a white solid: mp 138–140 °C; IR (KBr) 1620, 1330, 1315, 1160, 1140, 1090 cm^{-1}; ^1H NMR δ 3.86 (s, 2 H), 4.02 (s, 2 H), 7.03 (br s, 1 H), 7.20–8.00 (m, 5 H); MS, m/z 258 (M^+), 194, 141, 125 (100%). Anal. Calcd for $C_{10}H_{10}O_4S_2$: C, 46.5; H, 3.9. Found: C, 46.5; H, 3.9.

4-(*N*-*n*-Butylamino)-2-sulfolene (20). A yellow solution of **4** (790 mg, 4.0 mmol) and *n*-$BuNH_2$ (0.68 mL, 6.8 mmol) in THF (25 mL) was stirred at room temperature for 2.5 days. The solvent was removed under reduced pressure, the crude complex mixture was purified with a silica gel column (EtOAc), and **20** was isolated in 14% yield as a colorless oil: IR (neat) 3600, 1640, 1610, 1305, 1120 cm^{-1}; ^1H NMR δ 0.88 (t, 3 H, J = 6 Hz), 1.08–1.80 (m, 4 H), 2.46–2.80 (m, 2 H), 3.05 (dd, 1 H, J = 4.5, 14 Hz), 3.50 (dd, 1 H, J = 7, 14 Hz), 4.10–4.32 (m, 1 H), 6.66 (s, 2 H); MS, m/z 189 (M^+), 146 (100%), 125, 117, 110. Anal. Calcd for $C_8H_{15}NO_2S$: C, 50.8; H, 8.0. Found: C, 50.8; H, 8.0.

***cis*-(3a,6a)-1,3-Di-*n*-butylhexahydro-1*H*-thieno[3,4-*d*]-imidazole 5,5-Dioxide (22).** A solution of **4** (320 mg, 1.6 mmol) and *n*-$BuNH_2$ (1.6 mL, 160 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 2 days. Saturated brine (5 mL) was added, and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude oil was purified by HPLC (LiChrosorb column, hexane/EtOAc, 1:1) to give **22** in 75% yield as a white solid: mp 46.5–47.5 °C; IR (KBr) 1640, 1310, 1190, 1130, 1080 cm^{-1}; ^1H NMR (200 MHz) δ 0.91 (t, 6 H, J = 7 Hz), 1.30–1.50 (m, 8 H), 2.40–2.68 (m, 4 H), 3.00 (d, 1 H, J = 4.5 Hz), 3.02–3.50 (m, 6 H), 4.05 (d, 1 H, J = 4.5 Hz); MS, m/z 274 (M^+), 273 (100%), 231, 112, 70. Although a satisfactory microanalysis of **22** was not obtainable owing to its instability, the close similarity of the NMR spectra of **22** and **23**[6] provides other strong evidence for the structural assignment.

4-Hydroxy-2-sulfolene (25). A solution of **4** (112 mg, 0.56 mmol) and $NaNO_2$ (118 mg, 1.7 mmol) in DMF (2 mL) was sonicated for 5 min with a laboratory ultrasonic cleaner at room temperature. Saturated brine (2 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude oil was eluted through a silica gel column with EtOAc to remove DMF and then purified by HPLC (LiChrosorb column, EtOAc) to give **25** in 46% yield as a colorless oil: IR (neat) 3450, 1280, 1130, 1080, 1020 cm^{-1}; ^1H NMR δ 3.13 (dd, 1 H, J = 4, 14 Hz), 3.76 (dd, 1 H, J = 7, 14 Hz), 4.91 (s, 1 H), 5.17 (br s, 1 H), 6.55–6.70 (m, 2 H); MS, m/z 134 (M^+), 91, 87, 86, 80, 71 (100%). The spectral data are identical with those of the product prepared by a known procedure.[19]

Reaction of Compound 4 with (Trimethylsilyl)lithium. To a solution of Me_3SiLi[20] (1.67 mmol) in THF (10 mL) at −78 °C was added dropwise a solution of **4** (263 mg, 1.33 mmol) in THF (2 mL), and the resulting dark red solution was stirred at this temperature for 20 min. MeI (0.5 mL) was added, and the reaction mixture was allowed to warm to room temperature. Saturated brine (5 mL) was then added, and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (4 × 40 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude oil was eluted through a silica gel column (hexane/EtOAc, 1:1) to remove HMPA

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to give essentially pure 1 in 36% yield.

3,5-Dimethyl-3a,7a-dihydro-1-benzothiophene 1,1-Dioxide (38) and 3,5-Dimethyl-2,3-dihydro-1-benzothiophene 1,1-Dioxide (39). To a solution of LiHMDS [generated from HMDS (1.44 mmol) and *n*-BuLi (1.5 mmol) in THF (5 mL) at −78 °C for 45 min] was added dropwise a solution of **27** (305 mg, 1.44 mmol) in THF (15 mL) at −78 °C. The resulting dark purple solution was allowed to warm to room temperature and stirred overnight. Saturated brine (10 mL) was added, and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (4 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude yellow oil was purified by HPLC (LiChrosorb column, hexane/EtOAc, 2:1) to give **38** and **39** in 67% and 28% yields, respectively.

Compound 38: colorless oil; IR (neat) 1645, 1300, 1150, 1100 cm^{-1}; ^1H NMR δ 1.79 (s, 3 H), 2.04 (s, 3 H), 3.62–3.90 (m, 1 H), 4.08 (dd, 1 H, J = 5, 11 Hz), 5.39 (br s, 1 H), 5.83 (dd, 1 H, J = 5, 10 Hz), 6.12 (d, 1 H, J = 10 Hz), 6.49 (s, 1 H); MS, m/z 196 (M^+), 148, 132, 117, 91 (100%). Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.2; H, 6.2. Found: C, 61.1; H, 6.1.

Compound 39: white solid, mp 61–62 °C; IR (neat) 1615, 1300, 1180, 1135 cm^{-1}; ^1H NMR (200 MHz) δ 1.48 (d, 3 H, J = 6.5 Hz), 2.43 (s, 3 H), 2.95–3.25 (m, 1 H), 3.45–3.80 (m, 2 H), 7.17 (s, 1 H), 7.24 (d, 1 H, J = 10 Hz), 7.59 (d, 1 H, J = 10 Hz); MS, m/z 196 (M^+, 100%), 181, 132, 117, 91, 77. Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.2; H, 6.2. Found: C, 61.2; H, 6.1.

Thermolyses of 3-sulfolenes 8 and 31 to 40 and 41, Respectively. A solution of the 3-sulfolene (0.5 mmol) in xylene (4 mL) was heated to reflux for 3 h. After the solvent was removed under reduced pressure, the essentially pure diene product was obtained in quantitative yield. The same results could be obtained by the thermolyses of the 3-sulfolenes by preparative gas chromatography (column Carbowax 20M, 10 ft long; injection temperature 240 °C; oven temperature 180 °C; detector temperature 280 °C; carrier gas N_2; flow rate 30 mL/min). The spectral data of **40**[21] and **41**[22] are identical with those reported in the literature.

Thermolysis of 3-(Phenylsulfonyl)-3-sulfolene (19). A solution of **19** (258 mg, 1 mmol) in xylene (6 mL) containing pyridine (79 mg, 1 mmol) and hydroquinone (ca. 10 mg) was heated to reflux for 2 h. After addition of ethyl acetate (20 mL) and 1 M HCl (1 mL), the organic layer was washed with saturated brine (2 × 5 mL), dried ($mgSO_4$), and concentrated under reduced pressure. The crude product mixture was purified by HPLC (LiChrosorb column, hexane/EtOAc, 2.5:1) to give **43–45** (6:2:1) in nearly quantitative yield.

1,4-Bis(phenylsulfonyl)-4-vinylcyclohexene (43): white solid; mp 155–156.5 °C; IR (KBr) 1645, 1585, 1305, 1090 cm^{-1}; ^1H NMR δ 1.90–3.18 (m, 6 H), 4.92 (d, 1 H, J = 18 Hz), 5.28 (d, 1 H, J = 12 Hz), 5.72 (dd, 1 H, J = 12, 18 Hz), 6.97 (br s, 1 H), 7.30–7.71 (m, 6 H), 7.71–7.92 (m, 4 H); MS, m/z 247 ($M^+ - PhSO_2$), 245, 125 (100%), 91, 77. Anal. Calcd for $C_{20}H_{20}O_4S_2$: C, 61,8; H, 5.2. Found: C, 61.7; H, 5.1.

1-(Phenylsulfonyl)-4-[1-(phenylsulfonyl)ethenyl]cyclohexene (44): pale yellow oil; IR (KBr) 1645, 1305, 1150, 1090 cm^{-1}, ^1H NMR δ 1.80–3.16 (m, 7 H), 5.74 (s, 1 H), 6.38 (s, 1 H), 6.95 (br s, 1 H), 7.33–7.71 (m, 6 H), 7.71–7.98 (m, 4 H); MS, m/z 388 (M^+), 247, 125 (100%), 105, 91, 77. Anal. Calcd for $C_{20}H_{20}O_4S_2$: C, 61.8; H, 5.2. Found: C, 61.5; H, 5.2.

1,5-Bis(phenylsulfonyl)-5-vinylcyclohexene (45): white solid; mp 133–134 °C; IR (KBr) 1585, 1445, 1305, 1150, 1085 cm^{-1}; ^1H NMR δ 1.84–2.22 (m, 3 H), 2.31–2.70 (m, 3 H), 4.66 (d, 1 H, J = 17.5 Hz), 5.18 (d, 1 H, J = 11 Hz, 5.52 (dd, 1 H, J = 11, 17.5 Hz), 6.89 (br s, 1 H), 7.39–7.88 (m, 10 H); MS, m/z 247 ($M^+ - SO_2Ph$), 143, 141, 125 (100%).

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Optically Active Selenoxides: Chromatographic Separation and Absolute Configuration

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Asymmetric diaryl selenoxides were optically resolved by medium pressure column chromatography on an optically active column. The absolute configuration of the optically active selenoxides was estimated by comparison of their circular dichroism spectra with those of the optically active sulfoxides.

Recently, we have succeeded in preparing an air-stable optically pure diaryl selenoxide by fractional recrystallization of a diastereomer and subsequent removal of the chiral center other than the selenoxide group.[1] This method could not be applied for preparation of optically active selenoxides that have no functional group. We have also found that optical isomers of the asymmetric diaryl selenoxides could be separated by high-performance liquid chromatography using a chiral column.[2]

In this paper we describe the optical resolution of asymmetric diaryl selenoxides that possess no functional groups such as carboxylic or amino groups by chromatography using a chiral column. We also discuss the absolute configuration of the optically active diaryl selenoxides thus prepared, as inferred from their circular dichroism spectra.

The racemic diaryl selenoxides **1–7** were resolved on a medium pressure column chromatography system using a column (300 × 11 mm) packed with (*R*)-*N*-(3,5-dinitrobenzoyl)phenylglycine/aminopropylsilica (particle size 40 μm). This optically active column was commercially available. Hexane containing 2–10 vol % of 2-propanol

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