[2,3]-Sigmatropic Rearrangement of β-Phenylsulfonyl Propargylic Sulfenates as a Method for Preparing 1,4-Bis(phenylsulfonyl)-1,3-butadienes

Xiaoheng Wang,† Zhijie Ni,‡ Xiujing Lu,† Andrea Hollis,† Harold Banks,§ Augusto Rodriguez,*,† and Albert Padwa*,‡

Department of Chemistry, Clark Atlanta University, Atlanta, Georgia 30314, Department of Chemistry, Emory University, Atlanta, Georgia 30322, and U. S. Army, Chemical Research Development and Engineering Center, Aberdeen Proving Ground, Maryland 21010

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Several β-sulfoxy-substituted acetylenic carbinols were prepared by the addition of thiyl radicals and oxygen to conjugated enynes. The products obtained are derived from thiyl radical attack at the olefinic bond to generate a propargylic radical. Capture of this radical by oxygen followed by hydrogen transfer from thiophenol gives a hydroperoxide intermediate, which undergoes oxygen transfer by both intra- and intermolecular pathways. The resultant β-phenylsulfinyl propargylic alcohols proved to be versatile intermediates for the preparation of several different classes of compounds. The [2,3]-sigmatropic sulfinate to sulfoxide rearrangement was found to give 1,4-bis(phenylsulfonyl)-1,3-butadienes, α,β-unsaturated phenylsulfoxy ketones, and β-phenylsulfonyl α-allenic sulfoxides. Oxidation of the sulfoxy moiety to the sulfone followed by sulfinate formation with phenylsulfenyl chloride produces, after [2,3]-sigmatropic rearrangement, β-phenylsulfonyl α-allenic sulfoxides. In certain cases these allenes could be isolated, but were usually isomerized *in situ* and further oxidized to give 1,4-bis(phenylsulfonyl)-1,3-butadienes. The [2,3]-sigmatropic rearrangement of β-phenylsulfinyl-substituted propargylic alcohols proceeds by an entirely different course. With these systems, a double sigmatropic process occurs leading to the formation of vinyl sulfinates which are readily hydrolyzed to give α,β-unsaturated phenylsulfoxy ketones.

Conjugated dienes with electron-donating or electron-withdrawing substituents have attracted considerable attention during recent years.[1-4] Sulfur-substituted dienes, in particular, have been widely used in the Diels–Alder reaction.[5] More recently, phenylsulfonyl-substituted dienes have become established as useful synthetic intermediates.[6-14] The phenylsulfonyl group not only increases the reactivity of the diene but also adds control to the regioselectivity of the cycloaddition. Indeed, the phenylsulfonyl moiety is enjoying increasing popularity as an activating group undoubtedly as a consequence of its ability to act as a temporary control element in organic synthesis. The sulfonyl group can be removed both reductively and oxidatively with subsequent formation of ketones.[15] It stabilizes adjacent carbanions[16] which are extremely useful in carbon–carbon bond forming reactions. Benzenesulfinate anion also serves as a leaving group with S_N1-reactive substrates[17,18] and in the formation of cyclopropanes.[19] Elimination to olefins can also be accomplished, as for example, in the second step of the Julia alkene synthesis.[20] The bulkyl phenylsulfonyl group has also been shown to be useful for acyclic stereocontrol.[21]

In earlier reports, we demonstrated the use of 1,3- and 2,3-bis(phenylsulfonyl)-1,3-butadienes as versatile building blocks in organic synthesis, particularly for [4 +

† Clark Atlanta University.
‡ Emory University.
§ Edgewood Research, Development and Engineering Center.
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(1) Danishefsky, S. *Acc. Chem. Res.* **1981**, *14*, 400. Grayson, J.-I.; Petrizilka, M. *Synthesis* **1981**, 753. Hickmott, P. W. *Tetrahedron* **1984**, *40*, 2989.

(2) Evans, D. A.; Bryan, C. A.; Sims, C. L. *J. Am. Chem. Soc.* **1972**, *94*, 2891. Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 3554. Cohen, T.; Kosaych, Z. *J. Org. Chem.* **1982**, *47*, 4005.

(3) Halazy, S.; Magnus, P. *Tetrahedron Lett.* **1984**, *25*, 1421. Posner, G. H.; Wettlaufer, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 7373. Posner, G. H.; Harrison, W. *J. Chem. Soc., Chem. Commun.* **1985**, 1786.

(4) Akermark, B.; Nyström, J. E.; Rein, T.; Bäckvall, J. E.; Helquist, P.; Aslanian, R. *Tetrahedron Lett.* **1984**, *25*, 5719. Bloom, A. J.; Mellor, J. M. *Tetrahedron Lett.* **1986**, *27*, 873.

(5) *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum: New York, 1977. Bernardi, F.; Mangini, E. *Organic Sulfur Chemistry: Theoretical and Experimental Advances*; Elsevier: Amsterdam, 1985.

(6) Padwa, A.; Murphree, S. S. *Org. Prep. Proced. Int.* **1991**, *23*, 545.

(7) Trost, B. M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 107.

(8) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019.

(9) Schank, K. *Methoden der Organischen Chemie* (Houben-Weyl), 4th ed.; Thieme; Stuttgart, 1985; Vol. E11, p 1129.

(10) Durst, T. *Comprehensive Organic Chemistry*; Barton, D. H. R.; Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, pp 171, 197.

(11) *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappaport, Z., Stirling, C. J. M., Eds.; Wiley: Chichester, 1988; pp 1–1210.

(12) Fuchs, P. L.; Braish, T. F. *Chem. Rev.* **1986**, *86*, 903.

(13) Julia, M.; Paris, J. M. *Tetrahedron Lett.* **1973**, *12*, 4833. Hird, N. W.; Lee, T. V.; Leigh, A. J.; Maxwell, J. R.; Peakman, T. M. *Tetrahedron Lett.* **1989**, *30*, 4867. Kocienski, P. *Phosphorus Sulfur Relat. Elem.* **1985**, *24*, 97–127.

(14) Lythgoe, B.; Waterhouse, I. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2429.

(15) Little, R. D.; Myong, S. O. *Tetrahedron Lett.* **1980**, *21*, 3339. Hwu, J. R. *J. Org. Chem.* **1983**, *48*, 4432. Tanaka, K.; Matsui, S.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3619.

(16) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1173. Biellmann, J. F.; Ducep, J. B. *Org. React.* **1982**, *27*, 1.

(17) Brown, D. S.; Ley, S. V. *Tetrahedron Lett.* **1988**, *29*, 4869. Brown, D. S.; Hansson, T.; Ley, S. V. *Synlett* **1990**, 48. Harmata, S.; Gamlath, C. B. *J. Org. Chem.* **1988**, *53*, 6156. Trost, B. M.; Mikhail, G. K. *J. Am. Chem. Soc.* **1987**, *109*, 4124.

(18) Hoffmann, H. M. R. *J. Chem. Soc.* **1965**, 6762.

(19) Martel, J.; Huynh, Ch. *Bull. Soc. Chim. Fr.* **1967**, 985. Julia, M.; Guy-Ronalt, A. *Bull. Soc. Chim. Fr.* **1967**, 1411. Parker, W. L.; Woodward, R. B. *J. Org. Chem.* **1969**, *34*, 3085. Campbell, R. V. M.; Crombie, L.; Findley, D. A. R.; King, R. W.; Pattenden, G.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 897.

(20) Alvarez, E.; Cuvigny, T.; Hervee, J., du Penhoat, C.; Julia, M. *Tetrahedrron* **1988**, *44*, 119. Fehr, C. *Helv. Chim. Acta* **1983**, *66*, 2519. Mitchell, R. H.; Yan, J.-S. H.; Dingle, T.-W. *J. Am. Chem. Soc.* **1982**, *104*, 2551. Mandai, T.; Yanagi, T.; Araki, K.; Morisaki, Y.; Kawada, M.; Otera, J. *J. Am. Chem. Soc.* **1984**, *106*, 3670.

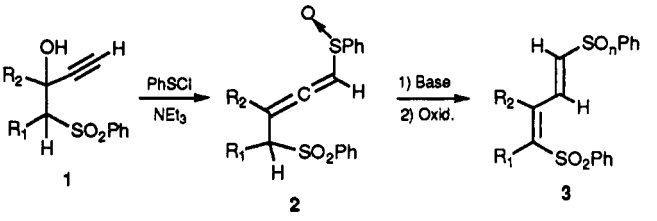
(21) Najera, C.; Mancheno, B.; Yus, M. *Tetrahedron Lett.* **1989**, *30*, 6085.

0022-3263/93/1958-5377$04.00/0

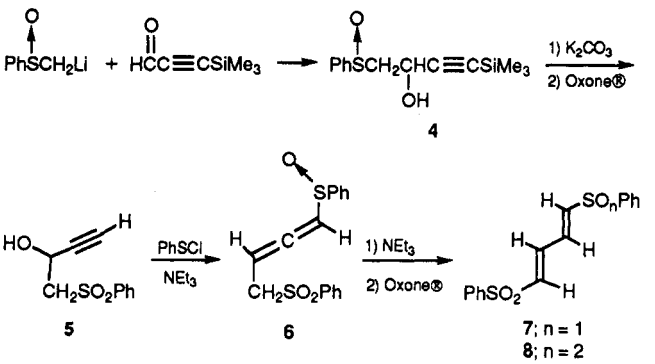
2]-cycloaddition chemistry.[22,23] As part of our studies in this area, we set out to prepare several 1,4-bis(phenylsulfonyl) 1,3-dienes with the intention of comparing their reactivity and cycloaddition behavior with the corresponding 1,3- and 2,3-isomers.[22] Although there are quite a number of synthetic routes available for the synthesis of monosulfonated dienes,[24-30] methods for preparing bis(phenylsulfonyl)-substituted dienes[31] are quite limited and not easily amenable to the preparation of the 1,4-isomer. In a preliminary report, we demonstrated that sulfinic esters of β-phenylsulfonyl-substituted acetylenic carbinols undergo a smooth reorganization to allenic sulfoxides, which, in turn, can be isomerized with base and oxidized to afford 1,4-bis(phenylsulfonyl) 1,3-dienes.[32] Our ongoing interest in the generality and synthetic utility of the [2,3]-sigmatropic rearrangement method[33] inspired us to take a detailed look at the scope and mechanistic details of this process. The present paper documents the results of these studies.

Results and Discussion

Since its discovery two decades ago,[34,35] the reversible interconversion of allylic sulfenates to sulfoxides has become one of the most studied and synthetically useful [2,3]-sigmatropic rearrangements known. Numerous synthetic applications of the rearrangement have been reported, including its use in the total synthesis of a variety of natural products such as steroids, prostaglandins, and leukotrienes.[36] Our strategy for the synthesis of 1,4-bis(phenylsulfonyl)-1,3-dienes relies on the well-precedented [2,3]-sigmatropic shift of propargylic sulfenates to α-allenic sulfoxides[37] and employs excess base to isomerize allene **2** to diene **3**. The first system we chose to examine was



carbinol **5**. This compound was prepared in 88% overall yield by addition of the lithio anion of methyl phenyl sulfoxide to 3-(trimethylsilyl)-2-propynal followed by desilylation and oxidation (Oxone). Treatment of **5** with 1 equiv of benzenesulfenyl chloride and 2 equiv of triethylamine in CH_2Cl_2 at 0 °C afforded allene **6** which was rapidly converted to diene **7** (n = 1) in 62% yield.



Oxidation of sulfoxide **7** with Oxone in methanol–water gave 1,4-bis(phenylsulfonyl)-1,3-butadiene **8** (n = 2) in 97% yield.

As part of our general program in this area, we decided to prepare a series of related 1,4-bis(phenylsulfonyl) 1,3-dienes so as to evaluate their chemical reactivity. In order to accomplish this goal, we required an efficient method to synthesize a variety of β-sulfur-substituted ynols. While several useful syntheses of acetylenic carbinols have been recorded,[38] a simple and general method for the preparation of β-sulfoxy-substituted ynols has not been established. To overcome this problem, we developed a general synthesis of these substrates through the coaddition of thiyl radicals and oxygen to olefins, a process termed cooxidation.[39,40] Our synthetic plan was based on the assumption that thiyl radical attack would occur at the

(22) Padwa, A.; Norman, B. H. *Tetrahedron Lett.* **1988**, *29*, 2417. Norman, B. H.; Gareau, Y.; Padwa, A. *J. Org. Chem.* **1991**, *56*, 2154. Padwa, A.; Harrison, B.; Norman, B. H. *Tetrahedron Lett.* **1989**, *30*, 3259. Padwa, A.; Gereau, Y.; Harrison, B.; Norman, B. H. *J. Org. Chem.* **1991**, *56*, 2713. Padwa, A.; Gareau, Y.; Harrison, B.; Rodriguez, A. *J. Org. Chem.* **1992**, *57*, 3540.

(23) For cycloaddition chemistry of phenylsulfonyl-substituted dienes, see: Bäckvall, J. E.; Rise, F. *Tetrahedron Lett.* **1989**, *30*, 5347. Bäckvall, J. E.; Juntunen, S. K. *J. Am. Chem. Soc.* **1987**, *109*, 6396. Chou, T.-S.; Hung, S. C. *J. Org. Chem.* **1988**, *53*, 3020. Chou, T.-S.; Hung, S. C.; Tso, H. H. *J. Org. Chem.* **1987**, *52*, 3394. Bäckvall, J. E.; Juntunen, S. K. *J. Org. Chem.* **1988**, *53*, 2398. Mashyama, Y.; Yamazaki, H.; Toyoda, Y.; Kurusu, Y. *Synthesis* **1985**, 964. Lee, S. J.; Lee, J.-C.; Peng, M. L.; Chou, T.-S. *J. Chem. Soc., Chem. Commun.* **1989**, 1020. Overman, L. E.; Petty, C. B.; Ban, T.; Huang, G. T. *J. Am. Chem. Soc.* **1983**, *105*, 6335. Eisch, J. J.; Galle, J. E.; Hallenbeck, L. E. *J. Org. Chem.* **1982**, *47*, 1608.

(24) Andell, O. S.; Bäckvall, J. E. *Tetrahedron Lett.* **1985**, *26*, 4555.

(25) Cuvigny, T.; Hervee du Penhoat, C.; Julia, M. *Tetrahedron* **1988**, *42*, 5329. *Tetrahedron Lett.* **1983**, 4315.

(26) Inomata, K.; Kinoshita, H.; Takemoto, H.; Murata, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3341.

(27) Chou, T.; Lee, S. J.; Peng, M. L.; Sun, D. J.; Chou, S. S. P. *J. Org. Chem.* **1988**, *53*, 3027.

(28) Naf, F.; Decorzant, R.; Escher, S. D. *Tetrahedron Lett.* **1982**, *23*, 5043.

(29) Akermark, B.; Mystrom, J. E.; Rein, T.; Bäckvall, J. E. *Tetrahedron Lett.* **1984**, *25*, 5719.

(30) Marino, J. P.; Long, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 7916.

(31) Jeganathan, S.; Okamura, W. H. *Tetrahedron Lett.* **1982**, *23*, 4763. Masuyama, Y.; Sato, H.; Kurusu, Y. *Tetrahedron Lett.* **1985**, *26*, 67.

(32) Ni, Z.; Wang, X.; Rodriguez, A.; Padwa, A. *Tetrahedron Lett.* **1992**, *33*, 7303.

(33) Padwa, A.; Bullock, W. H.; Norman, B. H.; Perumattam, J. *J. Org. Chem.* **1991**, *56*, 4252.

(34) Miller, E. G.; Rayner, D. R.; Mislow, K. *J. Am. Chem. Soc.* **1966**, *88*, 3139. Mislow, K. *Rec. Chem. Prog.* **1967**, *28*, 217. Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.

(35) Braverman, S.; Stabinsky, Y. *J. Chem. Soc., Chem. Commun.* **1967**, 270.

(36) Braverman, S. In *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappoport, Z., Stirling, C. J., Eds.; John Wiley: New York, 1988.

(37) Theobald, P. G.; Okamura, W. H. *J. Org. Chem.* **1990**, *55*, 741. Cutting, I.; Parsons, P. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1209.

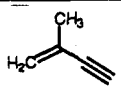
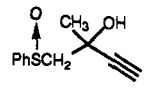
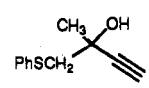
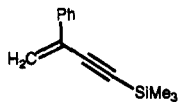
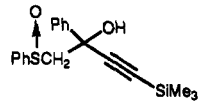
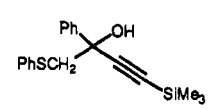
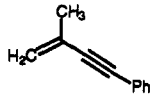
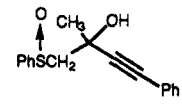
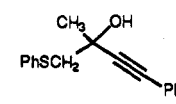
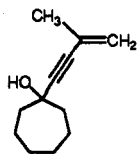
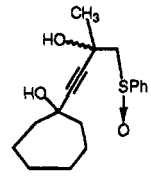
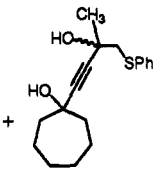
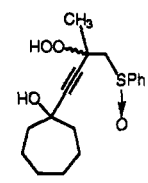
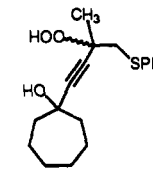
(38) Chanley, J. D. *J. Am. Chem. Soc.* **1948**, *70*, 244. Marshall, J. A.; Wang, X. *J. Org. Chem.* **1991**, *56*, 4913. Mandai, T.; Nakata, T.; Murayama, H.; Yamaoki, H.; Ogawa, M.; Kawada, M.; Tsuji, J. *Tetrahedron Lett.* **1990**, *31*, 7179. Earl, R. A.; Townsend, L. B. *Org. Synth.* **1981**, *60*, 81. Theobald, P. G.; Okamura, W. H. *J. Org. Chem.* **1990**, *55*, 741.

(39) Wang, X.; Ni, Z.; Lu, X.; Smith, T. Y.; Rodriguez, A.; Padwa, A. *Tetrahedron Lett.* **1992**, *34*, 5917.

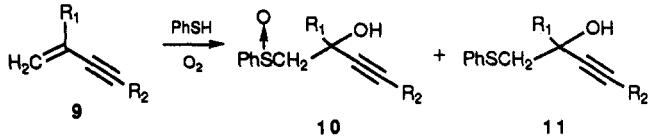
(40) Kharasch, M. S.; Nudenberg, W.; Mantell, G. J. *J. Org. Chem.* **1951**, *16*, 524. Oswald, A. A.; Griesbaum, K.; Hudson, B. E., Jr.; Bregman, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 2877. Griesbaum, K.; Oswald, A. A.; Hudson, B. E., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 1969.

(41) Petrov, A. A.; Sulimov, G. *J. Org. Chem. USSR* (Engl. *Transl.*) **1966**, *2*, 770. Stadnichuk, M. D.; Kryukova, T. B.; Petrov, A. A. *J. Gen. Chem. USSR* (Engl. Transl.) **1975**, *45*, 803. The addition of thiyl radicals to conjugated enynes with an alkoxy or thioalkoxy substituent on the double bond occurs exclusively at the terminal alkyne position: Shostakovskii, M. F.; Bogdanova, A. V.; Plotnikova, G. I.; Andreve, N. S. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (Engl. Transl.) **1960**, 1185. Prilezhaeva, E. N.; Guseinov, I. I.; Lopatin, B. V.; Shostakovskii, M. F. *J. Gen. Chem. USSR* (Engl. Transl.) **1959**, *2*, 770.

Table I. Cooxidation of Conjugated Enynes

enyne	conditions	products	diaster ratio	yields
 12	PhSH, O_2, 25°C	 13 +  14	1.5:1	13 = 33% 14 = 18%
 15	PhSH, O_2, 25°C	 16 +  17	1:1	16 = 21% 17 = 13%
 18	PhSH, O_2, 25°C	 19 +  20	1.2:1	19 = 49% 20 = 12%
 21	PhSH, O_2, 25°C	 22 +  23 +  24	+	 25

terminal olefinic carbon.[41] This assumption was made on the basis of earlier reports on the regiochemical outcome of thiyl additions to conjugated enynes.[41] Our results show that this indeed is the case and we were able to obtain several differently substituted β-sulfoxy and β-thio acetylenic alcohols in moderate yield (Table I). A typical experimental procedure consists of adding a heptane solution of thiophenol (1 mmol) over a course of 5–10 h


9 10 11

to an oxygenated heptane solution of the enyne (1 mmol). The complex product mixture obtained was readily separated by flash chromatography. When enyne **12** was cooxidized (Table I), the major sulfoxy carbinol **13** (33%) was isolated as a 1.5:1 mixture of diastereomers which could be readily separated by silica gel chromatography. Similar results were encountered with enyne **15**.

The β-phenylsulfoxy propargylic carbinols prepared in Table I were generally isolated as diastereomeric mixtures that could be easily separated by silica gel chromatography or else the mixture could be directly oxidized to the corresponding β-phenylsulfonyl carbinols in high yield. Minor modifications in the experimental conditions caused a significant effect in the product distribution. For example, if the cooxidation is conducted over long periods of time (>48 h) or KBr is added as a coreagent (*vide infra*), the amount of sulfoxy carbinol is enhanced. β-Thiophenyl carbinols are the exclusive products if a stoichiometric amount of triphenylphosphine is added to the reaction mixture. Conjugated enynes possessing an internal acetylene gave higher yields of product and proved less problematic than enynes with terminal acetylenes. The cooxidation of enynes proved to be highly regioselective. In all of the cases examined, the products formed are derived by preferential attack of the thiyl radical on the double bond of the enyne. The regiochemistry encountered holds for conjugated enynes that contain internal as well as terminal acetylenic π-bonds. These results are consistent with earlier observations on the addition of thiyl radicals to conjugated enynes[41] but are in marked contrast to recent studies by Back and co-workers.[42] The Back group investigated the free radical selenosulfonation of several conjugated enynes and found that the regioselectivity of the addition is controlled by steric factors. When the enyne contains an internal alkyne, radical addition occurs at the double bond. However, addition to the triple bond occurred preferentially with enynes possessing a terminal acetylenic π-bond. These differences are not all that surprising, however, since radical addition to conjugate enynes are complex and the regiochemistry is not only substrate-dependent but also depends on the nature of the attacking radical species.[43]

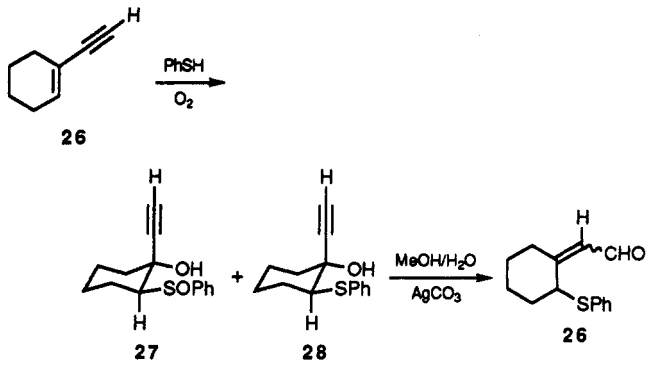
In contrast to the acyclic enynes, the cooxidation of cyclic enyne **26** gave sulfoxy carbinol **27** (26%) as a single diastereomer as well as a lesser amount (14%) of sulfide **28**. The structure of **27** has both the sulfoxy and hydroxyl groups in the equatorial position (*trans*), this assignment being based on an axial coupling constant of $J = 12.9$ Hz for the C_2-hydrogen. The fact that out of four possible diastereomers only one is observed is worth noting and suggests an intramolecular oxygen atom transfer process (*vide infra*). Sulfide **28** was converted to a mixture of *E*/*Z* aldehydes **29** using aqueous methanol containing a trace of silver carbonate (Rupe rearrangement[44]).

When the silyl-protected enyne **30** was cooxidized, sulfoxide **31** and sulfide **32** were formed in a 3:2 ratio. Once again, sulfoxy carbinol **31** was obtained as a single diastereomer even though four are possible. Desilylation of **31** with fluoride ion gave sulfoxide **27**, the same product obtained from the cooxidation of enyne **26**. When sulfide

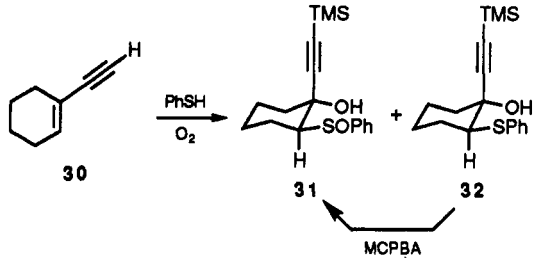
(42) Back, T. G.; Lai, E. K. Y.; Muralidharan, K. R. *J. Org. Chem.* **1990**, *55*, 4595.

(43) Poutsma, M. L.; Ibarbia, P. A. *J. Am. Chem. Soc.* **1973**, 95, 6000. Poutsma, M. L.; Ibarbia, P. A. *J. Org. Chem.* **1971**, *36*, 2572. Poutsma, M. L.; Ibarbia, P. A. *J. Org. Chem.* **1970**, *35*, 4038. Petry, R. C.; Parker, C. O.; Johnson, F. A.; Stevens, T. E.; Freeman, J. P. *J. Org. Chem.* **1967**, *32*, 1534.

(44) Pelletier, S. W.; Mody, N. V. *J. Org. Chem.* **1976**, *41*, 1069.

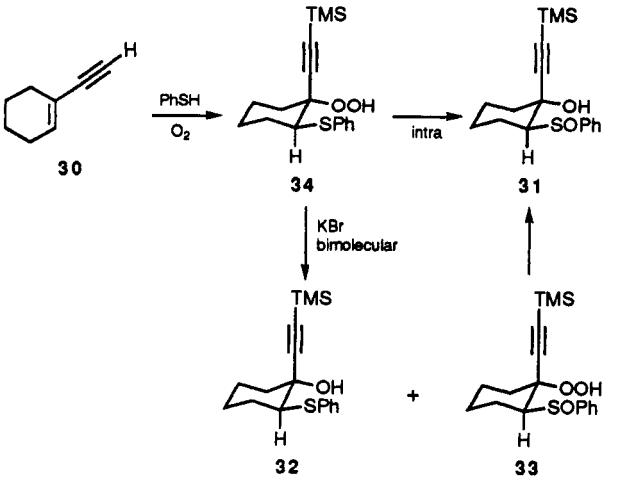


32 was treated with MCPBA, sulfoxide 31 was formed exclusively. The sole formation of 31 from the bimolecular

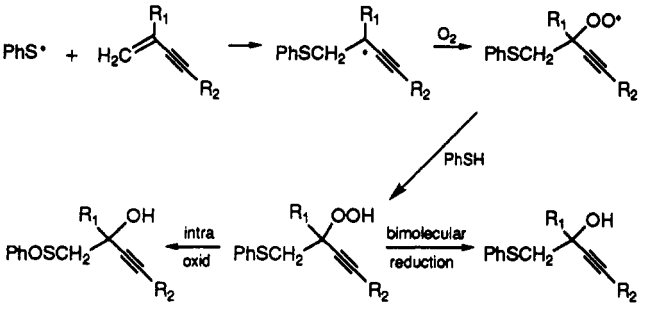


oxidation is undoubtedly related to hydrogen bonding between the hydroxy group and peracid with the specific delivery of oxygen to one face of the sulfide.

Our results are consistent with the cooxidation mechanism previously postulated for alkenes and which we now extend to conjugated enynes (Scheme I). Initial thiyl radical attack occurs exclusively at the double bond to generate a propargylic radical. Capture of the radical by oxygen followed by hydrogen transfer from thiophenol gives a hydroperoxide intermediate. This species has two available options; it can transfer an oxygen atom either by an intramolecular[45] or intermolecular[46] pathway. Support for this proposal was obtained by carrying out the cooxidation of enyne 30 in the presence of KBr. It has been reported that the absorption rate of oxygen is significantly accelerated in the presence of chloride or bromide ion.[47] The major products formed in the above reaction corresponded to sulfoxide 31, sulfide 32, sulfoxy hydroperoxide 33, and sulfide hydroperoxide 34 in a 1:1:1:1 ratio. Hydroperoxide 33 was isolated from the reaction mixture and was reduced to 31 by triphenylphosphine. Hydroperoxide 34, on the other hand, was too unstable



Scheme I



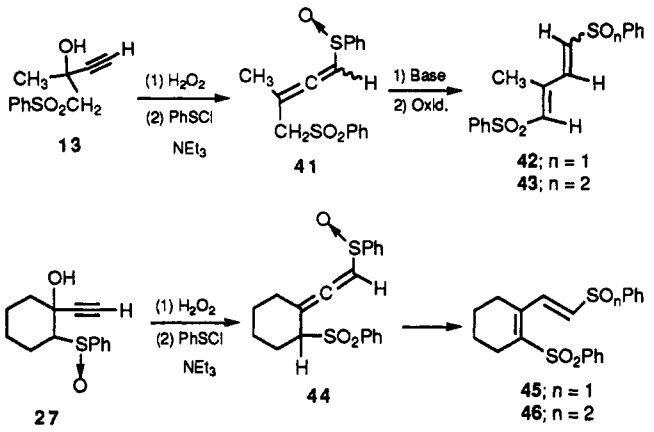
and consequently could not be isolated. Sulfoxide 33 was not detected in the absence of KBr and could only have arisen from an intermolecular oxygen transfer process since it still contains the hydroperoxide moiety. After standing for an additional 12 h, hydroperoxide 34 is no longer present and has been converted to 31 *via* the intramolecular pathway and at a slower rate to compounds 32 and 33 by a bimolecular disproportionation process. When triphenylphosphine was added to the reaction mixture in the cooxidation of 30, only sulfide 32 was obtained and no sulfoxide product was observed. This indicates that the oxygen atom donor species must be the hydroperoxide intermediate since reduction of this intermediate with the added triphenylphosphine suppresses the formation of sulfoxide 31. The cooxidation of enyne 21 proceeded in a similar fashion giving rise to a mixture of compounds 22–25. When left at 25 °C for 48 h, this mixture was cleanly converted to 24 in 90% yield. This observation is also consistent with the intermolecular pathway for oxygen transfer.

In addition to both sulfide and sulfoxy carbinols, the cooxidation of enynes possessing terminal alkynes also produced variable amounts of aldehydes as coproducts. The amount of aldehyde actually formed was dependent upon the rate at which oxygen was bubbled through the reaction mixture. This would tend to suggest that aldehyde formation is related to oxygen capture by radical intermediates rather than from propargylic alcohol rearrangements and is consistent with the pathway outlined in Scheme II. The initially formed radical (*i.e* 35) derived by thiyl radical addition to the alkene is trapped by oxygen to give mainly hydroperoxide 36 as well as minor amounts of the allenic hydroperoxide 37 as a transient intermediate. Although allenic hydroperoxides related to 37 are rare, they have been postulated in the radical triggering of neocarzinostatin analogs.[48] Decomposition of 37 *via* peroxide bond cleavage generates radical 38 which, we believe, is ultimately responsible for the formation of both aldehyde 29 and 40.

Having established that the cooxidation of enynes represents a general method for preparing β-sulfoxy-substituted propargylic carbinols, we next proceeded to examine the [2,3]-sigmatropic shift chemistry of the corresponding propargylic sulfenates.[27] A typical example involves the oxidation of 13 to the corresponding sulfone

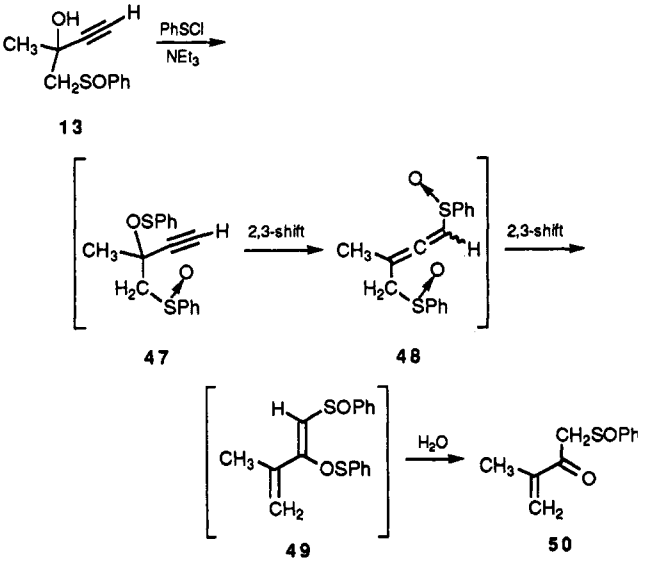
(45) Szmant, H. H.; Rigan, J. J. *Tetrahedron Lett.* **1967**, 3337. *J. Org. Chem.* **1972**, *37*, 447.
(46) Stacey, F. W.; Harriis, J. F. *Org. React.* **1963**, *13*, 186. Ford, J. F.; Pitkethly, R. C.; Young, V. O. *Tetrahedron* **1958**, *4*, 325.
(47) Bredereck, H.; Wagner, A.; Kottenbahn, A. *Chem. Ber.* **1960**, *93*, 2415.
(48) Fujiwara, K.; Kurisaki, A.; Hirama, M. *Tetrahedron Lett.* **1990**, *31*, 4329. Tanaka, T.; Fujiwara, K.; Hirama, M. *Tetrahedron Lett.* **1990**, *31*, 5947.

followed by treatment with phenylsulfenyl chloride and triethylamine producing a 1:1 mixture of *E,E*- and *E,Z*-



dienes **42** in 62% yield. A subsequent oxidation of **42** with hydrogen peroxide afforded bis-sulfone **43** ($n = 2$) in 65% yield. Sulfoxide **44** is stable enough to be isolated as a 1:1 mixture of *E*/*Z* isomers when carbinol **27** was oxidized to the sulfone followed by reaction with PhSCland triethylamine. This allene was subsequently transformed to diene **46** (*via* **45**) in 70% yield.

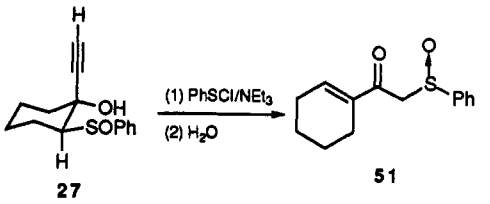
The sigmatropic reactions described above occur smoothly and produce the expected dienes in good yield. However, when β-sulfoxy carbinols are employed, the reaction proceeds in an entirely different manner. This is illustrated by the isolation of ketone **50** in 75% yield from the treatment of carbinol **13** with phenylsulfenyl chloride and triethylamine. The reaction proceeds *via* the initial formation of sulfenate **47** which then undergoes the expected 2,3-sigmatropic rearrangement to produce β-allenic sulfoxide **48**. This transient species undergoes



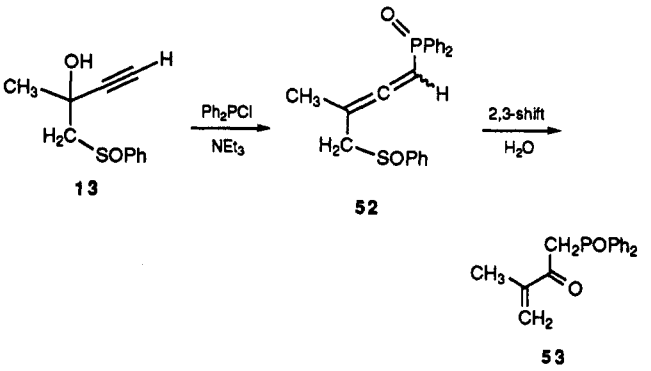
another [2,3]-sigmatropic shift to form vinyl sulfinate **49** which is eventually hydrolyzed to **50** upon aqueous workup. A somewhat related β-allenic sulfoxide → vinyl sulfenate rearrangement has recently been described by Posner and co-workers thereby providing good analogy for the proposed sequence of reactions.[49]

(49) Posner, G. H.; Carry, J. C.; Crouch, R. D.; Johnson, N. *J. Org. Chem.* **1991**, *56*, 6987.

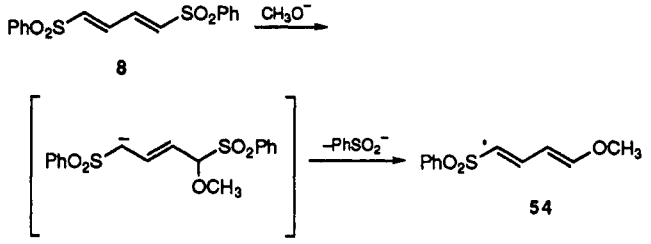
An analogous set of tandem [2,3]-sigmatropic shifts occurred with sulfoxy carbinols **27** and **13** under uniquely different reaction conditions. Treatment of **27** with phenylsulfonyl chloride followed by aqueous hydrolysis afforded enone **51** in 44% yield. We also examined the



reaction of carbinol **13** with diphenylchlorophosphine in the presence of triethylamine. The initially formed allene **52** was identified by IR spectroscopy (1954 cm^{-1}) and, on standing, underwent another [2,3]-sigmatropic shift to eventually give β-keto phosphine oxide **53**.[50]



α,β-Unsaturated sulfones are extremely useful as Michael acceptors with a host of nucleophilic partners.[51] We had previously demonstrated that 2,3-bis(phenylsulfonyl)-1,3-butadiene undergoes a [4 + 1]-annulation reaction with a variety of nucleophiles producing five-membered hetero[52] and carbocyclic ring systems.[53] As part of our studies in this area, we became interested in determining whether an analogous reaction would occur with the 1,4-bis(phenylsulfonyl) 1,3-diene system. As our first model, we examined the reaction of diene **8** with sodium methoxide. Addition of alkoxide ions to vinyl sulfones usually occurs at the β-position of the sulfone in analogous fashion to conjugate addition to enones.[54] The formation of **54** from the above reaction can be rationalized in terms of an initial

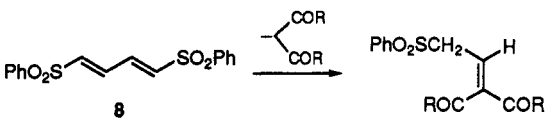


Michael addition of methoxide ion to one of the terminal carbon atoms followed by ejection of the benzenesulfinate group so as to regenerate a double bond. Such a mechanism has been suggested to be operative in the addition of

(50) For a related sigmatropic shift, see: Nicolaou, K. C.; Maligres, P.; Shin, J.; de Leon, E.; Rideout, D. *J. Am. Chem. Soc.* **1990**, *112*, 7825.
(51) Simpkins, N. S. *Tetrahedron* **1990**, *46*, 6951.
(52) Padwa, A.; Norman, B. H. *J. Org. Chem.* **1990**, *55*, 4801.
(53) Padwa, A.; Filipkowski, M. A. *Tetrahedron Lett.* **1993**, *34*, 813.
(54) Stirling, C. J. M. *J. Chem. Soc.* **1964**, 5856.

alkoxides to certain styryl sulfones producing enol ethers rather than furnishing Michael adducts.[55] One possible explanation to account for the exclusive formation of **54** from the reaction of **8** with methoxide ion is that, under the conditions used, Michael addition at the 2-position of the diene is reversible. Even if only a minor pathway, addition to the terminal carbon will give a stabilized allylic carbanion, that eventually produces the observed product by benzenesulfinate ejection.

The reaction of **8** with enolates derived from simple ketones proved to be too harsh for the base-sensitive bis(phenylsulfonyl) diene **8**. Use of softer carbanion nucleophiles such as the anion derived from dimethyl malonate, however, resulted in clean addition–elimination to provide **55** in 76% yield. Diketones may also be used for this reaction. Thus, treatment of **8** with the sodium salt of 2,4-pentanedione gave **56** in moderate yield. Both of these reactions presumably involve a 1,5-sigmatropic shift of hydrogen from the initially formed diene.



8

55; R = OCH_3
56; R = CH_3

In conclusion, a series of 1,4-bis(phenylsulfonyl) 1,3-dienes were readily prepared from β-sulfonyl-substituted acetylenic carbinols. These alcohols were converted to the corresponding propargylic sulfinates which were found to undergo [2,3]-sigmatropic rearrangement to produce allenylic sulfoxides that were subsequently converted to the desired dienes. The starting β-thio-substituted carbinols were conveniently synthesized by the addition of thiyl radicals and oxygen to a series of conjugated enynes. 1,4-Bis(phenylsulfonyl) dienes are versatile reagents that can be used as substrates for Michael type additions as well as in cycloaddition chemistry. The use of these dienes for [4 + 2]-cycloadditions is the object of ongoing investigations.

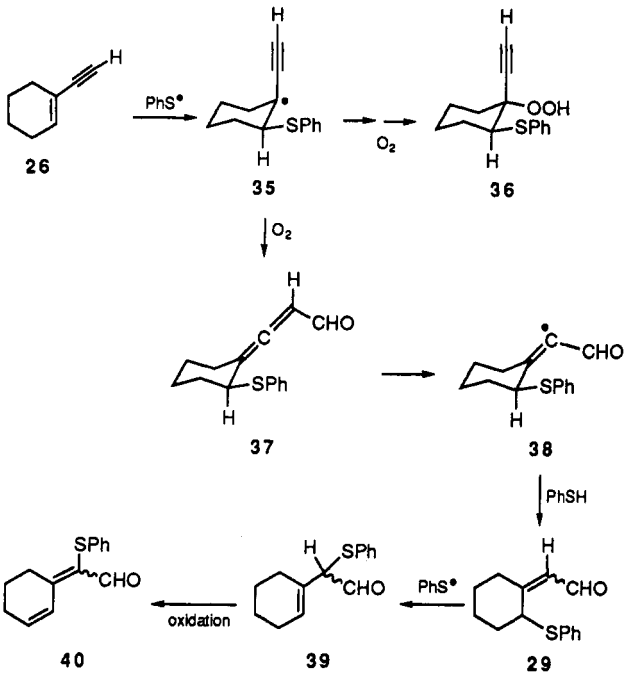
Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Unless otherwise noted, all reactions were performed in oven-dried glassware under an atmosphere of extra dry nitrogen. Solutions were evaporated under reduced pressure with a rotary evaporator and the residue was chromatographed on a silica gel column using a 1:1 ethyl acetate–hexane mixture as the eluent unless specified otherwise.

Preparation of 1,4-Bis(phenylsulfonyl)-1,3-butadiene (8). A solution of LDA prepared from 4.4 mL (31.5 mmol) of diisopropylamine and 21.6 mL of a 1.6 M (34.6 mmol) solution of *n*-butyllithium in 50 mL of THF at 0 °C was cooled to −78 °C. To this LDA solution was added a solution containing 4.4 g (31.5 mmol) of methyl phenyl sulfoxide in 50 mL of THF. After the addition, the solution was stirred at −78°C for 10 min and then 3.6 g (28.6 mmol) of 3-(trimethylsilyl)-2-propynal in 40 mL of THF was added dropwise. The mixture was stirred at −78 °C for 1 h, warmed to rt, and quenched with a saturated NH_4Cl solution. The solvent was removed under reduced pressure, and the residue was diluted with ether, washed with water, brine, dried, and concentrated under reduced pressure to give 7.43 g (97%) of 1-(trimethylsilyl)-4-(phenylsulfinyl)-1-butyn-3-ol (**4**) as a mixture of diastereoisomers which was used in the next reaction without further purification.

(55) Julia, M.; Righini, A.; Uguen, U. *J. Chem. Soc., Perkin Trans. 1* 1978, 1646.

Scheme II



A solution containing 0.5 g (1.88 mmol) of the above alcohol and 0.1 g (0.72 mmol) of potassium carbonate in 10 mL of methanol was stirred at rt for 3 h. To above the mixture was added 10 mL of water and 1.7 g (2.82 mmol) of Oxone. The mixture was stirred for an additional 2 h at rt. The solvent was removed under reduced pressure and the resulting residue was diluted with ether, washed with water, brine, and dried over sodium sulfate. Silica gel flash chromatography gave 360 mg (91%) of 4-(phenylsulfonyl)-1-butyn-3-ol (**5**): IR (neat) 2114, 1296, 1132, 1011 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 2.47 (d, 1H, J = 2.1 Hz), 3.44 (dd, 1H, J = 14.6 and 3.6 Hz), 3.50 (brd, 1H, J = 4.2 Hz), 3.57 (dd, 1H, J = 14.6 and 8.7 Hz), 4.90 (brd, 1H, J = 6.3 Hz), 7.56 (t, 2H, J = 7.8 Hz), 7.66 (t, 1H, J = 7.2 Hz), and 7.92 (d, 2H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 57.1, 61.7, 74.8, 80.8, 128.1, 129.3, 134.1, 138.9; HRMS calcd for $C_{10}H_{10}O_3S$: 210.0351, found 210.0350.

To a solution containing 420 mg (2.0 mmol) of carbinol **5** in 20 mL of CH_2Cl_2 at 0 °C was added dropwise 317 mg (2.2 mmol) of benzenesulfenyl chloride. The mixture was stirred overnight at rt, diluted with CH_2Cl_2, washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was recrystallized from ethyl acetate to give 395 mg (62%) of 1-(phenylsulfinyl)-4-(phenylsulfonyl)-1,3-butadiene (**7**): mp 163–164 °C; IR (KBr) 1619, 1445, 1316, 1149 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 6.61 (d, 1H, J = 14.7 Hz), 6.86 (d, 1H, J = 14.7 Hz), 6.97 (dd, 1H, J = 14.7 and 10.5 Hz), 7.26 (dd, 1H, J = 14.7 and 10.5 Hz), 7.41–7.61 (m, 8H), and 7.82 (d, 2H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 124.5, 127.5, 128.0, 129.2, 129.5, 131.5, 133.6, 134.5, 136.6, 139.5, 141.9, 146.1; HRMS calcd for $C_{16}H_{14}O_3S_2$ 318.0384, found 318.0381.

To a mixture of diene **7** in 50 mL of methanol and 20 mL of water was added 1.0 g (1.6 mmol) of Oxone in one portion. The mixture was stirred at rt for 5 h. Standard workup gave 0.32 g (97%) of 1,4-bis(phenylsulfonyl)-1,3-butadiene (**8**): IR (KBr) 1576, 1439, 1310, 1136, 809 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 6.82 (dd, 2H, J = 11.0 and 3.0 Hz), 7.26 (dd, 2H, J = 11.0 and 3.0 Hz), 7.56 (t, 4H, J = 7.5 Hz), 7.66 (t, 2H, J = 7.2 Hz), 7.88 (d, 4H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 128.0, 129.6, 134.1, 135.4, 138.9, 139.0; HRMS calcd for $C_{16}H_{14}O_4S_2$ 334.0334, found 334.0336.

General Procedure for the Cooxidation of Enynes. A solution containing 10 mmol of the enyne in 60 mL of heptane was stirred at 0–25 °C while oxygen was gently bubbled through a fritted disk. To this mixture was added a solution of thiophenol (10 mmol) in 10 mL of CH_2Cl_2 dropwise *via* syringe pump over a period of 5–10 h. After the addition of thiophenol was complete, the reaction mixture was stirred at rt for 2 h. Removal of the

solvent followed by silica gel chromatography gave β-phenylsulfenyl and β-phenylsulfinyl propargylic alcohols as the major reaction products.

Cooxidation of 2-Methyl-1-buten-3-yne (12). Using the general procedure described above, treatment of 5.0 g (75.6 mmol) of 2-methyl-1-buten-3-yne (12) with 7.8 mL (75.6 mmol) of thiophenol in the presence of oxygen followed by silica gel chromatography gave 3.1 g (20%) of 3-methyl-4-(phenylsulfenyl)-1-butyn-3-ol (**13a**), 2.1 g (13%) of the corresponding diastereomer **13b**, and 2.6 g (18%) of 3-methyl-4-(phenylthio)-1-butyn-3-ol (14). Sulfoxide **13a**: IR (neat) 1714, 1006 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.57 (s, 3H), 2.04 (s, 1H), 2.72 (s, 1H), 2.98 (AB, 2H, J = 13.1 Hz), 7.51–7.54 (m, 3H), 7.64–7.68 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 30.5, 66.5, 66.8, 74.0, 84.9, 123.9, 129.5, 131.6, 143.2; HRMS calcd for $C_{11}H_{12}O_2S$ 208.0558, found 208.0556.

Sulfoxide 13b: IR (neat) 1716, 1211, 1004 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.73 (s, 3H), 2.52 (s, 1H), 3.07 (d, 1H, J = 13.5 Hz), 3.20 (d, 1H, J = 13.5 Hz), 7.46–7.64 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 29.9, 66.0, 69.1, 73.4, 85.3, 124.0, 129.2, 131.1, 143.5; HRMS calcd for $C_{11}H_{12}O_2S$ 208.0558, found 208.0559.

3-Methyl-4-(phenylthio)-1-butyn-3-ol (14): IR (neat) 1663, 1095 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.57 (s, 3H), 2.40 (s, 1H), 3.98 (s, 1H), 3.38 (AB, 2H, J = 13.5 Hz), 7.18–7.45 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 28.6, 48.3, 67.3, 72.2, 86.2, 126.6, 128.9, 129.3, 130.1; HRMS calcd for $C_{11}H_{12}OS$ 192.0609, found 192.0607.

Cooxidation of 2-Phenyl-4-(trimethylsilyl)-1-buten-3-yne (15). Using the general procedure described above, treatment of 350 mg (1.75 mmol) of 2-phenyl-4-(trimethylsilyl)-1-buten-3-yne (15) with 230 mg (2.1 mmol) of thiophenol in the presence of oxygen followed by silica gel chromatography gave a 1:1 mixture (21%) of the diastereomers of 2-phenyl-1-(phenylsulfinyl)-4-(trimethylsilyl)-3-butyn-2-ol (16) as well as 2-phenyl-1-(phenylthio)-4-(trimethylsilyl)-3-butyn-2-ol (17, 13%). Sulfoxide **16a**: IR (neat) 3306, 1240, 1035, 829 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 0.29 (s, 9H), 2.97 (d, 1H, J = 13.2 Hz), 3.14 (d, 1H, J = 13.2 Hz), 5.64 (brs, 1H), 7.27–7.67 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ −0.18, 68.8, 72.1, 93.4, 104.8, 123.8, 125.3, 128.2, 128.4, 129.4, 131.4, 142.4, 143.3; HRMS calcd for $C_{19}H_{22}O_2SSi$ 342.1110, found 342.1108.

Sulfoxide 16b: IR (neat) 3306, 1238, 1033, 831 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 0.16 (s, 9H), 3.30 (d, 1H, J = 13.5 Hz), 3.47 (d, 1H, J = 13.5 Hz), 5.07 (brs 1H), 7.32–7.71 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ −0.32, 70.2, 71.6, 91.4, 105.6, 124.0, 125.5, 128.2, 128.5, 129.3, 131.2, 142.1, 143.6; HRMS calcd for $C_{19}H_{22}O_2SSi$ 342.1110, found 342.1113.

Sulfide 17: IR (neat) 3456, 1679, 1246, 840 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 0.17 (s, 9H), 3.25 (brs, 1H), 3.36 (d, 1H, J = 13.5 Hz), 3.54 (d, 1H, J = 13.5 Hz), 7.17–7.68 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ −0.26, 50.6, 61.2, 72.4, 91.4, 106.3, 125.5, 126.4, 128.1, 128.2, 128.8, 129.9, 136.4, 142.5; HRMS calcd for $C_{19}H_{20}SSi$ ($M^+ - H_2O$) 308.1055, found 308.1054.

Cooxidation of 2-Methyl-4-phenyl-1-buten-3-yne (18). Using the general procedure described above, treatment of 0.5 g (3.5 mmol) of 2-methyl-4-phenyl-1-buten-3-yne (18) with 0.39 mL (3.5 mmol) of thiophenol in the presence of oxygen followed by silica gel chromatography gave a 1:2 mixture of the diastereomers of 2-methyl-4-phenyl-1-(phenylsulfinyl)-3-butyn-2-ol (19, 49%) and 2-methyl-4-phenyl-1-(phenylthio)-3-butyn-2-ol (20, 12%). Sulfoxide **19a**: IR (neat) 3350, 1720, 1008 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.65 (s, 3H), 3.04 (d, 1H, J = 12.9 Hz), 3.12 (d, 1H, J = 12.9 Hz), 5.33 (brs, 1H), and 7.21–7.63 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 30.1, 66.9, 67.7, 85.2, 90.2, 121.8, 128.0, 128.3, 129.2, 131.1, 131.5, 143.2; HRMS calcd for $C_{17}H_{16}O_2S$ 284.0871, found 284.0870.

Sulfoxide 19b: IR (neat) 3360, 1716, 1215, 1004 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.81 (s, 3H), 3.18 (d, 1H, J = 13.5 Hz), 3.29 (d, 1H, J = 13.5 Hz), 4.70 (brs, 1H), 7.21–7.65 (m, 10 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 30.1, 66.6, 69.6, 85.1, 90.7, 122.0, 124.0, 128.1, 128.5, 129.3, 131.0, 131.7, 143.7; HRMS calcd for $C_{17}H_{16}O_2S$: 284.0871, found 284.0871.

Sulfide 20: IR (neat) 3342, 1665, 1090 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.67 (s, 3H), 3.01 (brs, 1H), 3.26 (d, 1H, J = 13.8 Hz), 3.50 (d, 1H, J = 13.8 Hz), 7.10–7.49 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 28.8, 48.5, 67.9, 84.1, 91.4, 126.4, 128.1, 128.3, 128.9, 129.9, 131.7, 135.3, 136.4; HRMS calcd for $C_{17}H_{16}OS$ 268.0922, found 268.0920.

Cooxidation of 1-(3-Methyl-3-buten-1-ynyl)cycloheptanol. Using the general procedure described above, 1.78 g (10 mmol) of 1-(3-methyl-3-buten-1-ynyl)cycloheptanol (21) and 1.10 g (10 mmol) of thiophenol afforded, after silica gel chromatography, 0.210 g (7%) of 1-[3-hydroxy-3-methyl-4-(phenylthio)-1-butynyl]cycloheptanol (23) as a colorless oil: IR (neat) 3408, 1481, 1157, 1123, 1086, 691 cm^{-1}; ^1H-NMR ($CDCl_3$, 250 MHz) δ 1.50–2.20 (m, 12H), 1.56 (s, 3H), 3.05 (brs, 1H), 3.17 and 3.40 (AB, 2H, J = 13.5 Hz), 7.20–7.32 (m, 3H), 7.40–7.50 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 22.1, 27.8, 28.9, 42.7, 48.3, 67.4, 71.4, 85.8, 88.7, 126.3, 128.9, 129.8, 136.6. Anal. Calcd for $C_{18}H_{24}O_2S$: C, 71.01; H, 7.95. Found: C, 70.81; H, 7.90.

The second fraction eluted from the column contained 0.23 g (7%) of 1-[3-hydroperoxy-3-methyl-4-(phenylsulfinyl)-1-butynyl]-cycloheptanol (24) as a 2:3 mixture of two diastereomers; IR (neat) 3337, 3044, 2243, 1375, 1250, 1120, 1024, 762, 691 cm^{-1}; ^1H-NMR ($CDCl_3$, 250 MHz) δ 1.50–2.10 (m, 24H, isomer **24a** and **24b**), 1.67 (s, 3H, isomer **24a**), 1.72 (s, 3H, isomer **24b**), 3.00 (br, 2H, isomer **24a** and **24b**), 3.15 and 3.48 (AB, J = 14 Hz, 2H, isomer **24a**), 3.09 and 3.53 (AB, J = 14 Hz, 2H, isomer **24b**), 7.50–7.56 (m, 6H, isomer **24a** and **24b**), 7.66–7.70 (m, 4H, isomer **24a** and **24b**), 10.60 (br, 2H, isomer **24a** and **24b**); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 22.0 (isomer **24b**), 22.1 (isomer **24a**), 25.0 (**24a**), 25.2 (**24b**), 27.7 (**24b**), 27.8 (**24a**), 42.6 (**24a**), 42.7 (**24b**), 67.9 (**24a**), 68.4 (**24b**), 71.5 (isomer **24a** and **24b**), 71.6 (isomer **24a** and **24b**), 81.4 (**24a**), 81.8 (**24b**), 91.9 (**24a**), 92.3 (**24b**), 124.0 (isomer **24a** and **24b**), 129.4 (**24b**), 129.5 (**24a**), 131.3 (**24b**), 131.4 (**24a**), 142.7 (**24a**), 142.9 (**24b**); KI test positive.

The final component to elute from the column contained 0.62 g (19%) of 1-[3-hydroxy-3-methyl-4-(phenylsulfinyl)-1-butynyl]-cycloheptanol (22) as a 2:3 mixture of diastereomers. Isomer **22a**: colorless oil; IR (neat) 3403, 1460, 1254, 1161, 891 cm^{-1}; ^1H-NMR ($CDCl_3$, 250 MHz) δ 1.50–2.13 (m, 12H), 1.59 (s, 3H), 2.97 and 3.11 (AB, 2H, J = 13 Hz), 3.20 (br, 1H), 5.16 (br, 1H), 7.52–7.57 (m, 3H), 7.65–7.70 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 22.1, 27.8, 30.2, 42.8, 66.6, 68.2, 71.3, 84.4, 90.9, 123.9, 129.4, 131.3, 143.4. Anal. Calcd for $C_{18}H_{24}O_3S$: C, 67.47; H, 7.55. Found: C, 67.35; H, 7.45.

Isomer 22b: colorless oil; IR (neat) 3300, 1736, 1653, 1445, 1121, 692 cm^{-1}; ^1H-NMR ($CDCl_3$, 250 MHz) δ 1.50–2.04 (m, 12H), 1.70 (s, 3H), 3.09 and 3.28 (AB, 2H, J = 13 Hz), 4.36 (br, 1H), 5.00 (br, 1H), 7.46–7.56 (m, 3H), 7.63–7.69 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 22.1, 27.9, 30.2, 42.6, 65.7, 71.2, 71.4, 84.7, 90.9, 124.0, 129.3, 131.0, 143.9. Anal. Calcd for $C_{18}H_{24}O_3S$: C, 67.47; H, 7.55. Found: C, 67.40; H, 7.51.

NMR analysis of the reaction mixture prior to separation showed a labile intermediate which was identified as 1-[3-hydroperoxy-3-methyl-4-(phenylthio)-1-butynyl]cycloheptanol (25): ^1H-NMR ($CDCl_3$, 250 MHz) δ 1.50–2.10 (m, 12H), 1.53 (s, 3H), 3.33 and 3.47 (AB, 2H, J = 13 Hz), 3.20 (br, 1H), 9.70 (brs, 1H), 7.46–7.56 (m, 3H), 7.63–7.69 (m, 2H). When a sample of the cooxidation mixture was allowed to stand at rt for 2 days, all the components present were converted to **22a,b** (1:2) in 90% yield.

Cooxidation of 1-Ethynylcyclohexene (26). Treatment of 1.06 g (10 mmol) of 1-ethynylcyclohexene with 1.10 g (10 mmol) of thiophenol in the presence of oxygen followed by silica gel chromatography gave a mixture of three products. The first product to elute from the column was a colorless oil whose structure was assigned as 1-ethynyl-2-(phenylthio)cyclohexanol (28) (14% yield): IR (neat) 3510, 1589, 1474, 1439, 736 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.15–2.24 (m, 8H), 2.56 (s, 1H), 2.98 (dd, 1H, J = 12.6 and 3.9 Hz), 3.51 (s, 1H), 7.20–7.54 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 23.2, 26.0, 32.8, 39.1, 61.3, 71.5, 74.6, 84.1, 127.1, 129.0, 131.9, 135.2; MS 232 [M^+], 215, 155, 135, 123, 110 (100), 95, 81, 53. Anal. Calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94. Found: C, 72.21; H, 6.91.

The second fraction (26%) was identified as 1-ethynyl-2-(phenylsulfinyl)cyclohexanol (27): IR (neat) 3317, 3057, 1727, 1581, 1444, 1124, 653 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 0.95–2.20 (m, 8H), 2.78 (dd, 1H, J = 12.9 and 3.9 Hz), 2.77 (s, 1H), 6.27 (s, 1H), 7.50–7.80 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 22.5, 23.0, 24.7, 40.1, 70.8, 71.5, 76.1, 83.2, 125.8, 129.3, 132.2, 142.0;

MS 248 [M+], 231, 202, 153, 135, 126 (100), 109, 78, 55. Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49. Found: C, 67.25; H, 6.44.

The last fraction obtained was identified as a 4:1 mixture of (*Z*)- and (*E*)-(2-cyclohexenylidene)(phenylthio)ethanal (12%) (**40**): IR (neat) 3466, 3303, 3060, 1721, 1660, 1478, 691 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) isomer **40a**: δ 1.05–2.60 (m, 6H), 6.35 (d, 1H, J = 9.6 Hz), 7.25 (d, 1H, J = 9.6 Hz), 7.20–7.65 (m, 5H), 9.76 (s, 1H), isomer **40b**: δ 1.05–2.60 (m, 6H), 6.02 (d, 1H, J = 15.3 Hz), 7.73 (d, 1H, J = 15.3 Hz), 7.20–7.65 (m, 5H), 9.76 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) isomer **40a**: δ 21.5, 23.4, 43.5, 119.5, 123.6, 128.1, 129.5, 130.7, 132.6, 149.2, 165.0, 193.0; MS 230 [M+], 202, 185, 179, 153, 137, 121, 109, 95, 91, 65, 55, 32, 28 (100). Anal. Calcd for $C_{14}H31_4OS$: C, 73.02; H, 6.13. Found: C, 72.80; H, 6.07.

If a slow flow of oxygen is utilized in the cooxidation of enyne **26**, then a fourth product (10%) was also isolated. This product was identified as a 7:3 *E*/*Z* mixture of [2-(phenylthio)cyclohexylidene]ethanal (**29**): IR (neat) 1670, 1623, 1201, 685 cm^{-1}; ^1H-NMR ($CDCl_3$, 250 MHz) isomer **29a** δ 1.40–2.35 (m, 6H), 3.85 (t, 1H, J = 4 Hz), 5.59 (d, 1H, J = 8 Hz), 7.24–7.43 (m, 5H), 9.93 (d, 1H, J = 8 Hz). Isomer **29b**: δ 1.40–2.35 (m, 6H), 4.76 (t, 1H, J = 4 Hz), 5.70 (d, 1H, J = 8 Hz), 7.24–7.43 (m, 5H), 9.17 (d, 1H, J = 8 Hz); ^{13}C-NMR ($CDCl_3$, 63 MHz) isomer **29a** δ 21.9, 25.5, 27.8, 33.6, 55.4, 125.8, 127.9, 129.1, 133.0, 137.4, 164.0, 190.2. Isomer **29b**: δ 21.3, 26.2, 27.8, 32.4, 47.5, 127.1, 127.9, 129.2, 133.0, 137.4, 163.0, 188.4; MS 232 [M+], 218, 135, 109 (100), 95, 81, 77, 65, 55. Anal. Calcd for $C_{14}H_{16}OS$: C, 72.39; H, 6.94. Found: C, 72.07; H, 6.89.

Cooxidation of 1-[2-(Trimethylsilyl)ethynyl]cyclohexene (30). A solution containing 0.89 g (5.0 mmol) of 1-[2-(trimethylsilyl)ethynyl]cyclohexene (**30**) and 0.55 g (5.0 mmol) of thiophenol was cooxidized in the presence of oxygen in the normal manner. Removal of the solvent under reduced pressure left a yellow oil which was purified by silica gel chromatography. The first fraction eluted from the column was identified as 2-(phenylthio)-1-[2-(trimethylsilyl)ethynyl]cyclohexanol (**32**) (20%): IR (neat) 3421, 1574, 1253, 846 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 0.23 (s, 9H), 1.20–2.25 (m, 8H), 2.96 (dd, 1H, J = 12.6 and 3.9 Hz), 3.40 (m, 1H), 7.20–7.35 (m, 3H), and 7.45–7.55 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ –0.1, 23.5, 26.2, 33.1, 39.1, 61.7, 71.8, 91.4, 105.8, 127.0, 128.9, 131.8, 135.8; MS 304 [M+], 227, 211, 195, 179, 165, 151, 135, 123, 110, 73 (100). Anal. Calcd for $C_{17}H_{24}OSSi$: C, 67.05; H, 7.94. Found: C, 66.86; H, 7.85.

The second fraction (34%) isolated from the column was identified as 2-(phenylsulfinyl)-1-[2-(trimethylsilyl)ethynyl]cyclohexanol (**31**): IR (neat) 3353, 1450, 1250, 1060, 695 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 0.24 (s, 9H), 1.05–2.15 (m, 8H), 2.74 (dd, 1H, J = 12.6 and 3.9 Hz), 6.20 (b, 1H), 7.50–7.58 (m, 3H), 7.71–7.75 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ –0.1, 22.7, 23.1, 24.8, 40.1, 71.1, 71.9, 93.0, 104.8, 125.8, 129.2, 132.1, 142.4. Anal. Calcd for $C_{17}H_{24}O_2SSi$: C, 63.71; H, 7.55. Found: C, 63.70; H, 7.50.

To a solution containing 0.5 g (2.8 mmol) of enyne **30** and 735 mg (2.8 mmol) of triphenylphosphine in 60 mL of heptane was added 0.30 mL (2.8 mmol) of a solution of thiophenol in 10 mL of CH_2Cl_2 *via* a syringe pump over 10 h while oxygen was bubbled into the solution. The mixture was stirred overnight and the triphenylphosphine oxide that formed was filtered. The filtrate was diluted with ether, washed with 10% NaOH, water, and brine, and dried over $NaSO_4$. Purification of the crude mixture on a silica gel column gave 282 mg (33%) of sulfide **32**.

To a solution containing 0.5 g (2.8 mmol) of enyne **30** and 1.0 g (2.8 mmol) of KBr in 60 mL of heptane was added 0.30 mL (8.4 mmol) of a solution of thiophenol in 10 mL of CH_2Cl_2 *via* a syringe pump over 10 h while oxygen was bubbled into the solution. The mixture was stirred overnight, diluted with ether, washed with water, dried over sodium sulfate, and concentrated under reduced pressure. Purification of the crude residue on silica gel gave 540 mg (60%) of sulfoxide **31**, 61 mg (7%) of sulfide **32**, and 114 mg (12%) of peroxide **33**; IR (neat) 1455, 1248, 1046, 850 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 0.16 (s, 9H), 0.95–1.20 (m, 2H), 1.35–1.69 (m, 4H), 1.91–2.12 (m, 3H), 3.24 (dd, 1H, J = 13.0 and 3.6 Hz), 7.40–7.69 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ –0.3, 23.2, 24.9, 25.3, 26.3, 72.0, 84.4, 96.7, 100.1, 125.9, 129.3, 132.2, 140.0.

Chemical support for structure **33** was obtained by its reduction to sulfoxide **31**. To a solution containing 20 mg (0.06 mmol) of peroxide **33** in 2 mL of CH_2Cl_2 was added 20 mg (0.7 mmol) of solid triphenylphosphine. After stirring for 10 min, the solvent was removed and the residue was purified by flash chromatography to give 17 mg (88%) of sulfoxide **31**. When the crude mixture was allowed to stir overnight, sulfide **32** and peroxide **33** were completely converted to sulfoxide **31** in 75% overall yield.

Preparation of 1,4-Bis(phenylsulfonyl)-2-methyl-1,3-butadiene (43). A mixture containing 350 mg (1.68 mmol) of 3-methyl-4-(phenylsulfinyl)-1-butyn-3-ol (**13**) and 1 mL of H_2O_2 (30%) in 2 mL of glacial acetic acid was heated to reflux for 10 h. The mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was washed with water and aqueous sodium bicarbonate and dried over sodium sulfate. Purification by silica gel flash chromatography afforded 350 mg (93%) of 3-methyl-4-(phenylsulfonyl)-1-butyn-3-ol: IR (neat) 2108, 1298, 1147, 1079 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.58 (s, 3H), 2.35 (s, 1H), 3.50 (AB, 2H, J = 14.4 Hz), 3.34 (s, 1H), 7.54 (t, 2H, J = 7.8 Hz), 7.64 (m, 1H), 7.93 (d, 2H, J = 6.9 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 30.3, 64.5, 65.5, 73.7, 83.8, 128.1, 129.1, 134.0, 140.1; HRMS calcd for $C_{11}H_{12}O_3S$ 224.0507, found 224.0507.

To a solution containing 170 mg (0.76 mmol) of the above carbinol and 0.28 mL (2.0 mmol) of triethylamine in 5 mL of CH_2Cl_2 at 0 °C was added 142 mg (1.0 mmol) of benzenesulfenyl chloride. The mixture was stirred at rt for 10 h. Standard workup and purification by silica gel flash chromatography afforded a 1:1 mixture of (1*E*,3*E*) (**42**) and (*E*,*Z*)-2-methyl-1-(phenylsulfonyl)-4-(phenylsulfinyl)-1,3-butadiene (**42b**) in 62% yield. **Isomer 42a**: IR (neat) 1605, 1434, 1309, 1138, 742 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.94 (s, 3H), 6.34 (s, 1H), 6.68 (d, 1H, J = 15.3 Hz), 7.50–7.70 (m, 8H), 7.94 (d, 2H, J = 8.4 Hz), 8.31 (d, 1H, J = 15.3 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 20.8, 124.6, 127.5, 129.3, 129.4, 129.6, 131.4, 131.8, 133.6, 141.2, 142.7, 143.0, 149.9; HRMS calcd for $C_{11}H_{11}OS$ (M^+ – $PhSO_2$) 191.0531, found 191.0536.

Isomer 42b: IR (neat) 1577, 1442, 1300, 1037, 750 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 2.33 (s, 1H), 6.35 (s, 1H), 6.44 (d, 1 H, J = 10.8 Hz), 7.42 (d, 1H, J = 10.8 Hz), 7.47–7.62 (m, 8H), 7.88 (d, 2H, J = 7.2 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 25.9, 124.4, 127.4, 129.4, 129.5, 130.9, 131.2, 133.4, 133.7, 139.7, 140.8; HRMS calcd for $C_{11}H_{11}OS$ (M^+ – $PhSO_2$) 191.0531, found 191.0527.

The above mixture of isomers was taken up in 2 mL of H_2O_2 and 5 mL of acetic acid. The mixture was heated at reflux for 4 h. Standard workup and purification by silica gel flash chromatography afforded a 1:1 mixture of (*E*,*E*) (**43a**) and (*E*,*Z*)-1,4-bis(phenylsulfonyl)-2-methyl-1,3-butadiene (**43b**) in 61% yield. **Isomer 43a**: IR (neat) 3068, 1716, 1445, 1131, 720 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 Mhz) δ 1.94 (s, 3H), 6.44 (s, 1H), 6.64 (d, 1H, J = 15.6 Hz), 7.53–7.66 (m, 6H), 7.87–7.94 (m, 4H), 8.52 (d, 1H, J = 15.6 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 20.6, 127.5, 128.2, 129.4, 129.5, 129.6, 133.8, 134.0, 134.6, 135.0, 135.5, 139.3, 142.9; HRMS calcd for $C_{17}H_{16}O_4S_2$: 348.0490, found 348.0492.

Isomer 43b: IR (neat) 1588, 1310, 1082, 741 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 2.24 (s, 3H), 6.24 (s, 1H), 6.32 (d, 1H, J = 11.7 Hz), 7.16 (d, 1H, J = 11.7 Hz), 7.51–7.66 (m, 6H), 7.92 (d, 4H, J = 7.8 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 25.5, 126.9, 127.4, 127.7, 129.2, 129.3, 129.9, 133.5, 133.8, 138.5, 139.8, 140.7, 147.5; HRMS calcd for $C_{17}H_{16}O_4S_2$ 348.0490, found 348.0489.

The [2,3]-sigmatropic rearrangement reaction of **13** was also carried out using a 2.0 mole excess of benzenesulfinyl chloride. To a solution containing 200 mg (0.96 mmol) of **13** and 0.3 mL (2.1 mmol) of triethylamine in 10 mL of CH_2Cl_2 at 0 °C was added 144 mg (1.0 mmol) of benzenesulfenyl chloride dropwise. The solution was stirred at 0 °C for 30 min and was heated at reflux for 1 h. Standard workup followed by silica gel flash chromatography gave 150 mg (75%) of 2-methyl-4-(phenylsulfinyl)-1-buten-3-one (**50**): IR (neat) 1674, 1446, 1040, 738 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.79 (s, 3H), 3.99 (d, 1H, J = 4.1 Hz), 4.26 (d, 1H, J = 14.1 Hz), 5.90 (brs, 2H), 7.46–7.48 (m, 3H), 7.62–7.65 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 17.1, 65.0, 124.1, 128.6, 129.2, 131.5, 143.2, 144.5, 192.5; HRMS calcd for $C_{11}H_{12}O_2S$: 208.0558, found 208.0557.

Preparation of *trans*-2-[2-(Phenylsulfonyl)ethenyl]-1-(phenylsulfonyl)cyclohexene (46). A solution containing 400 mg (1.61 mmol) of 1-ethynyl-2-(phenylsulfinyl)cyclohexanol (**27**) and 0.5 mL of H_2O_2 (30%) in 10 mL of glacial acetic acid was heated at reflux for 1 h, treated with ice water, and extracted with 60 mL of CH_2Cl_2. The organic layer was washed with

aqueous $NaHCO_3$ and water, the solvent was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column to give 276 mg (65%) of a white solid, mp 129–131 °C, whose structure was assigned as 1-etehynyl-2-(phenylsulfonyl)cyclohexanol: IR ($CDCl_3$) 3487, 3309, 1443, 1134, 1071, 642 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.05–2.10 (m, 8H), 2.58 (s, 1H), 3.09 (dd, 1H, J = 12.6 and 3.3 Hz), 5.25 (s, 1H), 7.50–7.93 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 22.5, 24.7, 25.3, 40.9, 68.7, 71.9, 76.3, 82.1, 128.9, 129.0, 134.0, 138.0. Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.62; H, 6.10. Found: C, 62.83; H, 6.02.

Using the standard procedure for the preparation of α-allenic sulfoxides, 180 mg (0.68 mmol) of the above cyclohexanol, 150 mg (0.68 mmol) of benzenesulfenyl chloride, and 0.15 mL of triethylamine gave, after silica gel chromatography, 191 mg (76%) of a mixture of the *cis–trans* isomers of 2-[2-(phenylsulfinyl)-ethylidene]-1-(phenylsulfonyl)cyclohexane (**44**): IR ($CDCl_3$) 3063, 1445, 1304, 1150, 1037 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.17–2.71 (m, 8H), 3.52 (d, 1H, J = 5.4 Hz, isomer **44a**), 3.61 (d, 1H, J = 5.7 Hz, isomer **44b**), 5.35 (d, 1H, J = 4.2 Hz), 7.40–7.80 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 20.8, 24.4, 24.9, 26.7, 63.2, 101.4, 104.2, 124.1, 124.2, 129.0, 129.1, 131.2, 133.6, 136.8, 143.9, 201.0. Anal. Calcd for $C_{20}H_{20}O_3S_2$: C, 64.49; H, 5.41. Found: C, 64.41; H, 5.44.

A solution containing 70 mg (0.19 mmol) of allene **44** and 0.3 mL of triethylamine in 15 mL of chloroform was heated at reflux for 16 h, after which the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography to give 43 mg (61%) of *trans*-2-[2-(phenylsulfinyl)ethenyl]-1-(phenylsulfonyl)cyclohexene (**45**) as a colorless oil: ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.50–2.50 (m, 8H), 6.51 (d, 1H, J = 15.3 Hz), 7.47–7.90 (m, 10 H), 8.44 (d, 1H, J = 15.3 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.1, 21.9, 27.3, 28.0, 124.5, 127.5, 129.3, 129.4, 131.1, 132.3, 133.4, 138.5, 138.6, 140.4, 141.6, 143.5; MS 372 [M^+], 356, 215 (100), 173, 121, 109, 91, 77.

A solution containing 116 mg (0.311 mmol) of **45** and 0.5 mL of H_2O_2 (30%) in 10 mL of glacial acetic acid was heated at reflux for 1 h. After cooling to rt, the reaction mixture was worked up with aqueous $NaHCO_3$, water, and brine, and dried over $MgSO_4$. The organic layer was concentrated under reduced pressure and the residue was chromatographed on silica gel to give 86 mg (71%) of *trans*-2-(2-(phenylsulfonyl)ethenyl)-1-(phenylsulfonyl)cyclohexene (**46**) as a colorless oil: ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.40–1.85 (m, 4H), 2.22–2.27 (m, 2H), 2.24–2.29 (m, 2H), 6.50 (d, 1H, J = 15.3 Hz), 7.44–8.00 (m, 10H), 8.68 (d, 1H, J = 15.3 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 20.9, 21.8, 27.4, 27.9, 127.4, 127.9, 129.3, 129.4, 131.6, 133.5, 133.6, 138.2, 139.4, 139.9, 140.6, 144.9. Anal. Calcd for $C_{20}H_{20}O_4S_2$: C, 61.83; H, 5.19. Found: C, 61.43; H, 5.02.

The [2,3]-sigmatropic rearrangement reaction of **27** was also carried out using a 2.0 mole excess of benzenesulfinyl chloride. Using the standard procedure for the preparation of α-allenic sulfoxides, 181 mg (0.73 mmol) of **27**, 161 mg (0.73 mmol) of benzenesulfenyl chloride, and 0.15 mL of triethylamine afforded, after silica gel chromatography, 80 mg (44%) of 1-(1-cyclohexenyl)-2-(phenylsulfinyl)ethanone (**51**) as a colorless oil: IR ($CDCl_3$) 3161, 1651, 1269, 1041, 781 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.55 (br s, 4H), 2.13 (br s, 2H), 2.19 (br s, 2H), 6.83 (s, 1H), 3.90–4.27 (AB, 2H), 7.47–7.65 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.2, 21.5, 22.7, 26.3, 64.8, 124.2, 129.2, 131.4, 139.7, 143.5, 144.8, 191.5; MS, 248 [M^+], 232, 207, 198, 170, 141, 109 (100), 81, 53, 45, 28.

Preparation of 1-(Diphenylphosphoryl)-3-methyl-3-butene-2-one (53). Using the general procedure for the preparation of allenic sulfoxides, 320 mg (1.66 mmol) of 2-methyl-1-(phenylsulfinyl)-3-butyn-2-ol (**13**), 370 mg (1.66 mmol) of chlorodiphenylphosphine, and 0.3 mL of triethylamine produced an unstable α-allenic phosphine oxide as a transient intermediate. The structure of this intermediate was assigned on the basis of its spectroscopic properties as 4-(phenylsulfinyl)-1-(diphenylphosphoryl)-3-methyl-1,2-butadiene (**52**): IR ($CDCl_3$) 3059, 1954, 1588, 1439, 1045 cm^{-1}; ^1H-NMR ($CDCl_3$, 250 MHz) δ 1.59 (m, 3H), 3.33 (m, 2H), 5.64 (m, 1H), 7.2–7.8 (m, 15H). Upon standing or upon aqueous workup followed by silica gel chromatography, this allenic phosphine oxide intermediate afforded 50 mg (21%) of 1-(diphenylphosphoryl)-3-methyl-3-buten-2-one (**53**) as a labile oil: IR ($CDCl_3$) 3297, 3057, 1669, 1591, 1438, 1327, 1198, 927, 524 cm^{-1}; ^1H-NMR ($CDCl_3$, 250 MHz) δ 1.75 (s, 3H), 3.91 (d, 2H, J = 15 Hz), 5.93 (s, 1H), 6.17 (s, 1H), 7.40–7.83 (m, 10H).

Preparation of 1-Methoxy-4-(phenylsulfonyl)-1,3-butadiene (54). To a solution containing 100 mg (0.3 mmol) of 1,4-bis(phenylsulfonyl)-1,3-diene (**8**) in 5 mL of methanol was added 1.8 mL (0.9 mmol) of a 0.5 M methanolic solution of sodium methoxide at rt. The mixture was stirred for 16 h. Standard workup and purification gave 43 mg (64%) of 1-methoxy-4-(phenylsulfonyl)-1,3-butadiene; IR (neat) 2987, 1318, 1083, 784 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 3.67 (s, 3H), 5.54–5.57 (m, 2H), 5.98 (dd, 1H, J = 17.1 and 1.2 Hz), 7.41 (dd, 1H, J = 17.1 and 11.4 Hz), 7.48–7.92 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 55.8, 103.9, 123.2, 126.5, 126.6, 129.1, 132.7; HRMS calcd for $C_{11}H_{12}O_3S$ 224.0507, found 224.0512.

Preparation of Dimethyl [4-(Phenylsulfonyl)-2-butenylidene]propanedioate (55). To a suspension containing 13 mg (0.3 mmol) of NaH in 10 mL of THF at 0 °C was added 19 μL (0.16 mmol) of dimethyl malonate. After stirring for 30 min, a solution of 50 mg (0.15 mmol) of 1,4-bis(phenylsulfonyl)-1,3-butadiene (**8**) in 5 mL of THF was added. The mixture was stirred at rt for 10 h, quenched with a saturated ammonium chloride solution, and extracted with ether. The organic layer was washed with water and brine and dried over sodium sulfate. Flash chromatography on silica gel gave 37 mg (76%) of dimethyl [4-(phenylsulfonyl)-2-butenylidene]propanedioate (**55**): IR (neat) 1787, 1723, 1310, 1246, 1075 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 3.76 (s, 3H), 3.78 (s, 3H), 4.10 (d, 2H, J = 7.2 Hz), 6.14 (quin, 1H, J = 7.8 Hz), 6.47 (dd, 1H, J = 15.3 and 11.7 Hz), 7.26 (d, 1H, J = 11.7 Hz), 7.56 (t, 2H, J = 7.8 Hz), 7.66 (t, 1H, J = 7.5 Hz), 7.84 (d, 2H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 52.4, 52.6, 60.2, 126.8, 128.4, 129.3, 131.4, 133.2, 138.1, 142.7, 164.4, 164.8; HRMS calcd for $C_9H_{11}O_4$ ($M^+ - PhSO_2$) 183.0657, found 183.0655.

Preparation of 3-[4-(Phenylsulfinyl)-2-butenylidene]-2,4-pentanedione (56). To a solution containing 100 mg (0.3 mmol) of 1,4-bis(phenylsulfonyl)-1,3-butadiene (**8**) and 40 μL (0.39 mmol) of 2,4-pentanedione in 5 mL of THF was added 20 mg (0.5 mmol) of NaH. The mixture was stirred at rt overnight. Standard workup and purification gave 37 mg (43%) of 3-[4-(phenylsulfonyl)-2-butenylidene]-2,4-pentanedione (**56**): IR (neat) 1755, 1736, 1320, 1078, 763 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 2.24 (s, 3H), 2.35 (s, 3H), 3.93 (d, 1H, J = 6.9 Hz), 6.15–6.37 (m, 2H), 6.94 (d, 1H, J = 10.5 Hz), 7.40–7.88 (m, 6H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 26.3, 31.5, 60.1, 127.4, 128.2, 129.3, 130.9, 133.6, 134.1, 139.2, 143.5, 197.0; HRMS calcd for $C_9H_{11}O_2$ ($M^+ - PhSO_2$) 151.0759, found 151.0757.

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Supplementary Material Available: Copies of ^{13}C-NMR spectra of new compounds lacking analyses (26 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.