acetate (2 × 20 mL), and the combined organics were washed with brine (25 mL), dried ($MgSO_4$), and evaporated, to give 200 mg of an off-white solid. The solid was chromatographed on silica gel (eluting with 95/5 ethyl acetate/methanol), to give 182 mg (88%) of **31** as a white powder: mp 95–110 °C; $[\alpha]^{23}_D$ +61° (*c* 2.0, $CHCl_3$); IR (KBr) 2480–3700, 2105, 1729, 1642, 1160 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 1.18 (9 H, s), 1.55–1.98 (6 H, br m), 2.34 (3 H, s), 3.52 (1 H, br s), 3.81 (1 H, br s), 4.14 (1 H, br s), 4.24 (1 H, br s), 4.80 (1 H, br s), 5.20 (1 H, br s), 6.00 (1 H, br s), 6.77 (2 H, br s), 7.22 (2 H, d, *J* = 8.1), 7.70 (2 H, d, *J* = 8.1), 8.03 (1 H, br s), 8.12 (1 H, br s); exact mass calcd for $C_{26}H_{35}N_9O_7S$ (M^+ + H) 618.2462, found 618.2465.

Sinefungin (1). To a solution of 156 mg (0.252 mmol) of **31** in 10 mL of methanol was added 100 mg of palladium hydroxide on carbon (Pearlman's catalyst; weight includes 45% moisture; palladium hydroxide content 20% on a dry weight basis). The mixture was shaken under H_2 at 60 psi for 44 h, diluted with methanol (25 mL) and ammonium hydroxide (10 mL), stirred for 30 min, filtered through Celite, and evaporated, to give 129 mg of amine **32**. The Celite/catalyst mixture was boiled in methanol for 1 h and filtered again. Evaporation gave an additional 7 mg of **32** (total of 136 mg of **32**, 91%). The product was used immediately in the next step without characterization: **31** R_f 0.82 (silica TLC, 5/5/1 chloroform/2-propanol/ammonium hydroxide); **32** R_f 0.42.

A solution of 127 mg (0.215 mmol) of amine **32** in 20 mL of 9/1 trifluoroacetic acid/water was prepared and stirred at 22 °C for 1 h. The solvents were evaporated, to give 180 mg of crude acid **33** as its trifluoroacetate salts. This material was used directly in the next step without purification or characterization: **32** R_f 0.95 (silica TLC, 3/6/1 methanol/chloroform/ammonium hydroxide); **33** R_f 0.32.

To a vigorously stirred (mechanical stirrer with glass paddle) solution of 42 mg of crude **33** in 30 mL of liquid ammonia (freshly distilled from sodium) at −78 °C was added 108 mg of sodium in two portions. After 20–30 s, a blue color persisted. Stirring was continued for an additional 1 min, and then 300 mg of ammonium chloride was added in one portion. The ammonia was evaporated under a stream of nitrogen, and the solid residue was dissolved in water and applied to a column of Dowex 50W-X8 (200–400 mesh, hydrogen form) cation exchange resin which had been washed with methanol and then water. The column was eluted with water and then with 9/1 water/concentrated ammonium hydroxide. The basic fractions, which contained sinefungin, were evaporated, and the residue (22 mg) was subjected to preparative reverse-phase HPLC (Whatman Partisil 10 ODS-3; eluting with 99/1 water/acetonitrile containing 0.03 N ammonium acetate, pH 6.8). The fractions containing sinefungin were repeatedly lyophilized. Sinefungin was thus obtained as a white solid (9 mg; 49% from **33**). The synthetic sinefungin was shown to be identical with natural sinefungin (purchased from Sigma and purified) by HPLC, TLC (3/1/1 methanol/chloroform/ammonium hydroxide), ^1H NMR (D_2O), ^{13}C NMR (D_2O), and UV comparison. The stereochemistry is identical at C-6 (*S*) for the synthetic and the natural material as evidenced by the appearance of C1-H as a clean doublet[11c] (δ 5.80 ppm, *J* = 4.6 Hz) in the ^1H NMR [500 MHz, D_2O, δ relative to dioxane (3.53 ppm) as an internal standard] of a mixture. For synthetic **1**: $[\alpha]^{23}_D$ +10 ± 2° (*c* 0.240, H_2O). For natural **1**: $[\alpha]^{23}_D$ +12 ± 2° (*c* 0.227, H_2O).

Acknowledgment. We are grateful to Dr. Frederick Hollander[34] for performing the X-ray structure determination. We thank Drs. Bruce Watkins, Philip Mattingly, and Christopher Maycock for early contributions to this project. Finally, we thank Undergraduate Research Participants Domenico Perrella and Edith Reiner for assistance in the preparation of intermediates.

Registry No. **1**, 58944-73-3; **4**, 50-69-1; **5**, 70-26-8; **6**, 73-24-5; **7**, 110414-90-9; **8**, 124288-73-9; **9**, 124288-74-0; **9a**, 124288-95-5; **10**, 124288-75-1; **11**, 33985-40-9; **12**, 124288-76-2; **13a**, 124288-77-3; **13b**, 124288-96-6; **14a**, 124288-78-4; **14b**, 124288-97-7; **15**, 124288-79-5; **16**, 124288-80-8; **17**, 124288-81-9; **18**, 124316-44-5; **19a**, 124288-82-0; **19b**, 124288-98-8; **20a**, 124288-83-1; **20b**, 124288-99-9; **21**, 124288-84-2; **22**, 124376-12-1; **23**, 124288-85-3; **24a**, 124288-86-4; **24b**, 124289-00-5; α-**25**, 124288-87-5; β-**25**, 124289-01-6; **26**, 52854-12-3; **27**, 18055-47-5; **28**, 124288-88-6; **29**, 124288-89-7; **30**, 124288-90-0; **31**, 124288-91-1; **32**, 124288-92-2; **33**·CF_3CO_2H, 124288-94-4.

Supplementary Material Available: Crystallographic data for **22** including methods of structure determination, crystal and data parameters, tables of positional parameters and their estimated standard deviations, bond angles, bond distances, anisotropic thermal parameters, torsion angles, root-mean-square amplitudes of anisotropic displacement, least-squares planes, and ORTEP drawings (14 pages). Ordering information is given on any current masthead page.

Studies Dealing with the Alkylation–[1,3]-Rearrangement Reaction of Some Phenylthio-Substituted Allylic Sulfones

Albert Padwa,* William H. Bullock, and Andrew D. Dyszlewski

Department of Chemistry, Emory University, Atlanta, Georgia 30322

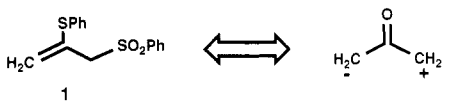
Received July 25, 1989

A series of 2-(phenylthio)-3-(phenylsulfonyl)alkenes are easily metalated with *n*-butyllithium, and the resulting carbanion is regioselectively alkylated by alkyl halides in the α-position to give β,γ-unsaturated sulfones in high yield. These substituted phenylthio allyl sulfones undergo a 1,3-sigmatropic phenylsulfonyl shift by thermal, light-induced, and in some cases acid-catalyzed pathways. Rearrangement occurs where the product sulfone is thermodynamically more stable than the starting material. Cross-over experiments and inhibition studies suggest that the thermal/photochemical reaction occurs by a radical chain mechanism involving a phenylsulfonyl radical. Alkylation of the rearranged sulfones could also be performed under mild conditions. A sequential 1,3-rearrangement–cyclization reaction of 3-alkenyl-substituted allylic sulfones was also studied. The cyclization reaction gives either five- or six-membered ring methyl ketones and was accomplished by using sodium phenylsulfinate in 60% aqueous acetic acid. The cyclization step can be considered as being closely analogous to an intramolecular metallo-ene reaction involving a phenylsulfonyl shift.

The stabilization of carbanion centers by adjacent sulfur groups is the basis of many valuable transformations in organic synthesis.[1-9] Monometalated allyl sulfones have played an important role as reactive intermediates in total

0022-3263/90/1955-0955$02.50/0

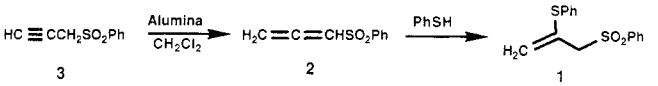
synthesis, for example in the synthesis of polyenes and Vitamin A,[10] in the preparation of specifically functionalized diquinanes,[11] and in asymmetric CC bond formation in the presence of chiral amines.[12] Allyl phenyl sulfones are easily metalated with alkyllithiums, and the resulting carbanion is regioselectively alkylated by alkyl halides in the α-position to give β,γ-unsaturated sulfones as the major product, with small amounts of dialkylated sulfones also being produced.[8] The proclivity of α,β-unsaturated sulfones to deconjugate from alkene groups during equilibration is presumably a significant factor associated with the preferential α-alkylation reaction.[13,14] Lately, there have been several reports in the literature which indicate that substituted allylic sulfones can undergo a 1,3-rearrangement.[15-25] During the course of our synthetic studies with unsaturated sulfones,[26] we became involved in the preparation and utilization of allyl sulfones of the general type 1, with the objective of performing metalation–alkylation, followed by 1,3-rearrangement, then a further metalation–alkylation and finally hydrolysis of the vinyl sulfide and reduction of the sulfonyl group. This would correspond to using 1 as an acetone dianion equivalent. In this paper we document the result of these studies.[27]



1

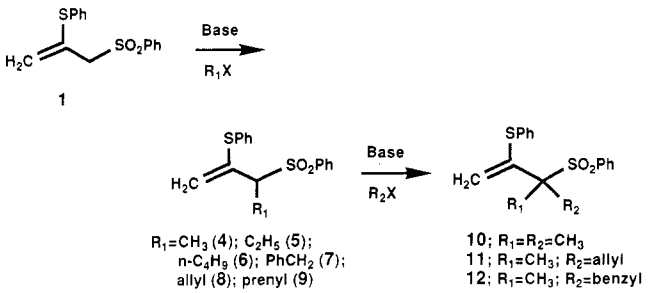
Results and Discussion

Reaction of 1-(phenylsulfonyl)-1,2-propadiene (2) with thiophenoxide according to the general procedure of Stirling[28] gave 3-(phenylsulfonyl)-2-(phenylthio)-1-butene (1) (ca. 60%) together with some of the isomeric vinyl sulfones. We found that the yield of 1 could be significantly enhanced (89%) by adding thiophenol to a stirred mixture of propargyl phenyl sulfone[29] and alumina in methylene chloride. Under these conditions the alkyne undergoes in situ isomerization to the allene, which subsequently adds a molecule of thiophenol. (Phenylsulfonyl)allene is highly activated toward nucleophilic addition as a consequence of its low LUMO energy level.[30] The reactions of allene 2 with heteronucleophiles have been well investigated.[31]



3 2 1

Exposure of allyl sulfone 1 to *n*-butyllithium (THF, −78 to 25 °C) followed by reaction with a primary alkyl halide produced the expected monoalkylated product in high yield (80–95%). The reaction is quite general, producing compounds 4–9 in good yield. However, in some cases it



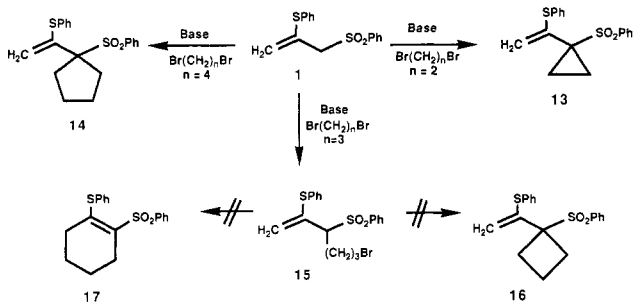
1

R_1=CH_3 (4); C_2H_5 (5); n-C_4H_9 (6); $PhCH_2$ (7); allyl (8); prenyl (9)

10; R_1=R_2=CH_3
11; R_1=CH_3; R_2=allyl
12; R_1=CH_3; R_2=benzyl

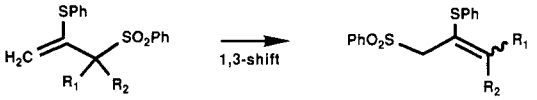
was necessary to add an excess of HMPA to promote the alkylation. Secondary alkyl halides failed to react, giving either recovered starting material or, under more forcing conditions, intractable tar. Sequential treatment of the mono-alkylated product with base followed by reaction with a second electrophile afforded α,α-dialkylated allylic sulfones 10–12. 1,2-Dibromoethane and 1,4-dibromobutane were also found to undergo dialkylation with sulfone 1 leading to the cyclized products 13 and 14 in high yield. Interestingly, in the case of 1,3-dibromopropane, the only material formed corresponded to the mono-alkylated product 15. All of our attempts to effect ring closure to either a four-membered (16) or six-membered (17) ring failed. Our inability to isolate 16 is presumably related to a combination of ring strain as well as unfa-

(1) Posner, G. H., Brunelle, D. J. *J. Org. Chem.* **1973**, *38*, 2747.
(2) Conrad, P. C.; Fuchs, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 346. Hutchinson, D. K.; Fuchs, P. L. *J. Am. Chem. Soc.* **1985**, *107*, 6137; *Tetrahedron Lett.* **1986**, 1429; *J. Org. Chem.* **1987**, *52*, 586.
(3) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1980**, *45*, 4534.
(4) Taber, D. F.; Saleh, S. A. *J. Org. Chem.* **1981**, *46*, 4817.
(5) Ford-More, A. H.; Peters, R. A.; Wakelin, R. W. *J. Chem. Soc.* **1949**, 1754.
(6) Trost, B. M.; Schmuff, N. R.; Miller, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 5981. Trost, B. M.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 7260; **1985**, *107*, 396.
(7) Moriyama, T.; Mandai, T.; Kawada, M.; Otera, J.; Trost, B. M. *J. Org. Chem.* **1986**, *51*, 3896.
(8) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019.
(9) Durst, T. *Compr. Org. Chem.* **1979**, *3*, 171.
(10) Julia, M.; Arnould, D. *Bull. Soc. Chim. Fr.* **1973**, 743.
(11) Vollhardt, J.; Gais, H. J.; Lukas, K. L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 610.
(12) Akiyama, T.; Shimizu, M.; Mukaiyama, T. *Chem. Lett.* **1984**, 611.
(13) Broaddus, C. D. *Acc. Chem. Res.* **1968**, *1*, 231.
(14) Lansbury, P. T.; Erwin, R. W. *Tetrahedron Lett.* **1978**, 2675.
(15) Bickart, P.; Carson, F. W.; Jacobus, J.; Miller, E. G.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4869.
(16) Bordwell, F. G.; Pagani, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 118.
(17) Manchand, P. S.; Rosenberger, M.; Saucy, G.; Wehrli, P. A.; Wong, H.; Chambers, L.; Ferro, M. P.; Jackson, W. *Helv. Chim. Acta* **1976**, *59*, 387.
(18) Baechler, R. D.; Bently, P.; Deuring, L.; Fisk, S. *Tetrahedron Lett.* **1982**, 2269.
(19) Inomata, K.; Yamamoto, T.; Kotake, H. *Chem. Lett.* **1981**, 1357.
(20) Kocienski, P. *J. Chem. Soc., Perkin Trans. 1* **1983**, 945.
(21) Julia, M.; Nel, M.; Righini, A.; Uguen, D. *J. Organomet. Chem.* **1982**, *235*, 113.
(22) Lin, P.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1102. Knight, D. J.; Lin, P.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2707.
(23) Ogura, K.; Iihama, T.; Kiuchi, S.; Kajiki, T.; Koshikawa, K.; Takahashi, K.; Iida, H. *J. Org. Chem.* **1986**, *51*, 700.
(24) Myong, S. O.; Linder, L. W.; Seike, S. C.; Little, R. D. *J. Org. Chem.* **1985**, *50*, 2244.
(25) Barre, V.; Uguen, D. *Tetrahedron Lett.* **1987**, 6045.
(26) Padwa, A.; Carter, S. P.; Chiacchio, U.; Kline, D. N. *Tetrahedron Lett.* **1986**, 2683. Padwa, A.; Wannamaker, M. W. *Tetrahedron Lett.* **1986**, 5817. Padwa, A.; Bullock, B.; Dyszlewski, A. D. *J. Org. Chem.* **1987**, *52*, 4760. Padwa, A.; Kline, D. N.; Norman, B. H. *Tetrahedron Lett.* **1988**, 265. Padwa, A.; Yeske, P. *J. Am. Chem. Soc.* **1988**, *110*, 1617. Padwa, A.; Norman, B. H. *Tetrahedron Lett.* **1988**, 2417; **1988**, 3041.
(27) For a preliminary report, see: Padwa, A.; Bullock, W. H.; Dyszlewski, A. D. *Tetrahedron Lett.* **1987**, 3193.
(28) Stirling, C. J. M. *J. Chem. Soc. C* **1964**, 5856.
(29) Pourcelot, G.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1966**, 3016, 3024.
(30) Hayakawa, K.; Nishiyama, H.; Kanematsu, K. *J. Org. Chem.* **1985**, *50*, 512.
(31) Stirling, C. J. M. *J. Chem. Soc. C* **1964**, 5863. Appleyard, G. D.; Stirling, C. J. M. *J. Chem. Soc. C* **1967**, 2686. Horner, L.; Lindel, H.; *Phosphorous Sulfur* **1984**, *20*, 165. McMullen, C. H.; Stirling, C. J. M. *J. Chem. Soc. B* **1966**, 1217, 1221. McDowell, S. T.; Stirling, C. J. M. *J. Chem. Soc. C* **1967**, 351. Fujii, I.; Ryu, K.; Hayakawa, K.; Kanematsu, K. *J. Chem. Soc., Chem. Commun.* **1984**, 844. Thyagarajan, B. S.; Wood, B. F.; Glowienka, J. A.; Delgado, P. *Phosphorous Sulfur* **1985**, *25*, 1.



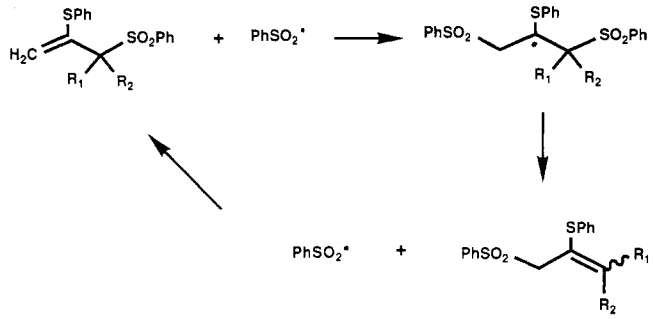
vorable entropic factors which raise the activation energy associated with ring closure.[32] As was pointed out earlier, it is well known that the reaction of lithiated allylic sulfones with alkyl halides affords only α-alkylated products.[8,33] Thus, cyclization to the six-membered ring system would require an unfavorable γ-alkylation.

A 1,3-sulfonyl shift was found to occur when we subjected the initially formed mono- or dialkylated sulfones to silica gel chromatography. An alternate way to induce the rearrangement was to heat the sulfone at 80 °C in solution. At first we thought that this was a thermal



reaction, but we found that it did not occur in solution in benzene, chloroform, or acetonitrile in the dark. The 1,3-shift does occur in solution on exposure to light, even daylight diffused through the window and a Pyrex flask. It can be prevented simply by wrapping the flask in aluminum foil.

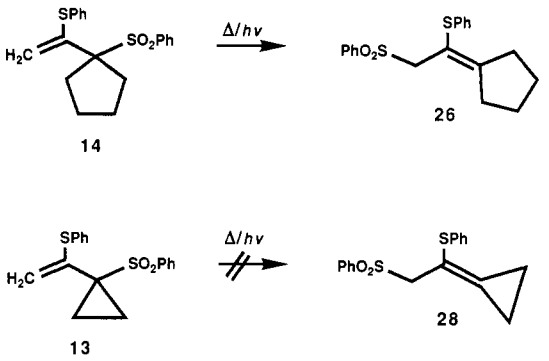
Two different paths can be put forth regarding the mechanism of this rearrangement. One route includes a fairly tight ion pair which is probably applicable to the silica gel induced rearrangement. The alternate path occurs in solution and involves a radical chain mechanism. The heat and/or light initiates the reaction by bringing about cleavage of the allyl–sulfone bond. The phenylsulfonyl radical so produced adds to the double bond of another molecule, leading to a new radical which loses the resident phenylsulfonyl group to generate the rearranged isomer. In all cases the thermodynamically rearranged alkene with the more substituted double bond is the exclusive product.



There are a number of excellent precedents for the proposed radical chain mechanism. Whitham and coworkers have studied the rearrangement of several acyclic and cyclic allylic *p*-tolyl sulfones using benzoyl peroxide in CCl_4 as a radical initiator.[22] Rearrangement with these simpler systems occurred in those cases where the product was thermodynamically more stable than the starting material. Sulfonyl radicals have previously been postulated in addition–elimination mechanisms of variously substituted alkenes.[34-36] γ-Radical attack on an allylic sulfone is known,[37] and there are some examples reported which involve sulfonyl radical elimination from β-sulfonyl radicals.[38]

Several aspects of the radical chain mechanism deserve some discussion. First, the relative rate of rearrangement was monitored in various solvents with different dielectric constants. The following order was observed: chloroform > benzene > carbon tetrachloride ≫ acetonitrile ~ dimethyl sulfoxide. If an ionic mechanism was occurring in solution, the more polar solvents should have increased the rate of rearrangement. This was not the case. The addition of *p*-toluenesulfonic acid did not increase the rate of reaction for any of the five solvents studied. When the rearrangement was monitored in the presence of a catalytic amount of hydroquinone, a known free-radical inhibitor, the reaction could be completely suppressed.[39]

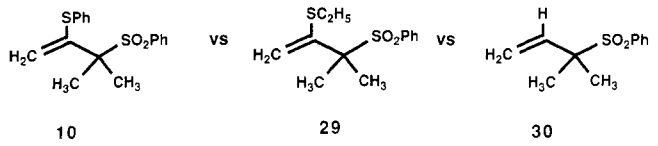
A number of 1-substituted allyl sulfones underwent the 1,3-rearrangement under the standard thermal/light conditions, and the results are summarized in the Experimental Section. In general, the more substituted double bond (more stable) isomer predominated, and *Z*/*E* isomeric mixtures were obtained, except for the case of **13** where only recovered starting material was observed. This can be readily rationalized since methylenecyclopropanes are known to be thermodynamically less stable than vinyl-substituted cyclopropanes.[40] In fact, MMX calculations showed that compound **13** is 12 kcal/mol more stable than **28**.[41]



We also investigated the 1,3-rearrangement of allylic sulfones **29** and **30** in order to evaluate the role of the substituent group on the 2-position of the sulfone. By finding conditions under which only partial rearrangement occurred, we observed that the relative rate of rearrangement of the unsubstituted sulfone **30** was 2 orders of

(32) The only material isolated from the reaction corresponded to the 1,3-sulfonyl rearrangement product.

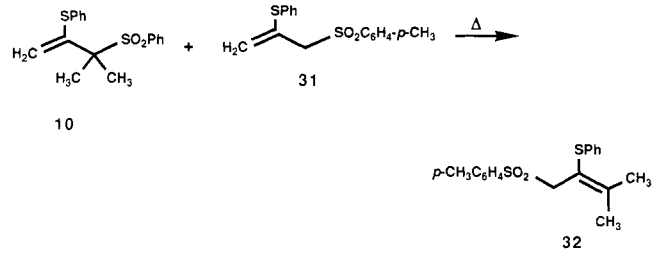
(33) Biellmann, J. F.; Ducep, J. B. *Org. React.* **1982**, *27*, 1.
(34) Kice, J. L. In *Free Radicals*; Kochi, J. K., Ed.; Interscience: New York, 1973; Vol. 1, p 715.
(35) Stacey, F. W.; Sauer, J. C.; McKusick, B. C. *J. Am. Chem. Soc.* **1959**, *81*, 987.
(36) Frydman, N.; Mazur, Y. *J. Am. Chem. Soc.* **1970**, *92*, 3203.
(37) Ueno, Y.; Aoki, S.; Okawara, M. *J. Am. Chem. Soc.* **1979**, *101*, 5414; *J. Chem. Soc., Chem. Commun.* **1980**, 683. Ueno, Y.; Sano, H.; Aoki, S.; Okawara, M. *Tetrahedron Lett.* **1981**, 2675. Nokami, J.; Sudo, T.; Nose, H.; Okawara, R. *Tetrahedron Lett.* **1981**, 2899.
(38) Boothe, T. E.; Greene, J. L.; Shevlin, P. B. *J. Org. Chem.* **1980**, *45*, 794. Wagner, P. J.; Sedon, J. H.; Lindstrom, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 2579. Ueno, Y.; Miyano, T.; Okawara, M. *Tetrahedron Lett.* **1982**, 443.
(39) For some related processes, see: Brownbridge; P.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2125. Kozikowski, A. P.; Huie, E.; Spring, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 2059. Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846.
(40) Halton, B.; Banwell, M. G. *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley: New York, 1987.
(41) MMX calculations were performed on a Vax 11/785 using Model 2.92. We thank Professor Kosta Steliou for providing a copy of Model 2.92 and the Gajewski-Gilbert MMX-Vax program.



10 29 30

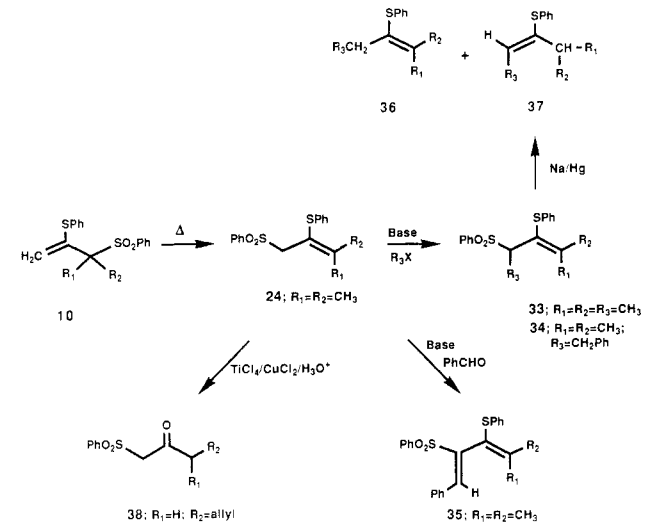
magnitude slower than either sulfone **10** or **29**. Clearly the presence of the thiophenyl group on the 2-position of the allylic sulfone plays a significant role in controlling the rate of rearrangement. This result is expected for a mechanism involving addition of the electrophilic $PhSO_2$ radical to the more electron-rich π-bond.

One additional piece of evidence for the proposed radical chain mechanism emerged from a cross-over experiment. Heating a mixture of **10** and a 10-mol excess of 2-(phenylthio)-3-(*p*-tolylsulfonyl)-1-propene (**31**) in benzene afforded a significant quantity (ca. 55%) of the mixed rearranged product **32**. This is perfectly consistent with the addition–elimination sequence outlined above.



10 31 32

Alkylation of the rearranged sulfones could also be performed under mild conditions. Thus, treatment of **24** with *n*-butyllithium at −78 °C followed by reaction with several alkyl halides proceeded uneventfully and in high yield.

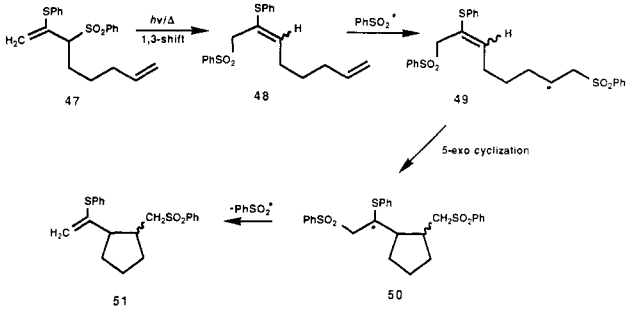


10 24; $R_1=R_2=CH_3$ 33; $R_1=R_2=R_3=CH_3$ 34; $R_1=R_2=CH_3$; $R_3=CH_2Ph$ 36 37 38; $R_1=H$; R_2=allyl 35; $R_1=R_2=CH_3$

Treatment of the anion derived from **24** with benzaldehyde followed by the addition of methanesulfonyl chloride and triethylamine afforded diene **35** in 70% yield. The trialkylated sulfone **34** was transformed into a mixture of vinyl sulfides **36** and **37** by reduction with sodium amalgam in methanol. While reductive cleavage of sulfone **8** in protic media effects desulfonylation, subjection of this material to hydrolytic conditions afforded keto sulfone **38** in good yield.

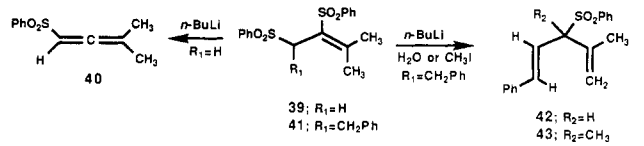
m-Chloroperbenzoic acid oxidation of **24** readily generates disulfone **39** in high yield. We were interested in the preparation and utilization of allyl anions derived from disulfones related to **39** with the object of cycloadding these 4-electron systems to unsaturated molecules.[42] We found,

Scheme I



47 48 49 50 51

however, that treating **39** with *n*-butyllithium results in the elimination of the sulfonyl group to give allene **40** in excellent yield. Reaction of the benzyl-substituted disulfone **41** with *n*-butyllithium resulted in elimination of the allylic sulfonyl group. Quenching the resulting anion with methanol or methyl iodide gave dienes **42** and **43**, respectively.



40 39; R_1=H 41; $R_1=CH_2Ph$ 42; R_2=H 43; $R_2=CH_3$

Within the last decade, new methods for the controlled production of carbon-centered free radicals have been coupled with intramolecular cyclization reactions of predictable regio- and stereoselectivity to provide a powerful technique for carbon–carbon bond formation in organic synthesis.[43] Methods utilized for free-radical generation are usually tin hydride mediated, and halides, selenides, and sulfur-containing compounds have been used as radical precursors in most studies.[43] Five-membered rings are readily prepared by this approach and the 5-exo cyclization mode is generally favored,[44] with even carbon radical cyclization to aldehydes and ketones possible.[45] In addition, sequential radical cyclizations have been used to construct multiple rings in one step,[46] and guidelines for understanding the stereochemical influence of ring substituents have been published.[47]

During the course of our studies, it occurred to us that the radical induced 1,3-shift of a 2-(phenylthio)-substituted allylic sulfone might be used to promote the intramolecular 5-exo cyclization reaction. While our work was in progress, Whitham and Smith eloquently demonstrated the viability of the sequence using 1-(*p*-tolylsulfonyl)cyclohex-2-enyl allyl ether **44**.[48] The overall transformation was considered to occur by a chain mechanism involving the addition–elimination of an aryl sulfonyl radical.

Our initial attempts centered on sulfone **47**, which we expected to undergo cyclization to **51** (Scheme I), since the

(42) Padwa, A.; Yeske, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 1617. Kempf, D. J.; Wilson, K. D.; Beak, P. *J. Org. Chem.* **1982**, *47*, 1610. Beak, P.; Wilson, K. D. *J. Org. Chem.* **1986**, *51*, 4627. Beak, P.; Burg, D. A. *Tetrahedron Lett.* **1986**, 5911. Beak, P.; Burg, D. A. *J. Org. Chem.* **1989**, *54*, 1647.

(43) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon: New York, 1986. Stork, G.; Mook, R. *Tetrahedron Lett.* **1986**, 4529. Hart, D. J. *Science (Washington, D.C.)* **1984**, *223*, 883. Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3943. Newcomb, M.; Park, S. U. *J. Am. Chem. Soc.* **1986**, *108*, 4132.

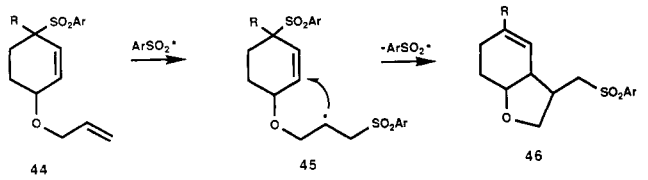
(44) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.

(45) Tsang, R.; Dickson, J. K.; Pak, H.; Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1987**, *109*, 3484. Dowd, P.; Choi, S. C. *J. Am. Chem. Soc.* **1987**, *109*, 3493.

(46) Curran, D. P.; Kuo, S. C. *J. Am. Chem. Soc.* **1986**, *108*, 1106.

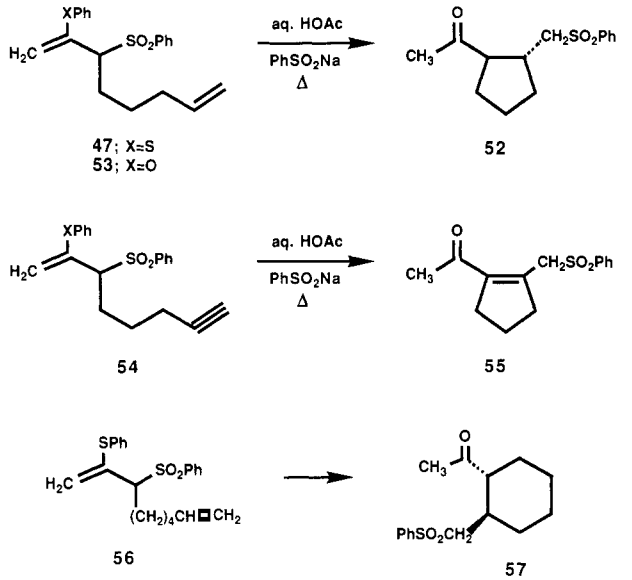
(47) Beckwith, A. L. J. *Rev. Chim. Intermed.* **1986**, *7*, 143.

(48) Smith, T. A. K.; Whitman, G. H. *J. Chem. Soc., Chem. Commun.* **1985**, 897; *J. Chem. Soc., Perkin Trans. 1* **1989**, 313.

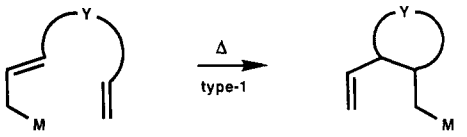


ring closure step would correspond to the formation of a five-membered ring from a hex-5-enyl radical. Although six-membered rings have been prepared by this method, the rate for 6-exo cyclization to alkenes is significantly less than for 5-exo cyclization.[49]

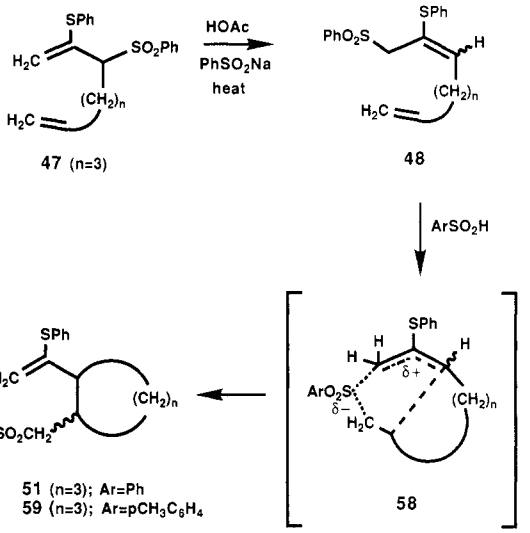
The required allylic sulfone was easily prepared by the alkylation of **1** with 5-bromo-1-pentene. Unfortunately, all of our attempts to effect cyclization under a variety of typical radical conditions were unsuccessful. The only material present in the crude NMR corresponded to the typical rearranged sulfone **48**. Heating the reaction mixture to higher temperatures (>100 °C) led to intractable tars. We did not pursue the radical cyclization any further when we discovered that a cyclization reaction could be effected using sodium phenyl sulfinate in 60% aqueous acetic acid at 100 °C for 16 h. Under these conditions, sulfone **47** was converted to ketone **52** in 45% yield.[50] More than likely the *trans*-methyl ketone **52** is formed via the cyclized intermediate **51**, which is hydrolyzed under the reaction conditions. The thermodynamically more stable *trans*-methyl ketone is produced as the exclusive cyclized product. This was also the case when the closely related phenoxy allylic sulfone **53** was allowed to cyclize under similar reaction conditions. An analagous cyclization also occurred with the acetylenic allylic thiophenyl-substituted sulfone **54**. We have also extended the cyclization reaction to the homologous 3-hexenyl-substituted sulfone **56**. Use of the aqueous acetic acid–sodium phenyl sulfinate procedure gave the six-membered ring *trans*-methyl ketone **57** in 52% isolated yield.



A number of substituted acyclic allylic sulfones have been found to undergo 1,3-rearrangement when heated in acetic acid–water.[16,21,22] Evidence was presented by Whitham in favor of an ion-pair dissociation–recombination mechanism in these cases.[22] The ion pair was presumed to be fairly "intimate" since solvolysis products were not found. On the basis of the earlier work, we too believe that the cyclization of **47** (or **53**) to **52** proceeds by an initial 1,3-rearrangement of the allylic sulfone.[51] The next step can be considered as being somewhat analogous to a metallo-ene reaction recently exploited by Oppolzer and coworkers for natural product synthesis.[52] The intramolecular type 1 metallo-ene reaction dates back to 1972 when



Felkin described the conversion of 2,7-octadienylmagnesium bromide to *cis*-1-methyl-2-vinylcyclopentane in 67% yield.[53] Similar processes have been uncovered with lithium,[54] palladium,[55] platinum,[52] nickel,[52] and zinc.[56] The synthetic exploitation of this reaction is still in its infancy and has focused mainly on allylmagnesium/alkene cyclizations because of their diastereoselectivity and propensity of the cyclized Grignard intermediates to be trapped with many different electrophiles. It is our opinion that the sulfone version of the metallo-ene reaction also holds considerable promise as a synthetic method. It should be noted that the above allylic sulfones do not cyclize by heating in acetic acid–water in the absence of added sodium phenyl sulfinate but rather undergo the 1,3-sigmatropic sulfonyl shift. One possibility to account for the role of phenyl sulfinate is to invoke some sort of nucleophilic-assisted ion-pair process best symbolized by figure **58**. The ion-pair mechanism is supported by



cross-over experiments involving the rearrangement of **48** in the presence of excess sodium *p*-tolyl sulfinate. Under these conditions a 1:5 mixture of **52** and the *trans*-methyl ketone derived from **59** is obtained. The above interpretation should be treated with some caution, however, in

(49) Beckwith, A. L. J.; Easton, C. J.; Lawrence, T.; Serelis, A. K. *Aust. J. Chem.* **1983**, *36*, 545.

(50) A related set of observations were recently made by Smith and Whitham using *p*-tolylsulfonyl-substituted sulfones; see: Smith, T. A. K.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1989**, 319.

(51) Allylic sulfone **47** cleanly underwent a 1,3-sulfonyl shift upon exposure to light affording the expected rearranged product **58** ($n = 3$) in 91% yield. This material cyclized to **52** (48% yield) when allowed to react with sodium phenylsulfinate in 60% aqueous acetic acid at 100 °C for 16 h.

(52) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 38.

(53) Felkin, H.; Umpleby, J. D.; Hagaman, E.; Wenkert, E. *Tetrahedron Lett.* **1972**, 2285. Felkin, H.; Kwart, L. D.; Swierczewski, G.; Umpleby, J. D. *J. Chem. Soc., Chem. Commun.* **1975**, 242.

(54) Josey, A. D. *J. Org. Chem.* **1974**, *39*, 139.

(55) Oppolzer, W. *Chimia* **1988**, *42*, 6. Oppolzer, W.; Gaudin, J. M.; Birkinshaw, T. N. *Tetrahedron Lett.* **1988**, 4705.

(56) Louw, van der J.; Baan, van der J. L.; Stieltjes, H.; Bickelhaupt, F.; Klumpp, G. W. *Tetrahedron Lett.* **1987**, 5929.

light of the earlier results of Whitham[22] who suggested that the role of sulfinic acid is to behave as a source of $ArSO_2$ radicals. Thus, an alternate possibility would involve an addition–elimination mechanism as was previously outlined in Scheme I.

In conclusion, several trends have surfaced from our studies in this area. First and foremost, phenylthio-substituted allyl sulfones undergo ready alkylation and 1,3-rearrangement by a radical addition–elimination mechanism. Further α-alkylation and regioselective replacement of the sulfonyl group by hydrogen can be used to prepare a variety of substituted alkenes. Secondly, in those cases where the allylic sulfone has an alkenyl side chain, initial 1,3-rearrangement is followed by cyclization to give both five- and six-membered rings. We are continuing to explore the scope, generality, and synthetic applications of the sulfone cyclization reaction and will report additional findings at a later date.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer Model 283 infrared spectrometer. Proton NMR spectra were obtained on a Varian EM-390, a Nicolet 360 MHz, and a GE QE-300 MHz spectrometer. ^{13}C NMR spectra were recorded on an GE QE-300 75 MHz spectrometer. Microanalyses were performed at Atlantic Microlabs, Atlanta, GA. Mass spectra were determined with a VG MM-7070S mass spectrometer at an ionizing voltage of 70 eV.

General Procedure for the Preparation and Rearrangement of 3-Substituted 3-(Phenylsulfonyl)-2-(phenylthio)-propenes. A solution containing 0.2 g of 3-(phenylsulfonyl)-2-(phenylthio)-1-propene (**1**) in 5 mL of dry tetrahydrofuran was cooled to −78 °C under a nitrogen atmosphere. To this mixture was added 0.6 mL of a 1.4 M *n*-butyllithium solution in hexane (1.2 equiv). The resulting yellow solution was stirred for 10 min at −78 °C, and then the appropriate electrophile was added by syringe. The reaction was allowed to warm to room temperature and was quenched with a saturated ammonium chloride solution. Evaporation of the solvent under reduced pressure left a yellow oil, which was dissolved in chloroform. The organic layer was washed with a saturated sodium bicarbonate solution and a 10% sodium metabisulfite solution and dried over sodium sulfate. Concentration of the solvent under reduced pressure left a yellow oil that was chromatographed on a short silica gel column using a 10% ethyl acetate–hexane mixture to give the appropriate alkylated compound. In this manner the following unsaturated sulfones were prepared.

3-(Phenylsulfonyl)-2-(phenylthio)-1-butene (4) as a clear oil in 80% yield: IR (neat) 3080, 3000, 2940, 1740, 1600, 1480, 1440, 1310, 1240, 1140, 1080, 880, and 750 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 1.64 (d, 3 H, J = 7.2 Hz), 3.77 (q, 1 H, J = 7.2 Hz), 5.09 (s, 1 H), 5.53 (s, 1 H), 7.20–7.40 (m, 5 H), 7.55–7.70 (m, 3 H), and 7.85–7.95 (m, 2 H). A 0.2-g sample of sulfone **4** was chromatographed on a silica gel column using a 10% ethyl acetate–hexane mixture to give 0.16 g (75%) of a clear oil. This material was irradiated with sunlight in a Pyrex flask for 48 h to give rise to a 3:1 mixture of (*Z*,*E*)-1-(phenylsulfonyl)-2-(phenylthio)-2-butene (**18**): IR (neat) 3060, 3000, 2920, 1590, 1470, 1450, 1320, 1250, 1140, 1100, 1080, 960, 880, 750, and 600 cm^{-1}; NMR ($CDCl_3$, 300 MHz) (minor isomer) δ 1.67 (d, 3 H, J = 7.2 Hz), 3.94 (s, 12 H), 6.26 (q, 1 H, J = 7.2 Hz), 6.90–7.35 (m, 5 H), 7.45–7.50 (m, 3 H), and 7.75–7.95 (m, 2 H); (major isomer) δ 1.88 (d, 3 H, J = 6.7 Hz), 3.83 (s, 2 H), 6.19 (q, 1 H, J = 6.7 Hz), 6.90–7.35 (m, 5 H), 7.45–7.50 (m, 3 H), and 7.75–7.95 (m, 2 H). Anal. Calcd for $C_{16}H_{16}O_2S_2$: C, 63.12; H, 5.30; S, 21.06. Found: C, 63.01; H, 5.34; S, 20.90.

3-(Phenylsulfonyl)-2-(phenylthio)-1-pentene (5) as yellow oil in 90% yield: IR (neat) 3160, 2980, 2940, 2880, 1610, 1480, 1450, 1310, 1150, 1090, 890, 750, 720, and 700 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 1.01 (t, 3 H, J = 7.4 Hz), 1.90–2.18 (m, 1 H), 2.20–2.40 (m, 1 H), 3.56 (dd, 1 H, J = 11.0 and 3.5 Hz), 4.85 (s, 1 H), 5.35 (s, 1 H), 7.20–7.35 (m, 5 H), 7.55–7.70 (m, 3 H), and 7.85–7.95 (m, 2 H); UV (95% ethanol) 252 nm (ϵ 5400); HRMS calcd for $C_{17}H_{18}O_2S_2$ 318.0748, found 318.0735. A sample containing 0.21 g of **5** was chromatographed on a silica gel column using a 10% ethyl acetate–hexane mixture to give 0.19 g (87%) of a clear oil. This material was irradiated with sunlight in a Pyrex flask for 72 h to give rise to a 3:1 mixture of (*Z*,*E*)-1-(phenylsulfonyl)-2-(phenylthio)-2-pentene (**19**): IR (neat) 3065, 2980, 2940, 2880, 1590, 1480, 1450, 1320, 1160, 1090, 920, 650, and 600 cm^{-1}; NMR ($CDCl_3$, 300 MHz) (major isomer) δ 0.80–1.10 (m, 3 H), 2.00–2.40 (m, 2 H), 3.83 (s, 2 H), 6.08 (t, 1 H, J = 7.2 Hz), 7.00–7.40 (m, 5 H), 7.45–7.78 (m, 3 H), and 7.80–7.95 (m, 2 H); (minor isomer) δ 0.80–1.10 (m, 3 H), 2.00–2.40 (m, 2 H), 3.96 (s, 2 H), s, 2 H), 6.20 (t, 1 H, J = 7.2 Hz), 7.00–7.40 (m, 5 H), 7.45–7.78 (m, 3 H), and 7.80–7.95 (m, 2 H); *m*/*e* 318 (M^+), 218, 176, 135, 109, 86, 84 (base), and 77. Anal. Calcd for $C_{17}H_{18}O_2S_2$: C, 64.12; H, 5.70. Found: C, 64.06; H, 5.64.

3-(Phenylsulfonyl)-2-(phenylthio)-1-heptene (6) as a viscous oil in 60% yield: IR (neat) 3060, 2960, 2940, 2880, 1580, 1480, 1450, 1310, 1140, 1090, 750, and 690 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.07–1.10 (m, 3 H), 1.10–1.70 (m, 4 H), 1.70–2.30 (m, 2 H), 3.66 (dd, 1 H, J = 12.0 and 4.5 Hz), 4.86 (s, 1 H), 5.36 (s, 1 H), and 7.20–8.10 (m, 10 H). A sample containing 100 mg of **6** in 100 mL of benzene was irradiated with sunlight in a Pyrex flask for 48 h to give 87 mg (87%) of a 3:1 *Z*/*E* mixture of 1-(phenylsulfonyl)-2-(phenylthio)-2-heptene (**20**): IR (neat) 3060, 2960, 2920, 2880, 1590, 1470, 1450, 1310, 1150, 1030, 750, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) (major isomer) δ 0.91 (t, 3 H, J = 7.0 Hz), 1.20–1.40 (m, 4 H), 2.32 (q, 2 H, J = 7.0 Hz), 3.85 (s, 2 H), 6.20 (t, 1 H, J = 7.0 Hz), 7.0–7.4 (m, 5 H), 7.5–7.7 (m, 3 H), and 7.8–8.0 (m, 2 H); (minor isomer) δ 0.91 (t, 3 H, J = 7.0 Hz), 1.2–1.4 (m, 4 H), 2.05 (q, 2 H, J = 7.0 Hz), 3.98 (s, 2 H), 6.40 (t, 1 H, J = 7.0 Hz), 7.0–7.4 (m, 5 H), 7.5–7.7 (m, 3 H), and 7.8–8.0 (m, 2 H). Anal. Calcd for $C_{19}H_{22}O_2S_2$: C, 65.86; H, 6.40. Found: C, 65.65; H, 6.34.

4-Phenyl-3-(phenylsulfonyl)-2-(phenylthio)-1-butene (7) as a light yellow oil in 90% yield: IR (neat) 3060, 3020, 2930, 1630, 1600, 1500, 1490, 1340, 1320, 1090, 730, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.29 (dd, 1 H, J = 12.8 and 11.8 Hz), 3.63 (dd, 1 H, J = 13.0 and 3.4 Hz), 3.87 (dd, 1 H, J = 11.5 and 3.4 Hz), 4.89 (s, 1 H), 5.43 (s, 1 H), 6.95 (m, 2 H), 7.00–7.42 (m, 8 H), 7.50–7.80 (m, 3 H), and 7.85–8.00 (m, 2 H); UV (95% ethanol) 276 nm (ϵ 5850); HRMS calcd for $C_{22}H_{20}O_2S_2$ 380.0904, found 380.0909. A sample containing 0.64 g of sulfone **7** was chromatographed on a silica gel column using a 10% ethyl acetate–hexane mixture to give 0.47 g (70%) of a clear oil. This material was irradiated with sunlight in a Pyrex flask for 48 h to give a 3:1 *Z*/*E* mixture of 4-phenyl-1-(phenylsulfonyl)-2-(phenylthio)-2-butene (**21**): IR (neat, 3:1 mixture) 3060, 3020, 2930, 1630, 1600, 1590, 1500, 1490, 1310, 1140, 1090, 730, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) (major isomer) δ 3.67 (d, 2 H, J = 7.4 Hz), 3.85 (s, 2 H), 6.22 (t, 1 H, J = 7.4 Hz), and 7.0–8.0 (m, 15 H); (minor isomer) δ 3.47 (d, 2 H, J = 7.4 Hz), 4.04 (s, 2 H), 6.34 (t, 1 H, J = 7.4 Hz), and 7.0–8.0 (m, 15 H); *m*/*e* 380 (M^+), 238, 218, 184, 147, 129 (base), 110, 91, and 77. Anal. Calcd for $C_{22}H_{20}O_2S_2$: C, 69.44; H, 5.30. Found: C, 69.16; H, 5.34.

3-(Phenylsulfonyl)-2-(phenylthio)-1,5-hexadiene (8) as a light yellow oil in 91% yield: IR (neat) 3080, 3000, 2940, 1650, 1610, 1590, 1480, 1450, 1310, 1240, 1150, 1090, 1030, 1000, 950, 750, and 700 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.65–2.87 (m, 1 H), 2.90–3.20 (m, 1 H), 3.65–3.74 (dd, 1 H, J = 11.0 and 4.0 Hz), 4.90 (s, 1 H), 5.10–5.25 (m, 2 H), 5.40 (s, 1 H), 5.65–5.75 (m, 1 H), 7.24–7.40 (m, 5 H), 7.55–7.75 (m, 3 H), 7.85–7.95 (m, 2 H); HRMS calcd for $C_{18}H_{18}O_2S_2$ 330.0748, found 330.0747. A sample containing 0.25 g of **8** was chromatographed on silica gel using a 10% ethyl acetate–hexane mixture to give 0.21 g (92%) of a clear oil. This material was irradiated with sunlight in a Pyrex flask for 48 h to give rise to a 3:1 mixture of (*Z*,*E*)-6-(phenylsulfonyl)-5-(phenylthio)-1,4-hexadiene (**22**): IR (neat) 3080, 3020, 2990, 2940, 1590, 1480, 1450, 1340, 1140, 1090, 1000, 940, 750, 690, and 600 cm^{-1}; NMR ($CDCl_3$, 360 MHz) (major isomer) δ 3.11 (t, 2 H, J = 7.2 Hz), 3.85 (s, 2 H), 4.95–5.15 (m, 2 H), 5.65–5.85 (m, 1 H), 6.14 (t, 1 H, J = 7.2 Hz), 7.10–7.35 (m, 5 H), 7.50–7.70 (m, 3 H), and 7.80–7.95 (m, 2 H); (minor isomer) δ 2.90 (t, 2 H, J = 7.6 Hz), 3.96 (s, 2 H), 4.95–5.20 (m, 2 H), 5.60–5.80 (m, 1 H), 6.18 (t, 1 H, J = 7.6 Hz), 7.10–7.35 (m, 5 H), 7.5–7.7 (m, 3 H), and 7.80–7.95 (m, 2 H); *m*/*e* 330 (M^+), 218, 188 (base), 173, 147, 110, and 77. Anal. Calcd for $C_{18}H_{18}O_2S_2$: C, 65.42; H, 5.49. Found: C, 65.26; H, 5.34.

To a solution containing 0.16 g of sulfone **8** in 10 mL of a 9:1 acetic acid–water mixture was added 0.19 g of anhydrous cupric chloride and 0.16 mL of titanium tetrachloride under a nitrogen atmosphere. The mixture was heated at 50 °C for 48 h and was then quenched with water. The aqueous layer was extracted with ether, and the combined organic layers were washed with a saturated sodium bicarbonate solution and dried over sodium sulfate. Evaporation of the solvent under reduced pressure left a clear oil that was chromatographed on silica gel using a 10% ethyl acetate–hexane mixture as the eluent gave 0.04 g (35%) of 6-(phenylsulfonyl)-1-hexen-5-one (**38**) as a clear oil: IR (neat) 3080, 3000, 2940, 1720, 1580, 1440, 1320, 1150, 1090, 920, 750, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.30 (q, 2 H, J = 7.0 Hz), 2.81 (t, 2 H, J = 7.0 Hz), 4.15 (s, 2 H), 4.95–5.15 (m, 2 H), 5.7–5.9 (m, 1 H), 7.5–7.7 (m, 3 H), and 7.8–8.0 (m, 2 H). Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92. Found: C, 60.26; H, 5.74.

6-Methyl-3-(phenylsulfonyl)-3-(phenylthio)-1,5-heptadiene (9) as a yellow oil in 85% yield: IR (neat) 3080, 3000, 2940, 1650, 1610, 1590, 1480, 1450, 1310, 1240, 1150, 1090, 1030, 1000, 930, 750, and 700 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.56 (s, 1 H), 1.66 (s, 3 H), 2.56–2.96 (m, 2 H), 3.63 (dd, 1 H, J = 11.0 and 4.0 Hz), 4.87–5.16 (m, 1 H), 4.90 (s, 1 H), 5.40 (s, 1 H), 7.24–7.40 (m, 5 H), 7.55–7.75 (m, 3 H), and 7.85–7.95 (m, 2 H). A solution containing 0.11 g of **9** in 10 mL of toluene was heated at 160 °C in a sealed tube for 18 h. Concentration of the solvent under reduced pressure followed by silica gel chromatography using a 10% ethyl acetate–hexane mixture gave 0.09 g (82%) of a 3:1 mixture of 6-methyl-1-(phenylsulfonyl)-2-(phenylthio)-2,5-heptadiene (**23**): IR (neat) 3060, 2980, 2920, 1580, 1470, 1450, 1320, 1140, 1090, 740, and 690 cm^{-1}; NMR ($CDCl_3$, 360 MHz) (major isomer) δ 1.60 (s, 3 H), 1.70 (s, 3 H), 3.02 (t, 2 H, J = 7.2 Hz), 3.82 (s, 2 H), 4.95 (t, 1 H, J = 7.2 Hz), 6.04 (t, 1 H, J = 7.2 Hz), 7.05–7.35 (m, 5 H), 7.50–7.75 (m, 3 H), and 7.80–7.95 (m, 2 H); (minor isomer) δ 1.60 (s, 3 H), 1.70 (s, 3 H), 2.77 (t, 2 H, J = 7.2 Hz), 3.97 (s, 2 H), 4.95 (t, 1 H, J = 7.2 Hz), 6.15 (t, 1 H, J = 7.2 Hz), 7.05–7.35 (m, 5 H), 7.50–7.75 (m, 3 H), and 7.80–7.95 (m, 2 H). Anal. Calcd for $C_{20}H_{22}O_2S_2$: C, 67.02; H, 6.19. Found: C, 66.83; H, 6.14.

3-Methyl-3-(phenylsulfonyl)-2-(phenylthio)-1-butene (10) as a light yellow oil in 95% yield: IR (neat) 3160, 3000, 2930, 1590, 1480, 1440, 1300, 1240, 1230, 1170, 1120, 880, 750, 730, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.68 (s, 6 H), 4.95 (s, 1 H), 5.48 (s, 1 H), 7.20–7.40 (m, 5 H), 7.45–7.70 (m, 3 H), and 7.65–8.00 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75, MHz) δ 22.7, 67.7, 119.4, 128.3, 129.5, 130.8, 133.6, 133.7, and 144.5; UV (acetonitrile) 218 (ϵ 17 300) and 252 nm (ϵ 5650). A sample containing 0.24 g of **10** was chromatographed on a silica gel column using a 10% ethyl acetate–hexane mixture to give 0.21 g (97%) of the rearranged 3-methyl-1-(phenylsulfonyl)-2-(phenylthio)-2-butene (**24**). Recrystallization of this material from methanol gave white needles: mp 106–107 °C; IR (KBr) 3080, 2980, 2920, 1580, 1480, 1450, 1310, 1140, 1090, 1030, 930, 750, 690, and 600 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.80 (s, 3 H), 1.97 (s, 3 H), 3.98 (s, 2 H), 6.8–7.3 (m, 5 H), 7.4–7.6 (m, 3 H), and 7.7–7.8 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.4, 23.9, 60.3, 114.3, 126.1, 128.5, 128.6, 129.0, 133.7, 135.2, 139.4, and 151.3. Anal. Calcd for $C_{17}H_{18}S_2O_2$: C, 64.12; H, 5.70; S, 20.14. Found: C, 64.16; H, 5.71; S, 20.22.

Preparation and Rearrangement of 3-Methyl-3-(phenylsulfonyl)-2-(phenylthio)-1,5-hexadiene (11). A solution containing 0.21 g of 3-(phenylsulfonyl)-2-(phenylthio)-1,5-hexadiene (**8**) in 5 mL of dry tetrahydrofuran was treated with methyl iodide in the normal fashion to give 0.19 g (91%) of 3-methyl-3-(phenylsulfonyl)-2-(phenylthio)-1,5-hexadiene (**11**) as a clear oil: IR (neat) 3060, 2980, 2920, 1730, 1580, 1470, 1440, 1300, 1140, 1060, 920, 750, and 680 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.56 (s, 3 H), 2.72 (dd, 1 H, J = 13.7 and 8.5 Hz), 3.32 (dd, 1 H, J = 13.4 and 5.4 Hz), 4.83 (s, 1 H), 5.20–5.40 (m, 2 H), 5.30 (s, 1 H), 5.75 (m, 1 H), 7.20–7.50 (m, 5 H), 7.45–7.70 (m, 3 H), and 7.65–8.00 (m, 2 H).

A sample containing 0.23 g of **11** was chromatographed on a silica gel column using a 10% ethyl acetate–hexane mixture to give 0.19 g (91%) of a clear oil. This material was irradiated with sunlight in a Pyrex flask for 96 h to give a 3:1 mixture of 4-methyl-6-(phenylsulfonyl)-5-(phenylthio)-1,4-hexadiene (**25**): IR (neat) 3060, 2980, 2920, 1580, 1470, 1450, 1320, 1310, 1140, 1090, 920, 750, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) (major isomer) δ 1.87 (s, 3 H), 3.20 (d, 2 H, J = 6.4 Hz), 4.04 (s, 2 H), 5.08 (d, 1 H, J = 9.0 Hz), 5.14 (d, 1 H, J = 5.4 Hz), 5.60–5.85 (m, 1 H), 6.95–7.40 (m, 5 H), 7.45–7.70 (m, 3 H), and 7.8–8.0 (m, 2 H); (minor isomer) δ 2.05 (s, 3 H), 3.06 (d, 2 H, J = 6.4 Hz), 4.06 (s, 2 H), 5.08 (d, 1 H, J = 9.0 Hz), 5.14 (d, 1 H, J = 5.4 Hz), 5.60–5.85 (m, 1 H), 6.95–7.40 (m, 5 H), 7.45–7.70 (m, 3 H), and 7.8–8.0 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.2, 21.7, 39.6, 41.6, 59.6, 59.65, 116.0, 116.8, 117.1, 126.4, 128.5, 128.7, 128.9, 129.0, 129.1, 133.7, 134.2, 134.6, 139.1, and 151.6; UV (acetonitrile) 254 nm (ϵ 9730). Anal. Calcd for $C_{19}H_{20}O_2S_2$: C, 66.25; H, 5.85. Found: C, 66.26; H, 5.61.

Preparation of 1-[1-(Phenylthio)ethenyl]-1-(phenylsulfonyl)cyclopropane (13). A suspension containing 90 mg of sodium hydride and 20 mL of dry *N,N*-dimethylformamide was cooled to −40 °C under a nitrogen atmosphere. To this suspension was added 500 mg of 3-(phenylsulfonyl)-2-(phenylthio)-1-propene (**1**) in 5 mL of *N,N*-dimethylformamide dropwise. The resulting solution was stirred for 15 min at −50 °C, and then 0.16 mL of 1,2-dibromoethane was added in one portion. The reaction was allowed to warm to room temperature and was quenched with a saturated ammonium chloride solution. The solution was extracted with ether, and the combined organic extracts were washed with water and then brine and dried over sodium sulfate. Concentration of the solution under reduced pressure afforded a yellow oil, which was subjected to flash chromatography on a silica gel column using a 20% ethyl acetate–hexane mixture as the eluent to give 1-[1-(phenylthio)-ethenyl]-1-(phenylsulfonyl)cyclopropane (**13**) as a pale yellow oil in 84% yield: IR (neat) 2980, 2930, 1600, 1590, 1480, 1450, 1310, 1150, 1085, 760, 735, 695, and 630 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.131 (dd, 2 H, J = 7.2 and 4.9 Hz), 1.88 (dd, 2 H, J = 7.2 and 4.9 Hz), 4.71 (s, 1 H), 5.27 (s, 1 H), 7.29–7.34 (m, 5 H), 7.52–7.68 (m, 3 H), and 7.91–7.94 (m, 2 H); HRMS calcd for $C_{17}H_{16}O_2S_2$ 316.0577, found 316.0577.

Preparation of 1-[1-(Phenylthio)ethenyl]-1-(phenylsulfonyl)cyclopentane (14). A solution containing 0.036 g of oil-free sodium hydride (2.2 equiv) in 5 mL of dry dimethylformamide was cooled in an ice bath under a nitrogen atmosphere. To this material was added 0.2 g of 3-(phenylsulfonyl)-2-(phenylthio)-1-propene (**1**) in one portion. The resulting yellow solution was stirred for 10 min at 0 °C, and then 0.09 mL of 1,4-dibromobutane was added by syringe. The mixture was stirred for 3 h at 0 °C and was then allowed to warm to room temperature. The rection was quenched with a 10% aqueous hydrochloric acid solution, and 20 mL of ether was added to the mixture. The organic layer was washed with another portion of 10% aqueous hydrochloride acid followed by a saturated sodium bicarbonate solution and was then dried over sodium sulfate. Concentration of the solvent afforded a yellow oil, which was chromatographed on a silica gel column using a 10% ethyl acetate–hexane mixture as the eluent to give 0.16 g (70%) of 1-[1-(phenylthio)ethyl]-1-(phenylsulfonyl)cyclopentane (**14**) as a clear oil: IR (neat) 3060, 2960, 2880, 1580, 1470, 1440, 1300, 1140, 1090, 890, 760, 730, and 690; NMR ($CDCl_3$, 300 MHz) δ 1.50–2.00 (m, 4 H), 2.25–2.70 (m, 4 H), 4.90 (d, 1 H, J = 1.0 Hz), 5.40 (d, 1 H, J = 1.0 Hz), 7.20–7.46 (m, 5 H), 7.50–7.76 (m, 3 H), and 7.80–8.13 (m, 2 H); HRMS calcd for $C_{19}H_{20}O_2S_2$ 344.0904, found 344.0904.

A sample containing 0.26 g of **14** was chromatographed on a silica gel column using a 10% ethyl acetate–hexane mixture to give 0.18 g (70%) of a clear oil. This material was irradiated with sunlight in a Pyrex flask for 48 h to give 1-[2-(phenylsulfonyl)-1-(phenylthio)ethylidene]cyclopentane (**26**) as a clear oil: IR (neat) 3060, 2960, 2870, 1590, 1480, 1310, 1140, 1090, 1130, 930, 740, and 690 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.54–2.10 (m, 4 H), 2.30–2.60 (m, 4 H), 3.86 (s, 2 H), and 6.8–7.7 (m, 10 H); m/e 344 (M^+), 218, 210, 202, 185, 169, 161, 154, 147, 135, 125, 111, 93, 91, 84, and 77 (base). Anal. Calcd for $C_{19}H_{20}O_2S_2$: C, 66.25; H, 5.85. Found: C, 66.17; H, 5.62.

6-Bromo-3-(phenylsulfonyl)-2-(phenylthio)-1-hexene (15) was prepared in the normal manner as a clear oil in 80% yield: IR (neat) 3060, 2940, 2910, 1700, 1600, 1580, 1470, 1440, 1300, 1240, 1150, 1080, 1020, 870, 750, and 700 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.50–2.26 (m, 4 H), 3.20–3.50 (m, 2 H), 3.64 (dd, 1 H, J = 11.0 and 4.0 Hz), 4.83 (s, 1 H), 5.33 (s, 1 H), 7.10–7.40 (m, 5 H), 7.45–7.65 (m, 3 H), and 7.70–7.95 (m, 2 H). A sample containing 0.33 g of **15** was chromatographed on a silica gel column using a 10% ethyl acetate–hexane mixture to give 0.28 g (80%)

of a clear oil. This material was irradiated with sunlight in a Pyrex flask for 48 h to give a 3:1 mixture of 6-bromo-1-(phenylsulfonyl)-2-(phenylthio)-2-hexene (**27**): IR (neat) 3060, 2960, 2920, 1510, 1470, 1440, 1310, 1140, 1090, 890, 750, and 690 cm^{-1}; NMR ($CDCl_3$, 90 MHz) (major isomer) δ 1.50–2.13 (m, 2 H), 2.2–2.8 (m, 2 H), 3.2–3.6 (m, 2 H), 3.80 (s, 2 H), 6.06 (t, 1 H, J = 7.2 Hz), and 7.0–8.0 (m, 10 H); (minor isomer) δ 1.50–2.13 (m, 2 H), 2.2–2.8 (m, 2 H), 3.2–3.6 (m, 2 H), 4.16 (s, 2 H), 6.06 (t, 1 H, J = 7.2 Hz), and 7.0–8.0 (m, 10 H). Anal. Calcd for $C_{18}H_{19}O_2S_2Br$: C, 52.56; H, 4.66. Found: C, 52.37; H, 4.62.

Preparation and Rearrangement of 3,3-Dimethyl-3-(phenylsulfonyl)-2-(ethylthio)-1-propene (29). A solution containing 1.0 g of propargyl phenyl sulfone (**3**)[29] and 0.41 mL of ethanethiol in 30 mL of dry tetrahydrofuran was cooled in an ice bath under a nitrogen atmosphere. To this mixture was added small amounts of triethylamine (0.1 mL) and 0.05 mL of a 1.54 M *n*-butyllithium solution in hexane. The mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure, and the resulting oil was dissolved in chloroform. After washing with a saturated sodium bicarbonate solution, the organic layer was separated and dried over sodium sulfate. Concentration of the solvent under reduced pressure left 1.3 g (95%) of 3-(phenylsulfonyl)-2-(ethylthio)-1-propene as a pale yellow oil: IR (neat) 2980, 2940, 1590, 1440, 1320, 1140, 1080, 890, 760, 740, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.19 (t, 3 H, J = 7.4 Hz), 2.66 (q, 2 H, J = 7.4 Hz), 3.90 (s, 2 H), 5.00 (s, 1 H), 5.23 (s, 1 H), 7.40–7.70 (m, 3 H), and 7.80–8.00 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.5, 125.9, 63.4, 114.3, 128.4, 128.5, 128.7, 129.0, 132.6, 133.6, and 137.8; UV (acetonitrile) 220 (ϵ 10 060) and 252 nm (ϵ 3840).

A solution containing 0.21 g of the above sulfone in 5 mL of dry tetrahydrofuran was cooled to −78 °C under a nitrogen atmosphere. To this solution was added 1.4 mL of a 1.58 M *n*-butyllithium solution in hexane (2.5 equiv). The resulting deep orange solution was stirred at −78 °C for 10 min, and then 0.12 mL of methyl iodide was added to syringe. The reaction mixture was warmed to room temperature and was quenched with a saturated ammonium chloride solution. Evaporation of the solvent under reduced pressure left an oil that was taken up in chloroform. The organic layer was washed with a saturated sodium bicarbonate solution followed by a 10% aqueous sodium metabisulfite solution and dried over sodium sulfate. Concentration of the solvent followed by silica gel chromatography using a 10% ethyl acetate–hexane mixture as the eluent gave 0.2 g (85%) of 3,3-dimethyl-3-(phenylsulfonyl)-2-(ethylthio)-1-propene (**29**) as a clear oil: IR (neat) 2980, 2940, 1580, 1450, 1350, 1160, 1130, 1080, 730, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.21 (t, 3 H, J = 7.4 Hz), 1.65 (s, 6 H), 2.60 (q, 2 H, J = 7.4 Hz), 4.99 (s, 1 H), 5.40 (s, 1 H), 7.45–7.70 (m, 3 H), and 7.80–7.95 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.4, 22.5, 26.8, 67.6, 112.7, 128.1, 130.5, 133.4, 135.2, and 143.8; UV (acetonitrile) 218 (ϵ 10 740) and 254 nm (ϵ 3980); m/e 242 (M^+), 141, 101, 88, 84 (base), and 77.

This material was irradiated in benzene with sunlight in a Pyrex flask to give the rearranged 3-methyl-2-(ethylthio)-1-(phenylsulfonyl)-2-butene as a clear oil: IR (neat) 3060, 2950, 2940, 2880, 1620, 1590, 1450, 1310, 1140, 1090, 920, 740, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.12 (t, 3 H, J = 7.3 Hz), 1.68 (s, 3 H), 2.00 (s, 3 H), 2.55 (q, 2 H, J = 7.3 Hz), 4.17 (s, 2 H), 7.40–7.70 (m, 3 H), and 7.8–8.0 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.5, 22.0, 23.7, 27.5, 61.0, 114.9, 128.5, 128.7, 128.9, 133.6, and 148.9.

A competitive experiment using sulfone **10** and 3-methyl-3-(phenylsulfonyl)-1-butene (**30**)[57] indicated that sulfone **30** rearranged 100 times slower than either **10** or **29**, which showed comparable reaction rates.

Reaction of 3-(*p*-Tolylsulfonyl)-2-(phenylthio)-1-propene (31) with 3-Methyl-3-(phenylsulfonyl)-2-(phenylthio)-1-butene (10). A solution containing 1.0 g of 3-(*p*-tolylsulfonyl)-1-propyne[50] and 567 mg of thiophenol was stirred at room temperature under a nitrogen atmosphere. To this solution was added 0.072 mL of triethylamine. The mixture was allowed to stir at room temperature for 18 h. Removal of the solvent under reduced pressure left a yellow oil, which was subjected to flash chromatography on a silica gel column using a 20% ethyl acetate–hexane mixture as the eluent to give 3-(*p*-tolylsulfonyl)-2-(phenylthio)-1-propene (**31**) as a yellow oil in 75% yield: IR (neat) 2940, 2870, 1605, 1325, 1150, 1090, 915, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.46 (s, 3 H), 3.88 (s, 2 H), 5.16 (s, 1 H), 5.38 (s, 1 H), 7.24–7.36 (m, 7 H), and 7.77 (d, 2 H, J = 8.3 Hz); HRMS calcd for $C_{16}H_{16}S_2O_2$ 304.0592, found 304.0592.

A mixture containing 956 mg of **31** and 100 mg of 3-methyl-3-(phenylsulfonyl)-2-(phenylthio)-1-butene (**10**) in dry benzene was irradiated under a nitrogen atmosphere for 12 h using a sunlamp. Removal of the solvent under reduced pressure left a yellow oil, which was subjected to flash chromatography on a silica gel column using a 20% ethyl acetate–hexane mixture as the eluent. The major fraction was identified as 3-methyl-2-(phenylthio)-1-(*p*-tolylsulfonyl)-2-butene (**32**) as a pale yellow oil in 63% yield: IR (neat) 3040, 2940, 1605, 1445, 1330, 1150, 1090, 820, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.30 (s, 3 H), 2.41 (s, 3 H), 2.45 (s, 3 H), 4.50 (s, 2 H), 7.30–7.35 (m, 5 H), and 7.5–7.92 (m, 4 H); HRMS calcd for $C_{18}H_{20}S_2O_2$ 332.0904, found 332.0904.

Alkylation of the Anion Derivied from 3-Methyl-1-(phenylsulfonyl)-2-(phenylthio)-2-butene (24). A solution containing 0.1 g of 3-methyl-1-(phenylsulfonyl)-2-(phenylthio)-2-butene (**24**) in 5 mL of dry tetrahydrofuran was treated with methyl iodide in the normal manner to give 0.093 g (90%) of 4,5-dimethyl-1-(phenylsulfonyl)-2-(phenylthio)-2-butene (**33**) as a clear oil: IR (neat) 3080, 2980, 2940, 1590, 1480, 1450, 1310, 1150, 1090, 1040, 780, 740, 700, and 620 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.53 (d, 3 H, J = 6.7 Hz), 1.76 (s, 3 H), 1.95 (s, 3 H), 4.50 (q, 1 H, J = 6.7 Hz), 7.0–7.3 (m, 5 H), 7.5–7.7 (m, 3 H), and 7.8–7.9 (m, 2 H). Anal. Calcd for $C_{18}H_{20}O_2S_2$: C, 65.03; H, 6.06. Found: C, 65.07; H, 5.92.

A similar reaction with benzyl bromide gave 2-methyl-5-phenyl-4-(phenylsulfonyl)-3-(phenylthio)-2-pentene (**34**) (95%) as a clear oil: IR (neat) 3080, 3040, 2940, 1620, 1590, 1490, 1450, 1310, 1200, 1150, 1090, 1030, 780, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.49 (s, 3 H), 1.68 (s, 3 H), 3.55 (dd, 2 H, J = 10.2 and 4.2 Hz), 4.83 (dd, 1 H, J = 10.2 and 4.2 Hz), 6.7–6.8 (m, 2 H), 6.9–7.2 (m, 8 H), 7.4–7.7 (m, 3 H), and 7.8–7.95 (m, 2 H). Anal. Calcd for $C_{24}H_{24}O_2S_2$: C, 70.55; H, 5.92. Found: C, 70.37; H, 5.90.

Treatment of the anion derived from **24** with benzaldehyde followed by the addition of methanesulfonyl chloride and triethylamine affored a 1:1 *E,Z* mixture of 4-methyl-1-phenyl-2-(phenylsulfonyl)-3-(phenylthio)-1,4-pentadiene (**35**) (70%) as a clear oil: IR (neat) 3060, 3040, 2940, 1580, 1490, 1455, 1310, 1150, 1090, 790, 760, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) (first isomer) δ 1.44 (s, 3 H), 1.74 (s, 3 H), 4.74 (s, 1 H), and 6.8–7.8 (m, 15 H); (second isomer) δ 1.44 (s, 3 H), 1.74 (s, 3 H), 5.11 (s, 1 H), and 6.8–7.8 (m, 15 H); m/e 406 (M^+), 318, 265 (base), 249, 232, 223, 187, 176, 135, 123, 110, 91, and 77; HRMS calcd for $C_{24}H_{22}S_2O_2$ 406.1061, found 406.1064.

Sodium Amalgam Reduction of 2-Methyl-5-phenyl-4-(phenylsulfonyl)-3-(phenylthio)-2-pentene (34). A solution containing 0.075 g of 2-methyl-5-phenyl-4-(phenylsulfonyl)-3-(phenylthio)-2-pentene (**34**) in 8 mL of absolute methanol and 0.1 g of anhydrous disodium hydrogen phosphate was cooled to 0 °C. To this mixture was added 0.3 g of 6% sodium amalgam, and the mixture was stirred for 1 h at 0 °C. The reaction was quenched with a saturated ammonium chloride solution, and the solvent was removed under reduced pressure. The aqueous layer was extracted with ether, and the combined organic layer was washed with water and an aqueous 10% sodium hydroxide solution and dried over sodium sulfate. Concentration of the solvent under reduced pressure left a clear oil that was chromatographed on a silica gel column to give 0.047 g (95%) of a clear oil, which was identified as a 2:1 mixture of compounds **36** and **37**: IR (neat) 3080, 3040, 2980, 2940, 2880, 1580, 1505, 1480, 1460, 1450, 1210, 1090, 1030, 750, and 710 cm^{-1}; NMR ($CDCl_3$, 300 MHz) (major isomer) δ 1.75 (s, 3 H), 2.00 (s, 3 H), 2.51 (dd, 2 H, J = 8.4 and 7.2 Hz), 2.77 (dd, 2 H, J = 8.4 and 7.2 Hz), and 7.00–7.40 (m, 10 H); (minor isomer) δ 1.11 (d, 6 H, J = 6.7 Hz), 2.45 (q, 1 H, J = 6.7 Hz), 3.67 (d, 2 H, J = 7.0 Hz), 6.13 (t, 1 H, J = 7.0 Hz), and 7.00–7.40 (m, 10 H).

Peracid Oxidation of 3-Methyl-1-(phenylsulfonyl)-2-(phenylthio)-2-butene (24). A solution containing 1.3 g of 3-methyl-1-(phenylsulfonyl)-2-(phenylthio)-2-butene (**24**) was dissolved in 30 mL of dry methylene chloride, and the mixture

(57) Vollhardt, J.; Gais, H. J.; Lukas, K. L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 610.

was cooled to 0 °C under a nitrogen atmosphere. To this solution was added 2.2 g of *m*-chloroperbenzoic acid (2.5 equiv), and the reaction mixture was warmed to room temperature and stirred overnight. The organic layer was washed with a saturated potassium carbonate solution and dried over sodium sulfate. Concentration of the solvent under reduced pressure left a white solid, which was recrystallized from methanol to give 1.2 g (86%) of 3-methyl-1,2-(phenylsulfonyl)-2-butene (**39**) as white needles: mp 123–124 °C; IR (KBr) 3080, 3000, 2950, 1610, 1590, 1450, 1400, 1310, 1260, 1190, 1140, 1090, 800, 755, 730, 690, and 600 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.00 (s, 3 H), 2.18 (s, 3 H), 4.40 (s, 2 H), 7.4–7.8 (m, 6 H), and 7.9–8.1 (m, 4 H). Anal. Calcd for $C_{16}H_{16}O_2S_2$: C, 58.26; H, 5.18; S, 18.30. Found: C, 58.17; H, 5.22; S, 18.23.

A solution containing 0.1 g of the above compound in 5 mL of dry tetrahydrofuran was cooled to −78 °C under a nitrogen atmosphere. To this mixture was added 0.2 mL of a 1.55 M *n*-butyllithium solution in hexane (1.2 equiv). The reaction mixture was warmed to room temperature and was quenched with a saturated ammonium chloride solution. The solvent was removed under reduced pressure, and the mixture was taken up in chloroform. The organic layer was washed with water, followed by a saturated aqueous sodium bicarbonate solution and dried over sodium sulfate. Removal of the solvent under reduced pressure left a yellow oil that was chromatographed on a silica gel column using a 10% ethyl acetate–hexane mixture to give 0.04 g (72%) of 3,3-dimethyl-1-(phenylsulfonyl)allene (**40**) as a clear viscous oil: IR (neat) 3060, 3000, 2920, 2860, 1970, 1450, 1370, 1310, 1190, 1050, 980, 800, 770, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.77 (d, 6 H, J = 2.7 Hz), 6.05 (septet, 1 H, J = 2.7 Hz), 7.5–7.7 (m, 3 H), and 7.90–7.95 (m, 2 H). Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.44; H, 5.81. Found: C, 63.27; H, 5.72.

Peracid Oxidation of 2-Methyl-5-phenyl-4-(phenylsulfonyl)-3-(phenylthio)-2-pentene (34). A solution containing 0.31 g of 2-methyl-5-phenyl-4-(phenylsulfonyl)-3-(phenylthio)-2-pentene (**34**) in 10 mL of dry methylene chloride was cooled to 0 °C under a nitrogen atmosphere. To this mixture was added 0.4 g of a 80% *m*-chloroperbenzoic acid (2.5 equiv), and the mixture was allowed to warm to room temperature and was stirred at 25 °C overnight. The organic layer was washed with water, followed by a saturated potassium carbonate solution, and dried over sodium sulfate. Concentration of the solvent under reduced pressure left a clear oil, which was chromatographed on silica gel using chloroform as the eluent to give 0.33 g (98%) of 2-methyl-5-phenyl-3,4-bis(phenylsulfonyl)-2-pentene (**41**) as a clear oil: IR (neat) 3060, 3020, 2940, 1650, 1580, 1450, 1300, 1240, 1140, 1090, 750, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.90 (s, 3 H), 2.43 (s, 3 H), 3.40 (dd, 1 H, J = 14.0 and 9.8 Hz), 3.60 (dd, 1 H, J = 14.0 and 5.8 Hz), 5.66 (dd, 1 H, J = 9.8 and 5.8 Hz), 7.0–7.4 (m, 7 H), 7.45–7.70 (m, 6 H), and 7.9–8.0 (m, 2 H).

A solution containing 0.08 g of the above compound in 5 mL of dry tetrahydrofuran was cooled to −78 °C under a nitrogen atmosphere. To the above solution was added 0.18 mL of a 1.55 M *n*-butyllithium solution in hexane (1.5 equiv). The deep orange-brown solution was warmed to room temperature and was quenched with methanol followed by a 10% hydrochloric acid solution. The solvent was removed under reduced pressure, and the resulting oil was taken up in chloroform. The organic layer was washed with a saturated sodium bicarbonate solution and dried over sodium sulfate. Concentration of the solvent under reduced pressure left a clear oil, which was chromatographed on a silica gel column to give 0.045 g (83%) of 4-methyl-1-phenyl-3-(phenylsulfonyl)-1,4-pentadiene (**42**) as a clear oil: IR (neat) 3040, 2940, 2860, 1450, 1310, 1140, 1090, 980, 920, 750, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.98 (s, 3 H), 4.28 (dd, 1 H, J = 5.8 and 3.0 Hz), 5.05 (s, 1 H), 5.17 (s, 1 H), 6.32 (d, 1 H, J = 3.0 Hz), 6.35 (d, 1 H, J = 5.8 Hz), 7.20–7.40 (m, 5 H), 7.50–7.70 (m, 3 H), and 7.80–7.90 (m, 2 H); UV (95% ethanol) 262 nm (ϵ 14 000); m/e 298 (M^+), 157, 142, 129, 115, 87, 84 (base), and 77; HRMS calcd for $C_{18}H_{18}SO_2$ 298.1027, found 298.1030.

A solution containing 0.09 g of **41** in 5 mL of dry tetrahydrofuran was treated with methyl iodide in the normal manner to give 0.061 g (65%) of 3,4-dimethyl-1-phenyl-3-(phenylsulfonyl)-1,4-pentadiene (**43**) as a clear oil: IR (neat) 3060, 3020, 2960, 2940, 2880, 1600, 1590, 1450, 1300, 1145, 1070, 980, 920, 750, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.70 (s, 3 H), 2.10 (s, 3 H), 5.15 (s, 1 H), 5.27 (s, 1 H), 6.40 (d, 1 H, J = 16.1 Hz), 6.75 (d, 1 H, J = 16.1 Hz), and 7.10–7.90 (m, 10 H); UV (acetonitrile) 260 nm (ϵ 13 000). Anal. Calcd for $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45. Found: C, 73.07; H, 6.28.

Preparation of 2-[(Phenylsulfonyl)methyl]cyclopentyl Methyl Ketone (52). A solution containing 250 mg of 3-(phenylsulfonyl)-2-(phenylthio)-1-propene (**1**) and 0.75 mL of hexamethylphosphoramide in 10 mL of dry tetrahydrofuran was cooled to −78 °C under a nitrogen atmosphere. To this mixture was added 0.65 mL of a 1.6 M *n*-butyllithium solution in hexane. The resulting yellow solution was stirred at −78 °C for 10 min, and then 0.11 mL of 5-bromo-1-pentene was added in one portion. The reaction mixture was allowed to warm to room temperature and was quenched with a saturated ammonium chloride solution. Evaporation of the solvent under reduced pressure left a yellow oil, which was extracted with ether. The combined ether extracts were washed with water and brine. Removal of the solvent under reduced pressure left a yellow oil, which was taken up in 50 mL of a 60% aqueous acetic acid solution. The mixture was treated with 640 mg of sodium phenyl sulfinate and was heated to 100 °C for 16 h. The reaction mixture was cooled to 25 °C and extracted with ether. The combined ether extracts were washed with a dilute sodium hydroxide solution and water and then dried over sodium sulfate. Removal of the solvent under reduced pressure left a yellow oil, which was subjected to flash chromatography on a silica gel column using a 20% ethyl acetate–hexane mixture as the eluent to give 2-[(phenylsulfonyl)methyl]cyclopentyl methyl ketone (**52**) as a pale yellow oil in 45% yield: IR (neat) 3080, 2970, 2880, 1710, 1450, 1305, 1150, 1090, 750, and 695 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.31–1.43 (m, 1 H), 1.51–1.68 (m, 3 H), 1.95–2.06 (m, 2 H), 2.18 (s, 3 H), 2.62 (hx, 1 H, J = 7.5 Hz), 2.79–2.86 (m, 1 H), 3.07 (dd, 1 H, J = 14.2 and 7.3 Hz), 3.18 (dd, 1 H, J = 14.2 and 6.6 Hz), 7.53–7.67 (m, 3 H), and 7.85–7.89 (m, 2 H); HRMS calcd for $C_{14}H_{18}SO_3$ 266.0976, found 266.0974.

An analogous cyclization occurred upon heating a sample of 2-phenoxy-3-(phenylsulfonyl)-1,7-octadiene (**53**) [NMR ($CDCl_3$, 300 MHz) δ 2.0–2.5 (m, 6 H), 3.81 (dd, 1 H), 4.08 (d, 1 H), 4.36 (d, 1 H), 4.8–5.05 (m, 2 H), 5.7–5.93 (m, 1 H), and 6.8–8.0 (m, 10 H)] with sodium phenylsulfinate in 60% aqueous acetic acid for 16 h at 100 °C, giving rise to *trans*-ketone **52** in 53% yield.

Heating a sample of allylic sulfone **47** with 7 equiv of sodium *p*-tolylsulfinate in 60% aqueous acetic acid for 16 h afforded a 1:1 mixture of *trans*-ketone **52** as well as [(*p*-tolylsulfonyl)methyl]cyclopentyl methyl ketone (**60**) which was identical in all details with an authentic sample.[50] An analogous result was encountered using the rearranged allylic sulfone **48**. A sample of 7-(phenylthio)-8-(phenylsulfonyl)-1,6-octadiene (**48**) [*E*/*Z* mixture] was prepared in the standard fashion by irradiating a sample of **47** in benzene: NMR ($CDCl_3$, 300 MHz) δ 1.4–2.4 (m, 6 H), 3.80 (s, 2 H) [*E* isomer], 3.92 (s, 2 H) [*Z* isomer], 4.9–5.05 (m, 2 H), 5.7–5.85 (m, 1 H), 6.20 (t, 1 H) [*E* isomer], 6.20 (t, 1 H) [*Z* isomer], and 7.0–8.0 (m, 10 H).

Preparation of 2-[(Phenylsulfonyl)methyl]-1-cyclopentenyl Methyl Ketone (55). A solution containing 200 mg of 3-(phenylsulfonyl)-2-(phenylthio)-1-propene (**1**) and 0.59 mL of hexamethylphosphoramide in 10 mL of dry tetrahydrofuran was cooled to −78 °C under a nitrogen atmosphere. To this mixture was added 0.52 mL of a 1.6 M *n*-butyllithium solution in hexane. The resulting yellow solution was stirred at −78 °C for 10 min, and then 150 mg of 5-iodo-1-pentyne[58] was added in one portion. The reaction mixture was allowed to warm to room temperature and was quenched with a saturated ammonium chloride solution. Evaporation of the solvent under reduced pressure left a yellow oil, which was diluted with water and extracted with ether. The combined ether extracts were washed with water and brine followed by drying over sodium sulfate. Removal of the solvent under reduced pressure afforded a yellow oil, which was taken up in 50 mL of a 60% aqueous acetic acid solution. The mixture was treated with 800 mg of sodium phenylsulfinate and heated to 100 °C for 16 h. The reaction mixture was cooled to room temperature and extracted with ether. The ether extracts were washed with a dilute aqueous sodium hydroxide solution and water and dried over sodium sulfate. Re-

(58) Büchi, G.; Wuest, H. *J. Org. Chem.* **1979**, *44*, 546.

moval of the solvent under reduced pressure afforded a yellow oil, which was subjected to flash chromatography on a silica gel column using a 20% ethyl acetate–hexane mixture as the eluent to give 2-[(phenylsulfonyl)methyl]-1-cyclopentenyl methyl ketone (**55**) as a pale yellow oil in 43% yield: IR (neat) 3080, 2970, 2860, 1680, 1610, 1320, 1150, 1085, 740, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.78–1.95 (m, 2 H), 1.92 (s, 3 H), 2.58–2.65 (m, 2 H), 2.72–2.79 (m, 2 H), 4.53 (s, 2 H), 7.48–7.64 (m, 3 H), and 7.83–7.87 (m, 2 H); HRMS calcd for $C_{14}H_{16}SO_3$ 264.0820, found 264.0829.

Preparation of 2-[(Phenylsulfonyl)methyl]cyclohexyl Methyl Ketone (57). A solution containing 200 mg of 3-(phenylsulfonyl)-2-(phenylthio)-1-propene (1) and 0.59 mL of hexamethylphosphoramide in 10 mL of dry tetrahydrofuran was cooled to −78 °C under a nitrogen atmosphere. To this mixture was added 0.52 mL of a 1.6 M *n*-butyllithium solution in hexane. The resulting yellow solution was stirred at −78 °C for 10 min, and then 0.10 mL of 6-bromo-1-hexene was added in one portion. The reaction mixture was allowed to warm to room temperature and was quenched with a saturated ammonium chloride solution. Evaporation of the solvent under reduced pressure left a yellow oil, which was dissolved in ether. The organic solution was washed with water and brine. Removal of solvent under reduced pressure afforded a yellow oil, which was taken up in 50 mL of a 60% aqueous acetic acid solution. The mixture was treated with 800 mg of sodium phenylsulfinate and heated to 100 °C for 16 h. The solution was cooled and extracted with ether. The combined ether extracts were washed with a dilute sodium hydroxide solution, water, and brine and then dried over sodium sulfate. Removal of the solvent under reduced pressure left a clear oil, which was subjected to flash chromatography on a silica gel column using a 20% ethyl acetate–hexane mixture as the eluent. The major fraction was identified as 2-[(phenylsulfonyl)methyl]cyclohexyl methyl ketone (**57**) as a pale yellow oil in 50% yield: IR (neat) 3020, 2950, 2870, 1705, 1430, 1310, 1145, 1090, and 695 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.19–1.39 (m, 4 H), 1.73–1.81 (m, 2 H), 1.94–1.98 (m, 1 H), 2.11 (s, 3 H), 2.17–2.28 (m, 2 H), 2.47–2.54 (m, 1 H), 3.01 (d, H, J = 5.3 Hz), 7.54–7.68 (m, 3 H), and 7.87–7.90 (m, 2 H); HRMS calcd for $C_{15}H_{20}SO_3$ 280.1133, found 280.1138.

Acknowledgment. We gratefully acknowledge the National Science Foundation for generous support of this work. Use of the high-field NMR spectrometers used in these studies was made possible through equipment grants from the National Science Foundation and the National Institutes of Health.

Registry No. 1, 2525-54-4; **3**, 2525-40-8; **4**, 113881-68-8; **5**, 113881-69-9; **6**, 124418-78-6; **7**, 113881-71-3; **8**, 113881-70-2; **9**, 124418-79-7; **10**, 124418-80-0; **11**, 113881-80-4; **13**, 124418-81-1; **14**, 124418-82-2; **15**, 124418-83-3; **16**, 124418-84-4; **17**, 124418-85-5; (*E*)-**18**, 113881-72-4; (*Z*)-**18**, 113881-73-5; (*E*)-**19**, 113881-74-6; (*Z*)-**19**, 113881-75-7; (*E*)-**20**, 124418-86-6; (*Z*)-**20**, 124419-03-0; (*E*)-**21**, 113881-77-9; (*Z*)-**21**, 113881-78-0; (*E*)-**22**, 113881-76-8; (*Z*)-**22**, 113881-76-8; (*Z*)-**22**, 113921-81-6; (*E*)-**23**, 124418-87-7; (*Z*)-**23**, 124419-04-1; **24**, 113881-82-6; (*E*)-**25**, 124418-88-8; (*Z*)-**25**, 124419-05-2; **26**, 124418-89-9; **27**, 124418-90-2; **29**, 124418-91-3; **30**, 72863-20-8; **31**, 97479-46-4; **32**, 124418-92-4; **33**, 124418-93-5; **34**, 113881-89-3; (*E*)-**35**, 124441-43-6; (*Z*)-**35**, 124441-44-7; **36**, 113881-97-3; **37**, 124418-97-9; **38**, 80945-31-9; **39**, 113881-90-6; **40**, 18955-77-6; **41**, 113881-91-7; **42**, 124418-95-7; **43**, 124418-96-8; **47**, 124419-00-7; (*E*)-**48**, 124419-07-4; (*Z*)-**48**, 124419-08-5; **52**, 124418-98-0; **53**, 124418-99-1; **54**, 124419-09-6; **55**, 124419-01-8; **56**, 124419-10-9; **57**, 124419-02-9; **60**, 124419-06-3; $Br(CH_2)_2Br$, 106-93-4; $Br(CH_2)_4Br$, 110-52-1; $Br(CH_2)_3Br$, 109-64-8; CH_3CH_2SH, 75-08-1; PhSH, 108-98-5; $PhCH_2Br$, 100-39-0; PhCHO, 100-52-7; $Br(CH_2)_3CH{=}CH_2$, 1119-51-3; $CH_3(CH_2)_2C{\equiv}CI$, 14752-61-5; $Br(CH_2)_4CH{=}CH_2$, 2695-47-8; 3-(phenylsulfonyl)-2-(ethylthio)-1-propene, 2525-54-4; 3-methyl-2-(ethylthio)-1-(phenylsulfonyl)-2-butene, 124418-94-6; sodium benzenesulfinate, 873-55-2; sodium *p*-toluenesulfinate, 824-79-3.

1,6-Addition of Organocopper Reagents to 3-Alkynyl-2-cycloalkenones: Regiospecific Syntheses of Dienones and Allenes

Menyan Cheng and Martin Hulce*

Department of Chemistry and Biochemistry, University of Maryland Baltimore County, Baltimore, Maryland 21228

Received July 13, 1989

To investigate the preparation of allenes by means of 1,6-addition reactions to 2-alken-4-ynones, 3-ethynyl-2-cycloalkenones (**5**) were synthesized and reacted with a variety of organocopper nucleophiles. Such nucleophiles undergo regiospecific 1,6-additions to generate intermediate allenyl enolates (**10**), which are regiospecifically and stereoselectively protonated to yield a preponderance of (*Z*)-3-alkenyl-2-cycloalkenones (**6–8**). The reaction is sensitive to the nature of the organocopper reagent used; higher order cyanocuprates derived from organolithium reagents are the reagents of choice. The intermediate allenyl enolates (**10**) can be trapped as their enol triflates (**13**), which in turn can be converted into enallenes (**14**). Non-organocopper nucleophiles also can add to the terminal carbon of the alkynyl moiety of the enynones studied, but the mechanism may be distinct from that of 1,6-addition: (phenylthio)lithium adds to 3-ethynyl-2-methyl-2-cyclopentenone (**5a**) by a syn-carbometalation-like mechanism and upon protic quenching yields a preponderance of (*E*)-2-methyl-3-(2-(phenylthio)ethenyl)-2-cyclopentenone (**6h**).

Conjugate addition reactions of organometallic nucleophiles to α,β-unsaturated carbonyl substrates in aprotic solvents are powerful, versatile synthetic tools extensively exploited by organic chemists.[1-3] In contrast, vinylogous conjugate additions such as 1,6-additions to $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl substrates and, more generally, 1,(4 + 2n)-additions to more extensively conjugated polyenones

(1) (a) Yamoto, Y. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 947. (b) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59. (c) Posner, G. H. *Org. React.* **1972**, 19, 1.

(2) (a) Chapdelaine, M. J.; Hulce, M. *Org. React.*, **1990**, *38*, 327. (b) Noyori, R.; Suzuki, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 262. (c) Taylor, R. J. K. *Synthesis* **1985**, 364.

(3) For recent examples: (a) Yanagisawa, A.; Habaue, S.; Yamamoto, *J. Am. Chem. Soc.* **1989**, *111*, 366. (b) Ruggeri, R. B.; Hansen, M. M.; Heathcock, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 8734. (c) Ihara, M.; Suzuki, M.; Fukumoto, K.; Kametani, T.; Kabuto, C. *J. Am. Chem. Soc.* **1988**, *110*, 1963. (d) Mizuno, K.; Ikeda, M.; Toda, S.; Otsuji, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1288. (e) Corey, E. J.; Kang, M.; Desai, M. C.; Gosh, A. K.; Houpis, I. N. *J. Am. Chem. Soc.* **1988**, *110*, 649.

0022-3263/90/1955-0964$02.50/0