[3 + 2] Cyclization–Elimination Route to Cyclopentenyl Sulfones Using (Phenylsulfonyl)-1,2-propadiene

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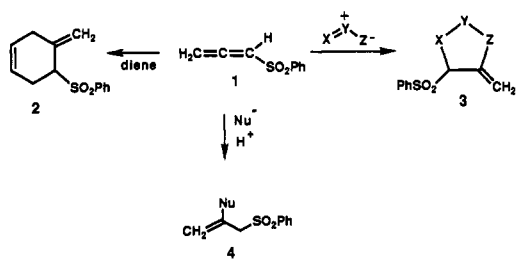
Received May 24, 1991

Treatment of (phenylsulfonyl)-1,2-propadiene (1) with bis(phenylsulfonyl)methane in the presence of sodium hydride affords 2,4,4-tris(phenylsulfonyl)-1-butene in 94% yield. Similar rearranged products were obtained using other soft nucleophiles and related allenes. The formation of these products involves addition of benzenesulfinate anion onto allene 1. The initially formed carbanion undergoes proton transfer with bis(phenylsulfonyl)methane followed by a S_N2' reaction of the resulting anion with 2,3-bis(phenylsulfonyl)-1-propene. Supporting evidence for the proposed mechanism is provided by the observation that the reaction of dimethyl malonate with the activated allene in the presence of sodium benzenesulfinate gives mostly abnormal products. When allene 1 is allowed to react with olefins bearing an electron-withdrawing group in the presence of sodium benzenesulfinate, a substituted cyclopentenyl sulfone is formed. The reaction proceeds in a stepwise fashion by addition of the initially produced carbanion onto the activated π-bond of the olefin followed by a 5-*endo*-*trig* cyclization and elimination of benzenesulfinate. This approach represents a mild and versatile anionic [3 + 2] route to five-membered unsaturated sulfones.

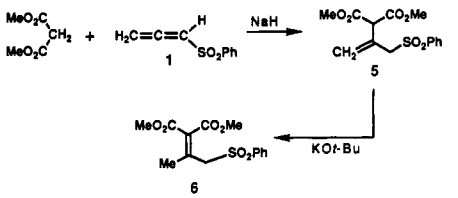
The greatly enhanced reactivity of activated allenes has long been recognized amongst organic chemists, but little application has been made of this functional unit in synthetic operations.[1] (Phenylsulfonyl)-1,2-propadiene (1)



represents one of the more reactive allenes known.[2-4] This compound contains a three-carbon array with an electron-rich π-bond, an electron-deficient alkene, and a pendant sulfone moiety that can be utilized for subsequent synthetic manipulations.[5-7] Allene 1 is a stable, crystalline compound having a shelf life of several years under normal laboratory conditions. MNDO calculations indicate that the introduction of a sulfonyl group causes a significant lowering of the LUMO energy level compared with allene (ΔE = 1.3 eV), and the largest LUMO coefficient resides on the central carbon and the next on the position bearing the sulfonyl group.[8,9] This suggests that the reaction 1 with various 4π-systems will proceed in a highly regioselective fashion and undergo cycloaddition across the activated C_1–C_2 π-bond. In fact, this reagent has proven to be a useful synthetic equivalent of allene as a dienophile due to its enhanced reactivity as well as the easy removal of the phenylsulfonyl group from the adducts 2.[9-12] Other phenylsulfonyl-substituted allenes are also becoming increasingly important in organic synthesis, particularly as dienophiles and dipolarophiles in cycloadditions[13,15] and in addition reactions with various nucleophiles.[16-19] While the reactions with heteronucleophiles have been reasonably well investigated[20-23], much less attention has been paid to the C–C bond forming reactions of 1 with carbon nucleophiles.[24,25] Our ongoing interest[13] in the synthetic utility of (phenylsulfonyl)allene 1 inspired us to take a detailed look at its reactions with soft carbanions. The present paper documents the results of these studies.[26]

Results and Discussion

We began our studies by examining the reaction of 1 with dimethyl malonate in the presence of a trace of sodium hydride. The major product formed (92%) corresponded to the expected Michael-type adduct 5. This



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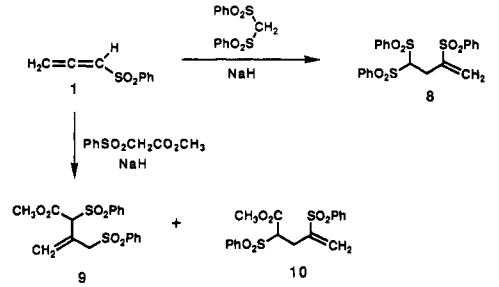
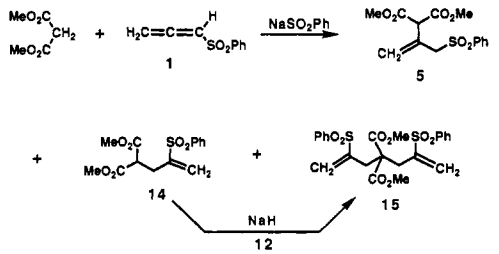
material readily rearranged to the thermodynamically more stable isomer **6** by stirring with potassium *tert*-butoxide in THF for longer periods of time. In marked contrast to this result, the reaction of **1** with bis(phenylsulfonyl)-methane in the presence of a trace of base afforded the Michael-type adduct in only 4% yield. The major product obtained (94%) corresponded to structure **8**. An inde-



pendently synthesized sample of **8** was obtained by treating the anion derived from bis(phenylsulfonyl)methane with 3-chloro-2-(phenylsulfonyl)-1-propene. Since we were interested in the mechanism by which compound **8** was formed, we undertook a study of the reaction of allene **1** with methyl (phenylsulfonyl)acetate. Under conditions identical with those used for the addition of bis(phenylsulfonyl)methane to allene **1**, a 2:1 mixture of **9** and **10** was formed in 98% overall yield.

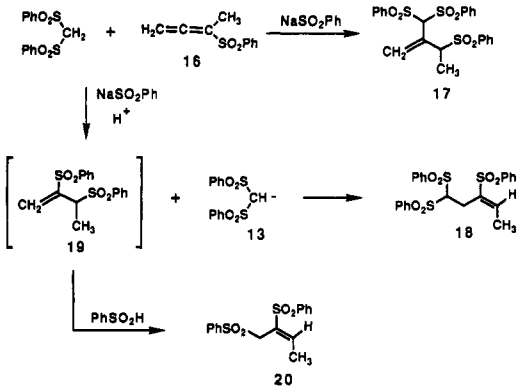
A mechanism that rationalizes the formation of **8** (and **10**) and that is consistent with all the data (vide infra) is outlined in Scheme I. Carbanion **11** is the probable key intermediate in this novel chain process. Proton transfer of **11** with bis(phenylsulfonyl)methane followed by an S_N2' reaction of the resulting carbanion with 2,3-bis(phenylsulfonyl)-1-propene (**12**) generates **8** and an additional quantity of benzenesulfinate anion. This material undergoes a subsequent nucleophilic addition with allene **1** and regenerates carbanion **11**. The origin of the trace amount of benzenesulfinate anion required to initiate the chain process is unclear. Highly purified samples of allene **1** and bis(phenylsulfonyl)methane were prepared, and their reaction still produced the abnormal product **8** in high yield. The benzenesulfinate anion could arise from conjugate addition of bis(phenylsulfonyl)methane anion followed by an intramolecular S_N2 reaction.

Supporting evidence for the proposed mechanism is provided by the observation that the reaction of dimethyl malonate with allene **1** in the presence of sodium benzenesulfinate afforded the abnormal products **14** and **15** in addition to the Michael-type adduct **5**. This is com-



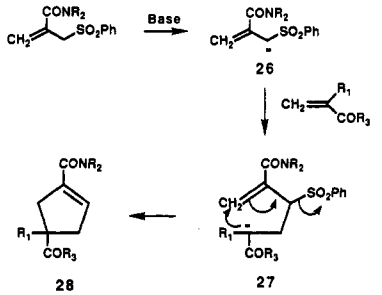
patible with the reaction sequence outlined in Scheme I. The anion derived from compound **14** apparently reacts with some additional 2,3-bis(phenylsulfonyl)-1-propene (**12**) present in the reaction mixture to give the diadduct **15**. In fact, a pure sample of **15** can be prepared by treating **14** with sodium hydride in the presence of **12**.

An additional piece of data that supports the S_N2' sequence was obtained by carrying out the reaction of bis(phenylsulfonyl)methane with 3-(phenylsulfonyl)buta-1,2-diene (**16**) in the presence of sodium benzenesulfinate.



In this case, a 1:1 mixture of **17** and **18** was obtained in 92% yield. The formation of **18** is readily explained in terms of an attack of anion **13** onto the methylene carbon of the initially formed disulfone **19**. We have attempted to prepare an authentic sample of **19** by treating **16** with benzenesulfinic acid in THF. However, the only product that could be isolated (93%) corresponded to (*E*)-1,2-bis(phenylsulfonyl)-2-butene (**20**).[27] More than likely, compound **20** is formed from **19** by a 1,3-bis(phenylsulfonyl) shift under the acidic conditions used.[28]

Considering the great utility of vinyl sulfones in organic synthesis,[29] we sought to develop an annulation strategy for cyclopentenyl sulfone formation that involves treating (phenylsulfonyl)allene **1** with an activated olefin in the presence of a nucleophilic reagent (see Scheme II). In this approach, generation of carbanion **21** by reaction of the nucleophile with **1** is follwed by a cyclization–elimination sequence to provide the five-membered ring. The cycloaddition of an allyl anion with an activated olefin to give a cyclopentyl anion has been an active area of investigation for many years. The anionic [3 + 2] cyclization route was initially exploited by Kauffmann[30] with additional contributions from Boche[31] and Ford.[32] More recently, Beak reported cyclopentene ring formation by reaction between a [1-(phenylthio)-2-carbamoylallyl]lithium reagent **26** and



an acrylamide in a sequence that involves a formal anionic [3 + 2] cycloaddition as the key step.[33] He subsequently found that a β'-phenylsulfonyl group not only increased

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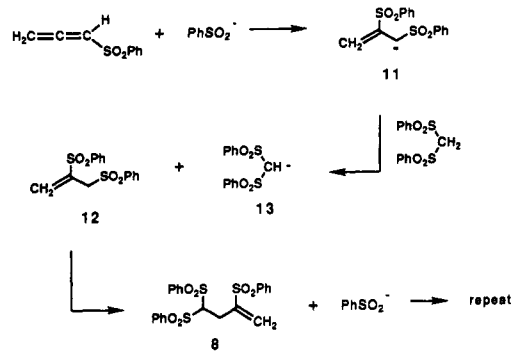
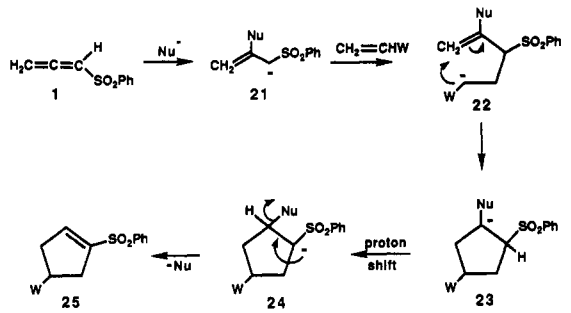
Scheme I



Scheme II



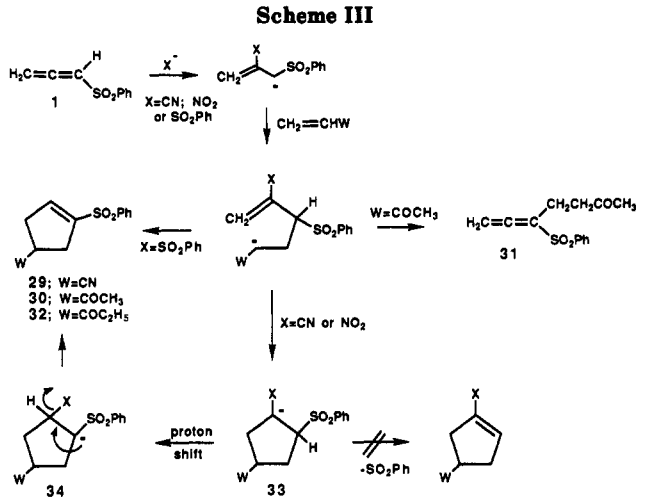
the ease of anion formation but also directed addition to the π-bond and, following the cyclization step, acted as a leaving group to drive the reaction thermodynamically to the cyclopentene product.[34] This sequence of reactions has characteristics similar to that outlined in Scheme II.[26]

Our approach toward carrying out the synthesis of cyclopentenyl sulfones requires that the allyl anion synthon meet the following criteria: (1) that the allyl anion be generated under essentially neutral conditions by the addition of a nucleophile to (phenylsulfonyl)-1,2-propadiene, (2) that the stability of the allyl anion is not so great as to diminish the nucleophilicity of the carbanion, (3) that the nucleophile be an electron-withdrawing moiety which, when cross conjugated with the allyl system, will stabilize the resulting cyclopentyl anion, and (4) following the cyclization step, the nucleophile also be capable of acting as the leaving group so as to drive the reaction thermodynamically to the cyclopentenyl sulfone. While these requirements are not inherent for a concerted $4\pi s + 2\pi s$ process, we did not expect them to perturb the "concertedness" of the cycloaddition, and in fact we anticipated that they would provide maximum driving force for the reaction to proceed.

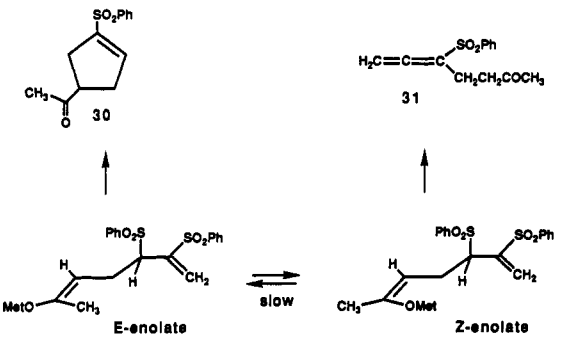
To implement our plans for the anionic [3 + 2] cyclization, allene **1**, acrylonitrile, and sodium benzenesulfinate (trace) were stirred in THF at ambient temperature. The major product, formed in 73% yield, corresponded to cycloadduct **29**. Similar results were obtained when sodium cyanide or sodium nitrite was used as the catalyst. Addition of these reagents to the allene generates a cyclized intermediate (i.e., **33**), which undergoes a 1,2-proton shift to give **34** prior to sulfinate ejection. A subsequent elimination of cyanide (or nitrite) ion gives rise to the observed product (Scheme III). A related set of reactins takes place when methyl (or ethyl) vinyl ketone was used as the trapping agent. For example, treatment of **1** with $PhSO_2Na$ and MVK led to a 2:1 mixture of cycloadduct **30** and allene **31** in 76% overall yield. The ratio of these

(34) Beak, P.; Burg, D. A. *J. Org. Chem.* **1989**, *54*, 1647.

Scheme III



two products was found to be dependent on the additive used. Addition of sodium nitrite to **1** and MVK gave predominantly cycloadduct **30** (75%) with lesser quantities of allene **31** (8%). Use of lithium benzenesulfinate, on the other hand, afforded a 1:1 mixture of **30** and **31**. When KCN was used, the only product formed corresponded to cycloadduct **30** (80%). Although Scheme III is written in terms of a stepwise reaction, the mechanism for the formation of cycloadduct **29** could be either concerted or stepwise. The isolation of allene **31**, however, strongly suggests a stepwise mechanism for the anionic [3 + 2] cyclization reaction, albeit the cyclization is a 5-*endo-trig* process.[35] All attempts to isolate or detect the formation of products from a possible acyclic intermediate failed.



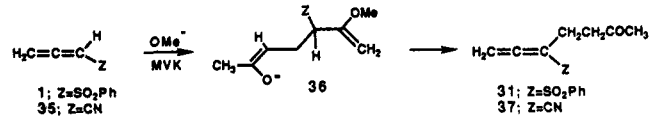
The formation of allene **31** can best be rationalized by a process involving intramolecular proton transfer of the hydrogen adjacent to the sulfonyl group to the enolate oxygen followed by loss of sulfinate anion. The nature of the counterion seems to significantly influence the product distribution. Small counterions (Met = Li) generate significant quantities of the *Z* enolate, which readily undergoes internal proton transfer. When the counterion is large (Met = K), however, the sterically less encumbered *E* enolate is formed and only the cyclization reaction occurs. Presumably, the barrier of interconversion of *E* and *Z* enolates is high under the experimental conditions used.[36]

We have also employed sodium methoxide as the attacking nucleophile in order to determine whether anionic cyclization would occur with this reagent. Treatment of allene **1** with MVK in the presence of catalytic quantities

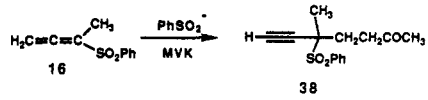
(35) Baldwin, J. E.; Lusch, M. J. *Tetrahedron* **1982**, *38*, 2939 and references cited therein.

(36) An alternative possibility is that coordination between lithium cation, the anion, and MVK results in an internal conjugate addition that demands an *s-cis* conformation of MVK, while such coordination is absent in the potassium ion case.

of NaOMe afforded allene **31** as the exclusive product (81%). An analogous reaction occurred upon treating cyanoallene (**35**) with NaOMe. Allene **37** is formed by attack of methoxide ion on the activated π-bond of **1** followed by conjugate addition of MVK. In this case, the initially produced carbanion **36** cannot cyclize and instead undergoes exclusive proton transfer followed by methoxide ejection to give **37**.



In an effort to extend the methodology to other phenylsulfonyl-activated 1,2-propadienes, allene **16** was treated with sodium benzenesulfinate in the presence of MVK. Addition of $PhSO_2Na$ to the central allene carbon is totally suppressed as a consequence of the methyl substituent. Instead of adding to the π-bond, the phenylsulfinate anion acts as a base and removes one of the vinylic protons. The resulting carbanion then undergoes conjugate addition with MVK to give alkyne **38** in 45% yield as the only identifiable product.



In conclusion, we have demonstrated that (phenylsulfonyl)-1,2-propadiene reacts with several carbon nucleophiles to give novel rearranged products. When this activated allene is treated with olefins bearing an electron-withdrawing substituent under phase-transfer conditions, cyclopentenyl-substituted sulfones are formed in high yield via an anionic [3 + 2] cyclization–elimination sequence. This approach represents a mild and versatile anionic [3 + 2] route to five-membered unsaturated sulfones.

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 an ethyl acetate–hexane mixture as the eluent unless specified otherwise.

Methyl 2-Carbomethoxy-3-[(phenylsulfonyl)methyl]-3-butenoate (5). To a stirred solution containing 200 mg (1.1 mmol) of (phenylsulfonyl)-1,2-propadiene (**1**)[2] and 0.13 mL of dimethyl malonate in 5 mL of THF was added 5 mg of NaH. The reaction was stirred for 18 h at 25 °C under N_2. Concentration of the mixture under reduced pressure followed by chromatography gave 318 mg (92%) of **5** as a white solid: mp 104–105 °C; IR ($CHCl_3$) 1745, 1320, 1165, 1035, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.76 (s, 6 H), 3.98 (s, 2 H), 4.51 (s, 1 H), 5.17 (s, 1 H), 5.41 (s, 1 H), 7.53–7.58 (m, 2 H), 7.63–7.68 (m, 1 H), and 7.86–7.89 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.0, 56.5, 61.4, 125.6, 128.6, 129.0, 129.1, 133.9, 137.9, and 167.6. Anal. Calcd for $C_{14}H_{16}O_6S$: C, 53.84; H, 5.16; S, 10.26. Found: C, 53.85; H, 5.17; S, 10.30.

Treatment of **5** in THF with a catalytic amount of *t*-BuOK for 12 h at 25 °C afforded methyl 2-carbomethoxy-3-[(phenylsulfonyl)methyl]-2-butenoate (**6**) in 98% yield: mp 84–85 °C; IR (KBr) 1730, 1310, 1160, 800, and 630 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.10 (s, 3 H), 3.45 (s, 3 H), 3.70 (s, 3 H), 4.50 (s, 2 H), 7.43–7.66 (m, 3 H), and 7.73–7.93 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.7, 52.1, 52.5, 59.8, 128.7, 128.9, 129.8, 133.8, 138.1, 143.5, 163.2, and 165.8. Anal. Calcd for $C_{14}H_{16}O_6S$: C, 53.84; H, 5.16; S, 10.26. Found: C, 53.70; H, 5.20; S, 10.17.

When the reaction was carried out using 9 mg of $PhSO_2Na$ instead of NaH, a mixture of **5** (70%) and compounds **14** (19%) and **15** (11%) was obtained. These two compounds were separated by silica gel chromatography. Structure **14** exhibited the following spectral properties: IR (neat) 1750, 1310, 1210, 1100, 860, and 670 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.83 (d, 2 H, J = 7.6 Hz), 3.69 (s, 6 H), 3.83 (t, 1 H, J = 7.6 Hz), 5.83 (s, 1 H), 6.41 (s, 1 H), 7.56 (t, 2 H, J = 7.3 Hz), 7.65 (t, 1 H, J = 7.3 Hz), and 7.88 (d, 2 H, J = 7.3 Hz); HRMS calcd for $C_{14}H_{16}O_6S$ 312.0667, found 312.0667. Anal. Calcd for $C_{14}H_{16}O_6S$: C, 53.83; H, 5.17. Found: C, 54.02; H, 5.11.

Structure **15** was a crystalline solid: mp 152–153 °C; IR ($CHCl_3$) 1740, 1310, 1210, 1090, and 700 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 2.96 (s, 4 H), 3.70 (s, 6 H), 5.69 (s, 2 H), 6.35 (s, 2 H), 7.55 (t, 4 H, J = 7.4 Hz), 7.64 (t, 2 H, J = 7.4 Hz), and 7.83 (d, 4 H, J = 7.4 Hz). Anal. Calcd for $C_{23}H_{24}O_8S_2$: C, 56.08; H, 4.91; S, 13.02. Found: C, 55.99; H, 4.98; S, 12.93.

An authentic sample of **15** was prepared in the following fashion. To a solution containing 0.10 mL of dimethyl malonate in 10 mL of THF at 0 °C under N_2 was added 1.04 mmol of *n*-BuLi dropwise via syringe. The mixture was stirred for 20 min at 0 °C, and then a solution containing 189 mg of 3-chloro-2-(phenylsulfonyl)-1-butene[37] in 2 mL of THF was rapidly added via syringe. The mixture was allowed to warm to rt and, after being stirred for 2 h, was poured into water and extracted with CH_2Cl_2. The organic extracts were washed successively with water and then a saturated NaCl solution. The organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude mixture was dissolved in 10 mL of THF and treated with 9 mg of sodium hydride. The resulting solution was stirred for 1 h at 25 °C under N_2. After standard aqueous workup, the residue was shown to contain 386 mg (90%) of compound **15**, which was identical with a sample prepared from the reaction of allene **1** with dimethyl malonate.

2,4,4-Tris(phenylsulfonyl)-1-butene (8). To a stirred solution containing 200 mg (1.1 mmol) of allene **1** and 329 mg of bis(phenylsulfonyl)methane in 50 mL of THF was added 5 mg of NaH. The reaction was stirred for 18 h at 25 °C under N_2. Concentration of the mixture under reduced pressure left a crude residue, which was subjected to silica gel chromatography. The first fraction contained 497 mg (94%) of **8**: mp 133–134 °C; IR (KBr) 1585, 1310, 1160, 725, and 620 cm^{-1}: NMR ($CDCl_3$, 300 MHz) δ 3.21 (d, 2 H, J = 6.0 Hz), 5.57 (t, 1 H, J = 6.0 Hz), 6.07 (s, 1 H), 6.49 (s, 1 H), 7.54 (t, 6 H, J = 7.7 Hz), 7.63–7.71 (m, 3 H), and 7.77–7.86 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.6, 80.1, 128.4, 129.2, 129.4, 131.0, 134.0, 134.6, 137.7, 138.2, and 143.2. Anal. Calcd for $C_{22}H_{20}O_6S_3$: C, 55.44; H, 4.23; S, 20.18. Found: C, 55.47; H, 4.26; S, 20.22.

The second fraction isolated from the column contained 21 mg (4%) of 1,1-bis(phenylsulfonyl)-2-[(phenylsulfonyl)methyl]-2-propene (**7**): mp 182–183 °C; IR (KBr) 1600, 1335, 1075, and 820 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.95 (s, 2 H), 5.26 (s, 1 H), 5.68 (s, 1 H), 5.91 (s, 1 H), 7.50–7.65 (m, 6 H), 7.65–7.75 (m, 3 H), and 7.92–8.05 (m, 6 H). Anal. Calcd for $C_{22}H_{20}O_6S_3$: C, 55.45; H, 4.23; S, 20.18. Found: C, 55.34; H, 4.24; S, 20.12.

An authentic sample of **8** was prepared in the following manner. To a solution containing 200 mg (0.8 mmol) of bis(phenylsulfonyl)methane in 10 mL of THF at 0 °C under N_2 was added 0.8 mmol of *n*-BuLi dropwise via syringe. The resulting yellow solution was stirred for 30 min at 0 °C, and then a solution containing 216 mg of 3-chloro-2-(phenylsulfonyl)-1-propene in 2 mL of THF was rapidly added. The resulting clear solution was allowed to warm to rt. After being stirred for 1 h, the reaction mixture was poured into water and extracted with CH_2Cl_2. The organic extracts were washed successively with water and then a saturated NaCl solution. The organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give **8** in 81% yield.

Methyl 2,4-Bis(phenylsulfonyl)-4-pentenoate (10). To a stirred solution containing 200 mg of allene **1** (1.1 mmol) and 238 mg of methyl(phenylsulfonyl)acetate in 5 mL of THF was added 4 mg of NaH. The reaction was stirred for 18 h at 25 °C under N_2. Concentration of the mixture under reduced pressure left a crude residue that was subjected to silica gel chromatography. The first fraction contained 307 mg (67%) of **10**: mp 113–114 °C; IR (neat) 1750, 1450, 1270, 1085, 965, 850, 755, and 695 cm^{-1};

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NMR ($CDCl_3$, 300 MHz) δ 2.84 (dd, 1 H, J = 14.6 and 2.9 Hz), 3.04 (dd, 1 H, J = 14.6 and 11.3 Hz), 3.61 (s, 3 H), 4.53 (dd, 1 H, J = 11.3 and 2.9 Hz), 5.88 (s, 1 H, 6.44 (s, 1 H), 7.52–7.69 (m, 5 H), 7.72–7.77 (m, 3 H), and 7.86–7.88 (m, 2 H). Anal. Calcd for $C_{18}H_{18}O_6S_2$: C, 54.81; H, 4.60; S, 16.26. Found: C, 54.89; H, 4.64; S, 16.18.

The second fraction isolated from the column contained 143 mg (33%) of methyl-3-[(phenylsulfonyl)methyl]-2-(phenylsulfonyl)-3-butenoate (**9**): mp 103–104 °C; IR ($CHCl_3$) 1750, 1455, 1330, 1155, 1030, and 630 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.67 (s, 3 H), 4.06 (s, 2 H), 5.03 (s, 1 H), 5.35 (s, 1 H), 5.64 (s, 1 H), 7.55 (t, 4 H, J = 7.5 Hz), 7.67 (q, 2 H, J = 7.5 Hz), and 7.84 (d, 4 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 53.1, 61.3, 72.7, 124.5, 128.4, 128.8, 129.1, 129.8, 130.3, 134.0, 134.5, 136.0, 137.8, and 164.4. Anal. Calcd for $C_{18}H_{18}O_6S_2$: C, 54.81; H, 4.60; S, 16.26. Found: C, 54.58; H, 4.64; S, 16.07.

When the reaction was repeated using 9 mg of $PhSO_2Na$ instead of NaH, a 4:1 ratio of **10** to **9** was obtained in 98% yield.

3,5,5-Tris(phenylsulfonyl)-2-pentene (18). To a stirred solution containing 500 mg (1.88 mmol) of bis(phenylsulfonyl)-methane and 328 mg of 3-(phenylsulfonyl)-1,2-butadiene (**16**)[38] in 20 mL of THF was added 4 mg of $PhSO_2Na$. The reaction was heated for 16 h at reflux under N_2 and then cooled to rt and concentrated under reduced pressure. The crude residue was subjected to silica gel chromatography using a 30% ethyl acetate–hexane mixture as the eluent. The first fraction contained 382 mg (46%) of 2-[bis(phenylsulfonyl)methyl]-3-(phenylsulfonyl)-1-butene (**17**): mp 78–79 °C; IR ($CHCl_3$) 1590, 1450, 1230, 1080, and 955 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.35 (d, 3 H, J = 7.0 Hz), 4.04 (q, 1 H, J = 7.0 Hz), 5.29 (s, 1 H), 5.78 (s, 1 H), 6.04 (s, 1 H), 7.48–7.58 (m, 6 H), 7.64–7.69 (m, 3 H), 7.87–7.90 (m, 2 H), 7.98–8.01 (m, 2 H), and 8.06–8.09 (m, 2 H). Anal. Calcd for $C_{23}H_{22}O_6S_3$: C, 56.31; H, 4.52. Found: C, 56.36; H, 4.58.

The second fraction contained 380 mg (46%) of **18** as a white solid: mp 161–162 °C; IR ($CHCl_3$) 1650, 1450, 1300, and 1120 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.02 (d, 3 H, J = 7.2 Hz), 3.22 (d, 2 H, J = 6.4 Hz), 5.84 (t, 1 H, J = 6.4 Hz), 7.18 (q, 1 H, J = 7.2 Hz), and 7.46–7.79 (m, 15 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.3, 21.6, 78.9, 127.9, 128.9, 129.0, 129.2, 133.4, 134.4, 134.8, 138.2, 138.6, and 144.1. Anal. Calcd for $C_{23}H_{22}O_6S_3$: C, 56.31; H, 4.52. Found: C, 56.39; H, 4.54.

A solution containing 1.0 g of 3-(phenylsulfonyl)-1,2-butadiene (**16**), 2.54 g of benzenesulfinic acid sodium salt, and 0.32 mL of glacial acetic acid in 10 mL of tetrahydrofuran was heated at reflux for 12 h. The solution was cooled to room temperature and filtered through a Celite pad. The organic solution was washed with brine and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave 1.47 g (85%) of a white solid, mp 137–138 °C, which was identified as (*E*)-1,2-bis(phenylsulfonyl)-2-butene (**20**) on the basis of its spectral properties: IR (CCl_4) 1645, 1450, 1150, and 870 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.97 (d, 3 H, J = 7.2 Hz), 4.21 (s, 2 H), 7.37 (q, 1 H, J = 7.2 Hz), 7.49–7.69 (m, 6 H), and 7.77–7.82 (m, 4 H). Anal. Calcd for $C_{16}H_{16}O_4S$: C, 57.12; H, 4.79. Found: C, 56.90; H, 4.80.

1-(Phenylsulfonyl)-4-cyanocyclopent-1-ene (29). To a stirred solution containing 200 mg (1.1 mmol) of allene **1** and 15 equiv of acrylonitrile in 5 mL of THF was added 5 mol % of $PhSO_2Na$. The reaction was stirred for 14 h at 25 °C under N_2. Removal of the solvent was followed by silica gel chromatography. The major compound (73%) was 1-(phenylsulfonyl)-4-cyanocyclopent-1-ene (**29**): IR (neat) 2245, 1625, 1315, 780 and 695 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.78–3.08 (m, 4 H), 3.24–3.36 (m, 1 H), 6.68 (br s, 1 H), 7.57 (t, 2 H, J = 7.5 Hz), 7.67 (t, 1 H, J = 7.5 Hz), and 7.88 (d, 2 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.5, 35.6, 37.7, 120.9, 128.0, 129.5, 134.1, 138.5, 139.7, and 143.4; HRMS calcd for $C_{12}H_{11}NO_2S$ 233.0511, found 233.0506. Anal. Calcd for $C_{12}H_{11}NO_2S$: C, 61.79; H, 4.76; N, 6.01. Found: C, 61.68; H, 4.55; N, 6.09.

1-[3-(Phenylsulfonyl)-3-cyclopenten-1-yl]ethanone (30). To a stirred solution containing 200 mg of allene **1** (1.1 mmol) and 0.09 mL of methyl vinyl ketone in 5 mL of THF was added 5 mol % of $PhSO_2Na$. The reaction was stirred for 14 h at 25 °C under N_2. Removal of the solvent was followed by silica gel chromatography. Two products were isolated from the silica gel column. The first component (51%) consisted of 1-[3-(phenylsulfonyl)-3-cyclopenten-1-yl]ethanone (**30**) as a light yellow oil: IR (neat) 1720, 1590, 1155, and 695 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.11 (s, 3 H), 2.65–2.90 (m, 4 H), 3.34–3.45 (m, 1 H), 6.63 (br s, 1 H), 7.53 (t, 2 H, J = 7.5 Hz), 7.63 (t, 1 H, J = 7.5 Hz), and 7.87 (d, 2 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.2, 32.7, 34.6, 50.0, 127.7, 129.2, 133.5, 138.9, 104.8, 142.6, and 206.7; HRMS calcd for $C_{13}H_{14}O_3S$ 250.0664, found 250.0673. Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.17; H, 5.57.

The second component isolated from the column (25%) was identified as 5-(phenylsulfonyl)-5,6-heptadien-2-one (**31**): IR (neat) 1980, 1720, 1320, 860, and 735 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.08 (s, 3 H), 2.44–2.50 (m, 2 H), 2.60–2.65 (m, 2 H), 5.36–5.38 (m, 2 H), 7.53 (t, 2 H, J = 7.5 Hz), 7.62 (t, 1 H, J = 7.5 Hz), and 7.88 (d, 2 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.7, 29.6, 40.5, 84.6, 111.9, 127.6, 128.9, 133.4, 139.5, 205.9, and 207.1; HRMS calcd for $C_{13}H_{14}O_3S$ 250.0664, found 250.0666. Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.05; H, 5.41.

1-[3-(Phenylsulfonyl)-3-cyclopenten-1-yl]propanone (32). To a stirred solution containing 400 mg of allene **1** (2.2 mmol) and 0.24 mL of ethyl vinyl ketone in 10 mL of THF was added 168 mg of 5 mol % of $PhSO_2Na$. The reaction was stirred for 14 h at 25 °C under N_2. Removal of the solvent was followed by silica gel chromatography. The major fraction contained 458 mg (78%) of 1-[3-(phenylsulfonyl)-3-cyclopenten-1-yl]propanone (**32**) as a light yellow oil: IR (neat) 1715, 1450, 1160, and 695 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, 3 H, J = 7.2 Hz), 2.31 (q, 2 H, J = 7.2 Hz), 2.58–2.73 (m, 4 H), 3.27–3.37 (m, 1 H), 6.53 (s, 1 H), 7.41–7.54 (m, 3 H), and 7.75–7.77 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.4, 32.8, 34.1, 34.8, 48.7, 127.5, 129.0, 133.4, 138.8, 140.0, 142.4, and 209.5; HRMS calcd for $C_{14}H_{16}O_3S$ 264.0820, found 264.0825. Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.62; H, 6.11. Found: C, 63.44; H, 5.93.

5-Cyano-5,6-heptadien-2-one (37). To a stirred solution containing 500 mg (7.7 mmol) of 1-cyano-2,3-propadiene[39] (**35**) and 0.64 mL of methyl vinyl ketone in 70 mL of THF was added 5 mg of NaOMe. The resulting solution was stirred for 14 h under N_2 at 25 °C. Removal of the solvent under reduced pressure left a crude residue that was purified by distillation at 200 °C (0.3 mm). The resulting pale yellow oil (920 mg, 89%) was identified as 5-cyano-5,6-heptadien-2-one (**37**) on the basis of its spectral properties: IR (neat) 2240, 1980, 1715, 1375, 1020, and 880 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.18 (s, 3 H), 2.40–2.51 (m, 2 H), 2.62–2.70 (m, 2 H), and 5.21–5.23 (m, 2 H); HRMS calcd for C_8H_9NO 135.0684, found 135.0683. Anal. Calcd for C_8H_9NO: C, 71.08; H, 6.72; N, 10.37. Found: C, 70.96; H, 6.63; N, 10.32.

5-Methyl-5-(phenylsulfonyl)hept-6-yn-2-one (38). To a stirred solution containing 200 mg (1.1 mmol) of 1-methyl-1-(phenylsulfonyl)allene (**16**) and 0.09 mL of methyl vinyl ketone in 10 mL of THF was added 8 mg of $PhSO_2Na$. The resulting solution was heated under N_2 at 67 °C for 13 h. The reaction was cooled to rt, and the solvent was removed under reduced pressure. The crude residue was diluted with CH_2Cl_2, and the mixture was washed with water followed by a saturated NaCl solution. The organic layer was dried ($NaSO_4$), filtered, and concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave 122 mg (45%) of alkyne **38**: mp 86–87 °C; IR (CCl_4) 1730, 1560, 1160, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.51 (s, 3 H), 2.15 (s, 3 H), 2.07–2.31 (m, 2 H), 2.51 (s, 1 H), 2.65–2.87 (m, 2 H), 7.53–7.58 (m, 2 H), 7.65–7.70 (m, 1 H), and 7.95–7.98 (m, 2 H); HRMS calcd for $C_{14}H_{16}O_3S$ 264.0820, found 264.0819. Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.62; H, 6.11. Found: C, 63.51; H, 6.04.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health (CA-26750). Use of the high-field NMR spectrometer used in these studies was made possible through equipment grants from the NIH and NSF.

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