Cyclization Reactions of 2,3-Bis(phenylsulfonyl)-1,3-butadiene with Various Carbanions. A [4 + 1] Anionic Annulation Approach to Phenylsulfonyl-Substituted Cyclopentenes†

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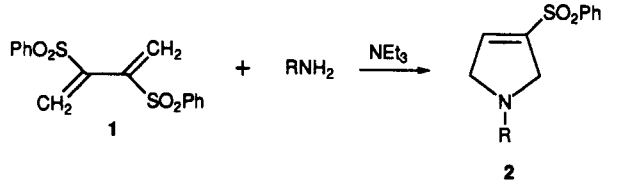
2,3-Bis(phenylsulfonyl)-1,3-butadiene undergoes conjugate addition in the presence of carbanions giving rise to a variety of unsaturated sulfones. Reaction with lithium enolates proceeds *via* an allylic anionic intermediate which undergoes a subsequent elimination of phenylsulfinate anion to produce an allene. Generation of enolates from silyl enol ethers results in conjugate addition to the diene without subsequent elimination. Substituted cyclopentenyl sulfones are available *via* a [4 + 1] annulation reaction of the diene with various distabilized carbanions. The reaction involves a tandem addition–proton exchange–addition sequence. In the special case of 2,4-pentanedione, pyrans are formed, the isomeric identity of which depends upon the reaction conditions. 2-Alkylated 1,3-dicarbonyl compounds react with the activated diene to produce substituted allenes in high yield. Phenylsulfonyl alkenyl substituted allenes were conveniently prepared by a similar protocol and were found to serve as substrates for intramolecular [2+2] cycloaddition chemistry.

With the development of several general routes to unsaturated sulfones has come an increasing appreciation of their potential as synthetic intermediates.[1-15] Unsaturated sulfones owe their attractiveness in part to the uncommon amalgamation of chemical properties.[1] Individual facets of their manifold reactivity may be invoked selectively, either by variation of reaction conditions or by choice of a particular substrate. Most methodology employing unsaturated sulfones are based on the sulfonyl group's electron-withdrawing character. When appended to an olefinic moiety, the sulfonyl group effects significant polarization of the double bond, making it susceptible to a host of addition reactions.[16] After the desired transformations have taken place, the sulfonyl group provides a convenient site for further elaboration; or it is easily removed, either by simple elimination or by oxidative[17] or reductive desulfonylation.[18]

In connection with our program dealing with the chemistry of unsaturated sulfones,[19] we have been exploring the chemical reactivity of 2,3-bis(phenylsulfonyl)-1,3-butadiene (1) as a versatile building block in organic synthesis, particularly for [4 + 2] cycloaddition chemistry.[20] Bis(phenylsulfonyl) diene 1 is a crystalline compound, is easily prepared,[21] and possesses indefinite shelf-life, adding to its attractiveness as a synthetic reagent. In an earlier report, we demonstrated that this diene is an extremely useful reagent for pyrrolidine formation, since



it is highly activated toward nucleophilic addition by amines.[22] While the reaction of 1 with other heteronucleophiles has been studied in some detail,[22] there have been no examples of carbon–carbon bond forming reactions of 1 with carbon-based nucleophiles. Toward this end, we have used diene 1 as a key reagent for a [4 + 1] annulation approach to substituted cyclopentenes.[23] The present paper documents the results of these studies.

† This paper is dedicated to Professor Harry M. Walborsky on the occasion of his 70th birthday.

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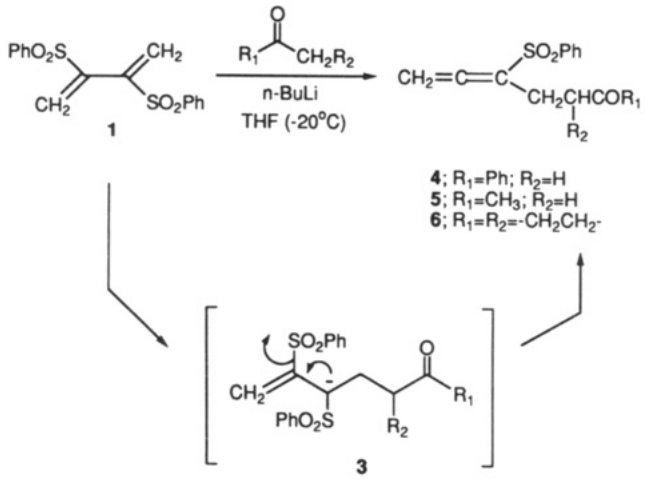
Scheme 1

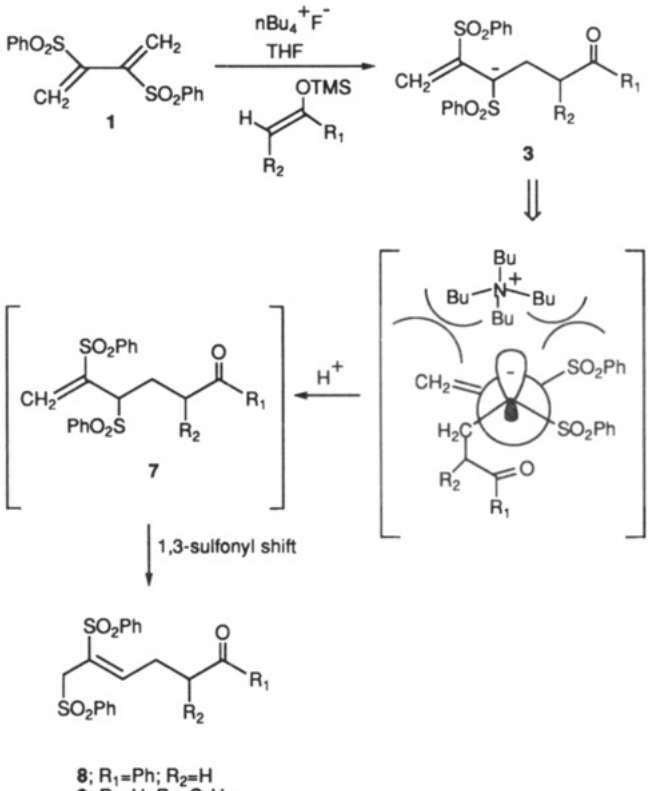


Results and Discussion

A. Behavior toward Enolates. The pivotal step in our annulation strategy involves addition of a carbanion onto the highly activated π-bond of diene **1**. We began our studies by examining the reaction of **1** with several enolate anions. Bis(phenylsulfonyl) diene **1** reacts with lithium enolates in a one-sided Michael addition to form allenes of type **4–6** (Scheme 1). This process most likely proceeds through an allylic anion intermediate **3** which undergoes subsequent elimination of phenylsulfinate ion. Thus, treatment of an equimolar mixture of acetophenone and 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) with *n*-butyllithium in THF at −20 °C results in the formation of (phenylsulfonyl) allene **4** in 60% yield. Analogous products (**5** and **6**) are observed when acetone and cyclohexanone are used, respectively.

A curious alteration in the course of the reaction occurs when the enolate is generated *via* the silyl enol ether (Scheme 2). In these cases, the resulting products retain both phenylsulfonyl groups. This crossover in behavior probably occurs at the stage of the sulfonyl-stabilized carbanion **3**. The larger tetrabutyl ammonium counterion may impose a rotational barrier which prohibits the synclinal or antiperiplanar geometry necessary for elimination. With this pathway effectively blocked, the anion is simply protonated with some H_2O present in solution to give an allylic bis-sulfone (*i.e.*, **7**) which, poised for a 1,3-sulfonyl shift, isomerizes to the observed product (*i.e.*, **8–11**). Earlier work in our laboratory[24] as well as Whitham[25] and others[26–35] has established that substituted acyclic allylic sulfones readily undergo a 1,3-sulfonyl shift

Scheme 2



thereby providing good precedent for the last step in Scheme 2.

B. Formation of Cyclopentenes. The biological importance and tremendous diversity of cyclopentanoid natural products have made these compounds important synthetic goals and have stimulated the development of new methods and reagents for the preparation of cyclopentene rings.[36,37] Several successful approaches have been designed through free radical intermediates,[38] ring expansion of three-[39] or four-membered[40] carbocycles, [3 + 2] cycloadditions,[41] [4 + 1] annulations,[42] and cyclization methods forming more than one bond in a single step using transition metal complexes.[43]

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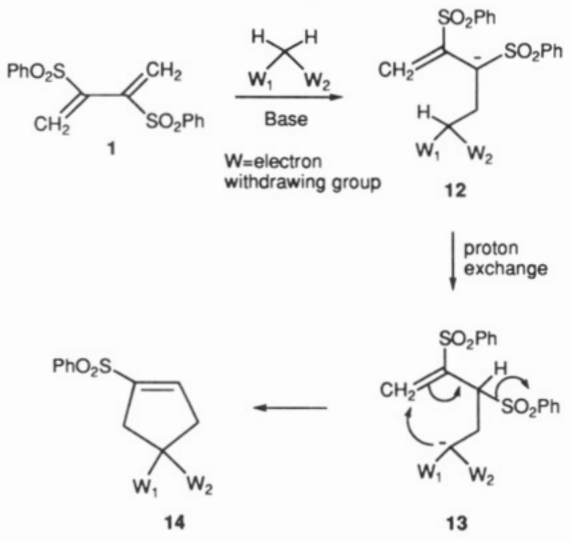
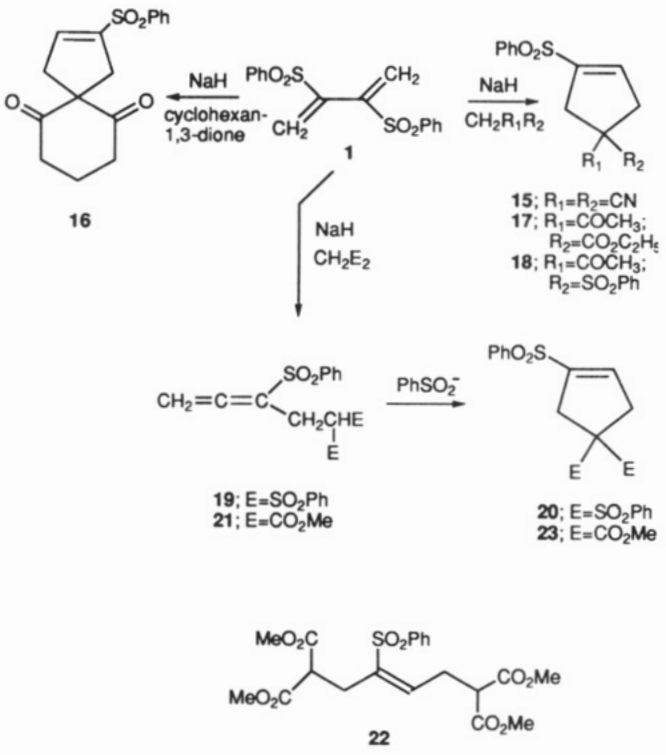
Scheme 3



Our interest in the reaction of bis(phenylsulfonyl) diene **1** with nucleophiles led us to develop a synthetic route toward cyclopentenyl sulfones. We envisaged a simple "one-pot" annulation sequence based on the tandem *addition–proton exchange–addition* protocol outlined in Scheme 3. The approach centers on the initial conjugate addition of a distabilized carbanion onto the highly activated π-bond of **1**. The resulting sulfonyl-stabilized carbanion **12** can be internally quenched *via* a proton shift to give a new carbanion **13**. The stage is now set for cyclopentene formation by a second conjugate addition. One might expect some difficulties with this latter step, as the ring closure is of the disfavored 5-*endo*-*trig* variety.[44] However, the literature supports the viability of this process in similar systems.[41,45] Indeed, we find this sequence proceeds smoothly for the majority of our substrates to provide sulfonyl-substituted cyclopentenes **14**.

We began our studies by examining the reaction of **1** with malonitrile in the presence of a slight excess of NaH in THF at 25 °C. The major product formed corresponded to cyclopentene **15** (60%). Similarly, treatment of diene **1** with cyclohexane-1,3-dione in the presence of NaH (THF) gave rise to the related spirocyclopentene **16** in 70% yield. An analogous cyclization reaction occurred using ethyl acetoacetate and phenylsulfonyl acetone producing cyclopentenes **17** and **18** in 60 and 75% yield, respectively. Interestingly, the reaction of **1** with bis(phenylsulfonyl)methane (NaH/THF) afforded allene **19** as the exclusive product in 75% isolated yield. When **19** was allowed to stir for longer periods of time in the presence of a catalytic amount of sodium benzenesulfinate, it was quantitatively transformed into cyclopentene **20**. Since we were interested in the mechanism by which **19** was converted to **20**, we studied the analogous reaction of **1** with dimethyl malonate. In this case, allene **21** is produced (50%) along with the diaddition product **22** (20%). More than likely the 5-*endo*-*trig* ring closure (*i.e.*, **13** → **14**) is hindered by the steric requirements of two methoxycarbonyl or phenylsulfonyl groups in an already demanding transition state environment (*cf.* **24**).[46]



The initially formed (phenylsulfonyl) allene is highly activated toward nucleophilic addition because of its low-lying LUMO energy level.[47] On treatment of **21** with a catalytic amount of sodium benzenesulfinate in acetonitrile at 25 °C, it was converted into cyclopentene **23** in excellent yield. Under these conditions, addition of phenylsulfinate anion onto the allene sets up an equilibrium process which allows for the reversion of allene **21** (or **19**) to the distabilized anion **13**. The equilibrium conditions, combined with the enhancement of conjugate addition by the more polar reaction medium,[48] results in the formation of the cyclopentene ring. Under the conditions used with dimethyl malonate, carbanion **13** is protonated, producing **25** which undergoes a subsequent addition/elimination reaction with dimethyl malonate anion to produce the diaddition product **22** as a minor reaction component.

C. Formation of Pyrans. An interesting anomaly in the reaction of diene **1** with active methylene compounds occurs when 2,4-pentanedione is used as the substrate. Here a 1:1 mixture of cyclopentene **26** and allene **27** is observed. In contrast with allenes **19** and **21**, the pentanedione derivative **27** is not equilibrated to the cyclopentene ring (*i.e.*, **26**) on treatment with sodium benzenesulfinate. Instead of adding across the activated double bond of the allene as in the previous cases, the benzenesulfinate anion abstracts the highly acidic methine

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(45) Tarnchompoo, B.; Thebtaranonth, C.; Thebtaranonth, Y. *Tetrahedron Lett.* **1987**, 6675.

(46) Significant nonbonded interactions in the transition state for ring closure are presumably present with the methoxycarbonyl and phenylsulfonyl groups thereby resulting in allene rather than cyclopentene formation.

24; R=CO_2CH_3 or SO_2Ph

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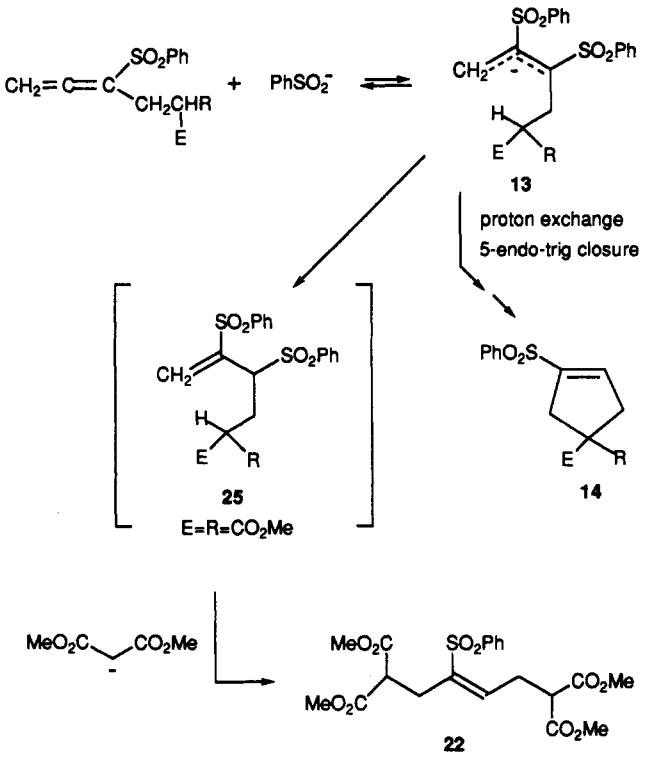
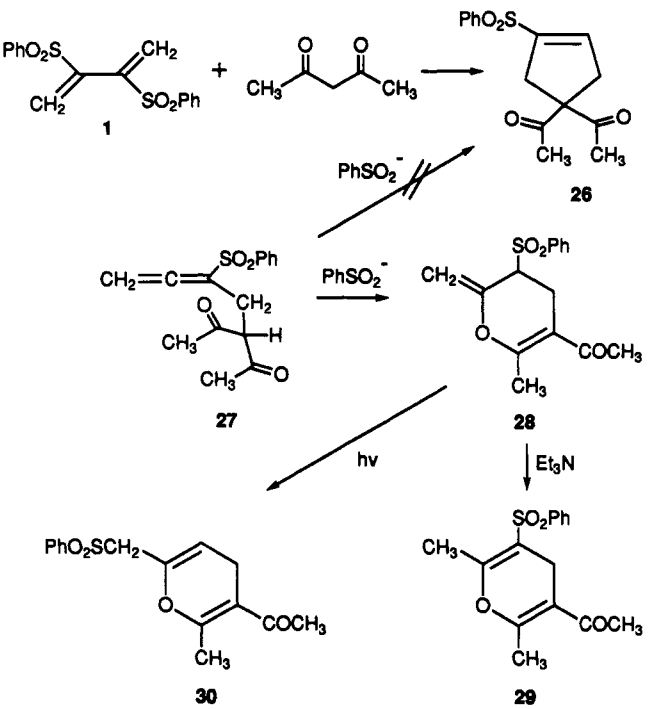
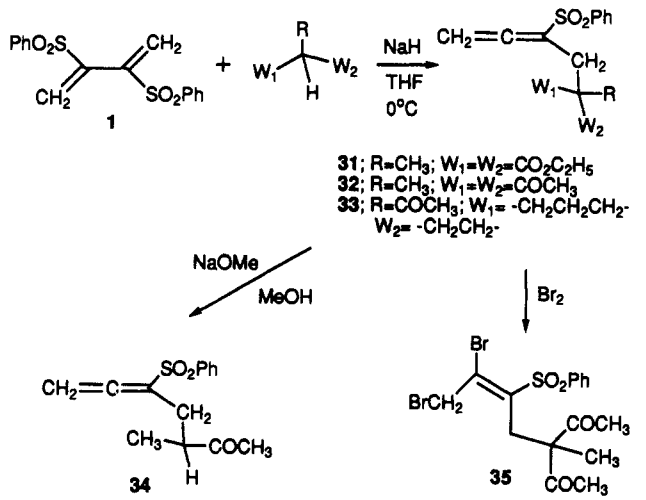


hydrogen. The resulting enolate then cyclizes on the



oxygen atom to give dihydro-4*H*-pyran **28** in 90% yield. Further treatment of **28** with triethylamine afforded the isomerized pyran **29** which is derived by a 1,3-proton shift. Interestingly, a 1,3-sulfonyl shift was found to occur when we subjected **28** to bright light. An alternate way to induce the rearrangement was to heat dihydro-4*H*-pyran **28** in benzene. 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 **30**. Clearly the isomerization of dihydro-4*H*-pyran **28** is markedly dependent upon the reaction conditions.

D. Behavior toward 2-Alkyl-1,3-Dicarbonyls. Intrigued by the subtleties in reaction of bis(phenylsulfonyl) diene **1** with various diactivated anions, we decided to examine the effect of blocking the second deprotonation by using monoalkylated dicarbonyl substrates. With no active hydrogen present in their addition products, many of the reaction pathways previously seen are not available. Indeed, the only viable process under these conditions appears to be the elimination of phenylsulfinate, resulting in the smooth formation of the phenylsulfonyl allenes **31**–**33**. These products contain an array of functionality which can be independently manipulated. For example, the



dicarbonyl adduct **32** undergoes smooth deacetylation in the presence of sodium methoxide without suffering involvement from the electrophilic allene center, thus providing dienone **34**. In addition, the allene moiety can be brominated to give dibromide **35** which retains the dione intact.

Allenes are particularly versatile in cycloaddition chemistry since the 10 kcal of strain associated with the cumulated double bond is relieved when the allene undergoes any kind of addition reaction.[49] Indeed, the [2 + 2] cycloaddition between an allene and an alkene has frequently been employed for the preparation of methylenecyclobutane derivatives.[49,50] The intramolecular [2 + 2] cycloaddition of allenes has also been studied,[51] and this process constitutes a particularly versatile method for the stereocontrolled synthesis of a variety of functionalized polycyclic compounds. Since the reaction of bis(phenylsulfonyl) diene **1** with dimethyl monoalkylmalonates proceeded so readily, we decided to extend this reaction with the intention of preparing a series of alkenyl-substituted allenes so as to investigate their thermal [2 + 2] cycloaddition behavior. With this in mind we examined the base induced reaction of diene **1** with 4,4-dicarbomethoxy-1-butene. This resulted in a 2:1-mixture of allene **38** (52%) and diene **39** (30%). The formation of **39**

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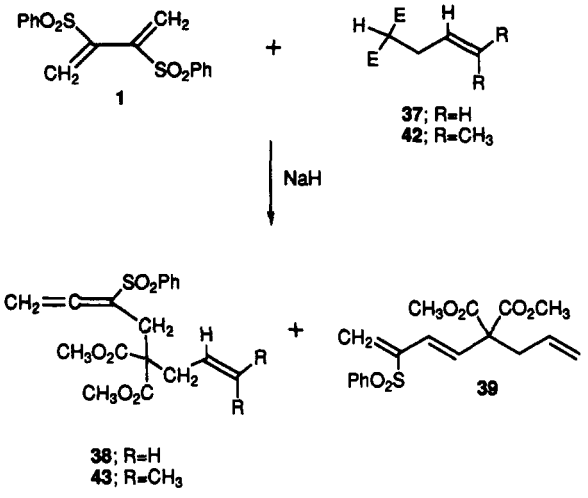
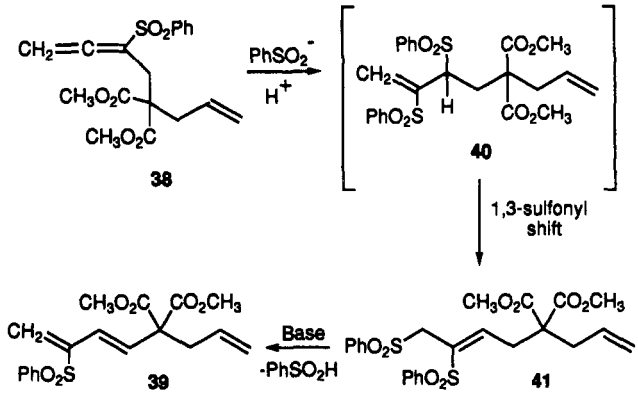
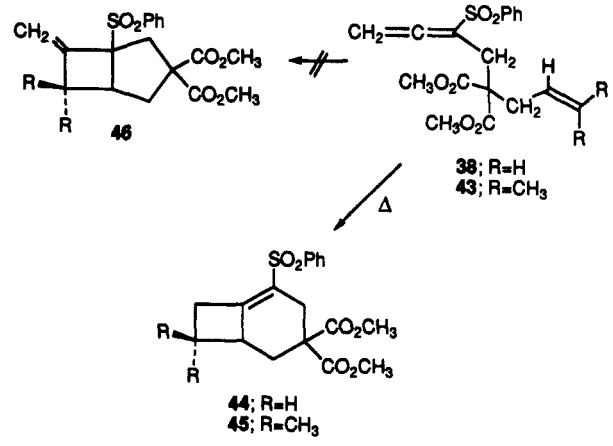


was somewhat unexpected since we had not previously encountered products of this type. A reasonable mechanism to account for its formation involves initial conjugate addition of the anion derived from **37** with diene **1**. The resulting adduct is quenched by acid on workup to give **40** which undergoes a ready 1,3-sulfonyl shift to afford the thermodynamically more stable product **41**. This substrate undergoes a subsequent 1,4-elimination of benzenesulfinic acid to give **39**. Another possibility is that benzenesulfinate anion engages in conjugate addition across the activated allene π-bond of **38** to eventually produce **39**, *via* intermediates **40** and **41**. Indeed, we found that the reaction of **38** with sodium benzenesulfinate in aqueous acetic acid smoothly afforded octa-1,6-diene **41**

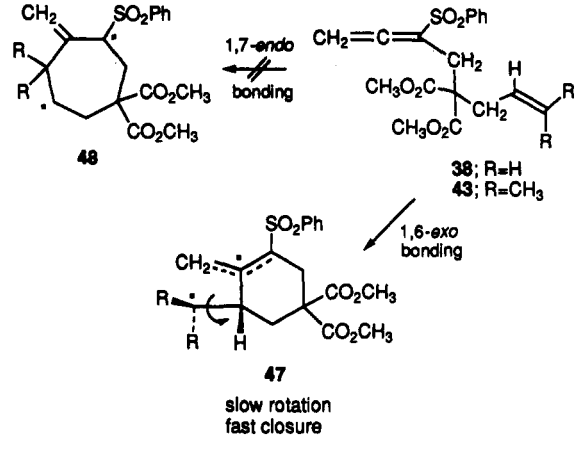


in 73% yield. When **41** was treated with base, it was converted to diene **39**.

E. Intramolecular Cycloaddition Behavior. The thermal reaction of allene **38** and the closely related prenyl analog **43** (prepared from **1** + **42** → **43**) was carried out by heating the reactants in xylene. The only products formed in both cases corresponded to the [2 + 2] cycloadducts **44** and **45** in 90 and 85% yield, respectively. It is particularly interesting to note that only the C_1–C_2 double bond of the allene participates in the cycloaddition. This result is somewhat surprising since phenylsulfonyl-substituted allenes react with various 4π-systems in a highly chemoselective fashion undergoing cycloaddition across the C_2–C_3 activated π-bond.[47] We believe that the high periselectivity observed is related to stereoelectronic factors. The primary spatial requirement for [2 + 2] cycloaddition is that the distance between the C_2 carbon of the allene and the olefinic π-bond should be sufficiently close that effective overlap of the π-systems can occur. Evidently, it is easier for stepwise bonding to occur in a 1,6-*exo* manner

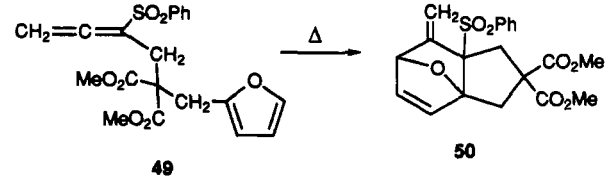


(leading to diradical **47**) than in a 1,7-*endo* fashion. The periselectivity encountered with these systems suggests that the reaction proceeds in a stepwise manner, since a concerted cycloaddition should have been expected to occur preferentially across the more activated π-bond of the allene. Since the allene adduct **47** contains two orthogonally twisted π-bonds, the initially formed allyl radical is also orthogonally twisted. Considering the lack



of significant stabilization of the nonallylic part of the diradical intermediate, it might be expected to cyclize rapidly, thereby accounting for the high stereoselectivity observed. In fact, rotation of the allylic radical site might well be subject to considerable barriers. The regioselectivity is probably due to efficient radical stabilization by the $PhSO_2$ group, which, unlike RCO_2, is free from anisotropic constraints of π-overlap.

To further illustrate the scope and synthetic utility of the intramolecular cycloaddition reaction of phenylsulfonyl alkenyl substituted allenes, we examined the thermal behavior of furanyl allene **49**. In this case, even though there is a potential competition between the [2 + 2] and [4 + 2] process, only the Diels–Alder adduct **50** was observed. This result is consistent with the general observation of Kanematsu that furanyl-substituted allenes readily undergo Diels–Alder chemistry.[51]



In conclusion, the work reported herein establishes the utility of 2,3-bis(phenylsulfonyl)-1,3-butadiene as a useful

reagent for the preparation of various unsaturated sulfones. Substituted cyclopentenyl sulfones are available *via* a [4 + 1] annulation reaction of the diene with various distabilized carbanions. Monoalkyl substituted dicarbonyl anions react with the activated diene to give phenylsulfonyl allenes *via* a conjugate addition–elimination sequence. Phenylsulfonyl alkenyl substituted allenes were found to undergo an intramolecular [2 + 2] cycloaddition reaction. Other aspects of the [4 + 1] annulation approach and further mechanistic details of the intramolecular [2 + 2] cycloaddition reaction will appear in forthcoming papers.

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.

Preparation of 6-Phenyl-3-(phenylsulfonyl)-1,2-hexadien-6-one (4). To a stirred solution containing 0.07 g (0.60 mmol) of acetophenone in 10 mL of anhydrous THF at −20 °C under N_2 was added 0.36 mL of a 1.48 M solution of *n*-butyllithium in THF dropwise *via* syringe. The mixture was maintained at −20 °C with stirring for 30 min, and then 0.20 g (0.60 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) in 5 mL of THF was slowly added. The reaction was allowed to warm to rt over a 30-min period and then a saturated NH_4Cl solution was added. The reaction mixture was extracted with CH_2Cl_2 and washed with water. The organic layer was collected and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. Silica gel chromatography gave 0.11g (60%) of a clear oil which was identified as **4** on the basis of its spectral data: IR (neat) ν 1965, 1706, 1310, and 727 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 2.70 (m, 2H), 3.20 (t, 2H, J = 7.2 Hz), 5.35 (t, 2H, J = 3.4 Hz), and 7.40–7.95 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.7, 36.3, 84.8, 112.4, 127.9, 128.1, 128.6, 129.2, 133.3, 133.6, 134.0, 136.5, 197.8, and 207.7; HRMS calcd for $C_{18}H_{16}O_3S$, 312.0820, found 312.0806.

Preparation of 3-(Phenylsulfonyl)-1,2-heptadien-6-one (5). To a stirred solution containing 0.09 mL (0.72 mmol) of diisopropylamine in 10 mL of anhydrous THF at −78 °C under N_2 was added 0.41 mL of a 1.48 M solution of *n*-butyllithium in THF. The reaction was allowed to warm to −20 °C and 0.05 mL (0.60 mmol) of acetone was added *via* syringe. After stirring for 15 min at −20 °C, the solution was cooled to −40 °C and 0.20 g (0.60 mmol) of diene **1** in 5 mL of dry THF was slowly added. After an additional 30 min of stirring at −40 °C, the solution was allowed to warm to rt and a saturated solution of NH_4Cl was added. The reaction mixture was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The crude residue was subjected to silica gel chromatography to give 0.12 g (80%) of **5** as a colorless oil: IR (neat) ν 1972, 1716, 1310, and 727 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 2.10 (s, 3H), 2.50 (m, 2H), 2.65 (t, 2H, J = 7.1 Hz), 5.35 (t, 2H, J = 3.4 Hz), and 7.45–7.80 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.1, 29.9, 41.0, 84.7, 112.3, 128.1, 129.2, 133.6, 139.9, 206.2, and 207.5; HRMS calcd for $C_{13}H_{14}O_3S$ 250.0664, found 250.0662.

Preparation of 2-[2-(Phenylsulfonyl)-2,3-butadienyl]cyclohexanone (6). The experimental procedure used for the preparation of **4** was repeated using the following reagents: 0.06 mL (0.60 mmol) of cyclohexanone, 0.45 mL of a 1.48 M solution of *n*-butyllithium, and 0.20 g (0.60 mmol) of diene **1**. Silica gel chromatography afforded 0.09 g (55%) of a clear oil which was identified as **6** from its spectral data: IR (neat) ν 1973, 1706, 1305, and 719 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.20–2.40 (m, 9H), 2.50 (sex, 1H, J = 6.3 Hz), 2.65 (ddt, 1H, J = 18.3, 12.3, and 3.0 Hz), 5.35 (q, 2H, J = 3.0 Hz), and 7.50–7.85 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 24.9, 27.1, 27.8, 33.6, 41.9, 48.6, 84.1, 111.1, 127.9, 129.0, 133.5, 139.9, 208.1, and 210.8; HRMS calcd for $C_{16}H_{18}O_3S$ 290.0977, found 290.0972.

Preparation of 6-Phenyl-1,2-bis(phenylsulfonyl)-2-hexen-6-one (8). To a 0 °C stirred solution containing 0.20 g (0.60 mmol) of diene **1** and 0.12 mL of 2-[(trimethylsilyl)oxy]styrene in 10 mL of anhydrous THF under N_2 was added 0.60 mL of a 1.0 M solution of tetrabutylammonium flouride in THF *via* syringe. The solution was allowed to warm to rt over a 25-min period and then 10 mL of water was added. The reaction mixture was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Recrystallization of the residue from CH_2Cl_2–hexane gave 0.16 g (60%) of a white solid, mp 132–133 °C, identified as **8** on the basis of its spectral properties: IR (neat) ν 1702, 1625, 1442, and 1139 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 2.80 (q, 2H, J = 6.7 Hz), 3.25 (t, 2H, J = 6.7 Hz), 4.35 (s, 2H), 7.30 (t, 1H, J = 7.8 Hz), and 7.40–7.90 (m, 15H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 24.7, 36.4, 53.8, 128.2, 128.3, 128.7, 129.1, 129.3, 132.1, 133.4, 133.5, 134.1, 136.2, 139.0, 139.3, 150.8, and 197.8. Anal. Calcd for $C_{24}H_{22}O_5S$: C, 63.42; H, 4.88; S, 14.08. Found: C, 63.22; H, 4.93; S, 14.00.

Preparation of 2-Ethyl-5,6-bis(phenylsulfonyl)-4-hexenal (9). To a 0 °C stirred solution containing 0.20 g (0.60 mmol) of diene **1** and 0.09 g (0.60 mmol) of 1-[(trimethylsilyl)oxy]butene in 10 mL of anhydrous THF under N_2 was added 0.60 mL of a 1.0 M solution of tetrabutylammonium fluoride in THF *via* syringe. The solution was allowed to warm to rt over a 25-min period and then 10 mL of water was added. The reaction mixture was extracted with CH_2Cl_2 and washed again with water. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Silica gel chromatography of the crude reaction mixture gave 0.14 g (60%) of **9** as a pale yellow oil: IR (neat) ν 1736, 1573, 1305, and 1140 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, 3H, J = 7.4 Hz), 1.45–2.60 (m, 5H), 4.35 (bs, 1H), 4.60 (bs, 1H), 7.20 (t, 1H, J = 7.5 Hz), 7.40–7.95 (m, 10H), and 9.60 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 11.2, 24.4, 29.1, 34.0, 65.0, 128.0, 128.8, 129.1, 132.6, 133.2, 134.1, 139.0, 152.0, and 190.2; HRMS calcd for $C_{14}H_{17}O_3S$ (M^+ − $SO_2C_6H_5$) 265.0898, found 265.0892.

Preparation of 2-[3,4-Bis(phenylsulfonyl)-2-butenyl]cyclopentanone (10). An identical procedure used for the preparation of **8** was followed except for the following reagents: 0.20 g (0.60 mmol) of diene **1**, 0.11 mL (0.60 mmol) of 1-[(trimethylsilyl)oxy]cyclopentene and 0.60 mL of a 1.0 M solution of tetrabutylammonium flouride in THF. Standard workup followed by silica gel chromatography yielded 0.17 g (70%) of a pale yellow oil identified as **10** on the basis of its spectral data: IR (neat) ν 1979, 1709, 1623, and 1139 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.70–2.25 (m, 7H), 2.40 (m, 1H), 2.60 (m, 1H), 4.20 (s, 2H), 7.25 (t, 2H, J = 7.3 Hz), and 7.45–7.95 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 20.6, 29.2, 29.9, 37.5, 48.1, 53.8, 128.2, 128.4, 129.2, 132.5, 133.6, 134.2, 138.9, 139.4, 149.8, and 218.9; HRMS calcd for $C_{15}H_{17}O_3S$ (M^+ − $SO_2C_6H_5$) 277.0898, found 277.0904.

Reaction of 2,3-Bis(Phenylsulfonyl)-1,3-butadiene (1) with 1-[(Trimethylsilyl)oxy]cyclohexene. The experimental procedure used for the preparation of **8** was repeated using the following reagents: 0.20 g (0.60 mmol) of diene **1**, 0.12 mL (0.60 mmol) of 1-[(trimethylsilyl)oxy]cyclohexene, and 0.6 mL of a 1.0 M solution of tetrabutylammonium fluoride in THF. Standard workup followed by flash silica gel chromatography gave 0.12 g (70%) of a clear oil which was identified as 2-[3,4-bis(phenylsulfonyl)-2-butenyl]cyclohexanone (**11**) from its spectral properties: IR (neat) ν 1715, 1581, 1310, and 1142 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.40–2.40 (m, 8H), 2.55 (m, 3H), 2.60 (dd, 2H, J = 7.5 and 6.8 Hz), 4.20 (d, 1H, J = 15.0 Hz), 4.55 (d, 1H, J = 15.0 Hz), 7.20 (t, 1H, J = 7.5 Hz), and 7.45–7.80 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 25.0, 27.7, 30.3, 34.2, 41.9, 49.7, 53.8, 128.0, 128.2, 129.0, 129.2, 131.7, 133.4, 134.0, 138.9, 139.4, 150.5, and 211.0; HRMS calcd for $C_{16}H_{19}O_3S$ (M^+ − $SO_2C_6H_5$) 291.1055, found 291.1061.

Preparation of 4,4-Dicyano-1-(phenylsulfonyl)-1-cyclopentene (15). To a stirred ice-cold suspension containing 0.03 g (0.78 mmol) of 60% NaH in 10 mL of THF under N_2 was added 0.04 g (0.60 mmol) of malononitrile. The solution was stirred for 15 min at 0 °C and then 0.20 g (0.60 mmol) of diene **1** in 5 mL of THF was added via syringe. The solution was allowed to warm to rt over 30 min and then a saturated NH_4Cl solution was added. The reaction mixture was extracted with CH_2Cl_2 and washed with water. The organic layer was collected and dried over anhydrous Na_2SO_4. Evaporation of the solvent under

reduced pressure left a crude residue which was subjected to flash silica gel chromatography. The major fraction contained 0.10 g (60%) of a viscous oil which was identified as **15** from its spectral data: IR (neat) ν 2256, 1623, 1573, 1317, and 1068 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.40 (dt, 4H, J = 16.1 and 2.0 Hz), 6.75 (t, 1H, J = 2.0 Hz), and 7.40–7.95 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 33.5, 44.0, 45.8, 115.8, 129.0, 130.7, 135.6, 137.8, 138.6, and 143.6; HRMS calcd for $C_{13}H_{10}N_2O_2S$: 258.0463, found 258.0460.

Preparation of 2-(Phenylsulfonyl)spiro[4.5]-2-decene-6,10-dione (16). The experimental procedure used for the preparation of **15** was repeated using the following reagents: 0.03 g (0.78 mmol) of 60% NaH, 0.07 g (0.60 mmol) of 1,3-cyclohexanedione, and 0.20 g (0.60 mmol) of diene **1**. After silica gel chromatography, the major component was recrystallized from CH_2Cl_2/hexane to give 0.09 g (50%) of a white solid, mp 140–141 °C, which was identified as **16** on the basis of its spectral properties: IR (neat) ν 1709, 1623, 1296, and 1139 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.95 (m, 2H), 2.70 (m, 4H), 3.05 (d, 2H, J = 1.1 Hz), 3.10 (d, 2H, J = 1.7 Hz), 6.60 (t, 1H, J = 1.7 Hz), and 7.55–7.90 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 16.8, 36.5, 36.6, 36.8, 70.5, 127.2, 128.7, 133.1, 138.3, 138.9, 139.9, and 204.0. Anal. Calcd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30; S, 10.53. Found: C, 63.02; H, 5.35; S, 10.59.

Preparation of Ethyl 1-Acetyl-3-(phenylsulfonyl)cyclopent-3-enecarboxylate (17). The experimental procedure used for the preparation of **15** was repeated using the following reagents: 0.03 g (0.78 mmol) of 60% NaH, 0.07 mL (0.60 mmol) of ethyl acetoacetate, and 0.20 g (0.60 mmol) of diene **1**. The major component isolated after chromatography contained 0.12 g (60%) of a light yellow oil identified as **17** on the basis of its spectral properties: IR (neat) ν 1716, 1306, 1155, and 723 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.20 (t, 3H, J = 7.0 Hz), 2.10 (s, 3H), 3.05 (m, 2H), 3.10 (d, 2H, J = 1.8 Hz), 4.15 (q, 2H, J = 7.0 Hz), 6.55 (t, 1H, J = 1.8 Hz), and 7.50–7.85 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 13.9, 25.7, 36.8, 38.9, 62.3, 65.9, 127.9, 129.3, 133.7, 138.9, 139.3, 141.7, 171.0, and 200.3; HRMS calcd for $C_{16}H_{18}O_5S$ 322.0875, found 322.0867.

Preparation of 4-Acetyl-1,4-bis(phenylsulfonyl)-1-cyclopentene (18). The experimental procedure used for the preparation of **15** was repeated using the following reagents: 0.03 g (0.78 mmol) of 60% NaH, 0.09 mL (0.60 mmol) of (phenylsulfonyl)acetone, and 0.20 g (0.60 mmol) of diene **1**. After purification on silica gel, the major compound isolated (70%) was identified as **18** on the basis of its spectral data: IR (neat) ν 1712, 1434, 1302, 1148, and 716 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.45 (s, 3H), 3.20 (m, 2H), 3.30 (d, 1H, J = 2.2 Hz), 3.35 (d, 1H, J = 2.0 Hz), 5.00 (t, 2H, J = 2.0 Hz), and 7.40–7.90 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 28.4, 35.8, 37.7, 82.5, 128.1, 129.2, 129.3, 129.4, 129.8, 134.0, 134.4, 134.8, 138.5, 141.7, and 199.6; HRMS calcd for $C_{19}H_{18}O_5S_2$ 390.0596, found 390.0596.

Preparation of 3,5,5-*Tris*(phenylsulfonyl)-1,2-pentadiene (19). The experimental procedure used for the preparation of **15** was repeated with the following reagents: 0.03 g (0.78 mmol) of 60% NaH, 0.18 g (0.60 mmol) of bis(phenylsulfonyl)methane, and 0.20 g (0.60 mmol) of diene **1**. After silica gel chromatography the major fraction isolated was recrystallized from CH_2Cl_2–hexane to give 0.20 g (75%) of **19** as a white solid: mp 141–142 °C; IR (neat) ν 1958, 1581, 1445, 1310, and 1154 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.20 (dt, 2H, J = 5.8 and 2.2 Hz), 5.15 (t, 1H, J = 5.8 Hz), 5.40 (t, 2H, J = 2.2 Hz), and 7.45–8.00 (m, 15H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 23.6, 79.2, 85.1, 107.2, 127.6, 128.6, 128.7, 129.0, 133.4, 134.1, 137.2, 138.5, and 208.6. Anal. Calcd for $C_{23}H_{20}O_6S_3$: C, 56.53; H, 4.13; S, 19.69. Found: C, 56.29; H, 4.16; S, 19.54.

Conjugate Addition of Dimethyl Malonate to 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1). The experimental procedure used for the preparation of **15** was repeated using the following reagents: 0.03 g (0.78 mmol) of 60% NaH, 0.07 mL (0.60 mmol) of dimethyl malonate, and 0.20 g (0.60 mmol) of diene **1**. Two major compounds were isolated after silica gel chromatography. The first compound contained 0.08 g (40%) of a pale yellow oil which was identified as 3-(phenylsulfonyl)-5,5-dicarbomethoxy-1,2-pentadiene (**21**): IR (neat) ν 1965, 1737, 1310, and 1147 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.80 (dt, 2H, J = 7.6 and 3.1 Hz), 3.60 (t, 1H, J = 7.6 Hz), 3.65 (s, 6H), 5.40 (t, 2H, J = 3.1 Hz), and 7.55–7.85 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 HMz) δ 26.2, 49.9, 52.8, 85.5, 110.2, 128.1, 129.2, 133.7, 139.7, 168.2, and 207.7; HRMS calcd for $C_{15}H_{16}O_6S$ 324.0667, found 324.0667.

The second fraction contained 0.06 g (20%) of a light yellow oil which was identified as tetramethyl 3-(phenylsulfonyl)-3-hexene-1,1,5,5-tetracarboxylate (**22**): IR (neat) ν 1737, 1303, 1145, and 734 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.85 (m, 2H), 3.50 (t, 1H, J = 7.5 Hz), 3.55–3.65 (m, 2H), 3.70 (s, 6H), 3.75 (s, 6H), 4.00 (t, 1H, J = 7.5 Hz), 6.95 (t, 1H, J = 7.5 Hz), and 7.45–7.80 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 25.4, 27.7, 47.8, 49.9, 50.1, 52.8, 128.1, 129.0, 129.3, 129.4, 133.5, 134.1, 139.7, 141.0, 168.4, and 168.8; HRMS calcd for $C_{19}H_{21}O_9S$ ($M^+ - CH_3O$) 425.0906, found 425.0895.

Preparation of 1,4,4-*Tris*(phenylsulfonyl)-1-cyclopentene (20). To a solution containing 230 mg (0.47 mmol) of 3,5,5-*tris*(phenylsulfonyl)-1,2-pentadiene (**19**) in 15 mL of CH_3CN at rt under N_2 was added 20 mg (0.12 mmol) of sodium benzenesulfinate. The suspension was allowed to stir for 36 h before being filtered through Celite and concentrated under reduced pressure to give 0.18 g (78%) of a viscous oil which was identified as **20** on the basis of its spectral properties: IR (neat) ν 1575, 1308, and 1160 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.50 (d, 4H, J = 7.2 Hz), 6.35 (bs, 1H), and 7.45–8.00 (m, 15H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 37.1, 39.2, 90.7, 128.1, 128.5, 129.1, 129.5, 129.6, 129.7, 130.9, 134.1, 135.1, 135.5, 137.8, 138.2, and 141.8; HRMS calcd for $C_{17}H_{15}O_4S_2$ ($M^+ - SO_2C_6H_5$) 347.0412, found: 347.0391.

Preparation of Dimethyl 3-(Phenylsulfonyl)-3-cyclopentene-1,1-dicarboxylate (23). A procedure similar to that used for the preparation of **15** was repeated using 50 mg (0.15 mmol) of 3-(phenylsulfonyl)-5,5-dicarbomethoxy-1,2-pentadiene (**21**). After stirring for 48 h, the reaction mixture was filtered through Celite and concentrated under reduced pressure to give 48 mg (96%) of a clear oil identified as **23** on the basis of its spectral properties: IR (neat) ν 1752, 1447, 1283 and 1158 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.15 (d, 2H, J = 2.0 Hz), 3.25 (d, 2H, J = 2.0 Hz), 3.70 (s, 6H), 6.55 (t, 1H, J = 2.0 Hz), and 7.50–7.90 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 38.5, 40.6, 53.4, 59.4, 127.9, 129.3, 133.7, 139.3, 141.6, 148.6, and 170.7; HRMS calcd for $C_{15}H_{16}O_6S$ 324.0668, found 324.0656.

Conjugate Addition of 2,4-Pentanedione to 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1). The same protocol used for the preparation of **15** was performed using the following reagents: 0.03 g (0.78 mmol) of 60% NaH, 0.07 mL (0.60 mmol) of 2,4-pentanedione, and 0.20 g (0.60 mmol) of diene **1**. Two major fractions were isolated after flash silica gel chromatography. The first fraction contained 0.05 g (30%) of a clear oil which contained an inseparable 2:3 mixture of 3-(phenylsulfonyl)-5-acetyl-1,2-hepten-6-one (**27**) and its enol tautomer: IR (neat) ν 1975, 1723, 1306, and 1155 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.90 (s, 6H), 2.75 (m, 1H), 3.20 (t, 2H, J = 3.1 Hz), 5.45 (t, 2H, J = 3.1 Hz), and 7.55–7.90 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 22.6, 25.1, 25.6, 29.3, 53.4, 65.9, 85.3, 85.6, 105.1, 112.9, 133.9, 139.6, 191.7, 202.0, and 207.3; HRMS calcd for $C_{15}H_{16}O_4S$ 292.0769, found 292.0767.

The second component contained 0.05 g (30%) of a colorless oil identified as 1-(phenylsulfonyl)-3,3-diacetyl-1-cyclopentene (**26**): IR (neat) ν 1716, 1702, 1303, 1147, and 684 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.00 (s, 6H), 3.05 (s, 2H), 3.10 (d, 2H, J = 2.0 Hz), 6.55 (bs, 1H), and 7.50–7.85 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 28.1, 35.2, 37.3, 74.1, 127.9, 129.4, 133.8, 139.2, 141.9, and 202.3; HRMS calcd for $C_{15}H_{16}O_4S$ 292.0769, found 292.0766.

Preparation of 5-Acetyl-6-methyl-2-methylene-3-(phenylsulfonyl)-2,3-dihydro-4*H*-pyran (28). To a stirred solution containing 100 mg (0.34 mmol) of **27** in 10 mL of CH_3CN at rt under N_2 was added 10 mg (0.06 mmol) of sodium benzenesulfinate. The suspension was allowed to stir for 2 h before being filtered through Celite and concentrated under reduced pressure to give 90 mg (90%) of a clear oil which was identified as **28** on the basis of its spectral properties: IR (neat) ν 1675, 1305, and 1130 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.90 (s, 3H), 2.25 (s, 3H), 2.75 (ddd, 1H, J = 17.7, 7.0 and 2.0 Hz), 3.35 (d, 1H, J = 17.7 Hz), 4.10 (d, 1H, J = 7.0 Hz), 4.50 (d, 1H, J = 1.0 Hz), 4.90 (d, 1H, J = 1.0 Hz), and 7.50–7.85 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 19.7, 22.2, 29.7, 29.9, 62.4, 100.2, 107.5, 128.2, 129.3, 129.4, 146.2, 160.7, and 196.8; HRMS calcd for $C_{15}H_{16}O_4S$ 292.0769, found 292.0769.

A solution containing 60 mg (0.21 mmol) of **28** in 10 mL of acetonitrile was allowed to stir in the presence of a 3-fold excess of triethylamine for 12 h. The solution was then concentrated under vacuum to give 54 mg (90%) of a yellow oil identified as 3-acetyl-2,6-dimethyl-5-(phenylsulfonyl)-4*H*-pyran (**29**) on the basis of its spectral properties: IR (neat) ν 1716, 1309, 1146, and 680 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.15 (s, 3H), 2.20 (s, 3H), 2.35 (s, 3H), 3.15 (s, 2H), and 7.55–7.90 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 17.4, 18.7, 23.7, 29.8, 110.1, 112.9, 127.1, 129.3, 133.4, 140.6, 156.8, 156.9, and 197.8; HRMS calcd for $C_{15}H_{16}O_4S$ 292.0769, found 292.0762.

A stirred solution containing 50 mg (0.17 mmol) of **28** in 10 mL of acetonitrile at rt under N_2 was allowed to sit under a bright visible light source for 48 h. The reaction mixture was filtered through Celite and concentrated under reduced pressure to give 45 mg (90%) of **30** which was identified from its spectral properties: IR (neat) ν 1660, 1335, and 1150 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.80 (s, 3H), 2.15 (s, 3H), 2.95 (d, 2H, J = 3.5 Hz), 3.80 (s, 2H), 5.10 (t, 1H, J = 3.5 Hz), and 7.55–7.90 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 19.1, 23.2, 29.8, 60.0, 106.9, 108.2, 128.1, 128.5, 133.9, 138.7, 139.7, 159.2, and 198.9; HRMS calcd for $C_{15}H_{16}O_4S$ 292.0769, found 292.0764.

Preparation of 3-(Phenylsulfonyl)-5,5-dicarboethoxy-1,2-hexadiene (31). To a 0 °C suspension containing 0.07 g (3.00 mmol) of 60% NaH in 50 mL of anhydrous THF under N_2 was added with stirring 0.39 g (2.25 mmol) of diethyl methylmalonate dropwise *via* syringe. After stirring for 15 min, 0.75 g (2.25 mmol) of diene **1** in 20 mL of THF was slowly added. The reaction mixture was brought to rt over a 30-min interval and then a saturated NH_4Cl solution was added. The mixture was extracted with CH_2Cl_2, washed with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude oil was subjected to flash silica gel chromatography to give 0.66 g (80%) of a clear oil which was identified as **31** on the basis its spectral properties: IR (neat) ν 1958, 1730, 1445, 1310, and 691 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.15 (t, 6H, J = 7.1 Hz), 1.30 (s, 3H), 2.80 (t, 2H, J = 3.1 Hz), 4.05 (dq, 4H, J = 7.1 and 3.1 Hz), 5.30 (t, 2H, J = 3.1 Hz), and 7.50–7.85 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 13.6, 18.9, 31.1, 52.6, 61.2, 85.2, 108.8, 127.8, 127.9, 133.4, 139.6, 170.3, and 207.8; HRMS calcd for $C_{18}H_{22}O_6S$ 366.1137, found 366.1138.

Preparation of 3-(Phenylsulfonyl)-5,5-diacetyl-1,2-hexadiene (32). The experimental precedure used for the preparation of **31** was repeated using the following reagents: 0.03 g (0.78 mmol) of 60% NaH, 0.07 mL (0.60 mmol) of 3-methyl-2,4-pentanedione, and 0.20 g (0.60 mmol) of diene **1**. The major component isolated after chromatography contained 0.15 g (80%) of a clear oil which was identified as **32** on the basis of its spectral properties: IR (neat) ν 1712, 1697, 1305, 1144, and 684 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.25 (s, 3H), 2.00 (s, 6H), 2.75 (t, 2H, J = 3.3 Hz), 5.25 (t, 2H, J = 3.3 Hz), and 7.55–7.80 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 17.8, 26.1, 29.9, 65.8, 85.9, 109.1, 128.0, 129.1, 133.5, 139.3, 205.0, and 207.5; HRMS calcd for $C_{16}H_{18}O_4S$ 306.0926, found 306.0926.

Preparation of 1-Acetyl-1-[2-(phenylsulfonyl)-2,3-butadienyl]cyclohexanone (33). To a stirred suspension containing 0.03 g (0.78 mmol) of 60% NaH in 10 mL of anhydrous THF under N_2 was added 0.07 mL (0.60 mmol) of 2-acetylcyclohexanone dropwise *via* syringe. After stirring for 15 min, 0.20 g (0.60 mmol) of diene **1** in 5 mL of THF was slowly added. The reaction flask was then fitted with a condenser and the solution was brought to reflux. After heating for 12 h, the mixture was allowed to come to rt and a saturated NH_4Cl solution was added. The reaction mixture was extracted with CH_2Cl_2 and washed with water. The organic layer was collected, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Silica gel chromatography of the crude mixture afforded 0.12 g (65%) of a pale yellow oil which was identified as **33** from its spectral data: IR (neat) ν 1709, 1445, 1303, and 690 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.45–1.60 (m, 4H), 1.95 (m, 1H), 2.05 (s, 3H), 2.35 (m, 1H), 2.45 (m, 2H), 2.60 (dt, 1H, J = 16.2 and 3.2 Hz), 2.85 (dt, 1H, J = 16.2 and 3.2 Hz), and 7.55–7.90 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.2, 25.5, 26.2, 29.2, 33.5, 40.6, 66.2, 85.2, 108.0, 127.5, 128.5, 133.0, 139.0, 204.1, 207.5, and 208.1; HRMS calcd for $C_{18}H_{20}O_4S$ 322.1082, found 322.1080.

Reaction of 3-(Phenylsulfonyl)-5,5-diacetyl-1,2-hexadiene (32) with Sodium Methoxide in Methanol. To a stirred solution containing 0.04 g (0.07 mmol) of $NaOCH_3$ in 10 mL of methanol was added 0.2 g (0.65 mmol) of **32** in 5 mL of methanol. After stirring for 1 h, the reaction mixture was poured into water, extracted with CH_2Cl_2, and washed with water. The organic layer was collected, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was subjected to flash silica gel chromatography to give 0.07 g (70%) of a pale yellow oil which was identified as 3-(phenylsulfonyl)-5-methyl-1,2-heptadien-6-one (**34**) on the basis of its spectral data: IR (neat) ν 1967, 1708, 1306, 1147, and 687 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.05 (d, 3H, J = 7.0 Hz), 2.10 (s, 3H), 2.25 (m, 2H), 2.60 (m, 1H), 2.80 (sext, 1H, J = 7.0 Hz), 5.35 (dd, 2H, J = 3.2 and 3.0 Hz), and 7.45–8.00 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 16.6, 28.3, 29.6, 44.9, 84.5, 111.3, 128.1, 129.1, 133.6, 139.8, 208.0, and 210.2; HRMS calcd for $C_{14}H_{16}O_3S$ 264.0820, found 264.0820.

Preparation of 1,2-Dibromo-3-(phenylsulfonyl)-5,5-diacetyl-2-hexene (35). To a solution containing 0.10 g (0.33 mmol) of **32** in 10 mL of glacial acetic acid was added 0.02 mL of bromine *via* syringe. The solution was stirred for 10 min and then poured into 50 mL of ice–water. The reaction mixture was carefully neutralized to pH 7 with a 50% NaOH solution, extracted with CH_2Cl_2, and washed with water, a saturated $NaHCO_3$ solution, and then again with water. The organic layer was collected and dried over anhydrous Na_2SO_4. The crude product was concentrated under reduced pressure and chromatographed on a silica gel column to give 0.14 g (90%) of a clear oil which was identified as **35** on the basis of its spectral properties: IR (neat) ν 1714, 1318, 1141, and 681 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.55 (s, 3H), 2.20 (s, 6H), 3.35 (s, 2H), 5.10 (s, 2H), and 7.60–7.90 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 16.8, 26.3, 32.8, 36.9, 65.9, 128.1, 129.5, 134.3, 141.0, 141.1, and 205.0.

Preparation and Thermolysis of 5,5-Dicarbomethoxy-3-(phenylsulfonyl)octa-1,2,7-triene (38). To a stirred ice-cold suspension containing 320 mg (8.0 mmol) of 60% NaH in 80 mL of THF under N_2 was slowly cannulated 0.8 mL (6.8 mmol) of dimethyl malonate. The solution was stirred for 15 min at 0 °C and then 0.70 mL (7.7 mmol) of allyl iodide was added *via* syringe. The solution was allowed to warm to rt and then was heated at reflux under argon for 5 h before being quenched with a saturated NH_4Cl solution. The reaction mixture was extracted with CH_2Cl_2 and the organic layer was collected, washed with water and brine, and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure left a crude residue which was subjected to silica gel chromatography. The major fraction contained 1.01 g (87%) of 4,4-dicarbomethoxy-1-butene (**37**); IR (neat) ν 1740, 1632, 1434, and 912 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.63 (t, 2H, J = 7.2 Hz), 3.45 (t, 1H, J = 7.2 Hz), 3.72 (s, 6H), 5.02–5.12 (m, 2H), and 5.68–5.82 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 32.8, 51.3, 52.4, 117.6, 133.9, and 169.2.

To a stirred ice-cold solution of 164 mg (0.95 mmol) of the above compound in 25 mL of THF was added 48 mg (1.2 mmol) of 60% NaH. The solution was stirred for 20 min at 0 °C under N_2 and then 314 mg (0.94 mmol) of diene **1** in 25 mL of THF was slowly added. The solution was stirred for 20 min at 0 °C and then allowed to warm to rt for 45 min before being quenched with a saturated NH_4Cl solution. The reaction mixture was extracted with CH_2Cl_2 and the organic layer was collected, washed with water and brine, and dried over Na_2SO_4. Standard workup followed by flash silica gel chromatography gave 178 mg (52 %) of 5,5-dicarbomethoxy-3-(phenylsulfonyl)octa-1,2,7-triene (**38**): mp 58–59 °C; IR (neat) ν 1965, 1730, 1631, 1439, and 727 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.64 (d, 2H, J = 7.5 Hz), 2.88 (t, 2H, J = 3.0 Hz), 3.63 (s, 6H), 4.95 (m, 2H), 5.36 (t, 2H, J = 3.0 Hz), 5.46–5.60 (m, 1H), 7.50–7.64 (m, 3H), and 7.86 (d, 2H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 28.4, 36.4, 52.5, 56.9, 85.5, 109.0, 119.6, 128.2, 129.1, 131.6, 133.6, 139.8, 169.9, and 208.1; HRMS calcd for $C_{18}H_{20}O_6S$ 364.0980, found 364.0982.

The second fraction isolated from the column contained 101 mg (30%) of 5,5-dicarbomethoxy-2-(phenylsulfonyl)octa-1,3,7-triene (**39**) as a clear oil; IR (neat) ν 1730, 1631, 1432, 1225, and 749 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.64 (d, 2H, J = 7.2 Hz), 3.69 (s, 6H), 4.98 (t, 2H, J = 16.2 Hz), 5.27 (s, 1H), 5.42 (s, 1H), 5.70–5.82 (m, 1H), 5.91 (s, 1H), 6.50 (s, 1H), 7.49–7.64 (m, 3H), and 7.84 (d, 2H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 39.9, 52.6, 63.8, 118.8, 125.9, 127.8, 128.8, 129.1, 133.3, 133.5, 136.9, 138.4, 149.3, and 169.7; HRMS calcd for $C_{18}H_{20}O_6S$ 364.0980, found 364.0979.

An authentic sample of **39** was prepared in the following manner. A suspen-sion containing 60 mg (0.16 mmol) of **38** and 80 mg (0.48 mmol) of sodium benzenesulfinate in 20 mL of 60% aqueous acetic acid was heated at 100 °C for 2 h. The mixture was cooled to 25 °C and extracted with ether. The combined ether extracts were washed with a dilute NaOH solution until the wash water was at pH 8 and then the organic layer was further washed with water and brine, and dried over anhydrous Na_2SO_4. Removal of the solvent followed by flash silica gel chromatography gave 60 mg (73%) of 4,4-dicarbomethoxy-7,8-bis(phenylsulfonyl)-octa-1,6-diene (**41**) as a clear oil: IR (neat) ν 1730, 1439, 1147, and 727 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.64 (d, 2H, J = 7.5 Hz), 2.87 (d, 2H, J = 7.5 Hz), 3.64 (d, 2H, J = 4.8 Hz), 3.68 (s, 6H), 4.20 (s, 1H), 4.97–5.12 (m, 2H), 5.56–5.66 (m, 1H), and 7.50–7.92 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 33.5, 38.7, 52.8, 53.7, 57.1, 120.1, 128.3, 128.5, 129.2, 129.3, 131.6, 133.6, 133.9, 134.3, 138.6, 139.4, 146.6, and 170.3. To a solution containing 30 mg of this compound in 8 mL of methanol and 6 mL of THF was added 0.9 mL of a 0.53 M solution of NaOMe in MeOH at rt under N_2. The mixture was stirred for 1 h at rt and then the solvent was removed under reduced pressure. The residue was dissolved in water, this mixture was extracted with CH_2Cl_2, and the organic layer was washed with water and brine and dried over Na_2SO_4. The major product isolated from the reaction mixture corresponded to 5,5-dicarbomethoxy-2-(phenylsulfonyl)-octa-1,2,7-triene (**39**) which was identical in all aspects with the sample isolated above.

A solution containing 43 mg (0.12 mmol) of **38** in 8 mL of xylene under N_2 was heated at reflux for 4.5 h. The solution was concentrated under reduced pressure to give 39 mg (90%) of 4,4-dicarbomethoxy-2-(phenylsulfonyl)bicyclo[4.2.0]oct-1-ene (**44**) after silica gel purification: mp 112–113 °C; IR (neat) ν 1730, 1681, 1446, 1311, and 713 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.57–1.76 (m, 2H), 2.27 (m, 1H), 2.39–2.50 (m, 2H), 2.92 (d, 2H, J = 15.3 Hz), 3.04–3.14 (m, 1H), 3.30–3.38 (m, 1H), 3.64 (s, 3H), 3.67 (s, 3H), 7.54–7.61 (m, 3H), and 7.87 (d, 2H, J = 7.2 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 25.1, 29.1, 31.9, 33.0, 40.3, 52.8, 52.9, 123.8, 127.3, 129.1, 133.2, 140.4, 155.7, 170.3, and 171.0; HRMS calcd for $C_{18}H_{20}O_6S$ 364.0980, found 364.0980.

Preparation and Thermolysis of 5,5-Dicarbomethoxy-8-methyl-3-(phenylsulfonyl)nona-1,2,7-triene (43). To a stirred ice-cold suspension containing 0.05 g (1.20 mmol) of 60% NaH in 25 mL of THF under N_2 was slowly cannulated 0.11 mL (0.96 mmol) of dimethyl malonate in 5 mL of THF. The solution was stirred for 15 min at 0 °C and then 0.12 mL (1.03 mmol) of 4-bromo-2-methyl-1-butene was added *via* syringe. The solution was allowed to warm to rt and was stirred for an additional 1.5 h before being quenched with a saturated NH_4Cl solution. The reaction mixture was extracted with CH_2Cl_2 and washed twice with water. The organic layer was collected and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure left a crude residue which was subjected to silica gel chromatography to give 0.12 g (60%) of 5,5-dicarbomethoxy-2-methyl-2-pentene (**42**); IR (neat) ν 1730, 1430, and 1140 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.60 (s, 3H), 1.65 (s, 3H), 2.55 (t, 2H, J = 7.4 Hz), 3.30 (t, 1H, J = 7.4 Hz), 3.70 (s, 6H), and 4.95 (t, 1H, J = 7.4 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 17.6, 25.7, 27.6, 51.8, 52.3, 119.4, 135.0, and 169.5.

A 0.08-g (0.40 mmol) sample of the above compound in 5 mL of THF was cannulated into a stirred ice-cold suspension containing 0.02 g (0.50 mmol) of 60% NaH in THF under N_2. The solution was stirred for 20 min at 0 °C, and then 0.13 g (0.40 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene in 10 mL of THF was slowly added. The solution was allowed to stir for 30 min before quenching with a saturated NH_4Cl solution. The reaction mixture was extracted with CH_2Cl_2, the extract was washed with water, and the organic layer was collected and dried over Na_2SO_4. Removal of the solvent under reduced pressure followed by flash silica gel chromatography gave 0.13 g (80%) of allene **43**: IR (neat) ν 1972, 1730, 1154, and 677 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.45 (s, 3H), 1.50 (s, 3H), 2.60 (d, 2H, J = 7.5 Hz), 2.85 (t, 2H, J = 3.5 Hz), 3.60 (s, 6H), 4.75 (t, 1H, J = 7.5 Hz), 5.35 (t, 2H, J = 3.5 Hz), and 7.50–7.85 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 17.7, 25.9, 28.3, 30.6, 52.4, 56.7, 85.6, 109.2, 116.7, 128.1, 129.0, 133.5, 136.3, 140.0, 170.2, and 207.8, HRMS calcd for $C_{20}H_{24}O_6S$ 392.1293, found 392.1281.

A solution containing 0.10 g (0.25 mmol) of **43** in 25 mL of xylene under N_2 was heated at reflux for 18 h. The solution was then concentrated under reduced pressure to give 4,4-dicarbomethoxy-7,7-dimethyl-2-(phenylsulfonyl)bicyclo[4.2.0]oct-1-ene (**45**) in 85% yield as a clear oil after silica gel purification: IR (neat) ν 1740, 1303, 1145, 717, and 685 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.95 (s, 3H), 1.25 (s, 3H), 1.50 (t, 1H, J = 12.3Hz), 2.20 (dd, 1H, J = 12.3 and 6.4 Hz), 2.40 (bd, 1H, J = 16.8 Hz), 2.55 (m, 1H), 2.85 (d, 1H, J = 14.7 Hz), 3.00 (d, 2H, J = 14.7 Hz), 3.60 (s, 3H), 3.65 (s, 3H), and 7.50–7.85 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 12.8, 26.6, 29.3, 29.7, 36.3, 45.9, 48.5, 52.9, 53.0, 53.7, 125.6, 127.3, 129.0, 133.1, 140.5, 152.3, 170.4, and 171.1; HRMS calcd for $C_{20}H_{24}O_6S$ 392.1293, found 392.1291.

Preparation and Thermolysis of 5,5-Dicarbomethoxy-6-furanyl-3-(phenylsulfonyl)-1,2-hexadiene (49). To a stirred ice-cold suspension containing 1.26 g (31.6 mmol) of 60% NaH in 50 mL of dry THF under N_2 was added 3.17 mL (24.3 mmol) of dimethyl malonate *via* syringe. The solution was stirred for 30 min at 0 °C before being cannulated into an ice-cold solution of furfuryl bromide in 50 mL of ether. The reaction was stirred for an additional 30 min and then quenched with a saturated NH_4Cl solution. The organic layer was extracted with CH_2Cl_2, washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was subjected to flash silica gel chromatography to give 3.86 g (63%) of a 1:1 mixture of dimethyl bis(furfuryl)malonate and dimethyl 3-furfurylmalonate. The latter compound was identified on the basis of its spectral properties: IR (neat) ν 1742, 1431, 1337, and 1153 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.25, (d, 2H, J = 7.8 Hz), 3.65 (s, 6H), 3.70 (t, 1H, J = 7.8 Hz), 6.05 (d, 1H, J = 3.4 Hz), 6.25 (dd, 1H, J = 3.4 and 1.8 Hz), and 7.30 (d, 1H, J = 1.8 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 29.4, 50.8, 52.7, 106.7, 110.3, 141.7, 151.5, and 168.9.

A 0.52-g sample of the above compound in 5 mL of THF was added to an ice-cold suspension containing 0.06 g (1.44 mmol) of 60% NaH in 15 mL of dry THF. After stirring for 15 min, a solution containing 400 mg (1.20 mmol) of diene 1 in 20 mL of THF was slowly cannulated into the reaction flask. The mixture was stirred for an additional 30 min and then a saturated NH_4Cl solution was added. The organic layer was extracted with CH_2Cl_2, washed with water, separated, and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure left a crude residue which was subjected to silica gel chromatography. The major product contained 358 mg (72%) of 5,5-dicarbomethoxy-6-furanyl-3-(phenylsulfonyl)-1,2-hexadiene (**49**): IR (neat) ν 1961, 1735, 1433, 1305, and 1146 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.90 (t, 2H, J = 3.3 Hz), 3.40 (s, 2H), 3.75 (s, 6H), 5.50 (t, 2H, J = 3.3 Hz), 6.00 (d, 1H, J = 3.0 Hz), 6.25 (t, 1H, J = 2.0 Hz), 7.25 (bs, 1H), and 7.55–8.00 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 28.1, 30.5, 52.6, 56.5, 85.7, 108.6, 110.1, 128.1, 128.9, 133.3, 139.7, 141.8, 149.4, 169.4, and 207.8.

Heating a sample of allene **49** in benzene for 10 min resulted in a quantitative yield of 2,2-dicarbomethoxy-3a,6-epoxy-7-methylene-7a-(phenylsulfonyl)-1,2,3,6,-7,7a-hexahydro-3a*H*-indene (**50**) as a clear oil: IR (neat) ν 1735, 1439, 1303, 1144, and 734 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.95 (d, 1H, J = 15.0 Hz), 3.00 (d, 1H, J = 16.0 Hz), 3.25 (d, 1H, J = 15.0 Hz), 3.60 (d, 1H, J = 16.0 Hz), 3.70 (s, 3H), 3.85 (s, 3H), 4.95 (bs, 1H), 5.30 (s, 1H), 5.35 (s, 1H), 6.05 (dd, 1H, J = 5.6 and 1.3 Hz), 6.50 (d, 1H, J = 5.6 Hz), and 7.45–7.85 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 35.3, 40.2, 53.3, 53.4, 61.6, 79.1, 84.1, 100.1, 111.4, 128.4, 130.9, 134.0, 134.6, 135.9, 136.9, 145.9, 170.7, and 171.0; HRMS calcd for $C_{20}H_{20}O_7S$ 404.0930, found 404.0926.

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Supplementary Material Available: Copies of ^{1}H- and ^{13}C-NMR spectra (75 MHz) of new compounds lacking analyses (31 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.