(Phenylsulfonyl)allenes as Substrates for Cycloaddition Reactions: Intramolecular Cyclizations onto Unactivated Alkenes

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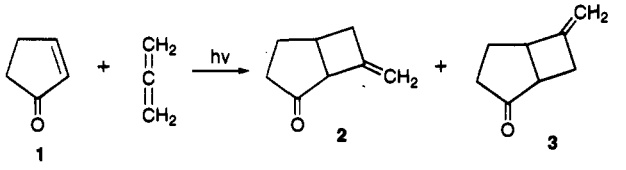
Abstract: The reaction of a series of allyl-substituted bis(phenylsulfonyl)methanes or dimethyl malonates with 2,3-bis(phenylsulfonyl)-1,3-butadiene in the presence of base afforded alkenyl-substituted allenes in good yield. The reaction proceeds by initial attack of the soft carbanion onto the terminal position of the diene, and this is followed by $PhSO_2^-$ elimination to give the phenylsulfonyl-substituted allene. Themal [2 + 2]-cycloaddition proceeded across the C_1-C_2 double bond of the allene with completely sterospecificity. Stepwise bonding prefers to occur in a 1,6-*exo* manner rather than in a 1,7-*endo* fashion. Substitution at the 7-position of the π-bond causes a crossover in the regioselectivity of the [2 + 2]-cycloaddition process. All products can be rationalized by a mechanism which includes an initial carbon−carbon bond formation involving the central allene carbon to give a diradical intermediate. The product distribution is then determined by the substitution pattern of the alkene and the fate of the diradical intermediate.

[2 + 2]-Cycloaddition reactions between allenes and ethylene derivatives have frequently been employed for the preparation of methylenecyclobutane derivatives.[1,2] Many of these reactions proceed by way of photochemical initiation, in which case the mechanistic pathway involves stepwise ring closure *via* diionic or diradical intermediates.[3−7] For example, allene itself undergoes [2 + 2]-photocycloaddition with cyclopentenone to give a 19:1 mixture of methylenecyclobutanes **2** and **3**.[3,4] Not only



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is there considerable regiochemical regularity in the [2 + 2]-photoaddition, but the products are also easily transformed into useful ring systems by one of several general methods,[9−12] making this a very synthetically useful reaction. While well-represented in the literature, these photochemical protocols are not the sole choice for allenic [2 + 2]-cycloadditions. Certain examples involve Lewis acid catalysis, where ionic intermediates are clearly involved.[13−16] Still others proceed under strictly thermal conditions.[17−21] The mechanistic details associated with these [2 + 2]-reactions constitute a topic of much study and debate.[22] Substitution on the allene not only enhances its reactivity but also allows for the formation of a mixture of regioisomers. In most cases it has not been unequivocally established whether the cyclizations are concerted or stepwise in nature. A concerted reaction would require an *antarafacial−suprafacial* orbital interaction and result in a stereospecific cyclization.[23] On the other hand, a stepwise mechanism would proceed by an initial rate-determining carbon−carbon bond formation, most likely involving the central carbon of the allene, due to allyl stabilization in the resulting diradical, followed by a subsequent radical coupling. This latter step has been termed the *"product-determining step"*[24] since there are two possible sites for secondary ring closure. If this process is rapid enough, the entire cyclization will occur with stereospecificity.

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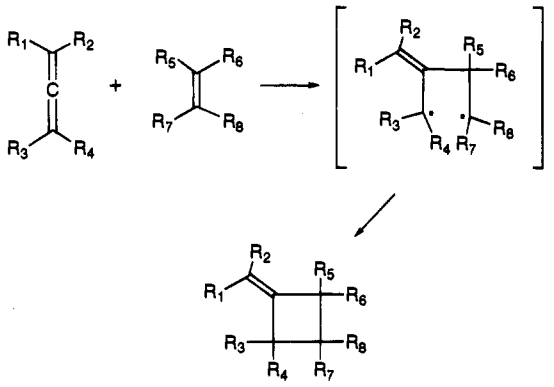
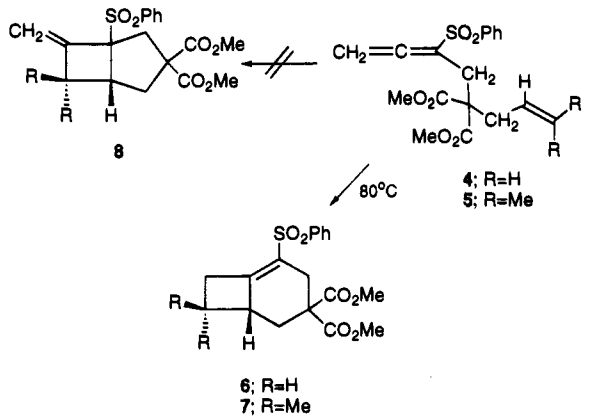


Thus, the distinction between a concerted and stepwise mechanism is not necessarily apparent in product distribution.[25,26] Furthermore, molecular orbital calculations indicate that the two mechanisms are comparable energetically.[27] Intramolecular [2 + 2]-cycloaddition of allenes has also been studied, and this process constitutes a particularly versatile method for the stereocontrolled synthesis of a variety of functionalized polycyclic compounds.[28-32]

In connection with our efforts toward the development of new methodologies using sulfonyl substituted allenes,[33] we uncovered a highly chemo- and stereospecific intramolecular [2 + 2]-cycloaddition of (phenylsulfonyl)allenes **4** and **5**.[34] The only products formed in both cases corresponded to the [2 + 2]-cycloadducts **6** and **7** in 90 and 85% yield, respectively. It is

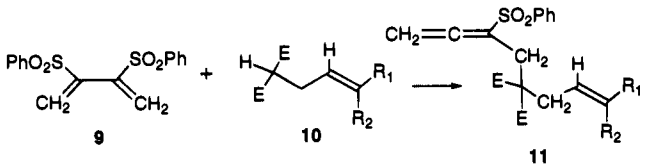


particularly interesting to note that only the C_1-C_2 double bond of the allene participates in the cycloaddition. This result was somewhat puzzling since phenylsulfonyl-substituted allenes react with various 4π-systems in a highly chemoselective fashion undergoing cycloaddition across the more activated C_2-C_3 π-bond.[35]

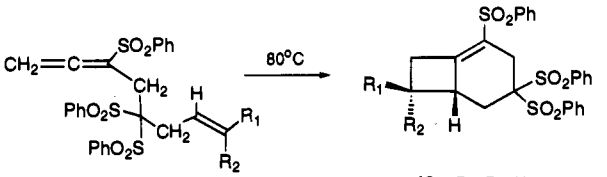
Our ongoing interest in the generality and synthetic utility of intramolecular cycloaddition reactions inspired us to take a more detailed look at the scope and mechanistic details of this process. The present paper documents the results of these studies.

Results and Discussion

Our general interest in this area originated from an earlier study of the reaction of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**9**) with soft carbanions.[36] Treatment of **9** with a series of allyl-substituted bis(phenylsulfonyl)methanes (**10**) afforded allenes **11** in 60–80% yield. The reaction proceeds by initial conjugate addition onto one of the vinyl sulfone groups to give a phenylsulfonyl-stabilized allyl anion which collapses with phenylsulfinate ejection to form the allene. Thus, through the use of bis(phenylsulfonyl)alkenes **10**, themselves conveniently prepared by the reaction of bis(phenylsulfonyl)methane with the corresponding alkyl halide, allenes **11** were easily generated. An analogous process also occurred when substituted dimethyl malonates were treated with 1 equiv of NaH in THF at 0 °C in the presence of diene **9**.



The thermal reactions of these allenes were performed by heating the reactants in benzene. The only products formed in all cases (*ca.* 80–98% yield) corresponded to the [2 + 2]-cycloadducts **12** which were fully characterized by their ^1H and ^{13}C NMR spectra. In the case of **11c**, the stereochemistry of the cycloadduct **12c** was unequivocally established by X-ray crystallographic analysis.



Several trends are evident upon inspection of these results. First of all, if the reaction had proceeded *via* the concerted pathway, the regioselectivity would be quite surprising, inasmuch as the observed products are the result of a formal [2 + 2]-cycloaddition across the nonactivated π-system of the allene. According to MNDO calculations, the largest and second largest LUMO coefficients reside on the sp^2 carbons β and α to the sulfonyl group, respectively. Indeed, this activated π-bond has been shown to engage in [4 + 2]-cycloadditions with very high

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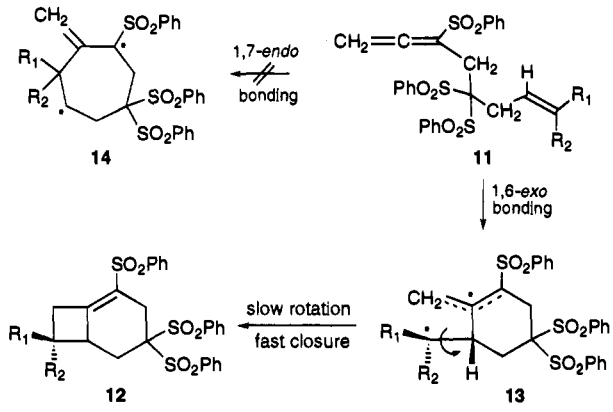
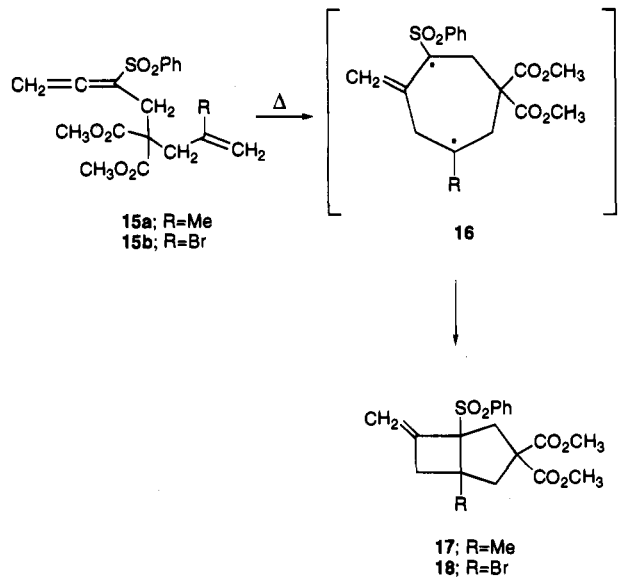
chemoselectivity.[35] We believe that the periselectivity observed is related to stereoelectronic factors. The primary spatial requirement for [2 + 2]-cycloaddition is that the distance between the C_2 carbon of the allene and the olefinic π-bond should be sufficiently close that effective overlap of the π-systems can occur. The initial rate-determining carbon–carbon bond formation occurs between the central allene carbon and the proximal alkene carbon atom. The regioselectivity on the alkene system is due to less clear-cut parameters. Evidently, it is easier for stepwise bonding to occur in a 1,6-*exo* manner (leading to diradical **13**) than in a 1,7-*endo* fashion. When one compares this type of ring closure with analogous radical cyclizations, the observed 6-*exo-trig* process on the proximal alkene carbon follows the empirically derived rule which disfavors the 7-*endo-trig* alternative involving the distal alkene carbon.[37]

Substitution on the alkene portion also affects the rate of the reaction, presumably by influencing the stability of that portion of the resulting diradical. Thus, cyclization of the dimethyl derivative **11b** (*via* the tertiary radical **13b**) is complete in 45 min, whereas the unsubstituted analog **11a** (giving rise to the primary radical intermediate **13a**) requires 22 h for completion. The rates of the two monomethyl variants **11c** and **11d** (secondary radical intermediates **13c** and **13d**) fall between the other two values (*i.e.*, 7 h), as expected.



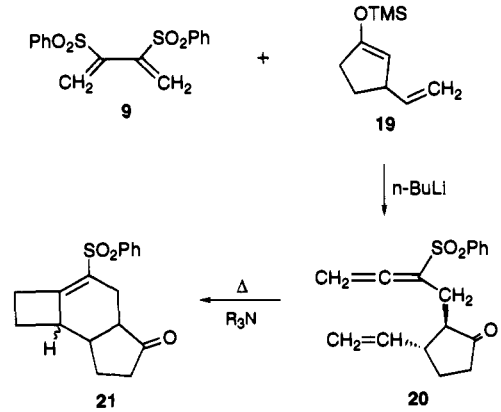
Another aspect of the cycloaddition worth noting is the complete stereospecificity of the process. Heating a sample of allene **11c** in benzene for 7 h produced cycloadduct **12c** as the exclusive product. Thermolysis of **11d**, on the other hand, gave rise to diastereomer **12d** in 90% yield with no detectable signs of **12c**. Since the allene adduct **13** 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 encountered may also be due to efficient radical stabilization by the $PhSO_2$ group, which, unlike RCO_2, is free from anisotropic constraints of π-overlap.

An interesting variation in the regioselectivity of the [2 + 2]-cycloaddition occurs with allenes **15a** and **15b**. The 7-methyl- (**15a**) and 7-bromooctatriene derivatives (**15b**) were prepared from bis(phenylsulfonyl)butadiene in 77% and 64% yield, respectively. Heating these substrates produced cycloadducts **17** and **18** which correspond to a formal [2 + 2]-cycloaddition across the more activated double bond. Thus, substitution at the 7-position effectively caused a crossover in the allene regioselectivity. We believe these reactions proceed through a similar mechanism in which the central allene carbon is involved



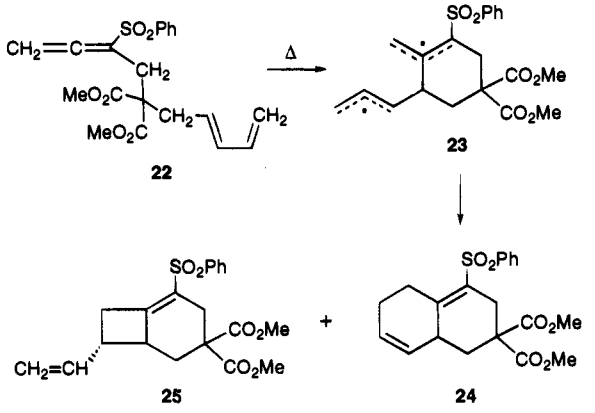
in the initial carbon–carbon bond formation to give an intermediate diradical (*i.e.*, **16**). The difference in these cases is that the initial bonding step now involves the distal alkene carbon. The resulting methylenecycloheptyl diradical **16** undergoes subsequent closure to form a bicyclo[3.2.0]heptane ring. The central question is then why substitution at the C_7 position prevents initial bond formation at this site. Obviously, the regioselectivity is governed by a fine balance of various factors, one of which is the steric demands involved in attaining proper geometry for bonding. The central carbon atom of the allene is flanked on one side by the very large phenylsulfonyl group and on the other side by the terminal hydrogen which projects perpendicularly from the plane of the activated π-bond. Substituents at C_7 apparently interact with these steric obstacles enough to tip the balance toward a 7-*endo-trig* type of cyclization, in which the C_7 substituent encounters relatively little steric interference. Moreover, the resulting radical is tertiary as opposed to primary, which if formed would arise from a corresponding 5-*exo-trig* type of cyclization. This electronic stabilization effect would certainly influence the regiochemistry as well.

To further illustrate the scope and synthetic utility of the intramolecular 2 + 2 process, we set out to explore this protocol for the synthesis of other ring systems. For example, bis(phenylsulfonyl)-1,3-butadiene (**9**) underwent smooth reaction with the enolate anion derived from **19** to form the disubstituted cyclopentanone **20**. This substrate was then heated in toluene at reflux for 72 h in the presence of a catalytic amount of tributylamine (to promote epimerization) to give the tricyclic enone **21** in 40% overall yield as a 4:1 mixture of diastereomers.

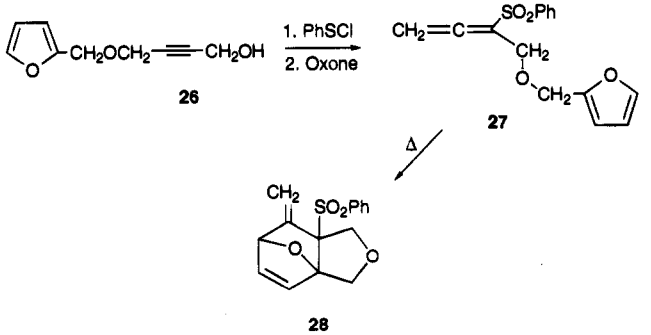


The low yield in this reaction is due in part to the lack of stabilization on the alkene portion of the intermediate diradical.

Further investigation into other ring systems included attachment of 4π-systems to the (phenylsulfonyl)allene. For example, the decatetraene **22** was prepared *via* diene **9**. This substrate underwent facile cyclization to give a 2:1 mixture of the bicyclic compounds **24** and **25**, which formally correspond to the products of [4 + 2]- and [2 + 2]-cycloaddition across the unactivated allenyl π-bond. In actuality, we believe these products arise from the same diradical intermediate **23**. The product distribution represents the relative propensity of the 4π-allylic radical **23** to undergo closure internally *vs* terminally. Kanematsu has observed the same preference of butadienyl-substituted allenes toward cyclobutane formation.[28]

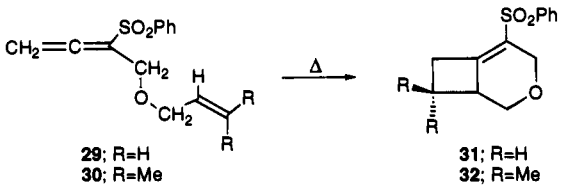


Another 4π-donor which was attached to the (phenylsulfonyl)allene moiety was the furan ring. In this case, the intramolecular bridge contained an ether linkage. Although, in principle, allene **27** might have been prepared by treating the phenylsulfonyl diene **9** with the appropriate alkoxide, in practice such a process resulted in a complex mixture of products. Fortunately, there is a convenient alternative for the preparation of **27**. This involved treating 4-(2-furfuryloxy)-2-butyn-1-ol (**26**) with benzenesulfenyl chloride through a sequence of sulfenylation and 2,3-sigmatropic rearrangement[38] to give a sulfinylallene which was subsequently oxidized with Oxone to afford the corresponding sulfone. Heating **27** in

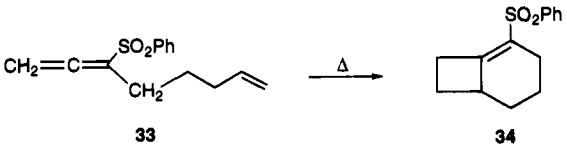


benzene at reflux for 1.5 h resulted in the smooth and high-yielding formation of the Diels–Alder cycloadduct **28**. This result is consistent with the general observation of Kanematsu[28] that furanyl-substituted allenes readily undergo Diels–Alder chemistry, whereas the closely related butadienyl substituted systems prefer [2 + 2]-cycloaddition.

Substitution about the alkene is certainly one variable affecting the course of the cyclization. Another important factor is the nature and length of the tether connecting the two reacting centers. In order to study the effects of altering this portion of the substrate, we prepared some oxa analogs which contain an ether linkage between the allenic and alkenyl regions. Upon heating, cyclization of these allenyl alkenyl ethers occurred with the same regioselectivity as their carbocyclic counterparts (*i.e.*, **11a,b**), thus providing an entry into the dihydropyran derivatives. Again, cyclization is more facile for the dimethyl derivative **30** (5 h at 110 °C) than the allyl system **29** (24 h at 140 °C) due to radical stabilization, a trend previously observed in the carbocyclic precursors. An interesting phenomenon that



we encountered while examining the thermal chemistry of these systems is the relative sluggishness of the cycloaddition reaction. A cause and effect relationship is difficult to rationalize, since in introducing the oxygen atom we had also removed the large bis(phenylsulfonyl)methane group. Thus, it was not clear whether the rate difference was due to the bond angle difference associated with the oxygen atom or to some property imparted by the sulfone groups. To separate these factors, we prepared allene **33**, in which the intramolecular tether consisted of a purely carbon backbone but lacked the bulky phenylsulfonyl groups of the previous examples. We found that the [2 + 2]-cycloaddition of this substrate was the least facile of all the systems examined (140 °C, 96 h, 60% conversion). The fact



that the steric bulk on the connecting chain of these alkenyl-substituted allenes enhances the cycloaddition rate is perfectly compatible with the well-known "*gem-dialkyl effect.*"[39] It has long been recognized that the cyclization of acyclic precursors is significantly accelerated by alkyl substituents.[40–43] Recent results by Jung and Gervay[44] showed that the rate acceleration is due primarily to the *reactive conformer effect* and not to angle compression. This same explanation nicely rationalizes the rate differences observed with the above allenyl sulfones.[45]

Expansion of the tether by another carbon atom was accomplished by synthesizing the homologous nonatrienes **35** and

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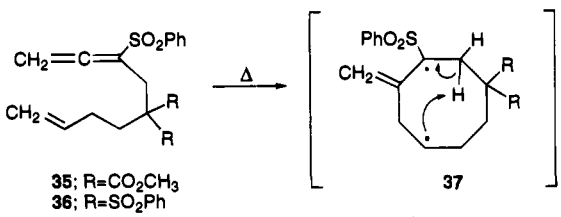
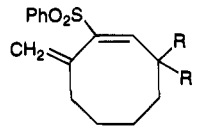
(45) Parrill and Dolata have recently suggested that the rate acceleration associated with the *gem*-dialkyl effect is not due to a change in concentrations of reactive rotamers, but instead is due to an overall reduction in the $\Delta G^{\ddagger}$ due to a facilitation of achieving the transition state from the ground state; see: Parrill, A. L.; Dolata, D. P. *Tetrahedron Lett.* **1994**, *35*, 7319.

36 from bis(phenylsulfonyl)butadiene **9**. Interestingly, exposure of these substrates to the thermolysis conditions did not result in bicyclic isomers at all, but rather the methylene-substituted cyclooctenes **38** and **39** in 80% and 81% yield, respectively.



35; R=CO_2CH_3
36; R=SO_2Ph

37



38; R=CO_2CH_3
39; R=SO_2Ph

The structural assignment of **39** was unequivocally established by X-ray crystal analysis. Here the carbon bridge is long enough to allow for an 8-*endo-trig* cyclization. The regioselectivity appears to be determined by formation of the more stable diradical intermediate (*i.e.*, **37**). Moreover, this diradical does not close to form the bicyclic species, but rather undergoes a competitive transannular hydrogen abstraction to provide the observed product.

In conclusion, the results from the above examples allow us to make the following generalizations in regard to the thermal cycloaddition behavior of the generic (phenylsulfonyl)allene **40**.

40

In cases where n = 1 and R_1 = H, these substrates tend to undergo a formal intramolecular [2 + 2]-cycloaddition involving the unactivated double bond of the allene giving bicyclo[4.2.0]-octene systems. The regioselectivity is unaffected by the introduction of heteroatoms into the intramolecular tether (*i.e.*, X = O), although the rate of reaction is enhanced by steric bulk at this site. When *n* = 1 and R_1 = alkyl, the regioselectivity is shifted and cycloaddition occurs formally across the activated double bond of the allene, to give methylenebicyclo-[3.2.0]heptane systems. When the tether is lengthened (*n* = 2), the substrates do not undergo [2 + 2]-cycloaddition but rather cyclize to give methylenecyclooctenes. All products can be rationalized by a mechanism which includes an initial carbon–carbon bond formation involving the central allene carbon to produce a diradical intermediate. The product distribution is then determined by the regioselectivity of the alkene and the fate of the diradical intermediate. These internal [2 + 2]-cycloadditions proceed in high yield and provide highly functionalized ring systems. Investigations into the synthetic utility of these cycloadducts are in progress and will be reported at a later date.

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 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 and Thermolysis of 3,5,5-Tris(phenylsulfonyl)octa-1,2,7-triene (11a). To a stirred ice-cold suspension containing 0.09 g (2.20 mmol) of 60% NaH in 40 mL of THF under a nitrogen atmosphere was slowly cannulated 0.50 g (1.7 mmol) of bis(phenylsulfonyl)methane in 10 mL of THF. The solution was stirred for 15 min at 0 °C, and then 0.06 mL (0.65 mmol) of allyl iodide was added dropwise *via* syringe. The solution was allowed to warm to room temperature and was heated at reflux for 12 h before being quenched with a saturated NH_4Cl solution. 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 silica gel chromatography to give 0.17 g (85%) of 4,4-bis(phenylsulfonyl)-1-butene: IR (neat) 1581, 1445, 1325, and 1140 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.90 (t, 2H, J = 6.3 Hz), 4.50 (t, 1H, J = 6.3 Hz), 5.00–5.10 (m, 2H), 5.75 (m, 1H), and 7.55–7.90 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 29.7, 83.5, 118.9, 128.5, 129.1, 129.6, 131.4, 132.2, 134.6, and 137.8.

A solution containing the above material in 5 mL of THF was slowly cannulated into a stirred ice-cold suspension of 0.05 g (1.2 mmol) of 60% NaH in 50 mL of dry THF under N_2. The solution was stirred for 30 min at 0 °C, and then 0.10 g (0.30 mmol) of 2,3-bis-(phenylsulfonyl)-1,3-butadiene in 10 mL of THF was slowly added. The solution was allowed to warm to room temperature over 30 min and was then quenched with a saturated NH_4Cl solution. The reaction mixture was extracted with CH_2Cl_2 and washed with water, and the organic layer was dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was subjected to silica gel flash chromatography to give 0.10 g (63%) of allene **11a**: IR (neat) 1978, 1964, 1586, 1438, 1326, 1144, 744, and 687 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.15 (d, 2H, J = 7.3 Hz), 3.30 (t, 2H, J = 3.3 Hz), 5.05 (s, 1H), 5.10 (d, 1H, J = 7.3 Hz), 5.35 (t, 2H, J = 3.3 Hz), 5.75 (m, 1H), and 7.45–8.00 (m, 15H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 26.5, 32.1, 86.5, 90.0, 106.6, 120.4, 128.1, 128.7, 129.2, 129.6, 131.4, 133.8, 134.7, 136.4, 139.5, and 209.6.

A solution containing 0.10 g (0.18 mmol) of allene **11a** in 25 mL of anhydrous benzene under N_2 was heated at reflux for 22 h. At the end of this time the solution was concentrated under reduced pressure, and the residue was subjected to flash silica gel chromatography to give 0.09 g (90%) of 2,4,4-tris(phenylsulfonyl)bicyclo[4.2.0]oct-1-ene (**12a**): IR (neat) 1444, 1312, 1140, 1070, 727, and 681 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.60 (m, 1H), 1.70 (dd, 1H, J = 13.7 and 10.9 Hz), 2.35 (ddd, 1H, J = 19.4, 9.7, and 2.8 Hz), 2.75 (dd, 1H, J = 7.3 and 6.5 Hz), 2.90 (d, 1H, J = 18.7 Hz), 3.05 (d, 1H, J = 18.7 Hz), 3.15 (m, 1H), 3.30 (m, 1H), 3.50 (m, 1H), and 7.50–7.50 (m, 15H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 25.1, 26.3, 29.6, 32.5, 39.4, 87.4, 122.5, 127.6, 128.8, 129.0, 129.2, 131.1, 131.2, 133.4, 134.8, 134.9, 135.1, 136.3, 139.9, and 156.7; HRMS calcd for $C_{26}H_{24}O_6S_3$ 528.0735, found 528.0710.

Preparation and Thermolysis of 3,5,5-Tris(phenylsulfonyl)-8-methylnona-1,2,7-triene (11b). The experimental procedure used for the preparation of allenyl sulfone **11a** was repeated using the following reagents: 0.03 g (0.78 mmol) sample of 60% NaH, 0.18 g (0.60 mmol) of bis(phenylsulfonyl)methane, and 0.08 mL (0.60 mmol) of 90% 4-bromo-2-methyl-2-butene. The major compound isolated after flash chromatography contained 0.15 g (69%) of 5,5-bis(phenylsulfonyl)-2-methyl-2-pentene: IR (neat) 1444, 1323, and 1149 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.40 (s, 3H), 1.55 (s, 3H), 2.85 (t, 2H, J = 6.3 Hz), 4.45 (t, 1H, J = 6.3 Hz), 4.95 (t, 1H, J = 6.3 Hz), and 7.50–7.90 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 17.6, 24.7, 25.6, 83.8, 118.1, 129.0, 129.4, 134.5, 135.9, and 138.1.

A 0.15 g (0.41 mmol) sample of the above compound in 5 mL of THF was subjected to the same experimental conditions used for the preparation of allene **11a** using the following reagents: 0.02 g (0.50 mmol) of 60% NaH and 0.14 g (0.41 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene. The major fraction isolated after silica gel chromatography contained 0.13 g (60%) of allene **11b**: IR (neat) 1971, 1957, 1445, 1305, 1143, 729, and 685 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.70 (s, 3H), 1.75 (s, 3H), 3.05 (d, 2H, J = 7.0 Hz), 3.30 (t, 2H, J =

3.4 Hz), 4.90 (t, 1H, J = 7.0 Hz), 5.35 (t, 2H, J = 3.4 Hz), and 7.45–7.95 (m, 15H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 17.9, 18.2, 25.4, 30.8, 34.9, 93.3, 108.2, 120.5, 128.0, 128.8, 129.5, 130.5, 131.0, 132.8, 134.6, 134.9, 136.1, 138.9, and 208.5.

A solution of 0.10 g (0.18 mmol) of allene **11b** in 15 mL of dry benzene under N_2 was heated at reflux for 45 min. Concentration under reduced pressure and flash silica gel chromatography gave 0.09 g (90%) of 7,7-dimethyl-2,4,4-tris(phenylsulfonyl)bicyclo[4.2.0]oct-1-ene (**12b**): IR (neat) 1433, 1306, 1139, 720, and 690 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.70 (s, 3H), 1.25 (s, 3H), 1.65 (dd, 1H, J = 13.8 and 10.8 Hz), 2.55 (dd, 1H, J = 13.8 and 6.9 Hz), 2.85 (d, 1H, J = 17.0 Hz), 2.95 (d, 1H, J = 17.0 Hz), 2.95 (s, 2H), 3.15 (m, 1H), and 7.50–7.80 (m, 15H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 20.8, 23.3, 24.7, 29.0, 36.4, 44.9, 47.0, 86.5, 123.4, 127.0, 128.2, 128.4, 128.7, 130.5, 130.7, 132.9, 134.3, 134.6, 135.8, 140.0, and 152.4; HRMS calcd for $C_{28}H_{28}O_6S_3$ 556.1048, found 556.1042.

Preparation and Thermolysis of *trans*-3,5,5-Tris(phenylsulfonyl)-nona-1,2,7-triene (11c). To a stirred ice-cold suspension containing 0.09 g (2.20 mmol) of 60% NaH in 40 mL of THF under N_2 was slowly cannulated 0.50 g (1.7 mmol) of bis(phenylsulfonyl)methane in 10 mL of THF. The solution was stirred for 15 min at 0 °C, and then 0.22 mL (1.7 mmol) of 80% crotyl bromide was added dropwise *via* syringe. The solution was allowed to warm to room temperature and was then heated at reflux for 12 h before being quenched with a saturated NH_4Cl solution. 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 silica gel chromatography to give 0.33 g (55%) of *trans*-5,5-bis(phenylsulfonyl)-2-pentene as a clear oil: IR (neat) 1573, 1445, 1323, and 1149 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.55 (d, 3H, J = 5.2 Hz), 2.90 (t, 2H, J = 5.9 Hz), 4.25 (t, 1H, J = 5.9 Hz), 5.35 (m, 2H), and 7.55–7.95 (m, 10H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 17.8, 23.5, 28.9, 88.6, 124.1, 124.8, 129.0, 129.6, 134.6, and 138.1.

A solution containing the above material in 5 mL of THF was slowly cannulated into a stirred ice-cold suspension of 0.05 g (1.2 mmol) of 60% NaH in 50 mL of dry THF under N_2. The solution was stirred for 30 min at 0 °C, and then 0.35 g (1.00 mmol) of 2,3-bis-(phenylsulfonyl)-1,3-butadiene in 10 mL of THF was slowly added. The solution was allowed to warm to room temperature over 30 min and was then quenched with a saturated NH_4Cl solution. The reaction mixture was extracted with CH_2Cl_2 and washed with water, and the organic layer was dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was subjected to silica gel flash chromatography using a 35% ethyl acetate–hexane mixture to give 0.33 g (60%) of allene **11c** as a clear oil: IR (neat) 1969, 1323, 1142, 727, and 680 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.85 (d, 3H, J = 5.5 Hz), 3.10 (d, 2H, J = 6.2 Hz), 3.25 (t, 2H, J = 3.5 Hz), 5.30 (m, 1H), 5.35 (t, 2H, J = 3.5 Hz), 5.50 (m, 1H), and 7.40–8.00 (m, 15H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 17.9, 26.6, 31.2, 86.5, 90.1, 106.6, 121.8, 128.0, 128.5, 129.1, 131.3, 131.4, 133.7, 134.6, 134.7, 136.6, 139.5, and 209.6.

A solution containing 0.14 g (0.25 mmol) of **11c** in 25 mL of anhydrous benzene under N_2 was heated at reflux for 7 h. The solution was then concentrated to give, after recrystallization from CH_2Cl_2–hexane, 0.10 g (80%) of *trans*-7-methyl-2,4,4-tris(phenylsulfonyl)-bicyclo[4.2.0]oct-1-ene (**12c**): mp 203–204 °C; IR (neat) 2247, 1702, 1573, 1437, 1308, 1149, 741, and 687 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.25 (d, 3H, J = 6.5 Hz), 1.60 (dd, 1H, J = 13.6 and 10.5 Hz), 1.90 (m, 1H), 2.75 (m, 2H), 2.80 (dd, 1H, J = 13.6 and 6.5 Hz), 3.00 (m, 2H), 3.45 (dd, 1H, 15.6 and 6.5 Hz), and 7.50–7.90 (m, 15H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 20.7, 25.3, 28.8, 35.8, 39.8, 46.5, 87.2, 122.1, 127.5, 128.3, 129.0, 129.2, 131.1, 131.2, 133.4, 134.7, 134.8, 135.0, 136.3, 139.9, and 153.5. Anal. Calcd for $C_{27}H_{26}O_6S_3$: C, 59.80; H, 4.83; S, 17.73. Found: C, 59.72; H, 4.83; S, 17.71.

Preparation and Thermolysis of *cis*-3,5,5-Tris(phenylsulfonyl)-nona-1,2,7-triene (11d). A sample of *cis*-1-bromo-2-butene was prepared by a modification of a procedure of Birch and McAllan.[46] A 1.0 g (13.89 mmol) sample of *cis*-2-butenol was mixed with 15 mL of ether and 0.375 mL of pyridine in a 50 mL flask fitted with a dropping funnel and calcium chloride tube. Phosphorus tribromide (0.54 mL) in 7 mL of ether was added dropwise in 15 min at −15 to −25 °C with stirring. The reaction mixture was transferred under reduced pressure to another flask. The solution was diluted with ether, washed with water and a $NaHCO_3$ solution, and dried over anhydrous Na_2SO_4. The ether layer was concentrated under reduced pressure to give *cis*-1-bromo-2-butene (60%): IR (neat) 1460, 1260, 1100, and 795 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.72 (d, 3H, J = 6.0 Hz), 4.01 (d, 2H, J = 7.5 Hz), and 5.65–5.78 (m, 2H).

To a stirred ice-cold suspension containing 90 mg of 60% NaH in 40 mL of THF under N_2 was slowly cannulated 0.50 g (1.7 mmol) of bis(phenylsulfonyl)methane in 10 mL of THF. The solution was stirred for 15 min at 0 °C, and then 2.3 mmol of *cis*-1-bromo-2-butene in 11 mL of ether was added dropwise *via* syringe. The solution was allowed to warm to room temperature and was then heated at reflux for 11 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 to give 351 mg (60%) of *cis*-5,5-bis(phenylsulfonyl)-2-pentene: IR (KBr) 1590, 1485, 1450, 1325, 1150, 725, and 680 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.49 (d, 3H, J = 6.6 Hz), 2.91 (t, 2H, J = 6.6 Hz), 4.44 (t, 1H, J = 9.0 Hz), 5.42 (m, 1H), 5.53 (m, 1H), 7.55–7.60 (m, 4H), 7.68–7.73 (m, 2H), and 7.97 (d, 4H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 12.7, 23.5, 84.0, 124.1, 127.9, 129.1, 129.6, 134.6, and 137.9.

A solution of 279 mg (0.80 mmol) of the above compound in 5 mL of THF was slowly cannulated into a stirred ice-cold suspension of 42 mg (1.10 mmol) of 60% NaH in 42 mL of dry THF under N_2. The solution was stirred for 1.5 h at 0 °C, and then 266 mg (0.80 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene in 8 mL of THF was slowly added. The solution was allowed to warm to room temperature over 30 min and was then quenched with a saturated NH_4Cl solution. The reaction mixture was extracted with CH_2Cl_2, and the combined organic layer was washed with water and brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was chromatographed on silica gel to give 311 mg (72%) of *cis*-3,5,5-tris(phenylsulfonyl)nona-1,2,7-triene (**11d**): IR (neat) 1980, 1700, 1590, 1485, 1310, 1145, 1080, and 725 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.51 (d, 3H, J = 6.3 Hz), 3.11 (d, 2H, J = 5.4 Hz), 3.31 (t, 2H, J = 3.6 Hz), 5.27–5.34 (m, 3H), 5.50 (m, 1H), and 7.52–7.96 (m, 15H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 13.2, 26.1, 26.2, 86.3, 89.6, 106.6, 121.0, 128.0, 128.1, 128.6, 129.2, 131.3, 133.8, 134.7, 136.3, 139.4, and 209.4.

A solution of 24 mg (0.044 mmol) of *cis*-allene **11d** in 2 mL of benzene was heated at reflux under argon for 1 h. The solvent was removed under reduced pressure, and the residue was subjected to flash chromatography on silica gel to give 24 mg (100%) of *cis*-7-methyl-2,4,4-tris(phenylsulfonyl)bicyclo[4.2.0]oct-1-ene (**12d**): IR (KBr) 1700, 1590, 1485, 1450, 1300, 1140, and 740 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.78 (d, 3H, J = 6.9 Hz), 1.73 (dd, 1H, J = 14.0 and 10.8 Hz), 2.47 (dd, 1H, J = 14.0 and 7.2 Hz), 2.69–2.83 (m, 2H), 2.99 (s, 2H), 3.26–3.35 (m, 1H), 3.52–3.57 (m, 1H), and 7.51–7.92 (m, 15H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.1, 23.6, 25.1, 29.3, 39.3, 40.8, 87.2, 124.6, 127.5, 128.8, 129.0, 129.3, 131.1, 131.3, 133.5, 134.8, 134.9, 135.2, 136.3, 140.1, and 155.7; HRMS calcd for $C_{27}H_{26}O_6S_3$ 542.0891, found 542.0849.

Preparation and Thermolysis of 2-[2-(Phenylsulfonyl)buta-2,3-dienyl]-2-(2-methylallyl)malonic Acid Dimethyl Ester (15a). A mixture containing 32.8 g (219 mmol) of sodium iodide, 5.0 mL (43.7 mmol) of 3-chloro-2-methylpropene, and 15 mL of distilled DMF was heated at reflux for 15 min. The reaction was poured into ice–water, extracted with ether, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was used in the next step without further purification.

To an ice-cold suspension containing 1.59 g (39.8 mmol) of 60% NaH in 250 mL of dry THF under N_2 was slowly added 3.5 mL (30.6 mmol) of dimethyl malonate. The solution was stirred for 20 min at 0 °C, and then 3-iodo-2-methylpropene in ether was added to the reaction mixture. The solution was allowed to warm to room temperature over 30 min and was quenched with a saturated NH_4Cl solution. The reaction mixture was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous Na_2SO_4 and

(46) Birch, S. F.; McAllan, D. T. *J. Chem. Soc.* **1951**, 2556.

concentrated under reduced pressure. The crude residue was subjected to silica gel chromatography to give 3.45 g (61%) of 2-(2-methylallyl)-malonic acid dimethyl ester: IR (neat) 1735, 1649, 1228, 1043, and 900 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.64 (s, 3H), 2.52 (d, 2H, J = 7.8 Hz), 3.52 (t, 1H, J = 7.8 Hz), 3.65 (s, 6H), 4.62 (s, 1H), and 4.68 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 22.0, 36.4, 50.1, 52.3, 112.1, 141.4, and 169.2.

A 0.33 g (1.79 mmol) sample of the above compound was slowly added to an ice-cold suspension containing 90 mg (2.32 mmol) of 60% NaH in 20 mL of dry THF under N_2. The solution was stirred for 20 min at 0 °C, and then 0.60 g (1.79 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene in 15 mL of dry THF was added. After the mixture was stirred for 5 min, the reaction was quenched with a saturated NH_4Cl solution. The mixture was extracted with CH_2Cl_2, washed with water, and dried over anhydrous Na_2SO_4. Concentration under reduced pressure afforded a crude yellow solid which was subjected to silica gel chromatography to give 0.52 g (77%) of 2-[2-(phenylsulfonyl)-buta-2,3-dienyl]-2-(2-methylallyl)malonic acid dimethyl ester (**15a**): mp 106−107 °C; IR (KBr) 1975, 1730, 1321, and 1083 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.54 (s, 3H), 2.72 (s, 2H), 2.92 (t, 2H, J = 3.7 Hz), 3.62 (s, 6H), 4.52 (s, 1H), 4.71 (s, 1H), 5.39 (t, 2H, J = 3.7 Hz), 7.53 (t, 2H, J = 7.5 Hz) 7.63 (t, 1H, J = 7.5 Hz), and 7.87 (d, 2H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 23.0, 28.4, 39.7, 52.5, 56.0, 85.8, 109.4, 116.0, 128.2, 128.9, 133.4, 139.7, 139.9, 170.2, and 207.7. Anal. Calcd for $C_{19}H_{22}O_6S$: C, 60.30; H, 5.86. Found: C, 60.27; H, 5.89.

A 0.22 g (0.58 mmol) sample of the above compound was heated at reflux in xylene for 6 h. Concentration of the mixture under reduced pressure afforded 5-(phenylsulfonyl)-1-methyl-6-methylenebicyclo-[3.2.0]heptane-3,3-dicarboxylic acid dimethyl ester (**17**) (98%): IR (neat) 1730, 1299, and 1148 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.68 (s, 3H), 2.04 (d, 1H, J = 14.0 Hz), 2.47 (d, 1H, J = 13.2 Hz), 2.67 (dt, 1H, J = 15.9 and 2.3 Hz), 2.83 (dt, 1H, J = 15.9 and 2.3 Hz), 2.91 (d, 1H, J = 14.0 Hz), 3.16 (d, 1H, J = 13.2 Hz), 3.55 (s, 3H), 3.71 (s, 3H), 4.42 (t, 1H, J = 2.3 Hz), 4.93 (s, 1H), 7.54 (t, 2H, J = 7.5 Hz), 7.65 (t, 1H, J = 7.5 Hz), and 7.88 (d, 2H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 24.0, 41.8, 42.9, 47.1, 50.0, 52.8, 53.1, 60.2, 78.5, 113.1, 128.7, 129.9, 133.8, 138.0, 142.7, 170.7, and 170.8; HRMS calcd for $C_{13}H_{17}O_4$ 237.1127 ($M^+ - C_6H_5SO_2$), found 237.1184.

Preparation and Thermolysis of 2-[2-(Phenylsulfonyl)buta-2,3-dienyl]-2-(2-bromoallyl)malonic Acid Dimethyl Ester (15b). To a solution of 2.28 mL (20.0 mmol) of dimethyl malonate in 100 mL of THF at 0 °C was added 0.88 g (60% in oil, 22.0 mmol) of NaH. After the mixture was stirred for 20 min, 2.01 mL (20.0 mmol) of 1,3-dibromo-2-propene was added. The mixture was stirred at 0 °C for 1 h and the reaction quenched with saturated NH_4Cl solution. Standard workup and purification on silica gel gave 3.16 g (63%) of 2-(2-bromoallyl)malonic acid dimethyl ester: IR (neat) 1745, 1624, 1239, and 891 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.95 (d, 2H, J = 7.5 Hz), 3.69 (s, 6H), 3.76 (t, 1H, J = 7.5 Hz), 5.41 (d, 1H, J = 1.5 Hz), and 5.62 (brs, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 40.3, 50.2, 52.6, 119.7, 129, and 168.3.

To a solution of 500 mg (2.0 mmol) of 2-(2-bromoallyl)malonic acid dimethyl ester in 60 mL of THF at 0 °C was added 88 mg (2.2 mmol) of NaH. After the mixture was stirred for 20 min, a solution of 635 mg (1.9 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene in 60 mL of THF was added. The mixture was stirred for an additional 20 min and then quenched with a saturated NH_4Cl solution. Standard workup and purification on silica gel gave 538 mg (64%) of 2-[2-(phenylsulfonyl)buta-2,3-dienyl]-2-(2-bromoallyl)malonic acid dimethyl ester (**15b**): mp 113−114 °C; IR (KBr) 1971, 1735, and 885 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.01 (t, 2H, J = 3.6 Hz), 3.19 (s, 2H), 5.38 (brs, 2H), 5.42 (t, 2H, J = 3.6 Hz), 5.45 (brs, 2H), 7.54 (t, 2H, J = 7.8 Hz), 7.64 (t, 1H, J = 7.2 Hz), and 7.88 (d, 2H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 27.6, 42.5, 52.9, 55.8, 86.2, 109.2, 122.4, 126, 128.2, 129.1, 133.6, 169.2, and 207.4. Anal. Calcd for $C_{18}H_{19}BrO_6S$: C, 48.77; H, 4.32. Found: C, 48.88; H, 4.33.

A solution of 371 mg (0.84 mmol) of **15b** in 20 mL of xylene was heated at reflux for 12 h. Removal of the solvent under reduced pressure and purification gave 304 mg (82%) of 5-(phenylsulfonyl)-1-bromo-6-methylenebicyclo[3.2.0]heptane-3,3-dicarboxylic acid dimethyl ester (**18**): IR (neat) 1728, 1299, and 907 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.60 (d, 1H, J = 13.5 Hz), 2.82 (d, 1H, J = 14.7 Hz), 3.18 (brd, 1H, J = 16.4 Hz), 3.32 (d, 1H, J = 13.5 Hz), 3.43 (brd, 1H, J = 16.4 Hz), 3.48 (d, 1H, J = 14.7 Hz), 3.57 (s, 3H), 3.71 (s, 3H), 4.68 (brs, 1H), 5.04 (brs, 1H), 7.55 (t, 2H, J = 7.8 Hz), 7.68 (t, 1H, J = 7.5 Hz), and 7.98 (d, 2H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 40.5, 49.0, 50.8, 53.1, 53.4, 56.6, 60.3, 82.2, 114.6, 128.7, 130.8, 134.2, 136.4, 140.4, 169.4, and 170.0; HRMS calcd for $C_{18}H_{19}BrO_6S$ 442.0086, found 442.0074.

A solution of 53 mg (0.12 mmol) of **18** and 0.1 mL (0.36 mmol) of tri(*n*-butyl)tin hydride and 5 mg of AIBN in 10 mL of benzene was heated at reflux for 12 h. Flash chromatography of the residue on silica gel gave 40 mg (91%) of 1-(phenylsulfonyl)-7-methylenebicyclo[3.2.0]-heptane-3,3-dicarboxylic acid dimethyl ester: IR (neat) 1730, 1296, and 1082 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.25 (dd, 1H, J = 13.8 and 9.0 Hz), 2.27−2.35 (m, 1H), 2.61−2.71 (m, 3H), 3.02 (d, 1H, J = 13.8 Hz), 3.31 (brt, 1H, J = 8.1 Hz), 3.60 (s, 3H,), 3.69 (s, 3H), 4.80 (brs, 1H), 4.96 (brs, 1H), 7.52 (t, 2H, J = 7.8 Hz), 7.64 (t, 1H, J = 7.2 Hz), and 7.87 (d, 2H, J = 7.2 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 34.6, 38.5, 39.2, 40.1, 52.8, 53.1, 62.7, 78.5, 114.1, 128.8, 130.0, 133.8, 136.4, 144.0, 170.6, and 170.9; HRMS calcd for $C_{18}H_{20}O_6S$ 364.0980, found 364.0979.

Preparation and Thermolysis of 3-Ethenyl-2-(2-(phenylsulfonyl)-2,3-butadienyl)cyclopentanone (20). To a solution containing 0.18 g (0.98 mmol) of 3-ethenyl-1-(trimethylsiloxy)-1-cyclopentene (**19**)[47] in 15 mL of dry THF at 0 °C under N_2 was added dropwise 0.69 mL (1.1 mmol) of a 1.6 M solution of *n*-butyllithium in THF. After 15 min, the solution was cooled to −78 °C and slowly cannulated into a −50 °C solution containing 0.30 g (0.90 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene in 20 mL of THF. The solution was stirred for an additional 30 min before the reaction was 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 flash silica gel chromatography to give 0.21 g (77%) of allenyl cyclopentane **20**: IR (neat) 1962, 1940, 1738, 1312, 1072, 721, and 677 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.60 (m, 2H), 2.00−2.60 (m, 6H), 4.95 (d, 1H, J = 7.7 Hz), 5.00 (s, 1H), 5.35 (t, 2H, J = 3.0 Hz), 5.70 (m, 1H), and 7.50−7.90 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 24.9, 27.0, 36.7, 46.3, 52.1, 84.6, 110.1, 115.3, 127.7, 128.6, 128.7, 129.9, 133.1, 139.2, 208.0, and 216.5.

A solution containing 0.10 g (0.33 mmol) of allene **20** and several drops of tributylamine in toluene was brought to reflux under N_2 and heated for 3 days. The reaction mixture was then concentrated under reduced pressure and subjected to silica gel chromatography to give 0.02 g (20%) of 3-(phenylsulfonyl)-2,4,4a,5,6,7,7a,7b-octahydro-1*H*-cyclobut[*e*]inden-5-one (**21**) as a 4:1 mixture of two diastereomers: IR (neat) 1733, 1433, 1300, and 1150 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.50−2.55 (m, 10H), 3.10 (m, 1H), 3.25 (m, 1H), 3.35 (m, 1H), and 7.55−7.90 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 20.5, 23.5, 24.4, 24.8, 25.7, 26.1, 31.8, 33.5, 37.7, 38.5, 42.9, 43.8, 48.4, 50.1, 51.0, 125.7, 127.5, 127.6, 129.1, 129.2, 133.2, 156.8, and 217.1; HRMS calcd for $C_{17}H_{18}O_3S$ 302.0977, found 302.0989.

Preparation and Thermolysis of 5,5-Dicarbomethoxy-3-(phenylsulfonyl)-1,2,7,9-decatetraene (22). To a suspension of 440 mg (11.0 mmol) of 60% NaH in 50 mL of THF at 0 °C was added 1.14 mL (10.0 mmol) of dimethyl malonate. After the mixture was stirred at 0 °C for 15 min, a solution containing 1.47 g (10.0 mmol) of 5-bromo-1,3-pentadiene[48] in 10 mL of THF was added. The mixture was stirred at room temperature for 2 h and quenched with NH_4Cl. Standard workup and purification by silica gel chromatography gave 680 mg (35%) of dimethyl (2,4-pentadienyl)propanedioate and 530 mg (20%) of dimethyl di(2,4-pentadienyl)propanedioate. The desired monoalkylated product exhibited the following spectral properties: IR (neat) 1742, 1426, 1148, and 901 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.64 (t, 2H, J = 7.5 Hz), 3.41 (t, 1H, J = 7.5 Hz), 3.67 (s, 6H), 4.98 (d, 1H, J = 9.6 Hz), 5.09 (d, 1H, J = 16.5 Hz), 5.58 (quin, 1H, J = 7.2 Hz), and 6.04−6.29 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 31.7, 51.5, 52.4, 116.5, 129.3, 133.7,136.4, and 169.1.

(47) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5253.
(48) Mebane, A. D. *J. Am. Chem. Soc.* **1952**, *74*, 5227.

To a solution of 198 mg (1.0 mmol) of the above compound in 10 mL of THF at 0 °C was added 44 mg (1.1 mmol) of NaH. The mixture was stirred at 0 °C for 15 min, and then 334 mg (1.0 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene in 15 mL of THF was added. After the mixture was stirred for 10 min, the reaction was quenched by adding aqueous NH_4Cl. Standard workup and purification by silica gel chromatography gave 313 mg (80%) of 5,5-dicarbomethoxy-3-(phenylsulfonyl)-1,2,7,9-decatetraene (**22**): IR (neat) 1962, 1727, 1441, 1316, and 1082 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.59 (d, 2H, J = 7.5 Hz), 2.80 (bs, 2H), 3.54 (s, 6H), 4.90 (d, 1H, J = 10.2 Hz), 4.99 (d, 1H, J = 17.1 Hz), 5.24−5.34 (m, 2H), 5.89 (dd, 1H, J = 14.7 and 10.5 Hz), 6.08 (dt, 1H, J = 17.1 and 10.2 Hz), and 7.43−7.79 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 28.3, 35.0, 52.3, 56.9, 85.3, 108.6, 116.5, 126.8, 127.8, 128.9, 133.4, 135.1, 136.1, 139.5, 169.6, and 207.9; HRMS calcd for $C_{20}H_{22}O_6S$ 390.1137, found 390.1124.

A solution of 276 mg (0.71 mmol) of allene **22** in 10 mL of benzene was heated at reflux for 5 h under N_2. Removal of the solvent afforded the [2 + 2] product **24** as well as the [4 + 2] product **25** in a 2:1 ratio in 96% combined yield. Cycloadduct **24** exhibited the following spectral properties: IR (neat) 1737, 1446, 1254, 1140, and 720 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.67 (dd, 1H, J = 12.9 and 10.2 Hz), 2.48 (dd, 1H, J = 12.6 and 6.3 Hz), 2.55 (m, 1H), 2.64 (dd, 1H, J = 14.5 and 7.3 Hz), 2.71 (m, 1H), 2.91−3.00 (m, 2H), 3.52−3.59 (m, 1H), 3.65 (s, 3H), 3.67 (s, 3H), 5.05 (s, 1H), 5.09 (d, 1H, J = 6.6 Hz), 5.87−5.99 (m, 1H), 7.52−7.65 (m, 3H), and 7.89 (d, 2H, J = 7.2 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 29.4, 31.1, 38.6, 42.1, 46.5, 52.9, 53.0, 54.2, 115.0, 124.6, 127.4, 129.2, 133.2, 139.2, 140.4, 152.0, 170.3, and 170.9; HRMS calcd for $C_{20}H_{22}O_6S$ 390.1137, found 390.1123.

The [4 + 2]-cycloadduct **25** exhibited the following spectral properties: IR (neat) 1730, 1440, 1295, and 1150 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.67 (dd, 1H, J = 13.3 and 12.2 Hz), 1.90−2.30 (m, 4H), 2.45 (dd, 1H, J = 13.3, 5.7 and 1.8 Hz), 2.79 (dt, 1H, J = 18.0 and 2.4 Hz), 2.89−3.00 (m, 1H), 3.29 (dd, 1H, J = 18.0 and 2.1 Hz), 3.57 (s, 1H), 3.72 (s, 3H), 5.42 (d, 1H, J = 9.9 Hz), 5.72−5.77 (m, 1H), 7.52−7.64 (m, 3H), and 7.95 (d, J = 6.9 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 27.5, 27.6, 32.1, 33.6, 37.1, 52.6, 52.8, 53.0, 126.9, 127.4, 127.5, 128.1, 129.0, 133.0, 142.0, 150.8, 170.1, and 171.0; HRMS calcd for $C_{20}H_{22}O_6S$ 390.1137, found 390.1149.

Preparation and Thermolysis of 1-(2-Furfuryloxy)-2-(phenylsulfonyl)-2,3-butadiene (27). To a solution containing 1.4 g (7.0 mmol) of 4-((*tert*-butyldimethylsilyl)oxy)-2-butyn-1-ol in 56 mL of THF at 0 °C was added 372 mg (9.24 mmol) of 60% NaH in one portion. The mixture was stirred at 0 °C for 30 min, and then a 1.49 g (9.24 mmol) sample of furfuryl bromide[49] in 5 mL of ether was added. The mixture was stirred at room temperature for 4 h, quenched with 40 mL of a NH_4Cl solution, and extracted with ether. The organic layer was washed twice with a $NaHCO_3$ solution, water, and brine and dried over Na_2SO_4. After concentration under reduced pressure, the residue was dissolved in 84 mL of THF and cooled to 0 °C, and 8.4 mL (8.4 mmol) of TBAF was added. The solution was stirred at room temperature for 1.5 h, and then 30 mL of an aqueous NH_4Cl solution was added. The solvent was removed under reduced pressure, and the mixture was extracted with ether. The organic layer was washed twice with $NaHCO_3$, water, and brine and dried over Na_2SO_4. Flash silica gel chromatography of the residue gave 0.80 g (69%) of 4-(2-furfuryloxy)-2-butyn-1-ol (**26**): IR (neat) 1619, 1499, 1431, 1342, 1140, 1058, and 736 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 2.05 (s, 1H), 4.19 (d, 2H, J = 1.5 Hz), 4.30 (s, 2H), 4.54 (s, 2H), 6.36 (m, 2H), and 7.41 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 50.9, 57.1, 63.2, 81.1, 85.1, 110.0, 110.4, 143.1, and 150.8.

To a solution containing 200 mg (1.2 mmol) of the above compound and 0.33 mL (2.36 mmol) of Et_3N in 28 mL of CH_2Cl_2 at −78 °C was added 0.20 mL (2.01 mmol) of benzenesulfenyl chloride dropwise, and the solution was stirred at this temperature for 45 min. The mixture was warmed with stirring to room temperature over 45 min, diluted with CH_2Cl_2, washed twice with an aqueous $NaHCO_3$ solution, water, and brine, and dried over Na_2SO_4. Concentration and purification by flash silica gel chromatography gave 300 mg (91%) of 1-(2-furfuryloxy)-2-(phenylsulfenyl)-2,3-butadiene: IR (neat) 1937, 1602, 1503, 1439, 1047, and 745 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 4.10−4.20 (m, 2H), 4.29 (d, 2H, J = 2.8 Hz), 5.33 (t, 2H, J = 1.7 Hz), 6.21 (d, 1H, J = 2.8 Hz), 6.30 (m, 1H), 7.36 (d, 1H, J = 1.7 Hz), 7.48 (m, 3H), and 7.65 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 63.3, 63.5, 83.0, 109.8, 110.2, 110.3, 124.6, 129.0, 131.1, 142.9, 143.0, 150.7, and 205.7; HRMS calcd for $C_{15}H_{14}O_3S$ 274.0663, found 274.0650.

To a solution containing 335 mg (1.12 mmol) of the above allenyl sulfoxide in 60 mL of water and 120 mL of methanol was added 48 mg (0.39 mmol) of Na_2CO_3 and then 2.38 g (3.88 mmol) of Oxone. The mixture was stirred at room temperature for 2.5 h and the methanol was removed *in vacuo* at room temperature. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was washed with water and brine and dried over Na_2SO_4. Flash silica gel chromatography gave 112 mg (35%) of 1-(2-furfuryloxy)-2-(phenylsulfonyl)-2,3-butadiene (**27**): IR (neat) 1958, 1726, 1570, 1493, 1140, 1071, and 727 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 4.27 (s, 2H), 4.32 (t, 2H, J = 1.8 Hz), 5.47 (t, 2H, J = 1.8 Hz), 6.19 (d, 1H, J = 3.3 Hz), 6.30 (m, 1H), 7.36 (s, 1H), 7.50 (m, 2H), 7.59 (m, 1H), and 7.91 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 63.6, 65.6, 84.0, 109.9, 110.1, 110.3, 128.1, 128.7, 128.9, 133.4, 142.9, 150.6, and 209.5; HRMS calcd for $C_{15}H_{14}O_4S$ 290.0612, found 290.0630.

The second component isolated from the silica gel column contained 138 mg (16%) of 7-methylene-3a,6-*endo*-epoxy-7a-(phenylsulfonyl)-1,3,3a,6,7,7a-hexahydrobenzo[*c*]furan (**28**): IR (neat) 1720, 1657, 1444, 1302, 1053, and 897 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 3.98 (m, 3H), 4.81 (d, 1H, J = 10.5 Hz), 5.14 (s, 1H), 5.44 (d, 2H, J = 11.4 Hz), 6.45 (m, 1H), 6.49 (m, 1H), 7.51−7.57 (m, 2H), 7.64−7.90 (m, 1H), and 7.87−7.90 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 67.3, 72.8, 80.5, 84.8, 100.4, 112.4, 128.6, 130.2, 132.0, 134.1, 137.3, 137.4, and 142.0; HRMS calcd for $C_{15}H_{14}O_4S$ 290.0612, found 290.0609. This same compound was prepared by heating a sample of **27** in benzene for 1.5 h in 90% yield.

Preparation and Thermolysis of 1-(2-Propenoxy)-2-(phenylsulfonyl)-2,3-butadiene (29). A 2.24 g (56 mmol) sample of NaH (60%) was washed with hexane and suspended in 85 mL of THF. To this mixture was added 4.82 g (56 mmol) of 2-butyne-1,4-diol in 75 mL of THF at room temperature. The mixture was stirred for 3.5 h, then 8.44 g (56 mmol) of *tert*-butyldimethylsilyl chloride was added, and vigorous stirring was continued for another 2.5 h. The mixture was poured into ether, washed with 10% aqueous K_2CO_3 and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The resulting oil was purified by flash silica gel chromatography to give 3.34 g (30%) of 4-((*tert*-butyldimethylsilyl)oxy)-2-butyn-1-ol: IR (neat) 3368, 1469, 1350, 1245, 1006, and 826 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 0.11 (s, 6H), 0.90 (s, 9H), 1.78 (s, 1H), 4.29 (d, 2H, J = 1.2 Hz), and 4.34 (s, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 5.2, 18.3, 25.8, 51.1, 51.7, 83.0, and 84.3.

To a solution of 1.4 g (7 mmol) of the above compound in 56 mL of THF at 0 °C was added 372 mg (9.24 mmol) of 60% NaH in one portion. The mixture was stirred at 0 °C for 30 min. Allyl iodide (0.84 mL, 9.24 mmol) was added, and the mixture was stirred at room temperature for 3 h, quenched with 40 mL of an NH_4Cl solution, and extracted with ether. The organic layer was washed with water, brine and dried over Na_2SO_4. After concentration under reduced pressure the residue was dissolved in 84 mL of THF and cooled to 0 °C, and 8.4 mL (8.4 mmol) of TBAF was added. The solution was stirred at room temperature for 1.25 h, and then an NH_4Cl solution was added and the THF was removed under reduced pressure. The mixture was extracted with ether, and the organic layer was washed with water and brine and dried over Na_2SO_4. Flash chromatography on silica gel gave 0.66 g (75%) of 4-(2-propenoxy)-2-butyn-1-ol: IR (neat) 3415, 1645, 1415, 1345, 1225, 1120 and 1010 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.78 (brs, 1H), 4.03 (d, 2H, J = 5.7 Hz), 4.16 (t, 2H, J = 1.5 Hz), 4.26 (t, 2H, J = 1.5 Hz), 5.19 (brd, 1H, J = 10.2 Hz), 5.28 (dd, 1H, J = 17.0 and 1.2 Hz), and 5.80−5.93 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 50.7, 57.3, 70.6, 81.2, 84.8, 117.9, and 133.7.

To a solution of 0.66 g (5.24 mmol) of the above compound and 1.09 mL (7.81 mmol) of triethylamine in 91 mL of CH_2Cl_2 at −78 °C was added 0.52 mL (5.24 mmol) of benzenesulfenyl chloride dropwise. The mixture was stirred, warmed to room temperature, diluted with CH_2Cl_2, washed with water and brine, and dried over Na_2SO_4. Concentration of the mixture under reduced pressure and purification by flash chromatography on silica gel gave 1.05 g (86%) of 1-(2-propenoxy)-2-(phenylsulfenyl)-2,3-butadiene: IR (neat) 1937, 1641, 1437,

(49) Zanetti, J. E. *J. Am. Chem. Soc.* **1927**, *49*, 1065.

1086, and 1043 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.68−3.92 (m, 2H), 4.03−4.20 (m, 2H), 4.09−4.16 (m, 2H), 5.32 (t, 2H, J = 1.8 Hz), 5.64−5.77 (m, 1H), 7.41−7.43 (m, 3H), and 7.56−7.61 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 63.2, 70.6, 82.6, 110.1, 117.3, 124.4, 128.8, 130.8, 133.5, 142.9, and 205.5.

To a solution of 500 mg (2.15 mmol) of the above sulfoxide in 50 mL of water and 100 mL of methanol was added 2.4 g (3.91 mmol) of Oxone. The mixture was stirred at room temperature for 24 h, and the methanol was removed *in vacuo*. The aqueous layer was extracted with ether, and the organic layer was washed with water and brine and dried over Na_2SO_4. Purification by silica gel chromatography gave 440 mg (82%) of 1-(2-propenoxy)-2-(phenylsulfonyl)-2,3-butadiene (**29**): IR (neat) 1969, 1641, 1314, 1148, 1086, and 734 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.75 (brd, 2H, J = 5.7 Hz), 4.26 (t, 2H, J = 1.5 Hz), 5.03−5.09 (m, 2H), 5.44 (t, 2H, J = 1.5 Hz), 5.58−5.71 (m, 1H), and 7.46−7.90 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 65.8, 70.7, 83.7, 110.0, 117.6, 127.9, 128.8, 133.3, 133.4, 141.0, and 209.3.

A solution of 107 mg (0.43 mmol) of **29** in 5 mL of xylene was heated at reflux under argon for 24 h. The solvent was removed under reduced pressure, and the residue was subjected to flash chromatography on silica gel to give 79 mg (74%) of 3-(phenylsulfonyl)-5,6-dihydro-2*H*-pyrano[5,4-*a*]cyclobutane (**31**): IR (neat) 1681, 1578, 1438, 1304, 1154, 1062, and 754 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.82 (quin, 1H, J = 8.1 Hz), 2.24 (ddd, 1H, J = 19.4, 9.6, and 2.7 Hz), 3.02 (t, 1H, J = 10.2 Hz), 3.21−3.35 (m, 2H), 3.37−3.50 (m, 1H), 3.99 (dd, 1H, J = 10.5 and 6.9 Hz), 4.22 (d, 2H, J = 1.8 Hz), and 7.52−7.92 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 23.3, 34.0, 42.5, 63.1, 66.9, 124.9, 127.2, 129.3, 133.4, 140.8, and 155.0; HRMS calcd for $C_{13}H_{14}O_3S$ 250.0664, found 250.0648.

Preparation and Thermolysis of 1-(3-Methyl-2-butenoxy)-2-(phenylsulfonyl)-2,3-butadiene (30). To a solution of 1.4 g (7 mmol) of 4-((*tert*-butyldimethylsilyl)oxy)-2-butyn-1-ol in 56 mL of THF at 0 °C was added 372 mg (9.24 mmol) of 60% NaH, and the mixture was stirred at 0 °C for 30 min. A 2.0 g (13.4 mmol) sample of 1-bromo-3-methyl-2-butene was added, and the mixture was warmed to room temperature over 2 h and was stirred for an additional 3 h at room temperature. The mixture was quenched with 40 mL of an NH_4Cl solution and extracted with ether, and the organic layer was washed with water and brine and dried over Na_2SO_4. After concentration under reduced pressure, the residue was subjected to flash chromatography on silica gel to give 1.76 g (94%) of the alkylated product. This compound was taken up in 84 mL of THF and cooled to 0 °C, and 8.4 mL (8.4 mmol) of TBAF was added. The solution was stirred at room temperature for 3.5 h, and then 40 mL of an NH_4Cl solution was added and the THF was removed under reduced pressure. The mixture was extracted with ether, and the organic layer was washed with water and brine and dried over Na_2SO_4. Flash chromatography on silica gel gave 864 mg (81%) of 4-(3-methyl-2-butenoxy)-2-butyn-1-ol: IR (neat) 3390, 1675, 1440, 1350, 1115, 1060, and 920 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.66 (s, 3H), 1.71 (s, 3H), 2.83 (brs, 1H), 4.00 (d, 2H, J = 7.2 Hz), 4.12 (s, 2H), 4.25 (s, 2H), and 5.26−5.31 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 17.9, 25.6, 50.7, 56.9, 66.0, 81.5, 84.5, 120.0, and 138.2.

To a solution of 288 mg (1.87 mmol) of the above compound and 0.39 mL (2.79 mmol) of triethylamine in 32 mL of CH_2Cl_2 at −78 °C was added 0.19 mL (1.87 mmol) of benzenesulfenyl chloride dropwise. The mixture was stirred at room temperature for 1 h, diluted with CH_2Cl_2, washed with water and brine, and dried over Na_2SO_4. Concentration under reduced pressure and purification by flash chromatography on silica gel gave 445 mg (91%) of 1-(3-methyl-2butenoxy)-2-(phenylsulfenyl)-2,3-butadiene: IR (neat) 1935, 1580, 1470, 1430, 1370, 1070, and 740 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.57 (s, 3H), 1.68 (s, 3H), 3.80 (m, 2H), 4.01 (dt, 1H, J = 12.6 and 2.4 Hz), 4.15 (dt, 2H, J = 12.9 and 1.8 Hz), 5.12 (m, 1H), 5.30 (t, 2H, J = 2.1 Hz), 7.46−7.51 (m, 3H), and 7.62−7.66 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 17.9, 25.7, 63.3, 66.4, 82.9, 110.8, 120.2, 124.7, 128.9, 131.0, 137.6, 143.2, and 205.4.

To a solution of 120 mg (0.46 mmol) of the above sulfoxide in 18 mL of water and 36 mL of methanol was added 436 mg (0.71 mmol) of Oxone at 0 °C. The mixture was warmed to room temperature and stirred for 7 h, and the methanol was removed *in vacuo*. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was washed with water and brine and dried over Na_2SO_4. Purification by silica gel chromatography gave 20 mg (16%) of 1-(3-methyl-2-butenoxy)-2-(phenylsulfonyl)-2,3-butadiene (**30**): IR (neat) 1961, 1586, 1420, 1325, 1146, and 725 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.57 (s, 3H), 1.67 (s, 3H), 3.79 (d, 2H, J = 6.9 Hz), 4.27 (s, 2H), 5.09 (m, 1H), 5.46 (t, 2H, J = 3.0 Hz), 7.50−7.64 (m, 3H), and 7.93 (d, 2H, J = 7.8 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 18.0, 25.7, 65.6, 66.4, 83.8, 116.0, 120.0, 128.1, 128.9, 133.4, 137.7, 141.0, and 209.3.

A solution of 50 mg (0.18 mmol) of **30** in 10 mL of toluene was heated at reflux under argon for 5.5 h. The solvent was removed under reduced pressure, and the residue was subjected to flash chromatography on silica gel to give 50 mg (100%) of 8,8-dimethyl-3-(phenylsulfonyl)-5,6-dihydro-2*H*-pyrano[5,4-*a*]cyclobutane (**32**): IR (neat) 1685, 1590, 1470, 1310, 1160, 1100, and 730 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.95 (s, 3H), 1.29 (s, 3H), 2.95 (m, 2H), 3.10 (m, 2H), 3.84 (m, 1H), 4.20 (s, 2H), 7.52−7.62 (m, 3H), and 7.87 (d, 2H, J = 7.2 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.8, 30.1, 37.5, 46.7, 50.4, 62.9, 63.2, 127.0, 127.2, 129.2, 133.4, 141.1, and 151.8; HRMS calcd for $C_{15}H_{18}O_3S$ 278.0976, found 278.0954.

Preparation and Thermolysis of 3-(Phenylsulfonyl)-1,2,7-octatriene (33). To a solution of 2.8 g (20.0 mmol) of tetrahydro-2-(2-propynyloxy)-2*H*-pyran in 100 mL of THF at −78 °C was added 13.1 mL of a 1.6 M *n*-butyllithium solution (21 mmol). After the mixture was stirred for 20 min, 5.2 mL (30 mmol) of HMPA was added, followed by the addition of 2.5 g (21 mmol) of 5-bromo-1-pentene. The mixture was warmed to room temperature and stirred overnight, the reaction was then quenched by adding a saturated NH_4Cl solution, and the mixture was finally diluted with 500 mL of ether. The organic layer was washed with water and brine and concentrated under reduced pressure. The residue was dissolved in 100 mL of methanol, and to this solution was added 0.4 g of *p*-toluenesulfonic acid and 2 mL of water. After the mixture was stirred for 4 h, the methanol was removed under reduced pressure, and the residue was diluted with ether, washed with water and brine, and dried. Removal of the solvent followed by silica gel chromatography gave 1.1 g (44%) of 7-octen-2-yn-1-ol: IR (neat) 2223, 1640, and 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.52 (quin, 2H, J = 7.2 Hz), 2.02−2.16 (m, 4H), 2.76−2.85 (m, 1H), 4.16 (s, 2H), 4.88−4.98 (m, 2H), and 5.63−5.77 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 17.9, 27.6, 32.6, 50.8, 78.5, 85.6, 115.0, and 137.6.

To a solution of 170 mg (1.37 mmol) of 7-octen-2-yn-1-ol and 0.23 mL (1.64 mmol) of NEt_3 in 10 mL of CH_2Cl_2 at −78 °C was added 0.16 mL (1.64 mmol) of benzenesulfenyl chloride. After the solution stirred at −78 °C for 40 min, the reaction was quenched with a saturated NH_4Cl solution. Standard workup followed by silica gel chromatography gave 250 mg (79%) of 3-(phenylsulfenyl)-1,2,7-octatriene: IR (neat) 1950, 1643, 1442, and 1045 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30−2.20 (m, 6H), 4.75−4.81 (m, 2H), 5.13−5.22 (m, 2H), 5.50−5.58 (m, 1H), and 7.35−7.51 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.7, 26.2, 32.5, 82.0, 112.6, 114.7, 124.1, 128.6, 130.5, 137.3, 143.2, and 205.1; HRMS calcd for $C_{14}H_{16}SO$ 232.0922, found 232.0922.

To a solution of 80 mg (0.25 mmol) of the above sulfoxide in 10 mL of water and 10 mL of methanol was added 300 mg (0.49 mmol) of Oxone. The mixture was stirred at room temperature for 2 days. Standard workup and flash silica gel chromatography gave 75 mg (88%) of 3-(phenylsulfonyl)-1,2,7-octatriene (**33**): IR (neat) 1968, 1732, 1442, 1300, and 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.50 (quin, 2H, J = 7.5 Hz), 1.99 (q, 2H, J = 7.2 Hz), 2.15−2.25 (m, 2H), 4.87−4.93 (m, 2H), 5.34 (t, 2H, J = 3.0 Hz), 5.60−5.71 (m, 1H), 7.50 (t, 2H, J = 7.8 Hz), 7.60 (t, 1H, J =7.2 Hz), and 7.86 (d, 2H, J = 7.2 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 25.9, 26.5, 32.6, 84.3, 113.1, 115.2, 128.0, 129.0, 133.4, 137.4, 140.1, and 207.6; MS *m/e* 248 (M^+), 125, and 79 (base).

A solution of 60 mg (0.081 mmol) of **33** in 10 mL of xylene was heated to reflux for 4 days. After the xylene was removed under reduced pressure, the residue was chromatographed on silica gel to give 36 mg (60%) of 2-(phenylsulfonyl)bicyclo[4.2.0]oct-1-ene (**34**): IR (neat) 1680, 1450, 1305, and 1148 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.96−1.10 (m, 1H), 1.35−1.51 (m, 1H), 1.59−1.73 (m, 2H), 1.78−1.89 (m, 2H), 2.08−2.26 (m 2H), 2.90−3.05 (m, 1H), 3.08−3.20 (m, 1H), 3.28−3.36 (m 1H), 7.50−7.62 (m, 3H), and 7.86 (d, 2H, J = 6.9 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.9, 23.3, 25.9, 26.7,

33.4, 44.1, 125.9, 127.5, 129.0, 132.9, 140.9, and 157.7; MS 248 (M^+), 79 (base); HRMS calcd for $C_{14}H_{16}O_2S$ 248.0871, found 248.0872.

Preparation and Thermolysis of 5,5-Dicarbomethoxy-3-(phenylsulfonyl)nona-1,2,8-triene (35). To a stirred ice-cold suspension containing 180 mg (4.5 mmol) of 60% NaH in 40 mL of THF under N_2 was slowly cannulated 0.4 mL (3.4 mmol) of dimethyl malonate. The solution was stirred for 15 min at 0 °C, and then 0.48 mL (4.6 mmol) of 4-bromo-1-butene was added *via* syringe. The solution was allowed to warm to room temperature 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 352 mg (60%) of 5,5-dicarbomethoxy-1-pentene: IR (neat) 1738, 1638, 1431, 1225, 1154, and 912 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.94−2.10 (m, 4H), 3.37 (t, 1H, J = 6.9 Hz), 3.71 (s, 6H), 4.97−5.04 (m, 2H), and 5.66−5.80 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 27.8, 31.2, 50.8, 52.4, 115.9, 136.7, and 169.7.

To a stirred ice-cold solution of 94 mg (0.5 mmol) of the above compound in 20 mL of THF was added 24 mg (0.6 mmol) of 60% NaH. The solution was stirred for 20 min at 0 °C under N_2, and then 169 mg (0.5 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene in 14 mL of THF was slowly added. The solution was stirred for 15 min at 0 °C and then allowed to warm to room temperature 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. Flash silica gel chromatography gave 125 mg (66%) of 5,5-dicarbomethoxy-3-(phenylsulfonyl)nona-1,2,8-triene (**35**): IR (neat) 1965, 1730, 1638, 1432, 1200, 1075, and 727 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.78−1.86 (m, 2H), 1.96−2.02 (m, 2H), 2.92 (t, 2H, J = 2.9 Hz), 3.65 (s, 6H), 4.91−4.98 (m, 2H), 5.34 (t, 2H, J = 2.9 Hz), 5.59−5.73 (m, 1H), 7.52−7.66 (m, 3H), and 7.86−7.89 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 28.2, 28.5, 30.9, 52.5, 56.5, 85.4, 108.9, 115.2, 128.2, 129.1, 133.6, 136.9, 139.8, 148.6, 170.4, and 208.2; HRMS calcd for $C_{19}H_{23}O_6S$ 378.1137, found 378.1154.

A solution containing 50 mg (0.13 mmol) of allene **35** in 7 mL of xylene under N_2 was heated at reflux for 89 h. Removal of the solvent under reduced pressure gave 20 mg (80%) of 3,3-dicarbomethoxy-8-methylene-1-(phenylsulfonyl)cyclooct-1-ene (**38**) after silica gel purification: IR (neat) 1730, 1602, 1502, 1445, 1304, 1132, and 713 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.34 (m, 2H), 1.51 (m, 2H), 1.94 (t, 2H, J = 5.7 Hz), 2.44 (t, 2H, J = 5.7 Hz), 3.78 (s, 6H), 4.79 (s, 1H), 5.26 (s, 1H), 7.48−7.60 (m, 4H), and 7.83 (d, 2H, J = 7.2 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 22.4, 25.4, 28.0, 35.6, 53.2, 60.5, 120.8, 128.8, 129.0, 133.4, 136.3, 138.3, 139.8, 142.0, and 169.2; HRMS calcd for $C_{19}H_{22}O_6S$ 378.1137, found 378.1144.

Preparation and Thermolysis of 3,5,5-Tris(phenylsulfonyl)nona-1,2,8-triene (36). To a stirred ice-cold suspension containing 0.09 g of 60% NaH in 40 mL of THF under N_2 was slowly cannulated 0.50 g (1.7 mmol) of bis(phenylsulfonyl)methane in 10 mL of THF. The solution was stirred for 20 min at 0 °C, and then 1.05 g (5.8 mmol) of 4-iodo-1-butene[50] was added dropwise *via* syringe. The solution was allowed to warm to room temperature and was heated at reflux for 3 days 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 to give 542 mg (91%) of 5,5-bis(phenylsulfonyl)-1-pentene: IR (neat) 1727, 1639, 1568, 1441, 1147, 908, 789, and 678 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.25−2.35 (m, 4H), 4.46 (t, 1H, J = 4.2 Hz), 5.00−5.07 (m, 2H), 5.49−5.59 (m, 1H), 7.55−7.73 (m, 6H), and 7.95 (d, 4H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 24.6, 31.5, 81.9, 117.8, 129.1, 129.6, 134.5, 135.4, and 137.9.

A solution containing 280 mg (0.80 mmol) of the above compound in 20 mL of THF was slowly cannulated into a stirred ice-cold suspension of 42 mg (1.10 mmol) of 60% NaH in 40 mL of dry THF under N_2. The solution was stirred for 3 h at 0 °C, and then 266 mg (0.80 mmol) of bis(phenylsulfonyl)butadiene in 8 mL of THF was slowly added. The solution was stirred at 0 °C for 45 min and then was allowed to warm to room temperature over 45 min. The reaction was quenched with a saturated NH_4Cl solution, the mixture was extracted with CH_2Cl_2, and the combined organic layer was washed with water and brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was chromatographed on silica gel to give 109 mg (25%) of 3,5,5-tris(phenylsulfonyl)nona-1,2,8-triene (**36**): mp 77−78 °C; IR (neat) 1965, 1723, 1638, 1574, 1439, 1311, 1147, 855, and 720 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.26−2.32 (m, 2H), 2.39−2.42 (m, 2H), 3.33 (t, 2H, J = 3.8 Hz), 4.91−4.97 (m, 2H), 5.22 (t, 2H, J = 3.8 Hz), 5.57−5.68 (m, 1H), and 7.53−7.95 (m, 15H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 25.9, 26.8, 28.0, 86.3, 90.7, 107.1, 115.8, 128.2, 128.7, 129.3, 131.3, 134.0, 134.7, 135.9, 136.6, 139.5, and 208.9; HRMS calcd for $C_{27}H_{26}O_6S_3Li$ 549.1051 (M + Li), found 549.1062.

A solution of 25 mg (0.046 mmol) of allene **36** in 9 mL of benzene was heated at reflux under argon for 20 days. The solvent was removed under reduced pressure, and the residue was subjected to flash chromatography on silica gel to give 20 mg (81%) of 8-methylene-1,3,3-tris(phenylsulfonyl)cyclooct-1-ene (**39**): mp 74−75 °C; IR (neat) 1716, 1581, 1439, 1325, 1076, 919, and 748 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.52−1.54 (m, 2H), 1.85 (m, 2H), 2.00 (m, 2H), 2.68 (t, 2H, J = 6.3 Hz), 3.69 (s, 1H), 4.78 (s, 1H), 7.47 (s, 1H), and 7.52−7.93 (m, 15H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.8, 25.3, 25.9, 35.5, 92.4, 120.4, 128.3, 128.6, 129.0, 129.1, 129.4, 131.4, 134.0, 134.9, 137.3, 138.9, and 147.6; HRMS calcd for $C_{27}H_{26}O_6S_3Li$ 549.1051 (M + Li), found 549.1050.

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Supporting Information Available: Tables of X-ray data and ORTEP diagrams for cycloadducts **12c** and **39** (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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