# 2,3-Bis(phenylsulfonyl)-1,3-butadiene: Substrate for Michael Donor/Acceptors in a Novel Synthesis of Fused Cyclopentenes

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The reaction of 2,3-bis(phenylsulfonyl)-1,3-butadiene with the anion of various 1-substituted dimethyl 1-pentenedioates has been investigated with the purpose of devising a tandem conjugate addition−[3 + 2]-anionic cyclization route for the synthesis of bicyclo[3.3.0]octenes. The reaction proceeds with complete stereospecificity as was evidenced by treating (*E*)- and (*Z*)-dimethyl (3-cyano-2-propenyl)propanedioate with NaH in the presence of the bis(phenylsulfonyl)diene. In both cases only a single cycloadduct was obtained with no detectable signs of the other diastereomer. The overall process involves a series of three sequential conjugate additions followed by benzenesulfinate ion ejection. The success of the method is dependent on the electrophilicity of the proximal $\pi$-bond. When 2-((5-oxo-2,5-dihydrofuranyl)methyl)malonic acid dimethyl ester was used, a mixture of the tricyclic adduct as well as an allene was obtained. In this case, elimination of the benzenesulfinate group from the initially formed sulfone-stabilized carbanion is competitive with the intramolecular [3 + 2]-annulation process. The base-induced reaction of dimethyl 2-(methoxycarbonyl)-2-pentenedioate with the bis(phenylsulfonyl)diene was also studied. Even though the position of the acceptor moiety on the $\pi$-bond was altered, the tandem Michael reaction sequence still occurs. The course of the reaction is dependent upon the length of the tether as well as the relative placement of the electron-withdrawing group on the olefin. Reaction with $\gamma$-substituted $\beta,\gamma$-alkenyl derivatives leads to bicyclo[3.3.0]octenes, whereas $\beta$-substituted $\beta,\gamma$-alkenyl reagents provide bicyclo[3.3.0]octenes derived from a novel α-elimination reaction.

Functionalized five-membered carbocycles are commonly found in many biologically active compounds derived from living systems.[1] Ever since Comer's structure elucidation of hirsutic acid in 1965,[2] the fused cyclopentanes have assumed a position of importance among synthetically significant targets.[3−5] As might be expected from the frequent occurrence and biological activity of fused cyclopentanoid natural products,[1] research in the area of cyclopentannulation has been brisk. While there are many ways to classify the various approaches, all synthetic strategies for fused cyclopentenes can be divided into two broad categories: those in which cyclization is carried out on an existing five-membered ring[6] and those in which two or more rings are formed simultaneously.[7] Over the past couple of decades, an impressive number of effective protocols for the synthesis of cyclopentanoids have been developed and many of these have proven to be of value in work directed toward the total synthesis of fused cyclopentanoid natural products.[8−16]

Although most of the cyclization methodologies have involved one-bond formation, an increased efficacy of cyclopentannulation is realized by simultaneous formation of fused rings from two moieties, as in [3 + 2]-annulation processes. Indeed, there has been considerable interest and activity in the development of single-step [3 + 2]-ring constructions.[17−43] Many such reactions have been developed in recent years with diverse applicability

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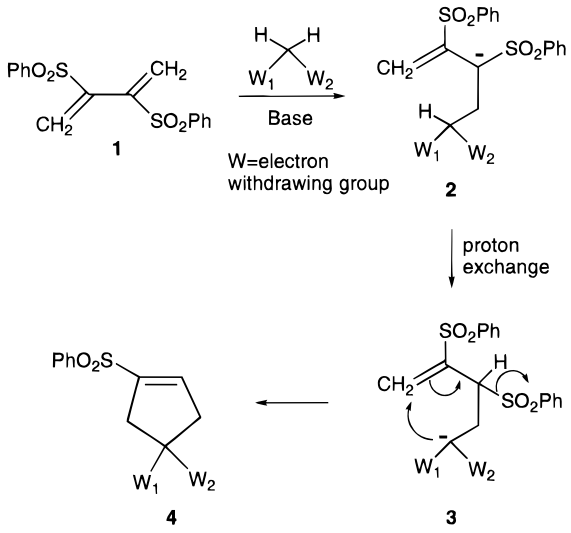
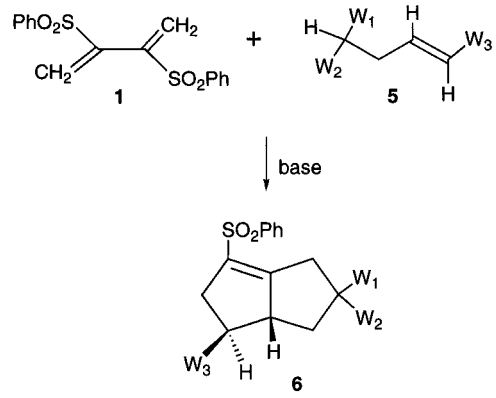
and limitations. The attractiveness of such methodology is enhanced by the ready availability of the two-carbon fragments and the possibility of obtaining a broad range of substitution on the resultant cyclopentanoids.

In connection with our program dealing with the tandem annulation chemistry of unsaturated sulfones,[44] we have been exploring the chemical reactivity of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**), a shelf-stable, highly functionalized compound exhibiting diverse chemical reactivity.[45] We have reported preliminary results of

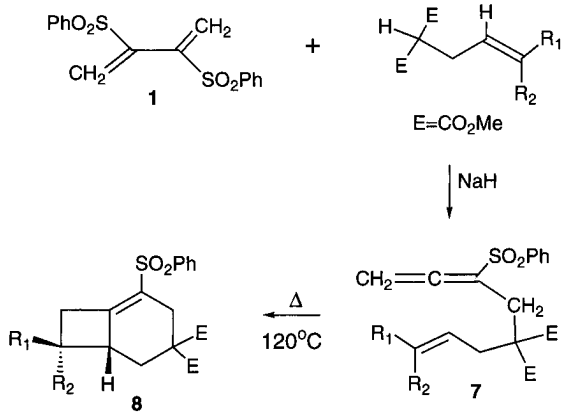



reactions of **1** with various bis-stabilized carbanions which produce cyclopentenyl sulfones.[46] This reaction involves a *tandem addition−proton exchange−addition* sequence. In the present paper we describe the outcome of reactions of diene **1** with dimethyl 1-pentenedioates **5** containing electron-withdrawing substituents at the 1-position, which lead to tetrahydro-1*H*-pentalenes **6** in high yield.[47] The overall reaction involves a series of three sequential conjugate additions[48−50] followed by benzenesulfinate ion ejection. The tandem cyclization sequence takes advantage of the usual role of the sulfonyl group as a carbanion stabilizer[51] and also illustrates its utility as a leaving group under extremely mild conditions.[52−55]




## Results and Discussion

We first became interested in the reaction of 2-allyl-substituted 1,3-dicarbonyl compounds with diene **1** in connection with the use of phenylsulfonyl-substituted allenes of type **7** as substrates for intramolecular [2 + 2]-cycloaddition chemistry.[56] The base-induced reaction of diene **1** with a series of allyl-substituted 1,3-dicarbonyl compounds (E = $CO_2Me$) proceeded by attack of the malonate anion onto the terminal position of the diene followed by elimination of $PhSO_2^-$ to give the phenylsulfonyl-substituted allene **7**. A subsequent thermolysis (80−120 °C) resulted in a highly chemo- and stereose-

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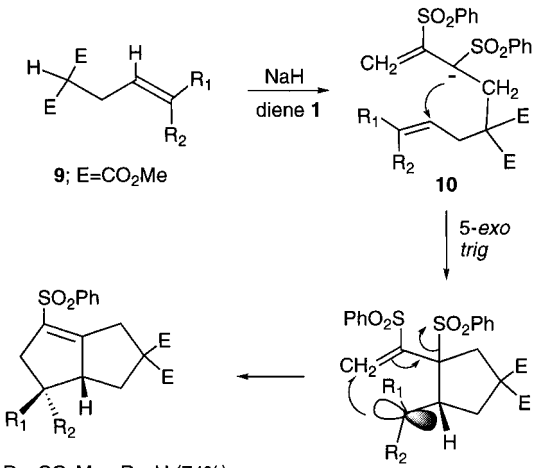
lective intramolecular [2 + 2]-cycloaddition reaction producing cycloadduct **8**. The formation of the [2 + 2]-cycloadduct was rationalized by a mechanism which includes an initial carbon−carbon bond formation involving the central allene carbon to give a diradical intermediate.[56] The periselectivity observed is related to stereoelectronic factors. Stepwise bonding prefers to occur in a 1,6-*exo* manner rather than in a 1,7-*endo* fashion.[56] The product distribution is then determined by the substituent pattern of the alkene and the fate of the diradical intermediate.

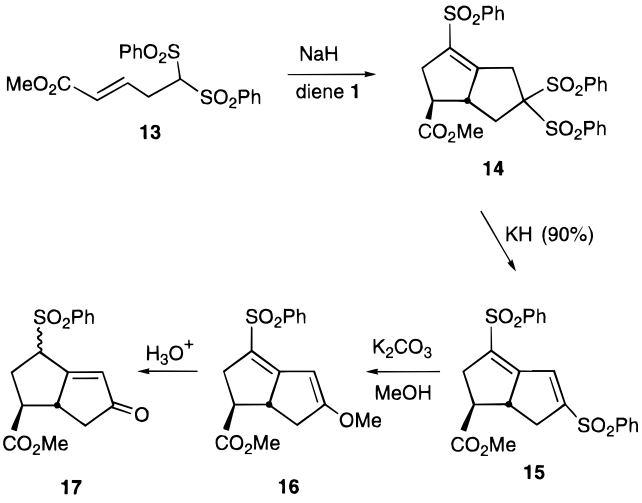
To further illustrate the scope and synthetic utility of the intramolecular [2 + 2]-process, we set out to expand this reaction into the synthesis of other ring systems. We found that an entirely different transformation occurred when an electron-withdrawing substituent was situated on the double bond. The compounds examined were those which contained dimethyl malonate to function as a Michael donor and a 1,2-disubstituted electron-deficient alkene to serve as the subsequent Michael acceptor (*vide infra*). These compounds (*i.e.*, **9**) react smoothly with diene **1** under mild conditions to undergo a bicycloaddition reaction, yielding functionalized bicyclo[3.3.0]octenes **12** in good to excellent yields. For example, treatment




of diene **1** with the sodium salt of malonate derivative **9b** in THF at 0 °C leads to the rapid formation of **12b** in 95% yield. This reaction most probably proceeds through a sequence initiated by Michael addition onto one vinyl sulfone moiety of the butadiene **1** to give a sulfone-stabilized carbanion intermediate (**10**), which collapses *via* a facile 5-*exo*-*trig* ring closure to form the presumed second intermediate **11**; a subsequent intramolecular addition−elimination reaction provides the observed products **12**.[57]

An aspect of the cycloaddition worth noting is the complete stereoselectivity of the process. For example, subjecting isomerically pure *E*-alkenes **9a**−**c** and **9e** to the tandem cyclization conditions produced only the cyclopentane which is *trans*-substituted. Likewise, *Z*-nitrile **9d** afforded the *cis*-substituted cyclopentane **12d** without detectable signs of **12c**. This phenomenon can be attributed to the combination of two effects. First of all, the relatively high steric demand about the carbanionic center present in **11** should impose a formidable hindrance to rotation around the C−C $\sigma$-bond. Furthermore, the ejection of benzenesulfinate ion prevents retrocyclization. We believe the observed facility of the ring closure is also related to the proximity of the reacting centers brought about by the 1,2-relationship in the rigid five-membered ring.

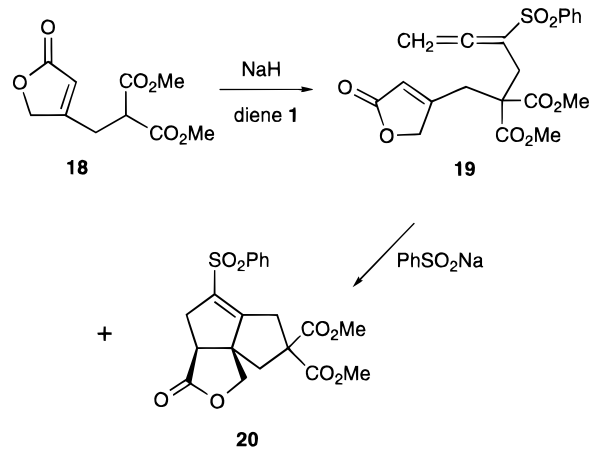
As this process could be useful for the synthesis of natural products containing fused bis(cyclopentanes),[6] we set out to probe its functional tolerance and control of stereochemistry. Toward this end, some interesting effects were observed upon modifying the Michael donor/acceptor. For example, the protocol is also viable using a reagent in which the active methine region is appended with phenylsulfonyl groups instead of methoxycarbonyl substituents (*i.e.*, **13**). The phenylsulfonyl groups permit ready activation of $C_5$ as a Michael donor and then, following cyclization, allow for the removal of this ver-



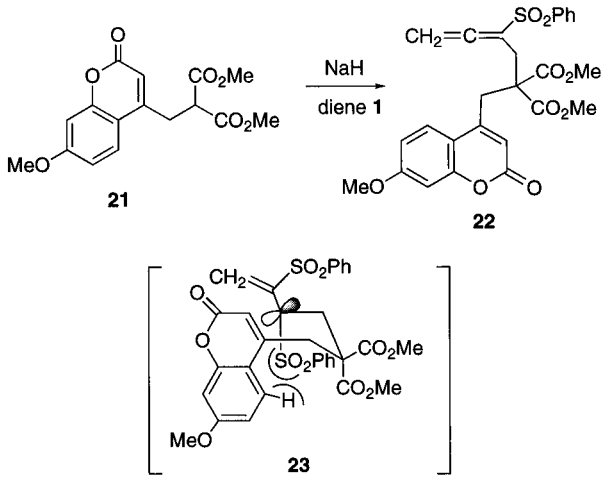

satile functionality. In this case, a mixture of the bicyclic compounds **14** and **15** was obtained, the latter being the product of a facile benzenesulfinate elimination. In fact, the *tris*-sulfone **14** can be readily converted to the diene **15** in 90% yield by treatment with potassium hydride. Embedded within the skeleton of the bicyclo[3.3.0]-octadiene **15** is an $\alpha,\delta$-bis(phenylsulfonyl)butadiene substructure, a system which we have found to undergo a facile methanolysis under mild conditions.[56] Indeed, this compound exhibits the same behavior; the resulting vinyl ether **16** can then be hydrolyzed upon treatment with acid to provide the synthetically attractive bicyclo[3.3.0]-octenone **17** as a 2:1 mixture of diastereomers. The exclusive regioselectivity observed in the methoxide addition/elimination reaction can be attributed to steric interactions which disfavor a proper trajectory to the alternate terminus (e.g., severe 1,3-interactions with the $\beta$-methoxycarbonyl group).

In examining further modifications to the Michael donor/acceptor, we were curious as to whether the incorporation of a ring in the starting material would allow for construction of analogous tricyclic systems. We found, as with the standard Michael process, that the success of this method is also dependent on the electrophilicity of the proximal $\pi$-bond. Thus, when diene **1** was treated with furanone **18** under the standard conditions, a mixture of allene **19** (48%) and tricyclic adduct **20** (42%)

(57) Alternatively, the reaction could proceed *via* an $S_N2'$ pathway.

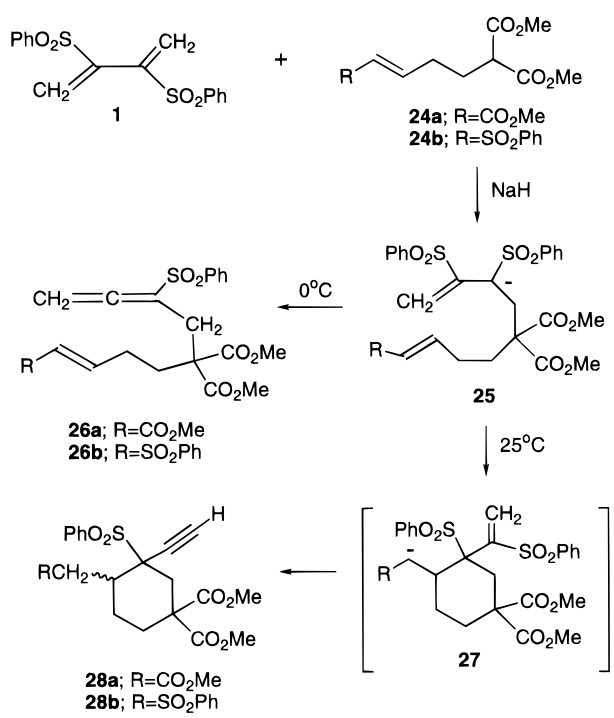



was obtained. In this case, elimination of the benzenesulfinate group from the initially formed sulfone-stabilized anion is competitive with the intramolecular [3 + 2]-annulation process, apparently due to the conformational restrictions imposed by the ring system. Inasmuch as allene formation should be a reversible process, owing to the double-bond activation by the phenylsulfonyl group, we theorized that the reestablishment of equilibrium should favor the irreversible carbocyclization.[44] Indeed, treatment of **19** with sodium benzenesulfinate induced quantitative conversion to lactone **20**, thus representing a rapid and high-yielding protocol for the construction of such tricyclic structures. However, there appears to be a limit to the dimensions of the cyclic appendage, as illustrated by the benzopyranone derivative **21**, the sodium salt of which reacts with butadiene **1** to form only allene **22**; no trace of cyclized product is observed. The extra steric bulk of the benzene ring $\beta$ to the $sp^2$ reactive site prohibits the proper attack of the equally demanding phenylsulfonyl-stabilized allylic anion **23**. Consequently, elimination of benzenesulfinate becomes the only productive process. Other factors such as electronic issues as well as the size of the ring onto which the spiro center is formed could also be involved here.




As to other structural modifications, it should not be surprising that the length of the tether connecting the Michael donor and Michael acceptor moieties influences the outcome of the reaction. Remarkably, however, such homologous donor/acceptor reagents (*i.e.*, **24a**,**b**) induced absolutely no bis-cyclization. In fact, if the reaction is

**Scheme 1**

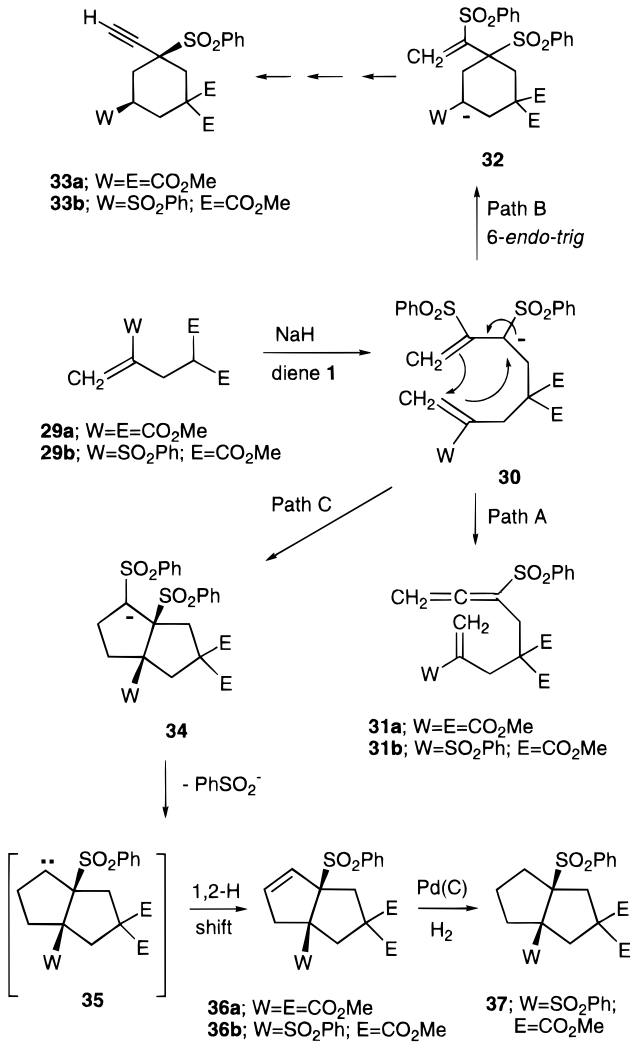



carried out at 0 °C (Scheme 1), simple Michael addition onto one of the vinyl sulfone moieties is the sole reactivity exhibited by the reagents; subsequent elimination of benzenesulfinate gives the observed allene **26**. Only at 25 °C is the reactive conformation of the intermediate **25** sufficiently populated to effect initial ring closure. However, in this case, the constraints of the more flexible six-membered ring fail to induce the second ring closure; the *endo-trig* cyclization remains disfavored. Instead, the intermediate anion **27** undergoes what is most likely an internal base-promoted elimination of benzenesulfinate[58] to give the alkynes **28**.

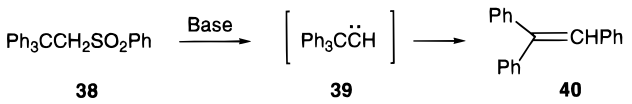
We have observed thus far that (1) active methine compounds tethered to $\gamma$-substituted $\beta,\gamma$-alkenyl residues are suitable reagents for the construction of fused bicyclic systems, (2) the steric bulk about the olefin can become critical for the initial cyclization, and (3) analogous $\gamma,\delta$-residues induce the first cyclization to give six-membered rings which, however, do not undergo a secondary cyclization. We were then curious as to what reactivity would be exhibited by $\beta$-substituted $\beta,\gamma$-alkenyl reagents under the same reaction conditions. Thus, we examined the base-induced reactions of dimethyl 2-(methoxycarbonyl)-2-pentenediote (**29a**) and dimethyl [2-(phenylsulfonyl)-2-propenyl]propanedioate (**29b**) with diene **1**. Even though the position of the acceptor moiety on the $\pi$-bond has been altered, the tandem Michael reaction sequence still occurs. The initially formed sulfonyl-stabilized 1,7-octadienyl anion **30** is poised to undergo a plurality of further transformations, a circumstance which is reflected by the fact that the product mixtures are highly dependent upon the reaction conditions. First of all, the steric and entropic factors associated with **30** would be expected to work against a facile cyclization, especially since the particularly rapid 5-*exo-trig* process is not an option in this case. Thus, we were not altogether surprised that this $\beta$-phenylsulfonyl anion also undergoes

(58) Otera, J.; Misawa, H.; Sugimoto, K. *J. Org. Chem.* **1986**, *51*, 3830.

**Scheme 2**




simple benzenesulfinate elimination to some degree, thus forming allene **31** [E = $CO_2Me$; $SO_2Ph$] (Scheme 2, path A). In addition, the allowed 6-*endo-trig* cyclization (path B) produces an intermediate cyclohexyl anion (**32**) which, like the analogous cyclohexylmethyl anion intermediate **27**, undergoes base-promoted ejection of benzenesulfinate to eventually form the alkynyl substituted cyclohexanes **33**. However, we were quite surprised by the occurrence of compound **36**, which is obviously not derived from the monocyclic intermediate anion **32**. The structure of **36b** was assigned on the basis of its spectroscopic properties and also by catalytic hydrogenation to bicyclo[3.3.0]-octane **37**. To account for the formation of **36**, we propose the intermediacy of the bicyclo[3.3.0]octyl anion **34**, which would arise from a tandem Michael/Michael reaction proceeding through an initial intramolecular $\gamma$-addition of the sulfonyl-stabilized allylic anion portion of **30** (path C). That the cyclized carbanion **34** does not induce elimination of the adjacent phenylsulfonyl group (as was observed with **11**) is noteworthy. The absence of this pathway may be related to conformational restrictions of sulfonyl carbanion **34**, which cannot adopt the anti-periplanar orientation necessary for $\beta$-elimination[59] since the three bulky substituents would be required to occupy the same side of the five-membered ring. One conceivable route by which carbanion **34** is converted to cycloadduct **36** involves protonation followed by a subsequent base-induced elimination. It should be noted that, although olefin-forming reactions involving sulfinic acid elimination of aryl sulfones are known, these reactions are generally promoted by α-heteroatom substitution[60−62] or by allylic ($\pi$)-activation of protons $\beta$ to the sulfone.[63−65] Clearly, $\beta$ elimination of an unactivated sulfone is a highly inefficient process requiring drastic conditions unless the resultant double bond is conjugated with some unsaturated group already present in the molecule.[66−68] It is for this reason that we propose the alternate path shown in the scheme which involves α-elimination of benzenesulfinate from carbanion **34** followed by a rapid 1,2-hydrogen shift of the resulting carbene **35**. Some precedence for this rare α-elimination of an α-sulfonyl anion can be found in an earlier report by Zimmerman and Munch.[69] The reaction of 2,2,2-triphenylethyl phenyl sulfone (**38**) with a strong base was found to give triphenylethylene (**40**). The reaction was suggested to proceed by an initial α-elimination to produce carbene **39** which then underwent a 1,2-phenyl shift to afford ethylene **40**.




In conclusion, the reactions outlined herein demonstrate the potential for using the tandem Michael addition−[3 + 2]-anionic cyclization sequence of unsaturated sulfones in the formation of five-membered rings. The ability to achieve high ring-juncture selectivity may find further application in natural product synthesis. Work is continuing in an effort to expand the scope of the present cyclopentannulation reaction.

## 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 flame-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.

**Reaction of Dimethyl 5-(Methoxycarbonyl)-2-hexenedioate (9a) with 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1).** To a suspension containing 125 mg (3.1 mmol) of NaH in 20 mL of THF at 0 °C was added 0.34 mL (3.0 mmol) of dimethyl malonate. After the solution was stirred at 0 °C for 20 min, 0.43 mL (3.1 mmol) of methyl 4-bromocrotonate was added. The mixture was stirred at rt for 5 h, washed with a

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saturated aqueous $NH_4Cl$ solution, and extracted with ether. The organic layer was washed with water and brine and dried over sodium sulfate. Concentration under reduced pressure followed by flash silica gel chromatography of the residue gave 380 mg (55%) of dimethyl 5-(methoxycarbonyl)-2-hexenedioate (**9a**) as a clear oil: IR (neat) 1737, 1431, 1268, 1033, and 727 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.79 (t, 2H, $J$ = 7.2 Hz), 3.51 (t, 1H, $J$ = 7.2 Hz), 3.70 (s, 3H), 3.74 (s, 6H), 5.98 (d, 1H, $J$ = 15.6 Hz), and 6.86 (dt, 1H, $J$ = 15.6 and 7.2 Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 30.9, 50.1, 51.3, 52.6, 123.3, 143.7, 166.1, and 168.5.

To a solution containing 315 mg (1.37 mmol) of the above triester in 10 mL of THF at 0 °C was added 71 mg (1.78 mmol) of NaH. After the solution was stirred at 0 °C for 30 min, a solution containing 458 mg (1.37 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) in 30 mL of THF was added. The mixture was stirred at 0 °C for 15 min, and then the reaction was quenched with a saturated aqueous $NH_4Cl$ solution. After removal of the solvent under reduced presure, the residue was extracted with ether, washed with water and brine, and dried over sodium sulfate. Flash silica gel chromatography of the residue gave 425 mg (74%) of *trans*-3-(phenylsulfonyl)-2,4,6,-6a-tetrahydro-1*H*-pentalene-1,5,5-tricarboxylic acid trimethyl ester (**12a**): IR (neat) 1730, 1438, 1147, 1075, and 727 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.86 (t, 1H, $J$ = 13.2 Hz), 2.56 (dd, 1H, $J$ = 13.2 and 7.8 Hz), 2.79−2.99 (m, 3H), 3.17 (brd, 1H, $J$ = 21.0 Hz), 3.34 (brd, 1H, $J$ = 21.0 Hz), 3.38−4.44 (m, 2H), 3.56 (s, 3H), 3.65 (s, 3H), 3.67 (s, 3H), 7.47 (t, 2H, $J$ = 7.5 Hz), 7.56 (t, 1H, $J$ = 7.5 Hz), and 7.78 (d, 2H, $J$ = 7.5 Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 33.2, 37.4, 39.4, 48.9, 51.9, 52.8, 53.0, 54.7, 63.1, 127.3, 129.0, 129.1, 133.4, 139.7, 161.0, 170.7, 171.2, and 172.4. Anal. Calcd for $C_{20}H_{22}O_8S$: C, 56.86; H, 5.25. Found: C, 56.75; H, 5.14.

**Reaction of Dimethyl (*E*)-(3-(Phenylsulfonyl)-2-propenyl)propanedioate (9b) with 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1).** To a suspension containing 220 mg (5.5 mmol) of NaH in 60 mL of THF at rt was added 0.57 mL (5.0 mmol) of dimethyl malonate dropwise. After the solution was stirred for 20 min, 1.30 g (5.0 mmol) of (*E*)-1-bromo-3-(phenylsulfonyl)-2-propene[70] was added in one portion at rt. The reaction was quenched after 30 min with a saturated $NH_4Cl$ solution. The solvent was removed under reduced pressure, and the residue was extracted with $CH_2Cl_2$. The organic layer was washed with brine and dried over sodium sulfate. Flash chromatography on silica gel gave 1.12 g (72%) of dimethyl (*E*)-(3-(phenylsulfonyl)-2-propenyl)propanedioate (**9b**): IR (neat) 1730, 1432, 1307, 1137, and 744 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.79 (dt, 2H, $J$ = 7.4 and 1.2 Hz), 3.64 (s, 6H), 3.69 (d, 1H, $J$ = 7.4 Hz), 6.38 (d, 1H, $J$ = 15.0 Hz), 6.89 (td, 1H, $J$ = 15.0 and 7.4 Hz), and 7.49−7.92 (m, 5H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 30.3, 49.8, 52.8, 127.6, 128.4, 129.2, 133.1, 133.4, 141.5, and 168.2.

To a solution containing 312 mg (1.0 mmol) of the above compound in 30 mL of THF was added 44 mg (1.1 mmol) of NaH. After 20 min of stirring at rt, the solution was cooled to 0 °C and a solution of 317 mg (0.95 mmol) of 2,3-bis-(phenylsulfonyl)-1,3-butadiene (**1**) in 30 mL of THF was added. After the solution was stirred for 10 min, the reaction was quenched with a saturated $NH_4Cl$ solution. Removal of the solvent under reduced pressure left a clear oil which was extracted with $CH_2Cl_2$. The organic layer was washed with water and brine and dried over sodium sulfate. Flash chromatography of the resulting residue on silica gel gave 457 mg (95%) of *trans*-4,6-bis(phenylsulfonyl)-3,3a,4,5-tetrahydro-1*H*-pentalene-2,2-dicarboxylic acid dimethyl ester (**12b**): mp 184−185 °C; IR (KBr) 1730, 1440, 1292, 1151, 900, and 728 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.77 (dd, 1H, $J$ = 13.2 and 10.8 Hz), 2.22 (dd, 1H, $J$ = 13.2 and 7.5 Hz), 2.91 (dd, 1H, $J$ = 14.7 and 7.8 Hz), 3.21 (brd, 1H, $J$ = 19.2 Hz), 3.29−3.35 (m, 1H), 3.43 (brd, 1H, $J$ = 19.2 Hz), 3.57−3.71 (m, 2H), 3.72 (s, 3H), 3.76 (s, 3H), 7.54−7.73 (m, 6H), and 7.83−7.87 (m, 4H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 33.2, 36.6, 37.1, 52.4, 53.0, 53.1, 62.9, 67.9, 127.4, 128.1, 128.6, 129.4, 129.5, 133.8, 134.2, 137.6, 139.4, 159.7, 170.4, and 170.8. Anal. Calcd for $C_{24}H_{24}O_8S_2$: C, 57.13; H, 4.80. Found: C, 56.97; H, 4.77.

**Reaction of Dimethyl (3-Cyano-2-propenyl)propanedioate with 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1).** A mixture containing 670 mg (60.0 mmol) of crotononitrile, 1.96 g (11.0 mmol) of NBS, and 10 mg of AIBN in 40 mL of $CCl_4$ was heated at reflux for 2 h and then filtered through a pad of Celite and washed with $CCl_4$. Concentration of the filtrate afforded 1-bromo-2-butenenitrile which was used in the next step without further purification. To a solution of sodium dimethyl malonate prepared from 1.03 mL (9.0 mmol) of dimethyl malonate and 400 mg (9.9 mmol) of NaH in 30 mL of THF at 0 °C was added a solution of the above bromide in 30 mL of THF. After the solution was stirred for 10 min at 0 °C, the reaction was quenched with a saturated $NH_4Cl$ solution. Standard workup and purification on silica gel gave 1.01 g (57%) of a 1:1-*cis*,*trans*-mixture of dimethyl (3-cyano-2-propenyl)propanedioate which could be separated by extensive silica gel chromatography. The *cis*-isomer **9d** exhibited the following spectral properties: IR (neat) 2217, 1738, 1428, 1231, 1020, and 731 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.93 (td, 2H, $J$ = 7.2 and 1.2 Hz), 3.50 (t, 1H, $J$ = 7.2 Hz), 3.71 (s, 6H), 5.38 (dt, 1H, $J$ = 10.8 and 1.2 Hz), and 6.43−6.51 (m, 1H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 36.4, 49.9, 52.6, 102.1, 116.1, 150.4, and 168.2; HRMS calcd for $C_9H_{11}NO_4$ 197.0688, found 197.0692.

The *trans*-isomer **9c** exhibited the following properties: IR (neat) 2221, 1745, 1432, 1225, and 969 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.76 (td, 2H, $J$ = 7.2 and 1.2 Hz), 3.47 (t, 1 H, $J$ =7.2 Hz), 3.72 (s, 6H), 5.40 (d, 1H, $J$ = 16.2 Hz), and 6.57−6.68 (m, 1H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 30.4, 49.9, 52.7, 102.2, 115.1, 149.5, and 168.2; HRMS calcd for $C_9H_{11}NO_4$ 197.0688, found 197.0688.

To a solution containing 197 mg (1.0 mmol) of the *cis*-isomer **9d** in 30 mL of THF was added 44 mg (1.1 mmol) of NaH at 0 °C. After the solution was stirred for 20 min, a solution of 317 mg (0.95 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) in 30 mL of THF was added at 0 °C. The reaction was quenched after 20 min with a saturated $NH_4Cl$ solution, extracted with $CH_2Cl_2$, and purified on silica gel to give 350 mg (91%) of *cis*-6-(phenylsulfonyl)-4-cyano-3,3a,4,5-tetrahydro-1*H*-pentalene-2,2-dicarboxylic acid dimethyl ester (**12d**): IR (neat) 2243, 1730, 1659, 1438, 1268, and 1069 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.09 (t, 1H, $J$ = 12.6 Hz), 2.61 (dd, 1H, $J$ = 13.2 and 7.8 Hz), 2.82 (d, 1H, $J$ = 14.7 Hz), 3.16 (d, 1H, $J$ = 21.0 Hz), 3.22−3.61 (m, 4H), 3.71 (s, 3H), 3.72 (s, 3H), 7.51−7.64 (m, 3H), and 7.84 (d, 2H, $J$ = 7.2 Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 31.9, 33.2, 34.5, 41.4, 53.0, 53.1, 53.2, 63.4, 118.4, 127.3, 129.2, 129.3, 133.8, 139.0, 160.9, 170.0, and 171.2. Anal. Calcd for $C_{19}H_{19}NO_6S$: C, 58.60; H, 4.92; N, 3.60. Found: C, 58.45; H, 4.82; N, 3.44.

Using similar conditions, reaction of *trans*-**9c** with 2,3-bis-(phenylsulfonyl)-1,3-butadiene (**1**) gave *trans*-6-(phenylsulfonyl)-4-cyano-3,3a,4,5-tetrahydro-1*H*-pentalene-2,2-dicarboxylic acid dimethyl ester (**12c**) in 89% yield: IR (neat) 2243, 1738, 1659, 1446, and 1268 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.92 (dd, 1H, $J$ = 13.1 and 11.4 Hz), 2.64 (dd, 1H, $J$ = 13.1 and 8.1 Hz), 2.84 (dd, 1H, $J$ = 18.9 and 9.6 Hz), 3.08 (brd, 1H, $J$ = 8.4 Hz), 3.18 (brd, 1H, $J$ = 19.6 Hz), 3.38 (brd , 1H, $J$ = 19.6 Hz), 3.45−3.65 (m, 2H), 3.69 (s, 3H), 3.71(s, 3H), 7.49−7.64 (m, 3H), and 7.80 (d, 2H, $J$ = 7.5 Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 32.2, 33.2, 36.5, 40.9, 50.0, 53.2, 55.8, 63.0, 119.0, 127.3, 129.3, 129.6, 133.8, 139.2, 160.3, 170.2, and 170.8. Anal. Calcd for $C_{19}H_{19}NO_6S$: C, 58.60; H, 4.92; N, 3.60. Found: C, 58.37; H, 4.76; N, 3.49.

**Reaction of Ethyl Methyl 7-(Methoxycarbonyl)-2,4-octadienedioate (9e) with 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1).** A solution containing 1.4 g (10.0 mmol) of ethyl sorbate, 1.96 g (11.0 mmol) of NBS, and 10 mg of AIBN in 50 mL of $CCl_4$ was heated at reflux with irradiation using a sunlamp for 3 days. Filtration of the mixture through a pad of Celite and purification of the residue on silica gel gave 0.80 g (30%) of ethyl 6-bromo-2,4-hexadienoate: IR (neat) 1723, 1325, 1296, and 1026 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.21 (t, 3H, $J$ = 7.2 Hz), 3.96 (d, 2H, $J$ = 7.8 Hz), 4.12 (q, 2H, $J$ = 7.2 Hz), 5.85 (d, 1H, $J$ = 15.4 Hz), 6.13−6.21 (m, 1H), 6.32

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(dd, 1H, $J$ = 15.0 and 12.0 Hz), and 7.17 (dd, 1H, $J$ = 15.4 and 10.8 Hz); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 14.0, 31.1, 60.2, 123.0, 131.6, 136.4, 142.2, and 166.1.

To a solution containing sodium dimethyl malonate prepared from 0.36 mL (3.2 mmol) dimethyl malonate and 153 mg (3.8 mmol) of NaH in 20 mL of THF was added a solution of 700 mg (3.2 mmol) of the above bromide. Standard workup and purification by silica gel chromatography gave 403 mg (47%) of ethyl methyl 7-(methoxycarbonyl)-2,4-octadienedioate (**9e**): IR (neat) 1745, 1638, 1431, 1268, 1026, and 855 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.20 (t, 3H, $J$ = 7.2 Hz), 2.68 (t, 2H, $J$ = 7.3 Hz) 3.42 (t, 1H, $J$ = 7.3 Hz), 3.66 (s, 3H), 3.67 (s, 3H), 4.11 (q, 2H, $J$ = 7.2 Hz), 5.74 (d, 1H, $J$ = 15.4 Hz), 5.91−6.01 (m, 1H), 6.17 (dd, 1H, $J$ = 15.0 and 11.0 Hz), and 7.13 (dd, 1H, $J$ = 15.4 and 11.0 Hz); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 14.1, 31.8, 40.9, 50.8, 52.3, 52.4, 60.1, 120.8, 130.8, 137.9, 143.6, 166.7, and 168.7.

To a solution of sodium ethyl methyl 7-(methoxycarbonyl)-2,4-octadienedioate prepared from 165 mg (0.61 mmol) of **9e** and 29 mg (0.73 mmol) of NaH in 30 mL of THF at 0 °C was added a solution of 167 mg (0.5 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) in 30 mL of THF. After the reaction was stirred for 10 min at 0 °C, the reaction was quenched with a saturated $NH_4Cl$ solution. Standard workup and purification on silica gel gave 182 mg (78%) of *trans*-6-(phenylsulfonyl)-4-(2-(ethoxycarbonyl)vinyl)-3,3a,4,5-tetrahydro-1*H*-pentalene-2,2-dicarboxylic acid dimethyl ester (**12e**): IR (neat) 1730, 1652, 1439, 1154, and 1069 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.25 (t, 3H, $J$ = 7.2 Hz), 1.87 (t, 1H, $J$ = 13.0 Hz), 2.54 (dd, 1H, $J$ = 13.0 and 7.8 Hz), 2.73−2.85 (m, 2H), 3.12−3.20 (m, 1H), 3.26 (brd, 1H, $J$ = 20.1 Hz), 3.41 (brd, 1H, $J$ = 20.1 Hz), 3.69−3.79 (m, 1H), 3.74 (s, 3H), 3.75 (s, 3H), 4.15 (q, 2H, $J$ = 7.2 Hz), 5.77 (d, 1H, $J$ = 15.6 Hz), 6.87 (dd, 1H, $J$ = 15.6 and 6.6 Hz), 7.52−7.64 (m, 3H), and 7.86 (d, 2H, $J$ = 7.2 Hz); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 14.1, 33.7, 37.0, 42.0, 49.2, 53.0, 53.2, 57.0, 60.5, 63.6, 122.2, 127.5, 127.9, 129.3, 129.9, 133.5, 140.0, 147.1, 162.2, 166.0, 170.9, and 171.5. Anal. Calcd for $C_{23}H_{26}O_8S$: C, 59.72; H, 5.67. Found: C, 59.63; H, 5.42.

**Reaction of Methyl 5,5-Bis(phenylsulfonyl)-2-pentenoate (13) with 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1).** To a suspension containing 380 mg (9.6 mmol) of NaH in 100 mL of THF was added 2.36 g (8.0 mmol) of bis(phenylsulfonyl)methane in several portions. The mixture was heated at reflux for 2 h and cooled to 0 °C. To this mixture was added 1.34 mL (8.8 mmol) of 4-bromocrotonate in 100 mL of THF. The mixture was stirred at rt for 2 days, and the reaction was then quenched with a saturated $NH_4Cl$ solution. Removal of THF under reduced pressure was followed by extraction with $CH_2Cl_2$, washing with water and brine, and drying over sodium sulfate. The resulting residue was purified by silica gel flash chromatography to give 1.36 g (43%) of methyl 5,5-bis(phenylsulfonyl)-2-pentenoate (**13**): mp 147−148 °C; IR (KBr) 1708, 1655, 1305, 1165, 1085, and 740 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 3.07 (t, 2H, $J$ = 6.3 Hz), 3.70 (s, 3H), 4.52 (t, 2H, $J$ = 6.3 Hz), 5.77 (d, 1H, $J$ = 15.6 Hz), 6.74−6.84 (m, 1H), and 7.56−7.98 (m, 10H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 28.0, 51.4, 81.7, 124.0, 129.0, 129.3, 134.6, 137.3, 141.6, and 165.6.

To a suspension containing 38 mg (0.95 mmol) of KH in 15 mL of THF at 0 °C was added 230 mg (0.58 mmol) of **13** in one portion. The mixture was stirred at rt for 45 min. To the above mixture was added a solution of 195 mg (0.58 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) in 15 mL of THF. After the solution was stirred for 1 h at 0 °C, the reaction was quenched with a $NH_4Cl$ solution. Standard workup and purification on silica gel gave 91 mg (27%) of 3,5,5-tris(phenylsulfonyl)-1,2,4,5,6,6a-hexahydropentalene-1-carboxylic acid methyl ester (**14**) and 80 mg (31%) of 3,5-bis(phenylsulfonyl)-1,2,6,6a-tetrahydropentalene-1-carboxylic acid methyl ester (**15**). Compound **14** exhibited the following spectral properties: IR (KBr) 1732, 1442, 1305, 1135, and 720 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 2.36 (dd, 1H, $J$ = 15.1 and 10.2 Hz), 2.76−2.86 (m, 3H), 2.91 (dd, 1H, $J$ = 15.1 and 9.0 Hz), 2.99−3.08 (m, 1H), 3.38 (dd, 1H, $J$ = 18.0 and 1.8 Hz), 3.55−3.65 (m, 1H), 3.66 (s, 3H), 4.05 (d, 1H, $J$ = 19.8 Hz), and 7.54−8.11 (m, 15H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 31.6, 35.1, 39.3, 49.7, 52.3, 54.6, 95.5, 127.7, 129.1, 129.4, 130.7, 131.3, 131.4, 133.8, 135.0, 135.1, 135.4, 135.6, 139.3, 157.4, and 172.1; HRMS calcd for $C_{22}H_{20}O_6S_2$ ($M^+$ − $PhSO_2H$) 444.0701, found 444.0672.

Compound **15** exhibited the following spectral properties: mp 153−154 °C; IR (KBr) 1730, 1440, 1305, 1145, and 1090 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 2.42 (ddd, 1H, $J$ = 17.1, 5.1 and 1.8 Hz), 2.84 (dd, 1H, $J$ = 16.8 and 8.1 Hz), 2.93−3.12 (m, 3H), 3.56−3.60 (m, 1H), 7.45 (s, 1H), 7.52−7.72 (m, 6H), 7.85 (d, 2H, $J$ = 7.2 Hz), and 7.92 (d, 2H, $J$ = 7.5 Hz); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 34.2, 39.6, 49.6, 52.2, 53.8, 127.7, 128.4, 129.4 129.6, 131.2, 133.8, 134.3, 138.0, 139.3, 159.2, 159.6, and 171.9. Anal. Calcd for $C_{22}H_{20}O_6S_2$: C, 59.45; H, 4.54. Found: C, 59.19; H, 4.86.

A solution containing 60 mg (0.01 mmol) of 3,5,5-tris(phenylsulfonyl)-1,2,4,5,6,6a-hexahydropentalene-1-carboxylic acid methyl ester (**14**) in 50 mL of THF was treated with 20 mg (50.0 $\mu$mmol) of KH at rt for 1 h to give 48 mg (90%) of 3,5-bis(phenylsulfonyl)-1,2,6,6a-tetrahydropentalene-1-carboxylic acid methyl ester (**15**) after workup and purification.

To a solution of 60.0 mg (0.017 mmol) of **14** in 10 mL of methanol was added 120 mg of $K_2CO_3$. The mixture was stirred at rt overnight. Standard workup and purification gave 23 mg (40%) of 3-(phenylsulfonyl)-5-methoxy-1,2,6,6a-tetrahydropentalene-1-carboxylic acid methyl ester (**16**): $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 2.39 (dd, 1H, $J$ = 16.2 and 5.7 Hz), 2.61 (dd, 1H, $J$ = 16.2 and 7.8 Hz), 2.80−3.03 (m, 3H), 3.36−3.45 (m, 1H), 3.67 (s, 3H), 3.83 (s, 3H), 5.91 (s, 1H), 7.48−7.60 (m, 3H), and 7.86 (d, 2H, $J$ = 7.5 Hz). This compound was easily hydrolyzed upon standing to 3-(phenylsulfonyl)-5-oxo-1,2,3,5,-6a-hexahydropentalene-1-carboxylic acid methyl ester (**17**) in quantitative yield as an inseparable 2:1-mixture of diastereoisomers: $^1$H NMR ($CDCl_3$, 300 MHz) major isomer $\delta$ 2.24 (t, 1 H, $J$ = 3.3 Hz), 2.39−2.56 (m, 1H), 2.59−2.77 (m, 2H), 2.86 (dd, 1H, $J$ = 10.8 and 7.8 Hz), 3.21−3.33 (m, 1H), 3.75 (s, 3H), 4.42 (t, 1H, $J$ = 8.1 Hz), 5.73 (t, 1H, $J$ = 1.8 Hz), and 7.58−7.90 (m, 5H); minor isomer $\delta$ 2.18 (t, 1H, $J$ = 2.7 Hz), 2.39−2.56 (m, 1H), 2.59−2.77 (m, 2H), 2.91 (dd, 1H, $J$ = 10.8 and 7.8 Hz), 3.13−3.20 (m, 1H), 3.71 (s, 3H), 4.77(d, 1H, $J$ = 9.6 Hz), 6.38 (t, 1H, $J$ = 1.8 Hz), and 7.58−7.90 (m, 5H). Anal. Calcd for $C_{16}H_{16}O_5S$: C, 59.99; H, 5.04. Found: C, 59.83; H, 4.96.

**Reaction of 2-((5-Oxo-2,5-dihydrofuran-3-yl)methyl)-malonic Acid Dimethyl Ester (18) with 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1).** To an ice-cold suspension containing 0.27 g (6.78 mmol) of NaH in 30 mL of dry THF under $N_2$ was slowly added 0.65 mL (5.65 mmol) of dimethyl malonate. The solution was stirred for 20 min at 0 °C, and then 1.0 g (5.65 mmol) of 3-(bromomethyl)-4-hydroxy-2-butenoic lactone[71] was slowly added *via* syringe. The solution was allowed to warm to rt over 30 min, and the reaction was then quenched by the addition of a saturated $NH_4Cl$ solution. The reaction mixture was extracted with $CH_2Cl_2$, and the organic layer was collected, washed with water, and dried over anhydrous $NaSO_4$. Concentration under reduced pressure afforded a crude yellow oil which was subjected to silica gel chromatography to give 0.68 g (53%) of **18** as a clear oil: IR (neat) 1766, 1730, 1439, 1303, and 1147 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 2.95 (d, 2H, $J$ = 7.4Hz), 3.68 (t, 1H, $J$ = 7.4 Hz), 3.71 (s, 6H), 4.73 (s, 2H), and 5.82 (s, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 27.4, 49.5, 53.0, 73.1, 116.8, 166.0, 168.2, and 173.2.

A 0.32 g (1.40 mmol) sample of **18** was slowly added into a stirred ice-cold suspension containing 73 mg (1.83 mmol) of NaH in 25 mL of dry THF under $N_2$. The solution was stirred for 20 min at 0 °C, and then 0.51 g (1.54 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) in 15 mL of dry THF was slowly added. The solution was allowed to warm to rt over 30 min, and the reaction was then 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,

(71) Boeckman, R. H.; Ho, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 1033.

and dried over anhydrous $NaSO_4$. Concentration of the mixture under reduced pressure afforded a crude yellow residue which was subjected to silica gel chromatography to give 0.24 g (41%) of 5-(phenylsulfonyl)-3-oxo-3,3a,4,6-tetrahydro-2-oxacyclopenta[*c*]pentalene-7,7-dicarboxylic acid dimethyl ester (**20**) as a clear oil: IR (neat) 1766, 1730, 1432, 1168, 1019, and 884 $cm^{-1}$; $^1H$ NMR (benzene-$d_6$) $\delta$ 1.73 (d, 1H, $J$ = 13.6 Hz), 2.07 (d, 1H, $J$ = 13.6 Hz), 2.29 (d, 1H, $J$ = 4.3 Hz), 2.74−2.84 (m, 1H), 2.90−2.98 (m, 1H), 3.11−3.23 (m, 1H), 3.20 (s, 6H), 3.63 (d, 1H, $J$ = 9.9 Hz), 3.70 (d, 1H, $J$ = 9.9 Hz), 4.03 (d, 1H, $J$ = 17.7 Hz), 7.09−7.11 (m, 3H), and 7.98−8.01 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 32.2, 40.2, 40.9, 44.4, 53.4, 53.5, 60.3, 64.6, 76.4, 127.8, 129.5, 132.5, 134.1, 139.3, 158.4, 170.7, 171.6, and 177.2. Anal. Calcd for $C_{20}H_{20}O_8S$: C, 57.13; H, 4.80. Found: C, 57.05; H, 4.68.

In addition to compound **20**, 0.28 g (48%) of 2-[2-(phenylsulfonyl)buta-2,3-dienyl]-2-((5-oxo-2,5-dihydrofuran-3-yl)methyl)malonic acid dimethyl ester (**19**) was also isolated from the chromatographic separation: IR (neat) 1958, 1930, 1745, 1723, 1147, and 1026 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.97 (t, 2H, $J$ = 2.5 Hz), 3.05 (s, 2H), 3.68 (s, 6H), 4.71 (s, 2H), 5.37 (t, 2H, $J$ = 2.5 Hz), 5.75 (s, 1H), 7.55 (t, 2H, $J$ = 7.5 Hz), 7.66 (t, 1H, $J$ = 7.5 Hz), and 7.83 (d, 2H, $J$ = 7.5 Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 29.9, 31.5, 53.1, 56.5, 73.9, 85.7, 108.3, 118.3, 128.1, 129.3, 134.0, 139.3, 164.6, 169.3, 173.2, and 208.3; HRMS Calcd for $C_{20}H_{20}O_8S$: 420.0878, found 420.0878.

A mixture containing 87 mg (0.21 mmol) of **19**, 41 mg (0.31 mmol) of $K_2CO_3$, and 2 mg (0.01 mmol) of sodium benzenesulfinate in 20 mL of dry THF under nitrogen was stirred at rt for 36 h. The solution was filtered through a pad of Celite and concentrated to give 5-(phenylsulfonyl)-3-oxo-3,3a,4,6-tetrahydro-2-oxacyclopenta[*c*]pentalene-7,7-dicarboxylic acid dimethyl ester (**20**) in quantitative yield.

**Reaction of 4-[2,2-Bis(methoxycarbonyl)ethyl]-7-methoxycoumarin (21) with 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1).** To a suspension containing 163 mg (4.08 mmol) of NaH in 30 mL of THF was added dimethyl malonate dropwise. The mixture was stirred for 20 min at rt and was then added to a solution of 1.0 g (3.72 mmol) of 4-(bromomethyl)-7-methoxycoumarin in 150 mL of THF at rt. The solution was stirred at rt for 20 min, and the reaction was quenched by the addition of a $NH_4Cl$ solution. Standard workup and purification gave 870 mg (73%) of 4-(2,2-bis(methoxycarbonyl)ethyl)-7-methoxycoumarin (**21**): IR (KBr) 2954, 1730, 1701, 1289, and 827 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 3.36 (d, 2H, $J$ = 7.5 Hz), 3.76 (s, 6H), 3.77 (t, 1H, $J$ = 7.5 Hz), 3.87 (s, 3H), 6.11 (s, 1H), 6.82−6.89 (m, 2H), and 7.54 (d, 1H, $J$ = 9.0 Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 30.2, 50.0, 53.0, 55.7, 101.1, 111.6, 111.9, 112.4, 124.9, 151.8, 155.4, 160.6, 162.7, and 168.3.

To a solution of 200 mg (0.62 mmol) of **21** in 50 mL of THF was added 28 mg (0.68 mmol) of NaH. The solution was stirred at rt for 30 min and then cooled to 0 °C. To the above mixture was added a solution of 187 mg (0.56 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) in 30 mL of THF. After the solution was stirred for 10 min, the reaction was quenched by the addition of a saturated $NH_4Cl$ solution. Standard workup and purification gave 165 mg (57%) of 4-[2,2-bis(methoxycarbonyl)-4-(phenylsulfonyl)-4,5-hexadienyl]-7-methoxylcoumarin (**22**): IR (KBr) 1930, 1609, 1282, and 1140 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.96 (t, 2H, $J$ = 3.0 Hz), 3.35 (s, 2H), 3.49 (s, 6H), 3.80 (s, 3H), 5.40 (t, 2H, $J$ = 3.0 Hz), 6.00 (s, 1H), 6.71−6.77 (m, 2H), 7.38 (d, 1H, $J$ = 9.0 Hz), 7.46−7.60 (m, 3H), and 7.80 (d, 2H, $J$ = 7.2 Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 29.6, 32.4, 52.7, 55.6, 56.5, 86.0, 101.0, 108.7, 111.9, 112.6, 113.2, 125.2, 127.9, 129.1, 133.7, 139.3, 150.3, 155.1, 160.1, 162.5, 169.1, and 207.8. Anal. Calcd for $C_{26}H_{24}O_9S$: C, 60.92; H, 4.72. Found: C, 60.75; H, 4.58.

**Reaction of Dimethyl (*E*)-6-(Methoxycarbonyl)-2-heptenedioate (24a) with 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1).** To a solution containing 244 mg (1.0 mmol) of dimethyl (*E*)-6-(methoxycarbonyl)-2-heptenedioate (**24a**)[72] in 30 mL of THF was added 44 mg (1.1 mmol) of NaH at 0 °C. After the solution was stirred for 20 min, a solution containing 317 mg (0.95 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) in 30 mL of THF was added. After the solution was stirred for 10 min, the reaction was quenched by the addition of a saturated $NH_4Cl$ solution. Standard workup and purification gave 334 mg (81%) of dimethyl 6-[2-(phenylsulfonyl)-2,3-butadienyl]-6-(methoxycarbonyl)-2-heptenedioate (**26a**): IR (neat) 1958, 1730, 1652, 1197, 1069 and 855 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.91 (brs, 4H), 2.80 (brs, 2H), 3.52 (s, 6H), 3.58 (s, 3H), 5.24 (brs, 2H), 5.64 (d, 1H, $J$ = 15.6 Hz), 6.05−6.71 (m, 1H), 7.40−7.53 (m, 3H), and 7.75 (d, 2H, $J$ = 7.5 Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 26.5, 28.3, 29.7, 51.1, 52.4, 56.0, 85.2, 104.7, 108.4, 121.3, 127.8, 128.9, 133.5, 139.4, 147.0, 166.3, 169.8, and 207.9; HRMS Calcd for $C_{21}H_{24}O_8S$ 436.1192, found 436.1179.

The reaction of **24a** with diene **1** was also carried out at 25 °C. To a solution of 500 mg (2.05 mmol) of **24a** in 30 mL of THF at 0 °C was added 90 mg (2.25 mmol) of NaH. After 20 min of stirring, the mixture was warmed to rt, and a solution of 634 mg (1.9 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) in 50 mL of THF was added. The mixture was stirred for an additional 10 min, and the reaction was quenched by the addition of a saturated $NH_4Cl$ solution. Standard workup and purification gave 627 mg (76%) of 3-ethynyl-4-((methoxycarbonyl)methyl)-3-(phenylsulfonyl)cyclohexane-1,1-dicarboxylic acid dimethyl ester (**28a**) as an inseparable 1:1 mixture of *cis*,*trans*-isomers: IR (KBr) 2111, 1723, 1439, and 1303 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.37 (dt, 1H, $J$ = 13.2 and 4.8Hz), 1.64−1.86 (m, 4H), 2.20−2.84 (m, 4H), 3.30 (dd, 1H, $J$ = 15.6 and 1.5 Hz), 3.49 (s, 3H), 3.53 (s, 3H), 3.61 (s, 3H), 3.65 (s, 6H), 3.68 (s, 3H), 7.48−7.70 (m, 6H), and 7.90−7.95 (m, 4H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 24.1, 24.3, 26.6, 29.5, 29.6, 31.8, 35.5, 36.1, 36.5, 36.7, 51.6, 51.7, 52.0, 52.2, 52.6, 53.0, 53.1, 64.8, 65.3, 76.4, 79.2, 79.5, 80.2, 128.4, 128.8, 130.6, 130.9, 134.2, 134.4, 134.9, 135.1, 169.6, 169.9, 171.0, 171.2, 171.8, and 172.2. Anal. Calcd for $C_{21}H_{24}O_8S$: C, 57.78; H, 5.55. Found: C, 57.62; H, 5.58.

**Reaction of Dimethyl (*E*)-[4-(Phenylsulfonyl)-3-butenyl]propanedioate (24b) with 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1).** To a solution of 2.55 g (8.7 mmol) of diethyl ((phenylsulfonyl)methyl)phosphonate[73] in 100 mL of THF at 0 °C was added 384 mg (9.6 mmol) of NaH. The mixture was stirred at rt for 30 min. To above solution was added 1.63 g (8.7 mmol) of 2-(3-oxopropyl)malonic acid dimethyl ester[72] in 50 mL of THF. The reaction was heated at reflux for 4 h. Standard workup and purification gave 1.45 g (51%) of dimethyl (*E*)-[4-(phenylsulfonyl)-3-butenyl]propanedioate (**24b**): IR (neat) 1730, 1439, 1311, and 1147 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.99 (q, 2H, $J$ = 7.8 Hz), 2.24, (dt, 2H, $J$ = 7.8 and 6.9 Hz), 3.29 (t, 1H, $J$ = 7.5 Hz), 3.64 (s, 6H), 6.30 (d, 1H, $J$ = 15.3 Hz), 6.86 (dt, 1H, $J$ = 15.3 and 6.9 Hz), 7.44−7.58 (m, 3H), and 7.79 (d, 2H, $J$ = 7.2 Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 26.4, 28.7, 50.4, 50.5, 127.4, 129.1, 131.4, 133.2, 140.2, 144.5 and 168.9.

To a solution of 326 mg (1.0 mmol) of **24b** in 30 mL of THF at 0 °C was added 48 mg (1.2 mmol) of NaH. After the solution was stirred for 10 min, a solution of 317 mg (0.95 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) in 30 mL of THF was added. The mixture was stirred for 10 min at 0 °C, and the reaction was quenched by the addition of a solution of $NH_4Cl$. Standard workup and purification gave 321 mg (65%) of 2-(2-(phenylsulfonyl)buta-2,3-dienyl)-2-(4-(phenylsulfonyl)but-3-enyl)malonic acid dimethyl ester (**26b**): IR (neat) 1958, 1730, 1439, and 1140 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.91−2.05 (m, 4H), 2.84 (t, 2H, $J$ = 2.7 Hz), 3.58 (s, 6H), 5.25 (t, 2H, $J$ = 2.7 Hz), 6.24 (d, 1H, $J$ = 15.0 Hz), 6.78 (td, 1H, $J$ = 15.0 and 6.0 Hz), 7.44−7.56 (m, 6H), and 7.76−7.81 (m, 4H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 26.0, 28.5, 29.4, 52.6, 56.1, 85.4, 108.5, 127.5, 128.1, 129.1, 129.2, 131.0, 133.2, 13.8, 139.4, 140.3, 144.8, 169.8 and 208.0. Anal. Calcd for $C_{25}H_{26}O_8S_2$: C, 57.90; H, 5.06. Found: C, 57.78; H, 4.89.

(72) Bunce, R. A.; Pierce, J. D. *Synth. Commun.* **1987**, *19*, 67.
(73) Shahak, I.; Almog, J. *Synthesis* **1970**, 145.

The reaction of **24b** with diene **1** was also carried out at 25 °C. To a solution containing 163 mg (0.5 mmol) of dimethyl (*E*)-[4-(phenylsulfonyl)-3-butenyl]propanedioate (**24b**) in 30 mL of THF at rt was added 30 mg (0.75 mmol) of NaH. After the solution was stirred for 10 min, a solution of 160 mg (0.48 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) in 30 mL of THF was added. The solution was stirred at rt for 10 min, and the reaction was quenched by the addition of a $NH_4Cl$ solution. Standard workup and purification gave 183 mg (72%) of 3-ethynyl-3-(phenylsulfonyl)-4-((phenylsulfonyl)-methyl)cyclohexane-1,1-dicarboxylic acid dimethyl ester (**28b**) as a 3:1-mixture of diastereoisomers. The major isomer showed the following properties: mp 186−187 °C; IR (KBr) 2108, 1730, 1439, 1311, and 1140 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.40 (td, 1H, $J$ = 13.5 and 3.9 Hz); 1.92 (qd, 1H, $J$ = 13.5 and 3.3 Hz), 2.23 (dd, 1H, $J$ = 13.5 and 2.1 Hz), 2.34 (d, 1H, $J$ = 13.5 Hz), 2.43 (brd, 1H, $J$ = 13.5 Hz), 2.60 (s, 1H), 2.62−2.74 (m, 2H), 3.26 (dd, 1H, $J$ = 14.4 and 9.9 Hz), 3.55 (s, 3H), 3.64 (s, 3H), 4.58 (d, 1H, $J$ = 14.4 Hz), and 7.52−7.98 (m, 10H); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 26.9, 29.5, 35.0, 36.4, 52.2, 52.3, 57.8, 64.6, 76.1, 79.8, 128.2, 129.0, 129.3, 130.9, 133.8, 134.6, 134.6, 134.7, 139.6, 169.5, and 170.9. Anal. Calcd for $C_{25}H_{26}O_8S_2$: C, 57.90; H, 5.06. Found: C, 57.82; H, 4.95.

The minor isomer was a viscous oil which exhibited the following properties: IR (KBr) 2108, 1730, 1446, 1303, and 1140 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.77 (dt, 1H, $J$ = 13.8 and 3.6 Hz), 2.25−2.53 (m, 4H), 2.59 (brd, 1H, $J$ = 14.4 Hz), 2.66 (d, 1H, $J$ = 14.4 Hz), 2.98 (brd, 1H, $J$ = 11.4 Hz), 3.38 (dd, 1H, $J$ = 11.7 and 11.4 Hz), 3.52 (s, 3H), 3.72 (s, 3H), 4.19 (brd, 1H, $J$ = 14.4 Hz), 7.49−7.68 (m, 6H), 7.89 (d, 2H, $J$ = 7.8 Hz), and 7.95 (d, 2H, $J$ = 7.5 Hz). Anal. Calcd for $C_{25}H_{26}O_8S_2$: C, 57.90; H, 5.06. Found: C, 57.71; H, 5.04.

**Reaction of 2-(Methoxylcarbonyl)-4-methylenepentanedioic Acid Dimethyl Ester (29a) with 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1).** To a suspension containing 0.12 g (2.90 mmol) of NaH in 50 mL of THF was slowly added 0.26 mL (2.23 mmol) of dimethyl malonate. The solution was stirred for 15 min, and then 0.27 mL (2.23 mmol) of methyl 2-(bromomethyl)acrylate was slowly added. After the solution was stirred for 30 min at rt, the reaction was quenched by the addition of a saturated solution of $NH_4Cl$. Workup and purification gave 460 mg (89%) of **29a**: IR (neat) 1730, 1631, 1439, 1232, and 1147 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.84 (d, 2H, $J$ = 7.5 Hz), 3.66 (s, 6H), 3.69 (t, 1H, $J$ = 7.5 Hz), 3.70 (s, 3H), and 5.60 (s, 1H), and 6.16 (s, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 31.4, 50.6, 51.9, 52.5, 128.0, 136.3, 166.6, and 169.

A solution of 0.38 g (1.67 mmol) of **29a** in 10 mL of THF was slowly added to an ice-cold suspension containing 0.09 g (2.17 mmol) of NaH in 20 mL of THF. The reaction mixture was stirred for 15 min at 0 °C, and then 0.56 g (1.67 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) in 10 mL of THF was slowly added. After the solution was stirred for 15 min at 0 °C, the reaction was quenched by the addition of a saturated solution of $NH_4Cl$. Standard workup and purification gave 0.30 g (43%) of 6a-(phenylsulfonyl)-4,6a-dihydro-1*H*-pentalene-2,2,3a-tricarboxylic acid trimethyl ester (**36a**): IR 1730, 1446, 1254, and 1147 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.34 (dd, 1H, $J$ = 17.4 and 2.5 Hz), 2.42 (d, 1H, $J$ = 14.3 Hz), 2.79 (d, 1H, $J$ = 14.3 Hz), 3.04 (dt, 1H, $J$ = 17.4 and 2.1 Hz), 3.23 (d, 1H, $J$ = 14.3 Hz), 3.54 (d, 1H, $J$ = 14.3 Hz), 3.63 (s, 3H), 3.76 (s, 3H), 3.79 (s, 3H), 5.19 (dd, 1H, $J$ = 5.4 and 2.5 Hz), 5.87 (dt, 1H, $J$ = 5.4 and 2.1 Hz), 7.49 (t, 2H, $J$ = 7.5 Hz), 7.62 (t, 1H, $J$ = 7.5 Hz), and 7.80 (d, 2H, $J$ = 7.5 Hz); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 39.0, 42.2, 46.9, 52.4, 53.0, 53.1, 58.8, 61.4, 88.0, 128.4, 129.5, 129.9, 133.7, 137.3, 137.7, 170.5, 171.3, and 172.4. Anal. Calcd for $C_{20}H_{22}O_8S$: C, 56.86; H, 5.25. Found: C, 56.63; H, 5.14.

In addition to compound **36a**, 0.34 g (48%) of 2-[2-(phenylsulfonyl)buta-2,3-dienyl]-2-(methoxycarbonyl)-4-methylenepentanedioic acid dimethyl ester (**31a**) was also isolated from the chromatographic separation as a clear oil: IR 1960, 1730, 1632, and 1304 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.84 (t, 2H, $J$ = 3.8 Hz), 3.01 (s, 2H), 3.61 (s, 6H), 3.68 (s, 3H), 5.42 (t, 2H, $J$ = 3.8 Hz), 5.47 (s, 1H), 6.14 (s, 1H), 7.54 (t, 2H, $J$ = 7.5 Hz), 7.64 (t, 1H, $J$ = 7.5 Hz), and 7.88 (d, 2H, $J$ = 7.5 Hz); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 28.6, 33.4, 52.0, 52.6, 56.2, 86.1, 109.3, 127.9, 128.2, 129.1, 129.6, 133.6, 135.1, 139.9, 166.9, and 169.84. Anal. Calcd for $C_{20}H_{22}O_8S$: C, 56.86; H, 5.25. Found: C, 56.78; H, 5.22.

**Reaction of Dimethyl [2-(Phenylsulfonyl)-2-propenyl]-propanedioate (29b) with 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1).** To a mixture of 240 mg (5.0 mmol) of NaH in 30 mL of THF at 0 °C was added 0.57 mL (5.0 mmol) of dimethyl malonate. After the solution was stirred for 10 min at 0 °C, a solution of 2,3-bis(phenylsulfonyl)-1-propene (**1**) in 30 mL of THF was added. The solution was stirred at 0 °C for 10 min, and the reaction was quenched with a saturated $NH_4Cl$ solution. Standard workup and purification on silica gel gave 0.97 g (62%) of dimethyl [2-(phenylsulfonyl)-2-propenyl]propanedioate (**29b**): IR (neat) 1735, 1434, 1302, 1079, and 747 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.79 (d, 2H, $J$ = 7.5 Hz), 3.64 (s, 6H), 3.78 (t, 1H, $J$ = 7.5 Hz), 5.80 (s, 1H), 6.37 (s, 1H), 7.51 (t, 2H, $J$ = 7.5 Hz), 7.61 (t, 1H, $J$ = 7.5 Hz), and 7.83 (d, 2H, $J$ = 7.5 Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 28.9, 50.1, 52.7, 126.6, 128.2, 129.3, 133.7, 138.3, 146.7, and 168.3.

To a solution of 156 mg (0.5 mmol) of **29b** in 15 mL of THF at 0 °C was added 24 mg (0.6 mmol) of NaH. After the solution was stirred for 10 min, a solution of 159 mg (0.48 mmol) of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) in 15 mL of THF was added. After 10 min, the mixture was quenched by the addition of a saturated $NH_4Cl$ solution. Standard workup followed by silica gel chromatographic separation and purification gave 75 mg (35%) of 2-[2-(phenylsulfonyl)allyl]-2-[2-(phenylsulfonyl)buta-2,3-dienyl]malonic acid dimethyl ester (**31b**), 73 mg (30%) of 3-ethynyl-3,5-bis(phenylsulfonyl)cyclohexane-1,1-dicarboxylic acid dimethyl ester (**33b**), and 75 mg (35%) of 3a,6a-bis(phenylsulfonyl)-3,3a,4,6a-tetrahydro-1*H*-pentalene-2,2-dicarboxylic acid dimethyl ester (**36b**). Compond **31b** showed the following properties: IR (neat) 2256, 1960, 1736, 1440, and 1152 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.96 (s, 2H), 2.99 (t, 2H, $J$ = 3.4 Hz), 3.65 (s, 6H), 5.29 (t, 2H, $J$ = 3.4 Hz), 5.74 (s, 1H), 5.34 (s, 1H), and 7.53−7.88 (m, 10H);$^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 28.8, 30.8, 53, 55.9, 86.1, 108.8, 127.0, 128.2, 128.3, 129.2, 129.3, 133.7, 133.8, 138.5, 139.6, 145.6, 169.2, and 207.7. Anal. Calcd for $C_{24}H_{24}O_8S_2$: C, 57.13; H, 4.80. Found: C, 56.83; H, 4.69.

Compound **33b** showed the following properties: mp 162−163 °C; IR (KBr) 2256, 1731, 1437, and 897 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.77 (t, 1H, $J$ = 12.9 Hz), 2.05 (dd, 1H, $J$ = 15.3 and 13.2 Hz), 2.48 (s, 1H), 2.49 (brd, 1H, $J$ = 15.3 Hz), 2.63 (d, 1H, $J$ = 16.2 Hz), 2.86 (brd, 1H, $J$ = 13.2 Hz), 3.37 (d, 1H, $J$ = 16.2 Hz), 3.70 (s, 3H), 3.75 (s, 3H), 4.04 (tt, 1H, $J$ = 12.9 and 3.3 Hz), 7.42 (t, 2H, $J$ = 7.8 Hz), 7.60−7.76 (m, 6H), and 7.92 (d, 2H, $J$ = 7.5 Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 28.2, 30.4 33.0, 52.2, 53.0, 53.4, 54.8, 60.0, 81.1, 128.5, 128.7, 129.4, 131.0, 133.6, 134.1, 134.4, 136.8, 169.0, and 170.4. Anal. Calcd for $C_{24}H_{24}O_8S_2$: C, 57.13; H, 4.80. Found: C, 57.21; H, 4.76.

Compound **36b** showed the following properties: mp 228−229 °C; IR (KBr) 1739, 1437, 1304, and 1143 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.12 (d, 1H, $J$ = 15.9 Hz), 2.21 (dd, 1H, $J$ = 15.9 and 2.7 Hz), 2.83 (d, 1H, $J$ = 13.8 Hz), 3.47 (brd, 1H, $J$ = 15.9 Hz), 3.52 (s, 3H), 3.53 (d, 1H, $J$ = 15.9 Hz), 3.46 (d, 1H, $J$ = 13.8 Hz), 3.78 (s, 3H), 5.30 (dd, 1H, $J$ = 5.7 and 1.8 Hz), 5.95 (t, 1H, $J$ = 2.4 Hz), 7.48−7.64 (m, 6H), 7.94 (d, 2H, $J$ = 7.5 Hz), and 8.00 (d, 2H, $J$ = 7.5 Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 39.8, 42.9, 44.9, 53.2, 53.4, 57.4, 79.8, 87.7, 128.6, 128.9, 130.3, 130.5, 131.4, 133.9, 135.4, 138.1, 138.5, 169.8 and 170.7. Anal. Calcd for $C_{24}H_{24}O_8S_2$: C, 57.13; H, 4.80. Found: C, 56.62; H, 4.79.

A mixture of 47 mg (0.09 mmol) of **36b** and 20 mg of $PtO_2$ in 30 mL of acetic acid and 30 mL of ethyl acetate under $H_2$ (70 psi) was hydrogenated overnight. Removal of the solvent and purification on silica gel gave 42 mg (87%) of 3a,6a-bis-(phenylsulfonyl)hexahydropentalene-2,2-dicarboxylic acid dimethyl ester (**37**): IR (KBr) 1730, 1439, 1303, and 1133 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.80−1.90 (m, 3H), 2.10−2.25

(m, 1H), 2.39 (d, 2H, $J = 15.0$ Hz), 2.67−2.75 (m, 2H), 3.60 (d, 2H, $J = 15.0$ Hz), 3.64 (s, 3H), 3.90 (s, 3H), 7.53−7.65 (m, 6H), and 8.02 (d, 4H, $J = 7.2$ Hz); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 20.2, 34.5, 42.0, 53.7, 58.1, 77.2, 82.3, 128.9, 130.6, 133.8, 138.7, 170.5, and 172.3. Anal. Calcd for $C_{24}H_{26}O_8S_2$: C, 56.90; H, 5.18. Found: C, 56.71; H, 5.09.

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**Supporting Information Available:** $^1$H NMR and $^{13}$C NMR spectra for new compounds lacking analyses (8 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.

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