aliquot. ^{13}C spectra consisted of 600 accumulations over 2250 Hz, and ^{1}H spectra were from nine accumulations over 4000 Hz.

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Registry No. **1a**, 502-42-1; **1b**, 17616-76-1; **2a**, 539-87-7; **2b**, 137435-12-2; **3a**, 6572-98-1; **3b**, 137435-13-3.

Use of 2,3-Bis(phenylsulfonyl)-1-propene as a Multicoupling Reagent

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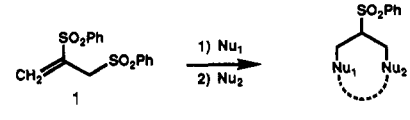
2,3-Bis(phenylsulfonyl)-1-propene (1) reacts with various amines to afford products derived from addition across the double bond as well as S_N2' displacement. When treated with 2-piperidinemethanol, bissulfone 1 gave the expected S_N2' product which was converted to the corresponding bromide and cyclized with tributyltin hydride to a bicyclic amine. Reaction of bissulfone 1 with furfurylamine followed by treatment with acetyl chloride afforded the product derived from a tandem S_N2' displacement–intramolecular Diels–Alder reaction. Several novel heterocyclic compounds were prepared by connecting two nucleophilic sites with a carbon–carbon bond and allowing this reagent to react with bissulfone 1. The reaction of 1 with the pyrrolidine enamine derived from cyclohexanone gave bicyclo[3.3.1]nonan-9-one in 78% yield. The soft nucleophile approach is not the only way to add carbon centers to bissulfone 1. Radical attack on the double bond of 1 leads to an intermediate sulfonyl-stabilized radical. This species readily fragments to produce a new vinyl sulfone which undergoes further radical cyclization to give six-membered ring sulfones.

Functionalized allylic reagents which contain both a leaving group and a π-activating substituent have been extensively utilized in organic synthesis.[1-11] These substituted 1-propenes have been referred to as multicoupling reagents.[5,12] In this context we have recently demonstrated that 2-alkoxy- or 2-thio-substituted 3-(phenylsulfonyl)-1-propenes[13] are versatile synthetic reagents. Owing to the phenylsulfonyl group's molecular weight and stability, the carbon backbone of such compounds can become very small without the drawback of volatility or thermal lability seen in other synthetic intermediates with the same carbon skeleton. They react with various electrophiles, leading to functionalized unsaturated sulfones, which can undergo further useful transformations. In connection with our program dealing with the chemistry of unsaturated sulfones,[14] we have been exploring the chemical reactivity of 2,3-bis(phenylsulfonyl)-1-propene (1).[15] This three-carbon backbone includes both a vinyl and allylic sulfone, which act in concert to provide unusual reactivity. Conveniently, bissulfone 1 is a crystalline compound, easily prepared and with indefinite shelf-life, adding to its attractiveness for use as a multicoupling reagent. The synthetic potential of bissulfone 1 was demonstrated by taking advantage of two properties of the phenylsulfonyl group: (1) its ability to activate double bonds toward Michael addition, and (2) its viability as a leaving group.[16] Indeed, treatment of 1 with a variety of nucleophiles results in S_N2' displacement followed by conjugate addition to give products of the general type 2. The present paper documents the results of these studies.



1 2

Results and Discussion

A. Heteroatom Additions. We began our studies by examining the reaction of 1 with various amines. Aniline was found to add efficiently across the double bond of 1

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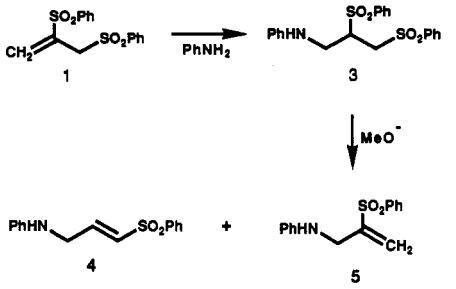
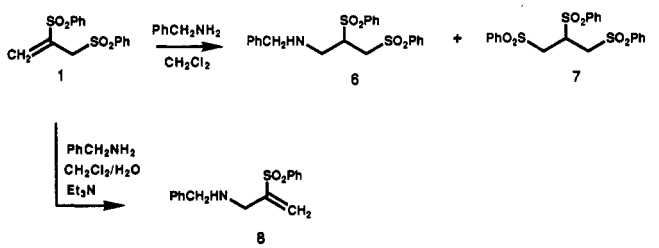
to give the saturated disulfone **3** which, upon treatment with sodium methoxide, afforded vinyl sulfones **4** and **5** in a 3:2 ratio. The addition of primary and secondary

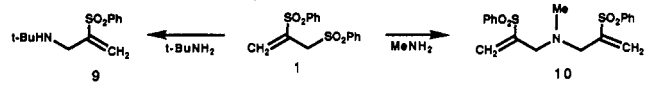


aliphatic amines to **1** is also possible. Here, however, the products were more dependent upon the reaction conditions. For example, treatment of **1** with benzylamine in methylene chloride resulted in a mixture of adduct **6** (70%) as well as 1,2,3-tris(phenylsulfonyl)propane, **7** (15%). This



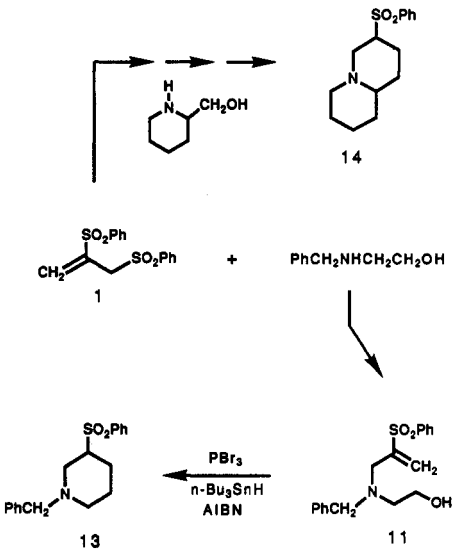
latter product is derived from attack of phenylsulfinate anion on structure **1**. The sulfinate anion is formed from the S_N2' reaction of benzylamine with **1**. In this case, the reaction of **6** with sodium methoxide did not lead to elimination of phenylsulfinate anion. We were able to overcome this obstacle in the preparation of amino sulfone **8** by modifying the reaction conditions. By using a biphasic solvent system (methylene chloride/water) with vigorous agitation, and adding 1 equiv of triethylamine to facilitate extraction of phenylsulfinate into the aqueous phase, amino sulfone **8** was obtained in 81% isolated yield.

Other primary amines also participate in the displacement protocol, although the use of sterically bulky groups is a requisite condition for exclusive monoaddition. Thus, *tert*-butylamine cleanly afforded **9** in excellent yield, whereas, when methylamine was used, the diadduct **10** was the exclusive product.



Once a monoadduct is formed, a new reactive site is present in the product. The introduction of an amine-containing pendant functionality would provide an avenue for further chemical manipulation. One attractive subsequent reaction appeared to be the use of a suitable halide precursor for a radical ring closure. Cyclization reactions involving free-radical chain processes are rapidly gaining ground in the repertoire of synthetic chemists.[17-19] In the construction of nitrogen-containing heterocycles, for instance, 1-aza,[20] 2-aza,[21] 3-aza,[22] and 4-aza-5-hexenyl[23] radical cyclizations have been shown to be quite useful. The majority of these closures involve 5-membered ring formation via a 5-*exo-trig* cyclization with varying amounts of 6-membered ring formed by 6-*endo-trig* cyclization.[24] A number of cases have also been reported in which 6-membered rings are formed predominantly or exclusively.[25]

Toward this end, bissulfone **1** was treated with *N*-benzylethanolamine, which resulted in the formation of adduct **11** in high yield. Conversion of **11** to the corresponding bromide **12** was accomplished by treating **11** with phosphorus tribromide. Subjection of **12** to reductive conditions using tributyltin hydride resulted in a 6-*endo-trig* cyclization to form the substituted piperidine **13** in 63% yield. This reaction is also successful with other



secondary amines, such as cyclic amines. For example, when treated with 2-piperidinemethanol, bissulfone **1** afforded the expected S_N2' product which was converted to the corresponding bromide with thionyl bromide and cyclized with tributyltin hydride to bicyclic amine **14**. This protocol constitutes a straightforward annulative approach to the structural backbone of the widely occurring lupine or quinolizidine alkaloids.[26]

Use of the vinyl sulfone moiety in an intramolecular 4 + 2-cycloaddition may provide an opportunity for subsequent chemistry and construction of polycyclic ring systems.[27] The intramolecular Diels–Alder reaction has been a valuable tool for the construction of polycyclic ring systems.[28] The versatility of furan as the diene in this process has been demonstrated by elaboration of its cycloadducts into aromatic compounds,[29] oxabicyclo[2.2.1]-

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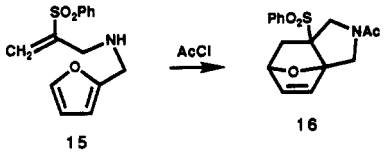
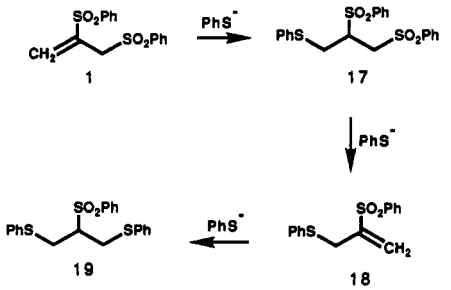
heptane systems,[30] and natural products.[31] We have found that treatment of 1 with furfurylamine gave adduct 15 in 85% yield. Attempted cyclization of 15 by thermolysis was unsuccessful. However, amidation with acetyl chloride resulted in a spontaneous cycloaddition reaction at room temperature to give cycloadduct 16 in excellent yield. The



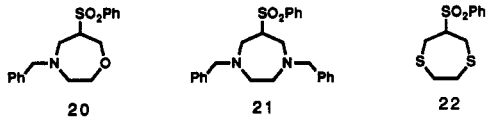
15 16

Diels–Alder reaction of allylfurfurylamines is known to be quite dependent on the steric demand of the N-substituent group.[32] Cycloaddition is more easily achieved with bulky substituents producing the exo-oriented product. The acceleration of the above cycloaddition with increasing bulk on the nitrogen atom is probably related to a lowering of the enthalpy of activation.[33]

In a similar vein, although not limited to the use of amines only, is the idea of adding a nucleophile to bissulfone 1 followed by attack of the newly formed vinyl sulfone with a secondary heteronucleophile. While the vinylsulfonyl group of the adduct is less reactive than 1, it will still allow a second addition, as demonstrated by the isolation of diadduct 19 upon treatment of 1 with excess thiophenol. The reaction of 1 with 1 equiv of thiophenol afforded mostly the addition product 17 (75%) together with lesser quantities of the S_N2' displacement product 18 (25%). The excess thiophenolate anion apparently induces the loss of phenylsulfinate, giving rise to 18 which rapidly reacts further to produce 19.



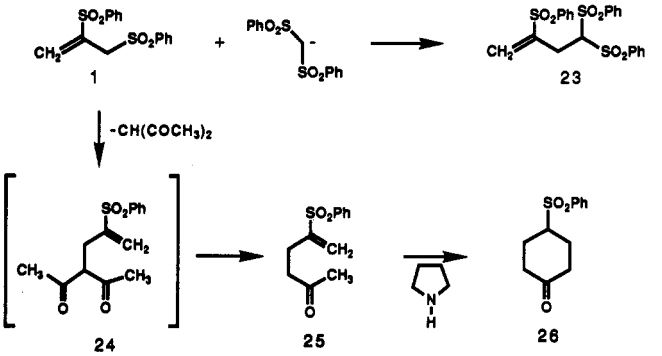
By connecting the two nucleophilic sites with a carbon-chain tether, this method can be used to prepare some novel heterocyclic compounds. Thus, treatment of adduct 11 with base-induced ring closure to form the perhydrooxazepine 20 in good yield. Other seven-membered heterocyclic compounds also could be easily prepared. The reaction of 1 with *N,N'*-dibenzylethylenediamine, using the biphasic conditions described previously, produced the perhydrodiazepine 21 in a one-pot procedure in 68% yield.



20 21 22

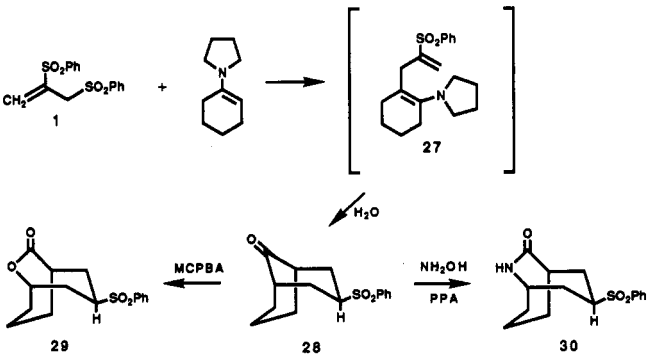
Likewise, treatment of 1 with ethanedithiol in methanol using a slight excess of triethylamine resulted in the formation of dithiepane 22 in 92% yield.

B. Carbon-Center Additions. Our ongoing interest in the synthetic utility of bissulfone 1 inspired us to take a detailed look at its reaction with various carbon nucleophiles, as this would provide an entry into the synthesis of various carbocycles. Enolates derived from simple ketones, however, proved to be too harsh for the base-sensitive bissulfone 1. Under these conditions, one of the active methylene protons was removed to form an α-sulfonyl anion which rapidly ejected phenylsulfinate anion to form (phenylsulfonyl)allene. The allene then simply polymerized under the reaction conditions. One way to circumvent this obstacle involved the use of "*softer*" carbon nucleophiles, such as enamines or diactivated methylene compounds. In fact, treatment of 1 with the lithium salt of bis(phenylsulfonyl)methane resulted in clean addition–elimination to provide adduct 23 in 81% yield.



Diketones may also be used for this reaction. Thus, treatment of 1 with the sodium salt of 2,4-pentanedione gave keto sulfone 25 in 78% yield, presumably arising from 24 which is deacetylated under the reaction conditions.[34] Stirring 25 with a catalytic amount of pyrrolidine resulted in smooth cyclization to produce the known 4-(phenylsulfonyl)cyclohexanone 26 in 90% yield.[35]

The reaction of 1 with the pyrrolidine enamine derived from cyclohexanone was also examined.[36] After acidic workup, crystallization from chloroform–hexane gave bicyclo[3.3.1]nonan-9-one 28 in 78% yield.[37] Initial nucleophilic attack of the enamine onto 1 produces a zwitterion, which is either neutralized directly by a 1,3-proton shift or indirectly by ejection of phenylsulfinate anion which can act then as a proton acceptor to give a new enamine (i.e. 27). With regeneration of the vinyl sulfone functionality, the substrate is poised for an iteration of the addition process, which after hydrolysis and purification affords the bicyclic keto sulfone 28. Substrate 28 can also



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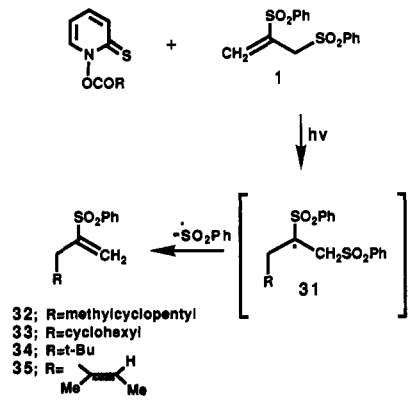
(36) For the reaction of cyclic enamines with (phenylsulfonyl)-1,2-propadiene, see: Hayakawa, K.; Takewaki, M.; Fujimoto, I.; Kanematsu, K. *J. Org. Chem.* **1986**, *51*, 5100.
(37) Anzeveno, P. B.; Matthews, D. P.; Barney, C. L.; Barbuch, R. J. *J. Org. Chem.* **1984**, *49*, 3134.

undergo further chemistry on the carbonyl group, independent of the sulfonyl functionality. For example, Baeyer–Villiger oxidation of **28** using MCPBA gave the bicyclic lactone **29** in very high yield. Likewise, Beckmann rearrangement of the oxime of **28** in the presence of polyphosphoric ester smoothly produced the corresponding amide **30**.

Use of a soft nucleophile is not the only way to add carbon centers to disulfone **1**. Another avenue is provided by the use of free radicals. The development of synthetic methodology permitting the radical construction of organic substrates remains an active area of research.[17-19] An attractive feature of this process is that in certain cases it may serve as a surrogate for synthetically inaccessible ionic reactions. Since treatment of **1** with various enolates or organometallic reagents results primarily in β-elimination of the phenylsulfonyl group producing (phenylsulfonyl)allene (vide supra), it seemed reasonable to assume that an analogous radical-based S_N2' reaction could provide a convenient alternative. The radical path would avoid the problem of elimination that is encountered with "*hard*" carbon nucleophiles. As an encouraging precedent, vinyl sulfones have been shown to be very efficient radical acceptors,[38] and the β-elimination of the phenylsulfonyl radical is also well precedented.[39-45]

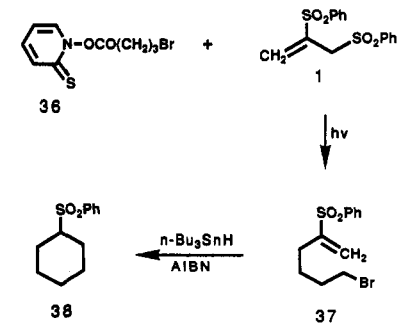
Free-radical addition reactions are recognized as a powerful method for inter- and intramolecular carbon–carbon bond formation.[17] The rate and regioselectivity of the reaction are affected by substituents on both the attacking radical and π-bond.[46] The exothermic addition of alkyl radicals to alkenes involves an early transition state, and molecular orbital calculations have suggested a dipolar complex.[47] This charge distribution is in accord with the concept that alkyl radicals behave as nucleophiles and will readily add to electron-deficient olefins. Indeed, addition to electronically activated π-bonds dominates even when unhindered, unactivated alkenes are available.[48] Methods utilized for free-radical generation are usually tin hydride mediated, and halides, selenides, and sulfur-containing compounds have been used as radical precursors in most studies.[49-51] More recently, Barton and co-workers have shown that the thermal or photochemical decomposition of thiohydroxamic esters represents an excellent method for generating alkyl radicals.[52] The synthetic utility of this procedure using various radical traps has been elegantly exploited to yield a variety of functional groups.[53]

By using Barton's method of generating alkyl radicals, we were able to add primary, secondary, and tertiary alkyl radicals to bissulfone **1**.[54] In a typical procedure, a solution of **1** and a 3-fold excess of a thiohydroxamic acid ester was irradiated with a 250-W tungsten lamp for ca. 1 h to produce adducts **32–34** in high yield. An sp^2 center could also be added using conventional tributyltin hydride conditions. The slow addition of 1.2 equiv of tributyltin hydride to a refluxing toluene solution of bissulfone **1**, 2-bromo-2-butene (1 equiv), and a catalytic amount of AIBN resulted in the formation of diene **35** in 83% yield.



The reaction proceeds by radical attack on the double bond of **1** to give an intermediate sulfonyl stabilized radical (i.e. **31**) which can undergo facile fragmentation to form a new vinyl sulfone. As exemplified in this sequence, vinyl sulfones function as efficient radical acceptors;[53] allylic sulfones are also known to promote S_N2' displacement reactions.[39-43]

Because there are two latent sites for radical attack, it seemed possible to effect dual addition to **1**. To demonstrate the viability of this process, a controlled stepwise sequence was envisioned by which the initial addition could be carried out by the Barton method, followed by ring closure via tin hydride reduction. For example, thiohydroxamic acid ester **36** was prepared from ω-bromobutyric acid. Irradiation of **36** in the presence of bissulfone **1** using a 300-W tungsten lamp produced bromo sulfone **37** in very high yield. Ring closure was then accomplished by treating **37** with an excess of tributyltin hydride, forming the known cyclohexyl phenyl sulfone **38** in 82% yield.[55]



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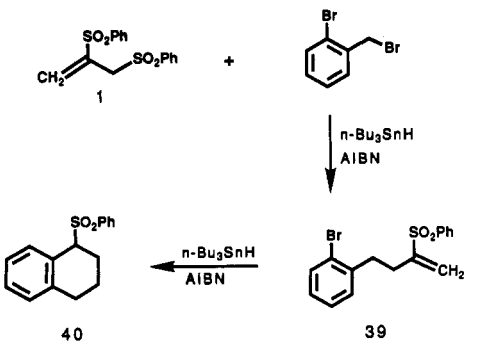
It was also possible to carry out this diaddition in one pot using only the tin hydride protocol. Thus, treatment of a solution containing bissulfone 1 and 1,3-dibromopropane with 3 equiv of tributyltin hydride in the presence of AIBN induced a sequential radical addition leading to the formation of 38 in 48% yield. Bromobenzyl sulfone 39 was also available by a similar addition, which could be subsequently cyclized with additional tributyltin hydride to produce the known tetrahydronaphthalene[56] 40 in 88% yield.



Ring closure reactions of 5-hexenyl radicals have received much synthetic attention in recent years.[57] In fact, sequential radical cyclizations have been used to construct multiple rings in one step,[58] and guidelines for understanding the stereochemical influence of ring substituents have been published.[57] A marked preference for exo ring closure generally exists giving rise to cycloalkylcarbinyl radicals. It should be noted, however, that in the above cases, cyclization gave only the six-membered ring. This result is in accord with earlier observations made in the literature where substitution at the 5-position causes a distinct preference for endo closure.[59]

Although other multifunctional electrophilic reagents are known, few can boast the straightforward preparation, high thermal stability and diverse reactivity shown by the crystalline bissulfone 1. Indeed, it is rare to encounter reagents which exhibit such excellent *shelf* stability, yet engage in such a variety of chemical transformations. In this regard, bissulfone 1 has proven to be an extremely versatile synthetic intermediate with much potential still to be explored. Extension of the scope and synthetic utilization of this reagent is being investigated further.

Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Unless otherwise noted, all reactions were performed in oven-dried glassware under an atmosphere of extra dry nitrogen. Solutions were evaporated under reduced pressure with a rotary evaporator, and the residue was chromatographed on a silica gel column using a 1:3 ethyl acetate–hexane mixture as the eluent unless specified otherwise.

Preparation of 2,3-Bis(phenylsulfonyl)-1-propene (1). To a solution containing 8.0 g of 3-(phenylsulfonyl)-2-(phenylthio)-1-propene[13] in 16.0 mL of glacial HOAc was added 20.0 mL of H_2O_2 over 1 h. The temperature was maintained between 90 and 100 °C. After the addition was complete, the solution was stirred overnight at 25 °C and was poured into 100 mL of water. The resulting precipitate was collected by filtration and washed with water, followed by recrystallization from CH_2Cl_2–hexane to give 2,3-bis(phenylsulfonyl)-1-propene (1) in 80% yield as a white solid: mp 125–126 °C; IR (KBr) 3120, 2980, 1590, 1310, 1140, and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 4.05 (s, 2 H), 6.50 (d, 1 H, J = 1.2 Hz), 6.67 (d, 1 H, J = 1.2 Hz), 7.45–7.56 (m, 4 H), 7.62 (d, 1 H, J = 7.5 Hz), 7.67 (d, 1 H, J = 7.5 Hz), and 7.74 (d, 4 H, J = 7.5 Hz). Anal. Calcd for $C_{15}H_{14}O_4S_2$: C, 55.89; H, 4.38; S, 19.86. Found: C, 55.62; H, 4.31; S, 19.75.

Reaction of 2,3-Bis(phenylsulfonyl)-1-propene (1) with Aniline. A solution containing 2.6 mL of aniline and 2.25 g (8 mmol) of bissulfone 1 in 25 mL of glacial HOAc was stirred at 25 °C for 72 h. The reaction mixture was poured into a saturated $NaHCO_3$ solution and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to leave a clear oil which crystallized on standing. Recrystallization using a $CHCl_3$–EtOH (3:1) mixture gave 1.6 g (80%) of 1,2-bis(phenylsulfonyl)-3-(*N*-phenylamino)propane (3) as a white solid: mp 143–144 °C; IR (KBr) 3340, 2950, 1590, 1450, 1310, 1150, and 740 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.40–3.78 (m, 4 H), 4.28–4.38 (m, 1 H), 6.48 (d, 2 H, J = 7.8 Hz), 6.62–6.70 (m, 1 H), 7.07 (t, 2 H, J = 7.8 Hz), and 7.35–7.74 (m, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 42.1, 51.5, 58.0, 113.6, 118.6, 127.9, 128.5, 129.3, 129.6, 129.7, 134.3, 134.5, 136.6, 138.2, and 146.6. Anal. Calcd for $C_{21}H_{21}O_4NS_2$: C, 60.71; H, 5.10; N, 3.37. Found: C, 61.03; H, 5.15; N, 3.31.

A solution containing 110 mg (0.24 mmol) of 3 and 40 mg of NaOMe in 40 mL of a 1:1 mixture of absolute EtOH and DME was stirred at 25 °C for 30 min. The reaction mixture was quenched with a saturated NH_4Cl solution, concentrated under reduced pressure, poured into water, and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting orange oil was subjected to silica gel chromatography using a 5% EtOAc–hexane mixture as the eluent. The first fraction isolated (58 mg, 60%) consisted of an orange oil which was identified as *N*-[3-(phenylsulfonyl)-2-propenyl]phenylamine (4): IR (neat) 3400, 2925, 1445, 1310, 1145, and 755 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 4.02 (d, 1 H, J = 4.0 Hz), 4.03 (d, 1 H, J = 4.0 Hz), 6.52 (d, 2 H, J = 7.9 Hz), 6.58 (d, 1 H, J = 15.0 Hz), 6.73 (t, 1 H, J = 7.9 Hz), 7.06 (dt, 1 H, J = 15.0, 4.0 Hz), 7.15 (t, 2 H, J = 7.9 Hz), 7.51 (t, 2 H, J = 7.8 Hz), 7.60 (t, 1 H, J = 7.8 Hz), and 7.84 (d, 2 H, J = 7.8 Hz); m/e 273 (M^+), 120 (base), and 110. Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.54; N, 5.13. Found: C, 66.07; H, 5.35; N, 5.02.

The second fraction isolated (39 mg, 40%) from the column was a white solid, mp 79–80 °C, which was identified as *N*-[2-(phenylsulfonyl)-2-propenyl]phenylamine (5): IR (CCl_4) 3460, 2925, 1450, 1320, 1140, and 740 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 4.00 (s, 2 H), 5.95 (s, 1 H), 6.33 (d, 2 H, J = 7.5 Hz), 6.41 (s, 1 H), 6.69 (t, 1 H, J = 7.5 Hz), 7.06 (t, 2 H, J = 7.5 Hz), 7.58 (t, 2 H, J = 7.5 Hz), 7.65 (t, 1 H, J = 7.5 Hz), and 7.93 (d, 2 H, J = 7.5 Hz). Anal. Calcd for $C_{15}H_{15}NO_2S$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.84; H, 5.57; N, 5.09.

Reaction of 2,3-Bis(phenylsulfonyl)-1-propene (1) with Benzylamine. To a solution containing 0.33 g (0.1 mmol) of 1 in 5 mL of CH_2Cl_2 was added 0.11 mL of benzylamine. The solution was allowed to stir overnight at rt, and the resulting white precipitate was removed by filtration. The filtrate was diluted with 15 mL of CH_2Cl_2 and washed twice with water. After being dried over anhydrous Na_2SO_4, the solution was concentrated, and the residue was chromatographed on silica gel to give 0.33 g (70%) of a white solid, mp 119–120 °C, whose structure was assigned as *N*-[2,3-bis(phenylsulfonyl)propyl]benzylamine (6): IR (KBr) 3440, 2925, 1455, 1310, 1150, and 740 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.73 (bs, 1 H), 3.02 (dd, 1 H, J = 13.7, 5.6 Hz), 3.17 (dd, 1 H, J = 13.7 and 2.2 Hz), 3.50–3.80 (m, 4 H), 3.92 (dd, 1 H, J = 13.8, 9.3 Hz), and 7.20–7.90 (m, 15 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 45.5, 50.9, 53.6, 59.4, 123.9, 127.1, 127.9, 128.1, 128.4, 128.6, 129.5, 134.2, 134.3, 136.7, 138.8, and 139.7. Anal. Calcd for $C_{22}H_{23}S_2O_4N$: C, 61.52; H, 5.40; N, 3.26. Found: C, 61.59; H, 5.46; N, 3.22

The second fraction (43 mg, 30%) isolated from the column consisted of a white solid, mp 126–127 °C, whose structure was assigned as 1,2,3-tris(phenylsulfonyl)propane (7) on the basis of its spectroscopic properties and by an independent synthesis: IR (KBr) 3065, 2990, 2980, 2945, 1305, 1145, 735, and 690 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 3.70–3.95 (m, 5 H) and 7.50–7.80 (m, 15 H). Anal. Calcd for $C_{21}H_{20}O_6S_3$: C, 54.30; H, 4.33; S, 20.70. Found: C, 54.11; H, 4.27; S, 20.59. An authentic sample of 7 was

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prepared by the oxidation of 1,3-bis(phenylthio)-2-(phenylsulfonyl)propane (19) (vide infra). To a solution containing 350 mg of 19 in 10 mL of glacial HOAc at 60 °C was added 5 mL of 30% hydrogen peroxide over a 30-min period. After being stirred for 2 h at 60 °C, the mixture was cooled to rt, poured into a 5% $NaHCO_3$ solution, extracted with CH_2Cl_2, and dried over $MgSO_4$. Removal of the solvent afforded trisulfone 7 in 85% yield.

The reaction of 1 with benzylamine was also carried out under a slightly different set of conditions. To a solution containing 1.0 g of 1 (3.1 mmol) in 67 mL of CH_2Cl_2 was added 67 mL of water, and then, with vigorous stirring, 0.42 mL of Et_3N and 0.33 mL of benzylamine were added. Stirring was continued for 5 h at rt, and the contents were diluted with 50 mL of water and the organic layer was dried over anhydrous Na_2SO_4. Evaporation of the solvent left a straw-colored oil which was subjected to silica gel chromatography to give 722 mg (81%) of *N*-[2-(phenylsulfonyl)-2-propenyl]benzylamine (8) as a clear oil: IR (neat) 3360, 2850, 1455, 1315, 1150, 1090, and 760 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 1.62 (bs, 1 H), 3.45 (s, 2 H), 3.61 (s, 2 H), 6.00 (s, 1 H), 6.46 (s, 1 H), and 7.22–7.95 (m, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 47.4, 52.2, 125.2, 127.0, 128.0, 128.3, 129.2, 133.5, 139.0, 129.4, 139.4, and 148.3; HRMS calcd for $C_{16}H_{17}NSO_2$ 287.0980, found 286.0911 ($M - H^+$).

Reaction of 2,3-Bis(phenylsulfonyl)-1-propene (1) with *tert*-Butylamine. To a solution containing 0.50 g (1.5 mmol) of 1 in 33 mL of CH_2Cl_2 at rt was added 33 mL of water, and then under vigorous agitation 0.21 mL of Et_3N and 0.17 mL of *t*-$BuNH_2$ were added. Stirring was continued for 4 h, after which the organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give 0.35 g of *N*-(*tert*-butyl)-3-(phenylsulfonyl)-3-propenamine (9): IR (neat) 2980, 1450, 1310, 1140, 1085, 960, and 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.94 (s, 9 H), 3.30 (s, 2 H), 6.03 (s, 1 H), 6.35 (s, 1 H), 7.50–7.95 (m, 5 H); HMRS calcd for $C_{13}H_{19}NO_2S$ 253.1137, found 253.1130.

Reaction of 2,3-Bis(phenylsulfonyl)-1-propene (1) with Methylamine. To a solution containing 0.50 g (1.5 mmol) of 1 in 33 mL of CH_2Cl_2 at rt was added 33 mL of water, and then under vigorous agitation 0.21 mL of Et_3N and 0.15 mL of a 40% aqueous solution of methylamine were added. Stirring was continued for 4 h, after which the organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a colorless oil. This material was subjected to silica gel chromatography to give 150 mg (82%) of *N,N*-bis[2-(phenylsulfonyl)-2-propenyl]methylamine (10): IR (KBr) 2975, 2820, 1590, 1450, 1310, 1090, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.82 (s, 3 H), 3.04 (s, 4 H), 5.86 (s, 2 H), 6.37 (s, 2 H), and 7.40–7.95 (m, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 41.3, 55.6, 126.0, 128.1, 129.2, 133.6, 139.0, and 147.3. Anal. Calcd for $C_{19}H_{21}NO_4S_2$: C, 58.30; H, 5.41; N, 3.58. Found: C, 58.17; H, 5.24; N, 3.56.

Reaction of 2,3-Bis(phenylsulfonyl)-1-propene (1) with *N*-Benzylethanolamine. To a solution containing 0.30 g (1.0 mmol) of 1 in 20 mL of CH_2Cl_2 were added 20 mL of water, 0.14 mL of Et_3N, and 0.13 mL of *N*-benzylethanolamine. Stirring was continued overnight at rt, and then the organic layer was separated, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give 0.31 g (98%) of *N*-benzyl-*N*-[2-(phenylsulfonyl)-2-propenyl]ethanolamine (11) as a pale straw-colored oil: IR (neat) 3490, 3060, 2820, 1450, 1310, 1140, and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.50 (t, 2 H, J = 5.3 Hz), 2.83 (bs, 1 H), 3.28 (s, 2 H), 3.46 (s, 2 H), 3.50 (t, 2 H, J = 5.2 Hz), 6.06 (s, 1 H), 6.43 (s, 1 H), and 7.00–7.90 (m, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 53.1, 54.8, 58.0, 59.0, 96.0, 127.2, 128.0, 128.2, 128.9, 129.1, 133.4, 137.5, 138.8, and 147.8.

To a solution of 0.08 mL of PBr_3 in 5 mL of CH_2Cl_2 at 0 °C was added a solution of 0.43 g (93%) of alcohol 11 in 5 mL of CH_2Cl_2. The mixture was allowed to warm to rt and was stirred for 5 h and then treated with 5 mL of EtOH and stirrer for 15 min. The solvent was removed, and the residue was taken up in CH_2Cl_2 and washed with $NaHCO_3$ solution. Concentration of the organic layer afforded 0.48 g of *N*-(2-bromoethyl)-*N*-[2-(phenylsulfonyl)-2-propenyl]benzylamine (12): IR (neat) 3030, 2820, 1450, 1310, 1180, 1140, 1080, and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.72 (t, 2 H, J = 7.2 Hz), 3.17 (t, 2 H, J = 7.2 Hz), 3.32 (s, 2 H), 3.49 (s, 2 H), 6.27 (s, 1 H), 6.50 (s, 1 H), 7.05–7.35 (m, 5 H), and 7.50–7.95 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.8, 52.1, 54.6, 57.5, 125.6, 126.8, 127.5, 127.8, 128.0, 128.6, 132.9, 137.0, 138.5, and 147.4; HRMS calcd for $C_{18}H_{20}BrNO_2S$ 393.0398, found 393,0385.

To a solution containing 210 mg of 12 in 20 mL of refluxing benzene was added over a period of 1 h a benzene solution containing 0.22 mL of *n*-Bu_3SnH and a catalytic amount of AIBN. The mixture was allowed to reflux overnight, after which the solvent was removed under reduced pressure. The residue was taken up in CH_3CN and washed three times with hexane to remove the bulk of the tin salts. The CH_3CN portion was concentrated under reduced pressure and subjected to silica gel chromatography. The major fraction contained 140 mg (63%) of *N*-benzyl-3-(phenylsulfonyl)-1-azacyclohexane (13): IR (neat) 2950, 2810, 1450, 1310, 1150, 1090, and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.40–2.15 (m, 5 H), 2.14 (t, 1 H, J = 11.0 Hz), 2.77 (d, 1 H, J = 11.0 Hz), 3.19 (m, 2 H), 3.50 (m, 2 H), 7.10–7.35 (m, 5 H), and 7.50–7.95 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.3, 23.6, 51.6, 51.9, 61.0, 62.4, 126.6, 127.6, 128.2, 128.3, 128.5, 133.1, 136.8, and 136.9; HRMS calcd for $C_{18}H_{21}NO_2S$ 315.1293, found 315.1290.

Reaction of 2,3-Bis(phenylsulfonyl)-1-propene (1) with 2-Piperidinemethanol. To a solution containing 0.30 g (1.0 mmol) of 1 in 20 mL of CH_2Cl_2 were added 20 mL of water, 0.14 mL of Et_3N, and a solution containing 0.12 g of 2-piperidinemethanol in 2 mL of CH_2Cl_2. Stirring was continued overnight at rt, and then the organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to silica gel chromatography to give 0.21 g of *N*-[2-(phenylsulfonyl)-2-propenyl]-2-piperidinemethanol: IR (neat) 3500, 2920, 1440, 1300, 1130, 1070, 750, and 680 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.50–1.55 (m, 6 H), 1.70 (m, 1 H), 2.15 (m, 1 H), 2.40 (m, 1 H), 2.80 (d, 1 H, J = 14.5 Hz), 3.31 (dd, 1 H, J = 12.1, 2.7 Hz), 3.76 (dd, 1 H, J = 12.1, 3.5 Hz), 3.91 (d, 1 H, J = 14.5 Hz), 5.93 (s, 1 H), 6.37 (s, 1 H), and 7.30–7.95 (m, 5 H).

To a solution of 0.06 mL of $SOBr_2$ in 5 mL of CH_2Cl_2 at 0 °C was added over a period of 30 min a solution containing 0.20 g of the above alcohol in 15 mL of CH_2Cl_2. The mixture was stirred for an additional 30 min at 0 °C and then for 2 h at rt. Ethanol (15 mL) was added, and the reaction mixture was heated at reflux for 3–5 min to decompose to excess $SOBr_2$. Evaporation of the solvent left the hydrochloride salt which was taken up in CH_2Cl_2 and washed with $NaHCO_3$ solution. Concentration of the organic layer afforded 0.22 g of 2-(bromomethyl)-*N*-[2-(phenylsulfonyl)-2-propenyl]piperidine: IR (neat) 2930, 1444, 1301, 1137, and 749 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.05–1.65 (m, 6 H), 1.90 (m, 1 H), 2.35 (m, 1 H), 2.55 (m, 1 H), 3.07 (d, 1 H, J = 15.7), 3.25 (m, 2 H), 3.45 (d, 1 H, J = 15.7), 6.05 (s, 1 H), 6.41 (s, 1 H), and 7.40–7.95 (m, 5 H).

To a solution of 0.22 g of the above bromide in 20 mL of refluxing benzene was added over a period of 1 h a benzene solution containing 0.25 mL of *n*-Bu_3SnH and a catalytic amount of AIBN. The mixture was refluxed overnight, after which the solvent was removed under reduced pressure. The residue was taken up in CH_3CN and washed three times with hexane to remove the bulk of the tin salts. The CH_3CN portion was concentrated and subjected to silica gel chromatography to give 0.13 g of 3-(phenylsulfonyl)-octahydroquinolizine (14): IR (neat) 2926, 1446, 1304, 1147, and 749 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.10–1.85 (m, 10 H), 2.05–2.15 (m, 2 H), 2.18 (t, 1 H, J = 11.2 Hz), 2.73 (d, 1 H, J = 11.2 Hz), 2.97 (dt, 1 H, J = 11.0 and 2.6 Hz), 3.23 (tt, 1 H, J = 12.0 and 3.5 Hz), and 7.50–8.05 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.6, 24.1, 25.6, 31.7, 32.6, 54.1, 56.2, 61.2, 61.4, 128.6, 129.0, 133.6, and 137.4; HRMS calcd for $C_{15}H_{21}O_2NS$ 279.1293, found 279.1296.

Reaction of 2,3-Bis(phenylsulfonyl)-1-propene (15) with Furfurylamine. To a solution containing 0.5 g (1.5 mmol) of 1 in 33 mL of CH_2Cl_2 was added 33 mL of water, and then, with vigorous stirring, 0.21 mL of Et_3N and 0.15 mL of furfurylamine were added. Stirring was continued for 5 h at rt, and the mixture was diluted with 50 mL. The organic layer was dried over anhydrous Na_2SO_4. Evaporation of the solvent left a straw-colored oil which was subjected to silica gel chromatography to give 0.34 g of *N*-[2-(phenylsulfonyl)-2-propenyl]furfurylamine (15): IR (neat) 3370, 3080, 2840, 1450, 1305, 1140, 1085, and 755 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.74 (br s, 1 H), 3.36 (s, 2 H), 3.56 (s, 2 H), 5.95 (s, 1 H), 5.98 (d, 1 H, J = 2.3 Hz), 6.20 (m, 1 H), 6.40 (s, 1 H), and 7.40–7.95 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ

43.9, 46.4, 106.7, 109.5, 124.7, 127.5, 128.6, 133.0, 138.3, 141.3, 147.4, and 152.3

To a solution containing 0.20 g of **15** in 15 mL of CH_2Cl_2 at 0 °C was added 0.06 mL of acetyl chloride. The solution was allowed to warm to rt and was stirred for an additional 2 h. The reaction mixture was diluted with CH_2Cl_2, washed with water and then a saturated $NaHCO_3$ solution, and finally dried over Na_2SO_4. Evaporation of the solvent left 0.20 g (80%) of 2,3,6,7-tetrahydro-2-acetyl-7a-(phenylsulfonyl)-3a,6-epoxyisoindole (**16**): mp 130–131 °C; IR (KBr) 3040, 1650, 1440, 1310, 1155, 870, and 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.94 (s, 3 H), 2.25 (m, 2 H), 3.25 (d, 1 H, J = 13.9 Hz), 3.74 (d, 1 H, J = 11.5 Hz), 4.02 (d, 1 H, J = 11.5 Hz), 4.38 (d, 1 H, J = 13.9 Hz), 5.25 (m, 1 H), 6.65 (s, 2 H), and 7.50–7.95 (m, 5 H). Anal. Calcd for $C_{16}H_{17}NO_4S$: C, 60.17; H, 5.37; N, 4.39. Found: C, 60.04; H, 5.23; N, 4.08.

Reaction of 2,3-Bis(phenylsulfonyl)-1-propene (1) with Thiophenol. A solution containing 210 mg (0.67 mmol) of **1**, 0.02 mL of thiophenol, and 0.03 mL of Et_3N in 50 mL of absolute MeOH was stirred at 25 °C for 15 h. The reaction mixture was concentrated under reduced pressure, poured into a 10% hydrochloric acid solution, and extracted with $CHCl_3$. The $CHCl_3$ extracts were washed with a 10% NaOH solution and then with water. The organic layer was dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and subjected to silica gel chromatography. The first fraction isolated (63 mg, 25%) consisted of 2-(phenylsulfonyl)-3-(phenylthio)-1-propene (**18**): IR (neat) 3060, 2920, 1450, 1310, 1150, 750, and 695 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 3.80 (s, 2 H), 6.05 (s, 1 H), 6.50 (s, 1 H), and 7.00–8.15 (m, 10 H); m/z 290 (M^+), 149, 147, and 77; HRMS calcd for $C_{15}H_{14}O_2S_2$ 290.0432, found 290.0427.

The second fraction isolated (160 mg, 75%) contained 1,2-bis(phenylsulfonyl)-3-(phenylthio)-1-propane (**17**): mp 151–152 °C; IR (KBr) 3070, 2995, 1455, 1320, 1290, 1150, 750, and 695 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.43 (dd, 2 H, J = 5.7 and 2.8 Hz), 3.61 (dd, 1 H, J = 14.4 and 8.1 Hz), 3.74 (ddd, 1 H, J = 8.1, 5.7, and 2.8 Hz), 3.83 (dd, 1 H, J = 14.4 and 2.8 Hz), 7.18–7.26 (m, 5 H), 7.48–7.58 (m, 4 H), and 7.62–7.83 (m, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 33.3, 52.7, 58.8, 127.2, 127.9, 128.9, 128.0, 129.3, 130.8, 134.0, 134.3, and 137.1; m/z 432 (M^+), 149, and 77; HRMS calcd for $C_{21}H_{20}O_4S_3$ 432.0524, found 432.0496.

The above reaction was also carried out using an excess of thiophenol. A solution containing 218 mg (0.67 mmol) of **1**, 0.17 mL of thiophenol, and 0.24 mL of Et_3N in 25 mL of absolute MeOH was stirred at 25 °C for 15 h. The reaction mixture was concentrated under reduced pressure, poured into a 10% hydrochloric acid solution, and extracted with $CHCl_3$. The $CHCl_3$ extracts were washed with a 10% NaOH solution and then with water. The organic layer was dried over anhydrous $MgSO_4$ and was then concentrated under reduced pressure to leave behind a clear oil which crystallized on standing. Recrystallization using a $CHCl_3$–hexane mixture gave 1,3-bis(phenylthio)-2-(phenylsulfonyl)propane (**19**) in 90% yield: mp 111–112 °C; IR (KBr) 3080, 2995, 1450, 1315, 1295, 1145, 740, and 695 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.28–3.40 (m, 3 H), 3.57–3.65 (m, 2 H), 7.19–7.31 (m, 10 H), 7.62 (t, 2 H, J = 8.0 Hz), 7.74 (t, 1 H, J = 8.0 Hz), and 7.88 (d, 2 H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.9, 63.4, 127.0, 129.0, 129.1, 129.3, 130.2, 134.1, 134.4, and 137.6; m/z 400 (M^+), 149, 123, and 77. Anal. Calcd for $C_{21}H_{20}O_2S_3$: C, 62.96; H, 5.04; S, 24.01. Found: C, 62.91; H, 5.04; S, 24.11.

Base-Induced Ring Closure of *N*-Benzyl-*N*-[2-(phenylsulfonyl)-2-propenyl]ethanolamine (11). To a solution containing 1.1 equiv of NaOEt in 10 mL of EtOH was added 0.31 g of *N*-benzyl-*N*-[2-(phenylsulfonyl)-2-propenyl]ethanolamine (**11**). The solution was allowed to stir at rt for 2 h and then a saturated NH_4Cl solution was added. The solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2. Concentration of the mixture followed by silica gel chromatography of the residue gave 83% of 1-benzyl-6-(phenylsulfonyl)-1-aza-4-oxacycloheptane (**20**): IR (neat) 3070, 2940, 1445, 1305, 1145, 1085, and 740 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.50–2.75 (m, 2 H), 3.05–3.25 (m, 2 H), 3.50–3.85 (m, 5 H), 4.07 (dd, 1 H, J = 13.0, 6.3 Hz), 4.24 (dd, 1 H, J = 13.0, 7.1 Hz), 7.10–7.35 (m, 5 H), and 7.40–7.85 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 53.0, 57.5, 62.3, 65.1, 67.6, 72.5, 127.1, 128.2, 128.5, 128.6, 129.1, 133.7, 137.8, and 138.3; HRMS calcd for $C_{18}H_{21}NO_3S$ 331.1242, found 331.1239.

Reaction of 2,3-Bis(phenylsulfonyl)-1-propene (1) with *N*,*N*′-Dibenzylethylenediamine. To a solution containing 0.50 g of **1** in 20 mL of CH_2Cl_2 was added 20 mL of water, 0.14 mL of Et_3N, and 0.22 mL of dibenzylethylenediamine. Stirring was continued for 15 h. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give a straw-colored oil, which was subjected to silica gel chromatography. The major fraction contained 0.23 g (68%) of 1,4-dibenzyl-6-(phenylsulfonyl)-1,4-diazacycloheptane (**21**): IR (neat) 3060, 2940, 1450, 1310, 1150, 1090, and 710 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.45–2.70 (m, 4 H), 3.05–3.25 (m, 4 H), 3.40–3.55 (m, 1 H), 3.55–3.75 (m, 4 H), 7.15–7.30 (m, 10 H), and 7.35–7.85 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.9, 55.6, 62.2, 64.0, 127.0, 128.2, 128.3, 128.5, 129.0, 133.5, 138.0, and 138.6. Anal. Calcd for $C_{25}H_{28}N_2O_2S$: C, 71.40; H, 6.71; N, 6.66. Found: C, 71.12; H, 6.75; N, 6.49.

Reaction of 2,3-Bis(phenylsulfonyl)-1-propene (1) with Ethanedithiol. To a solution containing 0.3 g (1.0 mmol) of **1** in 15 mL of MeOH were added 0.26 mL of ethanedithiol and 0.14 mL of Et_3N. The solution was allowed to stir for 24 h, after which the MeOH was removed under reduced pressure. The residue was extracted with CH_2Cl_2, washed with $NaHCO_3$ solution, and dried over Na_2SO_4. Concentration of the organic phase afforded a 92% yield of 6-(phenylsulfonyl)-1,4-dithiacycloheptane (**22**): mp 82–83 °C; IR (KBr) 3065, 2915, 1450, 1415, 1310, 1290, 1150, and 735 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.84–2.89 (m, 4 H), 3.26 (dd, 2 H, J = 15.3 and 6.1 Hz), 3.40 (dd, 2 H, J = 15.3 and 6.1 Hz), 3.52 (quintet, 1 H, J = 6.1 Hz), and 7.50–7.95 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.0, 38.0, 66.3, 128.5, 128.8, 133.6, and 136.5. Anal. Calcd for $C_{11}H_{14}O_2S_3$: C, 48.15; H, 5.14. Found: C, 48.26; H, 5.12.

Reaction of 2,3-Bis(phenylsulfonyl)-1-propene (1) with Bis(phenylsulfonyl)methane. To a solution containing 200 mg of bis(phenylsulfonyl)methane in 10 mL of THF at 0 °C under a N_2 atmosphere was added 0.8 mmol of *n*-butyllithium in hexane dropwise via syringe. The resulting yellow solution was stirred for 30 min at 0 °C, and then a solution containing 216 mg (0.67 mmol) of **1** in 2 mL of THF was added rapidly. The resulting solution was allowed to warm to rt. After being stirred for 1 h, the reaction mixture was poured into water and extracted with CH_2Cl_2. The organic extracts were washed successively with water and then saturated NaCl. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give 2,4,4-tris(phenylsulfony)-1-butene (**23**) in 81% yield: mp 133–134 °C; IR (KBr) 3060, 2940, 1335, 1310, 1160, 1150, and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.21 (d, 2 H, J = 6.0 Hz), 5.57 (t, 1 H, J = 6.0 Hz), 6.07 (s, 1 H), 6.49 (s, 1 H), 7.54 (t, 6 H, J = 7.7 Hz), 7.63–7.71 (m, 3 H), and 7.77–7.86 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.6, 80.1, 128.4, 129.2, 129.4, 131.0, 134.0, 134.6, 137.7, 138.2, and 143.2. Anal. Calcd for $C_{22}H_{20}O_6S_3$: C, 55.44; H, 4.23; S, 20.18. Found: C, 55.47; H, 4.26, 4.26; S, 20.22.

Reaction of 2,3-Bis(phenylsulfonyl)-1-propene (1) with 2,4-Pentanedione. To a solution containing 0.19 g (0.6 mmol) of **1** and 0.07 mL of 2,4-pentanedione in 5.0 mL of absolute MeOH at rt was added 1.4 mL of 0.5 N methanolic NaOMe. The mixture was allowed to stir at rt for 12 h and was then quenched with a saturated NH_4Cl solution. The MeOH was removed and the residue was extracted with CH_2Cl_2 and washed with water. Concentration of the organic layer was followed by silica gel chromatography to give 185 mg (78%) of 5-(phenylsulfonyl)-5-hexen-2-one (**25**): IR (neat) 3068, 2912, 1716, 1446, 1304, 1126, and 741 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.06 (s, 3 H), 2.45 (t, 2 H, J = 7.5 Hz), 2.67 (t, 2 H, J = 7.5 Hz), 5.72 (s, 1 H), 6.32 (s, 1 H), and 7.40–7.95 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$), δ 23.6, 29.7, 41.4, 124.5, 128.1, 129.1, 133.5, 138.4, 149.1, and 206.2.

To a solution containing 90 mg of **25** in 20 mL of benzene was added a catalytic amount of pyrrolidine. This mixture was refluxed overnight, after which the solvent was removed under reduced pressure. The residue was taken up in CH_2Cl_2 and washed first with 10% hydrochloric acid, then a saturated $NaHCO_3$ solution, and finally with water. Drying of the organic solution over Na_2SO_4, followed by concentration, left a yellow oil which was subjected to silica gel chromatography. The major fraction contained 80 mg (90%) of 4-(phenylsulfonyl)cyclohexanone (**26**), with properties in agreement to those reported in the literature.[35]

Reaction of 2,3-Bis(phenylsulfonyl)-1-propene (1) with 1-Pyrrolidino-1-cyclohexene. A solution containing 0.5 g of

1 and 0.24 g of 1-pyrrolidino-1-cyclohexene in 5 mL of absolute EtOH was heated at reflux for 18 h. Acidic workup of the solution followed by crystallization of the residue from $CHCl_3$–hexane afforded a 78% yield of 3-(phenylsulfonyl)bicyclo[3.3.1]nonan-9-one (**28**): mp 140–141 °C; IR (KBr) 2960, 1725, 1450, 1310, 1275, and 1145 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.50–1.75 (m, 1 H), 1.80–2.07 (m, 1 H), 2.09–2.25 (m, 4 H), 2.25–2.48 (m, 4 H), 2.49 (br s, 2 H), 4.05–4.25 (m, 1 H), and 7.50–8.05 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.3, 32.1, 33.4, 44.2, 57.5, 128.5, 128.7, 133.5, 135.9, and 216.6. Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52. Found: C, 64.63; H, 6.58.

To a solution containing 0.21 g of **28** in 5 mL of CH_2Cl_2 was added 0.28 g of 85% MCPBA. The reaction mixture was kept in the dark and swirled at intervals. After 3 h the mixture was washed with a 5% sodium thiosulfate–$NaHCO_3$ solution and dried over Na_2SO_4. Removal of the solvent under reduced pressure left 0.22 g of 3-(phenylsulfonyl)-9-oxobicyclo[3.3.2]decan-10-one (**29**): mp 162–163 °C; IR (KBr) 2950, 1725, 1280, 1180, 1145, and 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.45–2.55 (m, 10 H), 3.25 (m, 1 H), 3.73 (tt, 1 H, J = 13.1 and 4.1 Hz), 4.72 (m, 1 H), and 7.50–7.95 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 23.8, 26.8, 28.1, 32.4, 41.7, 58.2, 72.4, 128.7, 128.8, 133.7, and 135.2. Anal. Calcd for $C_{15}H_{18}O_4S$: C, 61.21; H, 6.16. Found: C, 61.06; H, 6.24.

A mixture containing 0.5 g of **28**, 0.5 g of hydroxylamine hydrochloride, 2.5 mL of pyridine, and 2.5 mL of absolute EtOH was heated at reflux for 2 h. The solvent was removed under reduced pressure, and the residue was thoroughly triturated with 5 mL of cold water. The solid was isolated by suction filtration and dried to give 3-(phenylsulfonyl)bicyclo[3.3.1]nonan-9-one oxime (87%): mp 186–187 °C; IR (KBr) 3440, 3280, 2930, 1445, 1305, 1140, 945, and 730 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.50–2.25 (m, 10 H), 2.62 (br s, 1 H), 3.62 (br s, 1 H), 3.94 (tt, 1 H, J = 12.4, 6.2), 7.55–7.95 (m, 5 H), and 8.20 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.8, 26.9, 30.0, 30.6, 31.3, 32.2, 34.5, 58.5, 128.4, 128.6, 133.3, 136.2, and 162.8.

A solution containing 0.15 g of the above oxime and 0.34 g of polyphosphate ester (PPE) in 2 mL of $CHCl_3$ was heated at reflux for 5 min. After the mixture was cooled to rt, 1 mL of water was added and the resulting mixture was stirred overnight in order to decompose the excess PPE. The mixture was diluted with $CHCl_3$, washed with water, and dried. Evaporation of the solvent provided an 85% yield of 3-(phenylsulfonyl)-9-azabicyclo-[3.3.2]decan-10-one (**30**) as a white solid: mp 240–241 °C; IR (KBr) 3210, 2950, 1660, 1310, 1140, and 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.25–2.45 (m, 10 H), 2.93 (t, 1 H, J = 7.3 Hz), 3.50–3.75 (m, 2 H), 6.70 (d, 1 H, J = 7.3 Hz), and 7.55–7.95 (m, 5 H). Anal. Calcd for $C_{15}H_{19}NO_3S$: C, 61.41; H, 6.53. Found: C, 61.37; H, 6.55.

Typical Procedure for Radical Additions. Method A. Addition of the Barton Intermediate to 2,3-Bis(phenylsulfonyl)-1-propene (1). To a refluxing suspension containing 1.2 mmol of dry sodium pyrithione and 0.1 mmol of 2-(dimethylamino)pyridine in 10 mL of benzene was added a solution containing 1 mmol of the appropriate acid chloride in 5 mL of benzene. The reaction vessel was covered with foil, and the solution was heated at reflux for 15 min. After removal of the solvent under reduced pressure, the residue was chromatographed on a short silica gel column using CH_2Cl_2 as the eluent. The filtrate was concentrated to a volume of 0.5 mL and was then transferred to a test tube containing 0.33 g of bissulfone 1. With efficient stirring, the bright yellow solution was irradiated with a 250-W tungsten lamp until the yellow color disappeared. Standard chromatographic workup afforded the alkylated sulfone.

Method B. Addition of Alkyl Bromides to 2,3-Bis(phenylsulfonyl)-1-propene (1) Using Tributyltin Hydride. To a solution containing 1 mmol of 1 and 1.2 mmol of the appropriate alkyl bromide in 10 mL of refluxing benzene was added a solution of 1.5 mmol of n-Bu_3SnH and 0.1 mmol of AIBN in 5 mL of benzene over an 18-h period. After removal of the solvent under reduced pressure, the residue was freed from most of the tin impurities by partitioning it between CH_3CN and hexane. The CH_3CN layer was concentrated under reduced pressure to give the crude product which was purified in the standard manner.

4-Cyclopentyl-2-(phenylsulfonyl)-1-butene (32). Sulfone **32** was obtained in 85% yield according to method A: IR (neat) 3080, 2980, 1145, 1085, and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.95 (m, 2 H), 1.30–1.75 (m, 9 H), 2.16 (t, 2 H, J = 7.9 Hz), 5.66 (s, 1 H), 6.29 (s, 1 H), and 7.50–7.95 (m, 5 H); HRMS calcd for $C_{15}H_{20}O_2S$ 264.1184, found 264.1182.

3-Cyclohexyl-2-(phenylsulfonyl)-1-propene (33). Sulfone **33** was obtained in 90% yield according to method A: IR (neat) 2930, 2880, 1450, 1310, 1150, 1090, and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.80–1.75 (m, 11 H), 2.08 (d, 2 H, J = 7.2 Hz), 5.68 (s, 1 H), 6.38 (s, 1 H), and 7.40–7.95 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.3, 25.6, 32.1, 35.1, 36.7, 123.8, 127.6, 128.5, 132.4, 148.1; HRMS calcd for $C_{15}H_{20}O_2S$ 264.1184, found 264.1179.

3-Cyclohexyl-2-(phenylsulfonyl)-1-propene (**33**) was also prepared by method B in 53% yield.

4,4-Dimethyl-2-(phenylsulfonyl)-1-pentene (34). Sulfone **34** was obtained in 80% yield according to method A: IR (neat) 2970, 1450, 1305, 1150, and 755 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.88 (s, 9 H), 2.17 (s, 2 H), 5.84 (s, 1 H), 6.43 (s, 1 H), and 7.40–7.95 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.0, 31.2, 40.9, 125.9, 127.7, 128.5, 132.7, 138.7, 148.2; HRMS calcd for $C_{13}H_{18}O_2S$ 238.1028, found 238.1025.

4-Methyl-2-(phenylsulfonyl)-1,4-hexadiene (35). Sulfone **35** was obtained in 83% yield as a mixture of isomers according to method B: IR (neat) 2920, 1450, 1310, 1170, 1130, 1090, 750, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) (major) δ 1.31 (s, 3 H), 1.48 (d, 3 H, J = 6.8 Hz), 2.90 (s, 2 H), 5.22 (q, 1 H, J = 6.8 Hz), 5.69 (s, 1 H), 6.40 (s, 1 H), and 7.40–7.95 (m, 5 H); (minor) δ 1.38 (d, 3 H, J = 6.7 Hz), 1.46 (s, 3 H), 2.90 (s, 2 H), 5.38 (q, 1 H, J = 6.7 Hz), 5.63 (s, 1 H), 6.36 (s, 1 H), and 7.40–7.95 (m, 5 H); HRMS calcd for $C_{13}H_1{}^6O_2S$ 236.0871, found 236.0869.

Cyclohexyl Phenyl Sulfone (38). Sulfone **37** was obtained in 88% yield according to method A: IR (neat) 2950, 1456, 1310, 1145, 1085, 750, and 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.50–1.85 (m, 4 H), 2.18 (t, 2 H, J = 7.5 Hz), 3.25 (t, 2 H, J = 6.6 Hz), 5.68 (s, 1 H), 6.30 (s, 1 H), and 7.40–7.95 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.4, 27.7, 31.0, 32.4, 122.9, 127.6, 128.6, 132.9, 138.1, 149.3.

To a solution containing 0.082 g of bromo sulfone **37** in 20 mL of refluxing benzene was added a solution containing 1.5 g (1.5 equiv) of n-Bu_3SnH and 10 mg of AIBN in 5 mL of benzene over an 18-h period. Workup as described above gave cyclohexyl phenyl sulfone (**38**) in 82% yield, which was identical with an authentic sample:[55] mp 70–71 °C; IR (KBr) 2930, 2860, 1450, 1305, 1290, 1230, 1150, 1090, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.05–2.15 (m, 22 H), 2.88 (tt, 1 H, J = 12.0, 3.4 Hz), and 7.40–7.95 (m, 5 H).

Cyclohexyl phenyl sulfone (**38**) could also be prepared by a one-pot method: To a solution containing 1 mmol of 1 and 1.2 mmol of 1,3-dibromopropane in 10 mL of refluxing benzene was added a solution of 3.0 mmol of n-Bu_3SnH and 0.1 mmol of AIBN in 5 mL of benzene over an 18-h period. After removal of the solvent under reduced pressure, the residue was freed from most of the tin impurities by partitioning between CH_3CN and hexane. The CH_3CN layer was concentrated under reduced pressure to give the desired product in 48% yield.

Preparation and Radical Cyclization of 2-[3-(Phenylsulfonyl)-3-butenyl]-1-bromobenzene (39). Sulfone **39** was obtained in 78% yield according to method B: mp 78–79 °C; IR (neat) 3070, 2950, 1450, 1310, 1160, 1140, and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.53 (t, 2 H, J = 7.9 Hz), 2.89 (t, 2 H, J = 7.9 Hz), 5.71 (s, 1 H), 6.40 (s, 1 H), 7.05–7.35 (m, 3 H), 7.40–7.75 (m, 4 H), and 7.88 (d, 2 H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.7, 34.0, 123.6, 123.7, 126.9, 127.6, 127.7, 128.6, 129.9, 132.3, 132.9, 138.1, 138.6, 148.6.

To a solution containing 0.18 g of **39** in 25 mL of refluxing benzene was added over a period of 1 h a benzene solution containing 0.21 mL of n-Bu_3SnH and a catalytic amount of AIBN. The mixture was allowed to reflux overnight, after which the solvent was removed under reduced pressure. The residue was taken up in CH_3CN and washed three times with hexane to remove the bulk of the tin salts. The CH_3CN portion was concentrated under reduced pressure and subjected to silica gel chromatography. The major fraction (88%) was identified as 2-(phenylsulfonyl)-1,2,3,4-tetrahydronaphthalene (**40**) which exhibited properties consistent with those found in the literature.[56]

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Registry No. 1, 2525-55-5; 3, 137091-70-4; 4, 137059-18-8; 5, 137059-19-9; 6, 137091-71-5; 7, 15515-75-0; 8, 137059-20-2; 9, 137059-21-3; 10, 137059-22-4; 11, 137059-23-5; 12, 137059-24-6; 13, 137059-25-7; 14, 137059-26-8; 15, 137059-27-9; 16, 137059-28-0; 17, 137059-29-1; 18, 137059-30-4; 19, 137059-31-5; 20, 137059-32-6; 21, 137059-33-7; 22, 137059-34-8; 23, 112841-18-6; 25, 137059-35-9; 26, 34259-63-7; 28, 137059-36-0; 29, 137059-37-1; 30, 137059-38-2; 32, 137059-39-3; 33, 129855-21-6; 34, 129855-24-9; 35, 129855-25-0; 36, 137059-40-6; 37, 129855-23-8; 38, 6947-57-5; 39, 129855-22-7; 40, 137059-41-7; $PhNH_2$, 62-53-3; $PhCH_2NH_2$, 100-46-9; *t*-$BuNH_2$, 75-64-9; $MeNH_2$, 74-89-5; $PhCH_2NH(CH_2)_2OH$, 104-63-2; PhSH, 108-98-5; *t*-BuCOCl, 3282-30-2; $Br(CH_3)C{=}CHCH_3$, 13294-71-8; $ClCO(CH_2)_3Br$, 927-58-2; BrC_6H_4-*o*-CH_2Br, 3433-80-5; $Br(CH_2)_3Br$, 109-64-8; 3-(phenylsulfonyl)-2-(phenylthio)-1-propene, 2525-54-4; 2-piperidinemethanol, 3433-37-2; *N*-[2-(phenylsulfonyl)-2-propenyl]-2-piperidinemethanol, 137059-42-8; 2-(bromomethyl)-*N*-[2-(phenylsulfonyl)-2-propenyl]piperidine, 137059-43-9; furfurylamine, 617-89-0; dibenzylethylenediamine, 140-28-3; ethanedithiol, 540-63-6; bis(phenylsulfonyl)methane, 3406-02-8; 2,4-pentanedione, 626-96-0; 1-pyrrolidino-1-cyclohexene, 1125-99-1; 3-(phenylsulfonyl)bicyclo[3.3.1]nonan-9-one oxime, 137059-36-0; sodium pyrithione, 15922-78-8; cyclopentaneacetyl chloride, 1122-99-2; cyclohexanecarbonyl chloride, 2719-27-9; cyclohexyl bromide, 108-85-0.

Supplementary Material Available: ^1H NMR and ^{13}C NMR spectra (75 MHz) for all compounds with high resolution mass spectra (13 pages). Ordering information is given on any current masthead page.

Reinvestigation on the Reaction of 2,6-Di-*tert*-butylbenzoquinone Methide and 2,6-Di-*tert*-butylphenol

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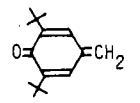
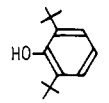
The reaction of quinone methide 1 and phenol 2 in equimolar amounts was investigated in pentane at 30 °C. Products were isolated by means of column chromatography on SiO_2. There was a marked difference in product distribution between the reactions in the presence and absence of added Et_3N. Dienones 3 and 10 were obtained only from the former reaction, while formation of 1,2-bis(4-hydroxyphenyl)ethane 18 and 4,4'-dihydroxybiphenyl 20 was overwhelming in the latter reaction. Other products from both reactions were relatively small quantities of 4,4'-stilbenequinone 17, 4,4'-diphenoquinone 21, and bis(4-hydroxyphenyl)methane 24, but dienone 4 was not obtained. Compounds 20 and 24 obtained from the latter reaction were formed by isomerization of dienones 19 and 23, respectively, during the chromatography. The reaction is initiated by dimerization of 1 to generate biradical 11. Subsequent processes involving hydrogenation–dehydrogenation, coupling–dissociation, and dienone–phenol rearrangement account for the formation or the lack of formation of the products. The difference in product distribution is ascribed to capability of Et_3N to catalyze the isomerization. Quinone methide 1 also adds to 2 to give 23. The decay of 1 in the presence of both 2 and phenol 6 gave dienone 8 additionally. The formation of 24 and 4 was facilitated by conducting the reaction of 1 and 2 in DMSO. Dehydrogenation of 10 and 3 with PbO_2 afforded spirodienones 27 and 28, respectively. Compounds 27 and 28 were unstable, and their decay in solution was investigated in the presence or absence of added 2. The results show that the decay is initiated by homolytic scission of the C–C bond connecting the dienone rings in the cyclopentane (in 27) and cyclohexane (in 28) rings. Compound 28 is novel in that it bears two kinds of such C–C bonds. Reversibility of the dimerization of 1 is suggested.

2,6-Di-*tert*-butylbenzoquinone methide (1) is a reactive species which can exist only in dilute solution, and its reactions have been investigated in considerable detail, partly in connection with the antioxidant activity of 2,6-di-*tert*-butyl-4-methylphenol (6).[1] Neureiter[2] studied the decay of 1 in the presence of 2,6-di-*tert*-butylphenol (2) in petroleum ether under various conditions and obtained bis-dienone 3 in generally low yields. Later, Chaser and Westfahl[3] conducted a similar reaction, but in the presence of base such as dimsyl anion or Et_3N, and isolated dienone 4.



1



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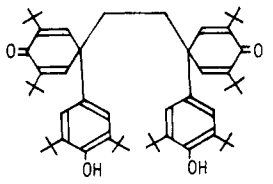

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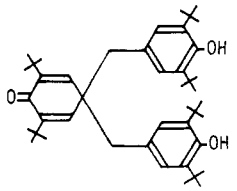

4

Recently, it has been suggested by a ^1H NMR study that addition of 2 to a solution containing 1 generated by disproportionation of phenoxy radical 5 slowly affords, in the presence of a base, dienone 8 among other products.[4] This

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