Diels–Alder Reactions of *S*-Vinyl-*S*-Arylsulfoximines

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Received September 6, 1983

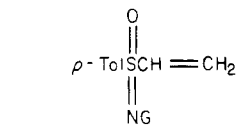
Cyclopentadiene and the known *S*-*p*-tolyl-*S*-vinyl-*N*-phthalimidosulfoximine (**1a**) undergo Diels–Alder reaction to give a mixture of cycloadducts in excellent yield. The structures of the cycloadducts including stereochemistry are assigned by ^{1}H NMR spectroscopy. The crystal and molecular structure of the major cycloadduct **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$ was determined unequivocally by X-ray crystallographic techniques. Treatment of this major cycloadduct with hydrazine in ethanol resulted in conversion of the sulfoximine to sulfoxide group concomitant with reduction of the carbon–carbon double bond. Use of allyl alcohol as solvent in this reaction allowed conversion to the corresponding unsaturated sulfoxide **8**. The previously unknown *S*-*p*-tolyl-*S*-vinyl-*N*-(*p*-tolylsulfonyl)-sulfoximine (**1b**) is somewhat more reactive than phenyl vinyl sulfone and undergoes Diels–Alder reactions with cyclic and acyclic 1,3-dienes in 81–95% yield. The endo selectivity of vinylsulfoximine **1b** is 9:2 with cyclopentadiene and 93:7 with 1,3-cyclohexadiene. With 2-methyl-1,3-butadiene the para adduct is produced regioselectively in a ratio of 4:1. Although formation of the endo adducts from vinylsulfoximine **1b** and cyclopentadiene and 1,3-cyclohexadiene is not diastereoselective, the diastereomers can be separated by HPLC. The cycloadducts from 1,3-cyclohexadiene and vinylsulfoximine **1b** have been converted to bicyclo[2.2.2]oct-2-ene and bicyclo-[2.2.2]oct-2-en-5-one.

Recently, Diels–Alder reactions of phenyl vinyl sulfoxide[1] and phenyl vinyl sulfone[2] have been exploited in organic synthesis. Cycloaddition of phenyl vinyl sulfoxide and thermal elimination under the conditions of the reaction render this dienophile a valuable synthetic equivalent of acetylene. Ethynyl *p*-tolyl sulfone,[3] 1-(phenylsulfonyl)-2-(trimethylsilyl)ethylene,[4] and 1,2-bis(phenylsulfonyl)ethylene[5] also are acetylene equivalents in Diels–Alder reactions and are more reactive than phenyl vinyl sulfoxide. The >$CHSO_2Ph$ moiety in the Diels–Alder adducts of phenyl vinyl sulfone has been transformed into >CH_2, >CHR, or >C=O groups.[2,6] This renders phenyl vinyl sulfone the synthetic equivalent of alkenes or ketene.

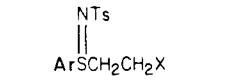
This paper reports the preparation of *S*-aryl-*S*-vinyl-*N*-(*p*-tolylsulfonyl)sulfoximines and their Diels–Alder reactions as well as those of *S*-*p*-tolyl-*S*-vinyl-*N*-phthalimidosulfoximine. Such reactions are complementary to those of phenyl vinyl sulfoxide and sulfone. Several unique and useful transformations of the N-(*p*-tolylsulfonyl)-sulfoximine moiety into other functional groups have been reported.[7] As examples, the α-anion derived from *S*,*S*-dialkyl- and *S*-alkyl-*S*-aryl-*N*-(*p*-tolylsulfonyl)sulfoximines reacts with aldehydes or ketones, α,β-unsaturated ketones or esters, and N-substituted amines to afford epoxides, cyclopropanes, and aziridines, respectively, and with epoxides to yield oxetanes. Arylvinylsulfoximines, unlike aryl vinyl sulfones, are chiral and may induce asymmetry in Diels–Alder reactions.

Results and Discussion

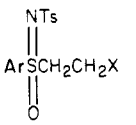
Both racemic and optically pure *S*-*p*-tolyl-*S*-vinyl-*N*-phthalimidosulfoximine (**1a**) were prepared by the method of Colonna and Stirling.[8] The previously unknown racemic *S*-*p*-tolyl-*S*-vinyl-*N*-(*p*-tolylsulfonyl)sulfoximine (**1b**)



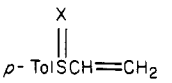
1a, G = 1,2-$C_6H_4(CO)_2N$
b, G = Ts



2a, X = Cl, Ar = *p*-Tol
b, X = OAc, Ar = Ph



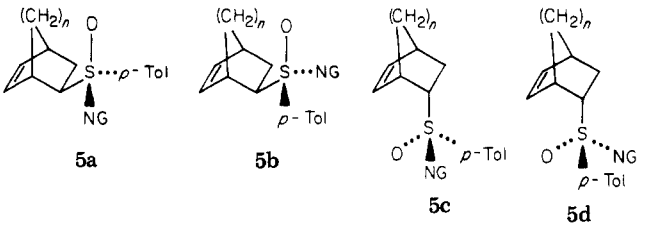
3a, X = Cl, Ar = *p*-Tol
b, X = OAc, Ar = Ph



4a, X = O
b, X = NTs

was prepared by oxidation of sulfilimine **2a**[8] with ruthenium tetroxide[9] to sulfoximine **3a** in 78% yield followed by dehydrochlorination with triethylamine to give **1b** quantitatively. *S*-Phenyl-*S*-vinyl-*N*-(*p*-tolylsulfonyl)sulfoximine is similarly prepared from *S*-(2-chloroethyl)-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfilimine. Ruthenium tetroxide oxidation of sulfilimine **2b** gave sulfoximine **3b**, but it could not be converted to the corresponding vinylsulfoximine.[8,10]

The Diels–Alder reaction of sulfoximine **1a** and cyclopentadiene produced a mixture of four cycloadducts in 95% yield. The first and last products in order of their HPLC elution times were well separated from the other products, but the second and third compounds were not resolvable from each other. The ratio of products (1:(2 + 3):4) was approximately 1:4:4. The major product from the reaction of (*S*)-**1a** and cyclopentadiene was secured pure by column chromatography on silica gel followed by recrystallization. Its structure has been unequivocally established by single-crystal X-ray analysis to be **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$. A stereoscopic view of the



5a **5b** **5c** **5d**

(1) Paquette, L. A.; Moerck, R. E.; Harirchian, B.; Magnus, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 1597.
(2) Carr, R. V. C.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 853.
(3) Davis, A. P.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1980**, 639.
(4) Paquette, L. A.; Williams, R. V. *Tetrahedron Lett.* **1981**, *22*, 4643.
(5) DeLucchi, O.; Modena, G. *J. Chem. Soc., Chem. Commun.* **1982**, 914.
(6) Little, R. D.; Myong, S. O. *Tetrahedron Lett.* **1980**, 3339.
(7) Johnson, C. R. *Acc. Chem. Res.* **1973**, *6*, 341. Huang, S. L.; Swern, D. *Phosphorus Sulfur* **1976**, *1*, 309. Kennewell, P. D.; Taylor, J. B. *Chem. Soc. Rev.* **1975**, *4*, 189. Kennewell, P. D.; Taylor, J. B. *Ibid.* **1980**, *9*, 477. Welch, S. C.; Prakasa Rao, A. S. C.; Lyon, J. T.; Assercq, J.-M. *J. Am. Chem. Soc.* **1983**, *105*, 252.
(8) Colonna, S.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2120.
(9) Veale, H. S.; Levin, J.; Swern, D. *Tetrahedron Lett.* **1978**, 503.
(10) Yamamoto, T.; Kakimoto, M.; Okawara, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 84.

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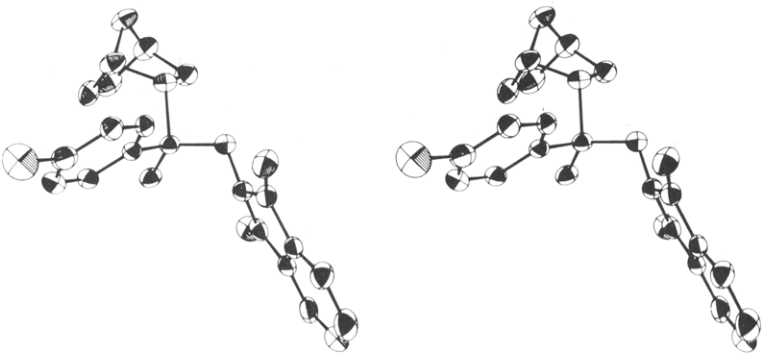


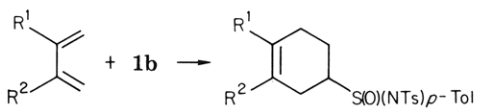
Figure 1. ORTEP[17] stereoview of **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$. The hydrogen atoms were assigned arbitrary thermal parameters. Thermal ellipsoids were drawn to enclose 30% of the probability distribution.

Table I. Selected NMR Spectroscopic Parameters Used in Stereochemical Assignments of Cycloadducts from 1b

cycloadduct	δH(2), ppm	$J_{1,2}$, Hz	δH(1), ppm
5a, n = 1, G = 1,2-$C_6H_4(CO)_2N$	3.44	1.3	3.93
b, n = 1, G = 1,2-$C_6H_4(CO)_2N$	3.34	1.3	2.78
c, n = 1, G = 1,2-$C_6H_4(CO)_2N$	4.14	3.1	3.81
d, n = 1, G = 1,2-$C_6H_4(CO)_2N$	4.16	3.5	2.67
5a, n = 1, G = Ts	3.21	1.1	3.53
b, n = 1, G = Ts	3.14	1.3	2.83
c, n = 1, G = Ts	3.93	3.2	3.56
d, n = 1, G = Ts	3.96	3.1	2.69
5c, n = 2, G = Ts	3.77		3.33
5d, n = 2, G = Ts	2.73		2.73

molecule is shown in Figure 1. The structures of the other adducts were assigned by ^{1}H NMR spectroscopy. The assignments at C(2) are based on the characteristic differences in chemical shift and coupling between exo and endo hydrogen atoms in 2-substituted bicyclo[2.2.1]-hept-5-enes[11] (Table I). The assignments of relative configurations for each exo and endo adduct is deduced from the chemical shift of H(1). As seen in Table I, H(1) resonates at higher field in exo adduct **5a**, n = 1, G = 1,2-$C_6H_4(CO)_2N$, and endo adduct **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$, than in their corresponding diastereomers **5b** and **5c**, n = 1, G = 1,2-$C_6H_4(CO)_2N$, respectively. Analysis using molecular models and the X-ray structure for **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$, suggested that the aromatic ring current of the p-tolyl group in **5a** and **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$, shields H(1).

Cycloaddition of vinylsulfoximine **1b** with acyclic and cyclic 1,3-dienes produced cycloadducts, as a mixture of



6a, $R^1 = R^2$ = H
b, R^1 = Me, R^2 = H
c, R^1 = H, R^2 = Me
d, $R^1 = R^2$ = Me

isomers, in 81–95% yield (Table II). The mixture of adducts obtained from vinylsulfoximine **1b** and cyclopentadiene could be separated into three fractions in a ratio of 2:4:5 by HPLC. The fractions, after separation, were analyzed by ^{1}H NMR spectroscopy. The first fraction was a 5:6 mixture of exo diastereomers **5a** and **5b**, n = 1, G = Ts, respectively. The second fraction was endo isomer **5c**, n = 1, G = Ts, and the third fraction was endo isomer **5d**, n = 1, G = Ts. The stereochemistry of the cycloadducts was assigned as before (Table I). Thus, the endo

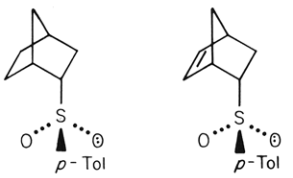
Table II. Diels–Alder Reactions of Vinylsulfoximine 1b with 1,3-Dienes

diene	product	yield, %
cyclopentadiene	**5**, n = 1, G = Ts	81[a]
1,3-butadiene	**6a**	90
2-methyl-1,3-butadiene	**6b**	95
2,3-dimethyl-1,3-butadiene	**6d**	95[b]
1,3-cyclohexadiene	**5**, n = 2, G = Ts	95[c]

[a] The ratio of isomers **5a**:**5b**:**5c**:**5d**, n = 1, G = Ts, was 1:1:4:5. [b] The ratio of regioisomers **6b**:**6c** was 4:1. [c] The exo:endo ratio was 7:93. The ratio of **5c**:**5d**, n = 2, G = Ts, was 4:5.

selectivity in this reaction is 9:2, but there is little diastereoselectivity in the formation of either the endo or exo adducts.

Further support for the structural assignment of **5d**, n = 1, G = Ts, was obtained by stereospecific conversion of this material and **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$ (whose structure has been unambiguously established by X-ray methods), to the identical sulfoxide **7**. Catalytic hydro-



7 **8**

genation of **5d**, n = 1, G = Ts, was followed by hydrolysis of the =NTs group to =NH with sulfuric acid. Treatment of this material with nitrous acid produces sulfoxide **7** in 32% overall yield; retention of configuration at sulfur[12] was presumed. On exposure to hydrazine in ethanol, **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$, afforded saturated sulfoxide **7** (retention of configuration at sulfur[8] presumed) in 81% yield, identical with that produced from **5d**, n = 1, G = Ts. Treatment of **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$, with hydrazine in ethanol in the presence of excess cyclohexene yielded a mixture of sulfoxides **7** and **8**. Unsaturated sulfoxide **8** was produced exclusively in 93% yield on treatment of **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$, with hydrazine in allyl alcohol. Sulfoxide **8** could not be obtained in good yield by the reaction of cyclopentadiene with p-tolyl vinyl sulfoxide due to sulfenic acid elimination concomitant with its formation.

The Diels–Alder reactions of vinylsulfoximine **1b** and 1,3-butadiene and 2,3-dimethyl-1,3-butadiene afford the corresponding cycloadducts **6a** and **6d**. Catalytic hydro-

(11) Davis, J. C.; VanAuken, T. V. *J. Am. Chem. Soc.* **1965**, *87*, 3900.

(12) Williams, T. R.; Nudelman, A.; Booms, R. E.; Cram, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 4684.

genation of cycloadduct **6a** provides *S*-cyclohexyl-*S*-*p*-tolyl-*N*-(*p*-tolylsulfonyl)sulfoximine in 81% yield. This product is identical with that produced by a two-step sequence from the known cyclohexyl *p*-tolyl sulfide. Treatment of this sulfide with Chloramine-T (*N*-chloro-*p*-tolylsulfonamide sodium salt) produced the corresponding N-*p*-tolylsulfilimine in 82% yield, which on two-phase oxidation with ruthenium tetroxide gave *S*-cyclohexyl-*S*-*p*-tolyl-*N*-(*p*-tolylsulfonyl)sulfoximine in 73% yield.

Cycloaddition of vinylsulfoximine **1b** and 2-methyl-1,3-butadiene provides a mixture of adducts **6b** and **6c**. The isomers could not be separated by HPLC under the conditions studied. However, ^{13}C NMR spectroscopic analysis suggested that the regioisomers were formed in a ratio of approximately 4:1. To unequivocally establish the structure of the major regioisomer, the cyclohexenyl moiety was dehydrogenated to a substituted benzene ring. Although 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[2] failed to effect this conversion, the following sequence provided the desired transformation. Cycloadducts **6b** and **6c** were treated sequentially with butyllithium followed by excess bromine. Exposure of the crude reaction product to 1,8-diazabicyclo[5.4.0]undec-7-ene in toluene followed by column chromatography provided *S,S*-di-*p*-tolyl-*N*-(*p*-tolylsulfonyl)sulfoximine in 25% yield. For comparison, authentic *S,S*-di-*p*-tolyl-*N*-(*p*-tolylsulfonyl)sulfoximine was secured in 34% yield by copper-induced decomposition of *p*-tolylsulfonyl azide[13] in the presence of di-*p*-tolyl sulfoxide.

Reaction of vinylsulfoximine **1b** with 1,3-cyclohexadiene gave a mixture of cycloadducts **5**, $n = 2$, G = Ts, which were separated into four components by HPLC. The first two, in order of elution time, were minor, i.e., each less than 5% of the mixture. The second two components were **5c**, $n = 2$, G = Ts, and **5d**, $n = 2$, G = Ts, in a ratio of 4:5. They were separated by HPLC and their stereochemistry assigned by analysis of their ^1H NMR spectra (Table I). Thus, this reaction is highly endo selective; the endo:exo ratio is 93:7. Although this reaction like that of vinylsulfoximine **1b** with cyclopentadiene shows little diastereoselectivity, the diastereomers of the endo adducts, i.e., **5c** and **5d**, could be separated by HPLC. Thus, reaction of optically pure vinylsulfoximine **1b** with cyclopentadiene or 1,3-cyclohexadiene followed by HPLC is expected to provide both optically pure diastereomers **5c** and **5d** (it is assumed that no racemization occurs under the conditions of the Diels–Alder reaction). Separation of diastereomeric sulfoximines constitutes part of the useful sulfoximine-mediated method for resolution of ketones recently reported.[14]

The usefulness of complex sulfoximines derives in part from the transformation of the sulfoximine moiety. Two new transformations of the sulfoximine group have been found for cycloadducts **5**, $n = 2$, G = Ts.[15] Desulfurization of the unseparated mixture of these cycloadducts with sodium amalgam produces bicyclo[2.2.2]oct-2-ene in 83% yield. Such desulfurization is analogous to that of sulfones with this reagent.[16] This selective reduction of the sulfoximine moiety in the presence of a carbon–carbon double bond with sodium amalgam complements the selective reduction of a carbon–carbon double bond in the presence of the sulfoximine group (both cycloadduct **5d**, $n = 1$, G = Ts, and **6a** have been so selectively reduced). Oxidation of an unseparated mixture of cycloadducts **5**, $n = 2$, G = Ts, by sequential treatment with lithium diisopropylamide and oxodiperoxymolybdenum (pyridine)(hexamethylphosphoric triamide), MoO_5·Py·HMPA (MoOPH), provides bicyclo[2.2.2]oct-2-en-5-one in 37% yield. Such transformation of a >CHS(O)(NTs)*p*-Tol moiety into a >C=O group is analogous to the reported >$CHSO_2Ar$ → >C=O conversion under similar conditions.[6]

Vinylsulfoximine **1b** is a reasonably good dienophile and is somewhat more reactive than phenyl vinyl sulfone. To determine the relative dienophilicities of these two compounds, they were allowed to compete for 2,3-dimethyl-1,3-butadiene. The mixture was analyzed by ^1H NMR spectroscopy after partial reaction. The ratio of unreacted phenyl vinyl sulfone to vinylsulfoximine **1b** was 2.6:1.

Experimental Section

Melting points were measured on a Thomas-Hoover apparatus and were uncorrected. IR spectra were recorded on a Perkin-Elmer Model 398 spectrophotometer, calibrated with the 1601 cm^{-1} band of polystyrene. ^1H NMR spectra were recorded at 250 MHz on a Bruker Model WM-250 spectrometer or at 60 MHz on a Varian EM-360 or T-60 spectrometer. Chemical shifts are reported as δ units from tetramethylsilane as internal standard. ^{13}C NMR were recorded at 63 MHz on a Bruker Model WM-250 spectrometer. Ethyl and methyl acetate were purified by washing with 5% aqueous sodium carbonate solution and then saturated aqueous calcium chloride solution, followed by drying over anhydrous magnesium sulfate and distillation from phosphorus pentoxide. Hexane and pentane were stirred with concentrated sulfuric acid and distilled from potassium hydroxide. Tetrahydrofuran was distilled from sodium/benzophenone under a nitrogen atmosphere. All other solvents were reagent grade and were used as purchased. Analytical and preparative thin-layer chromatography was carried out by using Merck HF-254 (Type 60) silica gel supplied by Brinkmann Instruments, Inc. Preparative thin-layer plates were prepared on 8 × 8 in. plates with 0.75-mm adsorbent. Column chromatography was carried out by using Woelm silica gel (63–200 μm) with ca. 20 times the weight of adsorbent as sample to be chromatographed. Analytical and semipreparative HPLC was performed on a commercially packed column (4.6 × 150 mm) of Beckman Ultrasphere ODS (5 μm) silica gel (normal phase) at a flow rate of 3 mL/min by using various compositions of methyl (or ethyl) acetate in hexane. Effluents were monitored by using an Altex Model 153 detector at 280 nm. On all chromatographic separations (analytical or preparative) the eluting solvent is listed in parentheses. Hydrazine hydrate (99%) was supplied by Mallinkrodt Chemical Works and was used as purchased. All other reagents were purchased from Aldrich Chemical Co., unless otherwise stated, and were used as purchased. Anhydrous Chloramine-T (Caution: explosive!) was prepared by storing the trihydrate over phosphorus pentoxide at 0.01 mm pressure and room temperature until constant weight was achieved.

***S*-*p*-Tolyl-*N*-(*p*-tolylsulfonyl)-*S*-vinylsulfoximine (1b).** A solution of *S*-*p*-tolyl-*S*-(2-chloroethyl)-*N*-(*p*-tolylsulfonyl)-sulfilimine (**2a**, 2.00 g, 5.62 mmol), prepared according to the method of Colonna and Stirling,[8] in methylene chloride (55 mL) was placed in a 200-mL three-necked flask fitted with a mechanical stirrer. Vigorous shaking was begun, and a solution of sodium metaperiodate (2.52 g, 11.8 mmol, 2.1 equiv) in water (28 mL) was added at once along with ruthenium dioxide dihydrate (17 mg). The black crystals of ruthenium dioxide gradually dispersed

(13) Kwart, H.; Khan, A. A. *J. Am. Chem. Soc.* **1967**, *89*, 1950. Johnson, C. R.; Katekar, G. F. *Ibid.* **1970**, *92*, 5753. Johnson, C. R.; Kirchhoff, R. A.; Reischer, R. J.; Katekar, G. F. *Ibid.* **1973**, *95*, 4287.

(14) Johnson, C. R.; Zeller, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 4021.

(15) Aluminum amalgam reduced the sulfur alkyl bond in N-unsubstituted and *N*-methyl-*S*-arylsulfoximines but not *N*-tosyl-*S*-arylsulfoximines: Schroeck, C. W.; Johnson, C. R. *J. Am. Chem. Soc.* **1971**, *93*, 5305. β-Hydroxy sulfoximines underwent reductive elimination to alkenes with aluminum amalgam but n-$C_5H_{11}CH(OH)C(CH_3)S(O)(NMe)Ph$ gave 2-octanol with sodium in liquid ammonia or sodium amalgam in ethanol: Johnson, C. R.; Kirchhoff, R. A. *Ibid.* **1979**, *101*, 3602.

(16) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.

(17) Johnson, C. K. ORTEP, Oak Ridge National Laboratory: Oak Ridge, TN.

to give the mixture a black color. The mixture, which slowly turned yellow, was stirred for 24 h at room temperature. When stirring was discontinued, the black color slowly returned. The reaction was conveniently followed by TLC (20% pentane in diethyl ether). The layers were separated and the aqueous layer was extracted once with methylene chloride (40 mL). To the extracts were added 2-propanol (1 mL) and anhydrous magnesium sulfate. Filtration and solvent removal at reduced pressure yielded a black oil. Diethyl ether (40 mL) was added and the precipitated black ruthenium complexes were removed by filtration through Celite. The pale yellow solution was reduced in volume on a rotary evaporator to ca. 15 mL. Once crystallization started, pentane was added, and the mixture was cooled and filtered to give sulfoximine **3a** (1.64 g, 4.40 mmol, 78% yield): mp 109–114 °C. An analytical sample was recrystallized from benzene/hexane and then methanol: mp 117–118 °C; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.10–7.95 (m, 8 H, Ar), 3.60–4.10 (m, 4 H, CH_2), 2.48 (s, 3 H, ArCH_3), 2.40 (s, 3 H, ArCH_3); IR (KBr) 1695, 1317, 1225, 1154, 1089, 1063, 1029, 1017, 875, 814, 755, 728 cm^{-1}. Anal. Calcd for $C_{16}H_{18}ClNO_3S_2$: C, 51.67; H, 4.88. Found: C, 51.73; H, 4.88.

To a solution of **3a** (1.64 g, 4.40 mmol) in toluene (50 mL) was added, with stirring, dried triethylamine (0.70 mL, 1.1 equiv) over a period of 1 min. At the end of the addition, a precipitate has formed and the mixture was stirred for 1 h. Filtration and removal of solvent at reduced pressure gave **1b** (1.48 g, 4.40 mmol, 100% yield): mp 130–135 °C; the analytical sample was recrystallized from methanol and then methylene chloride/hexane: mp 137–139 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.87 (d, 2 H, J = 8.2 Hz, Ar), 7.85 (d, 2 H, J = 8.4 Hz, Ar), 7.37 (d, 2 H, J = 8.2 Hz, Ar), 7.26 (d, 2 H, J = 8.1 Hz, Ar), 6.82 (dd, 1 H, J = 16.3 and 9.6 Hz, α-vinyl), 6.43 (dd, 1 H, J = 16.2 and 1.3 Hz, *cis*-β-vinyl), 6.14 (dd, 1 H, J = 9.6 and 1.3 Hz, *trans*-β-vinyl), 2.45 (s, 3 H, ArCH_3), 2.40 (s, 3 H, ArCH_3); IR (KBr) 1694, 1315, 1235, 1159, 1103, 1065, 817, 674 cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_3S_2$: C, 57.29; H, 5.11. Found: C, 57.09; H, 5.15.

***S*-(2-Chloroethyl)-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine.** A solution of 2-chloroethyl phenyl sulfide (6.86 g, 39.7 mmol), prepared according to the procedure of Bennett and Berry,[18] in absolute ethanol (20 mL) was added dropwise to a stirred solution of anhydrous Chloramine-T (Caution: explosive!) (9.82 g, 43.1 mmol) in absolute ethanol (100 mL) at 0 °C. The mixture was removed from the cold bath and was stirred at room temperature overnight. The ethanol was removed at reduced pressure. Column chromatography (50% hexane/ethyl acetate) gave an oil, which was a mixture of two compounds by TLC analysis (50% hexane/ethyl acetate, R_f 0.1 and 0.2). Diethyl ether trituration and methanol recrystallization gave *S*-(2-chloroethyl)-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfilimine as a white solid (2.63 g, 6.62 mmol, 17%), which showed impurities by ^{1}H NMR analysis: mp 90–95 °C. This material resisted purification and was used as is for oxidation. Thus, ruthenium tetroxide oxidation of *S*-(2-chloroethyl)-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfilimine (1.50 g, 4.39 mmol, 24-h reaction time) in a manner analogous to the oxidation of **3a** gave solid product after ether trituration (1.07 g, 2.99 mmol, 69% yield): mp 116–124 °C. The analytical sample was recrystallized from methanol/ethyl acetate and then methanol: mp 130–132 °C; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.15–8.15 (m, 9 H, Ar), 3.55–4.18 (m, 4 H, CH_2), 2.40 (s, 3 H, ArCH_3); IR (KBr) 1597, 1450, 1319, 1306, 1292, 1222, 1150, 1087, 1076, 1059, 1026, 763, 749, 733 cm^{-1}. Anal. Calcd for $C_{15}H_{16}ClNO_3S_2$: C, 50.34; H, 4.51. Found: C, 50.14; H, 4.40.

***S*-Phenyl-*N*-(*p*-tolylsulfonyl)-*S*-vinylsulfoximine.** The sulfoximine prepared above (264 mg, 0.750 mmol) was dissolved with heating in toluene (50 mL), and the solution was allowed to cool to room temperature. Triethylamine (0.12 mL, 87 mg, 0.86 mmol) was added and the solution was stirred for 3 h. The mixture was filtered, and the precipitated triethylamine hydrochloride was rinsed with toluene. The solvent was removed at reduced pressure. Recrystallization from methanol gave *S*-phenyl-*N*-(*p*-tolylsulfonyl)-*S*-vinylsulfoximine (204 mg, 0.634 mmol, 84%, mp 128–131 °C). The analytical sample was recrystallized from methanol: mp 131–133 °C; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.12–8.00 (m, 9 H, Ar), 6.72 (dd, 1 H, J = 9.0 and 16 Hz, α-vinyl), 6.40 (d, 1 H, J = 16 Hz, *cis*-β-vinyl), 6.10 (d, 1 H, J = 9.0 Hz, *trans*-β-vinyl), 2.40 (s, 3 H, ArCH_3); IR (KBr) 1599, 1448, 1312, 1289, 1235, 1155, 1103, 1064, 1017, 997, 768, 734 cm^{-1}. Anal. Calcd for $C_{15}H_{15}NO_3S_2$: C, 56.05; H, 4.70. Found: C, 55.66; H, 4.70.

***S*-(2-Acetoxyethyl)-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine (3b).** Ruthenium tetroxide oxidation of sulfilimine **2b**[10] (1.79 g, 4.19 mmol, 5-h reaction time) gave sulfoximine **3b** as a solid after ether trituration (1.37 g 3.58 mmol, 73% yield): mp 93–94 °C. The analytical sample was recrystallized from 95% ethanol: mp 93–94 °C; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.06–8.05 (m, 9 H, Ar), 4.20 and 3.92 (two br t, 4 H, J = 6 Hz, CH_2), 2.38 (br s, 3 H, ArCH_3), 1.72 (s, 3 H, COCH_3); IR (KBr) 1733, 1596, 1448, 1319, 1226, 1152, 1096, 1055, 747 cm^{-1}. Anal. Calcd for $C_{17}H_{19}NO_5S_2$: C, 53.52; H, 5.02. Found: C, 53.46; H, 4.88. Attempts to eliminate acetic acid from **3b** with potassium hydride, triethylamine, or 1,8-diazabicyclo[5.4.0]undec-5-ene did not yield the corresponding vinylsulfoximine.

Cycloaddition of Vinylsulfoximine 1a with Cyclopentadiene. A solution of vinylsulfoximine **1a** (428 mg, 1.31 mmol), prepared according to the procedure of Colonna and Stirling,[8] freshly distilled cyclopentadiene (1.2 mL, 0.96 g, 15 mmol, 11 equiv), and methylene chloride (8 mL) was heated at reflux for 16 h. The solvent was removed on a rotary evaporator and the residual yellow oil was stirred with hexane until it solidified. It was then filtered and washed with hexane to give the mixture of adduct isomers as a pale yellow solid (487 mg, 1.24 mmol, 95% yield). Semipreparative HPLC purification (15% methyl acetate in hexane) gave three fractions. The first fraction (11% of adduct mixture) was one exo diastereomer **5a**, n = 1, G = 1,2-$C_6H_4(CO)_2$N: mp 167–171 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.00 (d, 2 H, J = 8.4 Hz, ortho to sulfoximine), 7.69–7.77 (m, 2 H, *o*-1,2-C_6H_4-$(CO)_2$N), 7.58–7.67 (m, 2 H, *m*-1,2-$C_6H_4(CO)_2$N), 7.32 (d, 2 H, J = 8.2 Hz, meta to sulfoximine), 6.25 (br s, 2 H, HC=C), 3.92 (br s, 1 H, H1), 3.44 (ddd, 1 H, J = 1.3, 5.6, and 8.7 Hz, H2), 2.96 (br s, 1 H, H4), 2.41 (s, 3 H, ArCH_3), 2.01 (br d, 1 H, J = 9.2 Hz, H7syn), 1.86 (ddd, 1 H, J = 3.3, 5.5, and 12.5 Hz, H3exo), 1.55 (br d, 1 H, J = 9.1 Hz), 1.21–1.32 (m, 1 H, H3exo); IR (KBr) 1719, 1596, 1465, 1374, 1210, 1193, 1038, 1005, 883, 808, 718, 709 cm^{-1}. Exact mass calcd for $C_{22}H_{20}N_2O_3S$: m/e 392.1195. Found: 392.1155.

The second fraction (45% of adduct mixture) was a mixture of an exo (**5b**, n = 1, G = 1,2-$C_6H_4(CO)_2$N) and an endo (**5c**, n = 1, G = 1,2-$C_6H_4(CO)_2$N) diastereomer (ratio 1:1): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.11 (d, 2 H, J = 8.2 Hz, Ar), 7.98 (d, 2 H, J = 8.5 Hz, Ar), 7.70–7.78 (m, 4 H, *o*-1,2-$C_6H_4(CO)_2$N), 7.58–7.67 (m, 4 H, *m*-1,2-$C_6H_4(CO)_2$N), 7.39 (d, 2 H, J = 8.1 Hz, Ar), 7.31 (d, 2 H, J = 8.3 Hz, Ar), 6.41 (dd, 1 H, J = 2.8 and 5.7 Hz, HC=C), 6.30 (dd, 1 H, J = 2.9 and 5.6 Hz, HC=C), 6.23 (dd, 1 H, J = 3.0 and 5.6 Hz, HC=C), 6.00 (dd, 1 H, J = 3.3 and 5.4 Hz, HC=C), 4.18 (ddd, 1 H, J = 3.1, 5.1, and 9.3 Hz, H2 on endo isomer), 3.84 (br s, 1 H, H1 on endo isomer), 3.34 (ddd, 1 H, J = 1.3, 4.8, and 8.8 Hz, H2 on exo isomer), 3.06 (br s, 2 H, H4 on endo isomer), 2.98 (br d, 1 H, J = 1.2 Hz, H4 on exo isomer), 2.81 (br d, 1 H, J = 1.4 Hz, H1 on exo isomer), 2.68 (ddd, 1 H, J = 3.7, 5.0, and 12.8 Hz, H3exo in exo isomer), 2.45 (s, 6 H, ArCH_3), 2.40 (s, 6 H, ArCH_3), 1.95 (br d, 1 H, J = 9.0 Hz, H7anti in exo isomer), 1.91 (ddd, 1 H, J = 3.5, 9.3, and 12.8 Hz, H3exo in endo isomer), 1.76 (ddd, 1 H, J = 2.5, 8.6, and 12.7 Hz, H3endo in exo isomer), 1.60 (br d, 1 H, J = 8.8 Hz, H7anti in endo isomer), 1.48 (ddd, 1 H, J = 2.9, 4.8, and 12.3 Hz, H3endo in endo isomer), 0.69 (br d, 2 H, J = 8.8 Hz, H7syn in both isomers).

The third fraction was an endo (**5d**, n = 1, G = 1,2-$C_6H_4(CO)_2$N) diastereomer (44% of adduct mixture), and the analytical sample was recrystallized from absolute ethanol: mp 188–190 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.08 (d, 2 H, J = 8.2 Hz, ortho to sulfoximine), 7.20–7.77 (m, 2 H, *o*-1,2-$C_6H_4(CO)_2$N), 7.60–7.67 (m, 2 H, *m*-1,2-$C_6H_4(CO)_2$N), 7.39 (d, 2 H, J = 8.2 Hz, meta to sulfoximine), 6.31 (dd, 1 H, J = 3.1 and 5.5 Hz, HC=C), 5.86 (dd, 1 H, J = 2.7 and 5.6 Hz, HC=C), 4.16 (ddd, 1 H, J = 3.5, 5.2, and 8.9 Hz, H2), 3.03 (br s, 1 H, H4), 2.67 (br s, 1 H, H1), 2.45 (s, 3 H, ArCH_3), 2.31 (ddd, 1 H, J = 3.6, 9.1, and 12.7 Hz, H3exo), 2.05 (ddd, 1 H, J = 2.7, 4.9, and 12.6 Hz, H3endo), 1.43 (br d, 1 H, J = 9.6 Hz, H7anti), 1.29 (br d, 1 H, J = 8.6 Hz, H7syn); IR (KBr) 1720, 1593, 1468, 1373, 1362, 1352, 1229, 1222, 1188, 1088, 1032, 1002, 882, 818, 744, 713 cm^{-1}. Anal. Calcd for $C_{22}H_{20}N_2O_3S$:

(18) Bennett, G. M.; Berry, W. A. *J. Chem. Soc.* **1927**, 1676.

C, 67.33; H, 5.14. Found: C, 67.22; H, 5.18.

Crystal Structure Study of Cycloadduct 5d (n = 1, G = 1,2-$C_6H_4(CO)_2N$). Cycloaddition of cyclopentadiene and optically pure (*S*)-vinylsulfoximine **1a** was carried out as reported above for racemic **1a**. Column chromatography on silica gel, eluting with 5% acetone in benzene, provided separation. Cycloadduct **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$, was obtained as colorless needles: mp 194–195 °C; $[\alpha]_D$ −50.3° (acetone, c 2.2). Crystals of cycloadduct **5d** (n = 1, G = 1,2-$C_6H_4(CO)_2N$) suitable for X-ray crystallographic analysis were grown by vapor diffusion of a solution of the compound in diethyl ether with pentane. A needle was cut and mounted on a Syntex $P2_1$ autodiffractometer. The automatic centering and least-squares routines were carried out on 25 reflections, and the cell constants determined by least-squares treatment of these reflections are given in the supplementary material section. The orthorhombic space group was determined from systematic absences to be unambiguously $P2_12_12_1$. The data were reduced to F_o^2 and $\sigma(F_o^2)$. Lorentz and polarization but not absorption corrections were applied to all reflections. The θ–2θ data collection technique was used to collect the data of which those with $I \geq 3\sigma(I)$ were used in the calculations.

The structure was solved by the direct methods program MULTAN.[19] The positions of 21 of the 28 non-hydrogen atoms were obtained from an E map. The structure was refined by full-matrix least-squares techniques[20] by using neutral atom scattering factors[21] and treating the sulfur atom as an anomalous scatterer with $f' = 0.11$ and $f'' = 0.124$.[21] This led to isotropic convergence at $R = 0.24$ after five cycles. A difference map revealed the position of five additional non-hydrogen atoms. Further isotropic refinement converged at $R = 0.18$. A difference map at this point gave the position of an additional non-hydrogen atom. The position of the remaining atom of the bicyclo[2.2.1]heptyl ring was calculated. Final isotropic refinement converged at $R = 0.102$. Anisotropic refinement was accomplished by treating the *p*-tolyl ring and the rest of the molecule separately. This led to anisotropic convergence at $R = 0.073$. A difference map revealed the position of one hydrogen atom of the methyl moiety of the *p*-tolyl group. All other hydrogen atom positions were calculated. The hydrogen atom thermal parameters were set according to $B_H = B_N + 1$, where N is the atom to which H is bonded. The hydrogen atom parameters were not refined. Several cycles of anisotropic refinement led to convergence at $R = 0.0544$, $R_w = 0.0677$, and GOF = 2.68.

Reaction of Vinylsulfoximine 1b with Cyclopentadiene. A solution of vinylsulfoximine **1b** (687 mg, 2.05 mmol) and freshly distilled cyclopentadiene (0.4 mL) in methylene chloride (0.4 mL) was heated at reflux for 16 h. The workup was the same as that described for the reaction of vinylsulfoximine **1a** with cyclopentadiene. After workup the resulting solid was redissolved in chloroform, the solvent was removed, and the residual oil was triturated with pentane to give the adduct mixture (663 mg, 1.65 mmol, 81% yield). Semipreparative HPLC (10–15% methyl acetate in hexane–10 min gradient) gave three fractions. The first fraction (19% of adduct mixture) was a mixture of the two exo (**5a** and **5b**, n = 1, G = Ts) isomers (ratio 4:5): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.75–7.88 (m, 8 H, Ar on **a** and **b**), 7.32–7.42 (m, 4 H, Ar on **a** and **b**), 7.21 (coincidental d, 4 H, J = 8.1 Hz, Ar **a** and **b**), 6.22–6.28 (m, 2 H, HC=C of **a** and **b**), 6.15 (dd, 1 H, J = 3.2 and 5.5 Hz, HC=C of **a**), 5.96 (dd, 1 H, J = 3.3 and 5.6 Hz, HC=C of **b**), 3.54 (br dd, 1 H, J = 1.4 and 3.0 Hz, H1 of **a**), 3.20 (ddd, 1 H, J = 1.1, 5.2, and 8.6 Hz, H2 of **a**), 3.14 (ddd, 1 H, J = 1.3, 5.0, and 8.6 Hz, H2 of **b**), 2.90–2.98 (br, 2 H, H4 of **a** and **b**), 2.83 (br dd, 1 H, J = 1.4 and 3.0 Hz, H1 of **b**), 2.16–2.27 (m, 1 H), 1.55–1.83 (m, 4 H), 1.18–1.43 (m, 3 H).

The second fraction (36% of adduct mixture was an endo (**5c**, n = 1, G = Ts) diastereomer. When recrystallized from absolute ethanol, **5c**, n = 1, G = Ts, had the following: mp 145–148 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.80 (d, 2 H, J = 8.3 Hz, Ar), 7.75 (d, 2 H, J = 8.4 Hz, Ar), 7.33 (d, 2 H, J = 8.4 Hz, Ar), 7.22 (d, 2 H, J = 8.1 Hz, Ar), 6.14 (dd, 1 H, J = 3.1 and 5.6 Hz, HC=C), 5.82 (dd, 1 H, J = 2.8 and 5.6 Hz, HC=C), 3.93 (ddd, 1 H, J = 3.2, 5.0, and 9.2 Hz, H2), 3.57 (br s, 1 H, H1), 2.92 (br s, 1 H, H4), 2.43 (s, 3 H, ArCH_3), 2.39 (s, 3 H, ArCH_3), 1.78 (ddd, 1 H, J = 3.7, 9.2, and 12.7 Hz, H3exo), 1.49 (br ddd, 1 H, J = 1.9, 4.3, and 8.9 Hz, H7anti), 1.33 (ddd, 1 H, J = 2.8, 5.0, and 12.4 Hz, H3endo), 1.27 (br d, 1 H, J = 3.3 Hz, H7syn); IR (KBr) 1592, 1400, 1308, 1237, 1228, 1152, 1188, 1168, 1157, 762 cm^{-1}. Anal. Calcd for $C_{21}H_{23}NO_3S_2$: C, 62.81; H, 5.77. Found: C, 62.70; H, 5.79.

The third fraction (45% of adduct mixture) was an endo (**5d**, n = 1, G = Ts) diastereomer, which was recrystallized from absolute ethanol: mp 131.5–132.5 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.82 (d, 2 H, J = 8.4 Hz, Ar), 7.76 (d, 2 H, J = 8.2 Hz, Ar), 7.39 (d, 2 H, J = 8.3 Hz, Ar), 7.19 (d, 2 H, J = 8.1 Hz, Ar), 6.21 (dd, 1 H, J = 3.1 and 5.6 Hz, HC=C), 5.79 (dd, 1 H, J = 2.7 and 5.6 Hz, HC=C), 3.96 (ddd, 1 H, J = 3.1, 5.1, and 9.2 Hz, H2), 2.97 (br s, 1 H, H4), 2.69 (br s, 1 H, H1), 2.46 (s, 3 H, ArCH_3), 2.36 (s, 3 H, ArCH_3), 2.23 (ddd, 1 H, J = 3.7, 9.3, and 12.9 Hz, H3exo), 1.69 (br ddd, 1 H, J = 2.9, 5.0, and 12.8 Hz, H3endo), 1.48 (ddd, 1 H, J = 1.7, 6.6, and 8.8 Hz, H7anti), 1.25 (br d, 1 H, J = 8.8 Hz, H7syn); IR (KBr) 1595, 1401, 1315, 1245, 1235, 1153, 1092, 1063, 1016, 815, 763, 752 cm^{-1}. Anal. Calcd for $C_{21}H_{23}NO_3S_2$: C, 62.81; H, 5.77. Found: C, 62.71; H, 5.75.

General Procedure for Reaction of Vinylsulfoximine 1b with 1,3-Dienes. The diene (2–10 equiv), vinylsulfoximine **1b**, hydroquinone (5–20 mg), and enough chloroform or benzene (0.5–5 mL) to dissolve the entire contents when hot were placed in a sealed glass tube. The tube was put in an oven maintained at 110 °C for the required time (checked at least once to ensure solution), the tube was opened, and the volatiles were removed at reduced pressure. The adducts were isolated by pentane trituration, column chromatography, or recrystallization.

1,3-Butadiene. Vinylsulfoximine **1b** (372 mg, 1.11 mmol), 1,3-butadiene (ca. 0.25 mL, 2.6 equiv), and chloroform (0.60 mL) were allowed to react as described in the general procedure for 48 h. Hexane trituration and filtration gave cycloadduct **6a** as a solid (388 mg, 0.997 mmol, 90%). No conditions were found for separating the isomers by HPLC. Repeated recrystallization from diethyl ether and then ethanol gave the following: mp 104–106 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.83 (d, 2 H, J = 8.3 Hz, Ar), 7.82 (d, 2 H, J = 8.3 Hz, Ar), 7.38 (d, 2 H, J = 8.3 Hz, Ar), 7.23 (d, 2 H, J = 8.3 Hz, Ar), 5.50–5.70 (br m, 2 H, HC=C), 3.51–3.66 (br m, 1 H, H α to sulfoximine), 2.38–2.45 (two overlapping s and br m, 7 H), 2.02–2.36 (br m, 4 H, allylic CH_2), 1.42–1.62 (br m, 1 H); ^{13}C NMR ($CDCl_3$) δ 145.5, 142.3, 141.4, 131.7, 130.0, 129.4, 129.1, 126.6, 123.0, 62.7, 24.5, 21.9, 21.5, 21.4; IR (KBr) 1692, 1313, 1305, 1226, 1157, 1100, 1071, 817, 759, 721, 681, 637 cm^{-1}. Anal. Calcd for $C_{20}H_{23}NO_3S_2$: C, 61.67; H, 5.95. Found: C, 61.64; H, 5.97.

2-Methyl-1,3-butadiene. Vinylsulfoximine **1b** (1.189 g, 3.54 mmol) and 2-methyl-1,3-butadiene (4 equiv) were allowed to react in benzene (2 mL) as described above for 50 h. Pentane trituration gave the adducts **6b** and **6c** as a solid (1.354 g, 3.35 mmol, 95% yield). No HPLC conditions were found that would separate the products. ^{13}C NMR analysis, however, indicated the presence of more than one isomer: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.78–7.88 (br m, 4 H, Ar), 7.37 (d, 2 H, J = 7.5 Hz, Ar), 7.22 (d, 2 H, J = 8.0 Hz, Ar), 5.19–5.28 (br m, 1 H, HC=C), 3.25–3.64 (br m, 1 H, α-CH), 2.45 (s, 3 H, ArCH_3), 2.38 (s, 3 H, ArCH_3), 1.25–1.98 (br m, 4 H, allylic CH_2 and one of saturated methylene protons), 1.27–1.68 (br, 4 H allylic CH_3 and other saturated methylene proton); ^{13}C NMR ($CDCl_3$) δ 145.4, 142.4, 141.2, 134.1, 134.0, 131.5, 131.4, 130.0, 129.4, 129.3, 129.0, 126.5, 117.1, 117.0, 63.1, 62.6, 29.2, 24.5, 24.4, 24.2, 23.2, 22.8, 22.3, 21.7, 21.4.

2,3-Dimethyl-1,3-butadiene. Vinylsulfoximine **1b** (997 mg, 2.97 mmol) and 2,3-dimethyl-1,3-butadiene (3 equiv) were allowed to react in chloroform (2 mL) as described above for 60 h. Pentane trituration gave the adduct **6d** as a solid (1.139 g, 2.73 mmol, 92% yield). No HPLC conditions were found that separate the components: ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.16–7.94 (m, 8 H, Ar), 3.16–3.86 (br, 1 H, α-CH), 2.46 (s, 3 H, ArCH_3), 2.40 (s, 3 H, ArCH_3), 1.80–2.40 (br, 6 H, CH_2), 1.57 (br s, 6 H, allylic CH_3); ^{13}C NMR ($CDCl_3$) δ 145.5, 142.4, 141.4, 131.6, 131.5, 130.4, 130.0,

(19) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

(20) The major programs used during the structure determination are FORDAP (Fourier summation program by A. Zalkin), and NCLS (structure factor calculations and full-matrix least-squares refinement by J. Ibers adapted from ORFLS by W. R. Bussing, K. O. Martin, and H. A. Levy).

(21) Scattering factors are obtained from "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. II; pp 213, 222–223.

129.5, 129.1, 126.6, 125.8, 125.7, 122.4, 122.3, 63.4, 30.9, 30.4, 29.8, 22.7, 22.1, 21.6, 21.5, 19.0, 18.5.

1,3-Cyclohexadiene. Vinylsulfoximine **1b** (1.04 g, 3.10 mmol) and 1,3-cyclohexadiene (6 equiv) were allowed to react in chloroform (2.8 mL) as described above for 50 h. The volatiles were removed to give the mixture of adducts as a solid (1.24 g; 2.97 mmol, 96% yield). HPLC analysis (15% methyl acetate in hexane) showed four adduct peaks in the ratio 4:3:40:50. Recrystallization from methylene chloride/pentane gave two crops that are enriched in the first and second major peaks, respectively. HPLC purification of these fractions gave the two endo diastereomers. Peak 3 (**5c**, n = 2, G = Ts) was recrystallized from absolute ethanol: mp 172.5–173.5 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.82 (d, 2 H, J = 8.3 Hz, Ar), 7.73 (d, 2 H, J = 8.4 Hz, Ar), 7.32 (d, 2 H, J = 8.4 Hz, Ar), 7.21 (d, 2 H, J = 8.3 Hz, Ar), 6.08 (dd, 1 H, J = 7.4 and 7.4 Hz, HC=C), 5.78 (dd, 1 H, J = 7.3 and 7.3 Hz, HC=C), 3.77 (dd, 1 H, J = 7.4 and 8.8 Hz, H2), 3.32–3.34 (br m, 1 H, H1), 2.58–2.59 (br m, 1 H, H4), 2.44 (s, 3 H, ArCH_3), 2.38 (s, 3 H, ArCH_3), 1.19–1.81 (m, 6 H, ring CH_2); IR (KBr) 1591, 1311, 1302, 1238, 1222, 1155, 1096, 1074, 819, 766, 730 cm^{-1}. Anal. Calcd for $C_{22}H_{25}NO_3S_2$: C, 63.58; H, 6.06. Found: C, 63.63; H, 6.11.

Peak 4 (**5d**, n = 2, G = Ts) was recrystallized from absolute ethanol: mp 146–148 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.80 (d, 2 H, J = 8.5 Hz, Ar), 7.79 (d, 2 H, J = 8.4 Hz, Ar), 7.37 (d, 2 H, J = 8.1 Hz, Ar), 7.20 (d, 2 H, J = 8.1 Hz, Ar), 6.12 (dd, 1 H, J = 7.7 and 7.7 Hz, HC=C), 5.78 (dd, 1 H, J = 7.3 and 7.3 Hz, HC=C), 3.74 (dd, 1 H, J = 6.9 and 8.5 Hz, H2), 2.72–2.75 (br m, 1 H, H1), 2.64–2.66 (br m, 1 H, H4), 2.46 (s, 3 H, ArCH_3), 2.37 (s, 3 H, ArCH_3), 1.11–2.08 (m, 6 H, ring CH_2); IR (KBr) 1598, 1309, 1302, 1234, 1208, 1150, 1090, 1074, 818, 768, 705 cm^{-1}. Anal. Calcd for $C_{22}H_{25}NO_3S_2$: C, 63.58; H, 6.06. Found: C, 63.45; H, 6.07.

Competitive Reaction of Phenyl Vinyl Sulfone and Vinylsulfoximine 1b with 2,3-Dimethyl-1,3-butadiene. A solution of phenyl vinyl sulfone (39.3 mg, 0.216 mmol), vinylsulfoximine **1b** (72.3 mg, 0.216 mmol), 2,3-dimethyl-1,3-butadiene (50 μL, 0.442 mmol), and deuteriochloroform (0.5 mL, 1% tetramethylsilane) was placed in an NMR tube and sealed. The tube was put in an oven maintained at 110 °C for 16 h. ^{1}H NMR (250 Hz) analysis showed the ratio of remaining sulfone to sulfoximine to be 2.6:1.0.

Conversion of (±)-(2*S*,*R*)-*S*-*endo*-Bicyclo[2.2.1]hept-5-enyl-*N*-phthalimido-*S*-*p*-tolylsulfoximine (5d, n = 1, G = 1,2-$C_6H_4(CO)_2N$) to (±)-(2*S*,*S*)-*endo*-Bicyclo[2.2.2]heptyl *p*-Tolyl Sulfoxide (7). Vinylsulfoximine **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$, was purified by preparative thin-layer chromatography (twice eluted with 20% ethyl acetate in hexane). The most polar adduct band was collected and HPLC analysis (15% methyl acetate in hexane) showed it to be >90% pure. A sample of this adduct (26.4 mg, 6.73 μmol) was stirred with absolute ethanol (1 mL). Hydrazine hydrate (99%, 124 μL, 40 equiv), was added, and the solution was stirred and heated at 40 °C for 15 min. The solution was poured into water (10 mL) and extracted twice with diethyl ether (10 mL). The extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed at reduced pressure. Preparative thin-layer chromatography (ethyl acetate) gave the sulfoxide as an oil (12.5 mg, 54.6 μmol, 81% yield). Further purification by HPLC (25% methyl acetate in hexane) and bulb to bulb distillation (oven temperature 120–130 °C, 0.1 mm) gave the sample used for high-resolution mass spectrometry. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.60 (d, 2 H, J = 8.2 Hz, Ar ortho to sulfoxide), 7.29 (dd, 2 H, J = 8.3 and 0.8 Hz, Ar meta to sulfoxide), 3.12 (m, 1 H, α to sulfoxide), 2.84 (br, 1 H, bridgehead CH), 2.40 (s, 3 H, ArCH_3), 2.28 (br, 1 H, bridgehead CH), 2.14 (ddd, 1 H, J = 2.4, 9.0, and 9.0 Hz), 1.61–1.69 (br m, 2 H), 1.49 (ddd, 1 H, J = 1.7, 4.6, and 9.8 Hz), 1.23–1.42 (br complex m, 3 H), 0.90 (ddd, 1 H, J = 2.5, 5.6, and 13.2 Hz); IR (neat) 1600, 1496, 1455, 1314, 1086, 1042, 1018, 814, 714 cm^{-1}. Exact mass calcd for $C_{14}H_{18}OS$: m/e 234.1078. Found: 234.1052.

Using degassed solvents and reactions, lowering the initial temperature to 0 °C, and shortening the reaction time to 5 min still resulted in reduction of the carbon–carbon double bond.

Reaction of Vinylsulfoximine 5d, n = 1, G = 1,2-$C_6H_4(CO)_2N$, with Hydrazine in Ethanol Containing Cyclohexene. A sample of enriched **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$ (50.4 mg 128 μmol), purified as above, was stirred with degassed absolute ethanol (2 mL; nitrogen was bubbled through the absolute ethanol for 15 min prior to use) under a nitrogen atmosphere. Degassed cyclohexene (0.40 mL, 31 equiv) was added by syringe and the mixture cooled in an ice water bath. Degassed hydrazine hydrate (0.26 mL, 42 equiv) was added by syringe, the tube was removed from the cold bath, and the solution was stirred. The solid dissolved as the mixture warmed (5 min). Workup as for 7 above gave, after HPLC purification, a colorless oil (15.2 mg). ^{1}H NMR analysis showed it to be a 1:1 mixture of the saturated sulfoxide 7 and the unsaturated compound 8, whose preparation follows.

Conversion of Vinylsulfoximine (±)-5d, n = 1, G = 1,2-$C_6H_4(CO)_2N$, to (±)-(2*S*,*S*)-*endo*-Bicyclo[2.2.1]hept-5-enyl *p*-Tolyl Sulfoxide (8) with Hydrazine in Allyl Alcohol. A sample (88.2 mg, 0.225 mmol) of the pure diastereomer (±)-**5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$ (>99% one diastereomer by HPLC analysis) was stirred with allyl alcohol (5.0 mL) and hydrazine hydrate (0.26 mL, 24 equiv), was added. Gas evolution was evident after 5 min. After being stirred at room temperature for 20 h, the mixture was filtered. The filtrate was poured into water (100 mL) and extracted with diethyl ether (3 × 50 mL). The organic extracts were dried over anhydrous magnesium sulfate and filtered, and the volatiles were removed at reduced pressure. Bulb to bulb distillation using a hot air bath (oven temperature 140–150 °C, 0.1 mm) gave sulfoxide **8** (48.9 mg, 0.210 mmol, 93% yield): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.56 (m, 2 H, Ar), 7.29 (m, 2 H, Ar), 6.37 (dd, 1 H, J = 2.7 and 5.7 Hz, HC=C), 6.31 (dd, 1 H, J = 3.0 and 5.7 Hz, HC=C), 3.49 (br, 1 H, bridgehead H1), 3.40 (m, 1 H, Hα to sulfoxide), 2.91 (br, 1 H, bridgehead H4), 1.63 (ddd, 1 H, J = 1.9, 4.5, and 8.8 Hz, H7anti), 1.55 (ddd, 1 H, J = 3.7, 9.0, and 12.6 Hz, H3exo), 1.29 (br d, 1 H, J = 8.7 Hz, H7syn), 0.82 (ddd, 1 H, J = 2.8, 4.4, and 12.7 Hz, H3endo); IR (neat) 1596, 1493, 1337, 1083, 1043, 1015, 810, 738, 708 cm^{-1}; exact mass calcd for $C_{14}H_{16}OS$ m/e 232.0922, found 232.0912.

Catalytic Hydrogenation of (±)-(2*S*,*R*)-*S*-*endo*-Bicyclo[2.2.1]hept-5-enyl-*N*-(*p*-tolylsulfonyl)-*S*-*p*-tolylsulfoximine (5d, n = 1, G = Ts). A sample (38.1 mg, 94.9 μmol) of **5d**, n = 1, G = Ts, purified by HPLC (10–15% methyl acetate in hexane–10 min gradient), was reduced with platinum oxide in absolute ethanol as described for **6a** (see following experiment). After ethanol removal, concentrated sulfuric acid (0.5 mL) was added to the residue, and the contents were swirled for 15 min at room temperature to give a clear light brown solution. The solution was cooled in an ice bath while water (4.5 mL) was slowly added. Sodium nitrite (25 mg, 360 μmol) was added in one portion and brown gas evolved. The mixture was stirred at room temperature for 1 h, extracted with methylene chloride (2 × 10 mL), and dried over anhydrous magnesium sulfate. Solvent removal gave an oil that was purified as above to give an oil (7.2 mg, 31 μmol, 32% from adduct) that had HPLC retention time and ^{1}H NMR identical with sulfoxide **7** prepared from **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$.

Catalytic Hydrogenation of *S*-4-Cyclohexenyl-*N*-(*p*-tolylsulfonyl)-*S*-*p*-tolylsulfoximine (6a). A sample of the adduct (219 mg, 0.561 mmol) from 1,3-butadiene and vinylsulfoximine **1b** was dissolved in absolute ethanol (5 mL) with heating. The solution was added via syringe to platinum oxide (30 mg) prereduced by stirring under a hydrogen atmosphere for 15 min under absolute ethanol (1 mL) in a two-necked 10-mL pear-shaped flask. Stirring was begun and continued until hydrogen absorption ceased (ca. 15 min). The mixture was filtered through Celite and solvent removed at reduced pressure. Recrystallization from ethanol gave a solid (167 mg) whose melting point (114–117 °C), mixture melting point (111–115 °C), and ^{1}H NMR spectrum were identical with those of *S*-cyclohexyl-*S*-*p*-tolyl-*N*-(*p*-tolylsulfonyl)sulfoximine prepared by ruthenium tetroxide oxidation of *S*-cyclohexyl-*S*-*p*-tolyl-*N*-(*p*-tolylsulfonyl)sulfilimine. Preparative thin-layer chromatography (75% hexane in diethyl ether) gave an additional 15.7 mg (mp 114–117 °C, total yield of 83%).

***S*-Cyclohexyl-*S*-*p*-tolyl-*N*-(*p*-tolylsulfonyl)sulfilimine.** A solution of cyclohexyl p-tolyl sulfide (5.27 g, 25.4 mmol) in absolute ethanol (15 mL) was added dropwise to a solution of anhydrous Chloramine-T (Caution: explosive!) (6.36 g, 27.9 mmol) in absolute ethanol (75 mL) over 0.5 h. A white precipitate formed by the end of the addition, and the mixture was stirred at room temperature for 16 h. Ethanol was removed on a rotary evaporator; water (100 mL) was added; and the mixture was extracted

with methylene chloride (3 × 50 mL). The combined extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Column chromatography (50% ethyl acetate/hexane) gave an oil (7.82 g, 20.8 mmol, 82% yield): ^{1}H NMR ($CDCl_3$, 250 Hz) δ 7.70 (d, 2 H, J = 8.1 Hz, Ar ortho to sulfonyl), 7.52 (d, 2 H, J = 8.2 Hz, Ar ortho to sulfilimine), 7.27 (d, 2 H, J = 7.7 Hz, Ar meta to sulfonyl), 7.12 (d, 2 H, J = 8.0 Hz, Ar meta to sulfilimine), 3.18–3.99 (br m, 1 H, CH α to sulfilimine), 2.39 (s, 3 H, $ArCH_3$), 2.32 (s, 3 H, $ArCH_3$), 1.13–2.00 (br m, 10 H, ring CH_2); IR (KBr) 1598, 1493, 1452, 1307, 1296, 1282, 1143, 1090, 1021, 973, 813 cm^{-1}. This material was used directly in the ruthenium tetroxide oxidation.

Authentic S-Cyclohexyl-N-(p-tolylsulfonyl)-S-p-tolylsulfoximine. Ruthenium tetroxide oxidation of S-cyclohexyl-S-p-tolyl-N-p-tolylsulfilimine (7.18 g, 19.1 mmol), as already outlined for sulfilimine **2b** above (reaction time 8 h), gave a solid after ether evaporation (6.25 g, 16.0 mmol, 83% yield): mp 116–117 °C; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.72–8.16 (m, 4 H, Ar), 7.45 (d, 2 H, J = 8.5 Hz, Ar), 7.26 (d, 2 H, J = 8.4 Hz, Ar), 3.32 (br m, 1 H, α-CH), 0.8–2.40 (br, 10 H, ring CH_2); IR (KBr) 1601, 1455, 1315, 1308, 1225, 1210, 1152, 1108, 1094, 1071, 1015, 815, 750, 675 cm^{-1}. Anal. Calcd for $C_{20}H_{25}NO_3S_2$: C, 61.35; H, 6.44. Found: C, 61.36; H, 6.38.

Dehydrogenation of Mixture of Cycloadducts 6b and 6c. The mixture of cycloadducts from vinylsulfoximine **1b** and 2-methyl-1,3-butadiene (124 mg, 0.309 mmol) was dissolved in dry tetrahydrofuran (ca. 15 mL). The solution was cooled to −78 °C in a dry ice–acetone bath and butyllithium (0.15 mL, 2.32 M in hexane, 3.5 mmol) was added. The yellow solution was removed from the cold bath and allowed to warm and stirred for 20 min and recooled to −78 °C. Bromine (ca. 50 μL, ca. 0.98 mmol) was added. The solution turned blue and was removed from the cold bath. After 15 min of stirring, the solution turned yellow. Cyclohexene (0.1 mL) was added to consume excess bromine. Water (100 mL) was added and the mixture was extracted with methylene chloride (3 × 50 mL). Solvent was removed at reduced pressure. Toluene (ca. 15 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.37 mL, ca. 2.5 mmol) were added, and the solution was stirred overnight at room temperature and filtered. The solvent was removed at reduced pressure and the residue purified by preparative thin-layer chromatography (50% ethyl acetate/hexane) to give an oil (48.7 mg). A portion of the sample was subjected to HPLC analysis, which revealed three minor components and one major component. The major component comprised 64% of the mixture (7.8 mmol, 25% yield) and was collected. ^{1}H NMR and IR spectra were identical with authentic S,S-di-p-tolyl-N-(p-tolylsulfonyl)sulfoximine prepared below. A portion of the sample was recrystallized from absolute ethanol: mp 97–98 °C; mmp with authentic compound 97–100 °C.

Authentic S,S-Di-p-tolyl-N-(p-tolylsulfonyl)sulfoximine. Di-p-tolyl sulfoxide (2.46 g, 10.7 mmol) was dissolved in methanol (25 mL). p-Tolylsulfonyl azide (2.2 g, 11 mmol) and freshly precipitated copper (rinsed with methanol) were added. The mixture was refluxed for 8 h, and the green mixture was filtered through Celite. Dilute sulfuric acid (100 mL) was added and the mixture was extracted with methylene chloride (3 × 50 mL). The combined organic extracts were dried over anhydrous magnesium sulfate. The solvent was removed at reduced pressure to give a colorless oil. This material was ca. 40% product and 60% starting sulfoxide by ^{1}H NMR analysis. This material was ca. 40% product and 60% starting sulfoxide by ^{1}H NMR analysis. Recrystallization from ethanol gave S,S-di-p-tolyl-N-(p-tolylsulfonyl)sulfoximine (1.20 g, 3.01 mmol, 34%): mp 97–100 °C. The analytical sample was recrystallized from absolute ethanol: mp 100–102 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.82–7.92 (m, 6 H, Ar), 7.29 (d, 4 H, J = 8.3 Hz, Ar), 7.22 (d, 2 H, J = 8.2 Hz, Ar), 2.38 (s, 6 H, $ArCH_3$), 2.38 (s, 3 H, $ArCH_3$); IR (KBr) 1595, 1317, 1305, 1237, 1213, 1152, 1089, 1051, 1011, 811, 758, 701 cm^{-1}. Anal. Calcd for $C_{21}H_{21}NO_3S_2$: C, 63.13; H, 5.30. Found: C, 62.90; H, 5.23.

Bicyclo[2.2.2]oct-2-ene by Desulfurization of Cycloadducts 5, n = 2, G = Ts. A mixture of cycloadducts **5**, n = 2, G = Ts, (448 mg, 1.08 mmol) was dissolved in dry methanol (10 mL, distilled from magnesium methoxide). Anhydrous disodium hydrogen phosphate (613 mg, 4.32 mmol) was added and vigorous stirring begun. The mixture was cooled in a bath maintained at −20 °C, and sodium amalgam (2.07 g, 6%, 5.2 mol) was added and the flask removed from the cold bath. After 75 min at room temperature, the mixture was added to water (100 mL) and extracted with pentane (3 × 50 mL). The combined organic extracts were dried over magnesium sulfate and filtered, and the pentane was removed by distillation at atmospheric pressure. The residue was bulb to bulb distilled at atmospheric pressure to give a solid, which had IR and ^{1}H NMR spectra identical with commercially available bicyclo[2.2.2]oct-2-ene (97.0 mg, 0.897 mmol, 83% yield).

Conversion of Cycloadducts 5, n = 2, G = Ts, into Bicyclo[2.2.2]oct-2-en-5-one. To a dry three-necked round-bottomed flask was added dry tetrahydrofuran (1 mL) and butyllithium (0.62 mL, 2.3 M in hexane, 1.4 mmol). The solution was cooled in an ice water bath, and diisopropylamine (0.16 mL, 1.1 mmol) was added. After ca. 10 min at 0 °C, the cold bath was removed and replaced by a dry ice–acetone bath, and adduct **5**, n = 2, G = Ts, (490 mg, 1.18 mmol) suspended in dry tetrahydrofuran (10 mL) was added at once. The mixture turned yellow and was removed from the cold bath. Over 0.5 h the solid slowly dissolved to give a dark yellow solution. The flask was reimmersed in the −78 °C bath and MoOPH, prepared by the method of Vedejs and co-workers[22] (728 mg, 1.7 mmol), was added at once. The mixture was taken out of the bath, stirred, and allowed to warm to room temperature. During the next 20 min the solid slowly dissolved and the color went from yellow to green and back to yellow. After stirring for an additional 1 h, saturated sodium sulfite solution (5 mL) was added. The two-phase mixture was stirred for 15 min and poured into water (100 mL). The mixture was extracted with pentane (3 × 50 mL). The extracts were combined and washed with 5% hydrochloric acid (50 mL) and water (3 × 50 mL). The pentane was removed by distillation at atmospheric pressure, and the residue was distilled from bulb to bulb to give bicyclo[2.2.2]oct-2-en-5-one (52.8 mg, 0.432 mmol, 37%) as identified by its ^{1}H NMR and IR spectra.[23] The distillation residue was **5**, n = 2, G = Ts (51.2 mg, 10%). The aqueous layer, when extracted with diethyl ether, yielded additional **5**, n = 2, G = Ts (43.6 mg, 8.9%). The yield based on consumed material was 45%.

Registry No. **1a**, 71841-82-2; (S)-**1a**, 71841-93-5; **1b**, 89279-63-0; **2a**, 89279-64-1; **2b**, 89279-70-9; **3a**, 89279-65-2; **3b**, 89279-69-6; **5a** (n = 1, G = 1,2-$C_6H_4(CO)_2N$), 89279-71-0; **5a** (n = 1, G = Ts), 89279-75-4; **5a** (n = 2, G = Ts), 89279-82-3; **5b** (n = 1, G = 1,2-$C_6H_4(CO)_2N$), 89279-72-1; **5b** (n = 1, G = Ts), 89302-35-2; **5b** (n = 2, G = Ts), 89361-77-3; **5c** (n = 1, G = 1,2-$C_6H_4(CO)_2N$), 89279-73-2; **5c** (n = 1, G = Ts), 89279-76-5; **5c** (n = 2, G = Ts), 89361-78-4; **5d** (n = 1, G = 1,2-$C_6H_4(CO)_2N$), 89279-74-3; **5d** (n = 1, G = Ts), 89279-77-6; **5d** (n = 2, G = Ts), 89361-79-5; **6a**, 89279-78-7; **6b**, 89279-79-8; **6c**, 89279-80-1; **6d**, 89279-81-2; **7**, 89394-87-6; **8**, 89279-83-4; (S)-(2-chloroethyl)-S-phenyl-N-(p-tolylsulfonyl)sulfoximine, 89279-66-3; 2-chloroethyl phenyl sulfide, 5535-49-9; chloramine-T, 127-65-1; S-(2-chloroethyl)-S-phenyl-N-(p-tolylsulfonyl)sulfilimine, 89279-67-4; S-phenyl-N-(p-tolylsulfonyl)-S-vinylsulfoximine, 89279-68-5; cyclopentadiene, 542-92-7; 1,3-butadiene, 106-99-0; 2-methyl-1,3-butadiene, 78-79-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; 1,3-cyclohexadiene, 592-57-4; phenyl vinyl sulfone, 5535-48-8; cyclohexene, 110-83-8; allyl alcohol, 107-18-6; S-cyclohexyl-S-p-tolyl-N-(p-tolylsulfonyl)sulfoximine, 89279-84-5; S-cyclohexyl-S-p-tolyl-N-(p-tolylsulfonyl)sulfilimine, 89279-85-6; cyclohexyl p-tolyl sulfide, 59693-93-5; S,S-di-p-tolyl-N-(p-tolylsulfonyl)sulfoximine, 89279-86-7; di-p-tolyl sulfoxide, 1774-35-2; p-tolylsulfonyl azide, 941-55-9; bicyclo[2.2.2]-oct-2-ene, 931-64-6; bicyclo[2.2.2]oct-2-en-5-one, 2220-40-8.

Supplementary Material Available: Tables of crystal data, final atomic positional and thermal parameters, bond lengths, bond angles, and selected torsion angle data for **5d**, n = 1, G = 1,2-$C_6H_4(CO)_2N$ (7 pages). Ordering information is given on any current masthead page.

(22) Vedejs, E.; Engler, D. A.; Telschow, J. E. *J. Org. Chem.* **1978**, *43*, 188.

(23) "Aldrich Library of NMR Spectra", Vol. 2, 111B.