Chemistry of Conversions of [*o*-[1-Halo-1-(*p*-tolylsulfonyl)alkyl]benzyl]trimethylsilanes to *o*-Quinodimethanes and Benzocyclobutenes

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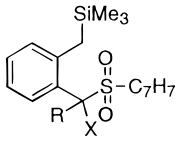
Received April 1, 1997 (Revised Manuscript Received October 14, 1997)

Trimethyl[*o*-[bromo(*p*-tolylsulfonyl)methyl]benzyl]silane (**10**) is prepared from *o*-[(trimethylsilyl)-methyl]benzyl *p*-tolyl sulfone (**9**), *n*-BuLi, and bromine. Sulfone **9** eliminates trimethylsilyl bromide upon reaction with TBAF in acetonitrile to give the presumed intermediate, α-sulfonyl-*o*-quinodimethane **11**, which (1) dimerizes to disulfone **12** and (2) is trapped by alkyl fumarates to yield (*p*-tolylsulfonyl)tetrahydronaphthalenes **17a**,**b** and **18a**,**b**, respectively. Sulfone **9** is converted by *n*-BuLi and alkyl halides to α-alkyl-α-bromosulfones **19a**−**f** which react with TBAF to give α-sulfonylbenzocyclobutenes **21a**−**f** and vinyl sulfones **23a**−**f**, apparently upon ring closure and upon 1,5-sigmatropic rearrangements of hydrogen in α-sulfonyl-*o*-quinodimethane intermediates **20a**−**f** and **22a**−**f**. Further, sulfone **9**, *n*-BuLi, and *tert*-butyl hypochlorite yield α-chlorosulfone **26** and α,α-dichlorosulfone **27**. TBAF effects dechlorotrimethylsilation of **27** to chloro(*p*-tolylsulfonyl)cyclobutene **28** presumably upon formation and cyclization of *o*-quinodimethane **29**. Silanes **10**, **19a**−**f**, and **27** are therefore practical synthons for *o*-quinodimethane intermediates **11**, **20a**−**f** and **22a**−**f**, and **29** respectively.

Introduction

α,α-Dialkyl-*o*-[(trimethylsilyl)methyl]benzyl *p*-tolyl sulfones (**1**) are eliminated by fluoride ion to α,α-dialkyl-*o*-quinodimethanes (**2**).[1] Such *o*-quinodimethanes (**2**) are of interest with respect to their multiplicities, ring closures to α,α-dialkylbenzocyclobutenes (**3**, eq 1), and Diels−Alder reactions with electron-deficient olefins (**4**, eq 2).[1] Of further significance is that **5**, with Z-α-alkyl groups with *β*-hydrogen, undergoes 1,5-sigmatropic rearrangements of hydrogen to give styrene derivatives **6** (eq 3). Study of synthesis and the behaviors of α-halo and α,α-dihalosilyl sulfones **7** and **8** with fluoride ion and the chemistry of the products thereof are now reported.[2] The uses of these reactions for advantageous synthesis have been emphasized in the present work.



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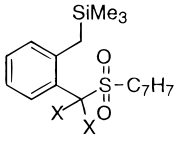

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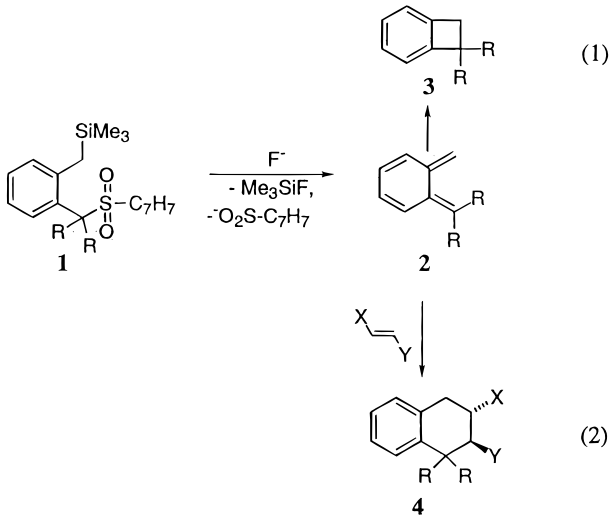
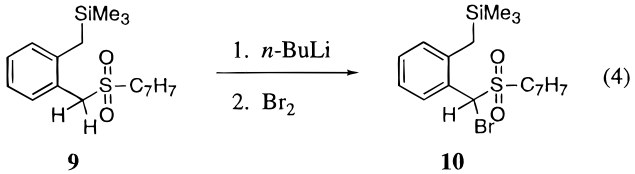


Results and Discussion

Synthesis and Reactions of Trimethyl[*o*-[bromo-(*p*-tolylsulfonyl)methyl]benzyl]silane (10). *o*-[(Trimethylsilyl)methyl]benzyl *p*-tolyl sulfone (**9**) reacts with *n*-BuLi (1 equiv) and then bromine (2 equiv) to give α-bromosulfone **10** (eq 4) in 65% yield. Use of less than 2 equiv of bromine results in recovery of large proportions



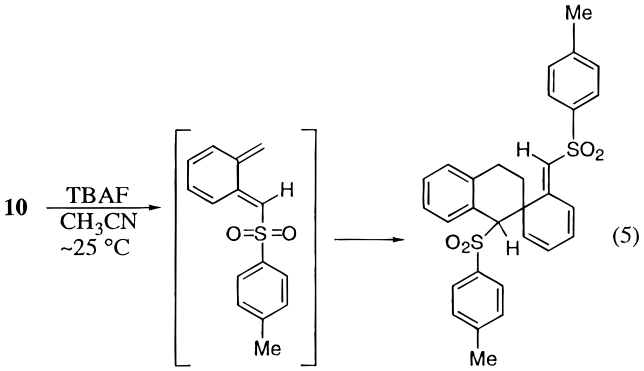
9 **10** (4)

(1) (a) Lenihan, B. D.; Shechter, H. *Tetrahedron Lett.* **1994**, *35*, 7505. (b) Lenihan, B. D.; Shechter, H. *J. Org. Chem.* **1998**, *63*, 2072.

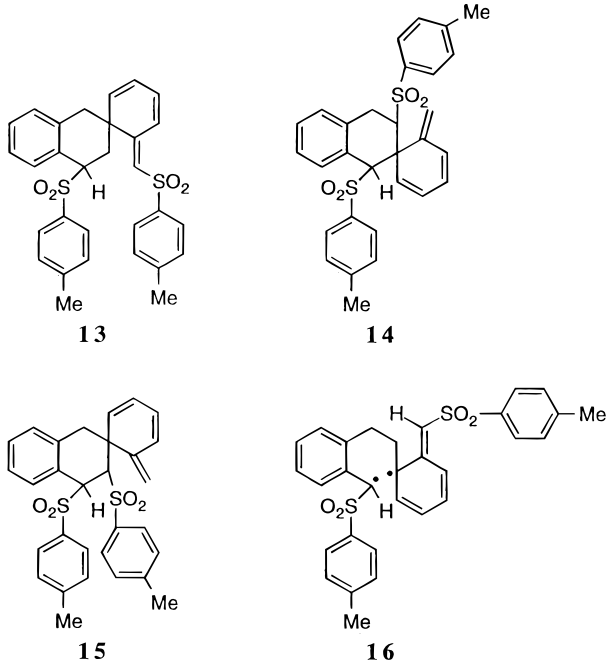
(2) Dechlorotrimethylsilylation of α-chlorosulfones is reported to be useful for synthesis of vinyl sulfones: (a) Hsiao, C.-N.; Shechter, H. *J. Org. Chem.* **1988**, *53*, 2688. (b) Hsiao, C. N.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 3455.

S0022-3263(97)00593-8 CCC: $15.00
Published on Web 03/17/1998

of the initial **9**. Reaction of **10** with TBAF in acetonitrile induces 1,4-elimination of trimethylsilyl bromide to give α-sulfonyl-*o*-quinodimethane **11** (eq 5) which dimerizes in situ to a disulfone assigned as **12**. Dimerization of **11**



via Diels−Alder reactions might also be expected to give **13**, **14**, and/or **15**. The ^{1}H NMR of the product reveals absorption, however, for only one aliphatic (sp^3-s) proton (δ 4−5) α to a sulfone group, and the signal for that proton is a sharp singlet. Structures **14** and **15** are ruled out for the dimer because they each have two aliphatic protons α to sulfone groups. Further, because the signal for the sp^3-s proton is a singlet, the proton is not on a carbon attached to carbon-containing hydrogen. The observations exclude the head to tail product **13**. The ^{1}H NMR therefore indicates that the dimer is the head to head product assigned as **12** (eq 5). Of interest is that **12** is the product predicted on the basis of stepwise dimerization of **11** as a diradical to give highly stabilized diradical **16**.



Generation of *o*-quinodimethane **11** from **10** in the presence of dimethyl fumarate and diethyl fumarate gives (*p*-tolylsulfonyl)tetrahydronaphthalenes **17a**,**b** and **18a**,**b**, respectively, in 71−93% yields. Isomers **17a** (R = Me) and **18a** (R = Et) are isolated pure in 31−38% yields upon crystallization from acetone. Isomers **17b**

Table 1. Coupling Constants[a] for Tetrahydronaphthalenes 17a,b and 18a,b

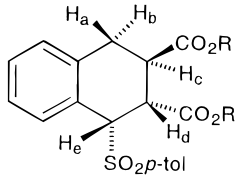
compd	J_{cd}	J_{de}	enhancement at H_d
17a	12.7	4.3	18.0%
17b	10.6	4.3	7.3%
18a	13[a]	4[a]	18.8%
18b	10.6	4.2	6.4%

[a] The coupling constants could not be determined accurately to the next decimal place in this experiment.

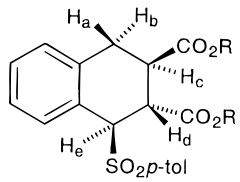
Table 2. Synthesis of α-Alkyl-α-bromosulfones 19a,b from Sulfone 9

product	R	yield, %
19a	methyl	70
19b	ethyl	52
19c	butyl	72
19d	benzyl	60
19e	4-pentenyl	58
19f	2-propyl	66

(R = Me) and **18b** (R = Et) are obtained in 30−31% yields by chromatography of the acetone mother liquors on silica gel. Reactions of **17a** with the fumarates using cesium fluoride instead of TBAF are slow (7−9 days), but the systems are cleaner and isomers **17b** and **18b** are easier to purify. Under conditions successful with the above fumarates, neither diethyl maleate nor acrylonitrile adds to **11**.



17a; R = Me
18a; R = Et

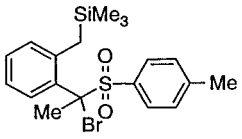
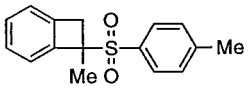
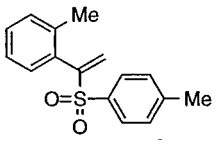
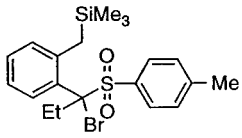
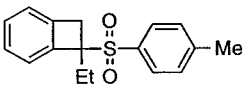
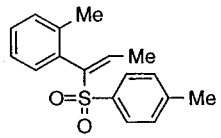
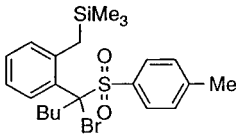
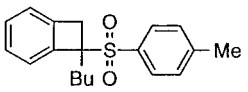
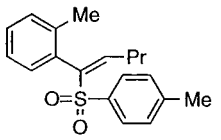
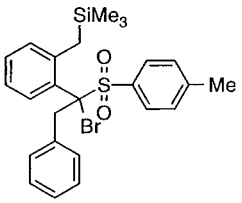
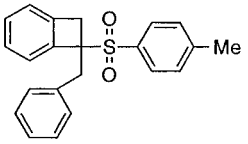
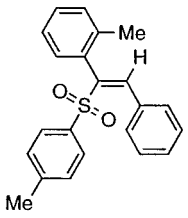
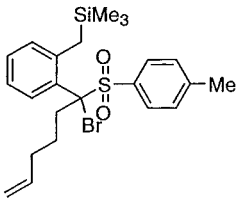
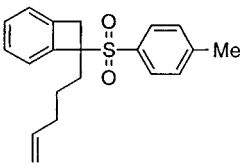
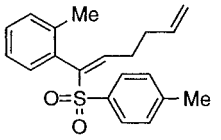
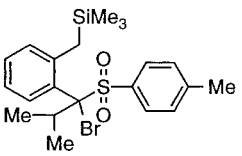
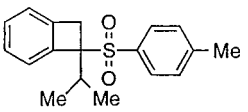
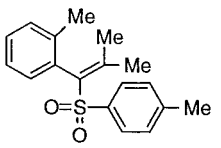


17b; R = Me
18b; R = Et

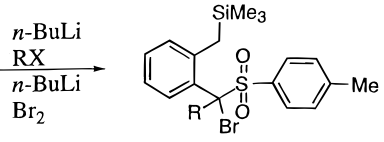
The configurations of **17a**−**18b** are assigned by NMR methods. The H_d−H_e coupling constants for **17a**−**18b** are similar and thus are not usable to establish configurations. NOE irradiation of the α-sulfonyl protons H_e in **17a** and **17b** (Table 2) do allow assignments. Isomer **17a** gives a much larger enhancement at H_d (18.0%) than does **17b** (7.3%). These data support cis stereochemistry for H_dH_e in **17a** and trans stereochemistry for H_dH_e in **17b**. Such NOE results are also obtained for **18a** and **18b** (Table 1). The coupling constants between H_c and H_d are large for **17a**,**b** and **18a**,**b** (Table 1) and support the trans stereochemistries as expected for cycloadditions of **11** to fumarate esters.

Synthesis of α-Alkyl-α-bromosulfones 19a−f and Their Conversions to Benzocyclobutenes 21a,b. α-Alkyl-α-bromosulfones **19a**−**f** are readily prepared (eq 6) from sulfone **9** by addition of *n*-BuLi and then a halide followed by *n*-BuLi and then bromine (Table 2). α-Bromo-α-methylsulfone **19a** could not be prepared efficiently in one pot because in the initial methylation methyl iodide was used and lithium iodide was formed. Unless the lithium iodide is removed, subsequent reactions of the product mixture with *n*-BuLi and bromine are complicated by oxidation of iodide ion to iodine. α-Alkyl-α-bromosulfones **19b**−**19e** are obtained satisfactorily, however, in single-pot procedures from the corresponding primary bromides (RX = R_pBr, eq 6). Alkylation of **9** upon reactions with *n*-BuLi and 2-bromopropane is complicated by elimination of the secondary bromide.

Table 3. Synthesis of Benzocyclobutenes 21a–f and Vinyl Sulfones 23a–f from α-Alkyl-α-bromosulfones 19a–f

α-Bromosulfone	Benzocyclobutene	Vinyl sulfone
 **19a**	 **21a** (11%)	 **23a** (61%)
 **19b**	 **21b** (54%)	 **23b** (15%)
 **19c**	 **21c** (61%)	 **23c** (15%)
 **19d**	 **21d** (59%)	 **23d** (17%)
 **19e**	 **21e** (50%)	 **23e** (22%)
 **19f**	 **21f** (49%)	 **23f** (21%)

Multiple additions of *n*-BuLi and 2-bromopropane are required, and the initial monoalkylated sulfone is best isolated pure before effecting its conversions by *n*-BuLi and then bromine to **19f**.



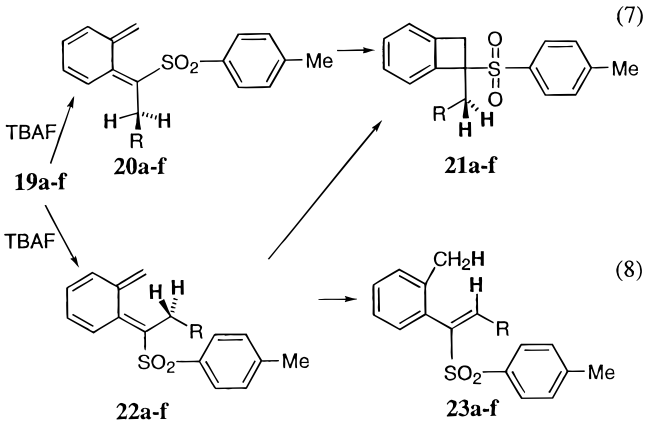
19a-f (6)

Of particular interest is that α-alkyl-α-bromosulfones **19a–f** are converted by TBAF in acetonitrile at 20–25 °C to benzocyclobutenes **21a–f** (eq 7) and vinyl sulfones **23a–f** (eq 8) as summarized in Table 3.[3,4] Other than for **21a**, benzocyclobutenes **21b–f** are the major products (49–61% yields); vinyl sulfones **23b–f** are formed in 15–

(3) For reviews of benzocyclobutenes and quinodimethanes, see ref 1 and its extensive references.

(4) 4,6-Dimethylbenzocyclobutenyl *p*-tolyl sulfone has been prepared by pyrolysis of the sodium salt of 4,6-dimethylbenzocyclobutenone (*p*-toluenesulfonyl)hydrazone: (a) Blomquist, A. T.; Heins, C. F. *J. Org. Chem.* **1969**, *34*, 2906. α-Sulfonylbenzocyclobutenes can also be synthesized by ring closures involving benzyne intermediates: (b) Bunnett, J. F.; Skorcz, J. A. *J. Org. Chem.* **1962**, *27*, 3836. (c) Gowland, B. D.; Durst, T. *Can. J. Chem.* **1979**, *57*, 1462. (d) Iwao, M. *J. Org. Chem.* **1990**, *55*, 3622. Ring closure through benzyne intermediates is a general method for synthesis of 1-substituted benzocyclobutenes: (e) Skorcz, J. A.; Kaminski, F. E.; Williams, V. Z.; Wiberg, K. B. *Org. Synth. Collect. Vol. V*, **1973**, 263. (f) Macdonald, D. I.; Durst, T. *Tetrahedron Lett.* **1986**, *27*, 2235. (g) Macdonald, D. I.; Durst, T. *J. Org. Chem.* **1988**, *53*, 3663.

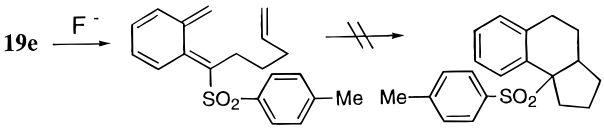
22% yields. The benzocyclobutenes give acceptable analyses and expected MS data. The most definitive evidence that **21a**−**f** are benzocyclobutenes are the ^{1}H NMR spectra of the cyclobutene ring hydrogens as doublets of doublets at δ 3−4 with the exception of the absorption for **21f**. The nonequivalent cyclobutene hydrogens in **21a**−**e** have geminal coupling constants of ∼14−15 Hz. The cyclobutene ring protons of **21f** appear as an NMR singlet because by coincidence the hydrogens all have the same chemical shifts. The vinyl sulfones **23a**−**f** are assigned from their analyses and/or HRMS and their ^{1}H NMR absorptions for vinyl hydrogens.



(7)

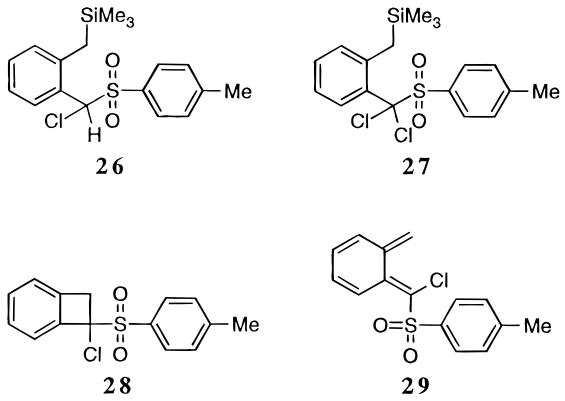
(8)

The reactions of **19a**−**f** with fluoride ion may be envisaged (eqs 7 and 8) to involve 1,4-eliminations to give isomeric *o*-quinodimethanes **20a**−**f** and **22a**−**f** which, depending on their stereochemistries, undergo intramolecular 2 + 2 cycloadditions yielding benzocyclobutenes **21a**−**f** or 1,5-sigmatropic rearrangements of hydrogen to form vinyl sulfones **23a**−**f**. Alternate mechanisms for formation of **21a**−**f** and **23a**−**f** which bypass *o*-quinodimethane intermediates involve eliminations with concerted ring closures to **21a**−**f** and eliminations with concerted hydrogen transfers to yield **23a**−**f**. What can be added to these questions of reaction mechanism are that efforts to generate and trap **20a**−**f** and **22a**−**f** with fumarate esters have failed and that elimination of α-bromo-α-(4-pentenyl)sulfone **19e** with TBAF gives benzocyclobutene **21e** and vinyl sulfone **23e** (eqs 7 and 8, Table 3) but none of the intramolecular capture product **25** (eq 9). On the basis that *o*-quinodimethane **11** is indeed formed from **10** (eq 5) and the intimate details of elimination of **19a**−**f** have not been established, steric effects are clearly important in the conversions to **21a**−**f** and **23a**−**f** and, as will be explained, the overall results are readily understandable on the basis of generation and subsequent reactions of *o*-quinodimethane intermediates **20a**−**f** and **22a**−**f** (eqs 7 and 8). Thus in elimination of **19a**, quinodimethane **22a** is formed (eqs 7 and 8) in preference to **20a** because the steric effect of the methyl group is less than that of the *p*-tolylsulfonyl group and then 1,5-sigmatropic rearrangement of one of the three hydrogen atoms of the methyl group in **22a** yields **23a** as the major product. In **19b**−**f** the α-alkyl groups are bulkier than methyl and then formation of *o*-quinodimethanes **20b**−**f** is more predominant than for **22b**−**f**. A further point is that the number of hydrogens in the 6-positions for sigmatropic rearrangement are less in **20b**−**f** than in **20a**. On the basis of steric and statistical factors, *o*-quinodimethanes **20b**−**f** form and then ring close more readily than does **20a**.



(9)

Synthesis and Conversion of [*o*-[Dichloro(*p*-tolylsulfonyl)methyl]benzyl]trimethylsilane (27) to α-Chloro-α-(*p*-tolylsulfonyl)benzocyclobutene (28). Sulfone **9** reacts with *n*-BuLi in hexane and then *tert*-butyl hypochlorite (4 equiv) to give α-chlorosulfone **26** (11%) and α,α-dichlorosulfone **27** (41%). α,α-Dichlorosulfone **27** undergoes fluoride-induced dechlorotrimethylsilylation in acetonitrile at 0 °C to yield α-chloro-α-(*p*-tolylsulfonyl)benzocyclobutene (**28**, 51%). The structure of **28** is assigned from its analyses, its MS patterns, and its ^{1}H NMR doublets at δ 3.62 and 4.20. *o*-Quinodimethane **29** may be a reaction intermediate in elimination of **27** although it could not be trapped by dimethyl fumarate or ethyl vinyl ether.



Conclusions

Halo(*p*-tolylsulfonyl)trimethylsilanes **10**, **19a**−**f**, and **27** undergo efficient dehalotrimethylsilations upon reactions with TBAF in acetonitrile at 0−25 °C to give the presumed intermediates, α-sulfonyl-*o*-quinodimethanes **11**, **20a**−**f**, **22a**−**f**, and **29**, respectively. *o*-Quinodimethane **11** undergoes directed 2 + 4 dimerization to disulfone **12** and is intercepted by dimethyl fumarate and diethyl fumarate to yield (*p*-tolylsulfonyl)tetrahydronaphthalenes **17a**,**b** and **18a**,**b**, respectively. Of note is that the α-alkyl-α-bromosulfones **19a**−**f** react with TBAF to give stable benzocyclobutenes **21a**−**f** and vinyl sulfones **23a**−**f**. Cyclobutenes **21a**−**f** are presumably formed by ring closures of **20a**−**f** and **22a**−**f**. Vinyl sulfones **23a**−**f** are apparently produced by 1,5-sigmatropic rearrangements of hydrogen in **22a**−**f**. Conversion of **27** by TBAF via quinodimethane **29** to α-chloro-α-sulfonylbenzocyclobutene (**28**) is an elegant preparative reaction, and various transformations of **28** are being studied.

Experimental Section

General Methods. The analytical, chromatographic, and spectral procedures used are identical with those previously described.[1b]

General Procedure for α-Bromination of Sulfones. [*o*-[Bromo(*p*-tolylsulfonyl)methyl]benzyl]trimethylsilane (10). To trimethyl[*o*-[(*p*-tolylsulfonyl)methyl]benzyl]-silane (**9**, 10.00 g, 30.1 mmol) in anhydrous THF (150 mL) at

−78 °C was added *n*-BuLi (23.4 mL, 31.6 mmol, 1.35 M in hexane). The yellow mixture was warmed to room temperature and then cooled to −78 °C. Bromine (3.1 mL, 60.1 mmol) was added in a single portion, and the mixture was then warmed to room temperature. After having been diluted with 1 M $NaHSO_3$, the mixture was extracted with diethyl ether. The aqueous layer was again extracted with diethyl ether, and the combined extracts were dried over $MgSO_4$ and concentrated. The resulting product was crystallized twice from methanol to yield **10** as a white crystalline solid (8.03 g, 65%, mp 98.5−101 °C): IR (KBr) 1596, 1319, 1250, 1150, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.01 (9H, s), 1.80 (1H, d, J = 14.4 Hz), 2.00 (1H, d, J = 14.4 Hz), 2.42 (3H, s), 5.95 (1H, s), 6.83−7.63 (8H, m); ^{13}C NMR ($CDCl_3$) δ −1.5 (q), 21.7 (q), 23.9 (t), 62.6 (d), 124.8 (d), 127.9 (s), 129.3 (d), 129.4 (d), 129.8 (d), 130.2 (d), 131.4 (d), 132.0 (s), 140.2 (s), 145.6 (s); MS(EI) *m/e* (relative intensity) 412.03 (1), 410.04 (1), 257.02 (49), 255.02 (48), 103.06 (49), 73.05 (100); HRMS calcd for $C_{18}H_{23}BrO_2SSi$ 410.0372; found 410.0373. Anal. Calcd for $C_{18}H_{23}BrO_2SSi$: C, 52.55; H, 5.63. Found: C, 52.77; H, 5.46.

Preparation of 3′,4′-Dihydro-1′-(*p*-tolylsulfonyl)-6-[(*p*-tolylsulfonyl)methylene]spiro[2,4-cyclohexadiene-1,2′-(1′*H*)-naphthalene] (12). To **10** (0.500 g, 1.22 mmol) in acetonitrile (8 mL) was added TBAF (2.5 mL, 2.5 mmol, 1.0 M in acetonitrile) over 40 min. The mixture was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and concentrated. The residue was crystallized from 1:1 acetone:chloroform to yield **12** as a pale yellow solid (85 mg, 27%, mp 208−209 °C): IR (neat) 1596, 1301, 1144, 1086 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72−1.79 (1H, m), 2.38 (3H, s), 2.40 (3H, s), 2.83−3.03 (2H, m), 3.08−3.17 (1H, m), 4.26 (1H, d, J = 1.3 Hz), 5.70 (1H, dd, J = 0.6, 9.5 Hz), 5.87 (1H, dd, J = 5.1, 9.5 Hz), 6.17 (1H, ddt, J = 5.2, 9.9, 1.4 Hz), 6.41 (1H, t, J = 1.3 Hz), 6.45 (1H, d, J = 7.6 Hz), 6.76−6.82 (1H, m), 7.07−7.20 (6H, m), 7.31 (2H, m), 7.48 (1H, d), 7.91−7.95 (2H, m); MS(EI) *m/e* (relative intensity) 361.12 (9), 206.11 (49), 205.10 (100), 191.09 (18), 139.03 (13), 91.06 (28).

Preparation of Dimethyl 1,2,3,4-Tetrahydro-1-(*p*-tolylsulfonyl)-2,3-naphthalenedicarboxylates (17a,b) Using Cesium Fluoride. A mixture of cesium fluoride (0.37 g), **10** (500 mg, 1.22 mmol), dimethyl fumarate (700 mg, 4.88 mmol), and acetonitrile (8 mL) was stirred for 7 days under argon. The mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, and concentrated to a white solid. The dimethyl fumarate was removed by vacuum sublimation, and the residue was recrystallized from acetone to yield **17a** (184 mg, 38%; mp 228−231 °C dec): IR (neat) 1732, 1317, 1170, 1142 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.43 (3H, s), 2.81 (1H, dd, J = 8.8, 17.7 Hz), 3.29 (1H, dd, J = 8.8, 17.7 Hz), 3.43 (1H, dd, J = 4.3, 12.7 Hz), 3.68−3.80 (7H, two s and superimposed m), 4.93 (1H, d, J = 4.3 Hz), 6.72−7.43 (8H, m); ^{13}C NMR ($CDCl_3$) δ 21.7 (q), 31.0 (t), 36.3 (d), 43.2 (d), 52.3 (q), 52.6 (q), 67.2 (d), 125.7 (d), 127.5 (s), 129.0 (d), 129.4 (d), 129.5 (d), 130.6 (d), 135.2 (s), 136.2 (s), 145.1 (s), 170.9 (s), 175.7 (s); NOE differences with irradiation at δ 4.94 give enhancements at δ 3.43 (dd, 18.0%), δ 6.7−6.8 (14.5%), and δ 7.35−7.5 (5.7%); MS(EI) *m/e* (relative intensity) 247.10 (12), 215.07 (30), 187.08 (70), 128.07 (43). Anal. Calcd for $C_{21}H_{22}O_6S$: C, 62.67; H, 5.51. Found: C, 62.44; H, 5.56.

Concentration and chromatography of the mother liquor using silica gel and $CHCl_3$ yielded **17b** as a white solid (118 mg, 24%, mp 140−146 °C): IR (neat) 1740, 1436, 1316, 1219, 1144 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (3H, s), 2.52 (1H, d), 2.64−2.75 (2H, m), 3.66 (3H, s), 3.74 (3H, s), 3.96 (1H, dd, J = 4.3, 10.6 Hz), 5.01 (1H, d, J = 4.3 Hz), 7.05 (1H, d), 7.15−7.28 (5H, m), 7.41−7.45 (2H, m); ^{13}C NMR ($CDCl_3$) δ 21.6, 31.9, 42.6, 43.8, 52.3, 52.8, 66.9, 126.3, 126.7, 128.0, 128.9, 129.4, 129.7, 131.7, 133.1, 138.3, 145.0, 172.5, 173.4; NOE differences with irradiation at δ 5.0 give enhancements at δ 2.6−2.8 (2.1%), δ 3.96 (dd, 7.2%), δ 7.15−7.25 (12.7%), and δ 7.4−7.5 (5.1%); MS(EI) *m/e* (relative intensity) 247.10 (6), 215.07 (27), 187.08 (100), 128.06 (83). Anal. Calcd for $C_{21}H_{22}O_6S$: C, 62.67; H, 5.51. Found: C, 62.74; H, 5.48.

Impure fractions (136 mg) from the chromatography were judged by NMR to be 25% **17a** and 75% **17b**, which corresponds to additional yields of 6% and 20%, respectively.

Preparation of Diethyl 1,2,3,4-Tetrahydro-1-(*p*-tolylsulfonyl)-2,3-naphthalenedicarboxylates (18a,b) Using Cesium Fluoride. A suspension of cesium fluoride (0.37 g), **10** (500 mg, 1.22 mmol), diethyl fumarate (800 mL, 4.88 mmol), and acetonitrile (8 mL) was stirred for 9 days. The reaction mixture was worked up as for **17a**,**b**. After the diethyl fumarate had been removed, recrystallization of the residue from acetone gave **18a** (195 mg, 37%; mp 206−208 °C): IR (KBr) 1730, 1325, 1175, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (3H, t, J = 7.1 Hz), 1.36 (3H, t, J = 7.1 Hz), 2.44 (3H, s), 2.76−2.87 (1H, dd, J = 8.7, 17.7 Hz), 3.34 (1H, dd, J = 9.1, 17.8 Hz), 3.42 (1H, dd, J = 4, 13 Hz), 3.75 (1H, dt, J = 9, 13 Hz), 4.17−4.93 (4H, two superimposed q, J = 7.1 Hz), 4.93 (1H, d, J = 4.1 Hz), 6.67−7.45 (8H, m); ^{13}C NMR ($CDCl_3$) δ 14.0 (q), 14.1 (q), 21.6 (q), 30.8 (s), 31.0 (t), 36.4 (d), 43.3 (d), 60.9 (t), 61.4 (t), 67.2 (d), 125.5 (d), 127.7 (s), 128.9 (d), 129.3 (d), 129.4 (d), 130.4 (d), 135.2 (s), 136.2 (s), 145.0 (s), 170.3 (s), 175.0 (s); NOE differences with irradiation at δ 4.92 give enhancements at δ 3.42 (dd, 18.8%), δ 6.65−6.75 (15.0%), and δ 7.4−7.5 (6.1%); MS(EI) *m/e* (relative intensity) 275.13 (14), 229.09 (44), 201.09 (73), 129.08 (94). Anal. Calcd for $C_{23}H_{26}O_6S$: C, 64.17; H, 6.09. Found: C, 64.39; H, 6.13.

The mother liquor on concentration and chromatography on silica gel gave **18b** (157 mg, 30%), an oil: IR (KBr) 1732, 1317, 1213, 1146, 757, 578 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (3H, t), 1.29 (3H, t), 2.41 (3H, s), 2.51 (1H, d), 2.59−2.73 (2H, m), 3.97 (1H, dd, J = 4.2, 10.6 Hz), 4.05−4.3 (4H, m), 5.04 (1H, d, J = 4.1 Hz), 7.06 (1H, d), 7.1−7.3 (5H, m), 7.4−7.5 (2H, m); NOE differences with irradiation at δ 5.04 gave enhancements at δ 2.6−2.75 (1.2%), δ 3.97 (6.4%), δ 7.2−7.3 (13.3%), and δ 7.4−7.5 (4.6%). Impure fractions yielded 170 mg of a mixture of **18a** and **18b** in a ratio of 15:85, respectively, as judged by NMR. The additional yields of **18a** and **18b** are 6% and 26%, respectively.

Preparation of Dimethyl 1,2,3,4-Tetrahydro-1-(*p*-tolylsulfonyl)-2,3-naphthalenedicarboxylates (17a,b) Using TBAF. A solution of **10** (250 mg, 0.61 mmol) and dimethyl fumarate (350 mg, 2.43 mmol) in CH_2Cl_2 (4 mL) at 0 °C was treated with TBAF (1.2 mL, 1.2 mmol, 1.0 M in acetonitrile) over 30 min. After product workup, the dimethyl fumarate was removed via sublimation and the residue was recrystallized from acetone to yield **17a** (77 mg, 31%). The ^1H NMR agreed with that of **17a** described previously. Chromatography of the mother liquor on silica gel using $CHCl_3$ yielded an impure mixture (117 mg) which NMR indicated to be 19% **17a** and 65% **17b**, which corresponds to yields of 9% and 31%, respectively.

Preparation of Diethyl 1,2,3,4-Tetrahydro-1-(*p*-tolylsulfonyl)-2,3-naphthalenedicarboxylates (18a,b) Using TBAF. TBAF (2.5 mL, 2.5 mmol, 1.0 M in acetonitrile) in acetonitrile (5 mL) was added in 100 min to **10** (506 mg, 1.23 mmol) and diethyl fumarate (1.00 mL, 6.10 mmol) in anhydrous acetonitrile (5 mL) at 0 °C. The white cloudy mixture was worked up as for **17a**,**b**. The residue was recrystallized from acetone to yield **18a** (203 mg, 38%) for which the ^1H NMR agreed with that of **18a** described previously. Chromatography of the mother liquor on silica gel using 1:19 ethyl acetate:ligroin gave **18b** (118 g, 22%) which has an ^1H NMR spectrum similar to that previously described.

[*o*-[1-Bromo-1-(*p*-tolylsulfonyl)ethyl]benzyl]trimethylsilane (19a). The product of reaction of trimethyl[*o*-[1-(*p*-tolylsulfonyl)ethyl]benzyl]silane[1b] (6.50 g, 18.8 mmol) with *n*-BuLi (13.2 mL, 19.7 mmol, 1.49 M in hexane) and then bromine (1.9 mL, 38 mmol) is an oil which was crystallized twice from methanol to yield **19a** as a white solid (5.57 g, 70%): IR (KBr) 1593, 1322, 1303, 1248, 1153, 848 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (9H, s), 2.33−2.39 (4H, s and superimposed d), 2.52 (3H, s), 3.12 (1H, d, J = 14.4 Hz), 6.86−7.45 (8H, m); ^{13}C NMR ($CDCl_3$) δ −0.5, 21.6, 26.9, 31.6, 79.2, 123.6, 129.0, 129.4, 130.6, 130.8, 131.0, 131.9, 144.5, 145.1; MS(EI) *m/e* (relative intensity) 218.99 (35), 191.12 (31), 131.00 (38), 117.07 (49), 91.06 (37), 73.05 (100). Two crystallizations from

methanol yielded an analytical sample (mp 106 °C). Anal. Calcd for $C_{19}H_{25}BrO_2SSi$: C, 53.64; H, 5.92. Found: C, 53.42; H, 5.89.

[*o*-[1-Bromo-1-(*p*-tolylsulfonyl)propyl]benzyl]trimethylsilane (19b). Alkylation of **9** (2.00 g, 6.01 mmol) with *n*-BuLi (2.30 mL, 6.2 mmol, 2.71 M in hexane) and ethyl bromide (0.47 mL, 6.32 mmol) followed by *n*-BuLi (2.30 mL, 6.2 mmol, 2.71 M in hexane) and bromine (0.62 mL, 12.0 mmol) and workup gave an oil which crystallized from methanol to yield **19b** (1.36 g, 52%, mp 92−97 °C): IR (KBr) 1594, 1319, 1304, 1247, 1147, 846 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.02 (9H, s), 1.11 (3H, t, J = 7.0 Hz), 2.01 (1H, d, J = 14.2 Hz), 2.39 (3H, s), 2.42−2.63 (1H, m), 2.84−3.02 (1H, m), 3.21 (1H, d, J = 14.2 Hz), 6.84−6.99 (2H, m), 7.05−7.40 (4H, m), 7.3−7.4 (2H, br d); ^{13}C NMR ($CDCl_3$) δ −0.6, 10.0, 21.6, 26.5, 32.6, 87.5, 123.4, 127.0, 128.9, 129.2, 130.9, 131.3, 131.4, 132.2, 145.0, 145.7; MS(EI) *m/e* (relative intensity) 285.05 (35), 283.05 (32), 229.07 (24), 131.09 (39), 91.07 (51), 73.05 (100). Recrystallization from ligroin yielded an analytical sample of **19b** (mp 97−98.5 °C). Anal. Calcd for $C_{20}H_{27}BrO_2SSi$: C, 54.66; H, 6.19. Found: C, 54.76; H, 6.22.

[*o*-[1-Bromo-1-(*p*-tolylsulfonyl)pentyl]benzyl]trimethylsilane (19c). Alkylation of **9** (2.00 g, 6.01 mmol) using *n*-BuLi (2.30 mL, 6.2 mmol, 2.71 M in hexane) and 1-bromobutane (0.68 mL, 6.32 mmol) followed by *n*-BuLi (2.30 mL, 6.2 mmol, 2.71 M in hexane) and bromine (0.61 mL, 12.0 mmol) yielded an oil which crystallized from methanol to give **19c** (mp 66−72 °C, 0.875 g): IR (KBr) 1596, 1325, 1246, 1148, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.02 (9H, s), 0.91 (3H, t), 1.30−1.50 (3H, m), 1.60−1.69 (1H, m), 1.95 (1H, d, J = 14.2 Hz), 2.39 (3H, s), 2.43−2.59 (1H, m), 2.80−2.95 (1H, m), 3.16 (1H, d, J = 14.2 Hz), 6.84−6.97 (2H, m), 7.03−7.22 (4H, m), 7.33−7.38 (2H, d); ^{13}C NMR ($CDCl_3$) δ −0.6, 13.8, 21.6, 22.5, 26.4, 27.5, 38.9, 86.6, 123.4, 127.5, 128.8, 129.2, 130.9, 131.3, 131.4, 132.1, 145.0, 145.4; MS(EI) *m/e* (relative intensity) 313.08 (15), 311.08 (15), 229.07 (17), 117.07 (56), 73.05 (100). A portion was recrystallized from ligroin to obtain an analytical sample (mp 69−72 °C). Anal. Calcd for $C_{22}H_{31}BrO_2SSi$: C, 56.52; H, 6.68. Found: C, 56.61; H, 6.72. The mother liquor was chromatographed on silica gel using 1:15 ethyl acetate:petroleum ether to yield additional **19c** (1.15 g, total yield 72%).

[*o*-[α-Bromo-α-(*p*-tolylsulfonyl)phenethyl]benzyl]trimethylsilane (19d). Sulfone **9** (3.00 g, 9.02 mmol) in THF (60 mL) was alkylated with *n*-BuLi (3.45 mL, 9.3 mmol, 2.71 M in hexane) and benzyl bromide (1.2 mL, 10.1 mmol) followed by reactions with *n*-BuLi (3.5 mL, 9.5 mmol, 2.71 M in hexane) and bromine (0.95 mL, 19 mmol). Product workup and crystallization from methanol yielded **19d** as a white solid (2.74 g, 60%, mp 129−131 °C): IR (KBr) 1596, 1322, 1247, 1148, 1082, 842 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.04 (9H, s), 1.82 (1H, d, J = 14.2 Hz), 2.41 (3H, s), 3.19 (1H, d, J = 14.3 Hz), 4.00 (1H, d, J = 16.7 Hz), 4.52 (1H, d, J = 16.7 Hz), 6.82−6.90 (1H, m), 7.05−7.25 (10H, m), 7.37−7.42 (2H, d); ^{13}C NMR ($CDCl_3$) δ −0.6, 21.6, 26.5, 43.2, 85.5, 123.3, 126.7, 127.4, 127.9, 128.9, 129.5, 130.1, 130.7, 131.3, 132.3, 132.7, 134.9, 145.2, 145.2; MS(EI) *m/e* (relative intensity) 420.06 (2), 347.06 (5), 345.07 (5), 266.14 (8), 229.07 (13), 193.14 (60), 115.05 (22), 91.05 (24), 73.05 (100). An analytical sample (mp 129−130.5 °C) of **19d** was obtained by recrystallization from ligroin. Anal. Calcd for $C_{25}H_{29}BrO_2SSi$: C, 59.87; H, 5.83. Found: C, 59.77; H, 5.86.

[*o*-[1-Bromo-1-(*p*-tolylsulfonyl)-5-hexenyl]benzyl]trimethylsilane (19e). Alkylation of **9** (2.00 g, 6.01 mmol) using *n*-BuLi (2.30 mL, 6.2 mmol, 2.71 M in hexane) and 5-bromo-1-pentene (0.78 mL, 6.6 mmol) followed by *n*-BuLi (2.30 mL, 6.2 mmol, 2.71 M in hexane) and bromine (0.32 mL, 6.3 mmol) and workup yielded **19e** which was crystallized from methanol (1.67 g, 58%, mp 110−113 °C): IR (KBr) 1596, 1323, 1246, 1147, 849 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.02 (9H, s), 1.44−1.61 (1H, m), 1.68−1.87 (1H, m), 1.93 (1H, d, J = 14.2 Hz), 2.15 (2H, q), 2.40 (3H, s), 2.43−2.59 (1H, m), 2.82−2.97 (1H, m), 3.15 (1H, d, J = 14.2 Hz), 4.95−5.07 (2H, m), 5.65−5.87 (1H, m), 6.84−6.95 (2H, m), 7.04−7.23 (4H, m), 7.36 (2H, d); ^{13}C NMR ($CDCl_3$) δ −0.6 (q), 21.6 (q), 24.7 (t), 26.4 (t), 33.3 (t), 38.7 (t), 86.6 (s), 115.6 (t), 123.4 (d), 127.5 (s), 128.9 (d), 129.2 (d), 130.9 (s), 131.3 (d), 131.5 (d), 132.2 (d), 137.5 (d), 145.1 (s), 145.5 (s); MS(EI) *m/e* (relative intensity) 229.07 (16), 171.12 (27), 129.07 (48), 91.06 (26), 73.05 (100). A portion of the solid was recrystallized from petroleum ether to obtain an analytical sample (mp 112−114 °C). Anal. Calcd for $C_{23}H_{31}BrO_2SSi$: C, 57.61; H, 6.52. Found: C, 57.46; H, 6.55.

[*o*-[1-Bromo-2-methyl-1-(*p*-tolylsulfonyl)propyl]benzyl]trimethylsilane (19f). Reaction of trimethyl[*o*-[2-methyl-1-(*p*-tolylsulfonyl)propyl]benzyl]silane[1b] (1.00 g, 2.67 mmol) with *n*-BuLi (1.15 mL, 2.80 mmol, 2.44 M in hexane) and bromine (0.27 mL, 5.3 mmol) and workup gave an oil which after chromatography on silica gel using 1:19 ethyl acetate:ligroin yielded **19f**, an oil, as the first eluent (1.09 g). Crystallization from petroleum ether gave pure **19f** (mp 89−93 °C, 0.801 g, 66%): IR (KBr) 1597, 1316, 1247, 1156, 854 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (9H, s), 0.95 (3H, d, J = 6.5 Hz), 1.57 (3H, d, J = 6.1 Hz), 2.34 (3H, s), 2.83 (1H, d, J = 14.4 Hz), 3.45−3.5 (1H, m), 6.8−7.2 (7H, m), 7.48−7.53 (1H, m); ^1H NMR (C_6D_6, 350 K) δ 0.04 (9H, s), 0.88 (3H, d, J = 6.5 Hz), 1.69 (3H, d, J = 6.1 Hz), 1.87 (3H, s), 2.03 (1H, d, J = 14.4 Hz), 3.05 (1H, d, J = 14.5 Hz), 3.55 (1H, septet, J = 6.3 Hz), 6.62−6.72 (3H, m), 6.83−6.93 (2H, m), 7.36 (2H, d), 7.56−7.60 (1H, d); ^{13}C NMR ($CDCl_3$) δ −0.4 (q), 20.5 (q), 21.1 (q), 21.5 (q), 26.2 (t), 35.5 (d), 123.7 (d), 128.5 (d), 128.7 (d), 130.9 (d), 132.4 (d), 132.8 (s), 144.6 (s); ^{13}C NMR (C_6D_6, 350 K) δ −0.2, 21.0, 21.1, 21.5, 26.9, 36.1, 98.5, 124.1, 128.6, 128.7, 131.5, 132.5, 132.7, 133.9, 134.7, 144.0, 144.3; MS(EI) *m/e* (relative intensity) 145.09 (33), 91.05 (16), 73.04 (100). Recrystallization from ligroin yielded an analytical sample of **19f**. Anal. Calcd for $C_{21}H_{29}BrO_2SSi$: C, 55.62; H, 6.45. Found: C, 55.79; H, 6.42.

Reaction of 19a with TBAF. Preparation of *p*-Tolyl 1-*o*-Tolylvinyl Sulfone (23a) and 7-Methyl-7-(*p*-tolylsulfonyl)bicyclo[4.2.0]octa-1,3,5-triene (21a). TBAF (2.3 mL, 1.0 M in acetonitrile) was added in 90 min to **19a** (0.497 g, 1.17 mmol) in acetonitrile (8 mL). The mixture was diluted with water and extracted with diethyl ether. The organic phase was washed with water and saturated NaCl, dried over $MgSO_4$, and concentrated. Crystallization from methanol yielded **23a** (0.137 g, 43%): IR (KBr) 1313, 1147 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.93 (3H, s), 2.38 (3H, s), 5.76 (1H, s), 6.69 (1H, s), 6.92−7.24 (6H, m), 7.47 (2H, d); ^{13}C NMR ($CDCl_3$) δ 19.2 (q), 21.5 (q), 125.1 (d), 126.4 (t), 128.8 (d), 129.1 (d), 129.4 (d), 130.0 (d), 130.6 (d), 131.6 (s), 135.3 (s), 137.6 (s), 144.5 (s), 150.1 (s); MS(EI) *m/e* (relative intensity) 272.09 (12), 117.07 (100); HRMS calcd for $C_{16}H_{16}O_2S$ 272.0871, found 272.0864. Two recrystallizations from methanol gave an analytical sample of **23a** (mp 90−92 °C). Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92. Found: C, 70.47; H, 5.97.

The mother liquor was chromatographed on silica gel using 1:9 ethyl acetate: petroleum ether. The first eluent contained additional **23a** (57 mg, 18%, total yield 61%). The next eluent contained **21a** (35 mg, 11%): IR (KBr) 2974, 2929, 1287, 1135 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.84 (3H, s), 2.42 (3H, s), 3.12 (1H, d, J = 14.5), 3.76 (1H, d, J = 14.6), 7.01−7.69 (8H, m); ^{13}C NMR ($CDCl_3$) δ 18.9, 21.6, 40.4, 69.3, 121.9, 123.4, 127.8, 129.2, 129.8, 129.9, 132.9, 141.8, 143.5, 144.5; MS(EI) *m/e* (relative intensity) 272.09 (1), 117.07 (100), 115.06 (32), 91.06 (20); HRMS calcd for $C_{16}H_{16}O_2S$ 272.0871, found 272.0876. Crystallization from ligroin yielded an analytical sample of **21a** (mp 103 °C). Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92. Found: C, 70.62; H, 5.93.

Reaction of 19b with TBAF. Preparation of 7-Ethyl-7-(*p*-tolylsulfonyl)-bicyclo[4.2.0]octa-1,3,5-triene (21b) and *p*-Tolyl 1-*o*-Tolylpropenyl Sulfone (23b). To **19b** (0.498 g, 1.13 mmol) in acetonitrile (10 mL) was added TBAF (2.3 mL, 2.3 mmol, 1.0 M in acetonitrile) in 45 min. After workup, the product was crystallized from methanol to give **21b** (0.140 g, 43%, mp 121−125 °C): IR (KBr) 2976, 2933, 1596, 1284, 1131 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (3H, t), 2.14 (1H, sextet), 2.31 (1H, sextet), 2.37 (3H, s), 3.18 (1H, d, J = 14.7 Hz), 3.55 (1H, d, J = 14.7 Hz), 6.95−6.98 (1H, m), 7.10−7.15 (1H, m), 7.19−7.26 (4H, m), 7.62 (2H, d); ^{13}C NMR ($CDCl_3$) δ 9.1, 21.5, 23.7, 36.9, 73.8, 122.9, 123.0, 127.6, 129.1, 129.6, 129.7, 133.2, 141.3, 142.3, 144.4; MS(EI) *m/e* (relative intensity) 131.09 (100), 116.06 (19), 115.06 (23), 91.05 (58). A portion of **21b**, on

crystallization from ligroin, yielded an analytical sample (mp 125−126 °C). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34. Found: C, 71.31; H, 6.35.

The mother liquor was chromatographed on silica gel using 1:15 ethyl acetate:petroleum ether as solvent. The first eluent gave **23b** (48 mg, 15%) as an oil: IR (neat film) 1641, 1597, 1312, 1301, 1148, 588 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.59 (3H, d, J = 7.0 Hz), 1.80 (3H, s), 2.38 (3H, s), 6.82−6.86 (1H,m), 7.08−7.30 (6H, m), 7.43 (2H, d); ^{13}C NMR ($CDCl_3$) δ 14.7, 18.9, 21.5, 125.4, 128.6, 129.0, 129.3, 129.6, 129.9, 131.0, 136.0, 137.9, 138.2, 142.8, 144.0; MS(EI) *m/e* (relative intensity) 286.10 (7), 131.09 (100), 116.06 (34), 115.05 (49), 91.05 (82); HRMS calcd for $C_{17}H_{18}O_2S$ 286.1027, found 286.1029. The next eluent contained additional **21b** (37 mg, 11%, total yield 54%).

Reaction of 19c with TBAF. Preparation of 7-Butyl-7-(*p*-tolylsulfonyl)-bicyclo[4.2.0]octa-1,3,5-triene (21c) and *p*-Tolyl 1-*o*-Tolyl-1-pentenyl Sulfone (23c). To **19c** (0.500 g, 1.07 mmol) in acetonitrile (10 mL) was added TBAF (2.1 mL, 2.1 mmol, 1.0 M in acetonitrile) in 45 min. After workup, the product was chromatographed on silica gel using 1:15 ethyl acetate:petroleum ether. The first eluent yielded **23c** (51 mg, 15%) as an oil: IR (KBr) 1639, 1597, 1313, 1302, 1148, 588 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84, (3H, t, J = 7.2 Hz), 1.44 (2H, sextet), 1.70−2.02 (2H, m), 1.83 (3H, s), 2.38 (3H, s), 6.80 (1H, dd), 7.01−7.25 (6H, m), 7.40−7.46 (2H, br d); ^{13}C NMR ($CDCl_3$) δ 13.7, 19.1, 21.4, 21.5, 31.0, 125.3, 128.7, 128.9, 129.3, 129.9, 131.2, 136.2, 138.3, 142.1, 142.7, 144.0; MS(EI) *m/e* (relative intensity) 314.13 (3), 159.11 (35), 117.07 (100); HRMS calcd for $C_{19}H_{22}O_2S$ 314.1340, found 314.1342.

The next eluent gave **21c** (204 mg, 61%): IR (KBr) 2958, 2940, 1597, 1292, 1133 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (3H, m), 1.1−1.4 (4H, m), 2.0−2.4 (2H, m), 2.39 (3H, s), 3.21 (1H, d, J = 14.8 Hz), 3.53 (1H, d, J = 14.8 Hz), 6.91−6.97 (1H, m), 7.08−7.23 (5H, m), 7.57−7.63 (2H, d); ^{13}C NMR ($CDCl_3$) δ 13.6, 21.4, 22.8, 26.8, 30.2, 37.6, 73.2, 122.8, 122.9, 127.5, 129.0, 129.5, 129.7, 133.1, 141.8, 142.1, 144.3; MS(EI) *m/e* (relative intensity) 159.12 (21), 117.08 (100), 115.05 (36), 91.05 (43). Crystallization from ligroin yielded an analytical sample of **21c** (mp 89−91 °C). Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.58; H, 7.05. Found: C, 72.66; H, 7.04.

Reaction of 19d with TBAF. Preparation of 7-Benzyl-7-(*p*-tolylsulfonyl)-bicyclo[4.2.0]octa-1,3,5-triene (21d) and 2-Methyl-α-(*p*-tolylsulfonyl)stilbene (23d). To **19d** (0.501 g, 1.00 mmol) in acetonitrile (10 mL) was added TBAF (2.0 mL, 1.0 M in acetonitrile) in 45 min. The mixture was diluted with water and extracted with diethyl ether. The organic layer was washed with saturated NaCl, dried over $MgSO_4$, and concentrated to an oil from which **21d** was obtained by crystallization from methanol (0.168 g, mp 136−139 °C): IR (KBr) 1286, 1149 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (3H, s), 3.06 (1H, d, J = 14.9 Hz), 3.40−3.50 (2H, two superimposed d, J = 14.9, 13.6 Hz), 3.63 (1H, d, J = 13.5 Hz), 6.70 (1H, d), 6.95−7.26 (10H, m), 7.64 (2H, d); ^{13}C NMR ($CDCl_3$) δ 21.5, 35.7, 36.0, 73.3, 122.8, 122.9, 126.7, 127.5, 127.8, 129.1, 129.7, 130.0, 130.3, 132.8, 134.7, 141.0, 142.1, 144.5; MS(EI) *m/e* (relative intensity) 193.10 (91), 178.08 (45), 115.05 (100), 91.05 (55); HRMS calcd for $C_{22}H_{20}O_2S$ 348.1184, found 348.1163. Recrystallization from ligroin yielded an analytical sample of **21d** (mp 137.5−139.5 °C). Anal. Calcd for $C_{22}H_{20}O_2S$: C, 75.83; H, 5.79. Found: C, 75.90; H, 5.80.

The mother liquor was concentrated and chromatographed on silica gel using 1:9 ethyl acetate:ligroin as solvent. The first eluent contained **23d** (60 mg, 17%) as an oil: IR (neat film) 1627, 1597, 1312, 1142, 1087 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73 (3H, s), 2.40 (3H, s), 6.95−7.35 (11H, m), 7.49 (2H, d), 7.97 (1H, s); ^{13}C NMR ($CDCl_3$) δ 19.0, 21.6, 126.0, 128.6, 128.9, 129.3, 129.4, 129.9, 130.1, 130.3, 130.4, 131.1, 133.1, 135.7, 137.6, 138.2, 140.2, 144.2; MS(EI) *m/e* (relative intensity) 348.12 (11), 209.10 (13), 193.10 (100), 178.08 (38), 115.06 (51), 91.06 (23); HRMS calcd for $C_{22}H_{20}O_2S$ 348.1184, found 348.1158. The next eluent contained additional **21d** (36 mg; total yield 204 mg, 59%).

Reaction of 19e with TBAF. Preparation of 7-(4-Pentenyl-7-(*p*-tolylsulfonyl)bicyclo[4.2.0]octa-1,3,5-triene (21e) and *p*-Tolyl 1-*o*-Tolyl-1,5-hexadienyl Sulfone (23e). To **19e** (0.499 g, 1.04 mmol) in acetonitrile (10 mL) was added in 50 min TBAF (2.1 mL, 2.1 mmol, 1.0 M in acetonitrile). After workup, the crude product was chromatographed on silica gel using 1:15 ethyl acetate:ligroin. The first eluent yielded **23e** (72 mg, 22%): IR (neat film) 1640, 1597, 1313, 1301, 1147 cm^{-1}; ^1H NMR δ 1.87 (3H, s), 1.9−2.4 (4H, m), 2.40 (3H, s), 4.95−5.03 (2H, m), 5.69 (1H, m), 6.77 (1H, d), 7.04−7.47 (8H, m); MS(EI) *m/e* (relative intensity) 171.11 (79), 143.08 (28), 129.06 (56), 105.06 (85); HRMS calcd for $C_{20}H_{22}O_2S$ 326.1340, found 326.1321.

The second eluent contained **21e** (168 mg, 50%) as an oil: IR (neat film) 2936, 1640, 1597, 1457, 1311, 1300, 1288, 1148 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35−1.52 (2H, m), 1.99−2.35 (4H, m), 2.39 (3H, s), 3.20 (1H, d, J = 14.8 Hz), 3.54 (1H, d, J = 14.8 Hz), 4.89−4.98 (2H, m), 5.70 (1H, m), 6.94−6.97 (1H, m), 7.13−7.26 (5H, m), 7.58−7.62 (2H, d); ^{13}C NMR ($CDCl_3$) δ 21.5, 24.2, 30.1, 33.8, 37.8, 73.2, 115.1, 123.0, 123.1, 127.7, 129.1, 129.7, 129.8, 133.1, 137.8, 141.8, 142.2, 144.4; MS(EI) *m/e* (relative intensity) 171.12 (20), 143.09 (18), 129.08 (100), 115.06 (41), 91.05 (50), 55.06 (24). The product was chromatographed on silica gel using 1:9 ethyl acetate:ligroin. Anal. Calcd for $C_{20}H_{22}O_2S$: C, 73.58; H, 6.79. Found: C, 73.51; H, 6.80.

Reaction of 19f with TBAF. Preparation of 7-(2-Propyl)-7-(*p*-tolylsulfonyl)bicyclo[4.2.0]octa-1,3,5-triene (21f) and 2-Methyl-1-*o*-tolylpropenyl *p*-Tolyl Sulfone (23f). To **19f** (0.500 g, 1.10 mmol) in acetonitrile (10 mL) in 35 min was added TBAF (2.2 mL, 2.2 mmol, 1.0 M in acetonitrile). Workup yielded an oil which solidified. Recrystallization from methanol gave **21f** as a white solid (0.138 g, 42%, mp 137−140 °C): IR (KBr) 1596, 1286, 1131, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (3H, d, J = 6.9 Hz), 1.21 (3H, d, J = 6.7 Hz), 2.33 (3H, s), 2.77 (1H, septet, J = 6.8 Hz), 3.31 (2H, s), 6.85 (1H, d), 7.04−7.26 (5H, m), 7.50 (2H, d); ^{13}C NMR ($CDCl_3$) δ 19.4, 20.1, 21.5, 29.0, 35.4, 77.4, 122.8, 123.5, 127.5, 128.8, 129.3, 129.6, 133.8, 142.3, 142.6, 144.0; MS(EI) *m/e* (relative intensity) 145.10 (100), 117.07 (38), 91.05 (30). One recrystallization from ligroin yielded an analytical sample of **21f**. Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.97; H, 6.71. Found: C, 72.04; H, 6.72.

The mother liquor was chromatographed on silica gel. An oil (94 mg) was obtained which NMR indicated to be 25% **21f** (additional yield of **21f**: 24 mg, 7%, total yield: 49%) and 75% **23f** (yield of **23f**: 70 mg, 21%): ^1H NMR ($CDCl_3$) δ 1.55 (3H, s), 2.02 (3H, s), 2.37 (3H, s), 2.43 (3H, s), 6.83−6.86 (1H, m), 7.0−7.2 (5H, m), 7.49−7.54 (2H, m).

[*o*-[Chloro(*p*-tolylsulfonyl)methyl]benzyl]trimethylsilane (26) and [*o*-[Dichloro(*p*-tolylsulfonyl)methyl]-benzyl]trimethylsilane (27). To sulfone **9** (5.00 g, 15 mmol) in THF (100 mL) at −78 °C was added *n*-BuLi (12.2 mL, 16.5 mmol, 1.35 M in hexane). After being warmed to room temperature, the solution was cooled to −78 °C, and *tert*-butyl hypochlorite (7.0 mL, 62 mmol) was added. The mixture was warmed to room temperature and protected from bright light. To the pale yellow solution were added two 1 mL portions of *tert*-butyl hypochlorite, and the mixture became colorless. The solution was diluted with 10% sodium bisulfite and extracted twice with diethyl ether. The combined diethyl ether extracts were washed with saturated NaCl, dried over $MgSO_4$, and concentrated. The material was recrystallized three times from methanol to obtain **27** (2.49 g, 41%): IR (KBr) 1594, 1337, 1159, 849 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (9H, s), 2.44 (3H, s), 2.70 (2H, s), 6.97−7.73 (8H, m); ^{13}C NMR ($CDCl_3$) δ −0.8 (q), 21.7 (q), 26.8 (t), 100.7 (s), 123.6 (d), 128.3 (s), 129.1 (d), 129.3 (s), 130.6 (d), 131.9 (d), 131.9 (d), 132.2 (d), 143.7 (s), 146.2 (s); MS(EI) *m/e* (relative intensity) 247.03 (22), 245.04 (32), 73.05 (100). Additional crystallizations from methanol yielded an analytical sample (mp 118−119.5 °C). Anal. Calcd for $C_{18}H_{22}Cl_2O_2SSi$: C, 53.86; H, 5.52. Found: C, 53.55; H, 5.48.

Concentration of the mother liquors from the first two crystallizations followed by crystallization from petroleum ether gave **26** (0.62 g, 11%) as a solid: ^1H NMR ($CDCl_3$) δ 0.01 (9H, s), 1.98 (1H, d, J = 14.5 Hz), 2.28 (1H, d, J = 14.3 Hz), 2.46 (3H, s), 5.89 (1H, s), 6.94−7.41 (6H, m), 7.61 (2H, d).

7-Chloro-7-(*p*-tolylsulfonyl)bicyclo[4.2.0]octa-1,3,5-triene (28). TBAF (5.0 mL, 5.0 mmol, 1.0 M in acetonitrile) was added in 45 min to **27** (979 mg, 2.44 mmol) in acetonitrile (20 mL) at 0 °C. The mixture was stirred at room temperature 15 min, diluted with dichloromethane, washed with water, dried over $MgSO_4$, and concentrated. The oily solid obtained was crystallized from methanol to yield **28** (374 mg, 51%), which was recrystallized from methanol to give a sample melting at 148−150 °C: IR (KBr) 1595, 1316, 1156 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.46 (3H, s), 3.62 (1H, d, J = 14.7 Hz), 4.20 (1H, d, J = 14.7 Hz), 7.03 (1H, d), 7.15 (1H, d), 7.26−7.44 (4H, m), 7.81 (2H, d); ^{13}C NMR ($CDCl_3$) δ 21.7 (q), 45.7 (t), 79.9 (s), 122.2 (d), 123.5 (d), 128.8 (d), 129.5 (d), 130.7 (d), 131.5 (s), 132.1 (d), 140.4 (s), 141.6 (s), 145.7 (s). The product was then recrystallized three times (using methanol and 1:4 ethyl acetate:ligroin) to obtain an analytical sample: MS(EI) *m/e* (relative intensity) 139.02 (36), 137.02 (100), 102.05 (22), 101.04 (21). Anal. Calcd for $C_{15}H_{13}ClO_2S$: C, 61.54; H, 4.48. Found: C, 61.12; H, 4.53.

Acknowledgment. We thank the National Science Foundation for support of this research.

Supporting Information Available: NMR spectra (60 pages). This material is contained in libraries on microfiche, immediately follows this article in the miocrofilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

JO9705935