Articles

Synthesis and Conversions of Substituted *o*-[(Trimethylsilyl)methyl]benzyl *p*-Tolyl Sulfones to *o*-Quinodimethanes and Products Thereof

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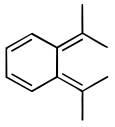
Use of *o*-[(trimethylsilyl)methyl]benzyl *p*-tolyl sulfone (**3**) for synthesis and cycloaddition of substituted *o*-quinodimethanes has been investigated. Sulfone **3** is prepared from 2-methylbenzyl alcohol (**4**) by reactions with *n*-BuLi and chlorotrimethylsilane to form *o*-[(trimethylsilyl)methyl]-benzyl alcohol (**7**) which phosphorus tribromide converts to *o*-[(trimethylsilyl)methyl]benzyl bromide (**8**). Displacement of **8** with sodium *p*-toluenesulfinate yields **3**. Sulfone **3** is alkylated at its α-sulfonyl position upon deprotonation with *n*-BuLi followed by methyl iodide, ethyl, butyl, allyl, and benzyl bromides, and 5-bromo-1-pentene, respectively. Acylations occur using acid chlorides. Dialkylation occurs upon further reaction with *n*-BuLi and an alkyl halide. 1,4-Eliminations of α,α-dialkyl sulfones **11** with tetrabutylammonium fluoride (TBAF) give α,α-dialkyl-*o*-quinodimethanes (**29**); **3** is therefore a synthon for the *o*-quinodimethane-α,α-dianion (**34**). *o*-Quinodimethanes **29** undergo (1) cycloaddition with acrylonitrile, acrylate esters, and alkyl fumarates to yield 1,1-disubstituted-tetrahydronaphthalenes (**30**) and (2) 1,5-sigmatropic rearrangements of hydrogen to give styrenes (**32**). The stereochemistries of the various cycloadditions reveal significant mechanism information.

Introduction

Synthesis and the chemistry of *o*-quinodimethanes (**1**) and benzocyclobutenes (**2**) are subjects of considerable interest.[1] Important to the inception of this research is that 1,4-elimination of [*o*-((trimethylsilyl)methyl)benzyl]-trimethylammonium halides by fluoride ion is a versatile method for generating substituted *o*-quinodimethanes which cycloadd with dienophiles to form substituted tetrahydronaphthalenes.[2] Preparation and utilization of trimethyl[*o*-[*p*-tolylsulfonyl)methyl]benzyl]silane (**3**) for generating and determining the detailed chemistry of **1** are now reported.[3] The present study has its specific origins in that (1) fluoride-induced (trimethylsilyl)benzenesulfonyl eliminations of 1-(benzenesulfonyl)-2-(trimethylsilyl)ethane and related derivatives yield their corresponding olefins efficiently[4] and (2) the fluoride eliminative methodology is excellent for preparing 1,3-dienes from varied 1-(benzenesulfonyl)-4-(trimethylsilyl)-2-butenes.[5]



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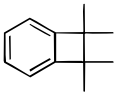

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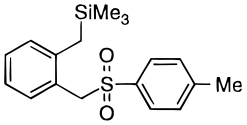

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Results and Discussion

Preparation of 3. Silyl sulfone **3** is now readily prepared in multigram quantities from 2-methylbenzyl alcohol (**4**) as shown in Scheme 1. Conditions which maximize the yield (71%) of *o*-[(trimethylsilyl)methyl]-benzyl alcohol (**7**) involve (1) reaction of **4** with *n*-BuLi (2.1 equiv) in diethyl ether at 30−35 °C followed by chlorotrimethylsilane (2.0 equiv) at −78 °C[6,7] and (2)

(1) For reviews of *o*-quinodimethanes, benzocyclobutenes, and related chemistry with important references therein, see: (a) Klundt, I. L. *Chem. Rev.* **1970**, *70*, 471. (b) Oppolzer, W. *Synthesis* **1978**, 793. (c) Thummel, R. P. *Acc. Chem. Res.* **1980**, 1370. (d) Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 41. (e) Magnus, P.; Gallagher, T.; Brown, P.; Pappalardo, P.; *Acc. Chem. Res.* **1984**, *17*, 35. (f) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873. (g) Pindur, U.; Erfanian-Abdoust, H. *Chem. Rev.* **1989**, *89*, 1681. (h) Martin, N.; Seoane, C.; Hanack, M. *Org. Prep. Proc. Intl.* **1991**, *23*, 237. (i) Oppolzer, W. *Compr. Org. Synth.* **1991**, *5*, 388. (j) Rigby, J. H. *Compr. Org. Synth.* **1991**, *5*, 622, 638. (k) Chou, T. *Rev. Heteroatom. Chem.*, Vol. 8; Shigeru, O., Ed.; MYU K.K.: Tokyo, Japan, 1993. (l) Footnote 2 and references therein.

(2) (a) Ito, Y. *Current Trends in Organic Synthesis*; Pergamon Press: New York, 1983; p 169. (b) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 863. (c) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1981**, *103*, 476. (d) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1982**, *104*, 7609. (e) Ito, Y.; Amino, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1983**, *105*, 1586. (f) Trahanovsky, W. S.; Macias, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 6820.

(3) The present results have been communicated in part by Lenihan, B. D.; Shechter, H. *Tetrahedron Lett.* **1994**, *35*, 7505.

(4) (a) Kocienski, P. J. *Tetrahedron Lett.* **1979**, 2649. (b) Kocienski, P. J. *J. Org. Chem.* **1980**, *45*, 2037. (c) Paquette, L. A.; Williams, R. V. *Tetrahedron Lett.* **1981**, *22*, 4643. (d) Hsiao, C.-N. Ph.D. Dissertation, The Ohio State University, 1982. (e) McCullough, K. J. *Tetrahedron Lett.* **1982**, *23*, 2223. (f) Kocienski, P. *Phosphorus Sulfur* **1985**, 24, 97. (g) Eisch, J. J.; Behrooz, M.; Dua, S. K. *J. Organomet. Chem.* **1985**, *285*, 121. (h) Williams, R. V.; Sung, C. A. *J. Chem. Soc., Chem. Commun.* **1987**, 590. (i) Hsiao, C.-N.; Shechter, H. *J. Org. Chem.* **1988**, *53*, 2688.

(5) (a) Hsiao, C.-N.; Shechter, H. *Tetrahedron Lett.* **1984**, *25*, 1219. (b) Pegram, J. J.; Anderson, C. B. *Tetrahedron Lett.* **1988**, *29*, 6719. (c) Meagher, T. P. Ph.D. Dissertation, The Ohio State University, 1988. (d) Yet, L. M.S. Thesis, The Ohio State University, 1990.

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Scheme 1

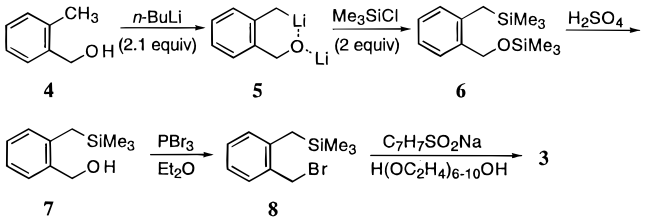
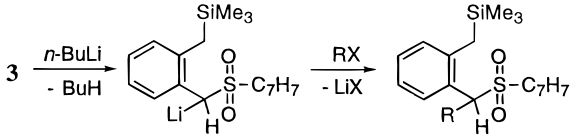


Table 1. Monoalkylations of Lithio Sulfone 9 to 10a−d with Primary and Secondary Halides (eq 1)

halide	sulfones **10a−d**	yield, %
methyl iodide	**10a**	77
allyl bromide	**10b**	81
benzyl bromide	**10c**	69
2-bromopropane	**10d**	66
cyclohexyl bromide	**10e**	0

hydrolysis of **6** with 10% H_2SO_4. Bromide **8** is obtained (95%) from **7** and phosphorus tribromide in diethyl ether at 25 °C. Displacement of **8** by sodium *p*-toluenesulfinate in poly(ethylene glycol) (PEG, av MW 400) at 60−80 °C then gives **3**.[8]

Alkylations and Acylations of Sulfones 3 and 10. Sulfone **3** in THF is monoalkylated α to its sulfone group to give **10a**−**c** in 69−81% yields by adding *n*-BuLi (1.05 equiv) in THF followed by a primary, allyl, or benzyl halide (eq 1, Table 1). A typical alkylation involves generation of lithio derivative **9** at −78 °C, warming to 20−25 °C, cooling to −78 °C, addition of a halide, and then warming to ∼25 °C. The reactions are followed by the fading of the yellow color of **9**, TLC, and NMR analyses of the products. In **10a**−**d** the α-sulfonyl hydrogens (*δ* 4−5) integrate to one proton.



(1)

Alkylations of **3** with secondary halides are less efficient because of competitive eliminations. Reaction of **9** with 2-bromopropane yields **10d** along with propene and **3**. Conversion of **3** to **10d** is accomplished effectively (66%), however, by successive additions of *n*-BuLi and 2-bromopropane in the presence of HMPA at 0 °C. ^{1}H NMR evidence for **10d** is the doublet for its α-sulfonyl proton. When cycloalkylation of **9** with cyclohexyl bromide is attempted, elimination to cyclohexene occurs and **3** is regenerated.

Dialkylations of **3** in one pot with primary halides are effected via successive additions of *n*-BuLi and a halide (eq 2, Table 2). Alkylations in which the second alkyl group is methyl give the best yields. Diethyl sulfone **11b** is produced (57%) by dialkylation of sulfone **3** with

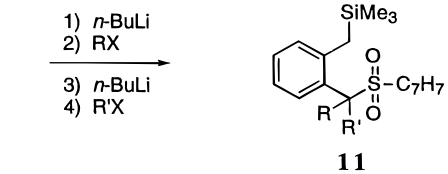
Table 2. Dialkylations of Lithio Sulfone 9 to 11 with Primary and Secondary Halides (eq 2)

sulfone product	R	R′	yield, %
11a	methyl	methyl	78
11b	ethyl	ethyl	57
11c	ethyl	methyl	60
11d	1-propyl	methyl	63
11e	butyl	methyl	70
11f	allyl	allyl	75
11g	allyl	methyl	82
11h	4-pentenyl	methyl	77
11i	2-propyl	methyl	72

Table 3. Reactions of Sulfones 10a−d with TBAF and Protonation To Give Sulfones 27a−d

sulfones **10a−d**	sulfones **27a−d**	yield, %
10a; R = methyl	**27a**	67
10b; R = allyl	**27b**	62
10c; R = benzyl	**27c**	70
10d; R = 2-propyl	**27d**	69

n-BuLi and ethyl bromide, but the synthesis requires HMPA and a third addition of *n*-BuLi and ethyl bromide. α-2-Propyl sulfone **10d** is alkylated by *n*-BuLi and methyl iodide in the presence of HMPA to give **11i** (72%). Evidence for dialkylations of **3** to **11a**−**i** include acceptable elemental analyses and the absence of ^{1}H NMR for α-sulfonyl protons in the products.[9] Most disubstituted sulfones (**11a**−**i**) do not give mass spectral molecular ions; a principal ion detected is the parent minus *p*-toluenesulfinate.



(2)

α,α-Dilithio derivatives such as dilithiomethyl phenyl sulfone (**12**)[10] and 1-(1,1-dilithio-2-trimethylsilyl)ethyl phenyl sulfone (**13**)[4g] are known. Reactions of *n*-BuLi and **3** have been investigated in efforts to prepare α,α-dilithio sulfone **14**. Addition of *n*-BuLi (2 equiv) in hexane to **3** at −78 °C followed by warming to 20−25 °C and then adding methyl iodide at −78 °C gives α,α-dimethyl sulfone **11a** (9%) and α,*o*-dimethyl sulfone **15** (57%), the product resulting from dimethylation of α,*o*-dilithio sulfone **16**. Generation of α,*o*-dilithiated phenyl sulfones has been previously reported[11] even though their α,α-dilithio isomers are more stable. Dimetalation of alkyl phenyl sulfones by *n*-BuLi at −78 °C occurs in general at the α,*o*-positions.[11] Upon warming the α,*o*-derivatives to room temperature, transmetalation occurs to form the α,α-dilithio derivatives.[11] It is not yet clear whether **11a** is formed by successive methylations of **14** or/and α-methylation of **16**, proton transfer, and then methylation of **17**.

Alkylation of α,α-dimethyl sulfone **11a** with *n*-BuLi and methyl iodide was attempted because of the possibil-

(6) Deprotonation of 2-methylbenzyl alcohol with *n*-BuLi in diethyl ether to **5** is complete in 24 h at room temperature and in 4 h under reflux. Braun, M.; Ringer, E. *Tetrahedron Lett.* **1983**, *24*, 1233.

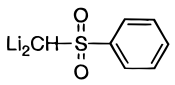
(7) Silane **7** is obtained in 79% yield using 3 equiv of *n*-BuLi (Dai-Ho, G.; Mariano, P. S. *J. Org. Chem.* **1988**, *53*, 5113) and in 87% yield using 5 equiv of *n*-BuLi and TMEDA (Lan, A. J. Y.; Heuckeroth, R. O.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 2738).

(8) Poly(ethylene glycol) is a useful solvent for preparing sulfones. Sukata, K. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 613.

(9) The NMR of some of the protons and carbons of sulfone **11i** are not defined at 303 K because restricted rotation causes signal broadening. At 350 K in C_6D_6, the signals become discrete because molecular rotation is increased.

(10) Eisch, J. J.; Dua, S. K.; Behrooz, M. *J. Org. Chem.* **1985**, **50**, 3674.

(11) (a) Gais, H.-J.; Vollhardt, J. *Tetrahedron Lett.* **1988**, *29*, 1529. (b) Vollhardt, J.; Gais, H.-J.; Lukas, K. L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 610.



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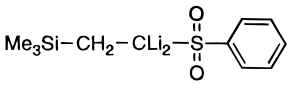

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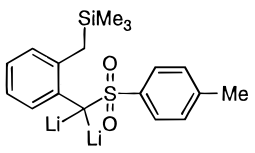

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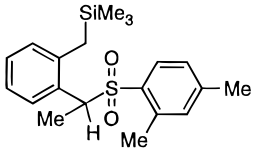

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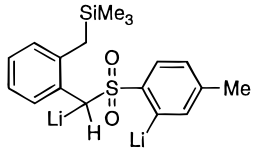

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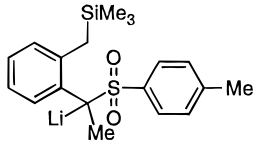

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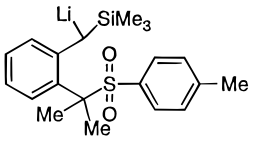
ity of methylation α to its silyl group via **18** to form **19**. Reaction gives however trimethyl[*o*-[1-methyl-1-(2,4-xylylsulfonyl)ethyl]benzyl]silane (**20**, 68%) and thus metalation of **11a** occurs *ortho* to its sulfone group. The abilities of phenyl sulfones to undergo *ortho*-metalation continue to be impressive.[12]



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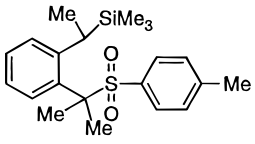

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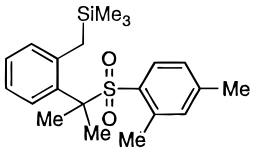

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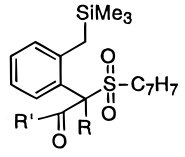
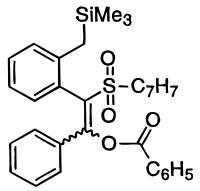
α-Metallo derivatives of **3** and **10** undergo other transformations. Thus, treatment of **3** with *n*-BuLi and then reactions with benzoyl chloride and with trimethylacetyl chloride in THF yield α-acyl sulfones **21a** (70%) and **21b** (69%). Similarly, α-benzoyl-α-methyl sulfone **21c** (72%) is obtained from **10a** and *n*-BuLi in THF and then benzoyl chloride. α-Acyl-α-sulfonyl derivative **21a**, an acid readily neutralized by sodium hydroxide (1.0 equiv), undergoes *o*-benzoylation (84%) upon addition of sodium hydroxide and benzoyl chloride to give **22**. That **22** is a sulfonyl enol benzoate is revealed by its ^{13}C NMR for 24 carbon atoms, its downfield ^{13}C absorption at δ 164 for ester carbonyl carbons, and its strong IR absorption at 1746 cm^{-1} for ester carbonyls. The stereochemistry of **22**, *E* or *Z*, is not yet assignable.

Behaviors of Trimethylsilyl Sulfones 10 and 11 with Fluoride Reagents. Fluoride-induced eliminations of α-monoalkyl sulfones **10a**−**d** were investigated in efforts to generate and capture α-monoalkyl-*o*-quinodimethanes **23** as 1,4-cycloadducts **24** (eq 3). In a typical experiment, TBAF (2 equiv) in acetonitrile is

(12) (a) Iwao, M.; Iihama, T.; Mahalanabis, K. K.; Perrier, H.; Snieckus, V. *J. Org. Chem.* **1989**, *54*, 24. (b) Lamothe, M.; Anderson, M. B.; Fuchs, P. L. *Synth. Commun.* **1991**, *21*, 1675.

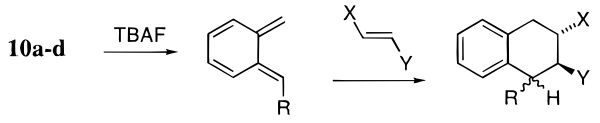




21a R = H; R' = C_6H_5
21b R = H; R'= $(CH_3)_3C$
21c R = CH_3; R' = C_6H_5

22

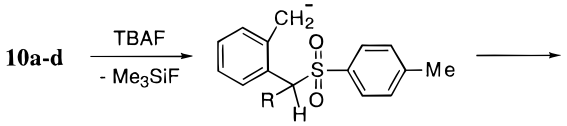
added slowly to an α-monoalkyl sulfone and a dienophile in acetonitrile. Each drop of TBAF produces a yellow color which fades after ∼5 s. The mixture is then diluted with an inert solvent, worked up, and chromatographed on silica gel.



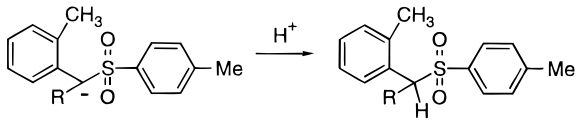
(3)

23 **24**

The study shows that **10a**−**d**, silanes containing hydrogen α to their sulfone groups, do not undergo 1,4-eliminations by TBAF. Only products resulting from loss of trimethylsilyl and from retention of *p*-tolylsulfonyl groups (**27a**−**d**, eq 4) are obtained. Reactions involving sulfones **10a**−**d** with TBAF along with the yields of **27a**−**d** are listed in Table 3. The results indicate formation of benzyl anions **25a**−**d** upon removal of the trimethylsilyl group, transfer of acidic hydrogen α to the sulfone group, and protonation of **26a**−**d** to **27a**−**d** on workup. Products **27a**−**d** are assigned from their elemental analyses and their ^1H NMR spectra.



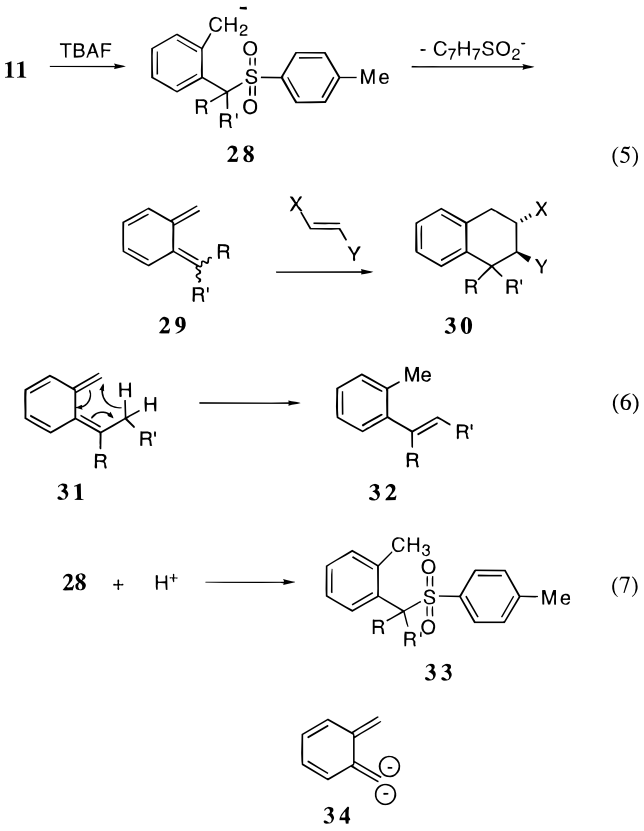
25a-d (4)



26a-d **27a-d**

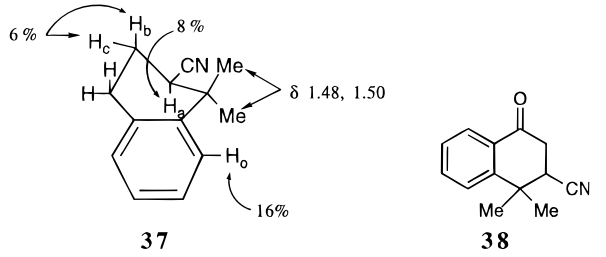
The behaviors of disubstituted sulfones **11** with fluoride ion were then studied. Such sulfones have no α-sulfonyl hydrogen and undergo 1,4-eliminations to form *o*-quinodimethanes **29** which are trappable by dienophiles to give tetrahydronaphthalenes **30** (eq 5; 30−60%). Sigmatropic 1,5-shifts of hydrogen in **31** (**29** which have (*Z*)-allylic hydrogen, eq 6) yield styrene derivatives (**32**) in competing processes. Sulfones **33** are also obtained by desilylation of **11** and then protonation of **28** (eq 7). The results obtained with **11** resulting in **29** reveal that **3** is a synthon for the *o*-quinodimethane-α,α-dianion (**34**) and are discussed specifically as follows.

α,α-Dimethyl sulfone **11a** in acetonitrile reacts with TBAF (2 equiv) in the presence of acrylonitrile (40 equiv) at 20−25 °C to give α,α-dimethyl-*o*-quinodimethane (**29a**, R and R′ = Me; eq 5, Table 4). *o*-Quinodimethane **29a** then undergoes (1) directed 1,4-cycloaddition of acrylonitrile yielding 2-cyano-1,1-dimethyltetrahydronaphthalene



(**35**, Table 4, 54%) and (2) sigmatropic hydrogen rearrangement to form styrene **36** (Table 4, 17%). Formation of sulfone **33a** (R and R′ = Me, eq 7, Table 4, 14%) along with polymerization of acrylonitrile and of styrene **36** are minor processes. Production of **33** (R and R′ = Me) suggests that 1,4-elimination of **11a** is stepwise via **28** (eq 7, R and R′ = Me) rather than concerted.

Reactions of **29a** (R and R′ = Me) with acrylonitrile can give two regioisomeric adducts. ^{1}H NMR and ^{13}C NMR show, however, that one isomer, **35** (Table 4), is greatly favored. Evidence for **35** is the ^{1}H NMR doublet of doublets at δ 2.83 for the α-cyano proton. NOE results as summarized in **37** provide further support of the regiochemical assignment in that irradiation at δ 1.50 gives an 8% enhancement of the doublet of doublets at δ 2.83 (H_a), a 16% increase of the aromatic doublet of doublets at δ 7.35 (H_o), and a 6% increase of the proton multiplet at δ 2.0−2.3 (H_b, H_c). Also, oxidation of **35** with chromium trioxide yields a product assignable as 3-cyano-4,4-dimethyl-1-tetralone (**38**).



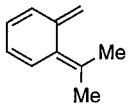
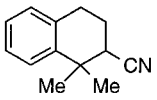
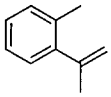
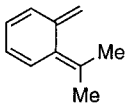
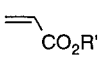
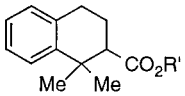
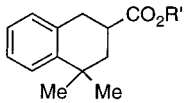
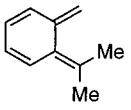
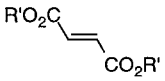
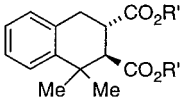
Reactions of α,α-dimethyl sulfone **11a** with TBAF−acetonitrile were then effected in the presence of methyl acrylate and ethyl acrylate. 1,4-Cycloadditions of **29a** with each acrylate (Table 4) give the corresponding 1,1-dimethyltetralin-2-carboxylate (**39a**, R′ = Me; **39b**, R′ = Et) and the 4,4-dimethyltetralin-2-carboxylate (**40a**, R′ = Me; **40b**, R′ = Et) esters in 3:1 ratios and 40% and 47% yields along with styrene **36** and sulfone **33a**. *o*-Quinodimethane **29a** therefore is not captured as efficiently or as regiospecifically by acrylates as by acrylonitrile. Poorer regioselectivity in cycloadditions of acrylate esters as compared to acrylonitrile has been reported previously.[13] The directions of addition of **29a** to the electronegatively substituted conjugated olefins are interpretable on the basis of favored transition states having diradical or dipolar character such as **41** and **42**. Further, the poorer regioselectivities with the acrylates leading to significant amounts of **40a** (R′ = Me) and **40b** (R′ = Et) are explained by steric interactions between the methyl groups in **29a** and the carboalkoxy groups in the dienophiles that cause retardation in cycloaddition to yield **39a** (R′ = Me) and **39b** (R′ = Et).

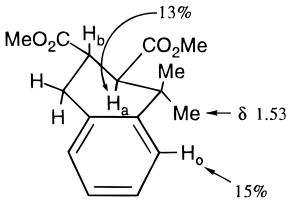
Cycloadducts (**43a** and **43b**) of **29a** with dimethyl and diethyl fumarates (Table 4) are obtained in 57% and 58% yields, respectively. The ^{1}H NMR spectrum of tetrahydronaphthyl dicarboxylate **43a** shows a doublet at δ 2.93 with a coupling constant of 11.5 Hz for its H_a proton (**44**, **45**). The large coupling constant suggests that the carbomethoxy groups are trans. NOE study of **44** and **45** involving irradiation of the methyl group at δ 1.53 results in 13% enhancement of the doublet at ∼δ 2.93 and 15% for the aromatic proton doublet at δ 7.35. Enlargement of the doublet at δ 2.9 upon irradiation at δ 1.53 indicates that the doublet arises from proton H_a and that the methyl which absorbs at δ 1.53 is cis to H_a. Irradiation of the methyl group at δ 1.21 causes increases of 13% in the multiplet at δ 3.0−3.4 and 8% in the aromatic doublet at δ 7.35. Because irradiation at δ 1.21 causes no enhancement in the H_a region, but does enlarge the H_b region, the methyl group which absorbs at δ 1.21 is trans to H_a. The conclusion that the methyl group which absorbs at δ 1.21 is close to H_b provides information regarding the conformation of **43a** and evidence that its carbomethoxy groups are trans (**44** and **45**). The NOE of **43b** (**46** and **47**) is similar to that of **43a** and leads to the conclusion that **43b** has trans stereochemistry. Cycloadducts of **29a** with dimethyl and diethyl fumarates are therefore totally trans.

Elimination of **11a** by TBAF after admixture with diethyl maleate was then studied. In all experiments the product from cycloaddition of *o*-quinodimethane **29a** (eq 5) is singularly *trans*-dicarboxylate **43b** (Table 4). The fact that the overall stereochemistries are identical in the cycloaddition reactions in the experiments with **11a**, TBAF, and either diethyl fumarate or diethyl maleate to give **43b** raise important mechanism questions as follows.

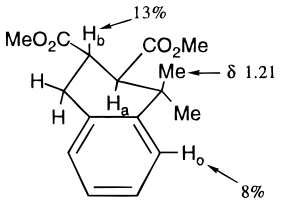
Maleate esters are known to (1) be isomerized by fluoride ion to fumarate esters[14] and (2) undergo cycloadditions of conjugated dienes slower and in lower yields than do fumarate esters.[15] Reaction of **11a**, TBAF, and diethyl maleate might thus involve partial or total isomerization of diethyl maleate to diethyl fumarate and stepwise (with steric control) or/and concerted addition

Table 4. Products Derived from Sulfone 11a, TBAF, and Dienophiles (eqs 5−7)

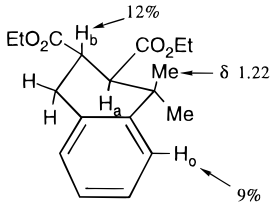
sulfone	*o*-quinodimethane	dienophile	cycloadduct	styrene **36**	sulfone byproduct **33a**
11a	 **29a**		 **35** (54%)	 17%	14%
11a	 **29a**	 R' = Me R' = Et	 **39a**, R' = Me (30%) **39b**, R' = Et (35%)	 **40a**, R' = Me (10%) **40b**, R' = Et (12%)	12% 14%	14% 12%
11a	 **29a**	 R' = Me R' = Et	 **43a**, R' = Me (57%) **43b**, R' = Et (58%)			10% 14%



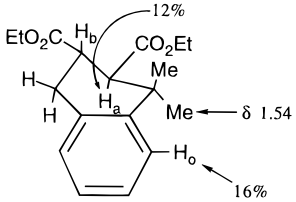
44



45



46



47

of **29a** to the diethyl fumarate to form **43b**. Admixture of **11a**, TBAF, and diethyl maleate (2 equiv) in acetonitrile at 20−25 °C for 90 min was then found to give *trans*-dicarboxylate **43b** in ∼32% yield along with ∼34% recovery of the diethyl maleate and, interestingly, ∼38% diethyl fumarate. Cesium fluoride also causes 1,4-elimination of **11a** in acetonitrile, but the reaction is considerably slower than that with TBAF because cesium fluoride is much less soluble in the acetonitrile. Of particular significance is that heterogeneous reaction of **11a** in acetonitrile with cesium fluoride in the presence of diethyl maleate (2 equiv) for 3 weeks at ∼25 °C produces *trans*-dicarboxylate **43b** in increased (59%) yield and diethyl maleate in increased (38%) conversion. Although the kinetics of the above reaction systems have not been studied in further detail, it is clear that (1) **29a** does not react concertedly with diethyl maleate[16] and (2) upon admixture of **11a**, diethyl maleate, and fluoride ion sources, isomerization of the diethyl maleate to diethyl fumarate is extensive and then cycloaddition of **29a** to the diethyl fumarate is a major or the (near) exclusive source of **43b**.

The behaviors of α,α-diethyl sulfone **11b** with TBAF−acetonitrile in the presence of dimethyl fumarate and diethyl fumarate were then investigated. The α,α-diethyl-*o*-quinodimethane (**29b**, Table 5) presumably generated undergoes 1,4-cycloadditions with the fumarate esters to give *trans*-dicarboxylates **48a** and **48b**. Competitive 1,5-hydrogen rearrangements of **29b** in the above experiments as in **50a** and **50b** result (Table 5) in 3-*o*-tolyl-2-pentenes: **49a**(**E**) and **49b**(**Z**). Desilylation of **11b** as in eq 7 yields **33b** (Table 5, R and R′ = Et). As expected, **29b** undergoes cycloadditions less effectively and hydrogen rearrangements more extensively than does **29a**, steric effects lead to **49a** in preference to **49b**, and desilylation to its sulfone is more prevalent in **11a** than **11b**.

Eliminations of α-ethyl-α-methyl sulfone **11c** by fluoride ion were then investigated to determine the various behaviors of α-ethyl-α-methyl-*o*-quinodimethanes **29c** and **29d** (Table 5). Reactions of **11c** with TBAF in acetonitrile at 20−25 °C yield styrene derivatives (eq 6)

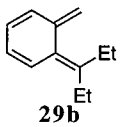
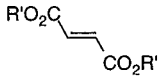
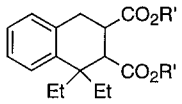
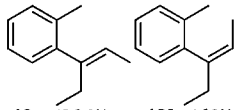
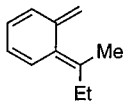
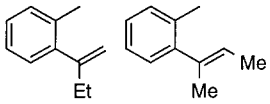
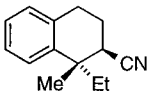
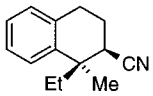
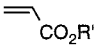
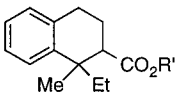
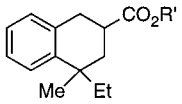
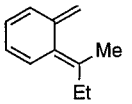
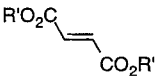
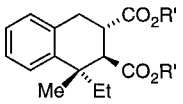
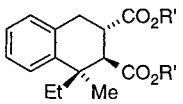
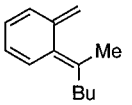
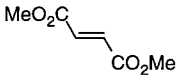
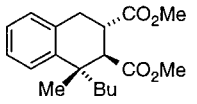
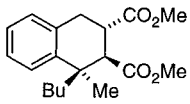
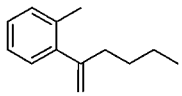
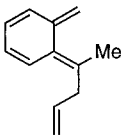
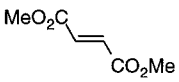
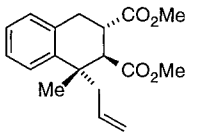
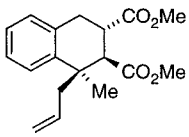
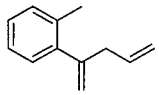
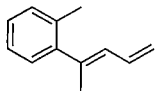
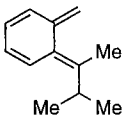
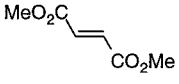
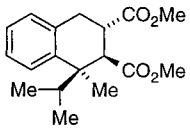
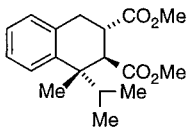
(13) Ito, Y.; Nakatsuda, M.; Saegusa, T. *J. Am. Chem. Soc.* **1982**, *104*, 7609.

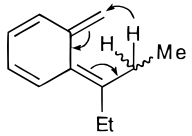
(14) Ito, Y.; Nakajo, E.; Saegusa, T. *Synth. Commun.* **1986**, *16*, 1073.

(15) (a) Arbuzov, B. A.; Fuzhenkova, A. V.; Devyatova, G. M. *J. Gen. Chem. USSR* **1971**, *41*, 721. (b) Blankenburg, V. B.; Fiedler, H.; Hampel, M.; Hauthal, H. G.; Just, G.; Kahlert, K.; Korn, J.; Müller, K.-H.; Pritzkow, W.; Reinhold: Y.; Röllig, M.; Sauer, E.; Schnurpfeil, D.; Zimmermann, G. *J. Prakt. Chem.* **1974**, *316*, 804. (c) Jung, M. E.; McCombs, C. A. *Tetrahedron Lett.* **1976**, 2935. (d) Inomata, K.; Kinoshita, H.; Takemoto, H.; Murata, Y.; Kotake, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3341. (e) Zutterman, F.; Krief, A. *J. Org. Chem.* **1983**, *48*, 1135. (f) Charlton, J. L.; Alauddin, M. M.; Penner, G. H. *Can. J. Chem.* **1986**, *64*, 793. (g) Meier, H.; Eckes, H.-L.; Niedermann, H.-P.; Kolshorn, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1046. (h) Noguchi, M.; Kiriki, Y.; Ushijima, T.; Kajigaeshi, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2938. The lower reactivity of dimethyl maleate is explained by steric effects between the dienophile substituents and the diene. The transition states become more crowded when the carboalkoxy groups are cis. (i) Miki, T.; Matsuo, T. *Chem. Pharm. Bull.* **1971**, *19*, 858 and references therein.

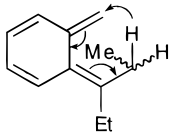
(16) (a) Reaction of dimethyl maleate with α,α′-dimethyl-*o*-quinodimethane generated by fluoride-induced elimination yields *cis*-2,3-dicarbomethoxy-1,4-dimethyl-1,2,3,4-tetrahydronaphthalene. The product is formed because the *o*-quinodimethane cannot undergo 1,5-sigmatropic rearrangement. Cycloaddition of dimethyl maleate to yield the cis adduct also occurs with the unsubstituted *o*-quinodimethane, which cannot undergo 1,5-sigmatropic rearrangement. Ito, Y.; Nakatsuda, M.; Saegusa, T. *J. Am. Chem. Soc.* **1982**, *104*, 7609. (b) Cycloadditions of *o*-quinonemethide *N*-alkylimines with fumarate esters give *trans*-2,3-dicarboalkoxy cycloadducts in good yields, whereas maleate esters give low yields of mixtures of *cis*- and *trans*-2,3-dicarboalkoxy cycloadducts in which the trans adducts dominate. Ito, Y.; Nakajo, E.; Saegusa, T. *Synth. Commun.* **1986**, *16*, 1073.

Table 5. Products Derived from Sulfones 11b, 11c, 11e, 11g, and 11i with TBAF in the Absence and Presence of Dienophiles

sulfone	*o*-quinodimethane	dienophile	cycloadduct	styrenes	sulfone byproduct **33**
11b	 **29b**	 R' = Me R' = Et	 **48a**, R' = Me (21%) **48b**, R' = Et (23%)	 **49a** (20%) **49b** (6%) **49a** (37%) **49b** (9%)	**33b** (2%) **33b** (5%)
11c	 **29c(E), 29d(Z)**			 **51a** (45%), **51b** (3.3%)	
11c	**29c(E), 29d(Z)**		 **54a** (14%)  **54b** (28%)	**51a** (24%), **51b** (5%)	**33c** (10%)
11c	**29c(E), 29d(Z)**	 R' = Me R' = Et	 **60**, R' = Me (30%) **61**, R' = Et (28%) 	**51a** (31%), **51b** (5%) **51a** (28%), **51b** (7%)	**33c** (13%)
11c	 **29c(E), 29d(Z)**	 R' = Me R' = Et	 **62a**, R' = Me (26%) **63a**, R' = Et (28%)  **62b**, (21%) **63b**, (23%)	**51a** (7%), **51b** (1%) **51a** (4%), **51b** (1%)	**33c** (8%) **33c** (10%)
11e	 **29e(E), 29f(Z)**		 **66a** (23%)  **66b** (22%)	 **67** (16%)	
11g	 **29g(E), 29h(Z)**		 **68a** (25%)  **68b** (19%)	 **69a** (8%)  **69b** (6%)	
11i	 **29i(E), 29j(Z)**		 **70a** (23%)  **70b** (3%)		

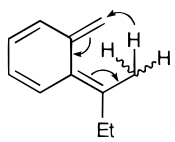


50a

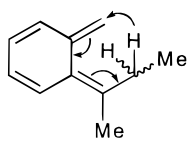


50b

51a (45%) and **51b** (3.3%) in a 93:7 ratio along with desilylated sulfone **33b** (eq 7; R = Me, R′ = Et) and nonvolatile materials. *o*-Quinodimethane **29c** is expected to be formed more extensively than **29d** because of steric



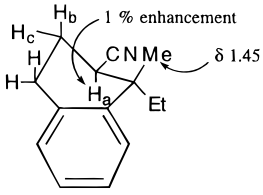
52



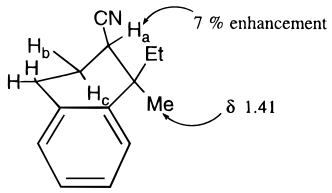
53

effects in elimination of **11c** by fluoride ion. Sigmatropic isomerizations of **29c** and **29d** with steric control as in **52** and **53** then yield **51a** in favor of **51b**.

Cyanotetrahydronaphthalenes **54a** [(*E*), 14%] and **54b** [(*Z*), 28%] (Table 5), the cycloadducts of **29c** and **29d** with acrylonitrile, are formed in a 1:2 ratio. Styrenes **51a** (24%) and **51b** (5%) along with desilylated sulfone **33c** (eq 7; R = Me, R′ = Et) are also produced. Diastereomers **54a** and **54b** were separated by gas chromatography and their stereochemistries determined by NOE methods. Cycloadduct **54a**, which has the shorter GC retention time, was irradiated at δ 1.45 (**55**) for its methyl group. The absorption for the α-cyano proton (H_a) at δ 3.05 in **55** is enhanced 1%. Irradiation of **54b** at δ 1.41 causes a 7% increase in absorption for the α-cyano proton at δ 2.90 (**56**). Because of the larger enhancement in **56**, its α-cyano proton and its methyl group are cis whereas the α-cyano proton H_a is trans to the methyl group in **55**. The regioselectivities in formation of **54a** and **54b** from **29c** and **29d** are similar to that for cycloadditions of unsymmetrical dienes and dienophiles[17] and are consistent with reaction mechanisms in which **29c** and **29d** add to acrylonitrile as diradical or dipolar reactants **57** and **58**. Of further interest, on the basis that the principal *o*-quinodimethane which reacts with acrylonitrile is **29c**, is that the transition state leading to **54b** as the major cycloadduct may be stabilized by Alder−Stein *endo* interaction as in **59**.



55



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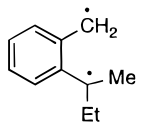

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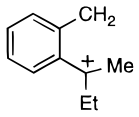
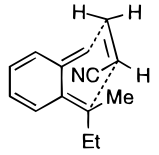


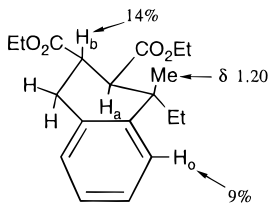
58



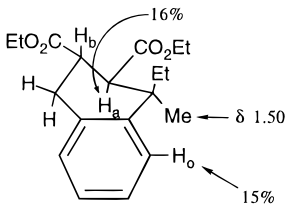
59

Sulfone **11c** in the presence of methyl acrylate is converted by TBAF in acetonitrile (Table 5) to 2- and 3-carbomethoxytetrahydronaphthalenes **60** (30%), styrenes **51a** (31%) and **51b** (5%), and desilylated sulfone **33c** (eq 7; R = Me, R′ = Et; 13%). Similar results are obtained with ethyl acrylate (Table 5). Four isomeric carbomethoxytetrahydronaphthalenes (**60**) are possible from 1,4-cycloadditions of methyl acrylate to **29c** and **29d**. The same possibilities exist in conversions of **29c** and **29d** by ethyl acrylate to **61**. All attempts to separate **60** or **61** or assign their structures precisely by NMR methods failed. It is clear however in the above elimination−cycloaddition experiments with **11c** that (1) acrylate esters are not captured as efficiently or as regioselectively by **29c** and **29d** as is acrylonitrile and (2) 1,5-sigmatropic rearrangements of **29c** and **29d** to **51a** and **51b** are more pronounced in the presence of methyl acrylate than in acrylonitrile.

Reactions of **11c** with TBAF were then effected in the presence of dimethyl fumarate and diethyl fumarate. The results are summarized in Table 5. Of note are (1) the fumarates are captured by **29c** and **29d** to give **62a**,**b** and **63a**,**b** in 47−51% yields, (2) the initial trans stereochemistries of the carboalkoxy groups are totally retained in the cycloaddition processes, and (3) styrenes **51a** and **51b** along with desilylated sulfone **33c** (R = Me, R′ = Et) are formed. The 2,3-dicarboethoxytetrahydronaphthalenes **63a** and **63b** are obtained in a 55:45 ratio as judged by NMR and are preparatively separable by GC. The configurations of **63a** and **63b** are assigned by NOE. Irradiation of the methyl group of the cycloadduct, **63a**, with the lower retention time gives a 14% enhancement at the multiplet corresponding to proton H_b as in **64**. Irradiation of the methyl group of the cycloadduct, **63b**, with the higher retention time results in a 16% increase at the doublet corresponding to proton H_a as in **65**. Further, the diastereomers with their 3-carboethoxy groups cis to the ethyl groups and therefore more hindered have the shorter retention times. Finally, as expected, the overall behavior of **11c** and TBAF with dimethyl fumarate is essentially identical to that with diethyl fumarate (Table 5).



64



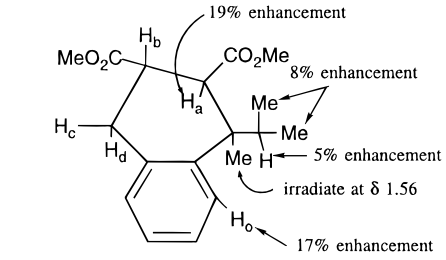
65

Study was then made of decompositions (Table 5) of α-methyl-α-substituted sulfones **11e** (R = Bu, R′ = Me), **11g** (R = Allyl, R′ = Me), and **11i** (R = 2-Propyl, R′ = Me) by TBAF in the presence of dimethyl fumarate (2−4 equiv). The principal purpose of these experiments was to determine if *o*-quinodimethanes more hindered and presumably less enophilic than those previously studied are readily captured by dimethyl fumarate. Further objectives were to assign the stereochemistries of cycloadducts and search for other intramolecular reactions of *o*-quinodimethanes. *o*-Quinodimethanes **29e** and **29f**, **29g** and **29h**, and **29i** and **29j**, presumed as generated from **11e**, **11g**, and **11i**, have thus been found to react with dimethyl fumarate (Table 5) to yield 2,3-dicarbomethoxytetrahydronaphthalenes **66a** and **66b**, **68a** and **68b**, and **70a** and **70b**, respectively. The *o*-quinodimethanes also undergo 1,5-hydrogen rearrangements to give their corresponding styrene derivatives (eq 6; Table 5; **67** and **69a** and **69b**). Desilylations of **11e**, **11g**, and **11i** occur as expected (eq 7); sulfones **33** were not characterized in detail.

The stereochemistries of **66a** and **66b**, **68a** and **68b**, and **70a** and **70b** were established as follows. In **43a**, **43b**, and **63b**, the methyl groups at C-1 which are trans to the carboalkoxy groups at C-2 show ^{1}H NMR at δ 1.50−1.54 whereas in **43a**, **43b**, and **63a**, the cis methyls at C-1 absorb at δ 1.20−1.22. Cycloadducts **66b**, **68b**,

(17) For reviews of the mechanisms of Diels−Alder reactions, see: (a) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16. (b) Martin, J. G.; Hill, R. K. *Chem. Rev.* **1961**, *61*, 537. (c) Alder, K.; Stein, G. *Angew. Chem.* **1937**, *50*, 510. (d) Woodward, R. B.; Baer, H. *J. Am. Chem. Soc.* **1944**, *66*, 645. (e) Sauer, J.; Sustmann, R. *Angew. Chem.* **1980**, *92*, 773. (f) Van Mele, B.; Huybrechts, G. *Int. J. Chem. Kinet.* **1989**, *21*, 967.

and **70a** having their C-1 methyls and their C-2 carbomethoxy groups trans are assigned from their ^{1}H NMR at δ 1.50, 1.51, and 1.56, respectively. The stereochemistry of pure **70a** upon isolation by MPLC is assigned much more comprehensively from its ^{1}H NMR and NOE as now described. Cycloadduct **70a** (Table 5) exhibits a doublet of doublets for H_d with a superimposed doublet for H_a at δ 2.8−2.9 (**71**). The large coupling constant of the superimposed doublet at 12.3 Hz for H_a supports the trans stereochemical assignments of the carbomethoxy groups. A doublet of doublets with coupling constants of 6.6 and 16.6 Hz for proton H_c is observed at δ 3.15−3.30, and H_b exhibits a doublet of doublet of doublets with coupling constants of 12.3, 11.2, and 6.6 Hz, respectively. The stereochemical assignment of **70a** is finalized from its NOE irradiation (**71**) at δ 1.56 resulting in 19% enhancement of the doublet at δ 2.90 corresponding to H_a rather than to H_b. Of particular interest is that **70a** and **70b** are produced in ~7:1 ratio when, upon consideration of conformational effects, **70b** is predicted to be less strained than **70a**. An interpretation of the observed stereochemical results is that endo transition states involving maximum overlap for formation of **70a** and **70b** come early and thus **70a** is formed in preference to **70b** because the steric repulsion of the C_1-carbomethoxy group with the 2-propyl and the methyl group in **72** is considerably less than that in **73**.



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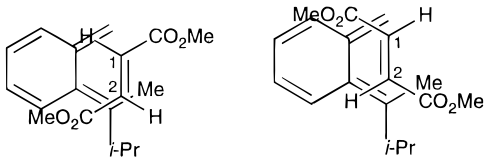
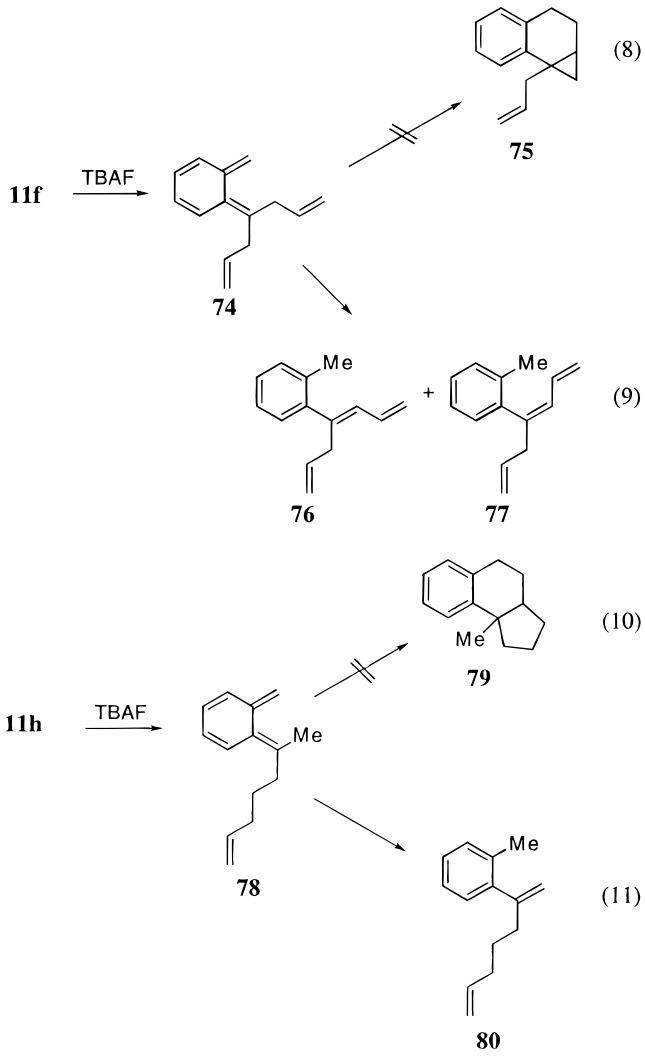


72 **73**

Fluoride ion elimination of α,α-diallyl sulfone **11f** (Table 2) in acetonitrile containing dimethyl fumarate (4 equiv) is instructive in that 4-(2-tolyl)-1,3,5-hexatrienes **76** and **77** (eq 9) are formed in 85:15 ratios in >55% yield by 1,5-hydrogen rearrangements of α,α-diallyl-*o*-quinodimethane (**74**). Of note are that **74** is not trapped by dimethyl fumarate and does not form the intramolecular Diels−Alder cycloadduct **75** (eq 8). Further, **11h** is converted by TBAF/acetonitrile to styrene derivative **80** (eq 11, 53%). Under the designated conditions, **78** does not form **79** (eq 10). As expected, appropriately α,α-disubstituted-*o*-quinodimethanes as generated by the present methodologies undergo (1,5)-sigmatropic shifts of hydrogen rather than intra- or intermolecular cycloadditions.

The generation and chemistry of various α,α-dialkyl-*o*-quinodimethanes (**29**) as obtained by fluoride ion eliminations of α,α-disubstituted sulfones **11** have been described. Determination of the chemistry of various



functionally substituted *o*-quinodimethanes as prepared from **3** is now in progress.

Experimental Section

All melting points are uncorrected. Proton shift values are reported in parts per million (ppm) from tetramethylsilane on the δ scale when $CDCl_3$ is used as the solvent with residual $CHCl_3$ at δ 7.26 as an internal reference. Carbon chemical shifts are reported in ppm relative to the center line of the $CDCl_3$ triplet (77.0 ppm). Elemental analyses of purified products were performed by Micro Analysis, Wilmington, DE, or Atlantic Microlab, Norcross, GA. All reactions were conducted under argon unless otherwise noted. Solvents and reagents were dried and purified when deemed necessary. Analytical thin-layer chromatography was performed with EM silica gel 60 F_{254} plates. Column chromatography was effected on EM 70−230 mesh silica gel 60 or Scientific Adsorbents 63−200 mesh silica gel. The chromatography solvent is denoted as the proportion of solvent by volume.

***o*-[(Trimethylsilyl)methyl]benzyl Alcohol (7).** *n*-BuLi (661 mL, 1719 mmol, 2.60 M in hexane) was added to 2-methylbenzyl alcohol (**4**, 100 g, 819 mmol) in anhydrous diethyl ether (1500 mL) at 0 °C. The mixture was warmed to room temperature, refluxed for 24 h, cooled to −78 °C, treated with chlorotrimethylsilane (260 mL, 2048 mmol), and warmed to room temperature. At −20 °C, the yellow color faded. After 2 h, 10% H_2SO_4 was added (dropwise initially) and the mixture was stirred overnight. The layers were then separated, and the aqueous phase was extracted with diethyl ether. The combined ether extracts were washed with saturated NaCl, dried over $MgSO_4$, and concentrated. Distillation of the

concentrate in a Vigreaux column gave **7** (bp 94 °C, 0.95 mmHg). Fractions contaminated with unhydrolyzed material were treated with 10% H_2SO_4 and diethyl ether, worked up as before, and distilled under reduced pressure to yield pure **7** (total yield 112.6 g, 71%). The spectroscopic properties of **7** agree with that reported:[7,18] MS(EI) *m/e* (relative intensity) 179,.09 (12), 161.08 (25), 104.06 (100), 73.05 (22).

[*o*-(Bromomethyl)benzyl]trimethylsilane (8). Phosphorus tribromide (20 mL, 211 mmol, 1.12 equiv) was added to **7** (109.4 g, 563 mmol) in diethyl ether (600 mL) at 0 °C. The mixture was stirred at room temperature 2 h, cooled in ice, and treated with water, and the layers were separated. The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with 1 M $NaHSO_3$, saturated $NaHCO_3$, and saturated NaCl, dried over $MgSO_4$, concentrated, and vacuum distilled to give **8** (137.3 g, 95%, bp 88 °C, 0.9 mmHg). Spectroscopic data for **8**[7] agree with those reported: MS(EI) *m/e* (relative intensity) 258.03 (3), 256.03 (3), 243.00 (11), 241.00 (10), 177.11 (57), 145.05 (18), 104.06 (100), 73.05 (70), 45.02 (22); HRMS calcd for $C_{11}H_{17}BrSi$ 256.0283, found 256.0281.

Trimethyl[*o*-[(*p*-tolylsulfonyl)methyl]benzyl]silane (3). A mixture of **8** (137.2 g, 533 mmol), sodium *p*-toluenesulfinate hydrate (137 g, 600 mmol), and poly(ethylene glycol) (220 mL, av MW 400, dried over 4 Å molecular sieves) was stirred at 80−100 °C for 5.5 h and then diluted with water. The precipitate formed was vacuum-filtered and recrystallized from methanol to yield **3** (136.6 g, 77%, mp 122−123 °C). A second crop of **3** was obtained (6.16 g, 3%, mp 120−122 °C, total yield 80%). Spectral data for **3**: IR (KBr) 1600, 1310, 1295, 1255, 1145, 1090, 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.06 (9H, s), 1.95 (2H, s), 2.42 (3H, s), 4.30 (2H, s), 6.91−7.48 (8H, m); ^{13}C NMR ($CDCl_3$) δ −1.6, 21.6, 23.5, 60.2, 124.3, 125.0, 128.6, 128.7, 129.4, 129.6, 132.1, 135.4, 140.9, 144.6; MS(EI) *m/e* (relative intensity) 177.11 (22), 104.06 (100), 73.05 (54); HRMS calcd for $C_{18}H_{24}O_2SSi$ 332.1266, found 332.1304. Additional crystallizations from carbon tetrachloride and ligroin yielded an analytical sample. Anal. Calcd for $C_{18}H_{24}O_2SSi$: C, 65.02; H, 7.27. Found: C, 64.66; H, 7.11.

Procedure A (Table 1) for Monosubstitution of o-[(Trimethylsilyl)methyl]benzyl *p*-Tolyl Sulfone (3) with Electrophiles. Trimethyl[*o*-[1-(*p*-tolylsulfonyl)ethyl]benzyl]silane (10a). *n*-BuLi (7.5 mL, 9.5 mmol, 1.27 M in hexane) was added to **3** (3.00 g, 9.02 mmol) in anhydrous THF (60 mL) at −78 °C. The mixture became yellow, was warmed to room temperature, and then cooled in dry ice−acetone, and methyl iodide (0.59 mL, 9.47 mmol) was added. The mixture was warmed to room temperature and diluted with water and dichloromethane, and the layers were separated. The organic layer was washed with saturated NaCl, dried over $MgSO_4$, and concentrated to an oil which solidified. The white product was recrystallized from ligroin to yield **10a** (2.41 g, 77%, mp 86−87 °C): IR (KBr) 1600, 1310, 1300, 1255, 1155, 860, cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.08 (9H, s), 1.64 (1H, d, J = 14 Hz), 1.72 (3H, d, J = 7 Hz), 1.97 (1H, d, J = 14.3 Hz), 2.37 (3H, s), 4.47 (1H, q, J = 7 Hz), 6.80−7.42 (8H, m); ^{13}C NMR ($CDCl_3$) δ −1.8, 14.5, 21.5, 23.4, 60.7, 124.3, 128.1, 128.2, 129.0, 129.2, 129.4, 130.4, 134.0, 140.4, 144.3; MS(EI) *m/e* (relative intensity) 191.13 (87), 73.05 (100). Anal. Calcd for $C_{19}H_{26}O_2SSi$: C, 65.85; H, 7.56. Found: C, 65.62; H, 7.60.

Trimethyl[*o*-[1-(*p*-tolylsulfonyl)-3-butenyl]benzyl]silane (10b). Procedure A (Table 1), a white solid, yield 81% (mp 67−69 °C): IR (KBr) 1645, 1600, 1315, 1290, 1260, 1150, 1090, 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.06 (9H, s), 1.58 (1H, d, J = 14.6 Hz), 1.95 (1H, d, J = 14.5 Hz), 2.39 (3H, s), 2.86 (1H, m), 3.15 (1H, m), 4.48 (1H, dd), 4.98 (1H, br d), 5.10 (1H, br d), 5.65 (1H, m), 6.84−7.37 (8H, m); ^{13}C NMR ($CDCl_3$) δ −1.1, 21.6, 23.0, 33.3, 65.5, 118.4, 124.4, 128.2, 128.7, 128.8, 129.1, 129.4, 129.6, 133.6, 134.3, 141.6, 144.4; MS(EI) *m/e* (relative intensity) 217.14 (16), 73.05 (100). Anal. Calcd for $C_{21}H_{28}O_2SSi$: C, 67.69; H, 7.57. Found: C, 67.19; H, 7.59.

Trimethyl[*o*-[α-(*p*-tolylsulfonyl)phenethyl]benzyl]silane (10c). Procedure A (Table 1), a white solid, yield 69% (mp 148−149.5 °C): IR (KBr) 1600, 1300, 1255, 1150, 1090, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.32 (9H, s), 1.38 (1H, d, J = 14.8 Hz), 1.66 (1H, d, J = 14.7 Hz), 2.39 (3H, s), 3.40 (1H, dd, J = 10.6, 13.8 Hz), 3.80 (1H, dd, J = 13.8, 3.8 Hz), 4.67 (1H, dd, J = 10.6, 3.8 Hz), 6.79 (13H, m); ^{13}C NMR ($CDCl_3$) δ −1.4 (q), 21.5 (q), 22.1 (t), 34.6 (t), 67.7 (d), 124.3 (d), 126.7 (d), 128.1 (d), 128.4 (d), 128.6 (s), 128.8 (d), 129.1 (d), 129.3 (d), 129.4 (d), 129.5 (d), 134.6 (s), 136.9 (s), 142.0 (s), 144.3 (s); MS(EI) *m/e* (relative intensity) 267.16 (9), 229.08 (12), 73.02 (100). Anal. Calcd for $C_{25}H_{30}O_2SSi$: C, 71.04; H, 7.15. Found: C, 71.00; H, 7.29.

Trimethyl[*o*-[2-methyl-1-(*p*-tolylsulfonyl)propyl]benzyl]silane (10d). To **3** (5.00 g, 15.0 mmol) in THF (100 mL) at −78 °C was added *n*-BuLi (6.5 mL, 15.0 mmol, 1 equiv, 2.30 M in hexane). After being warmed to room temperature, the solution was cooled to 0 °C and treated with HMPA (7.8 mL, 45 mmol, 3 equiv) and 2-bromopropane (1.42 mL, 15.0 mmol, 1 equiv). The mixture was maintained at 0 °C for 2.5 h and cooled to −78 °C, and then *n*-BuLi (1.30 mL, 3.0 mmol, 0.20 equiv, 2.30 M in hexane) was added. The mixture was warmed to 0 °C and treated with 2-bromopropane (0.35 mL, 3.75 mmol, 0.25 equiv). After 2.5 h at 0 °C, the mixture was reacted further with *n*-butyllithium (0.33 mL, 0.76 mmol, 0.05 equiv) followed by 2-bromopropane (0.07 mL, 0.76 mmol, 0.05 equiv). After 1.75 h at 0 °C, when TLC showed that almost all of the **3** had reacted, water and diethyl ether were added. The organic layer was worked up as for **10a** and concentrated to a solid (5.54 g) which was recrystallized from methanol to give **10d** (3.41 g, mp 74−78 °C, a white solid): IR (KBr) 1596, 1284, 1249, 1144, 1080, 844 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.06 (9H, s), 0.88 (3H, d, J = 6.8 Hz), 1.33 (1H, d, J = 14.8 Hz), 1.45 (3H, d, J = 6.5 Hz), 1.77 (1H, d, J = 14.7 Hz), 2.31 (3H, s), 2.77−2.95 (1H, m), 4.23 (1H, d, J = 9.3 Hz), 6.70−6.80 (1H, m), 7.00−7.13 (4H, m), 7.26−7.30 (2H, br d), 7.45−7.52 (1H, m); ^{13}C NMR ($CDCl_3$) δ −0.8, 21.4, 21.9, 22.4, 22.6, 29.1, 72.2, 124.4, 127.7, 128.6, 128.9, 129.2, 129.5, 130.5, 136.2, 141.0, 143.7; MS(EI) *m/e* (relative intensity) 219.16 (6), 73.04 (100). Anal. Calcd for $C_{21}H_{30}O_2SSi$: C, 67.33; H, 8.07. Found: C, 67.39; H, 8.10. Additional **10d** was obtained by crystallization from the mother liquor (0.33 g, total yield 3.74 g, 66%).

Procedure B (Table 2) for Dialkylation of 3. Trimethyl[*o*-[1-methyl-1-(*p*-tolylsulfonyl)ethyl]benzyl]silane (11a). *n*-BuLi (13.4 mL, 31.6 mmol, 2.35 M in hexane) was added to **3** (10.00 g, 30.1 mmol) in anhydrous THF (200 mL) at −78 °C. The yellow mixture was warmed to room temperature and cooled to −78 °C, and methyl iodide (1.97 mL, 31.6 mmol) was added. The solution was warmed to room temperature and cooled to −78 °C, and *n*-BuLi (13.4 mL, 31.6 mmol, 2.35 M in hexane) was added. The mixture was warmed to room temperature and then cooled to −78 °C. Methyl iodide (2.06 mL, 33.1 mmol) was added, and the mixture was warmed to room temperature. After the mixture was diluted with diethyl ether and extracted with water, the organic layer was washed with saturated NaCl, dried over $MgSO_4$, and concentrated to an oil which solidified. Recrystallization from methanol yielded **11a** as a white solid (8.48 g, 78%, mp 79−83 °C): IR (KBr) 1605, 1300, 1255, 1160, 1135, 1080, 855 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (9H, s), 1.89 (6H, s), 2.36 (3H, s), 2.56 (2H, s), 6.81−7.28 (8H, m); ^{13}C ($CDCl_3$) δ 0.5, 21.5, 26.1, 26.6, 67.7, 123.7, 128.0, 128.7, 130.1, 130.5, 131.9, 132.5, 133.6, 142.9, 144.0; MS(EI) *m/e* (relative intensity) 205.15 (52), 73.05 (100). Anal. Calcd for $C_{20}H_{28}O_2SSi$: C, 66.62; H, 7.83. Found: C, 66.29, H, 7.72.

[*o*-[1-Ethyl-1-(*p*-tolylsulfonyl)propyl]benzyl]trimethylsilane (11b). To **3** (2.00 g, 6.01 mmol) in THF (30 mL) at −78 °C was added *n*-BuLi (2.3 mL, 6.3 mmol, 2.71 M in hexane). The solution was warmed to room temperature, cooled to −78 °C, and treated with HMPA (3.1 mL, 18 mmol) and ethyl bromide (0.47 mL, 6.3 mmol). When TLC showed that all starting material had reacted, the mixture was cooled to −78 °C and *n*-BuLi (2.3 mL, 6.3 mmol, 2.71 M in hexane) was added. After being warmed to room temperature, the bright red solution was cooled to −78 °C, treated with ethyl bromide (0.49 mL, 6.6 mmol), and warmed to room temperature. TLC showed that the alkylations were about half

(18) Shih, C.; Swenton, J. S. *J. Org. Chem.* **1982**, *47*, 2668.

complete. The mixture was again treated with *n*-BuLi at −78 °C (1.1 mL, 3.0 mmol, 2.71 M in hexane) followed by ethyl bromide at −78 °C (0.30 mL, 4.0 mmol). TLC showed that reaction of **3** was mostly complete. The mixure was worked up (procedure B) and concentrated. Chromatography on silica gel using 1:19 ethyl acetate:ligroin yielded **11b** as a white solid (1.34 g, 57%, mp 70−76 °C): IR (KBr) 1597, 1300, 1244, 1143, 1078, 849 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.05 (9H, s), 1.07 (6H, t, J = 7.3 Hz), 2.30−2.38 (2H, m, J = 7.4 Hz), 2.35 (3H, s), 2.48 (2H, s), 2.61−2.75 (2H, sextet, J ∼ 7.3 Hz), 6.75−6.87 (2H, m), 7.00−7.18 (6H, m); ^{13}C NMR ($CDCl_3$) δ −0.2, 9.3, 21.5, 25.2, 26.8, 75.2, 123.5, 127.6, 128.6, 130.1, 131.8, 131.9, 132.6, 133.3, 143.8, 144.0 cm^{-1}; MS(EI) *m/e* (relative intensity) 233.17 (45), 73.05 (100). Recrystallization from ligroin yielded an analytical sample (mp 75−78 °C). Anal. Calcd for $C_{22}H_{32}O_2SSi$: C, 67.99; H, 8.30. Found: C, 67.97; H, 8.41.

Trimethyl[*o*-[1-methyl-1-(*p*-tolylsulfonyl)propyl]benzyl]silane (11c). Procedure B (Table 2), alkylation of **3** using *n*-BuLi and ethyl bromide followed by *n*-BuLi and methyl iodide, gave **11c** which crystallized from methanol as a white solid, yield 60% (mp 70−73 °C): IR (KBr) 1600, 1305, 1290, 1250, 1150, 1080, 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (9H, s), 0.84 (3H, t), 1.86 (3H, s), 1.98−2.15 (2H, d and superimposed m), 2.37 (3H, s), 2.53 (1H, d, J = 14.8 Hz), 2.67−2.78 (1H, m), 6.85−7.30 (8H, m); ^{13}C NMR ($CDCl_3$) δ −0.5, 8.2, 21.5, 23.1, 25.8, 29.5, 71.7, 123.7, 127.8, 128.7, 130.3, 130.8, 131.7, 132.0, 132.5, 143.7, 144.0; MS(EI) *m/e* (relative intensity) 219.15 (68) 73.05 (100). Recrystallizations from ligroin yielded an analytical sample (mp 77−79 °C). Anal. Calcd for $C_{21}H_{30}O_2SSi$: C, 67.33; H, 8.07. Found: C, 67.31; H, 8.23.

Trimethyl[*o*-[1-methyl-1-(*p*-tolylsulfonyl)pentyl]benzyl]silane (11e). Procedure B (Table 2), alkylation of **3** with *n*-BuLi and 1-bromobutane followed by *n*-BuLi and methyl iodide, gave **11c** which crystallized from methanol as a white solid, yield 70% (mp 70−76 °C): IR (neat film) 1600, 1305, 1250, 1150, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (9H, s), 0.87 (3H, t), 1.07−1.25 (2H, m), 1.29−1.39 (2H, m), 1.88 (3H, s), 1.96−2.06 (2H, d and superimposed m), 2.37 (3H, s), 2.50 (1H, d, J = 14.8 Hz), 2.63−2.73 (1H, m), 6.87−7.24 (8H, m); ^{13}C NMR ($CDCl_3$) δ −0.5 (q), 13.8 (q), 21.5 (q), 23.1 (t), 23.8 (q), 25.7 (t), 25.8 (t), 36.4 (t), 71.5 (s), 123.7 (d), 127.8 (d), 128.7 (d), 130.4 (d), 131.5 (s), 131.6 (d), 132.0 (d), 132.6 (s), 143.6 (s), 144.0 (s); MS(EI) *m/e* (relative intensity) 247.19 (16), 73.05 (100). Recrystallization of the product from methanol gave an analytical sample of **11e** (mp 73.5−77 °C). Anal. Calcd for $C_{23}H_{34}O_2SSi$: C, 68.60; H, 8.51. Found: C, 68.85; H, 8.58.

[*o*-[1-Allyl-1-(*p*-tolylsulfonyl)-3-butenyl]benzyl]trimethylsilane (11f). Procedure B (Table 2), alkylation of **3** using *n*-BuLi and allyl bromide, followed by *n*-BuLi and allyl bromide resulted in an oil which on chromatography on silica gel using petroleum ether/ethyl acetate as developer gave **11f**, yield 75%: IR (neat) 1637, 1597, 1301, 1248, 1145, 1083, 847 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (9H, s), 2.35 (3H, s), 2.48 (2H, s), 3.11 (2H, dd, J = 15.5, 7.2 Hz), 3.39 (2H, dd, J = 15.6, 6.2 Hz), 5.0−5.2 (4H, m), 5.79−5.95 (2H, m), 6.76−6.90 (2H, m), 7.03−7.18 (6H, m); ^{13}C NMR ($CDCl_3$) δ −0.2, 21.5, 26.7, 37.8, 73.3, 119.0, 123.5, 127.9, 128.7, 130.2, 131.6, 132.1, 132.5, 132.7, 143.7, 144.1.

Trimethyl[*o*-[1-methyl-1-(*p*-tolylsulfonyl)-3-butenyl]benzyl]silane (11g). Procedure B (Table 2), alkylation of **3** using *n*-BuLi and allyl bromide followed by *n*-BuLi and methyl iodide, workup, and then chromatography gave **11g**, a colorless oil, yield 82%: IR (neat) 1640, 1600, 1310, 1255, 1150, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (9H, s), 1.86 (3H, s), 2.15 (1H, d, J = 14.9 Hz), 2.39 (3H, s), 2.55 (1H, d, J = 14.8 Hz), 2.75 (1H, dd, J = 14.4, 8.6 Hz), 3.55 (1H, dd, J = 14, 4.5 Hz), 5.05 (1H, br d), 5.17 (1H, br d), 5.40−5.56 (1H, m), 6.86−7.27 (8H, m); ^{13}C NMR ($CDCl_3$) δ −0.4, 21.5, 23.6, 26.0, 41.1, 70.5, 119.4, 123.7, 128.0, 128.8, 130.3, 131.3, 131.7, 132.0, 132.1, 132.5, 143.6, 144.2; HRMS calcd for $C_{22}H_{30}O_2SSi$ 386.1736, found 386.1697. Anal. Calcd for $C_{22}H_{30}O_2SSi$: C, 68.34; H, 7.82. Found: C, 68.00; H, 7.71.

Trimethyl[*o*-[1-methyl-1-(*p*-tolylsulfonyl)-5-hexenyl]benzyl]silane (11h). Procedure B (Table 2), alkylation of **3** with *n*-BuLi and 5-bromo-1-pentene followed by *n*-BuLi and methyl iodide, and workup gave an oil which on chromatography yielded **11h** (0.478 g, 77%): IR (neat) 1641, 1597, 1298, 1248, 1143, 846 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (9H, s), 1.19−1.38 (2H, m), 1.89 (3H, s), 1.98−2.14 (4H, m), 2.39 (3H, s), 2.50 (1H, d, J = 14.8), 2.64−2.76 (1H, m), 4.94−5.03 (2H, m), 5.67−5.83 (1H, m), 6.85−7.25 (8H, m); ^{13}C NMR ($CDCl_3$) δ −0.5, 21.5, 23.0, 23.7, 25.6, 33.8, 36.1, 71.3, 115.2, 123.7, 127.9, 128.7, 130.3, 131.1, 131.6, 131.9, 132.4, 137.7, 143.5, 144.0; MS(EI) *m/e* (relative intensity) 177.11 (19), 91.05 (19), 73.05 (100).

[*o*-[1,2-Dimethyl-1-(*p*-tolylsulfonyl)propyl]benzyl]trimethylsilane (11i). To **10d** (3.00 g, 8.01 mmol) in THF (60 mL) at −78 °C was added *n*-BuLi (3.80 mL, 8.81 mmol, 2.35 M in hexane). The red-orange mixture was warmed to room temperature and then cooled to −78 °C, and HMPA (2.8 mL, 16 mmol) and methyl iodide (0.75 mL, 12 mmol) were added. The mixture was worked up (procedure B) and concentrated to an oil which crystallized from methanol to yield **11i** (2.00 g, mp 79−83 °C). A second crop of **11i** was obtained (0.24 g, total yield 72%): IR (KBr) 1597, 1283, 1248, 1149, 844 cm^{-1}; ^1H NMR ($CDCl_3$, 303 K) δ 0.02 (9H, s), 0.73 (3H, d, J = 6.9 Hz), 1.45 (3H, d, J = 6.5 Hz), 1.77 (3H, s), 2.29 (3H, s), 3.47−3.51 (1H, m), 6.85 (2H, br s), 6.94−7.09 (4H, m), 7.10−7.14 (2H, m); ^1H NMR (C_6D_6, 350 K) δ 0.03 (9H, s), 0.63 (3H, d, J = 6.9 Hz), 1.53 (3H, d, J = 6.5 Hz), 1.74 (3H, s), 1.85 (3H, s), 2.48 (1H, d, J = 14.1 Hz), 2.63 (1H, d, J = 14.9 Hz), 3.61 (1H, septet, J = 6.7 Hz), 6.63 (2H, d), 6.69−6.76 (1H, m), 6.86−6.90 (2H, m), 7.28−7.32 (3H, d and superimposed m); ^{13}C NMR ($CDCl_3$) δ −0.3, 17.3, 18.8, 19.9, 21.4, 25.7, 32.5, 76.1, 124.0, 127.5, 128.4, 129.6, 130.6, 132.5, 134.6, 142.5, 143.4; ^{13}C NMR (C_6D_6, 350 K) δ −0.09 (q), 17.8 (q), 19.1 (q), 20.1 (q), 21.0 (q), 26.4 (t), 32.9 (d), 76.6 (s), 124.4 (d), 127.6 (d), 128.6 (d), 130.3 (d), 131.2 (d), 132.9 (d), 136.0 (s), 136.5 (s), 143.0 (s), 143.1 (s). Recrystallization of **11i** from ligroin gave an analytical sample, mp 82−84 °C. Anal. Calcd for $C_{22}H_{32}O_2SSi$: C, 67.99; H, 8.30. Found: C, 68.06; H, 8.30.

Alkylation of Dilithio 3 with Methyl Iodide. Trimethyl[*o*-[1-(2,4-xylylsulfonyl)ethyl]benzyl]silane (15). *n*-BuLi (1.40 mL, 3.79 mmol, 2.5 equiv, 2.71 M in hexane) was added to **3** (0.498 g, 1.50 mmol) and THF (10 mL) at −78 °C. The dark red mixture was warmed to room temperature, stirred for 1 h, and cooled to −78 °C, and methyl iodide was added (0.28 mL, 4.5 mmol). The yellow solution was warmed to room temperature, diluted with water, and extracted with diethyl ether. The organic layer was washed with saturated NaCl, dried over $MgSO_4$, concentrated, and chromatographed on silica gel with 1:19 ethyl acetate:ligroin to yield a mixture (0.36 g) which NMR showed to be **15** and **11a** in an 86:14 ratio (adjusted yield of **15**: 0.310 g, 57%). Recrystallization from methanol gave pure **15** (mp 93−95 °C): IR (KBr) 1602, 1301, 1245, 1182, 1145, 1121 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.06 (9H, s), 1.66−1.77 (4H, d and superimposed d), 2.11 (1H, d, J = 14.4 Hz), 2.27 (3H, s), 2.34 (3H, s), 4.53 (1H, q), 6.85−7.31 (6H, m), 7.62 (1H, d); ^{13}C NMR ($CDCl_3$) δ −1.7, 15.0, 20.0, 21.3, 23.4, 60.5, 124.4, 126.8, 128.2, 128.8, 129.4, 130.1, 131.8, 132.6, 133.1, 139.3, 140.6, 144.2; MS(EI) *m/e* (relative intensity) 191.12 (97), 73.05 (100). α,α-Dimethyl sulfone **11a** was formed in 9% yield as judged by NMR.

Trimethyl[*o*-[1-methyl-1-(2,4-xylylsulfonyl)ethyl]benzyl]silane (20). A mixture of **11a** (2.00 g, 5.55 mmol), THF (40 mL), and *n*-BuLi (3.0 mL, 7.1 mmol, 2.35 M in hexane) was stirred 2 h at −78 °C, and then methyl iodide (0.43 mL, 6.9 mmol) was added. The solution was stirred at −78 °C for 30 min and then warmed to room temperature. The mixture changed from red-orange to colorless. After being stirred at room temperature 2 h, the mixture was processed as for **15** and concentrated. Chromatography on silica gel using 1:19 ethyl acetate:ligroin yielded solid **20** (1.59 g, 76%, mp 60−64 °C): IR (KBr) 1600, 1290, 1250, 1176, 1152, 1111, 849 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (9H, s), 1.89 (3H, s), 1.91 (6H, s), 2.33 (3H, s), 2.45 (2H, s), 6.85−6.90 (2H, m), 6.98−7.04 (3H, m), 7.11−7.17 (1H, m), 7.58 (1H, d); ^{13}C NMR ($CDCl_3$) δ −0.5, 19.7, 21.2, 26.2, 26.6, 68.6, 123.9, 126.2, 128.0, 130.5, 130.8, 132.1, 133.1, 133.9, 141.1, 143.2, 144.0; MS(EI) *m/e* (relative intensity), 205.13 (53), 73.04 (100). Recrystallization of **20** from ligroin gave an analytical sample (mp 63−65 °C). Anal. Calcd

for $C_{21}H_{30}O_2SSi$: C, 67.33; H, 8.07. Found: C, 67.29; H, 8.04.

2-(*p*-Tolylsulfonyl)-2-[α-(trimethylsilyl)-*o*-tolyl]acetophenone (21a). To **3** (5.00 g, 15.0 mmol) in THF (100 mL) at −78 °C was added *n*-BuLi (6.9 mL, 15.9 mmol, 2.30 M in hexane). After being warmed to room temperature, the mixture was cooled to −78 °C, reacted with benzoyl chloride (3.5 mL, 30 mmol), stirred at −78 °C for 30 min, and then treated with 10% HCl (20 mL).[19] The mixture was then worked up as for **15** and concentrated. The solid obtained was recrystallized from methanol to give pure **21a** (4.62 g, 70%, mp 132−133 °C): IR (KBr) 1682, 1594, 1320, 1274, 1220, 1145, 846 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.02 (9H, s), 2.20 (1H, d, J = 14.7 Hz), 2.32 (1H, d, J = 14.7 Hz), 2.39 (3H, s), 6.54 (1H, s), 6.89−6.98 (1H, m), 7.07−7.22 (4H, m), 7.33−7.57 (6H, m), 7.84−7.88 (2H, m); ^{13}C NMR ($CDCl_3$) δ −0.9, 21.6, 22.5, 70.9, 124.4, 125.5, 128.6, 128.7, 128.9, 129.7, 130.3, 130.5, 133.6, 134.0, 136.7, 141.2, 144.9, 191.3; MS(EI) *m/e* (relative intensity) 281.13 (11), 265.10 (7), 208.08 (19), 105.03 (41), 91.05 (20), 73.04 (100); HRMS calcd for $C_{25}H_{28}O_3SSi$ 436.1528, found 436.1547. Recrystallization from ligroin yielded an analytical sample. Anal. Calcd for $C_{25}H_{28}O_3SSi$: C, 68.77; H, 6.46. Found: C, 68.49; H, 6.45.

3,3-Dimethyl-1-(*p*-tolylsulfonyl)-1-[α-(trimethylsilyl)-*o*-tolyl]-2-butanone (21b). *n*-BuLi (1.20 mL, 1.62 mmol, 1.35 M in hexane) was added to **3** (0.496 g, 1.49 mmol) in THF (10 mL) at −78 °C. The mixture was warmed to room temperature and cooled to −78 °C, and trimethylacetyl chloride (0.20 mL, 1.6 mmol) was added. The solution, after warming to room temperature, became colorless. TLC showed that some **3** remained. The mixture was again treated with *n*-BuLi (1.20 mL) and trimethylacetyl chloride (0.21 mL) as before. The mixture was processed as for **15** and concentrated. Crystallization from 1:19 ethyl acetate:ligroin yielded initial **3** (54 mg). Chromatography of the mother liquor on TLC grade silica gel using 1:19 ethyl acetate:ligroin yielded **21b** (0.427 g, 69%) as a white solid (mp 54−77 °C): IR (KBr) 1712, 1597, 1318, 1249, 1150, 852 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (9H, s), 1.03 (9H, s), 2.26 (2H, dd), 2.40 (3H, s), 6.11 (1H, s), 6.79−6.92 (2H, m), 7.15−7.25 (5H, m), 7.43−7.48 (1H, br d); MS(EI) *m/e* (relative intensity) 332.12 (2), 261.17 (14), 188.12 (71), 73.05 (84), 57.07 (100).

2-(*p*-Tolylsulfonyl)-2-[α-(trimethylsilyl)-*o*-tolyl]propiophenone (21c). To benzoyl chloride (0.82 mL, 7.1 mmol) in THF (10 mL) at −78 °C was added in 100 min via cannula a solution prepared from **10a** (0.498 g, 1.44 mmol) and *n*-BuLi (1.32 mL, 1.51 mmol, 1.14 M in hexane) in THF (10 mL). The colorless mixture was warmed to room temperature, stirred with saturated $NaHCO_3$, and extracted with diethyl ether. The organic phase was processed and concentrated. The concentrate was chromatographed on silica gel using 1:19 ethyl acetate:petroleum ether as solvent to obtain **21c** as a foam (0.467 g, 72%): ^1H NMR δ −0.06 (9H, s), 1.75 (1H, d), 2.11 (3H, s), 2.40 (3H, s), 2.45 (1H, d), 7.05−8.15 (13H, m).

α-(*p*-Tolylsulfonyl)-2-[(trimethylsilyl)methyl]-α-stilbenol Benzoate (22). A mixture of sulfone **21a**, THF (7 mL), 3 M NaOH (3 mL), and benzoyl chloride (0.27 mL) was stirred for 1.5 h. When TLC showed that reaction was complete, the mixture was processed routinely and concentrated to a solid. Recrystallization from methanol yielded **22** (0.520 g, 84%, mp 167−170 °C): IR (KBr) 1746, 1614, 1597, 1315, 1246, 1209, 1151, 1094, 854 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (9H, s), 2.15 (1H, d, J = 14.9 Hz), 2.31 (1H, d, J = 14.9 Hz), 2.38 (3H, s), 7.05−7.28 (11H, m), 7.52 (2H, t), 7.64−7.70 (3H, m), 8.10−8.13 (2H, d); ^{13}C NMR ($CDCl_3$) δ −0.4 (q), 21.5 (q), 23.0 (t), 124.3 (d), 128.0 (d), 128.2 (d), 128.4 (d), 128.5 (d), 128.8 (s), 129.1 (d), 129.1 (d), 129.5 (d), 129.8 (d), 130.1 (s), 130.4 (d), 132.7 (d), 133.6 (s), 133.8 (d), 134.2 (s), 138.8 (s), 142.7 (s), 143.9 (s), 152.9 (s), 163.6 (s); MS(EI) *m/e* (relative intensity) 525.16 (2), 419.15 (12), 191.09 (9), 105.03 (100), 77.04 (20), 73.05 (15); HRMS calcd for $C_{32}H_{32}O_4SSi$ 540.1791, found 540.1801. Recrystallization from methanol yielded an analytical sample. Anal. Calcd for $C_{32}H_{32}O_4SSi$: C, 71.08; H, 5.96; S, 5.93. Found: C, 70.66; H, 5.92; S, 5.84.

General Procedure C (Table 3) for Reactions of Monoalkylated Sulfones with TBAF. *o*,α-Dimethylbenzyl *p*-Tolyl Sulfone (27a). A solution of 1 M TBAF in acetonitrile (2.15 mL, 2.15 mmol) was added in 40 min to **10a** (0.479 g, 1.38 mmol) in acetonitrile (5 mL). The mixture was diluted with water and extracted with dichloromethane. The organic phase was dried with $MgSO_4$ and concentrated to a solid which on recrystallization from 1:4 ethyl acetate:ligroin yielded **27a** as a white solid (0.223 g). A second crop of **27a** (0.032 g) was obtained (total yield 67%). The spectroscopic properties of **27a**: IR (KBr) 1600, 1315, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72 (3H, d, J = 7.1 Hz), 2.02 (3H, s), 2.39 (3H, s), 4.53 (1H, q, J = 7.1 Hz), 7.02−7.45 (4H, m); ^{13}C ($CDCl_3$) δ 14.8, 19.4, 21.5, 60.8, 126.2, 128.1, 128.4, 129.2, 130.3, 132.4, 134.4, 137.6, 144.5; MS(EI) *m/e* (relative intensity) 119.08 (100), 104.07 (15), 91.06 (19); HRMS calcd for $C_{16}H_{18}O_2S$ 274.1027, found 274.1027. The first crop on crystallization from 1:4 ethyl acetate:ligroin and from 2:1 ligroin:benzene melted at 146−147 °C. Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.62. Found: C, 69.77; H, 6.81.

***p*-Tolyl 1-*o*-Tolyl-3-butenyl Sulfone (27b).** Procedure C (Table 3), **10b** in acetonitrile, with TBAF in acetonitrile yielded a white solid which recrystallized from ligroin to give **27b**, yield 62%: IR (KBr) 1645, 1600, 1315, 1295, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.91 (3H, s), 2.38 (3H, s), 2.82−2.95 (1H, m), 3.12−3.22 (1H, m), 4.45 (1H, dd, J = 4.0, 11.4 Hz), 4.90−4.95 (1H, br d), 4.98−5.06 (1H, br d), 5.40−5.56 (1H, m), 6.98−7.47 (8H, m); ^{13}C ($CDCl_3$) δ 19.4, 21.5, 32.7, 65.5, 118.3, 126.2, 128.2, 128.4, 129.1, 129.2, 130.2, 130.4, 132.9, 134.7, 138.3, 144.5; MS(EI) *m/e* (relative intensity), 145.09 (100), 91.06 (36); HRMS calcd for $C_{18}H_{20}O_2S$ 300.1184, found 300.1176. An analytical sample (mp 84−86 °C) was obtained upon recrystallization from ligroin. Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.97; H, 6.71. Found: C, 71.55; H, 6.89.

***p*-Tolyl α-*o*-Tolylphenethyl Sulfone (27c).** Procedure C (Table 3), **10c** in acetonitrile, with TBAF in acetonitrile led to a solid which on crystallization from 1:4 ethyl acetate:ligroin gave **27c**, yield 70%: IR (KBr) 1600, 1320, 1310, 1300, 1290, 1150, 1095 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (3H, s), 2.37 (3H, s), 3.35 (1H, dd, J = 13.5, 11.67 Hz), 3.82 (1H, dd, J = 13.5, 3.17 Hz), 4.62 (1H, dd, J = 11.6, 3.17 Hz), 6.82−7.73 (13H, m); ^{13}C NMR ($CDCl_3$) δ 19.1, 21.5, 34.7, 67.4, 126.1, 126.5, 128.2, 128.3, 128.4, 128.8, 128.9, 129.2, 130.0, 130.4, 134.8, 136.9, 138.2, 144.5; MS(EI) *m/e* (relative intensity), 195.12 (65), 117.07 (16), 91.06 (15). Recrystallizations from 1:4 ethyl acetate:ligroin gave an analytical sample (mp 155−157 °C). Anal. Calcd for $C_{22}H_{22}O_2S$: C, 75.40; H, 6.32. Found: C, 75.04; H, 6.58.

***o*-Methylbenzyl-α-2-propyl *p*-Tolyl Sulfone (27d).** Procedure C (Table 3), **10d** in acetonitrile with TBAF in acetonitrile, and chromatography on silica gel using 1:19 ethyl acetate:petroleum ether gave **27d** as an oil which solidified, yield 69% (mp 83−84 °C): IR (KBr) 1597, 1313, 1286, 1139 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (3H, d, J = 6.8 Hz), 1.35 (3H, d, J = 6.6 Hz), 1.83 (3H, s), 2.29 (3H, s), 2.78−2.93 (1H, m), 4.20 (1H, d, J = 8.5 Hz), 6.85 (1H, d), 7.00−7.22 (3H, m), 7.32 (2H, d), 7.66 (1H, dd); ^{13}C NMR ($CDCl_3$) δ 19.6, 21.1, 21.4, 22.1, 30.0, 71.6, 126.1, 128.00, 128.5, 128.7, 130.0, 131.9, 136.5, 137.5, 143.7; MS(EI) *m/e* (relative intensity) 147.12 (57), 105.07 (100), 91.05 (13), 55.05 (19).

α,α-Dimethyl-*o*-quinodimethane (29a) and Its Cycloaddition with Acrylonitrile. 1,2,3,4-Tetrahydro-1,1-dimethyl-2-naphthonitrile (35). To **11a** (0.401 g, 1.11 mmol) and acrylonitrile (2.9 mL, 44 mmol) in acetonitrile (8 mL) was added TBAF (2.2 mL, 2.1 mmol, 1 M in acetonitrile) in acetonitrile (8 mL) over 60 min. The mixture was processed as for **7** and concentrated. Column chromatography on silica gel using 1:1 dichloromethane:petroleum ether (bp 35−60 °C) yielded styrene **36** (25 mg, 17%). The second eluent contained nitrile **35** as an oil (111 mg, 54%): IR (neat) 2238, 1491, 762 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (3H, s), 1.50 (3H, s), 2.05−2.27 (2H, m), 2.82 (1H, dd, J = 3.7, 9.5 Hz), 2.87−3.12 (2H, m), 7.05−7.36 (4H, m); ^{13}C NMR ($CDCl_3$) δ 22.9, 28.2, 28.3, 30.2, 36.0, 39.5, 121.0, 126.3, 126.3, 126.5, 129.1, 133.3, 142.2; NOE

(19) Allowing the mixture to warm to room temperature without HCl treatment caused formation of a small amount of **22** which is difficult to remove by crystallization.

differences with irradiation of the methyl singlets at δ 1.48 and 1.50 gave enhancements at δ 2.0−2.3 (6%), δ 2.82 (8%), and δ 7.34 (16%); MS(EI) *m/e* (relative intensity) 185.12 (42), 170.09 (100), 143.08 (64); HRMS calcd for $C_{13}H_{15}N$ 185.1204, found 185.1204. The third eluent contained **33a** as a solid (45 mg, 14%).

1,2,3,4-Tetrahydro-1,1-dimethyl-4-oxo-2-naphthonitrile (38). To nitrile **35** (0.109 g, 0.59 mmol) in glacial acetic acid (16 mL) was added a 10% solution of chromium trioxide in glacial acetic acid over 25 min (1.7 mL, 2.7 mmol).[20] After 20 min of stirring, the mixture was worked up as for **35** and concentrated. Chromatography on TLC grade silica gel using dichloromethane as eluent yielded **38** as a liquid (0.0377 g, 32%): IR (neat) 2240, 1690, 1600, 1300, 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.55 (3H, s), 1.62 (3H, s), 3.01−3.04 (2H, two superimposed d, J = 7.2, 8.4 Hz), 3.25 (1H, dd, J = 7.0, 8.5 Hz), 7.34−7.64 (3H, m), 8.04 (1H, dd); MS(EI) *m/e* (relative intensity) 199.10 (85), 184.07 (100), 146.07 (53), 131.05 (47), 91.05 (88); HRMS calcd for $C_{13}H_{13}NO$ 199.0997, found 199.0977.

α,α,-Dimethyl-*o*-quinodimethane (29a) and Its Cycloadditions with Methyl Acrylate. Methyl 1,2,3,4-Tetrahydro-1,1-dimethyl-2-naphthoate (39a) and Methyl 1,2,3,4-Tetrahydro-4,4-dimethyl-2-naphthoate (40a). A solution of 1 M TBAF in acetonitrile (2.8 mL, 2.8 mmol) was added in 60 min to **11a** (0.504 g, 1.40 mmol) and methyl acrylate (1.9 mL, 21 mmol) in acetonitrile (6 mL). The mixture was worked up and concentrated. Column chromatography (TLC grade silica gel, 1.19 ethyl acetate:ligroin) gave styrene **36** (22 mg, 12%) as the first eluent: IR (neat) 900, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.05 (3H, br s), 2.33 (3H, s), 4.86 (1H, br s), 5.20 (1H, br s), 7.12−7.26 (4H, m).

The second eluent, a liquid, contained isomers **39a** and **40a** (123 mg, 40%) in a 3:1 ratio as determined by ^1H NMR: IR (neat) 1738, 1731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3−1.6 (6H), 2.0−2.3 (2H), 2.65−3.15 (3H), 3.7−3.8 (3H), 7.0−7.4 (4H); MS(EI) *m/e* (relative intensity) 218.13 (9), 203.11 (9), 186.11 (11), 158.11 (19), 143.09 (83); HRMS calcd for $C_{14}H_{18}O_2$ 218.1307, found 218.1341. The third eluent contained **33a** (58 mg, 14%).

Ethyl 1,2,3,4-Tetrahydro-1,1-dimethyl-2-naphthoate (39b) and Ethyl 1,2,3,4-Tetrahydro-4,4-dimethyl-2-naphthoate (40b). To **11a** (492 mg, 1.37 mmol) and ethyl acrylate (2.2 mL, 21 mmol) in acetonitrile (5 mL) was added TBAF (2.75 mL, 2.8 mmol, 1 M in acetonitrile) over 60 min. After workup, the material was chromatographed on TLC grade silica gel using 1:19 ethyl acetate:ligroin. The first eluent was styrene derivative **36** (25 mg, 14%). The next eluent, an oil, consisted of isomers **39b** and **40b** in a 3:1 ratio (141 mg, 47%): IR (neat) 1731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2−1.6 (9H, m), 1.7−2.2 (2H, m), 2.6−3.1 (3H, m), 4.1−4.4 (2H, m), 7.0−7.5 (4H, m); MS(EI) *m/e* (relative intensity) 232.15 (30), 217.12 (11), 186.10 (23), 159.12 (26), 158.11 (51), 143.08 (100); HRMS calcd for $C_{15}H_{20}O_2$ 232.1463, found 232.1458. The third eluent was **33a** (46 mg, 12%).

Cycloaddition of α,α-Dimethyl-*o*-quinodimethane (29a) with Dimethyl Fumarate. Dimethyl *trans*-1,2,3,4-Tetrahydro-1,1-dimethyl-2,3-naphthalenedicarboxylate (43a). To **11a** (0.499 g, 1.38 mmol) and dimethyl fumarate (0.40 g, 2.77 mmol) in acetonitrile (8 mL) in 40 min was added TBAF (2.8 mL, 2.8 mmol, 1 M in acetonitrile). The mixture was stirred for 3 h and processed routinely. The organic product was concentrated to an oily solid, dissolved in hot methanol, and cooled to 0−5 °C to crystallize the dimethyl fumarate. The mother liquor was concentrated and chromatographed on silica gel using 1:19 ethyl acetate:ligroin as solvent to yield an oil (0.258 g) which NMR showed to be **43a** contaminated with 15 mol % **33a** (adjusted yield of **43a**: 0.22 g, 57%; yield of **33a**: 40 mg, 10%). Preparative GC yielded pure **43a**: IR (neat) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (3H, s), 1.53 (3H, s), 2.83−2.95 (2H, m and superimposed d, J (of doublet) = 11.5 Hz), 3.09−3.25 (2H, m), 7.03−7.24 (3H, m), 7.36 (1H, dd); ^{13}C NMR ($CDCl_3$) δ 28.3 (q), 29.6 (q), 33.3 (t), 37.1 (s), 39.9 (d), 51.5 (q), 51.9 (q), 53.4 (d), 126.0 (d), 126.5 (d), 126.7 (d), 128.6 (d), 132.5 (s), 144.0 (s), 173.8 (s), 175.4 (s); NOE differences with irradiation at δ 1.53 gave enhancements of a doublet at δ 2.93 (12.8%) and a doublet of doublets at δ 7.36 (15.0%); NOE differences with irradiation at δ 1.21 gave enhancements of a multiplet at δ 3.08−3.24 (12.6%), a multiplet at δ 7.0−7.3 (5.6%), and a doublet of doublets at δ 7.36 (7.9%); MS(EI) *m/e* (relative intensity) 276 (5), 245 (9), 244 (13), 216 (42), 201 (15), 157 (75); HRMS calcd for $C_{16}H_{20}O_4$ 276.1361, found 276.1366.

α,α-Dimethyl-*o*-quinodimethane (29a) with Diethyl Fumarate. Diethyl *trans*-1,2,3,4-Tetrahydro-1,1-dimethyl-2,3-naphthalenedicarboxylate (43b). A solution of TBAF (4.2 mL, 4.2 mmol, 1 M in acetonitrile) was added in 60 min to **11a** (1.00 g, 2.77 mmol) and diethyl fumarate (0.91 mL, 5.54 mmol) in acetonitrile (15 mL). The reaction mixture was chromatographed on silica gel using 1:19 ethyl acetate:ligroin as solvent. The first eluent contained **43b** as an oil (0.49 g, 58%): IR (neat) 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (3H, s), 1.29 (3H, t), 1.30 (3H, t), 1.55 (3H, s), 2.82−2.94 (2H, m and superimposed d, J (of doublet) = 11.7 Hz), 3.07−3.21 (2H, m), 4.14−4.28 (4H, m), 7.03−7.23 (3H, m), 7.36 (1H, dd); ^{13}C NMR ($CDCl_3$) δ 14.1, 14.2, 28.2, 29.6, 33.4, 37.1, 40.0, 53.4, 60.3, 60.6, 125.9, 126.5, 126.6, 128.2, 132.6, 144.1, 173.2, 174.9; NOE differences with irradiation at δ 1.22 gave enhancements at δ 3.0−3.2 (11.7%) and δ 7.36 (8.9%); NOE differences with irradiation at δ 1.54 resulted in enhancements of the doublet at δ 2.90 (12.2%) and the doublet at δ 7.36 (15.7%); MS(EI) *m/e* (relative intensity) 304.17 (3), 259.13 (12), 258.12 (8), 157.10 (100), 143.09 (41); HRMS calcd for $C_{18}H_{24}O_4$ 304.1674, found 304.1668.

The next eluent contained **33a** (0.11 g, 14%, mp 124−127 °C): IR (neat) 1594, 1285, 1152, 1129 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.92 (6H, s), 2.39 (3H, s), 2.45 (3H, s), 6.99−7.32 (8H, m); ^{13}C NMR ($CDCl_3$) δ 21.5, 24.3, 25.5, 67.8, 125.4, 128.5, 128.8, 130.3, 130.7, 132.3, 133.3, 135.1, 139.5, 144.2; MS(EI) *m/e* (relative intensity) 133.09 (37), 133.01 (100), 105.07 (37).

TBAF-Induced Elimination of 11a in the Presence of Diethyl Maleate. A solution of TBAF (2.8 mL, 2.8 mmol, 1.0 M in acetonitrile) was added in 90 min to **11a** (0.500 g, 1.39 mmol) and diethyl maleate[21] (0.45 mL, 2.77 mmol) in acetonitrile (10 mL). After an hour, additional TBAF (0.5 mL) was added. After routine workup, the mixture was concentrated. Chromatography on silica gel using 1:19 ethyl acetate:ligroin yielded diethyl fumarate (181 mg, 38%). The next eluent contained **43b** (133 mg, 32%). NMR indicated that the product is identical to that from cycloaddition with diethyl fumarate. The next eluent contained recovered diethyl maleate (162 mg, 34%).

Cesium Fluoride-Induced Elimination of 11a in the Presence of Diethyl Maleate. Silyl sulfone **11a** (0.500 g, 1.39 mmol), acetonitrile (10 mL), and diethyl maleate (0.45 mL, 2.8 mmol) were added to cesium fluoride (0.42 g, 2.8 mmol) in a flame-dried flask. After 3 weeks of stirring under argon, the mixture was processed routinely and concentrated. Chromatography on silica gel using 1:19 ethyl acetate:petroleum ether as elutent yielded diethyl fumarate as the first eluent (0.18 g, 36%). The next eluent contained **43b** (0.249 g, 59%).

Dimethyl *trans*-1,1-Diethyl-1,2,3,4-tetrahydro-2,3-naphthalenedicarboxylate (48a). TBAF (1.9 mL, 1.9 mmol, 1.0 M in acetonitrile) was added over 45 min to **11b** (0.359 g, 924 mmol) and dimethyl fumarate (0.53 g, 3.7 mmol) in acetonitrile (7 mL). The mixture was worked up routinely and concentrated. Dimethyl fumarate (0.34 g) was removed by crystallization from methanol. The mother liquor was concentrated and chromatographed on silica gel using 1:19 ethyl acetate:ligroin as solvent. The first eluent, a liquid, contained styrene derivatives **49a** and **49b** in a 3:1 ratio (38 mg, 26%): IR (KBr) 759, 730 cm^{-1}; MS(EI) *m/e* (relative intensity) 160.13 (65), 145.10 (41), 131.09 (100), 91.06 (44); HRMS calcd for $C_{12}H_{16}$ 160.1252, found 160.1257; ^1H NMR of isomer **49a** ($CDCl_3$) δ

(20) A solution of CrO_3 in acetic acid and water oxidizes the 1 position of tetrahydronaphthalenes. Burnham, J. W.; Duncan, W. P.; Eisenbraun, E. J.; Keen, G. W.; Hamming, M. C. *J. Org. Chem.* **1974**, *39*, 1416.

(21) Commercial diethyl maleate is contaminated with a small amount of diethyl fumarate. In the present work, the diethyl maleate was purified by chromatography and distillation.

1.04 (3H, t), 1.42 (3H, dt, J = 6.7, 1.2 Hz), 2.25 (3H, s), 2.3−2.35 (2H, m), 5.59 (1H, qt, J = 6.7, 1.2 Hz), 7.0−7.3 (4H, m); ^{1}H NMR of isomer **49b** ($CDCl_3$) δ 0.93 (3H, t), 1.82 (3H, d, J = 6.8 Hz), 2.31 (3H, s), 2.4−2.5 (2H, m), 5.35 (1H, q, J = 6.8 Hz), 7.0−7.3 (4H, m).

The next eluent was a mixture (69 mg) of **48a** and **33b** and a small amount of dimethyl fumarate. The mixture, as judged by ^{1}H NMR, contained 59 mg of **48a** (21%) and 7 mg of **33b** (2%). The spectral data of **48a**: IR (KBr) 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.66 (3H, t), 0.72 (3H, t), 1.57 (1H, sextet), 1.67 (1H, sextet), 1.84 (1H, sextet), 1.97 (1H, sextet), 2.77 (1H, dd, J = 12.2, 16.0 Hz), 3.06 (1H, dd, J = 4.8, 16.0 Hz), 3.18 (1H, d, J = 12.2 Hz), 3.30 (1H, td, J = 12.2, 4.8 Hz), 3.72 (3H, s), 3.73 (3H, s), 7.00−7.25 (4H, m); MS(EI) *m/e* (relative intensity) 243.10 (50), 215.11 (57), 183.08 (35), 143.08 (100), 129.07 (52); HRMS calcd for $C_{18}H_{24}O_4$ 304.1675, found 304.1668.

Diethyl *trans*-1,1-Diethyl-1,2,3,4-tetrahydro-2,3-naphthalenedicarboxylate (48b). TBAF (1.8 mL, 1.8 mmol) was added over 45 min to **11b** (0.351 g, 903 mmol) and diethyl fumarate (0.59 mL, 3.6 mmol) in acetonitrile (7 mL). The mixture was processed as for **48a** and concentrated. Chromatography on silica gel using 1:19 ethyl acetate:ligroin yielded a 4:1 mixture of **49a** and **49b** as the first eluent (67 mg, 46%).

The next eluent contained mostly diethyl fumarate, which after removal by distillation (70 °C, 0.65 Torr), yielded **48b** as an oil (32 mg, 23%): IR (neat) 1731 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.67 (3H, t), 0.72 (3H, t), 1.25−1.32 (6H, m), 1.54−1.73 (2H, m), 1.81−2.05 (2H, m), 2.77 (1H, dd, J = 12.2, 16.0 Hz), 3.06 (1H, dd, J = 4.8, 16.0 Hz), 3.15 (1H, d, J = 12.2 Hz), 3.27 (1H, td, J = 12.2, 4.8 Hz), 4.11−4.27 (4H, m), 7.04−7.20 (4H, m); ^{13}C NMR ($CDCl_3$) δ 8.4, 10.0, 14.1, 32.5, 33.5, 34.9, 40.3, 44.5, 48.0, 60.3, 60.6, 125.7, 126.4, 126.8, 128.5, 135.5, 139.2, 173.4, 175.3; MS(EI) *m/e* (relative intensity) 258.16 (14), 257.12 (18), 229.12 (54), 185.13 (43), 157.10 (82), 129.07 (100). The third eluent contained **33b** (R and R′ = Et, 14 mg, 5%).

Cycloadditions of Acrylonitrile to α-Ethyl-α-methyl-*o*-quinodimethanes (29c−d). 1-Ethyl-1,2,3,4-tetrahydro-1-methyl-2-naphthonitrile (54a−b). TBAF (2.1 mL, 2.1 mmol, 1 M in acetonitrile) in acetonitrile (8 mL) was added in 40 min to **11c** (0.402 mg, 1.07 mmol) and acrylonitrile (2.8 mL, 42 mmol) in acetonitrile (8 mL). The mixture was processed routinely and concentrated. Column chromatography on silica gel using 1:1 dichloromethane:petroleum ether (bp 35−60 °C) yielded as the first eluent a mixture of styrenes **51a** and **51b** in an 85:15 ratio (45 mg, 29%) whose spectral data are consistent with that reported.[22]

The second eluent, an oil, contained diastereomers **54a** and **54b** in a 1:2 ratio (92 mg, 43%): IR (neat) 2236, 758 cm^{-1}; MS(EI) *m/e* (relative intensity) 199.14 (12), 170.10 (100), 143.08 (63); HRMS calcd for $C_{14}H_{17}N$ 199.1361, found 199.1381. The isomers were separated by GC (10 ft × 0.25 in. Gas chromosorb Q GE SE30 15%). The compound with a lower retention time is assigned **54a**: ^{1}H NMR ($CDCl_3$) δ 0.73 (3H, t), 1.45 (3H, s), 1.78−2.07 (2H, m), 2.08−2.28 (2H, m), 2.78−2.95 (2H, m), 2.96−3.11 (1H, dd, J = 3.7, 9.9 Hz), 7.04−7.31 (4H, m); ^{13}C ($CDCl_3$) δ 8.5 (q), 22.8 (t), 27.9 (q), 28.5 (t), 33.4 (t), 34.7 (d), 39.6 (s), 121.0 (s), 126.1 (d), 126.5 (d), 129.2 (d), 134.5 (s), 140.5 (s). The NOE of **54a** upon irradiation at δ 1.45 gave enhancements at δ 0.73 (2%), δ 1.8−2.2 (10%), δ 3.0−3.1 (1%), and δ 7.1−7.3 (6%). The product with the higher retention time is assigned **54b**: ^{1}H NMR ($CDCl_3$) δ 0.98 (3H, t), 1.42 (3H, s), 1.81−2.02 (2H, m), 2.12−2.32 (2H, m), 2.81−2.94 (2H, dd with superimposed m), 3.06 (1H, dt, J = 6.5, 17.3 Hz), 7.07−7.31 (4H, m); ^{13}C NMR ($CDCl_3$) δ 9.0, 22.5, 27.0, 27.5, 32.5, 37.8, 38.7, 121.0, 126.1, 126.3, 126.7, 129.3, 133.9, 141.1. The NOE of **54b** with irradiation at δ 1.41 exhibited enhancements at δ 0.98 (5%), δ 1.8−2.1 (4%), δ 2.1−2.3 (2%), δ 2.85−2.95 (dd, 7%), and δ 7.25−7.35 (8%). The third eluent contained **33c** (35 mg, 10%).

Methyl 1-Ethyl-1,2,3,4-tetrahydro-1-methyl-2-naphthoates and Methyl 4-Ethyl-1,2,3,4-tetrahydro-4-methyl-2-naphthoates (60). To **11c** (497 mg, 1.33 mmol) and methyl acrylate (1.8 mL, 20 mmol) in acetonitrile (5 mL) was added TBAF (2.7 mL, 2.7 mmol, 1 M in acetonitrile) over 40 min. After workup, the material was chromatographed on TLC grade silica gel using 1:19 ethyl acetate:ligroin as solvent. Styrenes **51a** and **51b** (70 mg, 36%) were in the first eluent. The next eluent, an oil, contained **60** as a mixture of isomers (92 mg, 30%): IR (neat) 1733, 1205, 1156, 758 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.6−0.9 (3H, m), 1.2−1.5 (3H, m), 1.7−2.3 (4H, m), 2.6−3.0 (3H, m), 3.7−3.8 (3H, m), 7.0−7.4 (4H, m); MS(EI) *m/e* (relative intensity) 232.15 (4), 203.11 (36), 143.09 (100); HRMS calcd for $C_{15}H_{20}O_2$ 232.1463, found 232.1473. The third eluent contained **33c** (51 mg, 13%).

Ethyl 1-Ethyl-1,2,3,4-tetrahydro-1-methyl-2-naphthoate and Ethyl 4-Ethyl-1,2,3,4-tetrahydro-4-methyl-2-naphthoate (61). To **11c** (506 mg, 1.35 mmol) and ethyl acrylate (2.2 mL, 20 mmol) in acetonitrile (5 mL) was added TBAF (2.7 mL, 2.7 mmol, 1 M in acetonitrile) over 50 min. After workup, the material was chromatographed on TLC grade silica gel using 1:2 dichloromethane:ligroin as solvent. The first eluent contained styrenes **51a** and **51b** (70 mg, 35%). The next eluent yielded isomers **61** (93 mg, 28%) as an oil: IR (neat) 1731 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.7−1.0 (3H, m), 1.2−1.5 (6H, m), 1.6−2.3 (4H, m), 2.6−3.1 (3H, m), 4.1−4.3 (2H, m), 7.0−7.4 (4H, m); MS(EI) *m/e* (relative intensity) 246.16 (5), 217.13 (38), 143.09 (100); HRMS calcd for $C_{16}H_{22}O_2$ 246.1620, found 246.1618.

Cycloadditions of α-Ethyl-α-methyl-*o*-quinodimethanes (29c,d) and Dimethyl Fumarate; Dimethyl 1-Ethyl-1,2,3,4-tetrahydro-1-methyl-2,3-naphthalenedicarboxylates (62a,b). TBAF (3.0 mL, 3.0 mmol, 1.0 M in acetonitrile) was added to **11c** (0.749 g, 2.00 mmol) and dimethyl fumarate (0.58 g, 4.02 mmol) in acetonitrile (12 mL) in 1 h. The mixture was then worked up routinely and concentrated. Dimethyl fumarate was removed via crystallization from methanol, and the mother liquor was concentrated and chromatographed on TLC grade silica gel using 1:19 ethyl acetate:ligroin as solvent. The first eluent yielded styrenes **51a** and **51b** in a 4:1 ratio (23 mg, 8%). The second eluent yielded an oil (0.32 g) which NMR showed to be diastereomers **62a** and **62b** in a 58:42 ratio contaminated with 15% **33c** (adjusted yield of **62a** and **62b**, 0.27 g, 47%; yield of **33c**, 48 mg, 8%). Preparative GC yielded a pure mixture of **62a** and **62b**, an oil: IR (neat) 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.6−0.8 (3H, m), 1.19, 1.48 (3H, two s in 55:45 ratio), 1.5−1.8 (1H, m), 1.9−2.0 (1H, q), 2.8−3.5 (4H, m), 3.7 (6H, m), 7.0−7.3 (4H, m); MS(EI) *m/e* (relative intensity) 290.16 (8), 259.14 (14), 258.13 (20), 230.13 (53), 229.09 (41), 201.10 (100); HRMS calcd for $C_{17}H_{22}O_4$ 290.1518, found 290.1562. The mixture of diastereomers was chromatographed over silica gel (15 g) using 1:19 ethyl acetate:ligroin as solvent to obtain an analytical sample. Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 69.95; H, 7.67.

Cycloadditions of α-Ethyl-α-methyl-*o*-quinodimethanes (29c,d) with Diethyl Fumarate; Diethy1 Ethyl-1,2,3,4-tetrahydro-1-methyl-2,3-naphthalenedicarboxy-late (63a,b). To **11c** (0.498 g, 1.33 mmol) and diethyl fumarate (0.44 mL, 2.7 mmol) in acetonitrile (8 mL) was added TBAF (2.7 mL, 2.7 mmol, 1 M in acetonitrile) in 38 min. After 3 h, the mixture was worked up and concentrated. The residue was chromatographed with TLC grade silica gel using 1:19 ethyl acetate:ligroin as solvent. The first eluent contained styrenes **51a** and **51b** in a 4:1 ratio (9 mg, 5%).

The second eluent yielded diastereomers **63a** and **63b** as an oil in approximately a 55:45 ratio (213 mg, 51%): IR (neat) 1730 cm^{-1}; MS(EI) *m/e* (relative intensity) 318.18 (5), 273.15 (22), 272.15 (17), 244.15 (54), 215.11 (62), 171.12 (61), 143.09 (100). The isomers were separable by GC. Isomer **63a** had the lower retention time: ^{1}H NMR ($CDCl_3$) δ 0.69 (3H, t), 1.20 (3H, s), 1.29 (6H, t), 1.88−2.05 (2H, m), 2.77−3.04 (2H, m), 3.09−3.20 (2H, m), 4.09−4.26 (4H, m), 7.03−7.31 (4H, m); NOE differences with irradiation at δ 1.20 gave enhancements at δ 1.9−2.1 (6.2%), δ 3.1−3.2 (14.4%), δ 4.1−4.3 (2.3%), and δ 7.2−7.3 (9.3%). Isomer **63b** had the higher retention time: ^{1}H NMR ($CDCl_3$) δ 0.73 (3H, t), 1.28 (3H, t), 1.30 (3H, t), 1.50 (3H, s), 1.54−1.79 (2H, m), 2.87 (1H, dd, J = 11.9, 16.2 Hz), 2.92 (1H, d, J = 12.1 Hz), 3.15 (1H, dd, J = 5.8, 16.2 Hz), 3.27−

(22) Hornback, J. M.; Barrows, R. D. *J. Org. Chem.* **1982**, *47*, 4285.

3.39 (1H, m), 4.12−4.28 (4H, m), 7.06−7.32 (4H, m); NOE differences with irradiation at δ 1.50 gave enhancements of a multiplet at δ 1.55−1.8 (3.2%), a doublet at δ 2.92 (16.3%), and a doublet at δ 7.25−7.35 (14.6%).

The third eluent contained **33c** (39 mg, 10%): mp 110−113 °C; IR (neat) 1597, 1311, 1302, 1282 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (3H, t), 1.84 (3H, s), 2.05 (1H, sextet), 2.38 (3H, s), 2.44 (3H, s), 2.88 (1H, sextet), 7.00−7.28 (8H, m); ^{13}C NMR ($CDCl_3$) δ 8.2, 21.5, 22.8, 24.0, 27.9, 72.2, 125.5, 128.4, 128.7, 130.3, 131.6, 132.5, 132.5, 133.5, 140.1, 144.1; MS(EI) *m/e* (relative intensity) 147.10 (93), 131.05 (36), 105.08 (100), 91.05 (47).

Cycloadditions of α-Butyl-α-methyl-*o*-quinodimethanes (29e,f) to Dimethyl Fumarate; Dimethyl 1-Butyl-1,2,3,4-tetrahydro-1-methyl-2,3-naphthalenedicarboxylates (66a and 66b). Reaction of **11e** (0.501 g, 1.24 mmol) and dimethyl fumarate (0.36 g, 2.48 mmol) in acetonitrile (8 mL) with TBAF (2.5 mL, 2.5 mmol, 1.0 M in acetonitrile) followed by workup yielded an oily solid. Dimethyl fumarate was removed via crystallization from methanol, and the mother liquor was concentrated and chromatographed on silica gel using 1:19 ethyl acetate:ligroin. The first eluent contained styrene **67** as an oil (0.034 g, 16%): IR (neat) 905, 770, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (3H, t), 1.28−1.45 (4H, m), 2.29−2.37 (5H, s and superimposed q), 4.86 (1H, br s), 5.18 (1H, br s), 7.07−7.20 (4H, m); ^{13}C NMR ($CDCl_3$) δ 13.9 (q), 19.8 (q), 22.5 (t), 30.0 (t), 37.5 (t), 113.4 (t), 125.3 (d), 126.6 (d), 128.3 (d), 130.0 (d), 134.8 (s), 143.3 (s), 150.3 (s); MS(EI) *m/e* (relative intensity) 174.14 (6), 159.12 (15), 145.10 (23), 132.09 (100), 117.07 (63); HRMS calcd for $C_{13}H_{18}$ 174.1408, found 174.1401.

The next eluent contained diastereomers **66a** and **66b** (0.179 g, 45%) as a liquid: IR (neat) 1736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7−1.0 (5H, m), 1.0−1.4 (5H, m), 1.4−1.7 (3H, m), 1.7−2.0 (1H, m), 2.7−3.5 (2H, m), 3.7−3.8 (6H, 4s), 7.0−7.4 (4H, m); MS(EI) *m/e* (relative intensity) 318.18 (6), 263.99 (13), 258.16 (47), 229.09 (39), 201.09 (100); HRMS calcd for $C_{19}H_{26}O_4$ 318.1831, found 318.1835. Anal. Calcd for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found: C, 71.46; H, 8.19.

Dimethyl 1-Allyl-1,2,3,4-tetrahydro-1-methyl-2,3-naphthalenedicarboxylates (68a and 68b). To **11g** (500 mg, 1.29 mmol) and dimethyl fumarate (0.37 g, 2.6 mmol) in acetonitrile (8 mL) was added TBAF (2.6 mL, 2.6 mmol, 1 M in acetonitrile) in 50 min. After workup, dimethyl fumarate was removed by crystallization from methanol. The mother liquor was concentrated and chromatographed on silica gel using 1:19 ethyl acetate:ligroin. The first eluent contained a mixture of styrene derivatives **69a** and **69b** (28 mg, 14%). The next eluent contained diastereomers **68a** and **68b** as an oil (170 mg, 44%): IR (neat) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23, 1.51 (3H, two s), 2.3−3.1 (4H, m), 3.1−3.5 (2H, m), 3.70−3.75 (6H, m), 4.8−5.6 (3H, m), 7.0−7.4 (4H, m); MS(EI) *m/e* (relative intensity) 302.15 (1), 229.09 (61), 201.10 (100); HRMS calcd for $C_{18}H_{22}O_4$ 302.1518, found 302.1514.

Dimethyl 1,2,3,4-Tetrahydro-1-methyl-1-(2-propyl)-2,3-naphthalenedicarboxylates (70a and 70b). To **11i** (0.500 g, 1.02 mmol) and dimethyl fumarate (0.59 g, 4.08 mmol) in acetonitrile (10 mL) was added TBAF (2.0 mL, 2.0 mmol, 1 M in acetonitrile) in 30 min. Following workup, dimethyl fumarate was removed via crystallization from methanol. The mother liquor was concentrated and chromatographed on silica gel with 1:19 ethyl acetate:petroleum ether to obtain diastereomers **70a** and **70b** (103 mg, 26%) in a 7:1 ratio as judged by NMR: IR (neat) 1737 cm^{-1}; MS(EI) *m/e* (relative intensity) 304.17 (1), 273.15 (3), 261.11 (6), 244.14 (4), 229.08 (61), 201.09 (100); HRMS calcd for $C_{18}H_{24}O_4$ 304.1674, found 304.1675.

Chromatography by MPLC using Size A (240−10) LiChroprep Si60 (40−63 mm) and 1:19 ethyl acetate:petroleum ether yielded pure **70a** as the first eluent: ^1H NMR ($CDCl_3$) δ 0.76 (3H, d, J = 7.0 Hz), 0.91 (3H, d, J = 7.0 Hz), 1.56 (3H, s), 2.07 (1H, septet, J = 7.0 Hz), 2.84 (1H, dd, J = 11.2, 16.6 Hz), 2.91 (1H, d, J = 12.3 Hz), 3.21 (1H, dd, J = 16.6, 6.6 Hz), 3.53 (1H, ddd, J = 12.3, 11.2, 6.6 Hz), 3.72 (3H, s), 3.73 (3H, s), 7.04−7.34 (4H, m); ^{13}C NMR ($CDCl_3$) δ 19.3 (q), 19.6 (q), 26.7 (q), 32.7 (t), 36.9 (d), 39.9 (d), 43.5 (s), 51.6 (q), 51.9 (q), 52.7 (d), 126.0 (d), 126.1 (d), 126.9 (d), 128.5 (d), 133.4 (s), 143.0 (s), 174.6 (s), 176.0 (s); NOE differences with irradiation at δ 1.56 gave enhancements at δ 0.76 (7.7%), δ 2.07 (5.5%), δ 2.90 (d, 19.2%), and δ 7.3−7.4 (17.3%).

Elimination of Trimethyl[*o*-[1-(2-propenyl)-1-(*p*-tolylsulfonyl)-3-butenyl]benzyl]silane (11f); (*E*)-4-*o*-Tolyl-1,3,6-heptatriene (76), and (*Z*)-4-*o*-Tolyl-1,3,6-heptatriene (77). To **11f** (0.507 g, 1.23 mmol) and dimethyl fumarate (0.70 g) in acetonitrile (8 mL) was added TBAF (2.4 mL, 2.4 mmol, 1 M in acetonitrile) over 56 min. The mixture was worked up routinely and concentrated. The dimethyl fumarate was removed by crystallization from methanol, and the mother liquor was chromatographed twice with silica gel using 1:19 ethyl acetate:petroleum ether as solvent to obtain **76** and **77** as an oil in an 85:15 ratio as judged by ^1H NMR (125 mg, 55%): ^1H NMR ($CDCl_3$) of isomer **76** δ 2.32 (3H, s), 3.30 (2H, d), 4.93−5.31 (4H, m), 5.70−6.06 (2H, m), 6.79 (1H, dt), 7.11−7.22 (4H, m).

Elimination of Trimethyl[*o*-[1-methyl-1-(*p*-tolylsulfonyl)-5-hexenyl]benzyl]silane (11h). Preparation of 2-*o*-Tolyl-1,6-heptadiene (80). To **11h** (0.324 g, 0.781 mmol) in acetonitrile (5 mL) was added TBAF (1.5 mL, 1.5 mmol, 1 M in acetonitrile) in 20 min. The mixture was processed routinely and concentrated. Chromatography on silica gel using petroleum ether yielded **80** as an oil (77 mg, 53%): IR (neat) 1639, 905, 764, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.55 (2H, quintet), 2.17 (2H, q), 2.32−2.43 (5H, s with superimposed q), 4.92 (1H, br s), 4.96−5.08 (2H, m), 5.23 (1H, br s), 5.75−5.92 (1H, m), 7.10−7.22 (4H, m).

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Supporting Information Available: NMR spectra (96 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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