Periselective Intramolecular Cycloaddition of Allenyl Thioethers and Allenyl Sulfones

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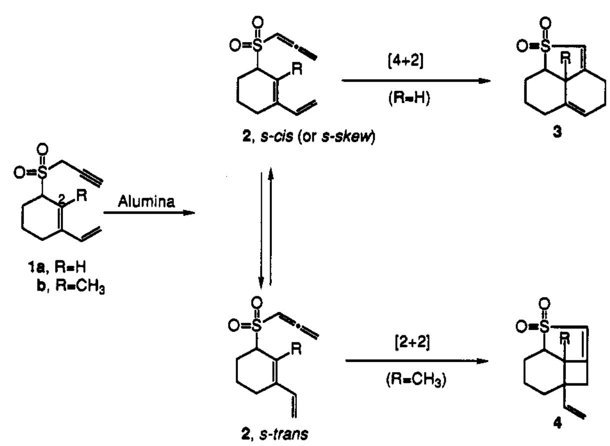
The thermal intramolecular cycloaddition reactions of variously substituted allenyl 3-vinyl-2-cyclohexenyl thioethers and sulfones and the base-catalyzed intramolecular cycloaddition reactions of several propargyl 3-vinyl-2-cyclohexenyl thioethers have been investigated. When there was no steric congestion in the transition state, the substrates gave Diels–Alder ([4 + 2]) adducts. When a substituent was introduced at C(2) of the cyclohexene in such way as to disfavor the *s-cis* conformation of the butadiene moiety in the transition state, novel [2 + 2] cycloadducts **4**, **37**, and **40** were obtained from allenyl sulfones, **1b**, **25**, and **27**, and allenyl thioether **20b** underwent a tandem [2 + 2] cycloaddition/[3,3]-sigmatropic rearrangement reaction sequence to produce **30** as the major product. C(4)-substituted compounds **22a,b** and **28** underwent Diels–Alder ([4 + 2]) reactions exclusively; C(6)-substituted allenyl thioethers **24a,b** and **26** did not afford the cycloadducts. The structure of [2 + 2] adduct **4** was confirmed by single-crystal X-ray analysis to be a strained tricyclic containing 4-, 5-, and 6-membered rings.

Introduction

The intramolecular Diels–Alder reaction of allenic dienophiles has proved to be an extraordinarily useful synthetic tool because the unique geometry of the allene molecule facilitates the cycloaddition and promotes a high degree of stereochemical control.[1–6] Recently, we have reported a dramatic substituent effect in the intramolecular cycloaddition reactions of allenyl 3-vinyl-2-cyclohexenyl ethers.[1] However, the ability of allenyl thioethers and allenyl sulfones to serve as dienophiles in intramolecular Diels–Alder reactions, which constitute a convenient route for the construction of complex ring systems, has received little attention.

Scheme 1



In 1985, we demonstrated the intermolecular Diels–Alder reactions of phenyl allenyl sulfones,[7] which was the first report of intermolecular Diels–Alder reactions of allenyl sulfones. More recently, one-pot preparations of benzo[*c*]thiophenes[8] and benzosulfolenes[9] *via* intramolecular cycloadditions of allenyl furfuryl sulfides and sulfones were reported.

In a continuation of our systematic studies of allene intramolecular cycloaddition reactions, we have recently reported a remarkable substituent effect in the intramolecular cycloaddition reactions of several allenyl sulfones.[10] The substrates underwent intramolecular Diels–Alder reactions and/or [2 + 2] cycloadditions, depending upon the substitution pattern of the 1,3-butadiene moiety (Scheme 1).

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(1) Hayakawa, K.; Aso, K.; Shiro, M.; Kanematsu, K. *J. Am. Chem. Soc.* **1989**, *111*, 5312–5320, and references cited therein.
(2) (a) Yamaguchi, Y.; Tatsuta, N.; Soejima, S.; Hayakawa, K.; Kanematsu, K. *Heterocycles* **1990**, *30*, 223–226. (b) Yamaguchi, Y.; Tatsuta, N.; Hayakawa, K.; Kanematsu, K. *J. Chem. Soc., Chem. Commun.* **1989**, 470–472. (c) Kanematsu, K.; Soejima, S. *Heterocycles* **1991**, *32*, 1483–1486. (d) Kanematsu, K.; Soejima, S.; Wang, G. *Tetrahedron Lett.* **1991**, *32*, 4761–4764. (e) Kanematsu, K.; Nishizaki, A.; Sato, Y.; Shiro, M. *Tetrahedron Lett.* **1992**, *33*, 4967–4970.
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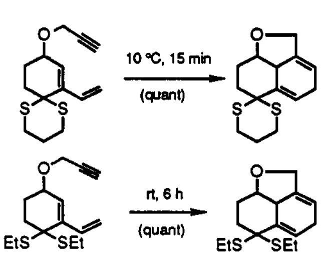
(6) (a) Kanematsu, K.; Nagashima, S. *J. Chem. Soc., Chem. Commun.* **1989**, 1028–1029. (b) Nagashima, S.; Kanematsu, K. *Tetrahedron: Asymmetry* **1990**, *1*, 743–749. (c) Nagashima, S.; Takaoka, Y.; Kawakami, K.; Kanematsu, K. unpublished results;



(7) Hayakawa, K.; Nishiyama, H.; Kanematsu, K. *J. Org. Chem.* **1985**, *50*, 512–517.
(8) Kanematsu, K.; Kinoyama, I. *J. Chem. Soc., Chem. Commun.* **1992**, 735–736.
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(10) Kanematsu, K.; Sugimoto, N.; Kawaoka, M.; Yeo, S.-K.; Shiro, M. *Tetrahedron Lett.* **1991**, *32*, 1351–1354.

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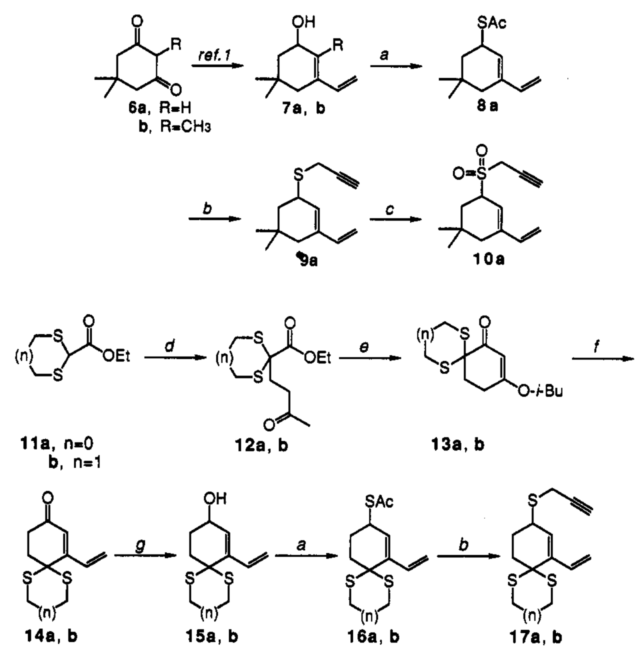
Scheme 2[a]



[a] (a) $Me_2NCH(OCH_2CMe_3)_2$, AcSH, PhMe, 0 °C; (b) (1) 0.2 N KOH, EtOH, rt, (2) $HC{\equiv}CCH_2Br$, Bu_4NHSO_4, aqueous NaOH, PhH, rt; (c) *m*-CPBA, CH_2Cl_2, 0 °C; (d) LDA, MVK, THF, −78 °C; (e) Na, *i*-BuOH, 50 °C-rt, then addition to *p*-TsOH, PhH, reflux; (f) $CH_2{=}CHMgBr$, THF, 0 °C, then addition to 10% H_2SO_4, Et_2O; (g) DIBALH, Et_2O, 0 °C.

The effect of the C(2) substituent on the reaction pathway is the key feature of these cycloadditions. The thermal reaction of allenyl 3-vinyl-2-cyclohexenyl sulfone (**2a**), prepared by the base-catalyzed rearrangement of the corresponding propargyl sulfone (**1a**, R = H), exclusively afforded Diels–Alder adduct **3a** in modest yield, whereas compound **2b**, bearing a substituent in C(2), gave a mixture of [2 + 2] adduct **4** and [4 + 2] adduct **3b**.[10] This intriguing substituent effect encouraged more detailed studies of these periselective cycloaddition reactions. For this purpose, we synthesized variously substituted allenyl thioethers and allenyl sulfones and then explored their thermal cycloaddition reactions in the hope of clarifying the factors controlling the periselection of the cycloadditions.

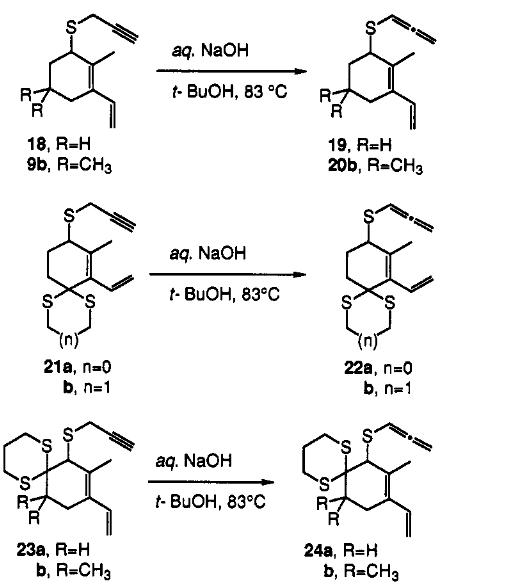
It is the aim of this paper to describe the full experimental details of our studies on cycloaddition reactions of substituted allenyl thioethers and allenyl sulfones, including an unequivocal structure determination of novel [2 + 2] adduct 10-methyl-6-vinyl-2-thiatricyclo[4.3.1.0^{4,10}]dec-3-ene 2,2-dioxide (**4**) by a single-crystal X-ray analysis. The remarkable effects of substituents at C(2), C(4), C(5), and C(6) are discussed in terms of conformational analysis.

Results

Synthesis of Propargyl 3-Vinyl-2-cyclohexenyl Thioethers and Sulfones. A variety of substituted 3-vinyl cyclohexenyl thioethers and sulfones used in cycloaddition reactions were prepared by the standard procedure, and a few representative examples are shown in Scheme 2.

Thioacetylation of 3-vinylcyclohexenols **7a,b**, prepared from dimedone (**6a**) and 2-methyldimedone (**6b**) by the standard method,[11] afforded various thioesters. For example, treatment of **7a** with thioacetic acid in the presence of *N,N*-dimethylformamide dineopentyl acetal in toluene gave thioester **8a** in 78% yield (Scheme 2). This procedure serves as a general method[12] for the thioacetylation of the dienols. The ethanolysis of **8a** in an ethanolic solution of 0.2 N KOH and propargylation of the resulting thiol provided the requisite propargyl thioether **9a** in 78% yield. Thioether **9a** was readily oxidized by *m*-CPBA (2.4 equiv) in CH_2Cl_2 and afforded propargyl sulfone **10a** in 78% yield.

Scheme 3



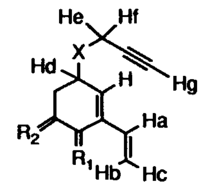
4,4-Dithiolane and dithane 3-vinylcyclohexenols **15a,b** were prepared in 37% and 43% overall yields, respectively, from ethyl 2,2-dithiolane- and 2,2-dithianecarboxylates **11a,b** by Michael condensation; intramolecular Aldol condensation and dehydration; Grignard reaction; and then reduction (Scheme 2). Compounds **15a,b** were transformed to propargyl thioethers **17a,b** by the method described above. The structural assignments were made on the basis of the 270-MHz ^1H NMR spectra (Tables 1 and 2).

Base-Catalyzed Rearrangement of 2-Substituted Propargyl Thioethers and Sulfones. When the 2-substituted propargyl thioethers were treated with aqueous NaOH (1 equiv) in *t*-BuOH at 83 °C, they rearranged rapidly to allenyl thioethers (Scheme 3). In contrast to the propargyl thioethers, the propargyl sulfones decomposed to uncharacterizable material upon treatment with aqueous NaOH. This problem was solved by the use of alumina as a weak base.

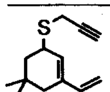
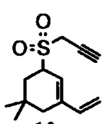
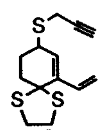
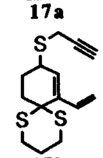
Cycloaddition Reactions. When the propargyl thioethers bearing no substituent at C(2) were treated with aqueous NaOH (1 equiv) in *t*-BuOH at 83 °C, a smooth cycloaddition took place with rapid disappearance of the starting materials. Apparently, the reaction was initiated by the base-catalyzed rearrangement of the propargyl thioether to an allenyl thioether[8,9,13] (e.g., **9a**, Table 3) prior to cycloaddition, since no reaction took place when these propargyl thioethers were heated without aqueous NaOH under otherwise identical reaction conditions. In

(11) Gannon, W. F.; House, H. O. *Org. Synth.* **1960**, *40*, 14, 41.
(12) This is a modified procedure of the reported acetylation of allylic alcohol in codeine: Barber, R. B.; Rapoport, H. *J. Med. Chem.* **1975**, *18*, 1074–1077.
(13) Brandsma, L.; Verkuijisse, H. D. *Synthesis of Acetylenes, Allenes, and Cumulenes*; Elsevier: New York, 1981.

Table 1. ^{1}H NMR Spectral Data[a] of Propargyl Thioethers and Sulfone

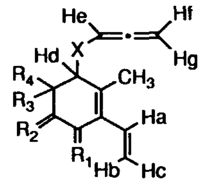


X = S, SO_2
R_1 = H_2, $-S(CH_2)_2S-$, $-S(CH_2)_3S-$
R_2 = H_2, $(CH_3)_2$

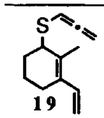
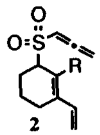
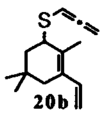
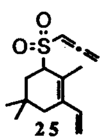
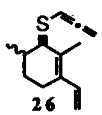
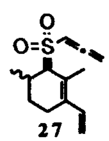
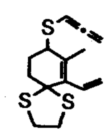
compd	δ[b], [multiplicities][c] (J, Hz)[d]								
	Ha	Ha	Hb	Hc	Hd	He	Hf	Hg	miscellaneous
 9a	5.73, [s]	6.38, [dd], (17.8, 10.8)	5.16, [d], (17.8)	4.99, [d], (10.8)	3.62–3.72, [m]	3.30, [d], 2.6, 2 H)		2.23, [t], (2.6)	0.91 (3 H, s), 1.06 (3 H, s), 1.47 (1 H, dd, 12.8, 10.8), 1.84 (1 H, ddt, 12.8, 5.9, 1.3), 1.90–1.96 (2 H, m)
 10a	5.84, [s]	6.43, [dd], (17.4, 10.8)	5.26, [d], (17.4)	5.12, [d], (10.8)	4.15–4.27, [m]	3.86, [d], (2.8, 2 H)		2.50, [t], (2.8)	0.91 (3 H, s), 1.15 (3 H, s), 1.68–2.44 (4 H, m)
 17a	6.07, [d], (4.2)	6.60, [ddt], (17.1, 10.8, 0.99)	5.49, [dd], (17.1, 1.5)	5.11, [dd], (10.8, 1.5)	3.69–3.74, [m]	3.30, [d], (2.6)	3.29, [d], (2.6)	2.26, [t], (2.6)	1.92–2.03 (1 H, m), 2.16–2.32 (2 H, m), 2.38–2.53 (1 H, m), 3.34–3.43 (4 H, m)
 17b	6.13, [d], (4.3)	6.70, [ddt], (17.1, 10.8, 0.99)	5.52, [dd], (17.1, 1.3)	5.11, [dd], (10.8, 1.3)	3.73, [dd], (10.2, 5.1)	3.33, [dd], (10.8, 2.6)	3.26, [dd], (10.8, 2.6)	2.25, [t], (2.6)	1.77–2.23 (4 H, m), 2.47 (1 H, ddd, 14.0, 7.7, 2.9), 2.56–2.74 (3 H, m), 3.02–3.14 (2 H, m)

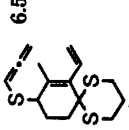
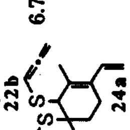
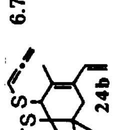
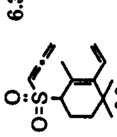
[a] $CDCl_3$. [b] Chemical shifts relative to TMS (δ 0.00). [c] Multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet. [d] Coupling constants in hertz.

Table 2. ^{1}H NMR Spectral Data[a] of Allenyl Thioethers and Sulfones



X = S, SO_2
R_1 = H_2, $-S(CH_2)_2S-$, $-S(CH_2)_3S-$
R_2 = H_2, $(CH_3)_2$
R_3, R_4 = H_2, $-S(CH_2)_3S-$, [H, CH_3]

compd	δ[b], [multiplicities],[c] (J, Hz)[d]							
	Ha	Hb	Hc	Hd	He	Hf	Hg	miscellaneous
 19	6.77, [dd], (17.4, 10.8)	5.20, [dd], (17.4, 1.3)	5.04, [dd], (10.8, 0.6)	3.45, [br s]	5.76, [t], (6.6)	4.99, [dd], (10.8, 6.6)	4.94, [dd], (10.8, 6.6)	1.94 (3 H, s), 1.67–2.17 (5 H, m), 2.25 (1 H, br d, 17.4)
 2	2a (R = H) 6.43, [dd], (17.4, 11.4)	5.26, [d], (17.4)	5.14, [d], (11.4)	3.58–4.17, [m]	6.07, [t], (6.0)	5.45, [d], (6.0, 2H)		1.50–2.55 (6 H, m), 5.78–5.92 (1 H, m)
	2b (R = CH_3) 6.86, [dd], (17.4, 11.4)	5.29, [d], (17.4)	5.17, [d], (11.4)	3.55–3.90, [m]	6.09, [t], (6.6)	5.43, [d], (6.6, 2H)		0.63–2.56 (6 H, m), 2.08 (3 H, s)
 20b	6.80, [dd], (17.3, 11.2)	5.17, [dd], (17.3, 1.1)	5.04, [d], (11.2)	3.45, [br t], (6.6)	5.63, [t], (6.2)	4.92, [d], (6.2, 2H)		0.87 (3 H, s), 1.03 (3 H, s), 1.72 (1 H, dd, 13.5, 9.7), 1.79–1.94 (3 H, m), 1.96 (3 H, s)
 25	6.82, [dd], (17.1, 11.2)	5.27, [d], (17.1)	5.17, [d], (11.2)	3.84, [br t], (9.0)	6.02, [t], (6.4)	5.44, [d], (6.4)	5.43, [d], (6.4)	0.82 (3 H, s), 1.10 (3 H, s), 1.69 (1 H, dd, 13.7, 10.7), 2.09 (3 H, t, 1.3), 1.83–2.15 (3 H, m)
 26	6.78, [dd], (17.3, 11.0)	5.20, [dd], (17.4, 1.4)	5.05, [dd], (11.0, 1.4)	3.07, [br s]	5.74, [t], (6.2)	4.96, [d], (6.2, 2H)		0.99 (3 H, dd, 6.9, 1.6), 1.41–1.51 (1 H, m), 1.93 (3 H, d, 1.6), 1.69–2.36 (4 H, m)
 27	6.83, [dd], (17.4, 10.8) (*cis*:*trans* = 1:7)	5.31, [d], (17.4)	5.17, [d], (10.8)	3.44, [br s]	6.06, [t], (6.2)	5.45, [dd], (14.1, 6.2)	5.39, [dd], (14.1, 6.2)	1.05 (3 H, d, 6.9), 1.38–1.48 (1 H, m), 2.06 (3 H, s), 2.00–2.13 (1 H, m), 2.22–2.27 (2 H, br m), 2.55–2.65 (1 H, m)
 22a	6.51, [dd], (17.8, 11.5)	5.23, [dd], (17.8, 2.3)	5.41, [dd], (11.5, 2.3)	3.41, [br s]	5.76 [t], (6.4)	5.01, [dd], (11.2, 6.4)	4.96, [dd], (11.2, 6.4)	1.95 (3 H, s), 2.00–2.10 (1 H, m), 2.13–2.26 (2 H, m), 2.53–2.64 (1 H, m), 3.16–3.38 (4 H, m)

 22b	6.55, [ddt], (17.4, 11.2, 1.3)	5.29, [dd], (17.4, 2.1)	5.46, [dd], (11.2, 2.1)	3.44, [br s]	5.79, [t], (6.4)	4.99, [dd], (6.4, 2.4, 2H)		1.99 (3 H, s), 1.78–2.11 (3 H, m), 2.26 (1 H, dddd, 14.0, 12.5, 4.6, 2.9), 2.48 (1 H, ddd, 13.8, 12.5, 2.6), 2.57–2.73 (3 H, m), 3.08 (2 H, tm, 13.5)
 24a	6.72, [dd], (17.4, 10.8)	5.20, [dd], (17.4, 1.3)	5.08, [d], (10.8)	3.13, [s]	6.02, [t], (6.2)	4.91, [dd], (11.8, 6.2)	4.85, [dd], (11.8, 6.2)	1.85–1.98 (2 H, m), 2.01 (3 H, s), 2.20–2.34 (4 H, m), 2.75–2.95 (3 H, m), 3.02 (1 H, dm, 14.8)
 24b	6.79, [dd], (17.4, 10.8)	5.17, [d], (17.4)	5.06, [d], (10.8)	4.02, [s]	6.08, [t], (6.2)	5.18, [dd], (10.8, 6.2)	5.13, [dd], (10.8, 6.2)	1.11 (3 H, s), 1.34 (3 H, s), 1.82–1.95 (2 H, m), 1.98 (3 H), 2.05 (1 H, br d, 17.4), 2.35 (1 H, br d, 17.4), 2.61–2.93 (3 H, m), 3.07 (1 H, ddd, 14.6, 9.9, 6.6)
 28	6.38, [dd], (17.4, 12.0)	5.06, [dd], (17.4, 2.4)	5.39, [dd], (12.0, 2.4)	3.75–4.20, [m]	6.08, [t], (6.0)	5.44, [d], (6.0, 2H)		1.08 (6 H, br s), 1.85 (3 H, s), 0.72–2.64 (4 H, m)

[a] $CDCl_3$. [b] Chemical shifts relative to TMS (δ 0.00). [c] Multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet. [d] Coupling constants in hertz.

fact, in some sterically hindered cases, the allenyl thioether intermediates could be isolated and fully characterized (Scheme 3). By contrast, the thermal reactions of 4,4-dithiane and dithiolane derivatives, having no substituents at C(2) (**17a,b**), gave another type of Diels–Alder adduct (**33a,b**, respectively) (Table 3).

Typically, the cycloadditions of propargyl thioethers bearing no substituents at C(2) and the cyclization of 5,5-*gem*-dimethyl-2-methyl propargyl thioether[15] (**9b**) were carried out as described previously (aqueous NaOH, *t*-BuOH, 83 °C, 1–3 h). However, the general procedure for thermal cycloaddition of allenyl thioethers and sulfones is as follows. The corresponding allenyl thioethers and sulfones were dissolved in toluene, and the solution was heated under reflux (110 °C) until the starting materials completely disappeared (1–5 h). After the aqueous workup, the products were isolated by column chromatography (silica gel). The results are summarized in Tables 3 and 4.

As shown in Tables 3 and 4, four kinds of products (the [4 + 2] adducts, the [2 + 2]/[3,3] adducts, the [2 + 2] adducts *via* the allenyl thioethers and sulfones, and the [4 + 2] adducts arising from the propargyl thioethers) were formed in moderate yields. It is almost certain that the substituent at C(2) plays an important role in determining the reaction pathway. Reactions of compounds having no substituents at C(2) (entries 1 and 3–7 in Table 3) gave exclusively the [4 + 2] adducts derived from the intramolecular Diels–Alder reactions of the propargyl and/or allenyl thioethers and allenyl sulfones. In addition, the substituents at C(5) may also influence the stability and reactivity of the initially formed allenyl thioethers (compare entries 1 and 2 in Table 3 with entries 1 and 2 in Table 4).

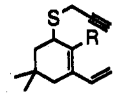
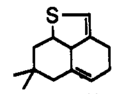
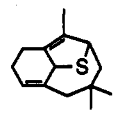
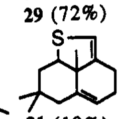
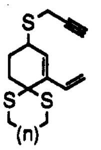
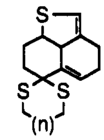
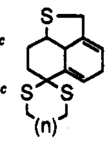
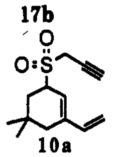
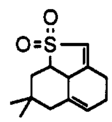
Introduction of a substituent at C(2) led to a remarkable change in chemical behavior. Thus, the 2-methyl derivative (entry 2 in Table 3 and entries 8, 9, and 11 in Table 4) underwent the tandem [2 + 2]/[3,3] and [2 + 2] reactions to give novel tricyclic compounds (**30** and **4**, **37**, **40**, respectively) as major products.

The C(4) substituents also influenced the periselectivity of the reaction depending on its stereochemistry. Whereas the reactions of 2-methyl-4-substituted compounds **22a,b** (entries 3 and 4 in Table 4) and **28**[6] (entry 10 in Table 4) gave only [4 + 2] adducts **36a,b** and **39**, the base-catalyzed reaction of 4,4-disubstituted derivatives **17a,b** (entries 3 and 4 in Table 3) afforded a mixture of [4 + 2] adducts **32a,b** *via* the allenyl thioether and [4 + 2] adducts **33a,b** from the propargyl thioether, respectively, in 5:1 (**32a**:**33a**) and 4:7 (**32b**:**33b**) ratios. Interestingly, the reactivities of dithiolane and dithiane derivatives (4,4-disubstituted) **17a,b** were remarkably different from those of other propargyl thioethers. Surprisingly, the thermal reactions of **17a,b** in benzene at 80 °C readily gave another type of

(14) The following characteristic spectral features were diagnostic in the stereochemical assignments: (1) the C(1) methine protons (Hd) of *trans* isomers **26**, **27**, and **40** appear at a higher field (δ 3.07, 3.44, and 2.70) than those of the *cis* isomers (δ 3.27, 3.70, and 3.24, respectively) because of the shielding effect of the C(6) substituent; (2) the coupling constant between two adjacent methine protons ($J_{1,6}$) is generally larger in *trans* isomer **40** (7.6 Hz) than in *cis* isomer **40** (3.2 Hz); and (3) the 2D NOESY experiments show a remarkable NOE interaction between the C-9 methyl groups (C-11 in **41**) and the C-1 methine protons in *trans*-**40** and **41** but not in *cis*-**40**, suggesting their spatial proximity in the former.

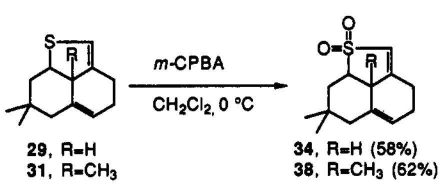
(15) Compound **9b** was also rearranged to the corresponding allenyl thioether by basic conditions (aqueous NaOH, 50 °C, 18 h, *t*-BuOH) in 36% yield.

Table 3. Base-Catalyzed Cycloaddition of Propargyl Thioethers and Sulfone

entry	substrate	reaction condition	product (yield, %) [2 + 2][3,3]	[4 + 2]	[4 + 2][a]
1	 9a (R = H)	aqueous NaOH, *t*-BuOH, 83 °C, 1 h		 29 (72%)	
2	9b (R = CH3)	aqueous NaOH, *t*-BuOH, 83 °C, 3 h	 30 (34%)	 31 (19%)	
3	 17a (*n* = 0)	aqueous NaOH, *t*-BuOH, 30 °C, 8 h		 32a (*n* = 0) (80%, 32a:33a = 5:1)[c]	 33a (*n* = 0)
4	17b (*n* = 1)	aqueous NaOH, *t*-BuOH, 50 °C, 5h		32b (*n* = 1) (80%, 32b:33b = 4:7)[c]	33b (*n* = 1)
5	17a	PhH, 80 °C, 4h			33a (83%)
6	17b	PhH, 80 °C, 1 h			33b (70%)
7[b]	 10a	alumina, PhH, 80 °C, 1 h		 34 (47%)	

[a] Cycloadduct arising from intramolecular cycloaddition at the propargylic triple bond. [b] The cycloaddition yield increased to 54% when Silica gel (*t*-BuOH, 83 °C, 5 h) was used instead of alumina. [c] The ratio was determined by the integration ratio of olefinic protons in 270-MHz ^{1}H NMR.

Scheme 4



[4 + 2] adduct (**33a,b**, respectively) in good yields (entries 5 and 6 in Table 3).[16]

In contrast, introduction of a substituent at C(6) led to an adverse change in the reactivity and stability of the allenyl thioether. Thus, 6-substituted allenyl thioethers **24a,b** (entries 5 and 6 in Table 4) and **26** decomposed to inseparable mixtures under the thermal conditions. However, the similar reaction of 6-substituted allenyl sulfone **27** (entry 11 in Table 4) gave a mixture of [2 + 2] adduct **40** and [4 + 2] adduct **41** in about a 2:1 ratio (and 2-substituted allenyl sulfones as well).

The determination of the structures of the Diels–Alder ([4 + 2]) adducts was based on the spectroscopic data (Table 5) as well as on chemical transformation. The most diagnostic feature of the ^{1}H NMR spectra is a peak appearing at low field (δ 5.54–6.33) that can be attributed to the olefinic proton of the dihydrothiophene or dihydrosulfolene moiety. These dihydrothiophene adducts could be easily converted into dihydrosulfolene adducts by an oxidation procedure, as exemplified by **29** and **31** (Scheme 4).

The structures of the [2 + 2] adducts were deduced from the ^{1}H NMR spectra (Experimental Section) and the ^{13}C NMR spectra (Table 6), which showed the characteristic signals of four sp^2 carbons (s + 2d + t) attributed to the tetra-, tri-, and disubstituted olefins. Unequivocal support for the proposed structures was obtained from a single-crystal X-ray analysis of **4** (Figure 1). The crystallographic data (see supplementary material) show standard bond lengths for all of the C=C, C—C, and C—S bonds of the 2-thiatricyclo[4.3.1.0^{4,10}]decene moiety in **4**, suggesting the stability of this novel ring system. The most interesting structural feature of [2 + 2] cycloadduct **4** is the presence of unusually long C–C bonds (nearly 1.6 Å) in the cyclobutane ring (C(5)–C(6), 1.590 Å; C(5)–C(8), 1.580 Å). The abnormal elongation of these two bonds is clearly not caused by steric effects and is very likely related to the well-documented π/σ* interaction enhanced by strain.[17] There are numerous examples in which an olefinic group destabilizes and elongates the adjacent strained C–C single bond when the π and σ* orbitals are parallel.

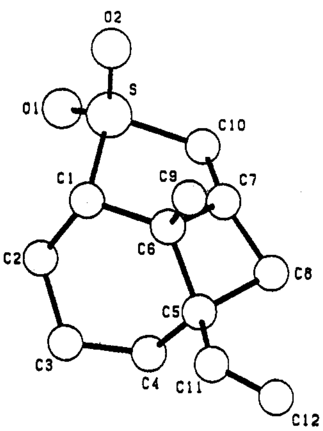


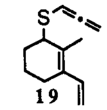
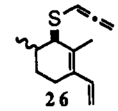
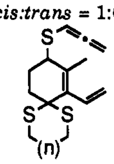
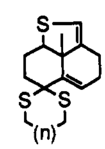
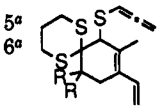
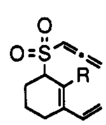
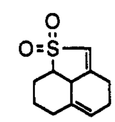
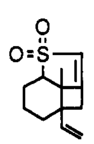
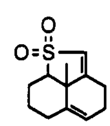
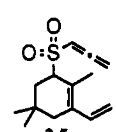
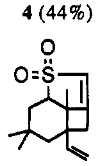
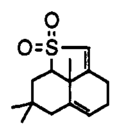
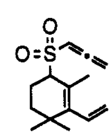
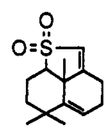
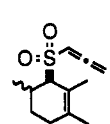
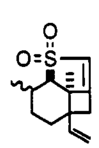
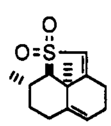
Figure 1. X-ray crystal structure of **4**.

The structure of novel [2 + 2]/[3,3] adduct **30** was assigned on the basis of the ^{1}H NMR and ^{13}C NMR spectra (Table 5 and Experimental Section) and on previous information[1] for the corresponding adduct from allenyl

(16) The thermal reactions of **17a,b** at 80 °C in benzene afforded another type of Diels–Alder adducts, **33a,b**, in 83% and 70% yields, respectively, arising from intramolecular cycloaddition at the propargylic triple bond.

(17) (a) Dougherty, D. A.; Choi, C. S.; Kaupp, G.; Buda, A. B.; Rudzinski, J. M.; Osawa, E. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1063. (b) Osawa, E.; Kanematsu, K. In *Molecular Structure and Energetics*; Greenberg, A., Liebman, J., Eds.; Verlag Chemie International: Deerfield Beach, FL, 1986; Vol. 3, Chapter 7.

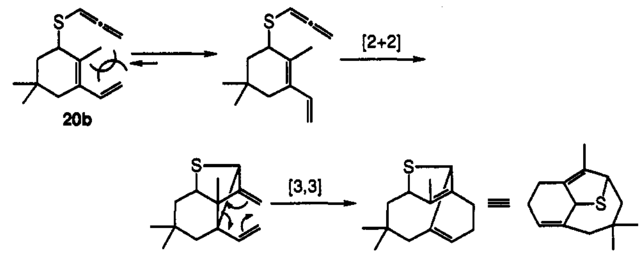
Table 4. Thermal Cycloadditions of Allenyl Thioethers and Sulfones

entry	substrate		product (yield, %) [2 + 2]	product (yield, %) [4 + 2]
1[a]	 19			
2[a]	 26 (*cis*:*trans* = 1:6)			
3		22a (*n* = 0)		 36a (45%)
4		22b (*n* = 1)	ND[b]	36b (71%)
5[a]		24a (R = H)		
6[a]		24b (R = CH_3)		
7		2a (R = H)	ND[b]	 3a (60%)
8			 4 (44%)	 3b (24%)
9	 25		 37 (27%)	 38 (16%)
10	 28		ND[b]	 39 (41%)
11[c]	 27 (*cis*:*trans* = 1:7)		 40 (47%) (*cis*:*trans* = 1:11)	 41 (24%)

[a] Cycloadducts were not obtained; the starting materials decomposed to inseparable mixtures under the thermal conditions. [b] ND; not detected. [c] The structure determination was made on the basis of the 270-MHz ^{1}H NMR spectra (Tables 2 and 5, Experimental Section, and supplementary material).[1,14]

ether. The ^{1}H NMR spectra showed the characteristic olefinic proton signal (δ 5.33) and two bridgehead methine proton signals (δ 3.96 and 3.77), and the ^{13}C NMR spectra showed the signals of four the sp^2 carbons (3s + d) attributed to tetra- and trisubstituted olefins. This spectral feature is compatible with that of the corresponding allenyl ether adduct.

Scheme 5



Discussion

Effects of the C(2) Substituent. Apparently, the substituent at C(2) plays the most important role in controlling the periselectivity of these cycloaddition reactions. The most obvious effect of the C(2) substituent is the effect on the conformational equilibrium of the 1,3-butadiene moiety in the starting material (and the allenyl thioethers as well) (Scheme 1). The *s-cis* (or *s-skew*) conformation of the butadiene moiety may be severely disfavored by the presence of the C(2) substituent.[18] In this regard, the ^{1}H NMR spectra (Tables 1 and 2 and Experimental Section) showed some instructive evidence. Whereas the olefinic proton signal (Ha) of the C(2) unsubstituted compounds, such as **2a**, **9a**, and **10a**, appeared at about δ 6.4 (dd), the Ha signal of the compounds bearing a C(2) substituent (**2b**, **19**, **20b**, **24a**, **24b**, **25**, **26**, and **27**) appeared at much lower field (δ 6.72–6.86) (see Tables 1 and 2 and Experimental Section). This remarkable low-field shift of the olefinic proton signal can be attributed to the deshielding effect of the proximate C(2)–C(3) double bond experienced in the *s-trans*-butadiene conformer.[1]

Consequently, when the *s-skew*-butadiene conformation is not sterically hindered, as in **9a** and **10a** as well as **2a**, the [4 + 2] cycloaddition, which gives the less-strained Diels–Alder adduct (**29** and **34** in Table 3), occurs. However, when the transition state is sterically congested by the C(2) substituent, as in **20b**,[18a] the [2 + 2] cycloaddition to give highly strained compound **5** is preferred. Compound **5** rapidly undergoes [3,3]-sigmatropic rearrangement to produce novel [2 + 2]/[3,3] product **30** (Scheme 5). The tandem [2 + 2]/[3,3] reaction proceeded in a stereoselective manner (see entry 2, Table 3), although a stepwise [2 + 2] cycloaddition involving diradical intermediates cannot be fully excluded.[19,20]

By contrast, **25** (as well as the other 2-substituted allenyl sulfones) underwent another type of [2 + 2] cycloaddition, which gave [2 + 2] adduct **37**. The cycloaddition of **25** was quite different from the intramolecular cycloaddition of allenyl ethers.[1] Obviously, the structural conditions in allenyl sulfones such as **2b**, the spatial proximity of the C(2)–C(3) double bond and a decrease in the internal bond angle (95.2°) of the allenyl sulfone moiety ("the reactive rotamer effect"[21]), provide an energetically favorable situation for this exceptional behavior. The sulfonyl

(18) (a) Jaime, C.; Osawa, E. *J. Mol. Struct.* **1985**, *126*, 363. (b) Lipnick, R. L.; Garbisch, E. W., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6370–6375. (c) Devaquet, A. J. P.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 4068–4076.

(19) For comprehensive reviews on allene [2 + 2] cycloadditions, see: (a) Hopf, H. *The Chemistry of Allenes*; Landor, S. D., Ed.; Academic Press: New York, 1982; Vol. 2, pp 525–562. (b) Pasto, D. J. *Tetrahedron* **1984**, *40*, 2805–2827.

(20) (a) Pasto, D. J.; Yang, S. H. *J. Am. Chem. Soc.* **1984**, *106*, 152–157. (b) Dolbier, W. R., Jr.; Wicks, G. E. *J. Am. Chem. Soc.* **1985**, *107*, 3626–3631.

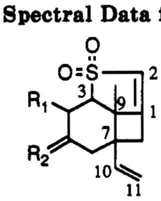
(21) Michael, L. C.; William, H. O. *J. Org. Chem.* **1990**, *55*, 5278–5287.

Table 5. Spectral Data for [4 + 2] Adducts

compd	IR, cm^{-1}	^1H NMR, δ, $CDCl_3$	mass, m/z	mp, °C
29	1625,[a] 2830, 2850, 2950	5.65 (br t, J = 1.9 Hz, 1 H), 5.41 (br d, J = 1.9 Hz, 1 H), 3.83 (ddd, J = 13.4, 9.5, 3.9 Hz, 1 H), 3.52 (br d, J = 9.5 Hz, 1 H), 2.48 (t, J = 6.2 Hz, 1 H), 2.27–2.20 (m, 3 H), 1.90–1.79 (m, 2 H), 1.44 (t, J = 13.2 Hz, 1 H), 1.25 (dd, J = 13.2, 3.9 Hz, 1 H), 1.00 (s, 3 H), 0.88 (s, 3 H)	206 (25, M^+), 204 (100, $M^+ - H_2$)	
31[d]	1630,[a] 2860, 2925, 2950	5.55 (d, J = 1.9 Hz, 1 H), 5.36–5.35 (m, 1 H), 3.32 (dd, J = 13.5, 3.6 Hz, 1 H), 2.46–2.06 (m, 4 H), 2.01 (br d, J = 14.2 Hz, 1 H), 1.71–1.64 (m, 1 H), 1.46–1.20 (m, 2 H), 1.22 (s, 3 H), 1.00 (s, 3 H), 0.86 (s, 3 H)	220 (26, M^+), 205 (100, $M^+ - CH_3$)	
36a	1240,[a] 1440, 2850, 2930	6.26 (t, J = 3.6 Hz, 1 H), 5.55 (d, J = 1.6 Hz, 1 H), 3.79 (dd, J = 6.4, 4.7 Hz, 1 H), 3.44–3.18 (m, 4 H), 2.57–2.08 (m, 7 H), 1.93–1.80 (m, 1 H), 1.52 (s, 3 H)	282 (100, M^+)	
36b[e]	1635,[b] 2850, 2920, 2960	6.37 (t, J = 3.8 Hz, 1 H), 5.54 (d, J = 1.6 Hz, 1 H), 3.75 (dd, J = 11.2, 4.9 Hz, 1 H), 3.03–2.83 (m, 3 H), 2.70–2.64 (m, 1 H), 2.49–2.23 (m, 5 H), 2.19–1.89 (m, 4 H), 1.80–1.65 (m, 1 H), 1.53 (s, 3 H)	296 (100, M^+)	146–147
3a[f]	1090,[c] 1280, 1640, 2950	6.33 (t, J = 1.7 Hz, 1 H), 5.51 (br t, J = 1.8 Hz, 1 H), 3.66 (br d, J = 6.6 Hz, 1 H), 3.43–3.34 (m, 1 H), 2.72–2.65 (m, 1 H), 2.47–1.59 (m, 9 H)	210 (100, M^+)	89
3b[g]	1090,[c] 1280, 1640, 2940	6.25 (s, 1 H), 5.47–5.44 (m, 1 H), 2.99 (dd, J = 11.1, 4.8 Hz, 1 H), 2.60–2.54 (m, 2 H), 2.45–2.12 (m, 5 H), 2.01–1.93 (m, 1 H), 1.90–1.76 (m, 1 H), 1.72–1.46 (m, 1 H), 1.52 (s, 3 H)	224 (100, M^+), 209 (69, $M^+ - CH_3$)	86–89
34[h]	1100,[b] 1270, 1625, 2840, 2900, 2950	6.30 (t, J = 2.0 Hz, 1 H), 5.53 (br t, J = 2.0 Hz, 1 H0, 3.68 (br s, 1 H), 3.42 (ddd, J = 14.1, 8.2, 4.2 Hz, 1 H), 2.70–2.64 (m, 1 H), 2.44–2.23 (m, 3 H), 1.94 (d, J = 13.2 Hz, 1 H), 1.85 (br d, J = 13.5 Hz, 1 H), 1.71 (dd, J = 13.5, 4.2 Hz, 1 H), 1.15 (t, J = 14.1 Hz, 1 H), 1.06 (s, 3 H), 0.95 (s, 3 H)	238 (100, M^+)	202–204
38[i]	1620,[b] 1665, 2850, 2900, 2930, 2950	6.20 (s, 1 H), 5.47–5.45 (m, 1 H), 3.04 (dd, J = 14.6, 3.6 Hz, 1 H), 2.57–2.49 (m, 2 H), 2.47–2.16 (m, 2 H), 2.02 (dd, J = 13.5, 1.6 Hz, 1 H), 1.80 (d, J = 13.5 Hz, 1 H), 1.69 (dd, J = 13.5, 3.6 Hz, 1 H), 1.53 (s, 3 H), 1.08 (t, J = 14.0 Hz, 1 H), 1.07 (s, 3 H), 0.94 (s, 3 H)	252 (100, M^+), 237 (43, $M^+ - CH_3$)	148–149
39[j]	1100,[c] 1290, 2950	6.22 (d, J = 1.7 Hz, 1 H), 5.59 (t, J = 3.6 Hz, 1 H), 3.16 (dd, J = 9.7, 6.7 Hz, 1 H), 2.70–2.25 (m, 4 H), 2.16–2.05 (m, 1 H), 1.80–1.63 (m, 2 H), 1.57 (s, 3 H), 1.53–1.21 (m, 1 H), 1.19 (s, 3 H), 1.13 (s, 3 H)	252 (50, M^+), 237 (100, $M^+ - CH_3$)	108
41[k]	1635,[b] 2820, 2830, 2870, 2930, 2970	6.26 (s, 1 H), 5.42 (ddd, J = 6.6, 2.6, 1.7 Hz, 1 H), 2.73 (d, J = 10.9 Hz, 1 H), 2.55–2.16 (m, 6 H), 1.92–1.74 (m, 2 H), 1.50 (s, 3 H), 1.48–1.30 (m, 1 H), 1.26 (d, J = 6.3 Hz, 3 H)	238 (100, M^+), 223 (56, $M^+ - CH_3$)	135–136
33a	1450,[a] 2820, 2850, 2920	6.26–6.22 (m, 1 H), 5.73 (br d, J = 2.0 Hz, 1 H), 3.77 (ddd, J = 12.9, 9.2, 3.6 Hz, 1 H), 3.63 (dtd, J = 12.5, 3.6, 2.0 Hz, 1 H), 3.53–3.27 (m, 4 H), 3.22–3.05 (m, 2 H), 2.96–2.68 (m, 2 H), 2.46–2.30 (m, 2 H), 1.80–1.71 (m, 1 H), 1.52–1.36 (m, 1 H)	268 (53, M^+), 207 (100)	
33b[l]	1440,[b] 2800, 2850, 2900, 2950	6.32–6.28 (m, 1 H), 5.74 (br t, J = 2.3 Hz, 1 H), 3.88 (ddd, J = 12.8, 9.2, 3.6 Hz, 1 H), 3.58 (dm, J = 13.2 Hz, 1 H), 3.42–3.32 (m, 2 H), 3.12 (ddd, J = 13.2, 11.9, 3.6 Hz, 1 H), 2.95–2.89 (m, 2 H), 2.75–2.56 (m, 3 H), 2.08–1.80 (m, 1 H), 1.71–1.63 (m, 1 H), 1.47–1.22 (m, 1 H)	282 (100, M^+)	132–134

[a] Neat. [b] KBr. [c] $CHCl_3$. [d] HRMS calcd for $C_{14}H_{20}S$ 220.1285, fopund 220.1289. [e] Anal. Calcd for $C_{15}H_{20}S_3$: C, 60.76; H, 6.80. Found: C, 60.67; H, 6.85. [f] Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71. Found: C, 62.81; H, 6.82. [g] Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.14; H, 7.24. Found: C, 64.07; H, 7.25. [h] Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61. Found: C, 65.37; H, 7.58. [i] Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.62; H, 7.99. Found: C, 66.51; H, 7.97. [j] Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.62; H, 7.99. Found: C, 66.61; H, 7.89. [k] Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61. Found: C, 65.50; H, 7.50. [l] Anal. Calcd for $C_{14}H_{18}S_3$: C, 59.52; H, 6.42. Found: C, 59.31; H, 6.41.

Table 6. ^{13}C NMR Spectral Data for [2 + 2] Adducts[a]



$R_1 = CH_3, H$
$R_2 = H_2, (CH_3)_2$

compd	C(1) (s)	C(2) (d)	C(3) (d)	C(10) (d)	C(11) (t)	C(9) (s)	C(7) (s)	miscellaneous
4	162.3	121.4	70.8	141.3	114.3	50.4	46.7	40.4 (t), 34.6 (t), 23.7 (t), 21.9 (q), 17.9 (t)
37	160.3	120.3	70.6	142.4	114.0	49.7	47.2	46.5 (t), 42.8 (t), 36.5 (t), 31.5 (q), 30.7 (s), 24.4 (q), 21.2 (q)
40	160.5	121.1	78.3	139.7	114.4	51.5	47.0	40.9 (t), 33.1 (t), 30.6 (d), 27.9 (t), 22.4 (q), 22.2 (q)

[a] δ, ppm, $CDCl_3$; multiplicities: s, singlet; d, doublet; t, triplet; q, quartet.

moiety also affected the reaction pathway. Therefore, the formation of cycloadduct **4** can be expected to proceed in a stepwise manner *via* diradical intermediate **A** rather than **B**, which suffers from steric congestion between the sulfonyl oxygen and Hb (see Figure 2).

Effects of the C(4) Substituents. In comparison with the C(2) substituents, the C(4) substituents show the reverse effect on the conformational equilibrium of the butadiene moiety. The *s-trans*-butadiene conformation may be disfavored by the repulsive interaction between the C(4) substituents and the terminal olefinic protons (Scheme 6). In this regard, the ^1H NMR spectra showed

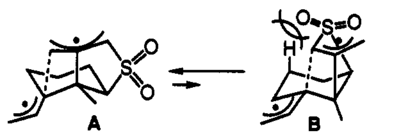
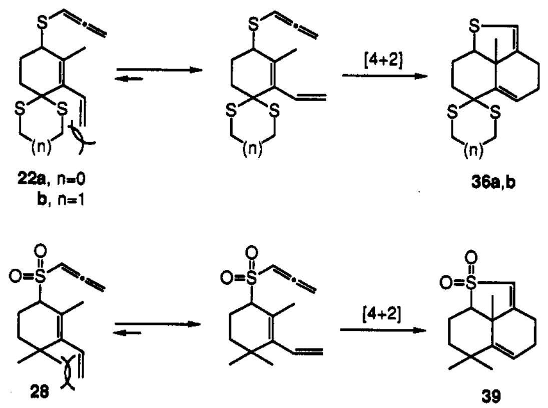


Figure 2. Proposed diradical intermediate in [2 + 2] cycloaddition of **2b**.

Scheme 6



some interesting evidence (Table 2). The olefinic signal (Ha) of a 2-methyl-4,4-disubstituted compound such as **22a,b** and **28** appeared at δ 6.38–6.55 (dd or ddt); the chemical shifts of the olefinic proton were similar to those of C(2) unsubstituted compounds (see Table 1). Furthermore, 2-substituted compounds **22a,b** and **28** exhibited terminal olefinic protons signals [Hb (*trans* olefin) and Hc (*cis* olefin)] at δ 5.06–5.29 (dd, Hb) and 5.39–5.46 (dd, Hc), respectively. These chemical shifts are different from those of the *s-skew-* or *s-trans*-butadiene moiety of the 4-unsubstituted analogues (see Tables 1 and 2). This finding seems to suggest that the butadiene moiety exists in an *s-skew* conformer with a dihedral angle of about 90°.

The above argument based on the conformational equilibrium of the butadiene moiety was substantiated by the following experiments. When compounds **22a,b** and **28** were subjected to the thermal cyclization (toluene, 160 °C, 1 h in a sealed tube, and 110 °C, 5 h), only the [4 + 2] adducts (**36a**, 45%; **36b**, 71%; **39**, 41%) were obtained, regardless of the substituent at C(2) (Scheme 6). Previously, the same results were also obtained for the corresponding allenyl ethers.[6]

Effects of the C(5) and C(6) Substituents. In contrast to the effects of the C(2) and C(4) substituents, those of the C(5) and C(6) substituents can be regarded as "secondary" (Tables 3 and 4), since the C(5) and C(6) substituents[1] alone show no remarkable effects (entries 1 and 5 in Table 3).

Thus, the *geminal* dimethyl groups at C(5) in **9a** (entry 1) and **10a** (entry 5) had no influence on the periselectivity of the reaction, and only [4 + 2] adducts **29** and **34** were formed, as in the case of **2a** (entry 7 in Table 4). However, the 5-substituent affected the reaction pathway of the 2-substituted allenyl thioether in an interesting manner. Whereas propargyl thioether **9b** (entry 2 in Table 3) underwent base-catalyzed competitive tandem [2 + 2]/3,3] reactions and Diels–Alder ([4 + 2]) reactions, the thermal reaction of C(5) unsubstituted 2-methyl allenyl thioether **19** (entry 1 in Table 4) afforded an inseparable mixture of decomposition products. These results may be explained by considering the conformational change in the cyclohexene ring caused by the C(5) substituents and the stability change of the cycloproduct containing the reactive thiovinyl moiety caused by the *geminal* dimethyl group.

The thermal reactions of the 6-substituted 2-methyl allenyl thioethers (entries 2, 5, and 6 in Table 4) gave decomposition mixtures. Although the steric hindrance caused by the C(6) substituent in the transition state can be considered, the rapid decomposition of unstable [2 + 2] cycloadducts cannot be fully excluded. Also, the instability of the allenyl thioethers under the thermal conditions was regarded as an alternative factor inhibiting the cycloadditions of the compounds. However, the outcome of the cyclization of the corresponding allenyl sulfone implied that there was no steric effect (**2b** vs **27** in Table 4).

In conclusion, the C(2) and C(4) substituents play the most important role in the intramolecular cycloadditions of allenyl thioethers and sulfones, since they affect the conformational equilibrium of *s-skew-* and *s-trans*-1,3-butadiene moieties. The 2-unsubstituted compounds exist as mixtures of *s-skew* and *s-trans* conformers and can move easily into an *s-cis* transition state whereas 2-substituted compounds exist almost completely in the *s-trans* conformation and must overcome a higher barrier to achieve an *s-cis* conformation. The 4-substituted compounds exist mainly in the *s-skew* conformation and face a still lower barrier, at least as far as rotation about this bond is concerned, to reach the transition-state geometry. Although the absence of a C(2) substituent promotes the Diels–Alder reactions, its presence makes the effects of the C(5) substituent of secondary importance. Since the C(5) substituents have an influence on the conformation of the cyclohexene ring and the stability of the compounds, the 5-substituted allenyl thioethers undergo competitive formation of tandem [2 + 2]/[3,3] and [4 + 2] adducts. It remains unclear whether the effect of C(6) substituents (in the allenyl thioethers) stems from unfavorable effects on the stability of the cycloproducts or from steric effects in the transition state of the intramolecular cycloaddition.

Experimental Section

The melting points were measured with a Yanaco micromelting point apparatus and are uncorrected. The ^{1}H NMR spectra were taken with a JOEL JNM-GX 270 or Hitachi R-1500 spectrometer with TMS as an internal standard; chemical shifts are expressed in δ values. The ^{13}C NMR spectra were determined with a JOEL JNM-GX 270 spectrometer with TMS as an internal standard. IR spectra were obtained with a JASCO A-100 infrared spectrophotometer. Mass spectra were determined on a JOEL-D 300 or a DX 300 spectrometer. Elemental analyses were performed on a Yanagimoto MT2 CHN recorder. Each reaction was monitored by TLC (silica gel 60 F_{254} plates). Column chromatography was done with E. M. Merck kieselgel 60 (70–230 mesh) as the stationary phase.

All solvents were purified before use: ether and THF were distilled from sodium benzophenone ketyl; benzene and CH_2Cl_2 were distilled from calcium hydride.

5,5-Dimethyl-3-vinyl-2-cyclohexenyl Thioacetate (8a): General Procedure for Thioacetylation. To a solution of **7a** (9.42 g, 61.8 mmol) in dry toluene (200 mL) at 0 °C were added *N,N*-dimethylformamide dineopentyl acetal (34.5 mL, 123.6 mmol) and thioacetic acid (8.8 mL, 123.6 mmol). After the reaction mixture was stirred for 10 min, the reaction was quenched by the addition of a saturated $NaHCO_3$ solution, and the separated organic phase was washed with water and brine prior to drying and evaporation. Purification of the residue by silica gel chromatography (elution with 2.5% ethyl acetate in hexane) gave **8a** (10.13 g, 78%) as a pale yellow oil: IR (neat, cm^{-1}) 2950, 1690; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.35 (dd, J = 17.5, 10.9 Hz, 1 H), 5.59 (s, 1 H), 5.15 (dd, J = 17.5, 0.7 Hz, 1 H), 4.99 (dd, J = 10.9, 0.7 Hz, 1 H), 4.37–4.30 (m, 1 H), 2.33 (s, 3 H), 1.94 (br d, J = 2.0

Hz, 2 H), 1.82 (dd, J = 12.9, 6.3 Hz, 1 H), 1.42 (dd, J = 12.9, 9.6 Hz, 1 H), 1.03 (s, 3 H), 0.97 (s, 3 H); MS m/z 210 (14, M^+), 135 (100, M^+ − SAc).

8-(Thioacetoxy)-6-vinyl-1,4-dithiaspiro[4.5]dec-6-ene (16a): pale yellow oil (76%); IR (neat, cm^{-1}) 3000, 2950, 2920, 1680; ^1H NMR (270 MHz, $CDCl_3$) δ 6.59 (dd, J = 17.2, 10.9 Hz, 1 H), 5.96 (d, J = 4.3 Hz, 1 H), 5.48 (dd, J = 17.2, 1.5 Hz, 1 H), 5.12 (dd, J = 10.9, 1.5 Hz, 1 H), 4.30–4.27 (m, 1 H), 3.41–3.27 (m, 4 H), 2.34 (s, 3 H), 2.33–2.21 (m, 3 H), 1.94–1.85 (m, 1 H); MS m/z 272 (2, M^+), 197 (100, M^+ − SAc).

9-(Thioacetoxy)-7-vinyl-1,5-dithiaspiro[5.5]undec-7-ene (16b): colorless oil (81%); IR (neat, cm^{-1}) 2950, 2900, 1680; ^1H NMR (270 MHz, $CDCl_3$) δ 6.69 (dd, J = 17.5, 10.9 Hz, 1 H), 6.01 (d, J = 4.9 Hz, 1 H), 5.49 (dd, J = 17.5, 1.6 Hz, 1 H), 5.11 (dd, J = 10.9, 1.6 Hz, 1 H), 4.30 (br q, J = 4.9 Hz, 1 H), 3.07 (ddt, J = 14.5, 12.5, 2.9 Hz, 2 H), 2.72–2.53 (m, 3 H), 2.44–2.34 (m, 1 H), 2.33 (s, 3 H), 2.32–2.19 (m, 1 H), 2.13–2.05 (m, 1 H), 1.92–1.76 (m, 2 H); MS m/z 286 (1, M^+), 211 (100, M^+ − SAc).

5,5-Dimethyl-1-(2-propynylthio)-3-vinyl-2-cyclohexene (9a): General Procedure for Propargylation. To a solution of **8a** (2.0 g, 9.50 mmol) in ethanol (10 mL) was added an ethanolic solution of 0.2 N KOH (190 mL, 38.0 mmol). The mixture was stirred at rt for 10 min before the reaction was quenched with saturated NH_4Cl solution, diluted with ether, washed with water and brine, and dried over Na_2SO_4. The solvent was then removed under reduced pressure. To a solution of the residue and Bu_4NHSO_4 (322 mg, 0.95 mmol) in benzene (20 mL) were added propargyl bromide (1.7 mL, 19.07 mmol) and 6% NaOH solution. After standing for 30 min, the reaction mixture was diluted with ether, washed with saturated NH_4Cl solution and brine, dried, and concentrated. Chromatography of the residue on silica gel (elution with 1.2% ethyl acetate in hexane) afforded 1.53 g (78% overall) of **9a** as a colorless oil: IR (neat, cm^{-1}) 3300, 2950; MS m/z 206 (6, M^+), 135 (100, M^+ − $SCH_2C{\equiv}CH$).

The ^1H NMR spectra of propargyl thioethers are summarized in Table 1.

1-(2-Propynylthio)-2,5,5-trimethyl-3-vinyl-2-cyclohexene (9b): colorless oil (77%); IR (neat, cm^{-1}) 3300, 2950; ^1H NMR (270 MHz, $CDCl_3$) δ 6.80 (dd, J = 17.5, 11.2 Hz, 1 H), 5.18 (dd, J = 17.5, 1.0 Hz, 1 H), 5.04 (d, J = 11.2 Hz, 1 H), 3.49 (br t, J = 7.9 Hz, 1 H), 3.23 (dd, J = 16.6, 2.6 Hz, 1 H), 3.15 (dd, J = 16.6, 2.6 Hz, 1 H), 2.21 (t, J = 2.6 Hz, 1 H), 1.96 (s, 3 H), 1.95–1.87 (m, 2 H), 1.84–1.80 (m, 1 H), 1.71 (dd, J = 13.3, 9.4 Hz, 1 H), 1.03 (s, 3 H), 0.87 (s, 3 H); MS m/z 220 (6, M^+), 149 (100, M^+ − $SCH_2C{\equiv}CH$).

9-(2-Propynylthio)-2-vinyl-2-cyclohexen-1-one dimethylene dithioketal (17a): colorless oil (70%); IR (neat, cm^{-1}) 3280, 2920; MS m/z 268 (6, M^+), 197 (100, M^+ − $SCH_2C{\equiv}CH$).

4-(2-Propynylthio)-2-vinyl-2-cyclohexen-1-one trimethylene dithioketal (17b): colorless oil (85%); IR (neat, cm^{-1}) 3280, 2950, 2910; MS m/z 282 (M^+).

2-Methyl-1-(2-propynylthio)-3-vinyl-2-cyclohexene (18): colorless oil (82%); IR (neat, cm^{-1}) 3300, 2930; ^1H NMR (270 MHz, $CDCl_3$) δ 6.77 (dd, J = 17.5, 11.2 Hz, 1 H), 5.19 (dd, J = 17.5, 1.3 Hz, 1 H), 5.03 (d, J = 11.2 Hz, 1 H), 3.48 (br s, 1 H), 3.33 (dd, J = 16.8, 2.6 Hz, 1 H), 3.19 (dd, J = 16.8, 2.6 Hz, 1 H), 2.28–2.22 (m, 1 H), 2.24 (t, J = 2.6 Hz, 1 H), 2.10–1.69 (m, 5 H), 1.96 (s, 3 H); ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm) 135.0 (d), 132.1 (s), 131.2 (s), 112.5 (t), 80.7 (d), 70.9 (s), 49.1 (d), 28.7 (t), 24.6 (t), 19.7 (t), 18.3 (q), 18.1 (t); MS m/z 192 (8, M^+), 121 (100, M^+ − $SCH_2C{\equiv}CH$).

3-Methyl-4-(2-propynylthio)-2-vinyl-2-cyclohexen-1-one dimethylene dithioketal (21a): colorless oil (90%); IR (neat, cm^{-1}) 3260, 2880; ^1H NMR (270 MHz, $CDCl_3$) δ 6.50 (dd, J = 17.8, 11.5 Hz, 1 H), 5.40 (dd, J = 11.5, 2.3 Hz, 1 H), 5.23 (dd, J = 17.8, 2.3 Hz, 1 H), 3.46 (br s, 1 H), 3.41–3.16 (m, 4 H), 3.31 (d, J = 2.6 Hz, 1 H), 3.25 (d, J = 2.6 Hz, 1 H), 2.58 (tm, J = 2.6 Hz, 1 H), 2.08–1.99 (m, 1 H), 1.96 (s, 3 H); MS m/z 282 (2, M^+), 211 (100, M^+ − $SCH_2C{\equiv}CH$).

3-Methyl-4-(2-propynylthio)-2-vinyl-2-cyclohexen-1-one trimethylene dithioketal (21b): colorless oil (87%); IR (neat, cm^{-1}) 3300, 2920; ^1H NMR (270 MHz, $CDCl_3$) δ 6.53 (ddd, J = 17.8, 11.5, 0.9 Hz, 1 H), 5.45 (dd, J = 11.5, 2.1 Hz, 1 H), 5.27 (dd, J = 17.8, 2.1 Hz, 1 H), 3.48 (br s, 1 H), 3.36 (dd, J = 17.1, 2.6 Hz, 1 H), 3.23 (dd, J = 17.1, 2.6 Hz, 1 H), 3.08 (tm, J = 13.2 Hz, 2 H), 2.74–2.57 (m, 3 H), 2.47 (td, J = 13.2, 2.6 Hz, 1 H), 2.27 (tdd, J = 13.2, 4.6, 2.6 Hz, 1 H), 2.25 (t, J = 2.6 Hz, 1 H), 2.11–1.78 (m, 3 H), 2.01 (s, 3 H); MS m/z 296 (2, M^+), 225 (100, M^+ − $SCH_2C{\equiv}CH$).

3-Methyl-2-(2-propynylthio)-4-vinyl-3-cyclohexen-1-one trimethylene dithioketal (23a): colorless needles (43%), mp 95.5–96 °C; IR (KBr, cm^{-1}) 3280, 2940, 2920; ^1H NMR (270 MHz, $CDCl_3$) δ 6.72 (dd, J = 17.5, 10.9 Hz, 1 H), 5.22 (dd, J = 17.5, 1.3 Hz, 1 H), 5.09 (d, J = 10.9 Hz, 1 H), 3.62 (dd, J = 16.8, 2.6 Hz, 1 H), 3.45 (dd, J = 16.8, 2.6 Hz, 1 H), 3.11 (s, 1 H), 3.01 (dm, J = 14.8 Hz, 1 H), 2.85–2.73 (m, 3 H), 2.47–2.40 (br m, 1 H), 2.33–2.14 (m, 3 H), 2.20 (t, J = 2.6 Hz, 1 H), 2.06–1.85 (m, 2 H), 2.01 (s, 3 H); ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm) 134.2 (d), 129.5 (s), 129.4 (s), 113.5 (t), 80.9 (d), 70.7 (s), 67.2 (s), 64.0 (d), 36.1 (t), 31.9 (t), 29.2 (t), 27.6 (t), 23.3 (t), 19.6 (t), 19.5 (q); MS m/z 296 (26, M^+), 225 (79, M^+ − $SCH_2C{\equiv}CH$), 150 (100).

Anal. Calcd for $C_{15}H_{20}S_3$: C, 60.76; H, 6.80. Found: C, 60.66; H, 6.85.

3,6,6-Trimethyl-2-(2-propynylthio)-4-vinyl-3-cyclohexen-1-one trimethylene dithioketal (23b): colorless oil (52%); IR (neat, cm^{-1}) 3300, 2970, 2920; ^1H NMR (270 MHz, $CDCl_3$) δ 6.79 (dd, J = 17.1, 11.2 Hz, 1 H), 5.17 (d, J = 17.1 Hz, 1 H), 5.05 (d, J = 11.2 Hz, 1 H), 3.85 (br s, 1 H), 3.83 (dd, J = 16.5, 2.6 Hz, 1 H), 3.43 (dd, J = 16.5, 2.6 Hz, 1 H), 3.01–2.85 (m, 2 H), 2.72–2.57 (m, 2 H), 2.35 (br d, J = 17.1 Hz, 1 H), 2.32 (t, J = 2.6 Hz, 1 H), 2.06 (s, 3 H), 2.05 (br d, J = 17.1 Hz, 1 H), 1.98–1.83 (m, 2 H), 1.34 (s, 3 H), 1.13 (s, 3 H); ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm) 134.9 (d), 131.1 (s), 128.5 (s), 112.8 (t), 80.3 (d), 72.4 (s), 67.9 (s), 59.8 (d), 40.3 (s), 37.4 (t), 27.4 (t), 26.8 (q), 25.7 (q), 25.3 (t), 25.2 (t), 23.1 (t), 18.2 (q); MS m/z 324 (22, M^+), 253 (27, M^+ − $SCH_2C{\equiv}CH$), 160 (100).

5,5-Dimethyl-1-(2-propynylsulfonyl)-3-vinyl-2-cyclohexene (10a): General Procedure for Sulfonylation. A solution of **9a** (1.18 g, 5.7 mmol) in CH_2Cl_2 (20 mL) was treated with 80% m-CPBA (2.76 g, 12.8 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The reaction mixture was stirred for 20 min and then quenched by the sequential addition of a 10% $NaHSO_3$ solution and a saturated $NaHCO_3$ solution. CH_2Cl_2 (50 mL) was added to the stirred reaction mixture after 30 min, and the resulting solution was washed with brine (2 × 50 mL). The organic layer was dried and concentrated *in vacuo*. Purification by chromatography (silica gel, elution with 33% ethyl acetate in hexane) gave 1.24 g (91%) of **10a** as a colorless oil: IR (neat, cm^{-1}) 3270, 2950, 2920, 2870, 1310, 1240, 1120; MS m/z 238 (13, M^+), 135 (55, M^+ − $SO_2CH_2C{\equiv}CH$), 134 (41), 119 (100).

1-(2-Propynylsulfonyl)-2,5,5-trimethyl-3-vinyl-2-cyclohexene (10b): colorless oil (66%); IR (neat, cm^{-1}) 3310, 3030, 2960, 1460, 1360, 1320, 1120; ^1H NMR (270 MHz, $CDCl_3$) δ 6.82 (dd, J = 17.2, 10.9 Hz, 1 H), 5.29 (d, J = 17.2 Hz, 1 H), 5.18 (d, J = 10.9 Hz, 1 H), 4.17–4.10 (m, 1 H), 3.89 (dd, J = 16.8, 3.0 Hz, 1 H), 3.72 (dd, J = 16.8, 3.0 Hz, 1 H), 2.50 (t, J = 3.0 Hz, 1 H), 2.11 (s, 3 H), 2.20–1.65 (m, 4 H), 1.11 (s, 3 H), 0.84 (s, 3 H); MS m/z 252 (M^+).

1-(2-Propynylsulfonyl)-3-vinyl-2-cyclohexene (1a): colorless oil (85%); IR (neat, cm^{-1}) 3310, 1320, 1120; ^1H NMR (60 MHz, $CDCl_3$) δ 6.44 (dd, J = 17.4, 10.8 Hz, 1 H), 5.94–5.72 (br s, 1 H), 5.28 (d, J = 17.4 Hz, 1 H), 5.14 (d, J = 10.8 Hz, 1 H), 4.40–3.38 (m, 1 H), 3.86 (d, J = 2.4 Hz, 2 H), 2.50 (t, J = 2.4 Hz, 1 H), 2.70–0.84 (m, 6 H); MS m/z 210 (M^+).

2-Methyl-1-(2-propynylsulfonyl)-3-vinyl-2-cyclohexene (1b): colorless oil (98%); IR (neat, cm^{-1}) 3310, 1320, 1120; ^1H NMR (60 MHz, $CDCl_3$) δ 6.86 (dd, J = 16.8, 10.8 Hz, 1 H), 5.32 (d, J = 16.8 Hz, 1 H), 5.18 (d, J = 10.8 Hz, 1 H), 4.24–3.88 (m, 1 H), 3.87 (d, J = 3.0 Hz, 2 H), 2.53 (t, J = 3.0 Hz, 1 H), 2.10 (s, 3 H), 2.67–0.48 (m, 6 H); MS m/z 224 (M^+).

1-(2-Propynylsulfonyl)-2,4,4-trimethyl-3-vinyl-2-cyclohexene (42): colorless oil (99%); IR (neat, cm^{-1}) 3250, 1310, 1120; ^1H NMR (60 MHz, $CDCl_3$) δ 6.25 (dd, J = 17.4, 12.6 Hz, 1 H), 5.37 (dd, J = 12.6, 3.0 Hz, 1 H), 5.06 (dd, J = 17.4, 3.0 Hz, 1 H), 4.13–3.77 (m, 1 H), 3.89 (d, J = 3.0 Hz, 2 H), 2.51 (t, J = 3.0 Hz, 1 H), 1.88 (s, 3 H), 1.07 (br s, 6 H), 2.64–0.72 (m, 4 H); MS m/z 252 (M^+).

1-(Allenylthio)-2,5,5-trimethyl-3-vinyl-2-cyclohexene (20b): General Procedure for Base-Catalyzed Rearrangement of Propargyl Thioethers. A solution of **9b** (911 mg, 4.1 mmol) in t-BuOH (40 mL) was treated with 10% NaOH solution (1.6 mL, 4.0 mmol) and heated at reflux (83 °C) for 30 min. After being cooled, the reaction mixture was diluted with ether, washed with water (40 mL), a saturated NH_4Cl solution (40 mL), and brine (40 mL), dried, and concentrated. Purification of the residue by silica gel chromatography (elution with hexane) gave 610 mg (67%) of **20b** as a pale yellow oil: IR (neat, cm^{-1}) 2950, 2920, 2860, 1940; MS m/z 220 (M^+).

1-(Allenylthio)-2-methyl-3-vinyl-2-cyclohexene (19): pale yellow oil (50%); ^{13}C NMR (67.8 MHz, $CDCl_3$, 200 ppm) 134.9 (d), 132.6 (s), 130.7 (s), 112.7 (t), 87.5 (d), 79.6 (t), 50.4 (d), 29.3 (t), 24.7 (t), 18.4 (q), 18.1 (t); IR (neat, cm^{-1}) 2930, 2860, 2830, 1940; MS m/z 192 (M^+).

4-(Allenylthio)-3-methyl-2-vinyl-2-cyclohexen-1-one dimethylene dithioketal (22a): pale yellow oil (85%); IR (neat, cm^{-1}) 2950, 2920, 2850, 1940; MS m/z 282 (2, M^+), 211 (100, M^+ − SCH=CH=CH_2).

4-(Allenylthio)-3-methyl-2-vinyl-2-cyclohexen-1-one trimethylene dithioketal (22b): pale yellow oil (77%); IR (neat, cm^{-1}) 2930, 2900, 1930; MS m/z 296 (11, M^+), 225 (100, M^+ − SCH=C=CH_2).

2-(Allenylthio)-3-methyl-4-vinyl-3-cyclohexen-1-one trimethylene dithioketal (24a): pale yellow oil (55%); IR (neat, cm^{-1}) 2990, 2920, 1930; MS m/z 296 (38, M^+), 225 (42, M^+ − SCH=C=CH_2), 57 (100).

2-(Allenylthio)-3,6,6-trimethyl-4-vinyl-3-cyclohexen-1-one trimethylene dithioketal (24b): pale yellow oil (62%); IR (neat, cm^{-1}) 2975, 2925, 1940; MS m/z 324 (58, M^+), 253 (100, M^+ − SCH=C=CH_2).

***cis-/trans*-1-(Allenylthio)-2,6-dimethyl-3-vinyl-2-cyclohexene (26)**: pale yellow oil (57%); IR (neat, cm^{-1}) 2970, 2930, 1940, 1450; MS m/z 206 (3, M^+), 191 (34, M^+ − CH_3), 135 (100, M^+ − SCH=C=CH_2).

1-(Allenylsulfonyl)-3-vinyl-2-cyclohexene (2a): General Procedure for Base-Catalyzed Rearrangement of Propargyl Sulfones. A solution of **1a** (450 mg, 2.1 mmol) in CH_2Cl_2 (10 mL) was treated with alumina (1 g) at rt for 2–3 h. Filtration through a short path of alumina and concentration of the filtrate left a yellow oil, which was purified chromatographically (silica gel, elution with 20% ethyl acetate in hexane) to afford 420 mg (93%) of **2a** as a colorless oil: IR (neat, cm^{-1}) 1950, 1300, 1110; MS m/z 210 (M^+).

1-(Allenylsulfonyl)-2-methyl-3-vinyl-2-cyclohexene (2b): colorless oil (84%); IR (neat, cm^{-1}) 1960, 1300, 1110; MS m/z 224 (M^+).

1-(Allenylsulfonyl)-2,5,5-trimethyl-3-vinyl-2-cyclohexene (25): colorless oil (84%); IR (neat, cm^{-1}) 1960, 1940, 1310, 1120; MS m/z 252 (1, M^+), 149 (100, M^+ − SO_2CH=C=CH_2).

***cis-/trans*-1-(Allenylsulfonyl)-2,6-dimethyl-3-vinyl-2-cyclohexene (27)**: colorless oil (84%); IR (neat, cm^{-1}) 1950, 1920, 1290, 1110; MS m/z 238 (2, M^+), 135 (100, M^+ − SO_2CH=C=CH_2).

1-(Allenylsulfonyl)-2,4,4-trimethyl-3-vinyl-2-cyclohexene (28): colorless oil (92%); IR (neat, cm^{-1}) 1960, 1310, 1120; MS m/z 252 (M^+).

Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.62; H, 7.99. Found: C, 66.38; H, 8.13.

2-(Ethoxycarbonyl)-2-(3-oxobutyl)-1,3-dithiolane (12a). To a stirred solution of LDA (10.7 mmol) at −78 °C, prepared from diisopropylamine (1.5 mL, 10.7 mmol) and *n*-butyllithium (1.5 M in hexane, 7.1 mL, 10.7 mmol) in dry THF (10 mL), was added **11a** (1.25 g, 7.0 mmol) dissolved in 10 mL of dry THF. After 30 min, methyl vinyl ketone (MVK; 0.9 mL, 10.7 mmol) was added dropwise, and the mixture was stirred for 30 min. The reaction mixture was poured into 10% HCl (20 mL) and extracted with ether (2 × 15 mL). The combined extracts were washed with saturated NH_4Cl solution and brine and dried over Na_2SO_4. The concentrate was purified by silica gel chromatography (elution with 20% ethyl acetate in hexane) to give unchanged **11a** (205 mg, 16%) and **12a** (940 mg, 54%) in that order.

For **12a**: colorless oil; IR (neat, cm^{-1}) 2980, 2930, 1720; ^1H NMR (270 MHz, $CDCl_3$) δ 4.21 (q, J = 7.1 Hz, 2 H), 3.49–3.32 (m, 4 H), 2.71–2.61 (m, 2 H), 2.49–2.44 (m, 2 H), 2.16 (s, 3 H), 1.29 (t, J = 7.1 Hz, 3 H); MS m/z 248 (4, M^+) 177 (12, M^+ − CH_2CH_2Ac), 175 (100, M^+ − CO_2Et).

2-(Ethoxycarbonyl)-2-(3-oxobutyl)-1,3-dithiane (12b). By means of the procedure described above for **12a**, MVK (1.4 mL, 17.26 mmol) was added to a solution of **11b** (2.44 g, 12.69 mmol). After a similar workup, column chromatography on silica gel (elution with 20% to 10% ethyl acetate in hexane) afforded, in the order of elution, unchanged **11b** (776 mg, 32%) and **12b** (1.74 g, 52%) as a colorless oil: IR (neat, cm^{-1}) 2980, 2930, 1720; ^1H NMR (270 MHz, $CDCl_3$) δ 4.25 (q, J = 7.1 Hz, 2 H), 3.29 (ddd, J = 14.5, 9.6, 2.6 Hz, 2 H), 2.74–2.63 (m, 2 H), 2.16 (s, 3 H), 2.14 (dm, J = 12.2 Hz, 1 H), 1.85 (ddm, J = 26.4, 12.2 Hz, 1 H), 1.32 (t, J = 7.1 Hz, 3 H); MS m/z 262 (16, M^+), 191 (13, M^+ − CH_2CH_2Ac), 189 (100, M^+ − CO_2Et).

8-Isobutoxy-1,4-dithiaspiro[4.5]dec-7-en-6-one (13a). To a stirred solution of *i*-BuONa (6.3 mmol), prepared from Na (0.14 g) in *i*-BuOH (10 mL), was added **12a** (1.30 g, 5.25 mmol) dissolved in 10 mL of *i*-BuOH at 30 °C. After 30 min, 20 mL of benzene and 1.5 g of *p*-TsOH·H_2O (7.89 mmol) were added, and the reaction mixture was heated at reflux (85–90 °C) for 3 h (Dean-Stark trap). After cooling, the reaction mixture was diluted with benzene, washed with a saturated $NaHCO_3$ solution and brine, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and column chromatography on silica gel (elution with 20% ethyl acetate in hexane) afforded **13a** as colorless thin plates (1.22 g, 90%), mp 106–107 °C (from ether/petroleum ether): IR (KBr, cm^{-1}) 2970, 2930, 2850, 1650, 1610; ^1H NMR (270 MHz, $CDCl_3$) δ 5.33 (s, 1 H), 3.61 (d, J = 6.6 Hz, 2 H), 3.58–3.47 (m, 2 H), 3.44–3.33 (m, 2 H), 2.63–2.52 (m, 4 H), 2.03 (dq, J = 19.9, 6.6 Hz, 1 H), 0.97 (d, J = 6.6 Hz, 6 H); MS m/z 258 (39, M^+), 199 (59), 143 (47), 118 (51), 85 (100).

Anal. Calcd for $C_{12}H_{18}O_2S_2$: C, 55.78; H, 7.02. Found: C, 55.83; H, 7.11.

9-Isobutoxy-1,5-dithiaspiro[5.5]undec-8-en-7-one (13b). Compound **13b** was isolated by column chromatography on silica gel (elution with 20% ethyl acetate in hexane) as colorless thin plates (2.24 g, 90%), mp 95–96.5 °C (from ether/petroleum ether): IR (KBr, cm^{-1}) 2970, 2930, 2880, 1640, 1610; ^1H NMR (270 MHz, $CDCl_3$) δ 5.20 (s, 1 H), 3.60 (d, J = 6.6 Hz, 2 H), 3.55 (tm, J = 13.5 Hz, 2 H), 2.62 (ddd, J = 14.2, 4.5, 3.5 Hz, 2 H), 2.57 (t, J = 6.3 Hz, 2 H), 2.28 (t, J = 6.3 Hz, 2 H), 2.21 (dm, J = 13.9 Hz, 1 H), 2.01 (dq, J = 19.9, 6.6 Hz, 1 H), 1.88 (qm, J = 26.4, 12.5 Hz, 1 H), 0.96 (d, J = 6.0 Hz, 6 H); MS m/z 272 (42, M^+), 239 (35), 183 (45), 132 (100).

Anal. Calcd for $C_{13}H_{20}O_2S_2$: C, 57.31; H, 7.40. Found: C, 57.27; H, 7.35.

6-Vinyl-1,4-dithiaspiro[4.5]dec-6-en-8-one (14a). To a solution of **13a** (1.22 g, 4.7 mmol) in dry THF (30 mL) at 0 °C was added a 0.98 M solution of vinylmagnesium bromide (9.6 mL, 9.4 mmol). The mixture was stirred for 1 h at 0 °C, and then 20 mL of a saturated aqueous NH_4Cl solution was added. The organic layer was separated, and the aqueous layer was extracted twice with 20 mL of ether. The combined organic extracts were washed with 20 mL of 10% H_2SO_4 and 20 mL of brine. After drying (Na_2SO_4) and evaporation of the solvent, the crude product was purified by silica gel column chromatography (elution with 10% ethylacetate in hexane) to afforded **14a** (802 mg, 80%) as a colorless oil: IR (neat, cm^{-1}) 2960, 2920, 1660; ^1H NMR (270 MHz, $CDCl_3$) δ 6.72 (dd, J = 17.5, 10.9 Hz, 1 H), 6.20 (s, 1 H), 5.79 (dd, J = 17.5, 1.0 Hz, 1 H), 5.45 (dd, J = 10.9, 1.0 Hz, 1 H), 3.50–3.33 (m, 4 H), 2.69–2.62 (m, 2 H), 2.59–2.50 (m, 2 H); MS m/z 212 (13, M^+), 186 (96, M^+ − CH=CH_2), 175 (100).

7-Vinyl-1,5-dithiaspiro[5.5]undec-7-en-9-one (14b): pale yellow oil (94%); IR (neat, cm^{-1}) 2920, 2850, 1660; ^1H NMR (270 MHz, $CDCl_3$) δ 6.90 (ddd, J = 17.16, 10.9, 0.8 Hz, 1 H), 6.21 (s, 1 H), 5.80 (dd, J = 17.16, 1.0 Hz, 1 H), 5.45 (dd, J = 10.9, 1.0 Hz, 1 H), 3.09 (ddd, J = 14.8, 12.2, 2.6 Hz, 2 H), 2.79–2.71 (m, 4 H), 2.68–2.60 (m, 2 H), 2.19–2.02 (m, 1 H), 1.90 (ddm, J = 26.1, 12.2 Hz, 1 H); MS m/z 226 (34, M^+), 200 (78, M^+ − CH=CH_2), 74 (100).

6-Vinyl-1,4-dithiaspiro[4.5]dec-6-en-8-ol (15a). To a solution of **14a** (1.01 g, 4.8 mmol) in dry ether (30 mL) at 0 °C was added a 0.93 M solution of DIBALH (7.7 mL, 7.1 mmol). The mixture was stirred for 30 min at 0 °C, and then wet NaF (2 g) was added. After 30 min, the reaction mixture was filtered, and the organic layer was washed with brine and dried. The concentrate was purified by silica gel chromatography (elution with 20% ethyl acetate in hexane) to give **15a** (968 mg, 95%) as a colorless oil: IR (neat, cm^{-1}) 3450, 2950, 2920; ^1H NMR (270 MHz, $CDCl_3$) δ 6.58 (ddd, J = 17.8, 10.9, 1.0 Hz, 1 H), 6.05 (d, J = 3.3 Hz, 1 H), 5.52 (dd, J = 17.8, 1.6 Hz, 1 H), 5.13 (dd, J = 10.9, 1.3 Hz, 1 H), 4.28 (br s, 1 H), 3.41–3.26 (m, 4 H), 2.37 (ddd, J = 14.0, 7.6, 2.8 Hz, 1 H), 2.22–2.07 (m, 2 H), 1.85–1.72 (m, 1 H), 1.54 (br s, 1 H, D_2O exchange); MS m/z 214 (68, M^+), 196 (10, M^+ − H_2O), 188 (13, M^+ − CH=CH_2), 153 (98), 135 (100).

7-Vinyl-1,5-dithiaspiro[5.5]undec-7-en-9-ol (15b). According to the procedure described above, **15b** (850 mg, 98%) was obtained from **14b** as a colorless oil: IR (neat, cm^{-1}) 3400, 2940, 2900; ^1H NMR (270 MHz, $CDCl_3$) δ 6.70 (ddt, J = 17.2, 10.9, 1.0 Hz, 1 H), 6.10 (d, J = 3.3 Hz, 1 H), 5.54 (dd, J = 17.2, 1.6 Hz, 1 H), 5.13 (dd, J = 10.9, 1.6 Hz, 1 H), 4.29 (br s, 1 H), 3.14–3.02 (m, 2 H), 2.71–2.59 (m, 3 H), 2.30 (ddd, J = 14.0, 10.2, 2.8 Hz, 1 H), 2.15–2.00 (m, 2 H), 1.92–1.74 (m, 2 H), 1.63 (br s, 1 H, D_2O exchange); MS m/z 228 (33, M^+), 210 (11, $M^+ - H_2O$), 202 (17, $M^+ - CH{=}CH_2$), 153 (84), 135 (100).

General Procedure for Cycloaddition Reactions of Propargyl Thioethers. The reaction of **9b** is described as an illustrative case. To a solution of **9b** (920 mg, 4.2 mmol) in 40 mL of *t*-BuOH were added water (3 mL) and a 10% NaOH solution (1.6 mL, 4.0 mmol). The reaction mixture was heated to reflux for 3 h, cooled to rt, diluted with water, and extracted with ether (2 × 50 mL). The combined extracts were washed with water (40 mL), a saturated NH_4Cl solution (40 mL), and brine (40 mL), dried, and evaporated. The residue was purified by silica gel chromatography (elution with 1.2% ethyl acetate in hexane) to give, in order of elution, 10,10,12-trimethyl-2-thiatricyclo[6.3.1.0^{4,12}]dodeca-3,7-diene (**31**, 175 mg, 19%) and 2,5,5-trimethyl-12-thiatricyclo[5.3.1.1^{3,11}]dodeca-1,7-diene (**30**, 313 mg, 34%), each as a colorless oil. The results are summarized in Table 3 and spectral data of [4 + 2] adducts are given in Table 5.

For **30**: IR (neat, cm^{-1}) 3020, 2950, 2900, 1450; ^1H NMR (270 MHz, $CDCl_3$) δ 5.33 (br t, J = 5.0 Hz, 1 H), 3.96 (s, 1 H), 3.77 (br s, 1 H), 3.15 (d, J = 12.5 Hz, 1 H), 2.37–2.24 (m, 3 H), 2.06–1.94 (m, 1 H), 1.85–1.75 (m, 3 H), 1.54 (s, 3 H), 0.98 (s, 3 H), 0.61 (s, 3 H); ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm) 143.9 (s), 141.4 (s), 129.7 (s), 120.5 (d), 56.3 (d), 56.1 (d), 47.4 (t), 46.0 (t), 35.4 (s), 35.0 (q), 27.2 (q), 24.8 (t), 23.0 (t), 13.3 (q); MS m/z 220 (34, M^+), 205 (100, $M^+ - CH_3$); HRMS calcd for $C_{14}H_{20}S$ 220.1284, obsd 220.1270.

Spiro[2-thiatricyclo[6.3.1.0^{4,12}]dodeca-4,7-diene-9,2′-[1′,3′]-dithiane] (33b): colorless needles; ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm) 138.6 (s), 134.7 (s), 125.6 (d), 116.9 (d), 53.3 (s), 44.5 (d), 42.4 (d), 40.9 (t), 35.4 (t), 30.5 (t), 29.7 (t), 28.9 (t), 28.2 (t), 24.9 (t).

Cycloaddition Reaction of Propargyl Sulfone. To a solution of **10a** (1.24 g, 5.2 mmol) in *t*-BuOH (50 mL) was added alumina (2–3 g). The reaction mixture was heated at reflux for 5 h, cooled to rt, and filtered through a short path of Na_2SO_4, and the filtrate was concentrated. The residue was purified by silica gel chromatography (elution with 33% ethyl acetate in hexane) to give 10,10-dimethyl-2-thiatricyclo[6.3.1.0^{4,12}]dodeca-3,7-diene 2,2-dioxide (**34**, 582 mg, 47%) as colorless needles.

General Procedure for Cycloaddition Reactions of Allenyl Thioethers and Allenyl Sulfones. The reaction of **25** is described as an illustrative case. Compound **25** (125 mg, 0.5 mmol) was dissolved in 10 mL of dry toluene and heated at 110 °C for 5 h. After the reaction mixture cooled, the solvent was removed. Chromatographic purification (silica gel, elution with 11% ethyl acetate in hexane) afforded, in order of elution, 8,8,-10-trimethyl-6-vinyl-2-thiatricyclo[4.3.1.0^{4,10}]dec-3-ene 2,2-dioxide (**37**, 34 mg, 27%) and 10,10,12-trimethyl-2-thiatricyclo-[6.3.1.0^{4,12}]dodeca-3,7-diene 2,2-dioxide (**38**, 20 mg, 16%), each as colorless plates. The results are summarized in Table 4, spectral data of [4 + 2] adducts are given in Table 5, and ^{13}C NMR spectral data of [2 + 2] adducts are given in Table 6.

For **37**: mp 161–162 °C (from ether/petroleum ether); IR (KBr, cm^{-1}) 3100, 2970, 2925, 2900, 1270, 1130, 1100; ^1H NMR (270 MHz, $CDCl_3$) δ 6.26 (d, J = 1.7 Hz, 1 H), 6.17 (dd, J = 16.8, 10.6 Hz, 1 H), 5.16 (dd, J = 10.6, 0.7 Hz, 1 H), 5.06 (d, J = 16.8 Hz, 1 H), 3.44 (dd, J = 15.2, 2.3 Hz, 1 H), 3.19 (dd, J = 10.2, 8.9 Hz, 1 H), 2.67 (dd, J = 15.2, 0.7 Hz, 1 H), 1.85 (ddd, J = 14.1, 8.9, 2.3 Hz, 1 H), 1.77–1.62 (m, 2 H), 1.55 (s, 3 H), 1.43 (d, J = 14.1 Hz, 1 H), 0.97 (s, 3 H), 0.82 (s, 3 H); MS m/z 252 (10, M^+), 237 (19, $M^+ - CH_3$), 117 (100).

Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.62; H, 7.99. Found: C, 66.56; H, 7.99.

10-Methyl-6-vinyl-2-thiatricyclo[4.3.1.0^{4,10}]dec-3-ene 2,2-dioxide (4): colorless crystals; mp 156 °C (from ether/petroleum ether); IR (KBr, cm^{-1}) 1280, 1140; ^1H NMR (270 MHz, $CDCl_3$) δ 6.31 (d, J = 1.3 Hz, 1 H), 5.95 (dd, J = 17.2, 10.6 Hz, 1 H), 5.21 (d, J = 10.6 Hz, 1 H), 5.06 (d, J = 17.2 Hz, 1 H), 3.50 (dd, J = 15.2, 2.3 Hz, 1 H), 3.17 (dd, J = 8.8, 4.5 Hz, 1 H), 2.67 (dd, J = 15.2, 1.0 Hz, 1 H), 2.28–2.17 (m, 1 H), 1.91–1.81 (m, 1 H), 1.73–1.59 (m, 3 H), 1.48 (br s, 3 H), 1.45–1.32 (m, 1 H); MS m/z 224 (2, M^+), 209 (10, $M^+ - CH_3$), 91 (100).

Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.14; H, 7.24. Found: C, 64.14; H, 7.19.

Spiro[12-methyl-2-thiatricyclo[6.3.1.0^{4,12}]dodeca-3,7-diene-9,2′-[1′,3′]dithiolane] (36a): ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm) 143.3 (s), 140.9 (s), 126.4 (d), 112.1 (d), 69.5 (s), 53.8 (d), 53.4 (s), 39.4 (t), 39.2 (t), 38.2 (t), 28.4 (q), 27.0 (t), 26.9 (t), 23.2 (t).

Spiro[12-methyl-2-thiatricyclo[6.3.1.0^{4,12}]dodeca-3,7-diene-9,2′-[1′,3′]dithiane] (36b): ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm) 141.4 (s), 139.1 (s), 130.2 (d), 111.4 (d), 53.8 (d), 53.7 (s), 52.7 (s), 36.5 (t), 29.1 (t), 28.9 (q), 28.0 (t), 27.9 (t), 26.6 (t), 25.0 (t), 22.9 (t).

***trans,trans*-11,12-Dimethyl-2-thiatricyclo[6.3.1.0^{4,12}]dodeca-3,7-diene 2,2-dioxide (41)**; ^{13}C NMR (67.8 MHz, $CDCl_3$, ppm) 158.3 (s), 136.9 (s), 122.3 (d), 121.6 (d), 73.9 (d), 46.2 (s), 29.7 (d), 29.2 (q), 28.8 (t), 27.4 (t), 26.7 (t), 23.6 (t), 20.7 (q).

***cis,trans-/trans,trans*-11,12-Dimethyl-6-vinyl-2-thiatricyclo[4.3.1.0^{4,10}]dec-3-ene 2,2-dioxide (40)**: colorless plates; mp 130–131 °C (from ether/petroleum ether); IR (KBr, cm^{-1}) 3080, 2970, 2925, 1270, 1130; ^1H NMR (270 MHz, $CDCl_3$) δ 6.29 (d, J = 1.7 Hz 1 H), 6.01 (dd, J = 17.2, 10.6 Hz, 1 H), 5.21 (dd, J = 10.6, 0.7 Hz, 1 H), 5.07 (dd, J = 17.2, 0.7 Hz, 1 H), 3.42 (dd, J = 14.8, 2.1 Hz, 1 H), 2.70 (d, J = 7.6 Hz, 1 H), 2.60 (dd, J = 14.8, 0.7 Hz, 1 H), 2.16–2.01 (m, 1 H), 1.93 (ddd, J = 14.0, 5.6, 2.1 Hz, 1 H), 1.64–1.55 (m, 1 H), 1.52–1.39 (m, 1 H), 1.45 (s, 3 H), 1.16 (d, J = 6.9 Hz, 3 H), 1.08–0.93 (m, 1 H); MS m/z 238 (4, M^+), 223 (15, $M^+ - CH_3$), 170 (100).

Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61. Found: C, 65.52; H, 7.61.

X-ray Analysis of 4. Crystal Data. $C_{12}H_{16}O_2S$, M_r 224.3, monoclinic; space group $P2_1/c$; a = 7.254(2) Å, b = 14.911(2) Å, c = 12.056(2) Å, β = 120.03(1)°, V = 1128.9(4) Å^3, Z = 4, D_{calcd} = 1.320 g cm^{-3}; μ(Cu Kα) = 22.9 cm^{-1}; crystal dimension 0.3 × 0.15 × 0.15 mm. Colorless crystals were obtained from an ether/petroleum ether solution. Three-dimensional intensity data were collected on a Rigaku AFC-5 diffractometer. The intensities of 1674 independent reflections in the range of $2\theta \le 120°$ were measured by means of a 2θ–ω scanning technique with Ni-filtered Cu Kα radiation (λ = 1.54178 Å). Three standard reflections monitored every 100 reflections showed no significant change during data collection. The intensities of 1448 observed reflections with $F_o > 3\sigma(F_o)$ were corrected for Lorentz and polarization effects but not for absorption.

Structure Determination of 4. The structure was solved by direct methods and refined to minimize the function of $\sum w|\Delta F|^2$ by the block-diagonal least-squares method. All hydrogen atoms were located in a difference Fourier map. The positional parameters of all the atoms and anisotropic thermal parameters of the non-hydrogen atoms were variable. The temperature factor of each hydrogen atom was set equal to B_{eq} of the bonded atom. The weighting scheme was $w = [\sigma^2(F_o) + 0.00187|F_o|^2]^{-1}$ for observed reflections with $w^{1/2}|\Delta F| < 4$, and $w = 0$ otherwise. Final R, R_w, and S were 0.045, 0.068, and 1.345, respectively, for 1413 reflections. The relative configuration of the molecule is presented in Figure 1.

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Supplementary Material Available: ^1H NMR spectra of **1a, 1b, 2a, 2b, 8a, 9a, 9b, 10a, 12a, 12b, 14a, 14b, 15a, 15a** (D_2O), **15b, 15b** (D_2O), **16a, 16b, 17a, 17b, 18, 19, 20b, 21a, 21b, 22a, 22b, 23a, 23b, 24a, 24b, 25, 26, 27, 29, 30, 31, 33a, 33b, 36a, 36b, 40, 41, 32a/33a, 32b/33b**; ^{13}C NMR spectra of **4, 18, 19, 23a, 23b, 30, 33b, 36a, 36b, 37, 40, 41**; and 2D spectra of **40** and **41** (61 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.