

desire to maximize M–O bonding, the metal atoms (M = Mo and W) also want to maximize M–M bonding. Hence for $[M(OR)_3]_n$, where $n = 2$, the ethane-like $O_3M\equiv MO_3$ geometry, I, with the M–M bonding configuration $\sigma^2\pi^4$, is preferred over the $[Al(OR)_3]_2$ structure involving two fused MO_4 tetrahedra. For $n = 3$, there is no known example for M = Mo or W—perhaps not surprisingly since $n = 3$ yields nine electrons available for M–M bonding which would necessarily lead to paramagnetism and would not maximize M–M bonding. For $n = 4$, there are 12 cluster electrons that can be accommodated in a variety of structures as seen for $W_4(O-i-Pr)_{12}$, II, $Mo_4Cl_4(O-i-Pr)_8$, XIII, and $Mo_4Br_4(O-i-Pr)_8$, XIV, and in the new homoleptic class $M_2(OCH_2R)_{12}$, XII. The preference for XII over structures II, XIII, and XIV appears to represent a situation wherein one metal atom achieves the maximum number of M–O bonds, namely six for M = W and Mo, while the other three metal atoms maximize their M–M bonding at the expense of M–O bonding.

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Supplementary Material Available: Tables of anisotropic thermal parameters and bond distances and angles, VERSORT drawings and stereoviews of the molecules giving the atom numbering scheme, and NMR data for compounds $M_4(OCH_2R)_{12}$, where M = W, R = cyclohexyl (IV), R = cyclopentyl (VI) and M = Mo, R = *i*-Pr (IX), R = cyclohexyl (VIII), and $M_4(OCH_2-c-Bu)_4(HOCH_2-c-Bu)$ where M = Mo (XI) and M = W (VII) (29 pages); table of observed and calculated structure factors for $Mo_4(OCH_2-c-Bu)_{12}(HOCH_2-c-Bu)$ (21 pages). Ordering information is given on any current masthead page.

Competitive Intramolecular [4 + 2] Cycloaddition and Tandem [2 + 2] Cycloaddition/[3,3]-Sigmatropic Rearrangement Sequence of Allenyl 3-Vinyl-2-cyclohexenyl Ethers: Evidence for Switching of the Reaction Pathway by the Substituent Effects[†]

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Abstract: The base-catalyzed intramolecular cycloaddition reactions (*t*-BuOK, *t*-BuOH, 83 °C) of variously substituted propargyl 3-vinyl-2-cyclohexenyl ethers have been investigated. The reaction proceeded smoothly via the initial isomerization to the corresponding allenyl ethers followed by the intramolecular Diels–Alder ([4 + 2]) reaction and/or tandem [2 + 2] cycloaddition, [3,3]-sigmatropic rearrangement ([2 + 2] + [3,3]) depending upon the substitution pattern. The C(2) substituent showed a remarkable switching effect. While the compounds bearing no substituents at C(2) (**1a**, **b**, **21**, **22**) underwent selectively the [4 + 2] cycloaddition, the 2-substituted compounds (**1c**, **d**) performed exclusively the tandem [2 + 2], [3,3] reactions. On the other hand, the C(6) substituents also influenced the reaction pathway in a unique manner. While the reaction of the 1,6-trans compounds (**15**, **20**) gave exclusively the [2 + 2] + [3,3] products, the similar reaction of the 1,6-cis isomers (**14**, **19**) resulted in a concomitant formation of [4 + 2] and [2 + 2] + [3,3] products. In the latter case, the allene intermediates (**36**, **37**) could be isolated. The structure–reactivity relationship in the intramolecular cycloadditions of the allenyl ethers was discussed in detail.

The ability of allenes to undergo either inter- or intramolecular cycloaddition reactions with various unsaturated functionalities provides a convenient route for the construction of complex ring systems.² The intramolecular Diels–Alder reaction utilizing appropriate allenic dienophiles has proved to be an extraordinarily useful synthetic tool because of unusual facilitation of cycloaddition as well as a high degree of stereochemical control due to the unique geometry of allene molecules.^{3–10}

Recently, we have reported a remarkable substituent effect in the intramolecular cycloaddition reaction of allenyl 3-vinyl-2-cyclohexenyl ethers (**2**) prepared in situ by the base-catalyzed

rearrangement of the corresponding propargyl ethers **1** (Scheme I).⁷ The key feature of the substituent effect is switching of the

(1) (a) Kyushu University. (b) Shionogi & Co., Ltd.

(2) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; Wiley, New York, 1984.

(3) Hayakawa, K.; Yodo, M.; Ohsuki, S.; Kanematsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 6735.

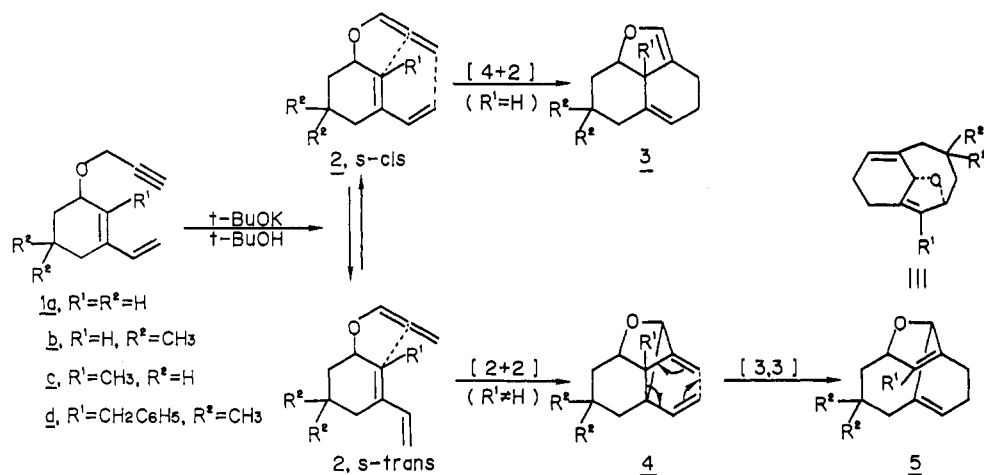
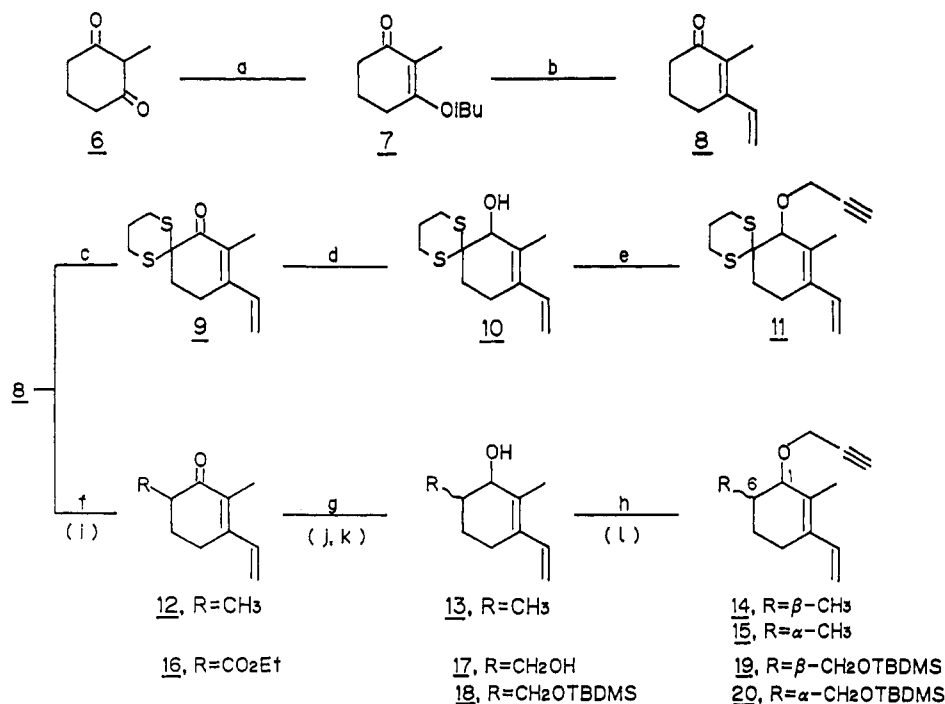
(4) (a) Hayakawa, K.; Yamaguchi, Y.; Kanematsu, K. *Tetrahedron Lett.* **1985**, *26*, 2689. (b) Yamaguchi, Y.; Hayakawa, K. *J. Chem. Soc., Chem. Commun.* **1987**, 515. (c) Yamaguchi, Y.; Yamada, H.; Hayakawa, K.; Kanematsu, K. *J. Org. Chem.* **1987**, *52*, 2040.

(5) (a) Hayakawa, K.; Yasukouchi, T.; Kanematsu, K. *Tetrahedron Lett.* **1986**, *27*, 1837. (b) *Ibid.* **1987**, *28*, 5895.

(6) Hayakawa, K.; Ohsuki, S.; Kanematsu, K. *Tetrahedron Lett.* **1986**, *27*, 947.

[†] This paper is dedicated to Professor Haruaki Yajima on the occasion of his retirement from Kyoto University in March, 1989.

Scheme I

Scheme II^a

^a(a) *i*-BuOH, *p*-TsOH, C₆H₆, Dean-Stark, 80 °C; (b) (1) CH₂CHMgBr, THF, 0 °C, (2) 10% H₂SO₄, Et₂O; (c) NaH, THF, 1,3-bis(*o*-nitrophenylthio)propane, 0 °C–room temperature; (d) DIBAL, Et₂O, 0 °C; (e) *n*-BuLi, HC≡CCH₂Br, C₆H₆/DMSO (1/1), 0 °C–room temperature; (f) LDA, CH₃I, THF, –78 °C; (g) = (d); (h) *n*-BuLi, HMPA, THF, HC≡CCH₂Br, 0 °C–room temperature; (i) LDA, ClCO₂Et, THF, –78 °C; (j) = (d); (k) TBDMSCl, imidazole, DMF, room temperature; (l) = (h).

reaction pathway depending on a substituent at C(2) position. Thus, while the base-catalyzed reaction of **1a,b** ($R^1 = H$) exclusively afforded the Diels–Alder ([4 + 2]) adducts **3a,b** in good yields, compounds **1c,d** bearing a substituent at C(2) gave the novel products **5c,d** arising from the initial intramolecular [2 + 2] cycloaddition of the allenyl ether **2** followed by the [3,3]-sigmatropic rearrangement of the highly strained **4** (tandem [2 + 2], [3,3] reaction).⁷ The observation of such an intriguing substituent effect encouraged more detailed studies on these periselective

cycloaddition reactions. For this purpose, we have synthesized variously substituted propargyl ethers and explored the base-catalyzed cycloaddition reactions via allenyl ether intermediates in the hope of clarifying the factors controlling the periselectivity of these cycloaddition reactions.

It is the aim of this article to describe the full experimental details of our studies on cycloaddition reactions of substituted allenyl ethers¹¹ including an unequivocal structural determination of the novel [2 + 2] + [3,3] adduct, 2-methyl-12-oxatrimethylene dithioketal (**23**), by a single-crystal X-ray analysis. The remarkable effects of substituents at C(2) and C(6) are discussed on the basis of the conformational analysis.

Results

Synthesis of Propargyl 3-Vinyl-2-cyclohexenyl Ethers. A variety of substituted 3-vinylcyclohexenyl ethers used in cycloaddition

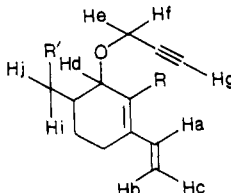
(7) Hayakawa, K.; Ohsuki, S.; Kanematsu, K. *Tetrahedron Lett.* **1986**, 27, 4205.

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(11) Some of this work appeared in preliminary forms, see: ref 5 and 6.

Table I. ^1H NMR Spectral Data^a of Propargyl Ethers


compd	$\delta, ^b$ [multiplicities], ^c (J , Hz) ^d							miscellaneous
	Ha	Hb	Hc	Hd	He	Hf	Hg	
1a	6.38, [dd], (17.4, 10.8)	5.19, [d], (17.4)	5.04, [d], (10.8)	4.04–4.36, [m]	4.21, [d], (2.4, 2 H)		2.40, [t], (2.4)	1.43–2.34 (6 H, m), 5.80 (1 H, m)
1b	6.41, [dd], (17.4, 11.0)	5.17, [d], (17.4)	5.01, [d], (11.0)	4.06–4.47, [m]	4.22, [d], (2.4, 2 H)		2.40, [t], (2.4)	0.91 (3 H, m), 1.05 (3 H, s), 1.75 (2 H, m), 1.96 (2 H, m), 5.76 (1 H, m)
1c	6.81, [dd], (17.4, 11.4)	5.20, [d], (17.4)	5.07, [d], (11.4)	3.75–4.05, [m]	4.20, [d], (2.4, 2 H)		2.40, [t], (2.4)	1.88 (3 H, br s), 1.34–2.50 (6 H, m)
1d	6.95, [dd], (17.4, 11.4)	5.29, [d], (17.4)	5.12, [d], (11.4)	3.60–4.15, [m]	4.07, [d], (2.4, 2 H)		2.32, [t], (2.4)	0.87 (3 H, s), 1.04 (3 H, s), 1.20–1.80 (2 H, m), 2.08 (2 H, m), 3.72 (1 H, d, 15.0), 3.80 (1 H, d, 15.0), 7.12 (5 H, s)
11	6.79, [dd], (17.4, 10.8)	5.21, [d], (17.4)	5.11, [d], (10.8)	3.98, [s]	4.57, [d], (2.4, 2 H)		2.51, [t], (2.4)	1.74–2.41 (6 H, m), 1.98 (3 H, s), 2.63–3.07 (4 H, m)
14	6.79, [dd], (17.5, 10.8)	5.21, [dd], (17.5, 1.4)	5.06, [dd], (10.8, 1.4)	3.78, [d], (3.8)	4.35, [dd], (16.0, 2.4)	4.25, [dd], (16.0, 2.4)	2.44, [t], (2.4)	1.04 (3 H, d, 7.0), 1.48–1.68 (2 H, m), 1.78–1.90 (1 H, m), 1.92 (3 H, s), 2.00–2.12 (1 H, m), 2.28 (1 H, dm, 16.2)
15	6.79, [dd], (17.5, 11.2)	5.22, [dd], (17.5, 1.5)	5.07, [dd], (11.2, 1.5)	3.59, [d], (4.3)	4.18, [dd], (2.4)	4.17, [dd], (2.4)	2.42, [t], (2.4)	0.96 (3 H, d, 7.3), 1.21–1.35 (1 H, m), 1.38–1.47 (1 H, m), 1.77–1.87 (1 H, m), 1.88 (3 H, s), 1.96–2.07 (1 H, m), 2.17 (1 H, m)
19	6.79, [dd], (17.8, 11.1)	5.21, [dd], (17.8, 1.1)	5.07, [dd], (11.1, 1.1)	3.93, [d], (3.0)	4.39, [d], (2.4)	4.38, [d], (2.4)	2.43, [t], (2.4)	0.07 (6 H, s), 0.81 (9 H, br s), 1.41–1.58 (2 H, m), 1.71–1.80 (2 H, m), 1.96 (3 H, s), 2.00–2.20 (1 H, m), 3.54 (1 H, dd, 10.3, 5.9, Hi), 3.70 (1 H, d, 10.3, Hj)
20	6.79, [dd], (17.9, 11.1)	5.20, [dd], (17.6, 1.1)	5.06, [dd], (11.1, 1.1)	3.88, [d], (4.3)	4.18, [d], (2.4)	4.17, [d], (2.4)	2.41, [t], (2.4)	0.04 (6 H, s), 0.89 (9 H, br s), 1.52–1.64 (2 H, m), 1.79–1.87 (1 H, m), 1.89 (3 H, s), 1.96–2.20 (2 H, m), 3.55 (1 H, d, 3.0, Hi) 3.57 (1 H, d, 3.2, Hj)
21	6.36, [dd], (17.6, 10.8)	5.20, [d], (17.6)	5.03, [d], (10.8)	4.07, [ddm], (4.6, 3.8)	4.26, [dd], (15.9, 2.4)	4.19, [dd], (15.9, 2.4)	2.41, [t], (2.4)	0.98 (3 H, d, 7.0), 1.52–1.69 (2 H, m), 1.90–2.07 (1 H, m), 2.11 (1 H, t, 6.8) 2.26 (1 H, dt, 17.6, 5.9) 5.81 (1 H, dm, 3.8)
22	6.36, [dd], (17.6, 10.8)	5.18, [d], (17.6)	5.03, [d], (10.8)	3.79, [dm], (7.3)	4.23, [d], (2.4, 2 H)		2.41, [t], (2.4)	1.05 (3 H, d, 6.5), 1.33–1.46 (1 H, m), 1.74 (1 H, ddd, 10.5, 7.3, 3.5), 1.79–19.0 (1 H, m), 2.12–2.21 (2 H, m), 5.76 (1 H, s)

^aCDCl₃. ^bChemical shifts relative to TMS (δ 0.00). ^cMultiplicities: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. ^dCoupling constants in hertz.

reactions were prepared by the almost unified procedure, and a few representative examples are shown in Scheme II.

Alkylation of 3-vinylcyclohexenone **8**, prepared from cyclohexa-1,3-dione **6** by the standard method¹² afforded various 6-substituted compounds. For example, treatment of **8** with 1,3-bis(*o*-nitrophenylthio)propane in the presence of sodium hydride in THF gave the dithiane derivative **9** in 64% yield (Scheme II). This procedure may serve as a general method¹³ of the α -dithianation of the carbonyl compounds.^{4b} The reduction of **9** by diisobutylaluminum hydride (DIBAH) (hexane/ether, 0 °C) and propargylation of the resulting alcohol **10** provided the requisite propargyl ether **11** in 98% yield (Scheme II).

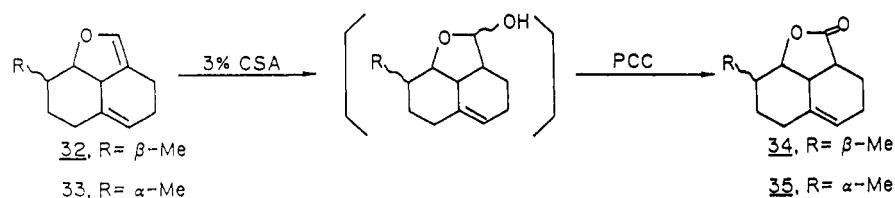
The DIBAH reduction of 6-methylcyclohexenone **12**, prepared from **8** by methylation (LDA, CH₃I, THF, -78 °C) gave an inseparable mixture of *cis/trans* alcohols **13** (Scheme II). The

propargylation, however, led to a readily separable mixture (8:1) of *cis-14* and *trans-15*, both of which were isolated in a pure form by medium-pressure column chromatography. Similarly, *cis-19* and *trans-20* were separately obtained in a 1:1 ratio after propargylation of a stereoisomeric mixture of alcohols **18** which were prepared from **8** as shown in Scheme II. The structural determination was made on the basis of the 270-MHz ^1H NMR spectra (Table I). Especially, the following characteristic spectral features were diagnostic in the stereochemical assignments. (1) The C(1) methine proton (Hd) of *trans* isomers **15** and **20** appears at the higher field (δ 3.59 and 3.88) compared with that of *cis* isomers **14** and **19** (δ 3.78 and 3.93, respectively) due to 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* isomers **15** and **20** (4.3 Hz) than in *cis* isomers **14** and **19** (3.8 and 3.0 Hz). (3) The geminal methylene protons of the C(6) substituent (Hi, Hj) or propargyl group (He, Hf) split at the larger extent in the *cis* isomers rather than in the *trans* isomers probably owing to the restricted free-rotation.¹⁴ (4) The 2D NOESY experiments

(12) Gannon, W. F.; House, H. O. *Org. Synth.* **1960**, *40*, 14, 41.

(13) This is a modified procedure of the reported α, α -disulfenylation of the carbonyl compounds: Nagao, Y.; Kaneko, K.; Kawabata, K.; Fujita, E. *Tetrahedron Lett.* **1978**, 5021.

Scheme III



showed a remarkable NOE interaction between the C-6 methyl group and the methylene protons (He, Hf) of propargyl group in *cis*-**14** but not in *trans*-**15**, suggesting their spatial proximity in the former.

Cycloaddition Reactions. When the propargyl ethers thus prepared were treated with *t*-BuOK in *t*-BuOH at 83 °C, a smooth cycloaddition reaction took place with rapid disappearance of starting materials. Apparently, the reaction was triggered by the base-catalyzed rearrangement of propargyl ether to the allenyl ether¹⁵ (e.g., **2**, Scheme I) prior to the cycloaddition, since no reaction took place on heating these propargyl ethers under the similar reaction conditions without *t*-BuOK.¹⁶ In fact, in some sterically hindered cases, the allenyl ether intermediates could be isolated and fully identified (*vide infra*).

A typical procedure for cycloaddition reactions is as follows. The appropriate propargyl ether (1 equiv) and *t*-BuOK (8 equiv) were dissolved in *t*-BuOH, and the solution was heated under reflux (83 °C) until the starting materials completely disappeared (30 min–1 h). After the aqueous workup, the products were isolated by medium-pressure column chromatography (SiO₂). The results are summarized in Table II.

As Table II shows, two kinds of products (the [4 + 2] adducts and [2 + 2] + [3,3] adducts) were formed in good to high yields. Apparently, the substituents at C(2) play an important role in determining the reaction pathway. Reactions of compounds having no substituents at C(2) (entries 1, 2, 10, and 11) afforded exclusively the [4 + 2] adducts derived from the intramolecular Diels–Alder reaction of the initially formed allenyl ethers. In this context, the substituent at C(5) had no remarkable influences (compare entries 1 and 2). In contrast, introduction of a substituent onto the C(2) position led to a remarkable change in the chemical behavior of **1**. Thus, the 2-methyl (**1c**) and 2-benzyl (**1d**) derivatives (entries 3, 4) underwent selectively the tandem [2 + 2],[3,3] reaction to give novel tricyclic **5c** and **5d**, respectively, as the sole product.

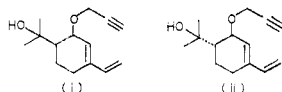
On the other hand, the C(6) substituents also influenced the periselectivity of the reaction in a unique manner depending on its stereochemistry. While the reaction of 6-*trans*-substituted compounds **15** (entry 7) and **20** (entry 9) gave only the [2 + 2] + [3,3] adduct, the similar reaction of 6-*cis*-substituted compounds **14** (entry 6) and **19** (entry 8) afforded a mixture of the [4 + 2] adduct and the [2 + 2] + [3,3] adduct. The dithiane derivative (6,6-disubstituted) **11** (entry 5) also afforded a mixture of [2 + 2] + [3,3] (**23**) and [4 + 2] adducts (**24**) in a 2.9/1 ratio. Interestingly, the reactivities of 6-substituted compounds were markedly different between *cis* and *trans* isomers. Thus, reaction of 6-*cis*-substituted compounds (**14** and **19**) was considerably retarded in comparison with that of the 6-*trans*-substituted com-

Table II. Base-Catalyzed Cycloaddition of Propargyl Ethers

entry	substrate	product (yield, %)	
		[2 + 2], [3, 3]	[4 + 2]
1, 2	1a , R=H 1b , R=CH ₃		3a (81) 3b (92)
3	1c	5c (88)	
4	1d	5d (92)	
5	11	23 (41)	24 (14)
6	14	25 (50)	26 (29)
7	15	27 (90)	
8	19	28 (56)	29 (22)
9 ^a	20	30 (86)	
10	21		32 (81)
11	22		33 (76)

^a A small amount (<3%) of [4 + 2] adduct **31** was formed.

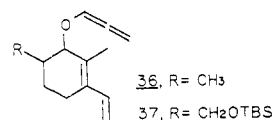
(14) The similar spectral differences were used for the stereochemical assignment of *i* and *ii*, which was confirmed by the stereoselective conversion of *ii* into (±)-platyphylide.⁶



(15) Brandsma, L.; Verkuijisse, H. D. *Synthesis of Acetylenes, Allenes, and Cumulenes*; Elsevier: New York, 1981.

(16) A prolonged heating of **1a** at 80 °C in benzene resulted in a slow formation of another type of Diels–Alder adduct arising from the intramolecular cycloaddition at the propargylic triple bond.⁶

pounds (**15** and **20**) and hence a prolonged heating (2–3 h) was required for completion of the reaction. In these cases, the formation of allenyl intermediates was detected (by TLC and IR) at the early stage of reaction. Actually, after quenching the reactions of **14** and **19** at 30 min, a rapid chromatography (silica gel column) led to the isolation of allenyl ethers **36** and **37**, re-



spectively [for **36**: IR 1950 cm⁻¹; ¹H NMR δ 6.82 (1 H, t, J =

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

compd	IR, cm ⁻¹	¹ H NMR, δ , CDCl ₃	mass, <i>m/z</i>
3a	1660, ^a 2850, 2940	1.20–1.90 (4 H, m), 1.90–1.60 (6 H, m), 3.16 (1 H, dm, <i>J</i> = 10.2 Hz), 4.59 (1 H, dt, <i>J</i> = 10.2, 6.0 Hz), 5.30 (1 H, m), 5.99 (1 H, m)	
3b	1650, ^a 2820, 2850, 2910, 2950, 3180	0.86 (3 H, s), 0.98 (3 H, s), 1.53 (2 H, d, <i>J</i> = 6.0 Hz), 1.84 (2 H, m), 2.09–2.53 (4 H, m), 3.14 (1 H, dm, <i>J</i> = 10.0 Hz), 4.68 (1 H, dt, <i>J</i> = 10.0, 6.0 Hz), 5.14–5.37 (1 H, m), 5.97 (1 H, m)	190 (100, M ⁺), 161 (38), 134 (96)
24^c	1650, ^b 2850, 2920	1.38 (3 H, s), 1.80–2.40 (10 H, m), 2.63–3.24 (4 H, m), 4.43 (1 H, m), 5.18 (1 H, br s), 6.03 (1 H, br s)	280 (100, M ⁺), 265 (54, M – CH ₃)
26^d	2870, ^a 2935, 2960	0.93–1.02 (1 H, m), 1.10 (3 H, d, <i>J</i> = 6.8 Hz), 1.22 (3 H, s), 1.51–1.61 (1 H, m), 1.81–1.98 (1 H, m), 2.02–2.11 (2 H, m), 2.16–2.27 (2 H, m), 2.33–2.42 (2 H, m), 3.93 (1 H, d, <i>J</i> = 4.1 Hz), 5.09 (1 H, br s), 6.00 (1 H, s)	190 (28, M ⁺), 175 (71, M – CH ₃), 131 (100)
29^e	1100, ^a 1250, 2850, 2925, 2960	0.06 (6 H, br s), 0.90 (9 H, br s), 1.22 (3 H, s), 1.71–1.90 (2 H, m), 1.92–2.11 (3 H, m), 2.19–2.29 (2 H, m), 2.32–2.43 (2 H, m), 3.58 (1 H, dd, <i>J</i> = 10.0, 7.8 Hz), 3.81 (1 H, dd, <i>J</i> = 10.0, 6.5 Hz), 4.05 (1 H, d, <i>J</i> = 3.8 Hz), 5.09–5.13 (1 H, m), 5.97 (1 H, s)	320 (1.5, M ⁺), 263 (100, M – <i>t</i> -Bu)

^aNeat. ^bCHCl₃. ^cmp 82.5–84 °C. Anal. Calcd for C₁₅H₂₀OS₂: C, 64.24; H, 7.19. Found: C, 64.05; H, 7.15. ^dHRMS Calcd for C₁₃H₁₈O 190.1357, found 190.1356. ^eHRMS Calcd for C₁₉H₃₂O₂Si 320.2170, found 320.2175.

Table IV. ¹³C NMR Spectral Data^a for [2 + 2] + [3,3] Adducts

compd	C(1) (s)	C(2) (s)	C(3) (d)	C(7) (s)	C(8) (d)	C(11) (d)	miscellaneous
5c	153.10	125.14	85.88	138.24	116.30	88.75	33.35 (t), 33.00 (t), 28.61 (t), 23.23 (t), 20.24 (t), 10.21 (q)
5d	155.86	145.97	85.87	138.41	118.87	86.31	129.44 (s), 128.42 (d), 126.08 (d), 46.06 (t), 45.81 (t), 34.55 (q), 33.82 (s), 32.31 (t), 26.66 (q), 23.64 (t), 20.47 (t)
23	150.94	141.93	85.94	123.50	117.21	91.21	58.39 (s), 40.66 (t), 29.37 (t), 26.21 (t), 25.62 (t), 25.21 (t), 23.45 (t), 20.12 (t), 13.10 (q)
25	153.26	137.66	86.06	125.85	116.04	93.70	35.39 (d), 35.18 (t), 28.80 (t), 23.43 (t), 20.05 (t), 18.56 (t), 10.19 (q)
27	153.01	139.83	85.84	124.52	116.13	92.87	42.86 (d), 37.31 (t), 32.55 (t), 23.23 (t), 20.21 (t), 17.67 (t), 12.11 (q)
28	152.77	139.87	85.87	124.30	116.29	89.32	77.22 (q), 64.47 (t), 51.02 (d), 32.15 (t), 31.96 (t), 25.90 (q), 23.22 (t), 20.20 (t), 18.23 (s), 11.39 (q)
30	152.98	137.97	86.31	125.30	116.14	89.20	77.22 (q), 64.48 (t), 44.05 (d), 29.75 (t), 29.29 (t), 26.00 (q), 23.42 (t), 20.11 (t), 18.37 (s), 10.12 (q)

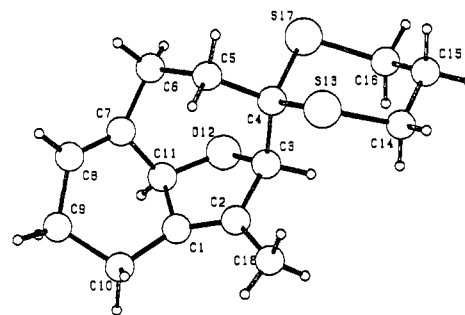
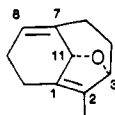
^a δ , ppm, CDCl₃; multiplicities: s, singlet; d, doublet; t, triplet; q, quartet.

5.9 Hz), 5.43 (2 H, d, *J* = 5.9 Hz)]. Heating of these allenyl ethers at 83 °C in *t*-BuOH (with or without *t*-BuOK) resulted in formation of the same mixture of products as above, indicating that **36** and **37** are the true intermediates in the above cycloaddition reaction.

The structural determination of the Diels–Alder ([4 + 2]) adducts was based on the spectroscopic data (Table III) as well as the chemical transformation. The most diagnostic feature of the ¹H NMR spectra is a singlet appearing at the low field (δ 5.9–6.0) which can be attributed to the vinyl proton of the dihydrofuran moiety. These adducts could be easily converted into the corresponding tricyclic lactones by a hydration–oxidation procedure^{6,8} as exemplified by **32** and **33** (Scheme III).

The structure of the [2 + 2] + [3,3] adducts was deduced from the ¹H NMR spectra (Experimental Section) and the ¹³C NMR spectra (Table IV) which showed the characteristic signals of four sp² carbons (3s + d) attributed to the tetra- and trisubstituted olefins and two sp³ carbons (2d) due to the methine carbon adjacent to the oxygen bridge. This was also confirmed by chemical transformations like hydrogenation and epoxidation.⁷ The unequivocal support for proposed structure was obtained by a single-crystal X-ray analysis of **23** (Figure 1). The crystallographic data (Tables V, VI, and VII) show the standard bond lengths for all C=C, C–C, and C–O bonds of the 12-oxatricyclo-[5.3.1.1^{3,11}]dodecadiene moiety in **23**, suggesting the stability of this novel ring system.

The stereochemical assignments of **25** and **27** were confirmed by the 270-MHz ¹H NMR spectra with the lanthanide shift reagent. In the presence of Eu(dpm)₃, compound **25** showed the largest shift for the Me(4) signal next to the H-3 and H-11 signals, while no prominent shift of the Me(4) signal was observed in **27**. This clearly indicates the proximity of the Me(4) group to the oxygen bridge in **25** (cis) rather than in **27** (trans).

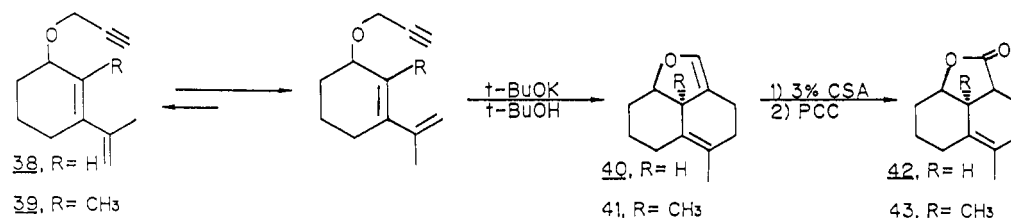
**Figure 1.** The X-ray crystal structure of **23**.

Discussion

Effects of C(2) Substituents. Apparently, the substituent at C(2) plays the most important role in controlling the periselectivity of the above cycloaddition reactions. The obvious effect of C(2) substituents is the one probably exerted on the conformational equilibrium of the 1,3-butadiene moiety in the starting materials (and the allenyl ethers as well) (Scheme I). The *s*-cis conformation of the butadiene moiety may be severely disfavored by the substituent at C(2) (R).¹⁷ In this regard, the ¹H NMR spectra (Table I) showed some instructive evidences. While the vinylic proton signal (Ha) of the unsubstituted compounds like **1a,b**, **21**, and **22** appeared at about δ 6.4 (dd), all other compounds having the 2-substituent (**1c,d**, **11**, **14**, **15**, **19**, and **20**) exhibited the Ha signal at the much lower field (δ 6.79–6.95) (see Table I). This remarkable low-field shift of the vinylic proton signal can be

(17) Conformation like **2c,d** involved highly repulsive 1,5-interaction: Jaime, C.; Osawa, E. *J. Mol. Struct.* **1985**, *126*, 363.

Scheme IV

**Table V.** Atomic Coordinates ($\times 10^4$; $\times 10^3$ for H) and Equivalent Isotropic Temperature Factors ($\text{\AA}^2 \times 10^2$) for **23^a**

atom	x	y	z	B_{eq}^b
C(1)	11113 (3)	2282 (2)	5676 (3)	364 (5)
C(2)	9466 (3)	2768 (2)	4216 (3)	334 (5)
C(3)	9271 (3)	3605 (2)	4742 (3)	296 (5)
C(4)	7971 (3)	3281 (2)	4369 (3)	282 (5)
C(5)	8519 (3)	2191 (2)	5260 (3)	366 (5)
C(6)	10546 (4)	2044 (2)	7279 (3)	454 (7)
C(7)	11831 (3)	1813 (2)	7661 (3)	406 (6)
C(8)	12413 (4)	823 (2)	7907 (3)	502 (7)
C(9)	13200 (4)	684 (2)	7724 (4)	572 (8)
C(10)	11988 (4)	1289 (2)	6037 (4)	513 (7)
C(11)	12087 (3)	2719 (2)	7257 (3)	371 (5)
O(12)	11139 (2)	3714 (1)	6650 (2)	348 (4)
S(13)	5563.1 (7)	3063.8 (5)	1998.1 (7)	366 (1)
C(14)	4864 (3)	4427 (2)	1073 (3)	437 (6)
C(15)	4965 (4)	5281 (2)	1838 (4)	461 (7)
C(16)	6926 (4)	5488 (2)	3810 (4)	462 (7)
S(17)	8053.9 (9)	4322.5 (5)	5255.9 (8)	400 (2)
C(18)	8011 (4)	2564 (3)	2331 (4)	539 (8)
H(C(3))	881 (4)	433 (2)	414 (4)	296
H(C(5))	823 (4)	155 (3)	461 (4)	366
H'(C(5))	779 (4)	214 (3)	512 (4)	366
H(C(6))	1058 (4)	140 (3)	768 (4)	454
H'(C(6))	1105 (5)	272 (3)	802 (5)	454
H(C(8))	1224 (5)	11 (3)	808 (4)	502
H(C(9))	1346 (5)	-16 (3)	783 (5)	572
H'(C(9))	1455 (5)	96 (3)	888 (5)	872
H(C(10))	1278 (5)	148 (3)	621 (5)	513
H'(C(10))	1091 (5)	76 (3)	492 (5)	513
H(C(11))	1342 (5)	291 (3)	826 (5)	371
H(C(14))	560 (4)	464 (3)	121 (4)	437
H'(C(14))	358 (5)	428 (3)	-21 (5)	437
H(C(15))	417 (5)	505 (3)	167 (4)	461
H'(C(15))	446 (5)	596 (3)	121 (5)	461
H(C(16))	685 (5)	607 (3)	420 (5)	462
H'(C(16))	770 (5)	576 (3)	397 (5)	462
H(C(18))	851 (5)	212 (3)	237 (5)	539
H'(C(18))	790 (5)	326 (3)	200 (5)	539
H''(C(18))	687 (5)	229 (3)	161 (5)	539

^a Esd values are in parentheses. ^b $B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i a_j$.

Table VI. Bond Lengths (\AA) for **23^a**

C(1)–C(2)	1.322 (7)	C(1)–C(10)	1.496 (8)
C(1)–C(11)	1.505 (7)	C(2)–C(3)	1.522 (7)
C(2)–C(18)	1.502 (8)	C(3)–C(4)	1.555 (7)
C(3)–O(12)	1.440 (6)	C(4)–C(5)	1.548 (7)
C(4)–S(13)	1.821 (5)	C(4)–S(17)	1.835 (5)
C(5)–C(6)	1.538 (8)	C(6)–C(7)	1.497 (8)
C(7)–C(8)	1.338 (8)	C(7)–C(11)	1.506 (7)
C(8)–C(9)	1.499 (9)	C(9)–C(10)	1.560 (9)
C(11)–O(12)	1.425 (6)	S(13)–C(14)	1.817 (5)
C(14)–C(15)	1.517 (8)	C(15)–C(16)	1.509 (9)
C(16)–S(17)	1.816 (7)		

^a Esd values are in parentheses.

attributed to the deshielding effect of the proximate C(2), C(3) double bond experienced in the *s-trans*-butadiene conformer.

Hence, when there is no severe steric hindrance to the *s-cis*-butadiene conformation as in **1a,b** (and **2a,b** as well), the [4 + 2] cycloaddition takes place preferentially to give the less strained Diels–Alder adduct (**3a,b**, Table II). However, when the [4 + 2] transition state is sterically congested by the C(2) substituent as in **2c,d**,¹⁷ the [2 + 2] cycloaddition is enforced to give the highly

Table VII. Bond Angles (deg) for **23^a**

C(2)–C(1)–C(10)	134.7 (5)	C(2)–C(1)–C(11)	108.4 (4)
C(10)–C(1)–C(11)	115.4 (4)	C(1)–C(2)–C(3)	109.0 (4)
C(1)–C(2)–C(18)	126.6 (5)	C(3)–C(2)–C(18)	124.4 (4)
C(2)–C(3)–C(4)	116.4 (4)	C(2)–C(3)–O(12)	104.2 (4)
C(4)–C(3)–O(12)	107.5 (4)	C(3)–C(4)–C(5)	114.0 (4)
C(3)–C(4)–S(13)	112.3 (3)	C(3)–C(4)–S(17)	110.7 (3)
C(5)–C(4)–S(13)	104.2 (3)	C(5)–C(4)–S(17)	105.3 (3)
S(13)–C(4)–S(17)	110.0 (3)	C(4)–C(5)–C(6)	118.6 (4)
C(5)–C(6)–S(7)	111.0 (5)	C(6)–C(7)–C(8)	126.2 (5)
C(6)–C(7)–C(11)	116.7 (4)	C(8)–C(7)–C(11)	115.0 (5)
C(7)–C(8)–C(9)	119.7 (5)	C(8)–C(9)–C(10)	111.6 (5)
C(1)–C(10)–C(9)	109.4 (5)	C(1)–C(11)–C(7)	103.2 (4)
C(1)–C(11)–O(12)	105.3 (4)	C(7)–C(11)–O(12)	114.6 (4)
C(3)–O(12)–C(11)	106.3 (3)	C(4)–S(13)–C(14)	102.3 (2)
S(13)–C(14)–C(15)	113.5 (4)	C(14)–C(15)–C(16)	113.5 (5)
C(15)–C(16)–C(17)	115.2 (5)	C(4)–S(17)–C(16)	102.2 (3)

^a Esd values are in parentheses.

strained compound **4** which in turn rapidly undergoes the [3,3]-sigmatropic rearrangement to produce the novel [2 + 2] + [3,3] product (**5c,d**, Table II). Although the tandem [2 + 2], [3,3] reaction proceeded in a stereospecific manner (see entries 6–9, Table II) which is reminiscent of the concerted mechanism, a stepwise [2 + 2] cycloaddition via diradical intermediates cannot be fully ruled out.^{18–21}

The above argument based on the conformational equilibrium of the butadiene moiety was substantiated by the following experiments. When compounds **38** and **39**, in which the *s-trans*-butadiene conformation is disfavored by the repulsive interaction ($A_{1,3}$ strain) between R and a Me group attached to the vinyl substituent, were subjected to the similar base-catalyzed reaction (*t*-BuOK, *t*-BuOH, 83 °C, 1 h), only the [4 + 2] adducts (**40**, 63%; **41**, 66%) were obtained regardless of the substituent (R) at C(2) (Scheme IV). The structure of these Diels–Alder adducts were confirmed by a smooth conversion into the lactones **42** and **43**.

Effects of C(6) Substituents. In contrast to the effects of the C(2) substituent, those of the C(6) substituents can be regarded as the “secondary” ones (Table II), since the C(6) substituents alone show no remarkable effects.²² Thus, the methyl group at C(6) in **21** (entry 10) and **22** (entry 11) had no influences on the periselectivity of their reaction without the C(2) substituent, and only the [4 + 2] adducts (**32** and **33**) were formed as in the case of **1a** (entry 1). However, in the 2-substituted compounds, the 6-substituent affected their reaction pathway in an interesting manner. While the 1,6-*trans* isomers [**15** (entry 7) and **20** (entry 9)] underwent a smooth and stereoselective tandem [2 + 2], [3,3] reaction on heating (83 °C) in the presence of *t*-BuOK, the similar base-treatment of the *cis* isomers [**14** (entry 6) and **19** (entry 8)] resulted in a rather dull reaction and competitive formation of

(18) 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.

(19) (a) Pasto, D. J.; Warren, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3670. (b) Pasto, D. J.; Heid, P. F.; Warren, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3676. (c) Pasto, D. J.; Yang, S. H. *J. Am. Chem. Soc.* **1984**, *106*, 152.

(20) (a) Dolbier, W. R., Jr.; Burkholder, C. R. *J. Org. Chem.* **1984**, *49*, 2381. (b) Dolbier, W. R., Jr.; Wicks, G. E. *J. Am. Chem. Soc.* **1985**, *107*, 3626.

(21) Komiya, Z.; Nishida, S. *J. Org. Chem.* **1983**, *48*, 1500.

(22) It was also observed that both *cis*-i and *trans*-ii (ref 14) underwent exclusively the intramolecular [4 + 2] cycloaddition on the similar base treatment.⁶

Scheme V

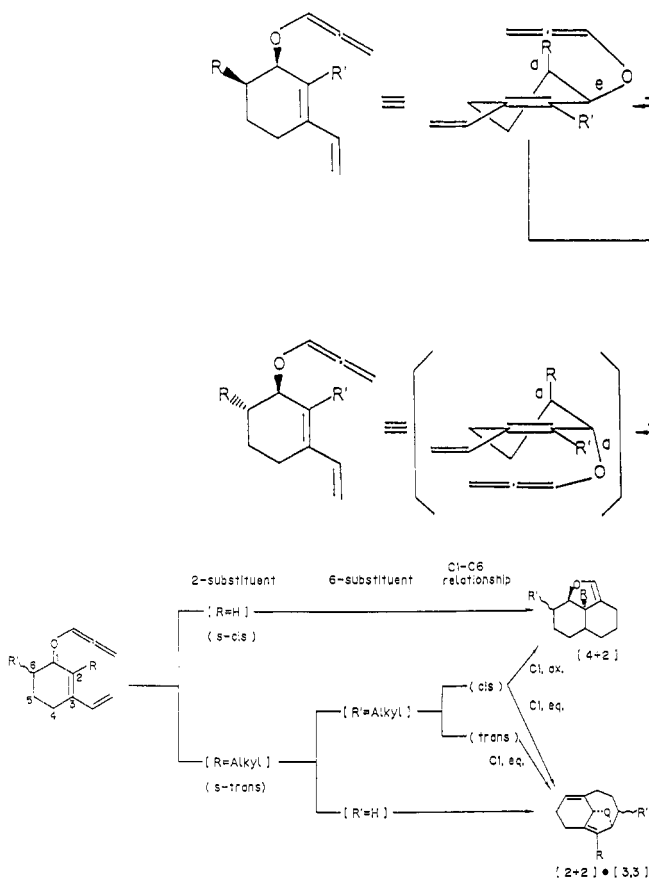


Figure 2. The structure-reactivity relationship in the intramolecular cycloaddition of allenyl ethers.

the [4 + 2] and [2 + 2] + [3,3] adducts.

These results can be reasonably explained by considering the conformational change of the cyclohexene ring affected by the C-6 substituent (Scheme V). Since the 1,6-cis isomers have pseudo-equatorial-axial or pseudo-axial-equatorial conformation, there are no difference in their stability. On the other hand, the 1,6-trans isomers remarkably prefer the pseudodiequatorial to the pseudodiaxial conformation. From these conformational analyses, the 1,6-trans compounds can be expected to proceed exclusively by the tandem [2 + 2], [3,3] reactions for the cycloadditions. Indeed, the allenyl ether groups having pseudoequatorial substituents give the [2 + 2] + [3,3] products, but in the pseudoaxial groups, only the [4 + 2] products are afforded.

In conclusion, the C(2) substituent plays the first important role in the intramolecular cycloaddition reactions of allenyl ethers, since it affects the conformational equilibrium of *s-cis*- and *s-trans*-1,3-butadiene moieties. While the absence of C(2) substituent promotes the Diels-Alder reactions, its existence brings about a consideration of the C(6) substituent as the secondary important effects. Since the C(6) substituent has a influence on the conformational changes of the cyclohexene rings, the 1,6-trans isomers cause a smooth and stereoselective tandem [2 + 2] + [3,3] reaction and the 1,6-cis isomers undergo a slower reaction and competitive formation of the [4 + 2] and [2 + 2] + [3,3] adducts (Figure 2).

Experimental Section

The melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. The ^1H NMR spectra were taken with a JEOL GX-270, JEOL PS-100, or Hitachi R-600 spectrometer with tetramethylsilane as an internal standard; chemical shifts are expressed in δ values. The ^{13}C NMR spectra were determined with a JEOL GX-270 or JEOL PS-100 with tetramethylsilane as an internal standard. IR spectra were obtained with a JASCO IR A-100 infrared spectrophotometer. Mass spectra were determined on a JEOL-D300 equipped with a JMA 3100/3500 at an ionization voltage 30–35 eV. Elemental

analyses were performed on Yanagimoto MT2 CHN recorder. For thin-layer chromatographic (TLC) analysis, Merck precoated TLC plates (Kieselgel 60 F₂₅₄, 0.2 mm) were used and column chromatography was done by using Merck Kieselgel 60 (70–200 mesh) as the stationary phase. The separation of the diastereomeric products was performed by a Kusano KHLC-201 liquid chromatograph using a C.I.G. column system.

All reactions were carried out under an atmosphere of dry argon. All solvents were purified by distillation before use: ether and THF were distilled from sodium benzophenone ketyl. *t*-BuOK was purified by sublimation before use.

2-Methyl-3-vinyl-2-cyclohexen-1-one (8). To a stirred solution of 2-methyl-1,3-cyclohexanedione (5.01 g, 39.7 mmol) and *p*-toluenesulfonic acid (0.5 g) in 40 mL of benzene was added *t*-BuOH (12 mL). The mixture was heated at reflux under a Dean-Stark trap for 3 h. The reaction mixture was cooled down to room temperature and poured into 30 mL of saturated aqueous NaHCO_3 solution and extracted with 3 \times 20 mL of ether. The combined extracts were washed with 30 mL of brine and dried over Na_2SO_4 . The solvent was removed under reduced pressure to give 3-isobutoxy-2-methyl-2-cyclohexen-1-one (7) as a yellow oil (7.15 g, 100%), which was used without further purification for the next step.

To a solution of 7 (7.15 g, crude from the foregoing step) in 70 mL of THF at 0 $^\circ\text{C}$ was added a 1.6 M solution of vinylmagnesium bromide (49 mL, 78.4 mmol). The mixture was stirred for 3 h at 0 $^\circ\text{C}$ and then 100 mL of saturated aqueous ammonium chloride solution was added. The organic layer was separated and the aqueous layer was extracted twice with 50 mL of ether. The combined organic extracts were washed with 100 mL of 10% H_2SO_4 and 100 mL of brine. After drying (Na_2SO_4) and evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1) to afford 5.40 g (100%) of 8 as a colorless oil: IR (neat) 1610, 1660, 2850, 2950 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.89 (3 H, s), 2.04–2.25 (2 H, m), 2.25–2.71 (4 H, m), 5.45 (1 H, d, J = 10.8 Hz), 5.62 (1 H, d, J = 17.4 Hz), 6.95 (1 H, dd, J = 10.8, 17.4 Hz).

3-Methyl-4-vinyl-3-cyclohexene-1,2-dione Trimethylene 1,1-Dithioacetal (9). Sodium hydride (60% in mineral oil, 3.43 g, 85.8 mmol) was washed in a flask with hexane (3 \times 20 mL) and suspended in 15 mL of THF. To this suspension at 0 $^\circ\text{C}$ were added dropwise a solution of 8 (5.30 g, 39.0 mmol) in 20 mL of THF and a solution of 1,3-bis(*o*-nitrophenylthio)propane (20 g, 48.2 mmol) in 40 mL of THF. The resulting mixture was allowed to warm up to room temperature. After 3 h, the mixture was poured into 100 mL of ice/water and extracted with 4 \times 80 mL of ether. The combined extracts were washed with 80 mL of saturated aqueous NaHCO_3 , 80 mL of brine, and 80 mL of water, and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, hexane/EtOAc = 20/1) to afford 5.99 g (64%) of 9 as a colorless viscous oil: IR (CHCl_3) 1625, 1690, 2930, 2995 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.94 (3 H, s), 2.03–2.83 (8 H, m), 3.10–3.70 (2 H, m), 5.45 (1 H, d, J = 10.8 Hz), 5.59 (1 H, d, J = 17.4 Hz), 6.90 (1 H, dd, J = 10.8, 17.4 Hz); mass spectrum, m/z (relative intensity) 240 (59, M⁺), 132 (100, M - 108), 108 (29, $\text{HS}(\text{CH}_2)_3\text{SH}$).

2-Hydroxy-3-methyl-4-vinyl-3-cyclohexen-1-one Trimethylene Dithioacetal (10): General Procedure for Diisobutylaluminum Hydride (DIBAH) Reduction. To a solution of 9 (5.99 g, 24.9 mmol) in 70 mL of ether was added dropwise a 1 M solution of DIBAH in hexane (37 mL, 37.0 mmol) over a 15-min period at 0 $^\circ\text{C}$. After the reaction mixture was stirred at

0 °C for 1 h, water (3.3 mL) and NaF (7.8 g) were added, and stirring at room temperature was continued for further 30 min. The reaction mixture was filtered, and the filtrate was washed with ether. Concentration of the filtrate afforded the crude product, which was purified by column chromatography (silica gel, hexane/EtOAc = 5/1) to give 5.43 g (90%) of **10** as a colorless crystal: mp 94–96 °C; IR (CHCl₃) 2910, 3450 cm⁻¹; ¹H NMR (CDCl₃) δ 1.83–2.46 (6 H, m), 2.00 (3 H, s), 2.59–3.03 (5 H, m), 4.14 (1 H, br s), 5.12 (1 H, d, *J* = 10.8 Hz), 5.20 (1 H, d, *J* = 17.4 Hz), 6.80 (1 H, dd, *J* = 10.8, 17.4 Hz).

3-Methyl-2-(3-propynyloxy)-4-vinyl-3-cyclohexen-1-one Trimethylene Dithioacetal (11): General Procedures for Propargylation. Method A. To a stirred solution of **10** (5.32 g, 21.9 mmol) in 100 mL of dimethyl sulfoxide and 100 mL of benzene was added dropwise 21 mL (32.8 mmol) of *n*-butyllithium (1.56 M in hexane) at 0 °C. When the addition was complete, the ice bath was removed and the mixture was stirred for 30 min. The solution was recooled to 0 °C and 7.8 mL (87.5 mmol) of propargyl bromide was added and the resulting solution was allowed to warm up to room temperature. After 3 h, the reaction mixture was poured into 100 mL of water and extracted with 3 × 80 mL of ether. The combined extracts were washed with 2 × 50 mL of brine and dried over Na₂SO₄. After evaporation under reduced pressure, the crude product was purified by column chromatography (silica gel, hexane/EtOAc = 4/1) to afford 6.00 g (98%) of **11** as a colorless oil.

Method B. A mixture of THF and hexamethylphosphoramide (HMPA, 1.5 equiv) was used as the solvent instead of a dimethyl sulfoxide/benzene (1/1) system and the reaction mixture was stirred for prolonged time (14–20 h). The same workup as above and chromatographic purification afforded **11** in a comparative yield.

The ¹H NMR spectra of propargyl ethers are summarized in Table I.

Compound 1a: colorless oil; IR (neat) 1600, 2120, 2850, 2940, 3300 cm⁻¹.

Compound 1b: colorless oil; IR (neat) 2120, 2900, 2950, 3010, 3300 cm⁻¹.

Compound 1c: colorless oil; IR (neat) 2100, 2850, 2920, 3070, 3290 cm⁻¹; mass spectrum, *m/z* 176 (16, M⁺), 79 (100).

Compound 1d: colorless oil; IR (neat) 2120, 2870, 2930, 2960, 3040, 3070, 3100, 3310 cm⁻¹.

Compound 11: IR (neat) 2100, 2920, 3290 cm⁻¹; mass spectrum, *m/z* 280 (11, M⁺), 224 (100); HRMS calcd for C₁₅H₂₀OS₂ 280.0955, found 280.0948.

Compound 21: colorless oil; IR (neat) 1600, 2100, 2840, 2920, 2950, 3300 cm⁻¹; mass spectrum, *m/z* 176 (9, M⁺), 161 (100, M - CH₃); HRMS calcd for C₁₂H₁₆O 176.1200, found 176.1196.

Compound 22: colorless oil; IR (neat) 1600, 2100, 2840, 2920, 2950, 3300 cm⁻¹; mass spectrum, *m/z* 176 (9, M⁺), 161 (100, M - CH₃).

Compound 38: colorless oil; IR (neat) 1600, 2310, 2855, 2945, 3300 cm⁻¹; ¹H NMR (CDCl₃) δ 1.32–1.99 (3 H, m), 1.91 (3 H, s), 2.04 (1 H, br s), 2.07–2.35 (2 H, m), 2.42 (1 H, t, *J* = 2.4 Hz), 4.10–4.35 (1 H, m), 4.23 (2 H, d, *J* = 2.4 Hz), 4.94 (1 H, br s), 5.05 (1 H, br s), 5.90 (1 H, br s).

Compound 39: colorless oil; IR (neat) 1625, 2300, 2850, 2925, 3300 cm⁻¹; ¹H NMR (CDCl₃) δ 1.35–1.82 (4 H, m), 1.76 (3 H, s), 1.77 (3 H, s), 1.88–2.20 (2 H, m), 2.40 (1 H, t, *J* = 2.4 Hz), 3.87 (1 H, br s), 4.20 (2 H, d, *J* = 2.4 Hz), 4.66 (1 H, m), 4.90 (1 H, m).

2,6-Dimethyl-3-vinyl-2-cyclohexen-1-one (12). To a stirred solution of LDA (10.6 mmol), prepared from diisopropylamine (1.5 mL, 10.6 mmol) and *n*-butyllithium (1.56 M in hexane, 6.8 mL, 10.6 mmol) in 10 mL of THF, was added **8** (965 mg, 7.09 mmol) dissolved in 10 mL of THF at -78 °C. After 30 min, 3.5 mL (56.2 mmol) of methyl iodide was added rapidly and the mixture was stirred at this temperature for 1.5 h. With vigorous stirring, acetic acid (0.3 mL, 5.24 mmol), ether (10 mL), and water (10 mL) were added successively. The organic layer was separated and the aqueous layer was extracted twice with 20 mL of ether. The combined extracts were washed with 15 mL of saturated aqueous NH₄Cl and 15 mL of brine and dried over Na₂SO₄. Removal of the solvent under reduced pressure and column chromatography of the residue on silica gel with 5/1 hexane/EtOAc afforded **12** (375 mg, 35%) and unreacted **8** (525 mg, 54%) in the order of elution.

Compound 12: colorless oil; IR (neat) 1605, 1660, 2850, 2940, 2960 cm⁻¹; ¹H NMR (CDCl₃) δ 1.15 (3 H, d, *J* = 6.0 Hz), 1.58–2.73 (5 H, m), 1.90 (3 H, s), 5.43 (1 H, d, *J* = 10.8 Hz), 5.61 (1 H, d, *J* = 17.4 Hz), 6.94 (1 H, dd, *J* = 10.8, 17.4 Hz).

cis-/trans-2,6-Dimethyl-3-vinyl-2-cyclohexen-1-ol (13). A solution of **12** (375 mg, 2.51 mmol) in 10 mL of ether was subjected to a DIBALH reduction according to the general procedure. After the similar workup, column chromatography on silica gel with 3:1 hexane/EtOAc afforded a *cis/trans* mixture of **13** (310 mg, 81%) as a colorless oil: IR (neat) 2860, 2935, 2960, 3400 cm⁻¹; ¹H NMR (CDCl₃) δ 0.85–1.08 (3 H, m), 1.14–1.82 (4 H, m), 1.94 (3 H, s), 2.03–2.40 (2 H, m), 3.50–3.87 (1 H,

m), 5.08 (1 H, d, *J* = 10.8 Hz), 5.21 (1 H, d, *J* = 17.4 Hz), 6.81 (1 H, dd, *J* = 10.8, 17.4 Hz).

cis- (14) and trans-2,6-Dimethyl-1-(2-propynyloxy)-3-vinyl-2-cyclohexene (15). A *cis/trans* mixture of **13** (310 mg, 2.04 mmol) was propargylated according to the general procedure B. After the usual workup, column chromatography of the reaction mixture on silica gel with 10/1 hexane/EtOAc afforded **13** (33 mg, 11%) and a mixture of **14** and **15** (250 mg, 65%). The latter diastereomeric mixture was further subjected to the medium-pressure liquid chromatography using a C.I.G. column system (hexane/EtOAc = 50/1) to give **14** (212 mg, 55%) and **15** (26 mg, 7%) both as colorless oils in the order of elution. ¹H NMR spectral data for these propargyl ethers are given in Table I.

Compound 14: IR (neat) 2110, 2860, 2930, 2970, 3300 cm⁻¹; mass spectrum, *m/z* 190 (19, M⁺), 119 (100); HRMS calcd for C₁₃H₁₈O 190.1357, found 190.1357.

Compound 15: IR (neat) 2100, 2850, 2900, 2940, 3290 cm⁻¹; mass spectrum, *m/z* 190 (19, M⁺), 119 (100).

cis-/trans-2-Methyl-6-(hydroxymethyl)-3-vinyl-2-cyclohexen-1-ol (17). According to the procedure described above for **12**, **8** (2.85 g, 20.9 mmol) was alkylated with ethyl chloroformate (8 equiv) to give crude **16** (4.2 g) as a yellow oil, which was used without further purification for the next step.

The crude **16** (4.2 g) was treated with a 1 M solution of DIBALH (84 mL) according to general procedure. After similar workup, column chromatography of the reaction mixture on silica gel with hexane/EtOAc (5/1 to 1/1) afforded in the order of elution of 2-methyl-3-vinyl-cyclohexen-1-ol (1.2 g, 48%) and **17** (389 mg, 11%) as a colorless oil: IR (neat) 2850, 2910, 3350 cm⁻¹; ¹H NMR (CDCl₃) δ 0.86–1.74 (4 H, m), 1.84 (3 H, s), 1.94–2.70 (3 H, m), 3.35–3.89 (2 H, m), 4.03–4.42 (1 H, m), 5.11 (1 H, d, *J* = 10.8 Hz), 5.47 (1 H, d, *J* = 18.6 Hz), 6.81 (1 H, dd, *J* = 10.8, 18.6 Hz).

cis-/trans-6-[[tert-Butyldimethylsilyloxy]methyl]-2-methyl-3-vinyl-2-cyclohexen-1-ol (18). To a solution of the diol **17** (389 mg, 2.33 mmol) in 5 mL of DMF were added *tert*-butyldimethylsilyl chloride (386 mg, 2.56 mmol) and imidazole (396 mg, 5.82 mmol), and the resulting mixture was stirred at room temperature for 12 h. After the reaction mixture was diluted with 20 mL of ether, the organic layer was washed with 10 mL of saturated aqueous NaHCO₃, 10 mL of water, and 10 mL of brine and dried over Na₂SO₄. The solvent was evaporated under reduced pressure and column chromatography on silica gel with 20/1 hexane/EtOAc afforded a *cis/trans* mixture of the silyl ether **18** (263 mg, 40%) as a colorless oil: IR (neat) 1095, 1250, 2850, 2930, 2955, 3450 cm⁻¹; ¹H NMR (CDCl₃) δ 0.08 (6 H, s), 0.91 (9 H, s), 1.47–2.00 (4 H, m), 1.94 (3 H, s), 2.00–2.44 (1 H, s), 2.63 (1 H, m, D₂O exchange), 3.50–3.89 (2 H, m), 4.01–4.25 (1 H, m), 5.07 (1 H, d, *J* = 10.8 Hz), 5.20 (1 H, d, *J* = 18.0 Hz), 6.82 (1 H, dd, *J* = 10.8, 18.0 Hz).

cis- (19) and trans-6-[[tert-Butyldimethylsilyloxy]methyl]-2-methyl-1-(2-propynyloxy)-3-vinyl-2-cyclohexene (20). A *cis/trans* mixture of **18** (190 mg, 0.673 mmol) was propargylated according to the general procedure B. After the similar workup, column chromatography of the reaction mixture on silica gel with 20/1 hexane/EtOAc afforded unreacted **18** (35 mg, 18%) and a mixture of **19** and **20** (136 mg, 67%). The latter diastereomeric mixture was further subjected to the medium-pressure liquid chromatography using a C.I.G. column system (hexane/EtOAc = 50/1) to give **19** (54 mg, 25%) and **20** (53 mg, 25%) both as colorless oils in the order of elution. ¹H NMR spectral data for these propargyl ethers are given in Table I.

Compound 19: IR (neat) 1080, 1240, 2090, 2825, 2900, 2940, 3280 cm⁻¹; mass spectrum, *m/z* 320 (3.2, M⁺), 305 (6.1, M - CH₃), 263 (100, M - *t*-Bu); HRMS calcd for C₁₉H₃₂O₂Si 320.2170, found 320.2162.

Compound 20: IR (neat) 1075, 1240, 2090, 2820, 2900, 2925, 3280 cm⁻¹; mass spectrum, *m/z* 320 (1.1, M⁺), 305 (2.5, M - CH₃), 263 (100, M - *t*-Bu); HRMS calcd for C₁₉H₃₂O₂Si 320.2170, found 320.2170.

General Procedure for Cycloaddition Reaction of Propargyl Ethers.

The reaction of **14** is described as an illustrative case. *t*-BuOK (1.00 g, 8.91 mmol) was dissolved in 10 mL of *t*-BuOH at 83 °C and a solution of **14** (212 mg, 1.11 mmol) in 10 mL of *t*-BuOH was added dropwise. After the addition was complete, the mixture was heated under reflux (83 °C) for 1 h. After cooling, the reaction mixture was poured into 20 mL of ice/water and extracted with 3 × 15 mL of ether. The combined extracts were washed with 20 mL of brine and dried over Na₂SO₄. The solvent was removed under reduced pressure, and the crude product was subjected to a medium-pressure liquid chromatography using a C.I.G. column system (hexane/EtOAc = 50/1) to give in the order of elution of 11,12-dimethyl-2-oxatricyclo[6.3.1.0^{4,12}]dodeca-3,7-diene **26** (56 mg, 26%), unreacted **14** (15 mg, 7%), and 2,4-*endo*-dimethyl-12-oxatricyclo[5.3.1.1^{3,11}]dodecane-1,7-diene **25** (102 mg, 52%) each as colorless oils. The results are summarized in Table II, spectral data of [4 + 2] adducts are given in Table III, and ¹³C NMR spectra data of [2 + 2] + [3,3] adducts are given in Table IV.

Compound 5c: colorless oil; IR (neat) 2920, 2850 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.08–1.54 (2 H, m), 1.48 (3 H, br s), 1.54–2.00 (4 H, m), 2.03–2.32 (4 H, m), 4.82 (1 H, s), 4.97 (1 H, m), 5.27 (1 H, m); mass spectrum, m/z 176 (21, M^+), 147 (100); HRMS calcd for $\text{C}_{12}\text{H}_{16}\text{O}$ 176.1200, found 176.1200.

Compound 5d: colorless oil; ^1H NMR (CDCl_3) δ 0.76 (3 H, m), 1.00 (3 H, m), 1.22–1.97 (4 H, m), 2.07–2.21 (3 H, m), 2.37 (1 H, d, $J = 6.0$ Hz), 2.54 (1 H, d, $J = 8.0$ Hz), 2.73 (1 H, d, $J = 8.0$ Hz), 4.80 (1 H, m), 4.86 (1 H, br s), 5.27 (1 H, m); mass spectrum, m/z 280 (100, M^+), 251 (93), 91 (67).

Compound 23: colorless crystal; mp 114–115 $^\circ\text{C}$ (ether/*n*-hexane); IR (CHCl_3) 2850, 2900, 2990 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.32 (1 H, dm, $J = 12.2$ Hz), 1.46 (1 H, dm, $J = 12.2$ Hz), 1.82 (3 H, s), 1.90–2.10 (2 H, m), 2.12–2.25 (4 H, m), 2.42 (1 H, ddm, $J = 13.5, 6.7$ Hz), 2.66–3.00 (5 H, m), 4.80 (1 H, br s), 5.18 (1 H, br s), 5.32 (1 H, m); mass spectrum, m/z 280 (4, M^+), 174 (11, $\text{M} - \text{S}(\text{CH}_2)_3\text{S}$), 148 (100). Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{OS}_2$: C, 64.12; H, 7.19. Found: C, 64.24; H, 7.19.

Compound 25: colorless oil; IR (neat) 2850, 2890, 2950 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.07 (1 H, td, $J = 12.7, 4.6$ Hz), 1.18 (3 H, d, $J = 6.8$ Hz), 1.49 (3 H, s), 1.59 (1 H, ddm, $J = 20.0, 6.2$ Hz), 1.93 (1 H, dm, $J = 6.2$ Hz), 1.98 (1 H, dm, $J = 6.2$ Hz), 2.01–2.11 (1 H, m), 2.15–2.34 (3 H, m), 2.54 (1 H, tm, $J = 12.7$ Hz), 4.66 (1 H, s), 4.81 (1 H, s), 5.23–5.28 (1 H, m); mass spectrum, m/z 190 (51, M^+), 175 (30, $\text{M} - \text{CH}_3$), 148 (100); HRMS calcd for $\text{C}_{13}\text{H}_{18}\text{O}$ 190.1357, found 190.1361.

Compound 27: colorless oil; IR (neat) 2845, 2900, 3000 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.80 (1 H, dd, $J = 14.0, 1.6$ Hz), 0.82–0.92 (1 H, m), 0.94 (3 H, d, $J = 9.2$ Hz), 1.24–1.33 (1 H, m), 1.60 (3 H, s), 1.76–1.87 (1 H, m), 2.09–2.31 (5 H, m), 2.42 (1 H, tm, $J = 12.2$ Hz), 4.77 (2 H, m), 5.23–5.30 (1 H, m); mass spectrum, m/z 190 (51, M^+), 175 (30, $\text{M} - \text{CH}_3$), 148 (100).

Compound 28: colorless viscous oil; IR (neat) 1100, 1250, 2850, 2935, 2960 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.08 (6 H, br s), 0.91 (9 H, br s), 0.95–1.03 (1 H, m), 1.24–1.30 (1 H, m), 1.50 (3 H, s), 1.81–2.03 (3 H, m), 2.15–2.27 (3 H, m), 2.42 (1 H, t, $J = 12.4$ Hz), 3.76 (1 H, dd, $J = 9.7, 7.8$ Hz), 3.85 (1 H, dd, $J = 9.7, 7.0$ Hz), 4.82 (1 H, s), 4.91 (1 H, s), 5.23–5.30 (1 H, m); mass spectrum, m/z 320 (1.4, M^+), 263 (44, $\text{M} - t\text{-Bu}$), 75 (100); HRMS calcd for $\text{C}_{19}\text{H}_{32}\text{O}_2\text{Si}$ 320.2170, found 320.2166.

Compound 30: colorless viscous oil; IR (neat) 1105, 1245, 2850, 2940, 2960 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.04 (6 H, br s), 0.89 (9 H, br s), 1.24–1.36 (1 H, m), 1.57 (3 H, s), 1.81–1.86 (1 H, m), 2.19–2.34 (6 H, m), 2.43 (1 H, t, $J = 11.9$ Hz), 3.46 (1 H, d, $J = 7.6$ Hz), 3.47 (1 H, d, $J = 7.6$ Hz), 4.78 (1 H, s), 5.10 (1 H, s), 5.24–5.31 (1 H, m); mass spectrum, m/z 320 (8.2, M^+), 263 (66, $\text{M} - t\text{-Bu}$), 75 (100). Anal. Calcd for $\text{C}_{19}\text{H}_{32}\text{O}_2\text{Si}$: C, 71.19; H, 10.06. Found: C, 71.35; H, 10.17.

Compound 31: colorless oil; IR (neat) 1100, 1250, 2850, 2925, 2960 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.06 (6 H, br s), 0.90 (9 H, br s), 1.21 (3 H, s), 1.60–1.80 (4 H, m), 1.85–2.09 (4 H, m), 2.16–2.30 (1 H, m), 3.68 (1 H, dd, $J = 10.0, 8.1$ Hz), 3.74 (1 H, dd, $J = 10.0, 6.5$ Hz), 3.97 (1 H, d, $J = 6.8$ Hz), 5.24 (1 H, t, $J = 4.6$ Hz), 5.46 (1 H, m); mass spectrum, m/z 320 (4.4, M^+), 263 (100, $\text{M} - t\text{-Bu}$).

Isolation of Allenyl Ethers. A mixture of **14** (36 mg) and *t*-BuOK (165 mg) in *t*-BuOH (5 mL) was heated at 83 $^\circ\text{C}$ for 20 min. After rapid cooling, the similar workup as above and chromatography on a silica gel column (hexane/EtOAc = 20/1) gave, besides **25**, **26**, and **14**, *cis*-1-(allenyl)-2,6-dimethyl-3-vinyl-2-cyclohexene, **36** (12 mg, 33%): IR (neat) 1950, 2860, 2940, 2975 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.01 (3 H, d, $J = 6.8$ Hz), 1.19–1.26 (1 H, m), 1.51–1.60 (1 H, m), 1.74–1.83 (1 H, m), 1.85 (3 H, s), 1.97–2.13 (1 H, m), 2.28–2.40 (1 H, m), 4.05 (1 H, d, $J = 3.8$ Hz), 5.08 (1 H, dd, $J = 11.1, 1.4$ Hz), 5.24 (1 H, dd, $J = 17.3, 1.4$ Hz), 5.43 (2 H, d, $J = 5.9$ Hz), 6.79 (1 H, dd, $J = 17.3, 11.1$ Hz), 6.82 (1 H, t, $J = 5.9$ Hz); mass spectrum, m/z 190 (18, M^+), 119 (100).

Similar short-time reaction (30 min) of **19** afforded *cis*-1-(allenyl)-6-[[*tert*-butyldimethylsilyloxy]methyl]-2-methyl-3-vinyl-2-cyclohexene, **37**: IR (neat) 1095, 1250, 1950, 2820, 2900, 2925 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.11 (6 H, br s), 0.90 (9 H, br s), 1.22–1.29 (1 H, m), 1.49–1.53 (1 H, m), 1.58–1.67 (1 H, m), 1.83 (3 H, m), 1.92–2.14 (1 H, m), 2.09–2.18 (1 H, m), 3.44 (2 H, d, $J = 7.3$ Hz), 3.92 (1 H, d, $J = 2.4$ Hz), 5.06 (1 H, dd, $J = 11.1, 1.4$ Hz), 5.19 (1 H, dd, $J = 17.3,$

1.4 Hz), 5.42 (2 H, d, $J = 5.9$ Hz), 6.73 (1 H, t, $J = 5.9$ Hz), 6.79 (1 H, dd, $J = 11.1, 17.3$ Hz); mass spectrum, m/z 320 (22, M^+), 263 (14, $\text{M} - t\text{-Bu}$), 75 (100).

General Procedure for the Lactone Formation from the [4 + 2] Adducts. The reaction of **33** is described as an illustrative case. To a solution of **33** (64 mg, 0.363 mmol) in 3 mL of THF was added dropwise 5 mL of 3% solution of 10-camphorsulfonic acid (CSA) in THF/ H_2O (30/1) at room temperature. After 30 min, the reaction mixture was diluted with 20 mL of ether, washed with 10 mL of saturated aqueous NaHCO_3 and 10 mL of brine, and dried over Na_2SO_4 . Removal of the solvent under reduced pressure afforded the crude lactol (66 mg, 94%), which was used for the next reaction without further purification.

The above lactol (66 mg, 0.340 mmol) dissolved in 5 mL of CH_2Cl_2 was added into a solution of pyridinium chlorochromate (125 mg, 0.705 mmol) in 7 mL of CH_2Cl_2 and the resulting mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with 50 mL of ether and filtered through a plug of Florisil (100–200 mesh). The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, hexane/EtOAc = 4/1) to afford 48 mg (69%) of 8-methylbicyclo[4.4.0]decan-1-ene-7,5-carbolactone **35** as a colorless crystal, mp 52–54 $^\circ\text{C}$ (ether/*n*-hexane): IR (neat) 1750, 2845, 2920, 3000 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.12 (3 H, d, $J = 7.6$ Hz), 1.42–1.53 (1 H, m), 1.61–1.80 (2 H, m), 1.96–2.06 (2 H, m), 2.08–2.18 (3 H, m), 2.21 (ddm, $J = 7.6, 3.5$ Hz), 2.84–2.97 (2 H, m), 4.25 (1 H, t, $J = 3.5$ Hz), 5.61 (1 H, dm, $J = 3.8$ Hz); mass spectrum, m/z 192 (56, M^+), 91 (100). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2$: C, 74.97; H, 8.39. Found: C, 75.01; H, 8.35.

Compound 34: colorless crystal; mp 67–69 $^\circ\text{C}$ (ether/*n*-hexane); IR (neat) 1750, 2845, 2920, 3000 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.10 (3 H, d, $J = 7.0$ Hz), 1.26 (1 H, dd, $J = 12.7, 3.5$ Hz), 1.35 (1 H, dd, $J = 12.7, 3.0$ Hz), 1.58–1.76 (2 H, m), 1.78–2.06 (3 H, m), 2.13 (1 H, ddm, $J = 7.0, 3.5$ Hz), 2.20 (1 H, dt, $J = 12.7, 3.5$ Hz), 2.77–2.84 (1 H, m), 2.90 (1 H, ddm, $J = 3.5, 3.0$ Hz), 4.38 (1 H, t, $J = 3.5$ Hz), 5.99 (1 H, m); mass spectrum, m/z 192 (55, M^+), 91 (100). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2$: C, 74.97; H, 8.39. Found: C, 74.95; H, 8.41.

Compound 42: colorless oil; IR (neat) 1760, 2860, 2940 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.13–2.36 (10 H, m), 1.60 (3 H, s), 2.54–2.93 (2 H, m), 4.53 (1 H, m); mass spectrum, m/z 192 (43, M^+), 147 (100).

Compound 43: colorless oil; IR (neat) 1770, 2850, 2930 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.67–2.14 (10 H, m), 1.26 (3 H, s), 1.60 (3 H, s), 2.35–2.55 (1 H, m), 4.19 (1 H, br s); mass spectrum, m/z 206 (100, M^+), 105 (87).

X-ray Analysis of 23. **Crystal Data.** $\text{C}_{15}\text{H}_{20}\text{OS}_2$, M_r 280.4, monoclinic; space group $P2_1/c$; $a = 15.499$ (2) \AA , $b = 12.188$ (1) \AA , $c = 16.212$ (2) \AA , $\beta = 152.54$ (1) $^\circ$, $V = 1412.4$ (4) \AA^3 , $Z = 4$, $D_{\text{calcd}} = 1.319$ g cm^{-3} ; $\mu(\text{Cu K}\alpha) = 31.7$ cm^{-1} ; $F(000) = 600$, crystal dimension $0.4 \times 0.2 \times 0.2$ mm. Colorless crystals were obtained from an ether/*n*-hexane solution. Three-dimensional intensity data were collected on a Rigaku AFC-5 diffractometer. The intensities of 2398 independent reflections in the range of $2\theta \leq 130^\circ$ were measured by using a ω - 2θ scanning technique with graphite-monochromated Cu K α radiation ($\lambda = 1.5418$ \AA). Three standard reflections monitored every 100 reflections showed no significant change during data collection. The intensities of 2161 observed reflections with $|F_o| > 2\sigma(F_o)$ were corrected for Lorentz and polarization effects, but not for absorption.

Structure Determination of 23. The structure was solved by direct methods and refined to minimize the function of $\sum w|F_o - F_c|^2$ by block-diagonal least-squares method. All hydrogen atoms were located on a difference electron-density map. The positional parameters of all the atoms and the 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 $w = [\sigma^2(F_o) + 0.00279|F_o|^2]^{-1}$ for observed reflections with $w^{1/2}|\Delta F| < 4$, and $w = 0$ otherwise. Final R , R_w , and S were respectively 0.045, 0.065, and 1.055 for 2148 reflections. Relative configuration of the molecule is presented in Figure 1.

Supplementary Material Available: Table of thermal parameters (1 page); structure factors for **23** (16 pages). Ordering information is given on any current masthead page.