Highly Stereoselective Cationic Cyclization Assisted by a Sulfenyl Group. Scope, Limitation, and Mechanism

Changqing Liu, Kazuaki Kudo, Yukihiko Hashimoto, and Kazuhiko Saigo*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

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When 8-acetoxy-2-methyl-9-(phenylthio)-2-nonene (**1a**) was treated with an acid, followed by a base, alkylative cyclization proceeded to give a mixture of 1,2-disubstituted cyclohexanes: **2a**, **3a**, and **4a.** The stereochemistry of the reaction was only slightly affected by the leaving group and the reaction conditions, such as the temperature, solvent, and acid. However, the bulkiness of the sulfenyl group had a great effect on the stereochemical course of the reaction. High trans selectivity was attained when **1c** (a derivative of **1a** with a bulkier sulfenyl group) was used as a substrate. On the other hand, the length and rigidity of the carbon chain of the substrate also had a major effect on the stereochemistry of the reaction; a high cis selectivity was observed when **10a** (a one-carbon-fewer analog of **1a**) or **15a** (a derivative with one more double bond in the carbon chain than in **1a**) was used as the substrate. The reaction proceeded via a 6,5- or 5,5-fused-ring intermediate. The sulfenyl-group-assisted reaction could be a useful method for the stereoselective cyclization of acetates of α-sulfenylated secondary alcohols.

Introduction

Alkylative cationic cyclization is one of the attractive methods for constructing carbocycles and has thus been widely applied for terpene syntheses.[1] Among them, the simplest reaction is the biomimetic synthesis of limonene/terpinolene by the cyclization of a nerol derivative. This reaction was originally studied by using biointermediate neryl pyrophosphate, itself, as a substrate.[2] Since then, the leaving group and/or activator was modified in order to apply the strategy to synthetic organic chemistry. Mukaiyama and co-workers showed that 2-halopyridinium salts effectively activate nerol to give the corresponding cyclized product in high yield.[3] Nozaki et al. reported on the cyclization of diethyl neryl phosphate by using organoaluminum species[4] and on the halogenative cyclization of nerol by utilizing a $TiCl_4$−amine complex.[5] An enantioselective version of the cyclization was also demonstrated by Yamamoto and co-workers by using a chiral leaving group and a suitably designed aluminum reagent.[6] Thus, cationic cyclizations to cyclohexene derivatives have been thoroughly investigated. However, the formation of the corresponding cyclohexane derivatives through cationic cyclization has been scarcely reported, except for cases in which the initially formed cations are tertiary or allylic;[7] one of the drawbacks for these simple cationic cyclizations is the dependence on the substrate structure.

We recently described that an allylic cation, to which a sulfenyl group participated, showed appropriate stability and that the reaction of the cation with silylated carbon nucleophiles proceeded regioselectively due to the neighboring participation of the sulfenyl group.[8] However, such a reaction could not be applied to a saturated secondary cation, even when the cation was stabilized by the participation of a sulfenyl group; this failure would arise from an instability of the cationic intermediate. We thus considered that such an unstable intermediate would successfully react with a nucleophilic moiety if the reaction is designed as an intramolecular version, which is entropically more favorable than an intermolecular counterpart. On the basis of this consideration, we tried to carry out the cyclization of some acetates of β-sulfenylated secondary alcohols and found that the corresponding cyclized products were obtained in good yields with high stereoselectivity.[9]

In this paper we report on the cationic cyclization reaction in detail along with mechanistic aspects.

Results and Discussion

When the acetate of β-sulfenylated secondary alcohol **1a** was treated with a 1.1 molar equivalent of trimethylsilyl trifluoromethanesulfonate (TMSOTf) for 24 h, the starting material was completely consumed. However, no cyclized product was detected, but instead, a very polar species was formed. The species decomposed quite slowly upon standing at room temperature to give a much less polar product, which was identified to be a mixture of cyclized products: **2a**, **3a**, and **4a.** On the basis of this result, the reaction conditions were at first examined concerning the conversion of the polar species into **2a**, **3a**, and **4a**. As a result, it was found that the decomposition was enhanced by treating the polar species with a base.

The present reaction is the first example concerning the formation of 1,2-dialkylcyclohexane by cationic cyclization; the reaction would proceed with the aid of a neighboring group participation of the sulfenyl group.

* Author to whom correspondence may be addressed: FAX, 03-5802-3348; e-mail, saigo@chiral.t.u-tokyo.ac.jp

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(2) Cramer, F.; Rittersdorf, W. *Tetrahedron* **1967**, *23*, 3015.

(3) Kobayashi, S.; Tsutsui, M.; Mukayama, T. *Chem. Lett.* **1976**, 1137.

(4) Kitagawa, Y.; Hashimoto, S.; Iemura, S.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1976**, *98*, 5030.

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(6) Sakane, S.; Fujiwara, J.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1983**, *105*, 6154; *Tetrahedron* **1986**, *42*, 2193.

(7) Sutherland, J. K. *Comprehensive Organic Synthesis*; Pergamon Press: Oxford, **1991**; Vol. 3, p 341.

(8) Kudo, K.; Hashimoto, Y.; Houchigai, H.; Hasegawa, M.; Saigo, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 848.

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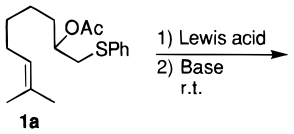
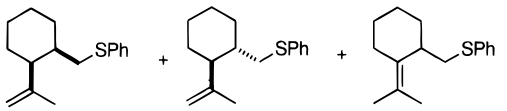
0022-3263/96/1961-0494$12.00/0

Table 1. Cyclization of 1a under Various Conditions



1a



2a **3a** **4a**

entry	Lewis acid	base	solvent	yield/%	**2a**:**3a**:**4a**[a]
1	TMSOTf	none	CH_2Cl_2	0	
2		Proton Sponge[b]		74	25:52:23
3		Et_2NH		78	36:55:9
4		$^iBuNH_2$		82	30:54:16
5		Et_3N		85	31:63:6
6			hexane	53	38:55:7
7			toluene	70	40:54:6
8			CH_3CN	72	40:60:0
9			Et_2O	50	39:55:6
10			$CHCl_3$	74	54:46:0
11	$TiCl_4$		CH_2Cl_2	39	40:46:14
12	$SnCl_4$			79	45:55:0
13	Ph_3CSbCl_6			65	50:50:0

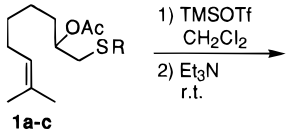
[a] Determined by GC analysis. [b] 1,8-Bis(dimethylamino)naphthalene.

This fact prompted us to thoroughly investigate various reaction conditions, such as the base, temperature, solvent, and Lewis acid as an activator. The results are given in Table 1.

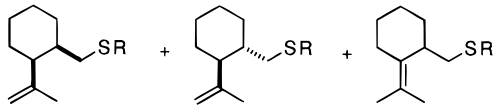
At first, the reaction was conducted at various temperatures in CH_2Cl_2 using TMSOTf as a Lewis acid. The reaction could not take place at temperatures below −23 °C, but proceeded quite slowly at −23 °C. Only at room temperature could the reaction proceed at a reasonable rate. Then, a subsequent study concerning the reaction was carried out at room temperature. Although bases could enhance the decomposition of the polar intermediate, in some cases the yield was low and the ratio of exo isomer **4a** increased (entries 2−4). In contrast, triethylamine suppressed the formation of exo isomer **4a** while maintaining high yield (entry 5). The reaction was then performed in various solvents with TMSOTf as an activator, followed by treatment with Et_3N (entries 5−10). The yield strongly depended on the solubility of the polar intermediate in each solvent; the highest yield was achieved when CH_2Cl_2 was used as a solvent. The effect of a Lewis acid was also studied (entries 5, 11−13). Among the Lewis acids examined, TMSOTf was the most preferable from the viewpoint of the yield, although the selectivity for diastereoisomers **2a** and **3a** was not observed. On the basis of these results, we concluded that the optimum reaction conditions for the present cationic cyclization were those of entry 5 in Table 1; subsequent reactions were carried out under such conditions.

In the next stage, we examined the effects of the leaving group and the sulfenyl group on the reaction. When the leaving group was an acetoxyl group, the yield was 85%, and the ratio of **2a**, **3a**, and **4a** was 31:63:6 (Table 1, entry 5); when the leaving group was a hydroxyl or trifluoroacetoxyl group, the yield and the isomer ratio were 85% and 40:60:0 and 85% and 43:57:0, respectively. These results indicate that the leaving group has little effect on the stereoselectivity of the reaction. However,

Table 2. Cyclization of 1a−c



1a-c

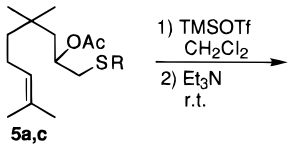


2a-c **3a-c** **4a-c**

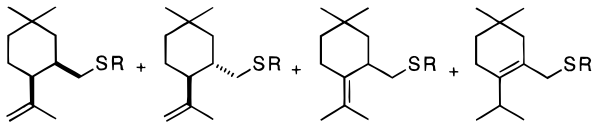
entry	substrate	R	yield/%	**2**:**3**:**4**[a]
1	**1a**	Ph	85	31:63:6
2	**1b**	Mes[b]	84	20:76:4
2	**1c**	TIPP[c]	78	4:96:0

[a] Determined by GC analysis [b] Mes = 2,4,6-trimethylphenyl (mesityl). [c] TIPP = 2,4,6-triisopropylphenyl.

Table 3. Cyclization of 5a,c



5a,c



6a,c **7a,c** **8a,c** **9a,c**

entry	substrate	R	yield/%	**6**:**7**:**8**:**9**[a]
1	**5a**	Ph	86	40:60:0:0
2	**5c**	TIPP[b]	91	0:91:0:9

[a] Determined by GC analysis. [b] TIPP = Triisopropylphenyl.

the bulkiness of the sulfenyl group greatly affected the stereoselectivity. The increase in the bulkiness of the sulfenyl group resulted in a higher yield of the trans isomer (Table 2); when 2,4,6-triisopropylbenzenesulfenyl was used as a sulfenyl group, the cis/trans ratio reached 4:96 (entry 3).

This cationic cyclization could also be applied to dimethylated substrate **5** (Table 3). In this case, the same tendency was also observed concerning the effect of the sulfenyl group on the stereoselectivity; the use of the bulkier 2,4,6-triisopropylbenzenesulfenyl group resulted in a higher trans selectivity. Noteworthy was that the product mixture consisted of trans isomer **7c** and endo isomer **9c** in a ratio of 91:9 and that neither the cis nor exo isomer was detected (entry 2).

In the next stage, we examined the effect of the length of the carbon chain on the stereoselectivity of the reaction. When **10a**, a one-carbon-fewer analog of **1a**, was treated with TMSOTf, the formation of a polar species was also observed on TLC. Treatment of the reaction mixture with Et_3N gave a mixture of the corresponding cyclized products in 70% yield, which comprised 83% of cis isomer **11a**, 17% of exo isomer **13a**, and a trace amount of endo isomer **14a**; surprisingly, the major product was the cis isomer, and no trans isomer was detected (Table 4, entry 1). We then optimized the reaction conditions. The results are listed in Table 4.

Although the yield of a mixture of the cyclized products and the ratio of the exo and endo isomers strongly

Scheme 1

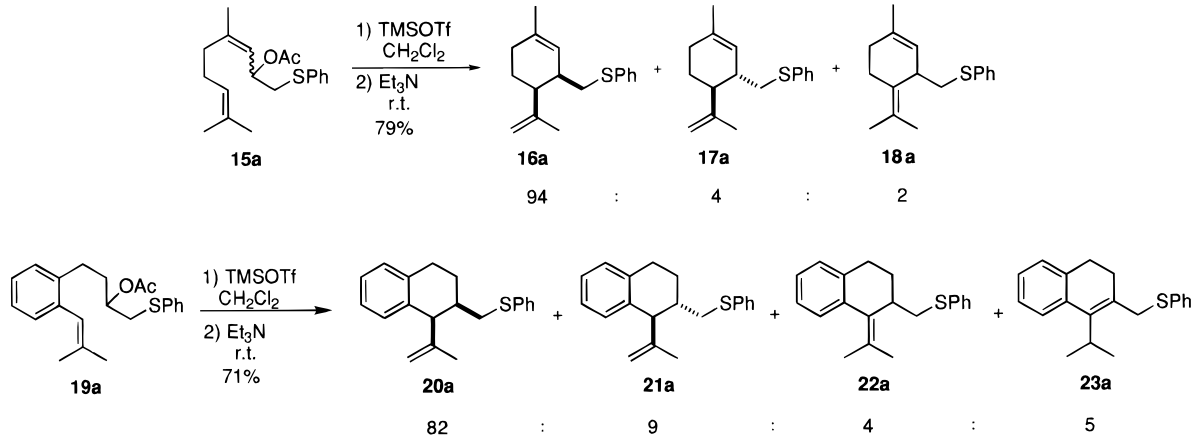
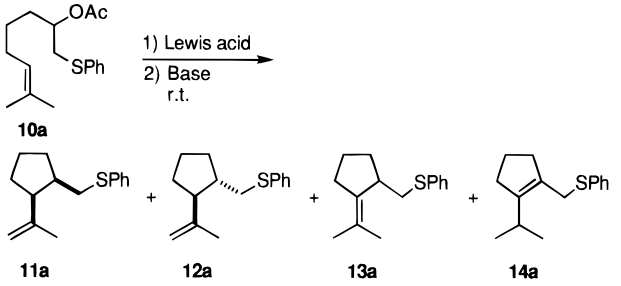


Table 4. Cyclization of 10a under Various Conditions



entry	Lewis acid	base	solvent	yield/%	**11a**:**12a**:**13a**:**14a**[a]
1	TMSOTf	Et_3N	CH_2Cl_2	70	83:0:17:trace
2		Et_3NH		68	77:0:45:3
3		$^iBuNH_2$		70	51:0:20:4
4		DBU		78	58:0:37:5
5		$^iPr_2NEt$		66	40:0:57:3
6		EtONa		85	52:0:42:6
7		2,6-lutidine		59	13:0:85:2
8		Proton Sponge[b]		65	34:0:62:4
9		Et_3N	CH_3CN	53	87:0:9:4
10			CH_3NO_2	64	76:0:18:6
11	Ph_3CClO_4		CH_2Cl_2	47	90:0:10:0
12	$SnCl_4$			77	32:66:2:0
13	$TiCl_4$			70	6:85:9:0

[a] Determined by GC analysis. [b] 1,8-Bis(dimethylamino)naphthalene.

depended on the base and solvent used, the exclusive cis selectivity was not affected by the solvent and base at all (entries 1−10). It is, however, noteworthy that the Lewis acid used had a great effect on the stereoselectivity. When TMSOTf was used as a Lewis acid, cis isomer **11a** was exclusively obtained (entry 1), whereas when a metal chloride was used as a Lewis acid, trans isomer **12a** became major; in the case of $TiCl_4$, the ratio of cis/trans reached 6:85 (entry 13). These results indicate that the length of the carbon chain has a major effect on the stereoselectivity of the reaction and that the cyclization of a substrate, which gives a five-membered ring product, can afford the cis or trans isomer selectively by using a suitable Lewis acid for activation of the substrate.

Since the length of the carbon chain had a great effect on the stereochemistry of the reaction, we considered that the rigidity of the carbon chain would also have some effect on the stereoselectivity of the reaction. On the basis of this consideration, we carried out cyclizations of substrates **15a** and **19a** (Scheme 1), which have one more double bond in the carbon chain than does **1**. When substrate **15a**, which could be easily synthesized from citral as a 3:2 mixture of (*Z*)- and (*E*)-isomers, was treated with 1.1 molar equivalents of TMSOTf in CH_2Cl_2 at room temperature, the starting material was quickly consumed, also giving a very polar species. The polar species was decomposed by treatment with Et_3N to give a mixture of the cyclized products in 79% yield; cis isomer **16a** was obtained with very high selectivity (the ratio of cis/trans was 94:4) in spite of the stereochemical heterogeneity of **15a**.

Treatment of **19a** with TMSOTf in CH_2Cl_2, followed by Et_3N, gave a mixture of the cyclized products in 71% yield; the cis isomer was also obtained with high selectivity (the ratio of cis/trans was 82:9), although there were small amounts of two other isomers. Thus, the rigidity of the carbon chain has a great effect on the stereochemistry of the reaction and strikingly increases the cis selectivity.

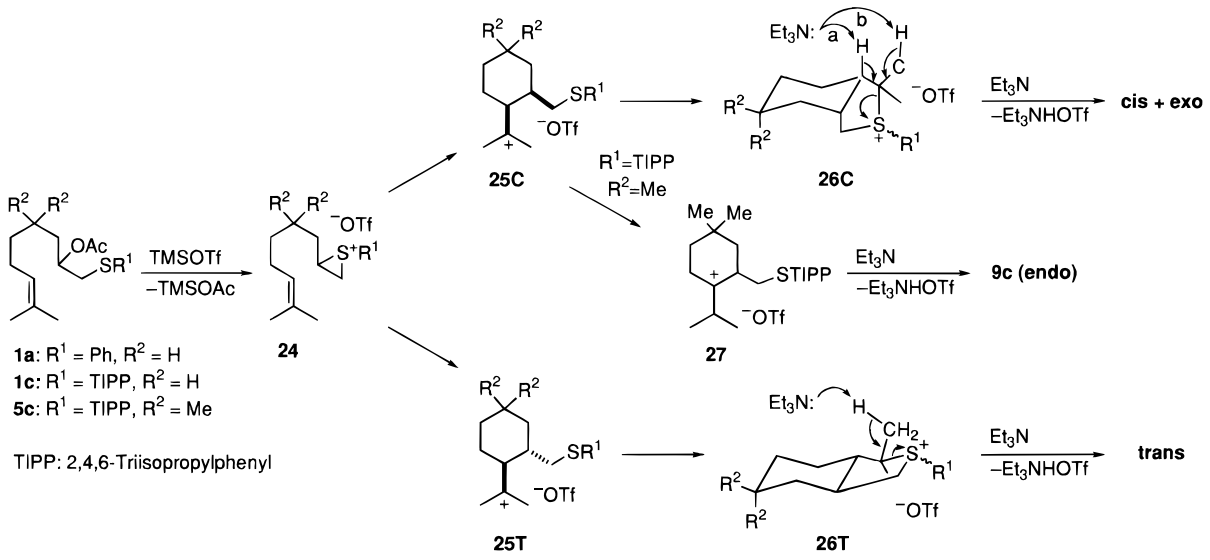
In order to clarify the mechanism of the reaction, we tried to identify the polar intermediate by monitoring the reaction of **1a** by ^1H NMR and ^{13}C NMR.

^1H NMR signals of **1a** slowly faded, and new peaks appeared upon the treatment of **1a** with TMSOTf in CD_2Cl_2 at room temperature. The characteristic changes of the ^1H NMR signals are the following: (1) low-field shift of the signals of the phenyl protons; (2) disappearance of the signals of the two protons at around 5 ppm, which can be assigned as the olefinic proton and the methyne proton on the carbon adjacent to the acetoxyl group; (3) disappearance of the signal of the methylene protons on the carbon adjacent to the phenylthio group; (4) appearance of new signals (at least six kinds) between 3.4 and 4.4 ppm, three of them are clear double doublets having a large *J* value, which is of geminal couplings; (5) shift of the signal of the methyl protons at 1.6 ppm to a higher magnetic field, which splits into three distinct singlets at 0.96, 1.17, and 1.20 ppm (the area ratio of the three peaks was roughly 1:2:2); (6) split of the signal of the other methyl protons at 1.7 ppm into three different peaks at 1.63, 1.70, and 1.82 ppm (the area ratio was roughly 2:2:1).

Moreover, the characteristic changes of ^{13}C NMR signals are the following: (1) disappearance of the signals at 73 (the carbon adjacent to the acetoxyl group), 125 (the olefinic carbon), and 127 ppm (the olefinic carbon); (2) appearance of signals around 45, 80, and 120 ppm.

Taking these observations into account, the intermediate was considered to be sulfonium ions **26** (Scheme 2). A precise investigation led us to conclude that intermediate **26** was a 2:3 mixture of cis diastereomeric sulfonium

Scheme 2



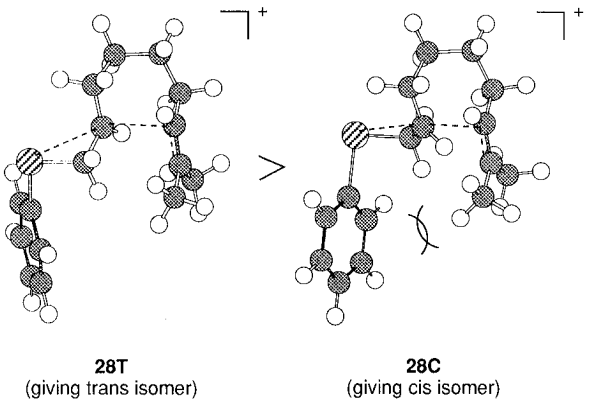


Figure 1. Possible transition states for the cyclization of **1a**.

salts **26C** and trans diastereomeric sulfonium salts **26T**, on the basis of a comparison of the ^{1}H NMR spectrum with those of 3,4,6,7,8,9-hexahydro-1,1,5-trimethylisobenzofuran isomers reported by Goldsmith and co-workers.[10] Cis isomer **2a** (via route a) and exo isomer **4a** (via route b) should be derived from cis intermediate **26C**, whereas trans isomer **3a** should be produced from trans intermediate **26T**, since the elimination reactions of these intermediates are considered to occur in an anti manner. The ratio of (**2a** + **4a**)/**3a** (about 2:3) is in good agreement with that of **26C**/**26T**. On the basis of these results, a possible mechanism for the cyclization would be as shown in Scheme 2.

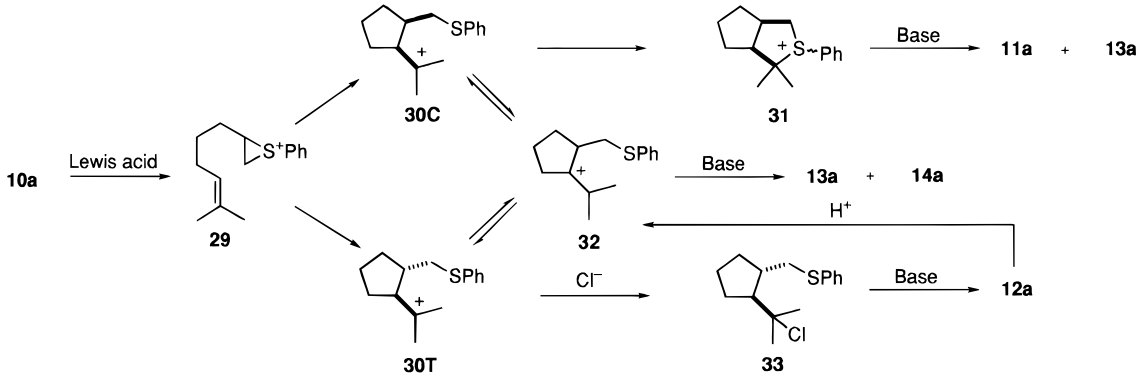
The facts that the leaving group has little effect on the stereoselectivity and that a bulky sulfenyl group favors the formation of the trans isomer could be explained on the basis of a conformational argument (Figure 1). Assuming a trans configuration for the episulfonium ion part and a "chair" conformation for the carbon chain in these cyclizations, transition state **28T**, leading to trans intermediate **25T**, would be more favorable than transition state **28C**, leading to cis intermediate **25C**, because of less steric congestion between the aryl group attached to the sulfur and the gem-diethyl group at the developing carbocationic center. Intermediates **25T** and **25C** would be immediately converted into stable 6,5-fused-ring intermediates **26T** and **26C**, respectively, before an interconversion between **25T** and **25C** takes place. Thus, the trans product is produced as a major product under kinetic control. Apparently, when the R^1 group is bulkier, the steric congestion in a cis transition state like **28C** would become more serious, resulting in the more predominant formation of **25T**. On the other hand, the leaving group does not affect the ratio of intermediates **26T** and **26C** at all, but rather affects the formation of episulfonium intermediate **24**. Hence, in these cyclizations the leaving group ought to have no effect on the stereochemistry, and a bulky sulfenyl group should be favorable in the formation of the trans product via trans intermediate **26T**.

The fact that endo isomer **9c** was obtained as a minor product in the place of cis isomer **6c** or exo isomer **8c** in the cyclization of **5c** could be explained as follows. A stable intermediate like **26C** could not be formed due to the severe interaction between the bulky 2,4,6-triisopropylphenyl and the gem-dimethyl group as well as the 1,3-diaxial interaction. Subsequently, cis cyclic exo cation **25C** is converted to cyclic endo cation **27** via hydrogen migration; a following deprotonation gives endo isomer **9c**.

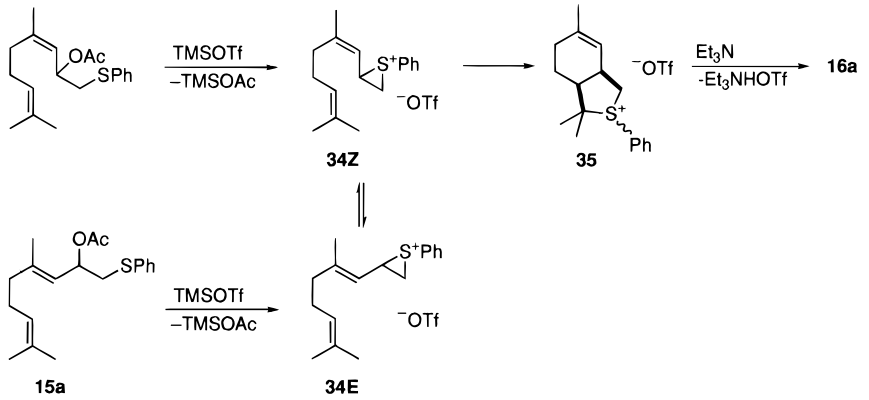
The ^{1}H NMR spectrum of the reaction mixture of **10a** and TMSOTf showed two singlets at 1.30 and 1.57 ppm, which were assigned to the gem-dimethyl group of cis diastereomeric intermediates **31**. As described above, the decomposition of **31** is responsible for the formation of cis product **11a** and exo product **13a**. Subsequently, the cyclization reaction of **10a** is considered to proceed in a mechanism similar to that of **1a** (Scheme 3); intermediates **30C** and **30T** are irreversibly formed from **29**. Although cis cyclic cation **30C** is considered to be less favorable than trans cyclic cation **30T**, due to a repulsion of the two cis-substituted groups, it is well-known that in a 5,5-fused system, a cis connection is much more favorable than a trans connection. Therefore, cis cation **30C** is attacked as soon as it is generated by the sulfur atom to form stable diastereomeric 5,5-fused sulfonium ion **31**. On the other hand, **30T** would be converted into **30C** and then into **31** via cyclic endo cation **32**, which is formed by hydrogen migration of **30T**, since the formation of a trans 5,5-fused system can scarcely take place. As a result, thermodynamically controlled cis product **11a**

(10) Goldsmith, D. J.; Clark, B. C., Jr.; Joines, R. C. *Tetrahedron Lett.* **1967**, 1211.

Scheme 3



Scheme 4



and exo isomer **13a** were obtained almost exclusively. Minor product **14a** may be produced from cyclic endo cation **32**.[11] When $TiCl_4$ is used as a Lewis acid, trans cation **30T** would be captured as soon as it is generated by a chloride ion to form neutral compound **33**.[12] Thus, kinetically controlled trans product **12a** was produced as a main product. This proposed mechanism is strongly supported by the fact that the treatment of a mixture, obtained in entry 13 of Table 4 (cis isomer **11a**:trans isomer **12a**:exo isomer **13a** = 6:85:9), with trifluoroacetic acid in CH_2Cl_2 for 6 h, followed by quenching with triethylamine, gave a mixture of cis isomer **11a** and exo isomer **13a** in a ratio of 74:26, and no trans isomer **12a** was detected.

The reaction of **15a** was monitored by ^{1}H NMR to explain the high cis selectivity. The signal of **15a** quickly faded upon the addition of TMSOTf, and new peaks appeared. The ^{1}H NMR spectrum of the reaction mixture showed two sets of singlets at 1.18 and 1.63 ppm and at 1.14 and 1.84 ppm, respectively; the ratio of the peak areas for the two sets of peaks was roughly 2:1. Although we could not assign the peaks exactly, we deduced that they belonged to the gem-dimethyl group of the two diastereomeric sulfonium salts **35** shown in Scheme 4. The decomposition of **35** would give rise to the cis and exo isomers. The high selectivity, irrespective of the stereochemical heterogeneity of the starting material **15a**, indicates that in this reaction, an isomerization of the double bond would take place in analogy with that in the intermolecular reaction of (α-sulfenylmethyl)allyl acetate.[8] On the other hand, it is known that an electrophilic attack toward a double bond occurs from the direction where the π-orbital of the double bond is maximally overlapped with the vacant lobe of the electrophile.[13] Two possible transition states for the cyclization of **15a** are illustrated in Figure 2. From the figure we can see that because of the rigidity of the carbon chain, the π-electron of the double bond is much more accessible to the electrophilic episulfonium cation in transition state **36C** (giving the cis isomer) than that in transition state **36T** (giving the trans isomer). Taking these considerations into account, the mechanism for the reaction of **15a** would be as shown in Scheme 4.

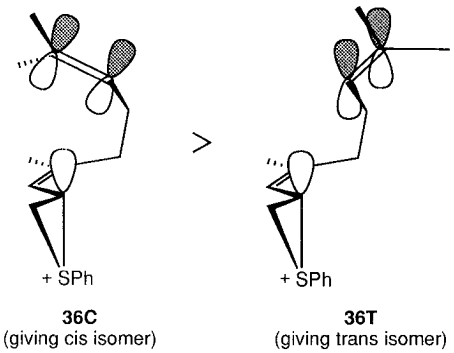


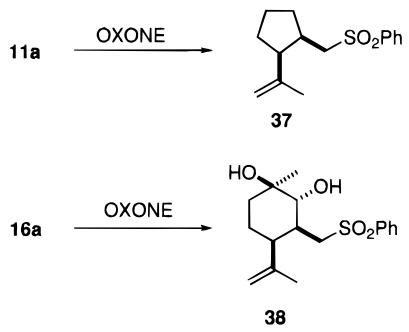
Figure 2. Possible transition states for the cyclization of **15a**.

Determination of Relative Stereochemistry of Products

X-ray crystallographic analyses were performed for sulfone **37** and sulfone **38**, derived from **11a** and **16a**, respectively (Scheme 5). On the basis of these results,

(11) Johnson, F.; Malhotra, S. K. *J. Am. Chem. Soc.* **1965**, *87*, 5492.
(12) A TLC analysis showed that the reaction intermediates consisted of species less polar than the starting material.
(13) Nagase; S.; Ray; N. K.; Morokuma, K. *J. Am. Chem. Soc.* **1980**, *102*, 4536.

Scheme 5



the relative configurations of **11a** and **16a** were confirmed to be cis.

The relative configurations of the other products were confirmed on the basis of a correlation of the ^{1}H NMR chemical shifts of selected peaks. The signals of the two terminal vinyl protons appeared at 4.5−5.0 ppm as two quasi-singlets. In the cases of the trans isomers, the difference in the chemical shift between the quasi-singlets was small, while it was large in the cases of the cis isomers.

In conclusion, we have provided a useful method for the highly stereoselective cyclization of secondary enyl alcohols. By cyclization, trans-1,2-disubstituted cyclohexane, cis-3,4-disubstituted cyclohexene, and cis- or trans-1,2-disubstituted cyclopentane could be obtained in fair-to-good yields with high stereoselectivity. Since the products have easily functionalizable moieties in the substituents, such as a sulfenyl group and a double bond, this reaction would be potent in the preparation of precursors for the synthesis of various kinds of cis- or trans-1,2-disubstituted five- and six-membered carbocycles.

Experimental Section

General. The starting materials and reagents, purchased from commercial suppliers, were used without further purification. All of the solvents were dried and distilled before use and stored over sodium wire or molecular sieves. "Concentration under reduced pressure" refers to the use of a rotatory evaporator at the water aspirator pressure. The residual solvent was removed at a pressure of less than 5 mmHg using a vacuum pump. The reaction flasks were flame-dried under a stream of argon. The syringes were oven-dried and cooled to room temperature in a desiccator over phosphorous pentoxide. Analytical thin-layer chromatography (TLC) was conducted on 1.0 × 4.0 cm precoated glass TLC plates (0.2 mm layer thickness of Silica Gel 60 F-254). The spots were visualized by an ultraviolet light, exposure to iodine vapor, or heating after dipping in a 3−5% solution of phosphomolybdic acid in ethanol. Flash chromatography was carried out using Silica Gel 60 (70−230-mesh ASTM). Preparative TLC (PTLC) was carried out with Wakogel B-5F (0.75 mm layer thickness).

The melting points were measured using a metal-block apparatus and an open capillary tube and are uncorrected. GC analyses were performed with a 25 m fused-silica capillary column using cyanopropyl silicone as a stationary phase. NMR spectra were measured on FT spectrometers operating at 270 or 400 MHz for ^{1}H and 68 or 100 MHz for ^{13}C or on a continuous-wave instrument at 60 MHz for ^{1}H. For ^{1}H NMR, the δ values are given in ppm with TMS as an internal standard; the coupling constants are recorded in Hz. For ^{13}C NMR, the chemical shifts are reported in ppm relative to TMS or $CDCl_3$ (δ 77.0). The unit for the values of IR spectra is cm^{-1}. Low-resolution mass spectra were recorded at an ionization potential of 70 eV, and the relative intensity is given in parentheses after the corresponding m/z value.

General Procedure for the Preparation of 1-(Arylthio)-2,3-epoxypropane: To a suspension of 1-chloro-2,3-epoxypropane (0.3 mol) and sodium hydroxide (0.3 mol, pellet) in dioxane (50 mL) was added arenethiol (0.1 mol) in dioxane (50 ml) over a period of 20 min at room temperature with stirring. Stirring was continued overnight. The precipitate was removed by filtration. Evaporation of the solvent, followed by distillation under reduced pressure, gave the title compound.

1,2-Epoxy-3-(phenylthio)propane: 95% yield; bp 110 °C/1 mmHg. ^{1}H NMR was identical with that in the literature.[14]

1,2-Epoxy-3-(mesitylthio)propane: 91% yield; bp 117−8 °C/1 mmHg; ^{1}H NMR (270 MHz, $CDCl_3$) 2.26 (s, 3H), 2.30 (dd, 1H, J = 2.6, 4.5), 2.52 (s, 6H), 2.57 (dd, 1H, J = 6.6, 13.5), 2.69 (ddd, 1H, J = 0.7, 4.0, 4.2), 2.88 (ddd, 1H, J = 0.7, 5.1, 13.5), 3.01−3.19 (m, 1H), 6.93 (s, 2H).

1,2-Epoxy-3-((2,4,6-triisopropylphenyl)thio)propane. The purification was carried out by column chromatography (eluent: hexane/AcOEt = 20/1) instead of distillation: 61% yield; pale-yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) 1.22 (d, 18H, J = 6.9), 2.27−2.50 (m, 1H), 2.50−2.97 (m, 4H), 2.97−3.14 (m, 1H), 3.97 (hept, 2H, J = 6.9), 7.08 (s, 2H).

8-Acetoxy-2-methyl-9-(phenylthio)-2-nonene (1a). In a similar manner to a method described in the literature,[15] 5-methyl-4-hexenal was obtained in 76% yield by the reaction of 2-methyl-3-buten-2-ol with ethyl vinyl ether in the presence of a catalytic amount of phosphoric acid at 150 °C under a pressure of 5 atm for 2 h.

To the thus-obtained aldehyde (63.79 g, 0.57 mol) was added sodium borohydride (8.93 g, 0.23 mol) in water (100 mL) in such a way that the temperature of the system was maintained at 40−50 °C with vigorous stirring. After the addition was completed, stirring was continued until the temperature of the system reached below 30 °C. The organic layer was then separated, and the aqueous phase was extracted with ether (3 × 20 mL). The organic and ethereal phases were combined, washed with brine (20 mL), and dried over anhydrous sodium sulfate. Evaporation of the solvent, followed by distillation at reduced pressure (100−105 °C/44 mmHg), gave 47.78 g (0.42 mol, 74% yield) of 5-methyl-4-hexen-1-ol. The ^{1}H NMR was identical with that given in the literature.[16]

The alcohol was transformed to 5-methyl-4-hexenyl bromide by NBS−PPh_3 in 47% yield according to the method described in the literature.[17] The ^{1}H NMR was identical with that reported in the literature.[17]

To a partially solidified solution of 5-methyl-4-hexenylmagnesium bromide in THF (10 mL), which was prepared from the bromide (3.61 g, 20.4 mmol) and Mg (0.53 g, 22 mmol), was added 1,2-epoxy-3-(phenylthio)propane (2.61 g, 15.7 mmol) in THF (5 mL) at room temperature. Then, CuI (200 mg, 1.0 mmol) was added to the mixture. After an induction period (ca. 1 min), an exothermic reaction occurred, and the solvent was vigorously refluxed. The reaction then settled after a few minutes. The reaction mixture was stirred for another 30 min, poured into ice water, and partitioned between EtOAc and water. The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Purification by column chromatography (eluent: hexane/EtOAc = 10/1) gave 8-methyl-1-(phenylthio)-7-nonen-2-ol (2.50 g, 60% yield): ^{1}H NMR (270 MHz, $CDCl_3$) 1.2−1.6 (m, 6H), 1.58 (s, 3H), 1.68 (s, 3H), 1.90−2.03 (m, 2H), 2.40 (d, 1H, J = 3.4), 2.84 (dd, 1H, J = 8.8, 13.7), 3.15 (dd, 1H, J = 3.3, 13.7), 3.60−3.72 (m, 1H), 5.04−5.15 (m, 1H), 7.18−7.42 (m, 5H); IR (neat) 3150−3600 (br), 3070, 2930, 2870, 1585, 1482, 1440, 1090, 1030, 740, 695. Anal. Calcd for $C_{16}H_{24}OS$: C, 72.67; H, 9.14. Found: C, 72.65; H, 9.19.

Acetylation of the alcohol by Ac_2O−pyridine in the presence of a catalytic amount of 4-(dimethylamino)pyridine (DMAP),

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followed by purification by column chromatography (eluent: hexane/EtOAc = 15/1), gave 2.74 g (95% yield) of **1a**: colorless oil; ^{1}H NMR (400 MHz, CD_2Cl_2) 1.2−1.4 (m, 4H), 1.61 (s, 3H), 1.69 (s, 3H), 1.6−1.75 (m, 2H), 1.95 (s, 3H), 1.90−2.00 (m, 2H), 3.07 (dd, 1H, J = 5, 14), 3.13 (dd, 1H, J = 6, 14), 4.90−5.00 (m, 1H), 5.00−5.10 (m, 1H), 7.20−7.40 (m, 5H); ^{13}C NMR (CD_2Cl_2, 100 MHz) 17.7, 21.1, 25.2, 25.8, 28.2, 30.0, 33.5, 38.0, 73.1, 124.8, 126.6, 129.3, 129.9, 131.8, 136.7, 170.7; IR (neat) 3070, 2970, 2930, 2865, 1740, 1585, 1485, 1440, 1375, 1240, 1025, 740, 694. Anal. Calcd for $C_{18}H_{26}O_2S$: C, 70.54; H, 8.55. Found: C, 70.36; H, 8.60.

8-Acetoxy-9-(mesitylthio)-2-methyl-2-nonene (1b). The procedure was the same as that for **1a**, except that 1,2-epoxy-3-(mesitylthio)propane was used in place of 1,2-epoxy-3-(phenylthio)propane: colorless oil; 62% yield for two steps from 5-methyl-4-hexenyl bromide; ^{1}H NMR (270 MHz, $CDCl_3$) 1.20−1.37 (m, 4H), 1.58 (br s, 3H), 1.68 (br s, 3H), 1.64−1.75 (m, 2H), 1.94 (s, 3H), 1.87−2.01 (m, 2H), 2.25 (s, 3H), 2.49 (s, 6H), 2.80 (d, 1H, J = 2.3), 2.82 (d, 1H, J = 2.0), 4.84−4.93 (m, 1H), 5.04−5.11 (m, 1H), 6.91 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) 17.7, 20.92, 20.97, 21.9, 24.8, 25.7, 27.8, 29.6, 33.1, 38.8, 73.6, 124.4, 129.0, 130.1, 131.5, 138.0, 142.6, 170.6; IR (neat) 3030, 2970, 2930, 2870, 1740, 1600, 1460, 1375, 1240, 1022, 852. Anal. Calcd for $C_{21}H_{32}O_2S$: C, 72.37; H, 9.25. Found: C, 72.41; H, 9.18.

8-Acetoxy-2-methyl-9-((2,4,6-triisopropylphenyl)thio)-2-nonene (1c). The procedure was the same as that for **1a**, except that 1,2-epoxy-3-((2,4,6-triisopropylphenyl)thio)propane was used in place of 1,2-epoxy-3-(phenylthio)propane: colorless oil; 60% yield for two steps from 5-methyl-4-hexenyl bromide; ^{1}H NMR (270 MHz, CD_2Cl_2) 1.24 (d, 18H, J = 6.9), 1.15−1.38 (m, 4H), 1.59 (s, 3H), 1.68 (d, 3H, J = 1.0), 1.63−1.73 (m, 2H), 1.90−2.30 (m, 2H), 2.74−2.88 (m, 2H), 2.86 (h, 1H, J = 6.9), 3.90 (h, 2H, J = 6.9), 4.98 (p, 1H, J = 6.0), 5.04−5.15 (m, 1H), 6.99 (s, 1H); IR (neat) 3050, 2970, 2930, 2870, 1742, 1600, 1465, 1375, 1240, 1024, 940, 880. Anal. Calcd for $C_{27}H_{44}O_2S$: C, 74.95; H, 10.25. Found: C, 74.94; H, 10.18.

8-Acetoxy-2,6,6-trimethyl-9-(phenylthio)-2-nonene (5a). To a THF (8 mL) solution of tetramethylethylenediamine (TMEDA) (0.81 g, 7 mmol) and thioanisole (0.87 g, 7 mmol) was added *n*-BuLi (4.09 mL, 1.71 M in hexane) at 0 °C; the resulting mixture was stirred at room temperature for 1 h. 3,3-Dimethyl-6-octenal (0.84 g, 5 mmol) in THF (4 mL), which was prepared by the methylation of citral with Me_2CuLi (73% yield),[18] was added to the mixture at −78 °C. After being stirred at −78 °C for 15 min, the reaction mixture was allowed to warm to room temperature. The reaction was then quenched with a saturated NH_4Cl aqueous solution (15 mL). The usual workup gave 1.37 g of crude 1-(methylthio)-4,4,8-trimethyl-7-nonen-2-ol. The alcohol was acetylated by Ac_2O−pyridine in the presence of a catalytic amount of DMAP to give 1.52 g of **5a** after purification by column chromatography (eluent: hexane/AcOEt = 20/1): 91% yield; colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) 0.85 (s, 6H), 1.14−1.20 (m, 2H), 1.57 (s, 3H), 1.66 (s, 3H), 1.50−1.72 (m, 2H), 1.83−1.20 (m, 2H), 1.93 (s, 3H), 2.95 (dd, 1H, J = 7.0, 13.5), 3.14 (dd, 1H, J = 5.0, 13.5), 4.97−5.08 (m, 1H), 7.15−7.52 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) 17.6, 21.2, 22.6, 25.7, 27.3, 32.6, 39.0, 42.4, 43.9, 70.4, 124.9, 126.2, 128.9, 129.4, 131.0, 135.8, 170.6; IR (neat) 3070, 2970, 2930, 2875, 1740, 1585, 1483, 1440, 1375, 1240, 1025, 740, 693. Anal. Calcd for $C_{20}H_{30}O_2S$: C, 71.80; H, 9.03. Found: C, 71.56; H, 8.84.

8-Acetoxy-2,6,6-trimethyl-9-((2,4,6-triisopropylphenyl)-thio)-2-nonene (5c). The procedure was the same as that for **5a**, except that methyl(2,4,6-triisopropylphenyl)methyl sulfide was used in place of thioanisole: 90% yield; colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) 0.90 (s, 6H), 1.23 (d, 12H, J = 6.9), 1.24 (d, 6H, J = 6.6), 1.18−1.30 (m, 2H), 1.56 (dd, 1H, J = 2.6, 14.8), 1.61 (s, 3H), 1.68 (d, 3H, J = 1.0), 1.76 (dd, 1H, J = 8.6, 14.8), 1.91 (s, 3H), 1.88−2.0 (m, 2H), 2.72 (dd, 1H, J = 5.1, 12.2), 2.86 (hept, 1H, J = 6.6), 2.88 (dd, 1H, J = 6.2, 12.2), 3.91 (hept, 2H, J = 6.9), 5.02−5.12 (m, 1H), 5.12−5.22 (m, 1H), 6.99 (s, 2H); IR (neat) 3050, 2970, 2930, 2875, 1740, 1598, 1465, 1370, 1240, 1022, 938, 880. Anal. Calcd for $C_{29}H_{48}O_2S$: C, 75.59; H, 10.05. Found: C, 75.40; H, 10.53.

7-Acetoxy-2-methyl-8-(phenylthio)-2-octene (10a). The title compound was prepared in the same manner as that for **1a**, except for the use of 4-methyl-3-pentenyl bromide[19] in place of 5-methyl-4-hexenyl bromide: 62% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) 1.2−1.4 (m, 2H), 1.57 (s, 3H), 1.67 (s, 3H), 1.6−1.78 (m, 2H), 1.95 (s, 3H), 1.87−2.03 (m, 2H), 3.04 (dd, 1H, J = 6, 14), 3.12 (dd, 1H, J = 6, 14), 4.96−5.12 (m, 2H), 7.15−7.42 (m, 5H); ^{13}C NMR (100 MHz, CD_2Cl_2) 17.7, 21.0, 256.4, 25.7, 27.6, 32.6, 37.7, 72.8, 124.0,126.3, 128.9, 129.6, 131.9, 136.0, 170.6; IR (neat) 3070, 2970, 2930, 2870, 1740, 1582, 1480, 1440, 1375, 124, 1025, 742, 695. Anal. Calcd for $C_{17}H_{24}O_2S$: C, 69.82; H, 8.27. Found: C, 69.99; H, 8.22.

8-Acetoxy-2,6-dimethyl-9-(phenylthio)-2,6-nonadiene (15a). The procedure was the same as that for **5a**, except for the use of citral in place of 3,3-dimethyl-6-octenal, giving **15a** as a 3:2 mixture of cis and trans isomers in 78% yield: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) 1.56 (s, 3H, minor), 1.59 (s, 3H, major), 1.649 (s, 3H, major), 1.652 (s, 3H, minor), 1.68 (s, 3H, major), 1.72 (d, 3H, J = 1.2, major), 1.94−2.10 (m, 4H), 1.96 (s, 3H, minor), 1.97 (s, 3H, major), 3.01 (dd, 1H, J = 6.1, 13.7, major), 3.02 (dd, 1H, J = 5.5, 13.4, minor), 3.16 (dd, 1H, J = 7.0, 13.4, minor), 3.19 (dd, 1H, J = 7.0, 13.7, major), 4.98−5.12 (m, 1H), 5.13−5.20 (m, 1H), 5.60−5.71 (m, 1H), 7.15−7.42 (m, 5H); IR (neat) 3070, 2975, 2930, 2860, 1740, 1582, 1480, 1440, 1372, 1240, 1020, 742, 695. Anal. Calcd for $C_{19}H_{26}O_2S$: C, 71.65; H, 8.22. Found: C, 71.37; H, 8.08.

1-[3-Acetoxy-4-(phenylthio)butyl]-2-(2-methyl-1-propenyl)benzene (19a). To a stirred solution of phthalide (2.68 g, 20 mmol) in CH_2Cl_2 (40 mL) at −90 °C was added over a period of 5 min diisobutylaluminum hydride (0.93 M in hexane, 21.5 mL, 20 mmol). After being stirred for 2 h at −90 °C, MeOH (3 mL) and a saturated potassium sodium tartrate solution (16 mL) were successively added; the mixture was allowed to warm up to room temperature. The usual workup, followed by purification by column chromatography (eluent: hexane/AcOEt = 1/1), gave 2.20 g of 2-(hydroxymethyl)-benzaldehyde in 81% yield as a 2:1 mixture of the ring-closed hemiacetal and the free aldehyde. The ^{1}H NMR was identical with that described in the literature.[20]

After dimethyl sulfide (5 mL) was introduced into a flask containing sodium hydride (55% dispersion in mineral oil, 0.436 g, 10 mmol), which was washed several times with pentane, the mixture was heated at 75−80 °C for 45 min. To the resulting solution of methylsulfenylmethyl carbanion,[21] cooled with an ice-water bath, was added 4.32 g (10 mmol) of isopropyltriphenylphosphonium iodide[22] in 10 mL of warm dimethyl sulfoxide (DMSO). After being stirred for 10 min at room temperature, 0.68 g (5 mmol) of 2-(hydroxymethyl)-benzaldehyde in DMSO (5 mL) was added to the mixture. The mixture was first stirred at room temperature for 30 min and then poured into a mixture of cold diluted hydrochloric acid (20 mL) and AcOEt (20 mL). The usual workup, followed by purification by column chromatography (eluent: hexane/AcOEt = 1/1), gave 0.65 g (80% yield) of 2-(2-methyl-1-propenyl)benzenemethanol: ^{1}H NMR (270 MHz, $CDCl_3$) 1.70 (d, 3H, J = 1.3), 1.66−1.78 (br, 1H), 1.92 (d, 3H, J = 1.3), 4.63 (s, 2H), 6.32 (s, 1H), 7.10−7.50 (m, 4H).

According to a method described in the literature,[23] 2-(2-methyl-1-propenyl)benzenemethanol was converted into 1-chloromethyl-2-(2-methyl-1-propenyl)benzene in 75% yield by a reaction with NCS/dimethyl sulfide, followed by purification by column chromatography (eluent: hexane/AcOEt = 20/1): ^{1}H NMR (270 MHz, $CDCl_3$) 1.69 (d, 3H, J = 1.3), 1.93 (d, 3H, J = 1.3), 4.57 (s, 2H), 6.37 (s, 1H), 7.10−7.45 (m, 4H).

The procedure for the preparation of the title compound (**19a**) was the same as that for **1a**, except for the use of

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1-chloromethyl-2-(2-methyl-1-propenyl)benzene in the place of 5-methyl-4-hexenyl bromide: 72% yield for two steps; colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) 1.66 (d, 3H, J = 1.3), 1.89 (d, 3H, J = 1.6), 1.96 (s, 3H), 1.86−2.0 (m, 2H), 2.50−2.67 (m, 2H), 3.03 (dd, 1H, J = 6.3, 13.9), 3.15 (dd, 1H, J = 5.9, 13.9), 4.93−5.07 (m, 1H), 6.23 (br s, 1H), 7.03−7.40 (m, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) 19.2, 21.0, 26.0, 29.1, 33.7, 37.4, 72.7, 123.5, 125.7, 126.3, 126.5, 128.7, 128.9, 129.7, 130.0, 135.7, 135.8, 137.5, 139.4, 170.6; IR (neat) 3070, 3020, 2970, 2930, 2870, 1740, 1585, 1485, 1442, 1378, 1240, 1030, 742, 695. Anal. Calcd for $C_{22}H_{26}O_2S$: C, 74.53; H, 7.39. Found: C, 74.51; H, 7.33.

General Procedure for Cyclization. To a solution of the substrate (0.35 mmol) in CH_2Cl_2 (2 mL) was added a CH_2Cl_2 solution of TMSOTf (1.2 M, 0.32 mL, 0.38 mmol) at room temperature; the resulting mixture was stirred for 24 h. During this period the color of the solution turned black. Then, triethylamine (0.5 mL, 3.6 mmol) was added to the mixture; the resulting pale-brown solution was stirred for 8 h. The mixture was partitioned between CH_2Cl_2 (5 mL) and a saturated NH_4Cl solution (5 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL), and combined organic layers were dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude material was purified by means of a preparative TLC (eluent: hexane) to give a mixture of the cyclized compounds.

***cis*-1-((Phenylthio)methyl)-2-(2-propenyl)cyclohexane (2a), *trans*-1-((phenylthio)methyl)-2-(2-propenyl)cyclohexane (3a), and 1-isopropylidene-2-((phenylthio)methyl)cyclohexane (4a)**: ^{1}H NMR (400 MHz, CD_2Cl_2) (only the characteristic peaks were recorded) for **2a** 1.62 (s, 3H), 2.77 (dd, 1H, J = 11, 13, PhSC*H*H), 2.89 (ddd, 1H, J = 1, 3, 13, PhSCH*H*), 4.64 (s, 1H), 4.85 (s, 1H); for **3a** 1.60 (s,3H), 1.86 (ddd, 1H, J = 3, 12, 12, $CH_2C(CH_3)CH$), 2.51 (dd, 1H, J = 10, 13, PhSC*H*H), 3.13 (dd, 1H, J = 3, 13, PhSCH*H*), 4.72 (s, 1H), 4.75 (s, 1H); for **4a** 1.90−2.00 (m), 2.5−2.6 (m), 3.0−3.1 (m); MS m/z (rel intensity) for **2a** 246 (M^+, 17), 164 (5), 149 (5), 137 (45), 123 (70),110 (21), 95 (40), 81 (91), 69 (100), 55 (54); for **3a** 246 (M^+, 12), 136 (17), 123 (100), 81 (52), 69 (31),67 (34), 55 (31); for **4a** 246 (M^+, 12), 136 (10), 123 (100), 81 (61), 67 (33), 55(21); IR (neat) 3075, 2930, 2860, 1640, 1584, 1480, 1440, 890, 735, 690. Anal. Calcd for $C_{16}H_{22}S$: C, 77.99; H, 9.00. Found: C, 77.80; H, 8.82.

***cis*-1-((Mesitylthio)methyl)-2-(2-propenyl)cyclohexane (2b), *trans*-1-((mesitylthio)methyl)-2-(2-propenyl)cyclohexane (3b), and 1-isopropylidene-2-((mesitylthio)methyl)cyclohexene (4b)**: ^{1}H NMR (400 MHz, CD_2Cl_2) (only the characteristic peaks were recorded) for **2b** 4.52 (br s, 1H), 4.74 (br s, 1H); for **3b** 1.46 (br s, 3H), 2.24 (s, 3H), 2.48 (s, 6H), 2.45−2.55 (m, 1H), 2. 69 (dd, 1H, J = 2.6, 12.2, MesSCH*H*), 4.60 (br s, 1H), 4.62−4.67 (m, 1H), 6.90 (s, 2H); for **4b** 1.93−2.06 (m); MS m/z (rel intensity) for **2b** 152 (M^+ − 136, 56), 137 (56), 119 (19), 95 (38), 81 (76), 69 (100); for **3b** 288 (M^+, 12), 273 (7), 165 (14), 152 (100), 137 (31), 123 (41), 119 (21), 95 (24), 81 (64), 69 (47); for **4b** 152 (M^+ − 136, 52), 123 (93), 81 (100), 67 (47); IR (neat) 3075, 2930, 2860, 1640, 1603, 1450, 13475, 890, 850. Anal. Calcd for $C_{19}H_{28}S$: C, 79.10; H, 9.78. Found: C, 78.95; H, 9.64.

***cis*-1-(2-Propenyl)-2-[((2,4,6-triisopropylphenyl)thio)methyl]cyclohexane (2c), *trans*-1-(2-propenyl)-2-[((2,4,6-triisopropylphenyl)thio)methyl]cyclohexane (3c):** ^{1}H NMR (400 MHz, CD_2Cl_2) (only the characteristic peaks were recorded) for **2c** 4.50, (br s, 1H), 4.71 (br s, 1H); for **3c** 1.21 (d, 6H, J = 6.9), 1.30 (d, 12H, J = 6.9), 1.42 (br s, 3H), 1.18−1.37(m, 4H), 1.40−1.64 (m, 2H), 1.67−1.84 (m, 3H), 2.21−2.34 (m, 1H), 2.28 (dd, 1H, J = 9.6, 11.9), 2.59 (dd, 1H, J = 2.3, 11.9), 2.86 (hept, 1H, J = 6.9), 3.92 (hept, 2H, J = 6.9), 4.61 (s, 1H), 4.62 (s, 1H), 6.98 (br s, 2H); MS m/z (rel intensity) for **2c** 372 (M^+, 17), 329 (15), 249 (22), 236 (100), 221 (34), 137 (73), 123 (30, 95 (39); for **3c** 372, (M^+, 12), 329 (9), 249 (21), 236 (100), 221 (33), 137 (70), 123 (37), 95 (31); IR (neat) 3070, 2970, 2930, 2870, 1640, 1595, 1464, 1383, 1363, 890, 870. Anal. Calcd for $C_{25}H_{40}S$: C, 80.58; H, 10.82. Found: C, 80.32; H, 10.82.

***cis*-1,1-Dimethyl-3-((phenylthio)methyl)-4-(2-propenyl)cyclohexane (6a), *trans*-1,1-dimethyl-3-((phenylthio)methyl)-4-(2-propenyl)cyclohexane (7a):** ^{1}H NMR (400 MHz, CD_2Cl_2) (only the characteristic peaks were recorded) for **6a** 0.90 (s, 3H), 0.97 (s, 3H), 1.71 (br s, 3H), 2.84 (dd, 1H, J = 8.9, 12.9), 2.94 (dd, 1H, J = 6.1, 12.9), 4.72 (br s, 1H), 4.85−4.89 (m, 1H); for **7a** 0.89 (s, 3H), 0.93 (s, 3H), 1.59 (br s, 3H), 2.44 (dd, 1H, J = 9.0, 12.2), 3.10 (dd, 1H, J = 2.3, 12.2), 4.73−4.78 (m, 2H); MS m/z (rel intensity) for **6a** 274 (M^+, 11), 1512 (37), 123 (28), 109 (37), 95 (37), 69 (100), 55 (41); for **7a** 274 (M^+, 17), 151 (100), 123 (34), 109 (51), 95 (66), 69 (74), 55 (50); IR (neat) 3075, 2950, 2930, 2870, 1645, 1585, 1480, 1440, 890, 738, 696. Anal. Calcd for $C_{18}H_{26}S$: C, 78.76; H, 9.45. Found: C, 78.94; H, 9.68.

***trans*-1,1-Dimethyl-4-(2-propenyl)-3-[((2,4,6-triisopropylphenyl)thio)methyl]cyclohexane (7c) and 4,4-dimethyl-1-isopropyl-2-[((2,4,6-triisopropylphenyl)thio)methyl]cyclohexene (9c):** ^{1}H NMR (400 MHz, CD_2Cl_2) (only the characteristic peaks were recorded) for **7c** 0.95 (s, 3H), 0.97 (s, 3H), 1.24 (d, 12H, J = 6.9), 1.32 (d, 6H, J = 6.9), 1.15−1.32 (m, 2H), 1.35−1.6 (m, 3H), 1.46 (br s, 3H), 1.62−1.8 (m, 2H), 1.85−1.95(m, 1H), 2.27 (dd, 1H, J = 9.6, 11.8), 2.44 (dd, 1h, J = 2.0, 9.6), 2.87 (hept, 1H, J = 6.9), 3.90 (hept, 2H, J = 6.90), 4.60−4.68 (m, 2H,), 6.99 (s, 2H); for **9c** 3.24 (s, 2H), 7.00 (s, 2H); MS m/z (rel intensity) for **7c** 249 (M^+ − 151, 27), 236 (90), 221 (30), 165 (23), 151 (47), 123 (13), 109 (72), 95 (40); for **9c** 249 (M^+ − 151, 36), 236 (71), 151 (19), 121 (20), 109 (69), 95 (30); IR (neat) 3080, 2970, 2930, 2870, 1644, 1600, 1560, 1465, 1385, 890, 878. Anal. Calcd for $C_{27}H_{44}S$: C, 80.93; H, 11.06. Found: C, 81.18; H, 11.24.

***cis*-1-((Phenylthio)methyl)-2-(2-propenyl)cyclopentane (11a), *trans*-1-((phenylthio)methyl)-2-(2-propenyl)cyclopentane (12a), 1-isopropylidene-2-((phenylthio)methyl)cyclopentane (13a), and 1-isopropyl-2-((phenylthio)methyl)cyclopentene (14a)**: ^{1}H NMR (400 MHz, CD_2Cl_2) for **11a** 1.5−1.9 (m, 6H), 1.73 (s, 3H), 2.2−2.3 (m, 1H), 2.43 (t, 1H, J = 12, PhSC*H*H), 2.4−2.5 (m, 1H), 2.86 (dd, 1H, J = 4, 12, PhSCH*H*), 4.74 (br s, 1H), 4.87 (br s, 1H), 7.1−7.3 (m, 5H); for **12a** (only the characteristic peaks were recorded) 1.59 (s, 3H), 1.9−2.0 (m, 1H), 2.2 (t, 1H, J = 8), 2.6−2.7 (m, 1H), 2.66 (dd, 1H, J = 9, 12, PhSC*H*H), 3.16 (dd, 1H, J = 3, 12, PhCH*H*), 4.59−4.71 (m, 2H); for **13a** (only the characteristic peaks were recorded) 2.63 (t, 1H, J = 12, PhSC*H*H), 3.02 (dd, 1H, J = 4, 12, PhSCH*H*); for **14a** 0.87 (d, 6H, J = 6.9), 3.62 (s, 2H); MS m/z (rel intensity) for **11a** 232 (M^+, 21), 189 (7), 164 (19), 123 (100), 109 (49), 81 (88), 67 (97), 55 (60); for **12a** 232 (M^+, 11), 123 (58), 109 (100), 79 (39), 67 (43), 55 (30); for **13a** 232 (M^+, 15), 123 (49), 109 (100), 81 (28), 67 (49), 45 (22); for **14a** 123 (M^+ − 109, 88), 81 (100); IR (neat) 3038, 2970, 2870, 1645, 1587, 1484, 1440, 1377, 1093, 1030, 895, 740, 695. Anal. Calcd for $C_{15}H_{20}S$: C, 77.52; H, 8067. Found: C, 77.23; H, 8048.

***cis*-1-Methyl-3-((phenylthio)methyl)-4-(2-propenyl)cyclohexene (16a), *trans*-1-methyl-3-((phenylthio)methyl)-4-(2-propenyl)cyclohexene (17a), and 4-isopropylidene-1-methyl-3-((phenylthio)methyl)cyclohexene (18a)**: ^{1}H NMR (400 MHz, CD_2Cl_2) (only the characteristic peaks were recorded) for **16a** 1.671 (s, 3H), 1.673 (s, 3H), 1.55−1.63 (m, 2H), 1.97−2.08 (m, 2H), 2.20−2.28 (m, 1H), 2.43−2.52 (m, 1H), 2.60 (dd, 1H, J = 10.3, 12.0, PhCH*H*), 2.98 (dd, 1H, J = 12.0, 3.6, PhSC*H*H), 4.71 (br s, 1H), 4.88 (br s, 1H), 5.68−5.73 (m, 1H), 7.10−7.35 (m, 5H); for **17a** 4.78−4.83 (m, 2H), 5.38−5.43 (m, 1H); for **18a** 5.54−5.9 (m, 1H); MS m/z (rel intensity) for **16a** 258 (M^+, 27), 189 (11), 164 (11), 149 (33), 135 (57), 124 (38), 107 (76), 93 (100), 81 (71), 77 (59); for **17a** 258 (M^+, 22), 189 (8), 149 (13), 135 (36), 124 (46), 107 (64), 93 (100), 81 (38); for **18a** 258 (M^+, 3), 135 (100), 107 (19), 97 (16); IR (neat) 3080, 2975, 2930, 1645, 1585, 1483, 1440, 1380, 895, 740, 693. Anal. Calcd for $C_{17}H_{22}S$: C, 79.01; H, 8.58. Found: C, 79.22; H, 8.42.

***cis*-2-((Phenylthio)methyl)-1-(2-propenyl)-1,2,3,4-tetrahydronaphthalene (20a), *trans*-2-((phenylthio)methyl)-1-(2-propenyl)-1,2,3,4-tetrahydronaphthalene (21a), 1-isopropylidene-2-((phenylthio)methyl)-1,2,3-trihydronaphthalene (22a), and 1-isopropyl-2-((phenylthio)methyl)-3,4-dihydronaphthalene (23a):** ^{1}H NMR (270 MHz, $CDCl_3$) (only the characteristic peaks were recorded) for **20a** 1.45 (br s, 3H), 1.45−1.6 (m, 2H), 1.85−2.0 (m, 1H), 2.26−2.38 (m, 1H), 2.71 (dd, 1H, J = 9.0, 12.9, PhCH*H*), 2.73−2.90 (m, 2H), 3.29 (dd, 1H, J = 3.6, 12.9, PhSC*H*H), 3.40 (d, 1H, J = 9.5), 4.83−

4.90 (m, 1H), 5.02−5.07 (m, 1H); for **21a** 1.61 (br s, 3H), 2.95 (dd, 1H, J = 6.0, 13.5), 3.76 (d, 1H, J = 4.9), 4.94−4.98 (m, 1H); for **22a** 1.77 (s, 3H), 1.85 (s, 3H), 3.10 (dd, 1H, J = 6.4, 13.1); for **23a** 1.22 (d, 6H, J = 7.3), 4.11 (s, 2H); MS m/z (rel intensity) for **20a** 294 (M^+, 34), 185 (31), 171 (100), 169 (82), 143 (65), 129 (80), 128 (63), 115 (36); for **21a** 185 (M^+ − 109, 10), 169 (8), 141 (8), 129 (12), 128 (7), 44 (40), 32 (100); for **22a** 294 (M^+, 18), 185 (11), 171 (31), 169 (15), 156 (10), 143 (18), 129 (20), 44 (29), 32 (100); for **23a** 294 (M^+, 15), 185 (40), 171 (20), 169 (23), 149 (34), 141 (29), 129 (55), 115 (29), 32 (100); IR (neat) 3075, 3020, 2925, 2860, 1645, 1480, 1440, 1375, 900, 740, 693. Anal. Calcd for $C_{20}H_{22}S$: C, 81.57; H, 7.53. Found: C, 81.67; H, 7.58.

***cis*-1-(Benzenesulfonylmethyl)-2-(2-propenyl)cyclopentane (37):**[24] colorless crystals; mp 49−50 °C (from EtOH); ^{1}H NMR (400 MHz, $CDCl_3$) 1.4−1.9 (m, 6H), 1.57 (s, 3H), 2.4−2.5 (m, 1H), 2.5−2.6 (m, 1H), 2.75 (dd, 1H, J = 11, 14, $PhSO_2$-CH*H*), 2.94 (dd, 1H, J = 1, 14, $PhSO_2$C*H*H), 4.64 (s, 1H), 4.83 (s, 1H),7.5−7.7 (m, 3H), 7.85−7.98 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) 22.1, 22.9, 217.1, 30.5, 35.6, 50.9, 56.6, 112.1, 128.0, 129.2, 133.5, 139.8, 144.5; IR (KBr pellet) 3070, 2970, 2880, 1648, 1450, 1310, 1155, 1090, 900, 755, 695. Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.14; H, 7.62. Found: C, 67.84; H, 7.69.

***c*-3-(Benzenesulfonylmethyl)-*t*-1-methyl-*c*-4-(2-propenyl)-*r*-1,*t*-2-cyclohexanediol (38):**[24] colorless crystals; mp 154−155 °C (from EtOH); ^{1}H NMR (400 MHz, $CDCl_3$) 1.30 (s, 3H), 1.10−1.95 (m, 6H), 2.45−2.60 (m, 2H), 2.95 (dd, 1H, J = 2.2, 14.3, $PhSO_2$CH*H*), 4.06 (dd, 1H, J = 11.5, 14.3, $PhSO_2$C*H*H), 4.18 (br s, 1H), 4.64 (br s, 1H), 4.85 (br s, 1H), 7.50−7.70 (m, 3H), 7.85−7.98 (m, 2H); IR (KBr pellet) 3465, 3410, 3190, 3175, 2990, 2975, 2930, 2870, 1645, 1450, 1300, 1150, 1090, 1045, 907, 731. Anal. Calcd for $C_{17}H_{24}O_4S$: C, 62.93; H, 7.45. Found: C, 62.81; H, 7.37.

(24) The author has deposited atomic coordinates for the structures of **37** and **38** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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