A Highly Regioselective Reaction of Allylic Acetates with Silylated Carbon Nucleophiles Directed by a Sulfenyl Group. Scope, Limitation, and Mechanistic Aspects

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α-(Sulfenylmethyl)allyl acetates reacted with silylated carbon nucleophiles in the presence of a catalytic amount of TMSOTf to give products substituted at the α-position of the sulfenylmethyl group in moderate to good yields with high regioselectivity. The theoretical calculation on an intermediate cationic species indicated that an episulfonium ion was a stable form; the observed regioselectivity was rationalized qualitatively on the basis of the coefficients of LUMO of the cation. Some transformations of the products were also demonstrated.

Allylic electrophiles are valuable building blocks in organic synthesis because of their high reactivity and synthetic versatility. However, the reaction of such substrates accompanies the problem of the regiochemistry, namely, the reaction can take place in S_N and S_N' fashions. Concerning the regiochemistry, the reaction of allylic electrophiles through organometallics is well studied. For example, the palladium-catalyzed reactions of allylic acetates take place at less hindered site,[1] while tungsten complexes are used to make C–C bond at more hindered site;[2] in general, the regiochemistry of the reaction of allylic electrophiles via η^3 allyl complexes does not depend on the position of the leaving group but on the metal, ligand, substituent on the substrate, and nucleophile.[3] On the other hand, the reaction of allylic electrophiles with copper reagents takes place in S_N2/S_N2' fashion. In this case, the position of the leaving group is as an important factor for the regiochemistry as other reaction conditions.[4]

In contrast to the above reactions, the study concerning the acid-catalyzed reaction of allylic electrophiles has not been thoroughly explored in the viewpoint of the regiochemistry. It is known that the acid-catalyzed reaction involves a cationic intermediate, and that the regiochemical course of the reaction is affected by a steric factor; the nucleophile attacks preferentially at less substituted site of the allylic system.[5] Hence, when both allylic sites are secondary, the reaction takes place randomly to give a mixture of regioisomers. To the best of our knowledge, an intramolecular reaction of allylic acetates having a silyl enol ether moiety is a unique example for distinction of two secondary allylic termini.[6] In this case, however, the regiochemical course of the reaction depends on the structure of the allylic acetate moiety.

We have recently reported the diastereoselective reaction of α-sulfenyl acetals and assumed that an intermediate episulfonium ion, generated by the neighboring group participation of the sulfenyl group, was responsible for the observed selectivity.[7] Although an episulfonium ion formed by a neighboring group participation is known to make the reaction stereospecific with the retention of the configuration,[8] this intermediate has not been studied in light of regio- or stereoselective reactions.[9] Then, we carried out the reaction of α-(sulfenylmethyl)allyl acetates with silyl enol ethers with the expectation that an *inter*molecular regioselective C–C bond formation via an episulfonium ion would take place, and found that such a selective reaction did occur at the α-position of the sulfenylmethyl group with the aid of the neighboring group participation of the sulfenyl group.[10] In this paper, we report on the reaction of α-(sulfenylmethyl)allyl acetates with silylated carbon nucleophiles in detail with mechanistic considerations.

Results and Discussion

At first, we attempted the reaction of allylic acetate **1a** and silyl enol ether **2a** in the presence of titanium(IV) chloride. Substrate **1a** was easily obtained in one pot by the reaction of lithiated (methylthio)benzene and crotonaldehyde, followed by treatment with acetyl chloride. A CH_2Cl_2 solution of titanium(IV) chloride (1.1 equiv) was added to a mixture of **1a** (1.0 equiv) and **2a** (1.2 equiv) in CH_2Cl_2 at −78°C. The reaction was very slow at −78°C, but completed within 30 min at room temperature. The substitution product **3** was obtained in 70% yield as a mixture of chromatographically inseparable isomers, which was found to consist of three isomers in a ratio of 96 : 2 : 2 by means of glc analysis. Then, the regiochemistry of the product was determined on the basis of ^{1}H NMR of the mixture; the main isomer and one of the minor isomers showed double–doublet signals of methyl groups adjacent to an olefin at around 1.7 ppm, whereas the other minor isomer showed a doublet methyl signal at 1.0 ppm. Moreover, the stereochemistry of double bond of main isomer was proved to be *trans* (J=15 Hz for the olefinic protons), whereas the stereochemistry of the other isomers could not be determined because their olefinic signals were overlapped with those of the main isomer. From

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the above information, the main isomer was concluded to be an (*E*)-α-substituted product and the two minor isomers were a (*Z*)-α-substituted product and a γ-substituted product. As already described, the reaction of an allylic electrophile under acidic conditions is usually affected by a steric hindrance. To our surprise the present reaction, however, occurred preferentially at the α-position of the sulfenylmethyl group in spite of steric disadvantage (Scheme 1).

In the next stage, we examined some reaction conditions by using more sterically demanding silyl enol ether **2b** as a nucleophile (Table 1). As anticipated, the regioselectivity for the reaction of **1a** with **2b** was slightly lower than that with **2a**. The metal halide-promoted reactions gave better selectivity, whereas the yield was higher when trimethylsilyl trifluoromethanesulfonate (TMSOTf) was used as a promoter even in a catalytic amount (Runs 1—4). Upon lowering the reaction temperature, the selectivity was slightly improved. However, it took very long time in order to complete the reaction (Runs 5, 6). The solvent effect indicates the formation of a cationic intermediate; in less polar toluene, which could not solvate the ionic intermediate, the reaction did not proceed (Run 9).

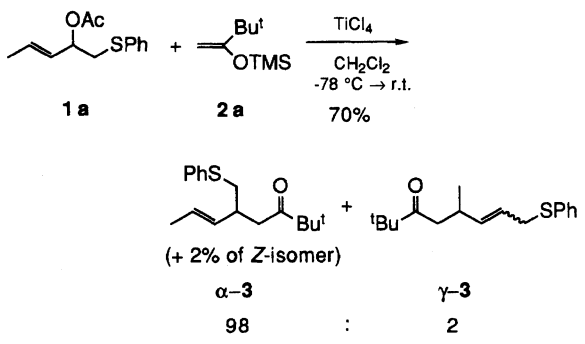
We also examined the effect of the sulfenyl group using substrate **1b**, a methylthio analog of **1a**. With a catalytic amount of TMSOTf, the reaction of **1b** did not give **5** but a small amount of unidentified very polar products, and most of **1b** remained unchanged. When 1.1 equiv of TMSOTf was used, substrate **1b** was completely consumed; **5** was obtained in almost the same degree of selectivity as the case of **4** (Run 10). However, the yield was a little low due to the formation of very polar by-products. Upon using excess **1b**, the yield was improved to some extent (Run 11). These observations can be reasonably explained by assuming that another substrate **1b** molecule quenches the intermediate cationic species to give a stable sulfonium salt, a very polar compound, and that the rate for this reaction is comparable to "normal" reaction with nucleophile **2b**. As the sulfur of a phenylthio group is less nucleophilic than that of an alkylthio group,[11] a phenylthio group would be better than a methylthio group for the sulfenyl moiety of the substrate in order to prevent side reactions and to achieve better yield. Finally, we deduced that the optimum reaction conditions were those used in Run 4 in Table 1.

The influence of terminal substitution mode of an allylic cation was also investigated. Substrate **1c**, which is considered to give an allyl cation with two tertiary ends, was tried to be synthesized, but was too labile to be isolated; we abandoned the reaction **1c**.[12] On the other hand, when the reaction of **1d** with **2a** was carried out in the presence of TMSOTf, no abstraction of the acetoxyl group occurred even with a stoichiometric amount of the activator. Moreover, when $TiCl_4$ was used instead of TMSOTf for the reaction of **1d** with **2a**, only a complex mixture was obtained. The presence of a primary allylic terminus might be disadvantageous for the formation of an intermediate cation having an appropriate stability.

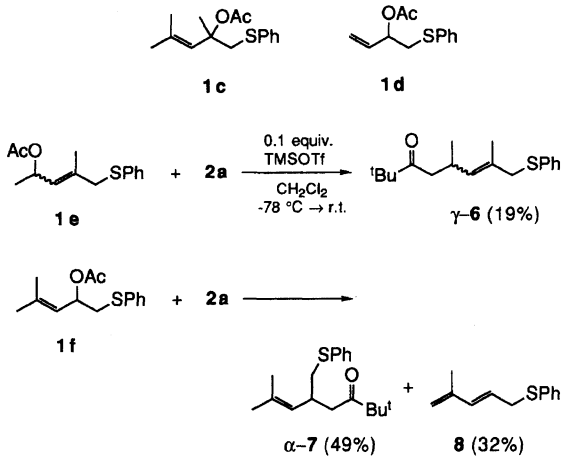
Since the sulfenylmethylated tertiary allylic acetate was labile as described above, we used secondary acetate **1e** for the reaction of an allylic cation bearing one secondary and one sulfenylmethylated tertiary ends. Although the reaction of **1e** with **2a** also showed complexity, the corresponding γ-substituted product could be isolated in 19% yield; the attack occurred only at the γ-position, sterically more favorable site. This result demonstrates that the steric factor is more important for determining the regiochemical course of the reaction.

Substrate **1f** was expected to give exclusively an α-substituted product from viewpoints of steric requirement and directing effect of the sulfenyl group. Actually, only α-**7** was obtained by the reaction of **1f** with **2a**. The yield was, however, a little lower compared to that of **3** from **1a**, due to the competing elimination reaction of acetic acid from **1f** to give diene **8** (Scheme 2).

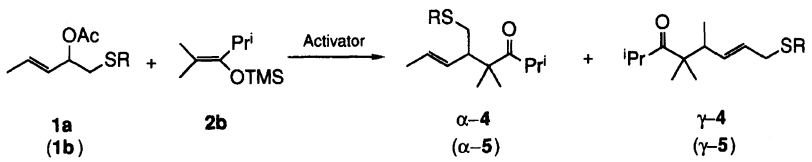
On the basis of the above observations, it is concluded that the present allylation reaction is useful when both ends of allylic cations are monosubstituted; side reactions are diminished and the corresponding α-substituted products are obtained in good yields. The present reaction is the first example for the discrimination of



Scheme 1.



Scheme 2.



1a (**1b**) **2b** α-**4** (α-**5**) γ-**4** (γ-**5**)

Table 1. Reaction of Allylic Acetate **1a** or **1b** with Silyl Enol Ether **2b** under Various Conditions[a)]

Run	Substrate	R	Lewis acid	Solvent	Temperature/°C	Product	Yield/%	$\alpha^{b)}/\gamma$
1	**1a**	Ph	$TiCl_4$	CH_2Cl_2	−78 to r.t.	**4**	61	93/7
2			$SnCl_4$				67	93/7
3			TMSOTf				79	89/11
4			TMSOTf[c)]				82	89/11
5					−23[d)]		61	92/8
6					0[d)]		75	89/11
7					r.t.		77	86/14
8				MeCN	−78 to r.t.		79	86/14
9				Toluene			0	—
10	**1b**	Me	TMSOTf	CH_2Cl_2		**5**	58	88/12
11[e)]							70	87/13

a) The reaction was carried out for 1 h by using 1.2 equiv of **2b** in the presence of 1.1 equiv of a Lewis acid. b) $E/Z \approx 98/2$. c) A catalytic amount (0.1 equiv) of the Lewis acid was used. d) The reaction was performed for 15 h. e) Substrate/nucleophile/Lewis acid=2.0/1.0/1.0.

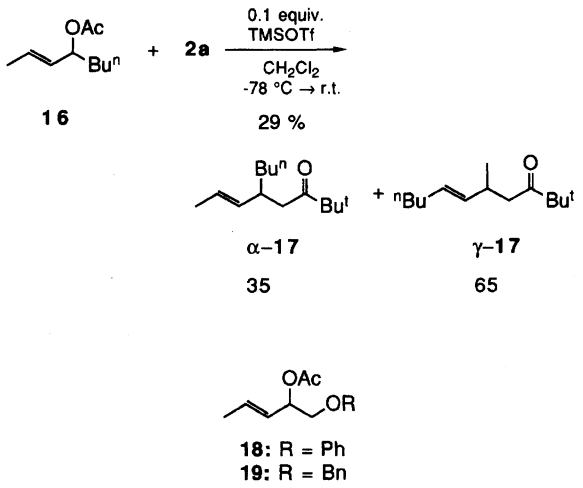
two secondary ends of an allylic cation in an intermolecular reaction with the aid of the electronic effect of a sulfenyl group.

The generality of this reaction for the discrimination of two secondary termini of an allylic cation is demonstrated in Table 2. In every case, the reaction proceeded with good to excellent α-selectivity. As far as using an identical substrate, the selectivity was almost the same degree, regardless of the nucleophile (Runs 1—8). This result is in contrast to the trityl perchlorate-mediated reaction of allyl methyl ethers, in which the regiochemistry was largely affected by the kind of nucleophile;[5a)] the synthetic usefulness of the present reaction should be emphasized. We also tested the possibility of stereoselective allylation by using β-monosubstituted nucleophile **2c**, but the result was completely disappointing (Run 4). Moreover, in order to elucidate stereospecificity, the reaction of diastereomerically pure substrate **1h** with **2a** was carried out. In this case, the reaction proceeded non-stereospecifically to give a 1 : 1 mixture of diastereomers with complete α-selectivity (Run 9), whereas only one diastereomer (*trans* isomer) was attained when cyclic substrate **1i** was employed (Run 10).

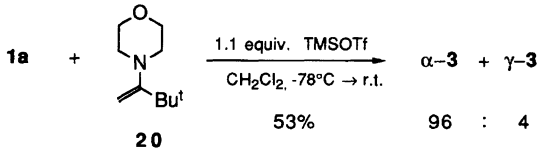
A control experiment was carried out by using **16** having no sulfenyl group; the reaction with **2a** gave **17** only in low yield with very low selectivity. This result strongly supports the idea that in the present reaction the sulfur function not only controls the regiochemistry of the reaction, but also stabilizes the cation to prevent the decomposition of the intermediate. Moreover, we tried the reaction of oxygen analogs of **1a**, namely **18** and **19**. However, both of the substrates gave only complex mixtures under the reaction conditions due to instability of the intermediates; this result also shows that a sulfenyl group is advantageous for neighboring group-participated reactions (Scheme 3).

It is noteworthy that not only silylated carbon nucleophiles but also enamine **20** reacted with **1a** in the presence of 1.1 equiv of TMSOTf with high α-selectivity (Scheme 4).

In order to look into the mechanism, the reaction of various precursors of 1-methyl-3-(phenylthiomethyl)allyl cation with **2b** or **2d** was carried out (Table 3).

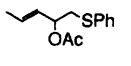
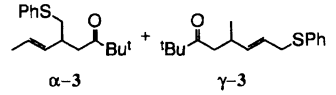
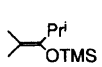
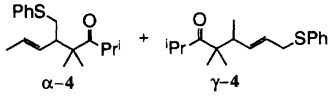
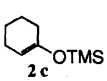
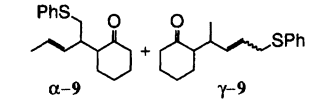
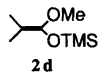
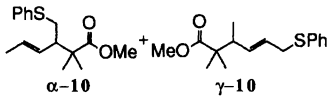
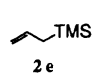
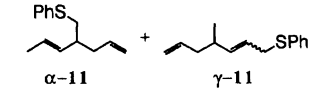
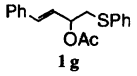
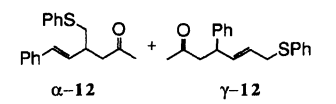
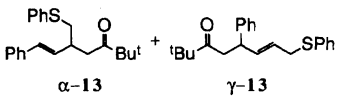
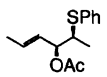
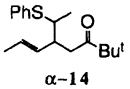
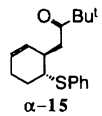


Scheme 3.



Scheme 4.

Table 2. Reaction of α-(Sulfenylmethyl)allyl Acetates with Various Nucleophiles[a)]

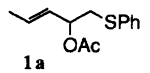
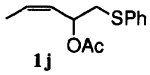
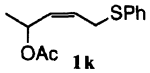
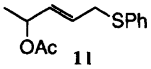
Run	Substrate	Nucleophile	Product(s)	Yield/%	α[b)]/γ
1	 **1a**	 **2a**	 **α-3** **γ-3**	68	94/6
2[c)]				70	98/2
3		 **2b**	 **α-4** **γ-4**	82	89/11
4		 **2c**	 **α-9** **γ-9**	84	91[d)]/9[d)]
5		 **2d**	 **α-10** **γ-10**	78	91/9
6		 **2e**	 **α-11** **γ-11**	59	91/9
7	 **1g**	 **2f**	 **α-12** **γ-12**	92	93/7
8		**2a**	 **α-13** **γ-13**	80	92/8
9	 **1h**		 **α-14**	49	100[d)]/0
10	 **1i**		 **α-15**	76	100/0

a) The reaction was carried out in CH_2Cl_2 in the presence of 0.1 equiv TMSOTf at $-78°C$ to room temperature for 2 h. b) $E/Z \approx 98/2$ except for **15**. c) $TiCl_4$ (1.1 equiv) was used as an activator. d) A 1 : 1 mixture of diastereomers.

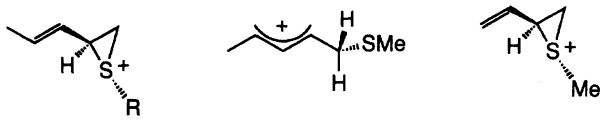
There observed apparent difference in reaction rate between the reactions with **2b**; relative rate was in the order **1a**>**1j**>**1k**≈**1l**. Nevertheless, in every case, the α/γ and E/Z ratios of the products were almost identical. These results can be consistently explained by assuming that the reaction proceeds via a unique intermediate, *E*-episulfonium ion **21a**. The formation of such a species can take place directly from **1a** by a neighboring group participation. Moreover, substrate **1j** also ionizes easily to give a *Z*-episulfonium ion, and it isomerizes very quickly to **21a**. In contrast, substrates **1k** and **1l** are more difficult to ionize because of the lack of the above anchimeric assistance. A cation like **21a** is also considered to epimerize rapidly, resulting in the loss of the stereochemical information in the reaction of **1h**. The reaction of **1i**, however, undergoes through the formation of an episulfonium ion having an annelated 6/3 ring system, which can exist only in *cis*-fused form, and then gives the *trans*-product exclusively.

Only by such an assumption for the presence of an episulfonium intermediate, the preferential formation of an α-substituted product is not directly explicable (Scheme 5). In order to account for the observed regioselectivity, a semiempirical calculation on model cation **21b** was performed using the PM3 Hamiltonian (Fig. 1, Table 4). Figure 1 clearly shows that LUMO of **21b** consists of two localized orbitals; LUMO of the simple allylic cation system C2–C3–C4 and the σ^* orbital of C4–S bond. As the absolute values of the coefficients on C4 are larger than those on C2, C4 is considered to be the most probable reaction site.[13)] This result is in good agreement with the observed α-selectivity. It is noteworthy that when the calculation was carried out on (sulfenylmethyl)allyl cation **22** instead of **21b**, the

Table 3. Reaction of Various Precursors for 1-Methyl-3-(phenylthiomethyl)allyl Cation[a)]

Run	Substrate	Nucleophile	Product	Yield/%	α[b)]/γ
1	 **1a**	**2b**	**4**	82	89/11
2	 **1j**			85	88[c)]/12
3	 **1k**			54	90/10
4	 **1l**			65	92/8
5		**2d**	**10**	82	92/8

a) The reaction was carried out in CH_2Cl_2 in the presence of 0.1 equiv TMSOTf at −78°C to room temperature for 2 h. b) E/Z=98/2 unless otherwise noted. c) E/Z=90/10.



21a: R = Ph
21b: R = Me

22 **23**

Scheme 5.

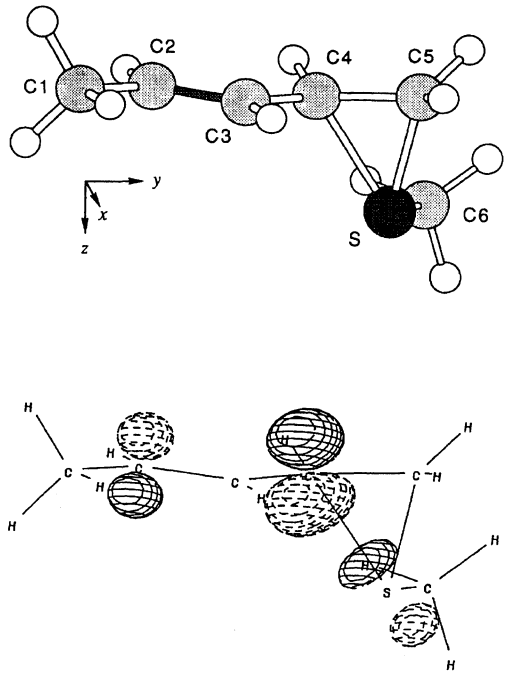


Fig. 1. Optimized structure and LUMO of model cation **21b**.

optimum structure was an episulfonium ion like **21b**.

The theoretical calculation on episulfonium ion **23**, which is a model cation for the reaction of **1d**, was also carried out by using the PM3 method; it was revealed that the heat of formation for **23** was 13.1 kcal mol^{-1} higher than that for **21b**. The observed complexity in the reaction of **1d** may arise from this instability of the intermediate.

Table 4. Coefficients of LUMO of Model Cation **21b**[a)]

	2s	$2p_x$	$2p_y$	$2p_z$
C1	0.006	0.003	0.012	0.041
C2	−0.009	0.003	−0.024	−0.398
C3	0.032	0.023	0.045	0.009
C4	−0.218	−0.025	−0.148	0.618
C5	−0.003	−0.007	−0.026	0.031
C6	−0.091	0.147	0.133	−0.054
S	0.158	0.312	−0.245	0.349

a) The absolute values of the coefficients of hydrogens were less than 0.083.

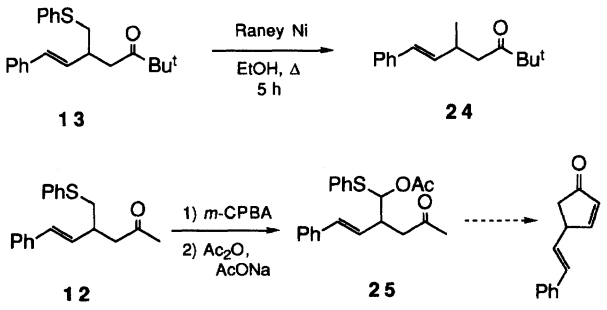
Since most of synthetically interesting compounds do not have a sulfur function, the removal of such function is an important step for a sulfur-assisted reaction. Then, we tried the desulfurization reaction of product **13**. By treatment of **13** with Raney Ni in refluxing ethanol for 4 h, the desulfurized product **24** was successfully obtained in 77% yield. Moreover, product **12** could be converted to acetoxy sulfide **25** by the Pummerer rearrangement,[14)] which is a potential precursor for 4-alkenyl-2-cyclopentenone (Scheme 6).

Experimental

General. ^{1}H NMR spectra were measured on a JEOL PMX-60SI or a JEOL GX-400 instrument with tetramethylsilane as an internal standard. Infrared spectra were recorded on a JASCO IR-810 spectrophotometer. Mass spectra were obtained with a Shimadzu QP-2000 or a JEOL JMSAX-505H instrument. Gas chromatography was performed on a Shimadzu GC-14A. Column chromatography was carried out with Merck Kieselgel 60 (70—230 mesh). Wakogel B-5F was used for preparative TLC. All solvents were distilled and stored over molecular sieves or sodium wire.

Silyl enol ethers **2a**—**2c**, **2f**, and ketene silyl acetal **2d** were synthesized according to a method in the literature.[15)] Enamine **20**,[16)] and Raney Ni[17)] were prepared by a known procedure, respectively.

(*E*)-4-Acetoxy-5-phenylthio-2-pentene (1a). To a stirred solution of (methylthio)benzene (2.99 g, 24.1 mmol) and *N*,*N*,*N*′,*N*′- tetramethylethylenediamine (TMEDA)



Scheme 6.

(2.82 g, 24.3 mmol) in THF (120 ml) was slowly added a hexane solution of *n*-BuLi (1.62 mol dm^{-3}, 15 ml, 24.3 mmol) at −78°C. The resulting mixture was allowed to warm up to 0°C and stirred for 30 min at that temperature. Then, crotonaldehyde (1.84 g, 26.3 mmol) in THF (15 ml) was added to the mixture at −78°C, and the stirring was continued for 1 h at that temperature and then for 1 h at room temperature. To the mixture was slowly added acetyl chloride (2.12 g, 27.0 mmol) in THF (15 ml) at −78°C. After stirring for 1 h, the reaction mixture was poured into ice-water (100 ml). The organic layer was washed twice with 1 mol dm^{-3} NaOH solution (50 ml) and once with brine (50 ml). The organic layer was dried over Na_2SO_4, and the solvent was stripped by using a rotary evaporator. Purification by column chromatography (eluent: ethyl acetate/hexane =1/20) gave 3.19 g (56% yield) of **1a** as an oil. ^{1}H NMR (CCl_4, 60 MHz) δ=1.8 (3H, d, J=6 Hz), 2.0 (3H, s), 3.2 (2H, d, J=6 Hz), 5.2—6.0 (3H, m), and 7.4 (5H, m); IR (neat) 1745, 1240, and 965 cm^{-1}. Found: C, 66.09; H, 6.75%. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82%.

In a similar manner, **1b**, **1f**, and **1g** were obtained. Allylic acetate **16** was also prepared by the same procedure (*n*-BuLi was used instead of lithiated (methylthio)benzene in the absence of TMEDA).

(*E*)-4-Acetoxy-5-methylthio-2-pentene (1b). 61% yield; an oil; ^{1}H NMR (CCl_4, 60 MHz) δ=1.8 (3H, d, J=6 Hz), 2.1 (3H, s), 2.2 (3H, s), 2.8 (2H, d, J=6 Hz), and 5.2—6.0 (3H, m); IR (neat) 1740, 1240, and 965 cm^{-1}. Found: m/z 114.0504. Calcd for $C_6H_{10}S$: M−AcOH, 114.0503.

(*E*)-4-Acetoxy-2-methyl-5-phenylthio-2-pentene (1f). 81% yield; an oil; ^{1}H NMR (CCl_4, 60 MHz) δ=1.6 (3H, s), 1.7 (3H, s), 1.9 (3H, s), 3.0—3.2 (2H, m), 5.0—5.9 (2H, m), and 7.2—7.6 (5H, m); IR (neat) 1740 and 1240 cm^{-1}. Found: m/z 190.0816. Calcd for $C_{12}H_{14}S$: M−AcOH, 190.0816.

(*E*)-3-Acetoxy-1-phenyl-4-phenylthio-1-butene (1g). 57% yield; an oil; ^{1}H NMR (CCl_4, 60 MHz) δ=2.0 (3H, s), 3.2 (2H, d, J=7 Hz), 5.6 (1H, q, J=7 Hz), 6.2 (1H, dd, J=7, 15 Hz), 6.7 (1H, d, J=15 Hz), and 7.2—7.6 (10H, m); IR (neat) 1745, 1240, and 965 cm^{-1}. Found: C, 72.54; H, 6.13%. Calcd for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08%.

(*E*)-4-Acetoxy-2-octene (16). An oil; NMR (CCl_4, 60 MHz) δ=1.0 (3H, m), 1.1—1.7 (6H, m), 1.7 (3H, d, J=6 Hz), 2.0 (3H, s), and 5.2—5.9 (3H, m); IR (neat) 1740, 1240, and 965 cm^{-1}. Found: m/z 170.1319. Calcd for $C_{10}H_{18}O_2$: M, 170.1307.

(*E*)-*rel*-(4*R*,5*R*)-4-Acetoxy-5-phenylthio-2-hexene (1h). (*E*)-2-Trimethylsiloxy-3-pentenenitrile[18] was deprotonated by LDA and allowed to react with 1-chloro-1-(phenylthio)ethane[19] according to a method in the literature.[20] Purification by column chromatography (eluent: ethyl acetate/hexane=1/20) gave (*E*)-2-phenylthio-4-hexen-3-one (30% yield) as an oil. ^{1}H NMR (CCl_4, 60 MHz) δ=1.4 (3H, d, J=7 Hz), 1.9 (3H, d, J=6 Hz), 3.8 (1H, q, J=7 Hz), 6.5 (1H, dm, J=16 Hz), 6.7—7.1 (1H, m), 7.3 (5H, s).

The above ketone was treated with lithium tri-*s*-butylborohydride according to a method in the literature,[21] and acetylated with Ac_2O/pyridine. Purification by column chromatography (eluent: ethyl acetate/hexane=1/20) gave the title compound (48% yield) as an oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.26 (3H, d, J=7 Hz), 1.72 (3H, dd, J=1, 6Hz), 1.99 (3H, s), 3.41 (1H, dq, J=7, 6 Hz), 5.30 (1H, dd, J=6, 7 Hz), 5.52 (1H, ddq, J=8, 15, 1 Hz), 5.78 (1H, dq, J=6, 15 Hz), and 7.2—7.5 (5H, m); IR (neat) 1745, 1240, and 965 cm^{-1}. Found: C, 67.06; H, 7.25%. Calcd for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.25%.

***rel*-(3*R*,4*R*)-3-Acetoxy-4-phenylthio-1-cyclohexene (1i).** Allylic acetate **1i** was prepared through acetylation of the corresponding alcohol which was prepared according to a procedure in the literature.[22] An oil; ^{1}H NMR (CCl_4, 60 MHz) δ=1.5—2.4 (4H, m), 2.0 (3H, s), 3.4 (1H, m), 5.2—6.2 (3H, m), and 7.4 (5H, m); IR (neat) 1735 and 1235 cm^{-1}; MS m/z (rel intensity) 248 (M^+, 60), 188 (100), 136 (36), 135 (20), 110 (40), 109 (36). Found: m/z 248.0839. Calcd for $C_{14}H_{16}O_2S$: M, 248.0871.

(*Z*)-4-Acetoxy-5-phenylthio-2-pentene (1j). To a stirred solution of (methylthio)benzene (12.4 g, 100 mmol) and TMEDA (10 ml, ca. 100 mmol) in THF (200 ml) was slowly added a hexane solution of *n*-BuLi (1.62 mol dm^{-3}, 62 ml, 100 mmol) at −78°C. The resulting mixture was allowed to warm up to 0°C and stirred for 30 min at that temperature. Then, a THF (10 ml) solution of 2-butynal, which was prepared from 2-butyn-1-ol (5 g, 70 mmol) and MnO_2 (64 g, 0.7 mol) according to a method in the literature,[23] was added to the mixture at −78°C. After removal of the cooling bath, the mixture was stirred overnight at room temperature and then poured into crushed ice. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3×50 ml). The organic layers were combined and dried over sodium sulfate, and then the solvent was evaporated. After most of unreacted (methylthio)benzene was distilled off under reduced pressure, the residue was purified by column chromatography (eluent: ethyl acetate/hexane =1/10) to give 1-phenylthio-3-pentyn-2-ol (1.8 g, 13% yield) as an oil. ^{1}H NMR (CCl_4, 60 MHz) δ=1.8 (3H, d, J=2 Hz), 2.5 (1H, br s), 3.1 (2H, d, J=6 Hz), 4.2—4.6 (1H, m), and 7.1—7.6 (5H, m).

The above alcohol was acetylated by a usual procedure (Ac_2O/pyridine, catalytic DMAP). Purification by column chromatography (eluent: ethyl acetate/hexane=1/20) gave the corresponding acetate in quantitative yield as an oil. ^{1}H NMR (CCl_4, 60 MHz) δ=1.8 (3H, d, J=2 Hz), 2.0 (3H, s), 3.2 (2H, d, J=7 Hz), 5.3—5.6 (1H, m), and 7.1—7.5 (5H, m).

A stirred mixture of the acetate (2.00 g, 8.5 mmol) and Lindlar catalyst (100 mg) in EtOH (50 ml) was exposed to hydrogen gas at 9.7 atm for 3 d. Filtration of the mixture, followed by evaporation of the solvent, gave the crude oil. Purification by means of column chromatography (ether/hexane=1/20) afforded **1j** (0.67 g, 33% yield) as an oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.65 (3H, dd, J=2, 7 Hz), 1.97 (3H, s), 3.01 (1H, dd, J=6, 14 Hz), 3.22 (1H, dd, J=7, 14 Hz), 5.39 (1H, ddt J=9, 11, 2 Hz), 5.6—5.8 (2H, m), and 7.2—7.4 (5H, m); IR (neat) 1740 and 1240 cm^{-1}. Found: C, 66.07; H, 6.90%. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82%.

(*Z*)-4-Acetoxy-1-phenylthio-2-pentene (1k). To a solution of phenyl propargyl sulfide (2.00 g, 13.5 mmol) and TMEDA (1.5 ml, 15 mmol) in THF (25 ml) was added a hexane solution of *n*-BuLi (1.62 mol dm^{-3}, 10.0 ml, 16.2 mmol) at −78°C. The resulting dark brown solution was stirred for 15 min at that temperature, then a THF (3 ml) solution of acetaldehyde (0.62 g, 14.1 mmol) was added to the solution. After being stirred for 15 min, a THF (3 ml)

solution of acetyl chloride (1.44 g, 18.3 mmol) was added, and the mixture was stirred overnight at room temperature. Usual aqueous workup, followed by column chromatography (eluent: ethyl acetate/hexan=1/20), gave 4-acetoxy-1-phenylthio-2-pentyne (1.80 g, 57% yield) as an oil. ^{1}H NMR (CCl_4, 60 MHz) δ=1.4 (3H, d, J=7 Hz), 2.0 (3H, s), 3.6 (2H, broad s), 5.4 (1H, broad q), and 7.2—7.6 (5H, m).

A stirred mixture of the above alkyne (2.00 g, 8.5 mmol) and Lindlar catalyst (100 mg) in 70 ml of EtOH was exposed to hydrogen gas at 9.7 atm for 5 d. Filtration of the mixture, followed by evaporation of the solvent, gave the crude oil. Purification by means of column chromatography (ether/hexane=1/20) afforded **1k** (0.87 g, 43% yield) as an oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.10 (3H, d, J=6 Hz), 2.00 (3H, s), 3.55 (1H, ddd, J=1, 7, 13 Hz), 3.76 (1H, ddd, J=1, 9, 13 Hz), 5.43 (1H, ddt, J=9, 10, 1 Hz), 5.49 (1H, dq, J=9, 6 Hz), 5.62 (1H, ddd, J=7, 9, 10 Hz), and 7.1—7.4 (5H, m); IR (neat) 1735 and 1250 cm^{-1}. Found: C, 66.13; H, 6.72%. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82%.

(*E*)-4-Acetoxy-1-phenylthio-2-pentene (1l). An ethereal solution of MeLi (1.06 mol dm^{-3}, 9.0 ml, 9.5 mmol) was diluted with 10 ml of THF, and the solution was cooled to 0°C. Then, a THF (5 ml) solution of 4-(phenylthio)-crotonaldehyde[24] (1.60 g, 9.0 mmol) was added to the above partially-solidified solution. The reaction mixture was allowed to warm up to room temperature, stirred for 10 min, and poured into ice-water (100 ml). The organic layer was washed successively with saturated aqueous NH_4Cl, water, and brine. After the organic layer was dried over Na_2SO_4, the solvent was evaporated. Column chromatography (eluent: ethyl acetate/hexane=1/5) was performed to remove less polar by-products. Then, the crude product obtained upon concentration of the fractions containing the main product was acetylated according to a usual procedure (Ac_2O/pyridine, catalytic DMAP) to give 1.27 g (60% yield) of **1l** after purification by column chromatography (eluent: ethyl acetate/hexane=1/20) as an oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.19 (3H, d, J=6 Hz), 2.00 (3H, s), 3.49 (2H, d, J=7 Hz), 5.26 (1H, dq, J=6, 6 Hz), 5.48 (1H, ddt, J=6, 15, 1 Hz), 5.73 (1H, ddt, J=1, 15, 7 Hz), and 7.1—7.4 (5H, m); IR (neat) 1740, 1240, and 955 cm^{-1}. Found: m/z 236.0845. Calcd for $C_{13}H_{16}O_2S$: M, 236.0871.

Allylic acetate **1e** was synthesized in a similar manner.

4-Acetoxy-2-methyl-1-phenylthio-2-pentene (1e). 55% yield (ca. 1:1 mixture of diastereomers); an oil; ^{1}H NMR (CCl_4, 60 MHz) δ=1.1 (3H, d, J=6 Hz), 1.8 (3H, s), 1.9 (3H, s), 3.4 (2H, s), 5.0—5.6 (2H, m), and 7.1—7.5 (5H, m); IR (neat) 1735 and 1245 cm^{-1}. Found: m/z 250.1041. Calcd for $C_{14}H_{18}O_2S$: M, 250.1027.

(*E*)-2,2-Dimethyl-5-phenylthiomethyl-6-octen-3-one (α-3) and 2,2,5-Trimethyl-8-phenylthio-6-octen-3-one (γ-3). To a solution of **1a** (0.41 mmol) and **2a** (0.50 mmol) in CH_2Cl_2 (4 ml) was added a CH_2Cl_2 solution of TMSOTf (1.0 mol dm^{-3}, 0.05 ml, 0.05 mmol) at −78°C. Then, the cooling bath was removed, and the mixture was stirred for 2 h. After addition of saturated aqueous $NaHCO_3$ (8 ml), the organic materials were extracted with CH_2Cl_2 (3×5 ml). The extracts were combined and then dried over Na_2SO_4, and the solvent was evaporated. Purification by preparative TLC gave **3** as an inseparable mixture of regioisomers. An oil; IR (neat) 1700, 1475, 960, 735, and 690 cm^{-1}. Found: C, 73.88; H, 8.78%. Calcd for $C_{17}H_{24}OS$: C, 73.86; H, 8.75%. ^{1}H NMR ($CDCl_3$, 400 MHz) for α-**3** δ=1.18 (9H, s), 1.71 (3H, dd, J=2, 6 Hz), 2.69 (1H, dd, J=7, 17 Hz), 2.81 (1H, dd, J=6, 17 Hz), 3.0 (1H, m), 3.04 (2H, d, J=7 Hz), 5.40 (1H, ddq, J=8, 15, 2 Hz), 5.56 (1H, dq, J=6, 15 Hz), and 7.1—7.4 (5H, m); for γ-**3** (only distinguishable peaks were recorded) δ=0.97 (3H, d, J=7 Hz), 1.16 (9H, s), 2.42 (1H, d, J=7 Hz), and 3.55 (2H, d, J=6 Hz).

In a similar nammer, other products **4**—**15** and **17** were obtained. The ratio of regioisomers was determined by means of GLC or ^{1}H NMR.

(*E*)-2,4,4-Trimethyl-5-phenylthiomethyl-6-octen-3-one (α-4) and (*E*)-2,4,4,5-Tetramethyl-8-phenylthio-6-octen-3-one (γ-4). An oil; IR (neat) 1690, 1460, 725, and 680 cm^{-1}. Found: m/z 290.1665. Calcd for $C_{18}H_{26}OS$: M, 290.1704. ^{1}H NMR ($CDCl_3$, 400 MHz) for α-**4** δ=0.99 (3H, d, J=7 Hz), 1.01 (3H, d, J=7 Hz), 1.09 (3H, s), 1.10 (3H, s), 1.70 (3H, dd, J=2, 7 Hz), 2.57 (1H, ddd, J=3, 10, 11 Hz), 2.76 (1H, dd, J=11, 12 Hz), 2.82 (1H, dd, J=3, 12 Hz), 3.04 (1H, quintet, J=7 Hz), 5.18 (1H, ddq, J=9, 15, 2 Hz), 5.53 (1H, ddq, J=1, 15, 7 Hz), and 7.1—7.3 (5H, m); for γ-**4** δ=0.78 (3H, d, J=7 Hz), 0.90 (3H, s), 0.92 (3H, s), 2.48 (1H, dq, J=7, 7 Hz), 3.51 (2H, dq like, J=7, 1 Hz), and 5.36 (1H, ddt, J=8, 15, 1 Hz).

(*E*)-2,4,4-Trimethyl-5-methylthiomethyl-6-octen-3-one (α-5) and 2,4,4,5-Tetramethyl-8-methylthio-6-octen-3-one (γ-5). An oil; IR (neat) 1705 and 970 cm^{-1}. Found: m/z 228.1563. Calcd for $C_{13}H_{24}OS$: M, 228.1548. ^{1}H NMR ($CDCl_3$, 400 MHz) for α-**5** δ=1.03 (3H, d, J=7 Hz), 1.05 (3H, d, J=7 Hz), 1.07 (3H, s), 1.09 (3H, s), 1.72 (3H, dd, J=1, 6 Hz), 2.05 (3H, s), 2.33 (2H, d, J=7 Hz), 2.56 (1H, dt, J=9, 7 Hz), 3.09 (1H, dq, J=7, 7 Hz), 5.18 (1H, ddq, J=9, 15, 1 Hz), and 5.56 (1H, ddq, J=1, 15, 6); for γ-**5** δ=0.90 (3H, d, J=7 Hz) and 2.04 (3H, s).

2,2,5,7-Tetramethyl-8-phenylthio-6-octene-3-one (γ-6). 1:1 mixture of diastereomers; an oil; ^{1}H NMR (CCl_4, 60 MHz) δ=0.8 (3H, two doublets, J=7 Hz), 1.1 (9H, s), 1.8 (3H, s), 2.2 (2H, d, J=7 Hz), 2.3 (1H, m), 3.4—3.7 (2H, m), 4.8—5.1 (1H, m), and 7.1—7.5 (5H, m); IR (neat) 1710, 740, and 690 cm^{-1}. Found: m/z 290.1717. Cacld for $C_{18}H_{26}OS$: M, 290.1705.

2,2,7-Trimethyl-5-phenylthiomethyl-6-octen-3-one (α-7). An oil; ^{1}H NMR (CCl_4, 60 MHz) δ=1.1 (9H, s), 1.6 (3H, s), 1.7 (3H, s), 2.4—3.2 (5H, m), 4.8—5.1 (1H, m), and 7.1—7.5 (5H, m); IR (neat) 1710, 1480, 735, and 690 cm^{-1}. Found: m/z 290.1703. Calcd for $C_{18}H_{26}OS$: M, 290.1705.

(*E*)-2-Methyl-5-phenylthio-1,3-pentadiene (8). An oil; ^{1}H NMR (CCl_4, 60 MHz) δ=1.8 (3H, s), 3.6 (2H, d, J=7 Hz), 4.9 (2H, broad s), 5.4—5.9 (1H, m), 6.2 (1H, d, J=16 Hz), and 7.1—7.5 (5H, m); IR (neat) 1480, 1440, 965, 740, and 690 cm^{-1}. Found: m/z 190.0780. Calcd for $C_{12}H_{14}S$: M, 190.0816.

(*E*)-2-(1-Phenylthiomethyl-2-butenyl)cyclohexanone (α-9) and 2-(2-Methyl-4-phenylthio-2-butenyl)cyclohexanone (γ-9). An oil; IR (neat) 1710, 970, 740, and 695 cm^{-1}. Found: C, 74.11; H, 8.02%. Calcd for $C_{17}H_{22}OS$: C, 74.40; H, 8.08%. ^{1}H NMR ($CDCl_3$, 400 MHz) for α-**9** (a mixture of two diastereomers which are tentatively named as αA and αB, and the assignment of every separated peak for each diastereomer is arbitrary) δ=1.65 (3H for αA, dd, J=1 Hz, another J value is missing because of the overlapping of the signal), 1.66 (3H for αB, dd, J=2

Hz, another J value is missing because of the overlapping of the signal), 1.4—2.0 (6H, m), 2.2—2.8 (4H, m), 2.96 (1H for αA, dd, J=7, 13 Hz), 2.99 (1H for αB, dd, J=8, 13 Hz), 3.02 (1H for αA, dd, J=6, 13 Hz), 3.22 (1H for αB, dd, J=6, 13 Hz), 5.24 (1H for αA, ddq, J=8, 15, 2 Hz), 5.4—5.6 (1H for αA and 2H for αB, m), and 7.1—7.4 (5H, m); for γ-**9** (γA and γB, tentatively) δ=0.89 (3H for γA, d, J=7 Hz), 0.90 (3H for γB, d, J=7 Hz), 3.48 (2H for γA, d, J=6 Hz), and 3.50 (2H for γB, d, J=5 Hz).

Methyl (*E*)-2,2-Dimethyl-3-phenylthiomethyl-4-hexenoate (α-10) and Methyl (*E*)-2,2,3-Trimethyl-6-phenylthio-4-hexenoate (γ-10). An oil; IR (neat) 1730, 1480, 970, 760, and 690 cm^{-1}. Found: C, 68.99; H, 7.96%. Calcd for $C_{16}H_{22}O_2S$: C, 69.02; H, 7.96%. ^1H NMR ($CDCl_3$, 400 MHz) for α-**10** δ=1.12 (3H, s), 1.13 (3H, s), 1.70 (3H, dd, J=2, 6 Hz), 2.51 (1H, ddd, J=3, 11, 11 Hz), 2.76 (1H, dd, J=11, 12 Hz), 2.96 (1H, dd, J=3, 12 Hz), 3.61 (3H, s), 5.17 (1H, ddq, J=8, 15, 2 Hz), 5.52 (1H, dd, J=15, 7 Hz), and 7.1—7.3 (5H, m); for γ-**10** δ=0.84 (3H, d, J=7 Hz), 0.97 (3H, s), 2.42 (1H, dq, J=7, 7 Hz), 3.50 (2H, d, J=7 Hz), 3.65 (3H, s), and 5.38 (1H, ddt, J=9, 15, 1 Hz).

(*E*)-4-Phenylthiomethyl-1,5-heptadiene (α-11) and 4-Methyl-7-phenylthio-1,5-heptadiene (γ-11). An oil; IR (neat) 1640, 1485, 965, 915, 740, and 690 cm^{-1}. Found: m/z 218.1146. Calcd for $C_{14}H_{18}S$: M, 218.1129. ^1H NMR ($CDCl_3$, 400 MHz) for α-**11** δ=1.66 (3H, dd, J=2, 6 Hz), 2.1—2.4 (3H, m), 2.88 (1H, dd, J=7, 13 Hz), 2.94 (1H, dd, J=6, 13 Hz), 4.9—5.1 (2H, m), 5.30 (1H, ddq, J=8, 15, 2 Hz), 5.47 (1H, ddq, J=1, 15, 6 Hz), 5.7—5.8 (1H, m), and 7.1—7.4 (5H, m); for γ-**11** δ=0.91 (3H, d, J=7 Hz) and 3.57 (2H, d, J=7 Hz).

(*E*)-6-Phenyl-4-phenylthiomethyl-5-hexen-2-one (α-12) and (*E*)-4-Phenyl-7-phenylthio-5-hepten-2-one (γ-12). An oil; IR (neat) 1715, 1360, 965, 745, and 690 cm^{-1}. Found: m/z 296.1255. Calcd for $C_{19}H_{20}OS$: M, 296.1275. ^1H NMR ($CDCl_3$, 400 MHz) for α-**12** δ=2.08 (3H, s), 2.61 (1H, dd, J=7, 17 Hz), 2.84 (1H, dd, J=5, 17 Hz), 3.0—3.1 (3H, m), 6.09 (1H, dd, J=7, 16 Hz), 6.41 (1H, d, J=16 Hz), and 7.1—7.4 (10H, m); for γ-**12** δ=2.00 (3H, s), 2.71 (2H, d, J=7 Hz), 3.46 (2H, d like, J=7 Hz), 3.83 (1H, q like, J=7 Hz), 5.46 (1H, dt, J=15, 7 Hz), and 5.61 (1H, dd, J=7, 15 Hz).

(*E*)-2,2-Dimethyl-7-phenyl-5-phenylthiomethyl-6-hepten-3-one (α-13) and (*E*)-2,2-Dimethyl-5-phenyl-8-phenylthio-6-octen-3-one (γ-13). An oil; IR (neat) 1710, 1480, 970, 750, and 695 cm^{-1}. Found: m/z 338.1683. Calcd for $C_{22}H_{26}OS$: M, 338.1704. ^1H NMR ($CDCl_3$, 400 MHz) for α-**13** δ=1.21 (9H, s), 2.84 (1H, dd, J=7, 18 Hz), 2.95 (1H, dd, J=5, 18 Hz), 3.2 (3H, m), 6.20 (1H, dd, J=8, 16 Hz), 6.50 (1H, d, J=16 Hz), and 7.2—7.4 (10H, m); for γ-**13** δ=1.10 (9H, s), 3.58 (2H, d, J=7 Hz), 4.02 (1H, qm, J=7 Hz), 5.58 (1H, ddt, J=1, 7, 15 Hz), and 5.74 (1H, ddt, J=1, 7, 15 Hz); MS for α-**13** m/z (rel intensity) 228 ($M-PhSH^+$, 15), 171 (11), 142 (15), 129 (29), 128 (49), 123 ($PhSCH_2^+$, 15), 85 (23), and 57 (100), for γ-**13** m/z (rel intensity) 229 ($M-PhS^+$, 27), 228 (10), 129 (42), 128 (25), 85 (52), and 57 (100).

(*E*)-2,2-Dimethyl-5-[1-(phenylthio)ethyl]-6-octen-3-one (α-14). An oil; ^1H NMR (CCl_4, 60 MHz) δ=1.1 (9H, s), 1.0—1.5 (3H, m), 1.7 (3H, m), 2.5—3.5 (4H, m), 5.3—5.5 (2H, m), and 7.1—7.5 (5H, m); ($CDCl_3$, 400 MHz) δ=1.09 (9H, s), 1.12 (9H, s), 1.63 (3H, dd, J=2, 6 Hz), 1.66 (3H, dd, J=2, 6 Hz); IR (neat) 1710, 1480, 970, 750 and 695 cm^{-1}; MS (identical for both diastereomers) m/z (rel intensity) 290 (M^+, 2), 190 (7), 137 ($M-PhSCHCH_3^+$, 100), and 57 (78). Found: C, 74.70; H, 9.07%. Calcd for $C_{18}H_{26}OS$: C, 74.43; H, 9.02%.

3,3-Dimethyl-1-[*rel*-(1*R*, 6*R*)-6-phenylthio-2-cyclohexenyl]-2-butanone (α-15). An oil; ^1H NMR ($CDCl_3$, 400MHz) δ=1.14 (9H, s), 1.7 (1H, m), 2.0—2.2 (3H, m), 2.55 (1H, dd, J=9, 18 Hz), 2.7 (1H, m), 3.00 (1H, dd, J=4, 18 Hz), 3.02 (1H, ddd, J=3, 9, 10 Hz, PhSC*H*), 5.45 (1H, dm, J=10 Hz), 5.7 (1H, m), 7.3 (3H, m), and 7.4 (2H, m); IR (neat) 1715, 1485, 1375, 745, and 700 cm^{-1}. Found: m/z 288.1564. Calcd for $C_{18}H_{24}OS$: M, 288.1548.

(*E*)-5-Butyl-2,2-dimethyl-6-octen-3-one (α-17) and (*E*)-2,2,5-Trimethyl-6-undecen-3-one (γ-17). An oil; IR (neat) 1715 and 975 cm^{-1}. Found: m/z 210.1996. Calcd for $C_{14}H_{26}O$: M, 210.1983. ^1H NMR ($CDCl_3$, 400 MHz) for α-**17** δ=0.8—0.9 (3H, m), 1.10 (9H, s), 1.2—1.3 (6H, m), 1.62 (3H, dd, J=2, 7 Hz), 2.3—2.5 (2H, m), 2.5—2.6 (1H, m), 5.17 (1H, ddq, J=9, 15, 2 Hz), and 5.4 (1H, m); for γ-**17** δ=0.95 (3H, d, J=7 Hz), 1.11 (9H, s), 1.9—2.0 (2H, m), 2.7—2.8 (1H, m), and 5.30 (1H, dd, J=7, 15 Hz).

Desulfurization of 13. To an EtOH (10 ml) solution of **13** (258 mg, 0.76 mmol; α/γ=92/8) was added an EtOH suspension of Raney Ni W-2 (ca. 5 g), and the mixture was heated to reflux for 4 h. Filtration, followed by evaporation and separation by preparative TLC, gave 135 mg (77% yield) of desulfurized product **24** as a 92/8 mixture of regioisomers. An oil; IR (neat) 1710, 970, 750, and 690 cm^{-1}. Found: m/z 230.1679. Calcd for $C_{16}H_{22}O$: M, 230.1670. ^1H NMR ($CDCl_3$, 400 MHz) for major isomer δ=1.08 (3H, d, J=7 Hz), 1.12 (9H, s), 2.50 (1H, dd, J=7, 17 Hz), 2.60 (1H, dd, J=6, 17 Hz), 2.9—3.0 (1H, m), 6.13 (1H, dd, J=7, 16 Hz), 6.37 (1H, d, J=17 Hz), and 7.2—7.4 (5H, m); for minor isomer δ=1.72 (3H, d, J=7 Hz) and 5.4—5.6 (2H, m); MS for major isomer m/z (rel intensity) 230 (M^+, 5), 173 (11), 131 (43), 91 (18), 85 (12), and 57 (100), for minor isomer m/z (rel intensity) 173 (20), 131 (72), 91 (21), and 57 (100).

(*E*)-4-[Acetoxy(phenylthio)methyl]-6-phenyl-5-hexen-2-one (25). To a CH_2Cl_2 (4 ml) solution of **12** (495 mg, 1.55 mmol; α/γ=93/7) was added a CH_2Cl_2 (6ml) solution of *m*-chloroperbenzoic acid (*m*-CPBA) (83% purity, 326 mg, 1.57 mmol) at −78°C. The mixture was allowed to warm up gradually to room temperature and stirred for 1 h. Then, saturated aqueous $NaHCO_3$ (5 ml) and Na_2SO_3 (2 ml) were added, and the organic materials were extracted with 5 ml of CH_2Cl_2. The extracts were dried over Na_2SO_4. After evaporation of the solvent, the crude oil was purified by means of column chromatography (eluent: ethyl acetate/hexane=2/1) to afford 474 mg (91% yield) of the intermediate sulfoxide as a viscous oil. ^1H NMR (CCl_4, 60 MHz) δ=2.1 (3×0.5 H, s), 2.2 (3×0.5 H, s), 2.6—3.6 (5H, m), 6.3—6.6 (2H, m), and 7.2—7.8 (10H, m); IR (neat) 1715, 1360, 1040, 965, 750 and 690 cm^{-1}.

The above sulfoxide (474 mg, 1.52 mmol) was dissolved in Ac_2O (10 ml), and anhydrous NaOAc (0.47 g, 5.73 mmol) was added to the solution. The mixture was refluxed for 5 h. Evaporation of the solvent, followed by column chromatography (eluent: ethyl acetate/hexane=1/10), gave **25** (108 mg, 20% yield) as a mixture of diastereomers. An oil; ^1H NMR (CCl_4, 60 MHz) δ=2.0 (3×0.5 H, s), 2.1 (3×0.5

H, s), 2.1 (3×0.5 H, s), 2.2 (3×0.5 H, s), 2.5—2.9 (2H, m), 3.1—3.5 (1H, m), 5.8—6.8 (3H, m), and 7.1—7.6 (10H, m); IR (neat) 1745, 1720, 1220, 1020, 965, 750 and 690 cm^{-1}. Found: m/z 294.1056. Calcd for $C_{19}H_{18}OS$: M − AcOH, 294.1078.

Theoretical Calculations. Molecular orbital calculations were performed on HITAC M-880 by using MOPAC Ver. 6.01 with complete geometry optimization.[25]

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