

Preparation and Reaction of 1-(Methylthio- and phenylthio)-vinyllithium Reagents

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An improved procedure for the preparation of 1-(methylthio- and phenylthio)vinyllithium reagents utilizing 2-methoxyalkyl sulfides was developed and their reactions with ketones, aldehydes, oxiranes, and alkyl halides were studied.

The utilization of various heteroatom-stabilized vinyl anions in organic synthesis has become increasingly important in recent years.¹⁾ The α -lithiated alkenyl sulfide (**3**) is one of these anions, and usefulness of **3** in the synthesis of certain organic compounds has well been demonstrated. For example, Oshima *et al.* showed that **3**, which are useful intermediates for the synthesis of ketones,²⁾ could be considered as acyl anion equivalents. It was also reported that the adducts of **3** with aldehydes might be valuable intermediates for the preparation of furans and 1,4-dicarbonyl compounds.³⁾

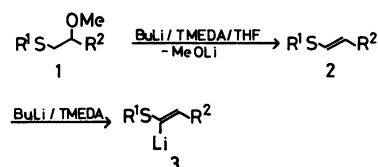
Since **3** is generally prepared by the treatment of alkenyl sulfide (**2**) with strong base, such as *s*-butyllithium, *t*-butyllithium, or lithium diisopropylamide (LDA), the preparation of alkenyl sulfides (**2**) is required at the first step of the aforementioned synthesis. However, the synthesis of **2** may not be straightforward in some cases.⁴⁾ We have thus investigated an improved procedure for the preparation of **3**. Recently, we found that the reaction of 2-methoxyalkyl sulfides (**1**) with two molar butyllithium in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) directly produced **3**, probably *via* **2**.⁵⁾

Concerning the formation of alkenyl sulfide from 2-methoxyalkyl sulfide and subsequent lithiation, Corey *et al.* reported that 1,3-bis(methylthio)propene (**4**) was obtained by the reaction of 1,3-bis(methylthio)-2-methoxypropane (**5**) with an equimolar amount of LDA, and 1,3-bis(methylthio)allyl anion (**6**) was directly produced when **5** was treated with two equivalents of LDA.⁶⁾ Unlike the above-mentioned result of us, the formation of vinylithium (**3**) was not observed in the lithiation of **4** with LDA. This selective formation of the allyl anion (**6**) is apparently due to the presence of methylthio group attached to the allylic position of **4**.

In this paper, we wish to report the scope and limitation for the generation of **3** with our method, and the results obtained in the reaction of **3** with carbonyl compounds, oxiranes, and alkyl halides are described.

Results and Discussion

1-(Methylthio- and phenylthio)vinyllithiums (**3**) were prepared by the reaction of the corresponding 2-methoxyalkyl sulfides (**1**) with butyllithium or LDA as indicated in Eq. 1. The yield of **3** was estimated on the basis of the isolated yield of adduct with benzaldehyde (Table 1). Satisfactory results were obtained when **1** was treated with butyllithium at -30°C or higher for 1 to 3 h in the presence of TMEDA. At -78°C , the yield of **3a**



- (1)
- 1a $\text{R}^1=\text{Me}$ $\text{R}^2=\text{H}$
 1b $\text{R}^1=\text{Me}$ $\text{R}^2=\text{Ph}(\text{CH}_2)_2$
 1c $\text{R}^1=\text{Me}$ $\text{R}^2=(\text{CH}_3)_2\text{CHCH}_2$
 1d $\text{R}^1=\text{Me}$ $\text{R}^2=\text{Ph}$
 1e $\text{R}^1=\text{Ph}$ $\text{R}^2=\text{Ph}(\text{CH}_2)_2$
 1f $\text{R}^1=\text{Ph}$ $\text{R}^2=(\text{CH}_3)_2\text{CHCH}_2$
 1g $\text{R}^1=\text{Ph}$ $\text{R}^2=\text{CH}_3(\text{CH}_2)_4$

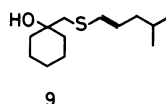
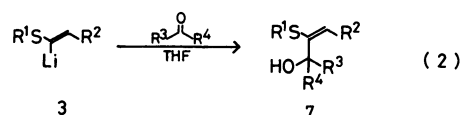


TABLE 1. THE REACTION OF **3** WITH BENZALDEHYDE

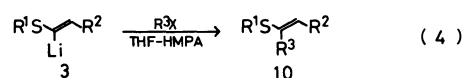
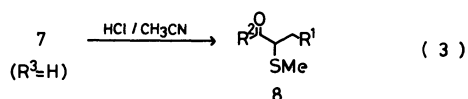
Run	2-Methoxy-alkyl sulfide	Temp $^{\circ}\text{C}$	Time h	Product	(Yield/%)
1	1a	-78	1	7e-1	(Trace) ^{a)}
2	1a	-78	1	7a-1	(11)
3	1a	-30	1	7a-1	(80)
4	1a	0	0.5	7a-1	(74)
5	1d	0	1	7d-1	(0)
6	1d	-30	2	7d-1	(0) ^{b)}
7	1d	-60	2.5	7d-1	(55) ^{b)}
8	1d	-30	1	7d-1	(22) ^{c)}
9	1e	-30	2	7e-1	(84)
10	1e	-23	3	7e-1	(74)
11	1e	0	0.5	7e-1	(82)
12	1f	0	0.5	7f-1	(66)
13	1f	-30	3	7f-1	(69)
14	1f	-23	3	7f-1	(74)

a) The reaction was carried out without TMEDA. b) The reaction was carried out in the presence of HMPA (0.6 ml/mmol) using LDA as a base. c) LDA was used as a base.

TABLE 2. THE REACTION OF **3** WITH ALDEHYDES AND KETONES

2-Methoxy-alkyl sulfide	Aldehyde or ketone		Product (Yield/%)	2-Methoxy-alkyl sulfide	Aldehyde or ketone		Product (Yield/%)
	R ³	R ⁴			R ³	R ⁴	
1a	Ph	H	7a-1 (80)	1e	CH ₃ CH ₂	H	7e-2 (64)
1a	Ph(CH ₂) ₂	H	7a-2 (81)	1e	(CH ₃) ₂ CHCH ₂	H	7e-3 (58)
1a	PhCH=CH	H	7a-3 (88)	1e	Ph	CH ₃	7e-4 (44)
1a	CH ₃ CH ₂	H	7a-4 (65)	1f	Ph	H	7f-1 (74)
1a	(CH ₃) ₂ CHCH ₂	H	7a-5 (70)	1f	Ph(CH ₂) ₂	H	7f-2 (77)
1a	Ph	CH ₃	7a-6 (68) ^{a)}	1f	PhCH=CH	H	7f-3 (84)
1c	-(CH ₂) ₅ -		7c-1 (15) ^{b)}	1f	CH ₃ CH ₂	H	7f-4 (72)
1d	Ph	H	7d-1 (55)	1f	(CH ₃) ₂ CHCH ₂	H	7f-5 (75)
1d	Ph(CH ₂) ₂	H	7d-2 (40)	1f	-(CH ₂) ₅ -		7f-6 (57)
1d	PhCH=CH	H	7d-3 (67)	1f	Ph	CH ₃	7f-7 (60)
1d	CH ₃ CH ₂	H	7d-4 (28)	1g	Ph	H	7g-1 (61)
1d	(CH ₃) ₂ CHCH ₂	H	7d-5 (33)	1g	-(CH ₂) ₅ -		7g-2 (50) ^{a)}
1e	Ph	H	7e-1 (84)	1g	Ph	CH ₃	7g-3 (59)

a) The reaction was carried out at -78°C . b) 1-[(4-Methyl-1-pentenylthio)methyl]-1-cyclohexanol (**9**) was isolated in 14% yield as a by-product.

TABLE 3. THE REACTION OF **3b** AND **3c** WITH ALDEHYDES

R ¹	R ²	Product	(Yield/%)
Ph(CH ₂) ₂	Ph	8b-1	(47)
Ph(CH ₂) ₂	Ph(CH ₂) ₂	8b-2	(39)
Ph(CH ₂) ₂	CH ₃ CH ₂	8b-3	(27)
(CH ₃) ₂ CHCH ₂	Ph	8c-1	(32)

was only 11% after 1 h. In the absence of TMEDA, only a trace amount of **3a** was produced under similar reaction conditions. In contrast to the reactions of **1a**, **1e**, and **1f**, the treatment of 2-methoxy-2-phenylethyl sulfide (**1d**) with butyllithium did not afford **3**, but produced the Michael type adduct of the intermediate alkenyl sulfide (**2**). When LDA was used as a base, however, this side reaction was suppressed.

The reaction of **3** with various aldehydes and ketones proceeded smoothly and produced β -methylthio and phenylthio β,γ -unsaturated alcohols (**7**) in good yields (Table 2). When allylic hydrogen was present in the intermediate methyl alkenyl sulfide (**2**), **7** was contaminated by some by-products. Since the purification of **7** was not successful in these cases, a mixture of the products was treated with hydrochloric acid in CH₃CN,⁷⁾ and the formation of **7** was proved by the isolation of the α -methylthio ketone (**8**) (Table 3). The NMR spectra of the by-products produced along with **7** suggested that not only α -lithiation but also lithiation of γ -position and the methylthio group proceeded in this case. In fact 2-hydroxyalkyl vinyl sulfide (**9**), which originated from the lithiation of methylthio group, was isolated in 14% yield in addition to α -adduct (**7c-1**) in the reaction of **1c** with cyclohexanone.

TABLE 4. THE REACTION OF **3** WITH ALKYL HALIDES

2-Methoxy-alkyl sulfide	RX	Product	(Yield/%)
1a	CH ₃ (CH ₂) ₇ I	10a-1	(77)
1e	CH ₃ I	10e-1	(76)
1e	CH ₃ (CH ₂) ₇ I	10e-2	(64)
1e	PhCH ₂ Br	10e-3	(34)
1f	CH ₃ I	10f-1	(92) ^{a)}
1f	CH ₃ (CH ₂) ₇ I	10f-2	(82)
1f	PhCH ₂ Br	10f-3	(32)
1f	CH ₂ =CHCH ₂ Br	10f-4	(43)
1f	(CH ₃) ₃ SiCl	10f-5	(84)
1g	CH ₃ I	10g-1	(84)
1g	CH ₃ CH ₂ I	10g-2	(85)
1g	CH ₃ (CH ₂) ₇ I	10g-3	(67)
1g	PhCH ₂ Br	10g-4	(31)

a) The reaction was carried out at -50°C without HMPA.

The alkylation of 1-(phenylthio)vinyl lithium (**3**) was also examined. When **3f** was allowed to react with octyl iodide at -30°C , the alkylated product (**10f-2**) was isolated only in 15% yield. On the other hand, **10f-2** was obtained in 67% yield by the reaction carried out at -78°C . Furthermore, it was found that the yield of **10f-2** increased by the use of hexamethylphosphoric triamide (HMPA) as an additive. Accordingly, the reactions of **3** with various alkyl halides were performed in the presence of HMPA (Table 4).

When primary alkyl halides were employed, the corresponding 1-alkyl-1-alkenyl sulfides (**10**) were produced in good yields. On the other hand, the reactions with benzyl bromide or allyl bromide resulted in the formation of **10** only in moderate yields. The coupl-

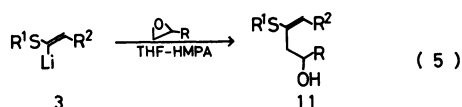
TABLE 5. THE REACTION OF **3** WITH OXIRANES

2-Methoxy-alkyl sulfide	Oxirane R	Product	(Yield/%)
1a	Ph	11a-1	(27) ^{a)}
1a	Ph	11a-1	(74)
1f	Ph	11f-1	(72)
1f	CH ₃ CH ₂	11f-2	(64)
1g	Ph	11g-1	(58)
1g	CH ₃ CH ₂	11g-2	(54)

a) The reaction was carried out without HMPA.

ing reactions of halides appeared to reduce the yield of **10**. Finally, it should be pointed out that the reaction of **3** with *s*-alkyl halide, such as isopropyl iodide or *s*-butyl bromide, gave no alkylated product.

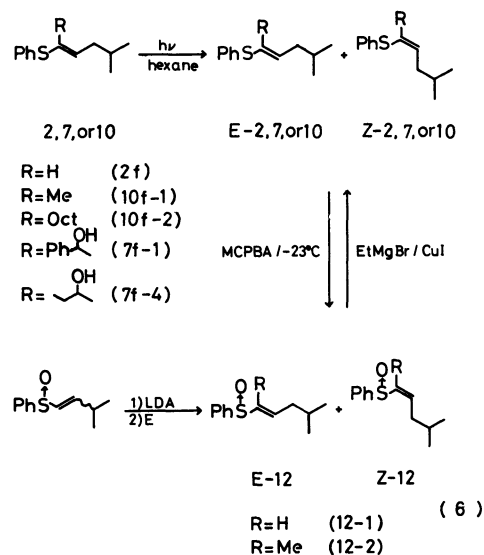
The reaction of **3** with oxiranes also took place smoothly and γ -alkylthio γ,δ -unsaturated alcohols (**11**) were obtained in good yields (Table 5). In this reaction, the addition of HMPA markedly increased the yield of **11** as well.



The first step of the present preparation of **3** may be the formation of alkenyl sulfide (**2**). In fact, the corresponding alkenyl sulfide (**2**) were isolated in high yields (**2e**; 90%, **2f**; 95%, **2g**; 85%) when 2-methoxyalkyl sulfides (**1**) were treated with an equimolar amount of butyllithium in the presence of TMEDA. The NMR spectra of the isolated alkenyl sulfides (**2**) suggested that they were *E*-isomers. In order to check the stereochemical purity of the resultant **2g**, we synthesized the authentic (*Z*)-**2f** by the following procedures. The alkenyl sulfide (**2f**) prepared by the present reaction was photoisomerized by the irradiation with high pressure mercury lamp to yield a mixture of (*Z*)- and (*E*)-**2f**. Although the separation of stereoisomers of **2f** was unsuccessful, the corresponding sulfoxides (**12-1**) were separated by TLC. The oxidation of **2f** was carried out by the treatment with *m*-chloroperbenzoic acid (MCPBA) in CH₂Cl₂ at -23 °C. The stereochemically pure alkenyl sulfoxides ((*E*)- and (*Z*)-**12-1**) were reduced with ethylmagnesium bromide in the presence of CuI⁸⁾ to give the authentic (*E*)- and (*Z*)-**2f**. The examination of the ¹H NMR spectra of these alkenyl sulfides showed that **2f** of the *E*-configuration was produced stereoselectively by the reaction of **1f** with butyllithium. Further, it was confirmed that **12-1** prepared by the oxidation of **2f** without photolysis contained no *Z*-isomer by its NMR spectrum.

Since alkenyl anions generally exhibit very high degree of retention of configuration,⁹⁾ we expected that the present reactions gave the 1-substituted alkenyl sulfides (**7**, **10**, and **11**) stereoselectively. Actually, the obtained alkenyl sulfides seemed to be pure *E*-isomers on the basis of their NMR spectra. In order to determine the configuration of alkenyl sulfides, we prepared sev-

eral authentic *E*-alkenyl sulfides ((*E*)-**7f-1**, (*E*)-**7f-4**, (*E*)-**10f-1**, and (*E*)-**10f-2**) from the alkenyl sulfoxide (**12-1**) by the method reported by Takei *et al.*¹⁰⁾ The NMR spectra of the authentic alkenyl sulfides were identical with those of the alkenyl sulfides obtained by the present reactions. Further, we concluded that the alkenyl sulfides (**7f-1**, **7f-4**, **10f-1**, and **10f-2**) contained no *Z*-isomer on the basis of the following experimental results. The alkenyl sulfides (**7f-1**, **7f-4**, **10f-1**, and **10f-2**) prepared by the reaction of **3f** with electrophiles were irradiated with high pressure mercury lamp to give the mixtures of two stereoisomers. The two isomers were separated each other by TLC with exception of **7f-4**. The structures of the stereoisomers produced by the photolysis were determined to be *Z*-alkenyl sulfides by the comparison of their IR and NMR spectra with those of the authentic *E*-isomers. It was confirmed that NMR signals characteristic to the *Z*-isomers were absent in the NMR spectra of the starting alkenyl sulfides. (*E*)- and (*Z*)-**10f-1** obtained by the above-mentioned procedure were oxidized with MCPBA to the corresponding sulfoxides (**12-2**). The NMR signal of vinyl proton of (*E*)-**12-2** appeared at $\delta=6.40$ and that of (*Z*)-**12-2** appeared at $\delta=5.94$. On the other hand, the NMR spectrum of the sulfoxide derived from **10f-1** without photolysis showed only one signal for the vinyl proton at $\delta=6.40$.



In conclusion, it is demonstrated that various alkenyl sulfides with β -substituents were easily synthesized in good to high yields by the use of 1-(methylthio- and phenylthio)vinyl lithium reagents (**3**) prepared by the treatment of 2-methoxyalkyl sulfides (**1**) with two molar butyllithium in the presence of TMEDA and the reactions of **3** with some electrophiles proceeded stereoselectively to give the *E*-isomers in all cases examined. The present method for the preparation of **3** would extend the applicability of α -lithiated alkenyl sulfides in organic synthesis.

Experimental

Measurements.

The boiling points and melting point

were uncorrected. NMR spectra were recorded with JEOL JNM-C-60HL spectrometer. IR spectra were measured with a JASCO DS-403G spectrometer.

2-Methoxyalkyl Sulfide (1). Phenyl (or methyl) 2-methoxyalkyl sulfides (**1b**, **c**, **d**, **e**, **f**, and **g**) were synthesized by the methylation (MeI/NaH/THF) of the corresponding 2-hydroxyalkyl sulfides prepared from aldehydes by the methods reported by Corey and Seebach,¹¹ and Peterson.¹² The boiling points, spectral data, and overall yields from aldehydes were as follows: 2-Methoxy-4-phenylbutyl methyl sulfide (**1b**); 45%, 102–105 °C/1 Torr (1 Torr=133.322 Pa), IR (neat): 3040, 2920, 1603, 1496, 1455, 1100, 744, and 700 cm⁻¹. ¹H NMR (CCl₄): δ =1.59–2.11 (2H, m), 2.02 (3H, s), 2.38–2.80 (4H, m), 3.03–3.37 (1H, m), 3.27 (3H, s), and 7.08 (5H, s). 2-Methoxy-4-methylpentyl methyl sulfide (**1c**); 52%, 89–92 °C/30 Torr, IR (neat): 2960, 1467, 1368, and 1096 cm⁻¹. ¹H NMR (CCl₄): δ =0.92 (6H, d, *J*=6 Hz), 1.15–1.88 (3H, m), 2.10 (3H, s), 2.28–2.52 (2H, m), 2.98–3.34 (1H, m), and 3.31 (3H, s). 2-Methoxy-2-phenylethyl methyl sulfide (**1d**); 64%, 85–87 °C/2 Torr, IR (neat): 2900, 1602, 1495, 1455, 1105, 742, and 702 cm⁻¹. ¹H NMR (CCl₄): δ =1.98 (3H, s), 2.58 and 2.69 (2H, 2d, *J*=6 and 7 Hz), 3.18 (3H, s), 4.09 and 4.21 (1H, 2d, *J*=6 and 7 Hz), and 7.24 (5H, s). 2-Methoxy-4-phenylbutyl phenyl sulfide (**1e**); 84%, 150–152 °C/0.6 Torr, IR (neat): 3030, 2930, 1583, 1480, 1438, 1097, 1026, 737, and 695 cm⁻¹. ¹H NMR (CCl₄): δ =1.54–2.06 (2H, m), 2.38–3.33 (5H, m), 3.24 (3H, s) and 6.72–7.37 (10H, m). 2-Methoxy-4-methylpentyl phenyl sulfide (**1f**); 69%, 98 °C/0.7 Torr, IR (neat): 2960, 1586, 1481, 1438, 1027, 737, and 692 cm⁻¹. ¹H NMR (CCl₄): δ =0.89 (6H, d, *J*=6 Hz), 1.13–1.97 (3H, m), 2.67 and 2.94 (2H, 2d, *J*=8 and 5 Hz), 3.03–3.41 (1H, m), 3.23 (3H, s), and 6.86–7.41 (5H, m). 2-Methoxyheptyl phenyl sulfide (**1g**); 83%, 94 °C/0.2 Torr, IR (neat): 2940, 1586, 1481, 1439, 1097, 1026, 738, and 692 cm⁻¹. ¹H NMR (CCl₄): δ =0.60–1.73 (11H, m), 2.72–3.00 (2H, m), 3.12–3.36 (1H, m), 3.24 (3H, s), and 6.83–7.40 (5H, m). 2-Methoxyethyl methyl sulfide (**1a**) (70%, bp 129–131 °C, lit.¹³, 132 °C) was prepared by the alkylation of 2-mercaptoethanol.

Preparation of 1-(Alkylthio)vinylolithium (3). 1-(Methylthio)vinylolithium (**3a**): To a THF (5 ml) solution of **1a** (212 mg, 2 mmol) and TMEDA (511 mg, 4.4 mmol) was added dropwise a hexane solution of butyllithium (4.4 mmol) at –30 °C. After stirring for 1 h, the resultant pale yellow solution of **3a** was used for the subsequent reactions.

1-Methylthio-2-phenylvinylolithium (3d). To a THF (0.5 ml) solution of LDA prepared from diisopropylamine (101 mg, 1 mmol) and butyllithium (1 mmol) was added a THF (1 ml) solution of **1d** (182 mg, 1 mmol) at –30 °C. After stirring for 40 min, HMPA (0.6 ml) and an additional THF (0.5 ml) solution of LDA (diisopropylamine; 121 mg, 1.2 mmol, butyllithium; 1.2 mmol) were successively added to the reaction mixture at –60 °C and stirring was continued for 2.5 h. The resultant dark green solution of **3d** was used in the subsequent steps.

4-Phenyl-1-phenylthio-1-butenylolithium (3e). To a THF (1 ml) solution of TMEDA (244 mg, 2.1 mmol) were added a hexane solution of butyllithium (2.1 mmol) and a THF (1 ml) solution of 2-methoxy-4-phenylbutyl phenyl sulfide (**1e**) (272 mg, 1 mmol) successively at –30 °C. After stirring for 2 h, the reddish purple solution of **3e** was obtained. By a similar procedure, the THF solutions of other vinylolithiums (**3b** and **c**; 0 °C, 30 min, **3f** and **g**; –23 °C, 3 h) were prepared.

The Reaction of 1-(Methylthio)vinylolithium (3a) with Benzaldehyde. To a THF solution of **3a** prepared from **1a** (212 mg, 2 mmol) by the above-mentioned procedure was added a THF (2 ml) solution of benzaldehyde (233 mg, 2.2 mmol) at –30 °C and the reaction mixture was allowed to

warm up to r.t. The reaction was quenched by the addition of a phosphate buffer solution (pH 7). The organic material was extracted with AcOEt and dried over Na₂SO₄. The extract was condensed under reduced pressure. The residue was chromatographed on silica gel (AcOEt–hexane) and 2-methylthio-1-phenyl-2-propen-1-ol (**7a-1**) was isolated (289 mg) in 80% yield. **7a-1**; a viscous oil. IR (neat): 3420, 1602, 1494, 1040, 861, 755, and 702 cm⁻¹. ¹H NMR (CCl₄): δ =2.12 (3H, s), 2.54 (1H, br s), 4.70 (1H, s), 5.08 (1H, s), 5.31 (1H, s), and 7.21 (5H, s). Found: C, 66.50; H, 6.70; S, 17.61%. Calcd for C₁₀H₁₂OS: C, 66.62; H, 6.71; S, 17.79%.

In a similar manner, the following β -alkylthio β,γ -unsaturated alcohols (**7**) and 2-hydroxyalkyl vinyl sulfide (**9**) were obtained. 2-Methylthio-5-phenyl-1-penten-3-ol (**7a-2**); a viscous oil. IR (neat): 3420, 1604, 1497, 1047, 861, 754, and 704 cm⁻¹. ¹H NMR (CCl₄): δ =1.63–2.10 (3H, m), 2.17 (3H, s), 2.44–2.89 (2H, m), 3.84–4.26 (1H, m), 4.56 (1H, s), 5.20 (1H, s), and 7.08 (5H, s). Found: C, 69.23; H, 7.77; S, 15.19%. Calcd for C₁₂H₁₆OS: C, 69.19; H, 7.74; S, 15.39%. 2-Methylthio-5-phenyl-1,4-pentadien-3-ol (**7a-3**); a viscous oil. IR (neat): 3410, 1601, 1497, 1030, 967, 863, 757, and 698 cm⁻¹. ¹H NMR (CCl₄): 2.18 (3H, s), 2.18–2.40 (1H, br s), 4.47 (1H, s), 4.47–4.83 (1H, br s), 5.31 (1H, s), 6.06 (1H, dd, *J*=16 and 6 Hz), 6.57 (1H, d, *J*=16 Hz), and 6.97–7.42 (10H, m). Found: C, 69.64; H, 6.84; S, 15.29%. Calcd for C₁₂H₁₄OS: C, 69.86; H, 6.84; S, 15.54%. 2-Methylthio-1-penten-3-ol (**7a-4**); a viscous oil. IR (neat): 3420, 1602, 1100, 983, and 859 cm⁻¹. ¹H NMR (CCl₄): δ =0.70–1.11 (3H, m), 1.36–1.80 (2H, m), 2.02–2.15 (1H, m), 2.20 (3H, s), 3.98 (1H, t, *J*=6 Hz), 4.67 (1H, s), and 5.20 (1H, s). Found: C, 54.39; H, 9.17; S, 24.11%. Calcd for C₆H₁₂OS: C, 54.51; H, 9.14; S, 24.25%. 5-Methyl-2-methylthio-1-hexen-3-ol (**7a-5**); a viscous oil. IR (neat): 3400, 2960, 1600, 1063, and 855 cm⁻¹. ¹H NMR (CCl₄): δ =0.94 (6H, d, *J*=6 Hz), 1.27–1.93 (3H, m), 1.93–2.15 (1H, m), 2.19 (3H, s), 4.11 (1H, t, *J*=6 Hz), 4.53 (1H, s), and 5.21 (1H, s). Found: C, 59.57; H, 10.09; S, 19.64%. Calcd for C₈H₁₆OS: C, 59.96; H, 10.06; S, 20.00%. 3-Methylthio-1-phenyl-3-buten-2-ol (**7a-6**); a viscous oil. IR (neat): 3450, 1597, 1496, 1070, 864, 718, and 701 cm⁻¹. ¹H NMR (CCl₄): δ =1.69 (3H, s), 2.13 (3H, s), 2.31 (1H, s), 4.78 (1H, s), 5.39 (1H, s), and 7.01–7.54 (5H, m). Found: C, 67.90; H, 7.30; S, 16.26%. Calcd for C₁₁H₁₄OS: C, 68.00; H, 7.26; S, 16.50%. 1-(4-Methyl-1-methylthio-2-pentenyl)-1-cyclohexanol (**7c-1**); a viscous oil. IR (neat): 3460, 2940, 1605, 1447, 1060, 982, and 913 cm⁻¹. ¹H NMR (CCl₄): δ =0.94 (6H, d, *J*=6 Hz), 1.14–2.14 (12H, m), 2.15 (3H, s), 2.14–2.60 (2H, m), and 5.18 (1H, t, *J*=7 Hz). Found: C, 67.97; H, 10.51; S, 13.66%. Calcd for C₁₃H₂₄OS: C, 68.37; H, 10.59; S, 14.04%. 1-[(4-Methyl-1-pentenylthio)methyl]-1-cyclohexanol (**9**); a viscous oil. IR (neat): 3450, 2940, 1613, 1448, 1056, 978, and 948 cm⁻¹. ¹H NMR (CCl₄): δ =0.88 (6H, d, *J*=6 Hz), 1.10–2.26 (14H, m), 2.68 (2H, s), 5.58 (1H, dt, *J*=15 and 6 Hz), and 5.93 (1H, d, *J*=15 Hz). Found: C, 68.40; H, 10.70; S, 13.95%. Calcd for C₁₃H₂₄OS: C, 68.37; H, 10.59; S, 14.04%. 2-Methylthio-1,3-diphenyl-2-propen-1-ol (**7d-1**); mp 63–64 °C (hexane–benzene). IR (neat): 3400, 1599, 1494, 1030, 753, and 698 cm⁻¹. ¹H NMR (CCl₄): δ =2.10 (3H, s), 2.85–3.27 (1H, br s), 5.65–5.95 (1H, br s), 6.32 (1H, s), and 6.88–7.42 (10H, m). Found: C, 74.81; H, 6.29; S, 12.50%. Calcd for C₁₆H₁₆OS: C, 74.96; H, 6.29; S, 12.51%. 2-Methylthio-1,5-diphenyl-1-penten-3-ol (**7d-2**); a viscous oil. IR (neat): 3400, 1602, 1497, 1053, 787, 756, and 699 cm⁻¹. ¹H NMR (CCl₄): δ =1.61–2.14 (2H, m), 2.18 (3H, s), 2.31–2.82 (3H, m), 4.51–4.84 (1H, m), 6.05 (1H, s), and 7.07 (10H, s). Found: C, 76.19; H, 7.11; S, 10.51%. Calcd for C₁₈H₂₀OS: C, 76.01; H, 7.09; S, 11.27%. 2-Methylthio-1,5-diphenyl-1,4-pentadien-3-ol (**7d-3**); a viscous oil. IR (neat): 3400, 1599, 1495, 1068, 964, 784, 750, and 694 cm⁻¹. ¹H NMR (CCl₄): δ =1.94–2.17 (1H, br s), 2.32 (3H, s), 5.21–5.47 (1H, br s), 6.30 (1H, s), 6.13 (1H, dd, *J*=16 and 4 Hz), 6.61 (1H, d, *J*=16 Hz), and 6.77–7.46 (10H, m). Found: C, 75.97; H, 6.51;

S, 11.02%. Calcd for $C_{18}H_{18}OS$: C, 76.56; H, 6.42; S, 11.35%. 2-Methylthio-1-phenyl-1-penten-3-ol (**7d-4**); a viscous oil. IR (neat): 3390, 2950, 1598, 1493, 1028, 753, and 697 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.85$ (3H, t, $J=7\text{ Hz}$), 1.38–1.90 (2H, m), 2.25 (3H, s), 4.17–4.73 (1H, m), 6.10 (1H, s), and 7.13 (5H, s). Found: C, 69.08; H, 7.82; S, 14.90%. Calcd for $C_{12}H_{16}OS$: C, 69.19; H, 7.74; S, 15.39%. 5-Methyl-2-methylthio-1-phenyl-1-hexen-3-ol (**7d-5**); a viscous oil. IR (neat): 3380, 2950, 1600, 1029, 755, and 694 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.59$ –1.03 (6H, m), 1.13–1.84 (3H, m), 1.97–2.22 (1H, br s), 2.25 (3H, s), 4.52–4.90 (1H, m), 6.09 (1H, s), and 7.16 (5H, s). Found: C, 71.15; H, 8.58; S, 13.15%. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; S, 13.56%. 1,5-Diphenyl-2-phenylthio-2-penten-1-ol (**7e-1**); a viscous oil. IR (neat): 3430, 3020, 1601, 1582, 1496, 1479, 1025, 743, and 698 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=2.19$ –2.97 (4H, m), 2.78 (1H, s), 5.52 (1H, s), 5.76 (1H, t, $J=7\text{ Hz}$), and 6.59–7.70 (15H, m). Found: C, 79.70; H, 6.33; S, 9.22%. Calcd for $C_{23}H_{22}OS$: C, 79.73; H, 6.40; S, 9.25%. 7-Phenyl-4-phenylthio-4-hepten-3-ol (**7e-2**); a viscous oil. IR (neat): 3420, 1602, 1582, 1496, 1478, 1086, 1024, 743, and 697 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.84$ (3H, t, $J=7\text{ Hz}$), 1.20–1.78 (3H, m), 2.26–2.83 (4H, m), 4.02–4.45 (1H, m), 5.74 (1H, t, $J=7\text{ Hz}$), and 6.97–7.38 (10H, m). Found: C, 76.38; H, 7.49; S, 10.52%. Calcd for $C_{19}H_{22}OS$: C, 76.47; H, 7.43; S, 10.74%. 2-Methyl-8-phenyl-5-phenylthio-5-octen-4-ol (**7e-3**); a viscous oil. IR (neat): 3420, 2960, 1603, 1583, 1497, 1480, 1068, 1026, 744, and 698 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.84$ and 0.88 (6H, 2d, $J=6$ and 7 Hz), 1.03–1.92 (4H, m), 2.33–2.86 (4H, m), 4.39 (1H, dd, $J=8$ and 5 Hz), 5.60 (1H, t, $J=8\text{ Hz}$), and 6.80–7.33 (10H, m). Found: C, 76.91; H, 8.15; S, 9.45%. Calcd for $C_{21}H_{26}OS$: C, 77.25; H, 8.03; S, 9.82%. 2,6-Diphenyl-3-phenylthio-3-hexen-2-ol (**7e-4**); a viscous oil. IR (neat): 3450, 1597, 1580, 1495, 1477, 1024, 743, and 696 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=1.64$ (3H, s), 2.08 (1H, s), 2.15–2.38 (4H, m), 5.64 (1H, t, $J=7\text{ Hz}$), and 6.58–7.48 (15H, m). Found: C, 79.94; H, 6.71; S, 8.77%. Calcd for $C_{24}H_{24}OS$: C, 79.96; H, 6.71; S, 8.89%. 5-Methyl-1-phenyl-2-phenylthio-2-hexen-1-ol (**7f-1**); a viscous oil. IR (neat): 3420, 2950, 1581, 1479, 1025, 740, and 697 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.91$ (6H, d, $J=7\text{ Hz}$), 1.17–1.92 (1H, m), 2.16 (2H, t, $J=8\text{ Hz}$), 2.59 (1H, d, $J=7\text{ Hz}$), 5.54 (1H, d, $J=7\text{ Hz}$), 5.79 (1H, t, $J=8\text{ Hz}$), and 6.70–7.37 (10H, m). Found: C, 76.60; H, 7.51; S, 10.51%. Calcd for $C_{19}H_{22}OS$: C, 76.47; H, 7.43; S, 10.74%. 7-Methyl-1-phenyl-4-phenylthio-4-octen-3-ol (**7f-2**); a viscous oil. IR (neat): 3420, 2950, 1601, 1581, 1497, 1478, 1024, 744, and 697 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.85$ (6H, d, $J=7\text{ Hz}$), 1.11–2.12 (6H, m), 2.60 (2H, t, $J=7\text{ Hz}$), 4.14–4.56 (1H, m), 5.69 (1H, t, $J=8\text{ Hz}$), and 6.77–7.38 (10H, m). Found: C, 77.01; H, 8.10; S, 9.52%. Calcd for $C_{21}H_{26}OS$: C, 77.25; H, 8.03; S, 9.82%. 7-Methyl-1-phenyl-4-phenylthio-1,4-octadien-3-ol (**7f-3**); a viscous oil. IR (neat): 3400, 2950, 1580, 1478, 1024, 966, 750, and 692 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.95$ (6H, d, $J=6\text{ Hz}$), 1.20–1.92 (1H, m), 2.19 (2H, t, $J=7\text{ Hz}$), 4.93–5.27 (1H, m), 5.88 (1H, t, $J=7\text{ Hz}$), 5.97 (1H, dd, $J=16$ and 5 Hz), 6.48 (1H, d, $J=16\text{ Hz}$), and 6.96–7.43 (10H, m). Found: C, 77.49; H, 7.47; S, 9.58%. Calcd for $C_{21}H_{24}OS$: C, 77.73; H, 7.46; S, 9.88%. 7-Methyl-4-phenylthio-4-octen-3-ol (**7f-4**); a viscous oil. IR (neat): 3420, 2960, 1582, 1480, 1024, 739, and 690 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.68$ –1.11 (3H, m), 0.91 (6H, d, $J=7\text{ Hz}$), 1.11–2.30 (6H, m), 4.18–4.66 (1H, m), 5.81 (1H, t, $J=8\text{ Hz}$), and 6.98–7.57 (5H, m). Found: C, 71.45; H, 8.77; S, 12.42%. Calcd for $C_{15}H_{22}OS$: C, 71.96; H, 8.85; S, 12.80%. 2,8-Dimethyl-5-phenylthio-5-nonen-4-ol (**7f-5**); a viscous oil. IR (neat): 3420, 2950, 1579, 1477, 1022, 736, and 687 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.93$ (12H, d, $J=7\text{ Hz}$), 1.16–2.25 (7H, m), 4.28–4.62 (1H, m), 5.69 (1H, t, $J=8\text{ Hz}$), and 6.89–7.41 (5H, m). Found: C, 73.38; H, 9.48; S, 11.14%. Calcd for $C_{17}H_{26}OS$: C, 73.33; H, 9.41; S, 11.51%. 1-(4-Methyl-1-phenylthio-1-pentenyl)-1-cyclohexanol (**7f-6**); a viscous oil. IR (neat): 3480, 2940, 2870, 1582, 1479, 1024, 738, and 690 cm^{-1} . $^1\text{H NMR}$

(CCl_4): $\delta=0.93$ (6H, d, $J=7\text{ Hz}$), 1.06–2.03 (12H, m), 2.39 (2H, t, $J=7\text{ Hz}$), 5.81 (1H, t, $J=7\text{ Hz}$), and 7.00–7.50 (5H, m). Found: 74.23; H, 8.98; S, 10.84%. Calcd for $C_{18}H_{26}OS$: C, 74.43; H, 9.02; S, 11.04%. 6-Methyl-2-phenyl-3-phenylthio-3-hepten-2-ol (**7f-7**); a viscous oil. IR (neat): 3450, 1598, 1580, 1495, 1478, 1066, 1024, 743, and 694 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.65$ and 0.70 (6H, 2d, $J=7\text{ Hz}$), 1.10–2.00 (3H, m), 1.70 (3H, s), 2.31 (1H, s), 5.70 (1H, t, $J=8\text{ Hz}$), and 6.84–7.51 (10H, m). Found: C, 76.86; H, 7.83; S, 10.09%. Calcd for $C_{20}H_{24}OS$: C, 76.88; H, 7.74; S, 10.26%. 1-Phenyl-2-phenylthio-2-octen-1-ol (**7g-1**); a viscous oil. IR (neat): 3400, 3020, 2880, 1575, 1470, 1430, 1015, 725, and 685 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.55$ –1.61 (9H, m), 1.96–2.50 (2H, m), 2.93 (1H, s), 5.61 (1H, s), 5.84 (1H, t, $J=7\text{ Hz}$), and 6.88–7.49 (10H, m). Found: C, 76.91; H, 7.84; S, 9.96%. Calcd for $C_{20}H_{24}OS$: C, 76.88; H, 7.74; S, 10.26%. 1-(1-Phenylthio-1-heptenyl)-1-cyclohexanol (**7g-2**); a viscous oil. IR (neat): 3490, 2930, 1584, 1482, 1432, 1028, 742, and 693 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.70$ –2.03 (20H, m), 2.25–2.73 (2H, m), 5.84 (1H, t, $J=7\text{ Hz}$), and 7.00–7.48 (5H, m). Found: C, 74.95; H, 9.42; S, 10.44%. Calcd for $C_{19}H_{28}OS$: C, 74.95; H, 9.27; S, 10.53%. 2-Phenyl-3-phenylthio-3-nonen-2-ol (**7g-3**); a viscous oil. IR (neat): 3460, 2920, 1598, 1580, 1493, 1478, 1439, 1024, 739, and 699 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.53$ –1.40 (9H, m), 1.68 (3H, s), 1.60–2.30 (2H, m), 2.56 (1H, s), 5.80 (1H, t, $J=7\text{ Hz}$) and 7.03–7.67 (10H, m). Found: C, 77.47; H, 8.13; S, 9.58%. Calcd for $C_{21}H_{26}OS$: C, 77.25; H, 8.03; S, 9.82%. The following α -methylthio ketones were obtained by the reaction of **3b** and **3c** with aldehydes followed by the isomerization by hydrochloric acid. 2-Methylthio-1,5-diphenyl-1-pentanone (**8b-1**); a viscous oil. IR (neat): 3020, 2920, 1673, 1498, 1449, 742, and 699 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=1.41$ –2.06 (4H, m), 1.81 (3H, s), 2.41–2.78 (2H, m), 3.94 (1H, t, $J=7\text{ Hz}$), 7.09 (5H, s), 7.17–7.48 (3H, m), and 7.67–8.02 (2H, m). Found: C, 76.04; H, 7.18; S, 11.18%. Calcd for $C_{18}H_{20}OS$: C, 76.01; H, 7.09; S, 11.27%. 4-Methylthio-1,7-diphenyl-3-heptanone (**8b-2**); a viscous oil. IR (neat): 3020, 2920, 1700, 1453, 746, and 697 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=1.30$ –1.87 (4H, m), 1.70 (3H, s), 2.27–3.12 (7H, m), and 7.12 (10H, s). Found: C, 76.49; H, 7.70; S, 10.07%. Calcd for $C_{20}H_{24}OS$: C, 76.88; H, 7.74; S, 10.26%. 4-Methylthio-7-phenyl-3-heptanone (**8b-3**); a viscous oil. IR (neat): 3020, 2940, 1703, 1453, 747, and 698 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=1.04$ (3H, t, $J=8\text{ Hz}$), 1.35–1.88 (4H, m), 1.82 (3H, s), 2.10–2.79 (4H, m), and 7.11 (5H, s). Found: C, 71.32; H, 8.61; S, 13.14%. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; S, 13.56%. 5-Methyl-2-methylthio-1-phenyl-1-hexanone (**8c-1**); a viscous oil. IR (neat): 3020, 2940, 1672, 1448, 739, and 695 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.92$ (6H, d, $J=6\text{ Hz}$), 1.03–2.13 (5H, m), 1.85 (3H, s), 3.92 (1H, t, $J=7\text{ Hz}$), 7.08–7.51 (3H, m), and 7.73–8.02 (2H, m). Found: C, 71.20; H, 8.55; S, 13.38%. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; S, 13.56%.

Reaction of 4-Phenyl-1-phenylthio-1-butenyllithium (3e) with Octyl Iodide. To a THF solution of **3e** prepared from **1e** (272 mg, 1 mmol) was added an HMPA (0.6 ml) solution of octyl iodide (360 mg, 1.5 mmol) at -78°C . After stirring for 30 min at -78°C , the reaction mixture was warmed up to r.t. The reaction was quenched by the addition of aqueous NH_4Cl . The usual work up gave 1-phenyl-4-phenylthio-3-dodecene (**10e-2**) (439 mg, 64%). **10e-2**; an oil. IR (neat): 2930, 1602, 1598, 1583, 1480, 1455, 1440, 1027, 742, and 699 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.60$ –1.67 (15H, m), 1.82–2.90 (6H, m), 5.77 (1H, t, $J=7\text{ Hz}$), and 7.17 (10H, s). Found: C, 81.55; H, 9.25; S, 8.90%. Calcd for $C_{24}H_{32}S$: C, 81.76; H, 9.15; S, 9.09%.

In a similar manner, the following alkenyl sulfides (**10**) were obtained. 2-Methylthio-1-decene (**10a-1**); an oil. IR (neat): 2920, 1710, 1598, and 840 cm^{-1} . $^1\text{H NMR}$ (CCl_4): $\delta=0.62$ –1.88 (15H, m),

1.92–2.40 (2H, m), 2.16 (3H, s), 4.50 (1H, s), and 4.94 (1H, s). Found: C, 70.92; H, 11.87; S, 16.80%. Calcd for $C_{11}H_{22}S$: C, 70.90; H, 11.90; S, 17.20%. 5-Phenyl-2-phenylthio-2-pentene (**10e-1**); an oil. IR (neat): 2920, 1601, 1582, 1496, 1478, 1453, 1439, 1026, 745, and 697 cm^{-1} . 1H NMR (CCl_4): δ =1.72 (3H, s), 2.08–2.85 (4H, m), 5.81 (1H, t, J =6 Hz), and 7.15 (10H, s). Found: C, 80.41; H, 7.26; S, 12.27%. Calcd for $C_{17}H_{18}S$: C, 80.27; H, 7.13; S, 12.60%. 1,5-Diphenyl-2-phenylthio-2-pentene (**10e-3**); an oil. IR (neat): 3020, 2920, 1600, 1582, 1497, 1476, 1453, 1438, 1024, 742, and 698 cm^{-1} . 1H NMR (CCl_4): δ =2.22–2.86 (4H, m), 3.36 (2H, s), 5.85 (1H, t, J =7 Hz), and 6.74–7.41 (15H, m). Found: C, 83.52; H, 6.80; S, 9.51%. Calcd for $C_{23}H_{22}S$: C, 83.59; H, 6.71; S, 9.70%. 5-Methyl-2-phenylthio-2-hexene (**10f-1**); an oil. IR (neat): 2950, 1581, 1476, 1437, 1023, 737, and 688 cm^{-1} . 1H NMR (CCl_4): δ =0.95 (6H, d, J =6 Hz), 1.07–2.43 (3H, m), 1.88 (3H, br s), 5.79 (1H, br t, J =7 Hz), and 7.21 (5H, s). Found: C, 75.81; H, 8.96; S, 15.36%. Calcd for $C_{13}H_{18}S$: C, 75.67; H, 8.79; S, 15.54%. 2-Methyl-5-phenylthio-4-tridecene (**10f-2**); an oil. IR (neat): 2920, 1582, 1479, 1467, 1439, 1025, 737, and 690 cm^{-1} . 1H NMR (CCl_4): δ =0.65–2.44 (20H, m), 0.93 (6H, d, J =6 Hz), 5.79 (1H, t, J =7 Hz), and 7.26 (5H, s). Found: C, 78.81; H, 10.65; S, 10.34%. Calcd for $C_{20}H_{32}S$: C, 78.88; H, 10.59; S, 10.53%. 5-Methyl-1-phenyl-2-phenylthio-2-hexene (**10f-3**); an oil. IR (neat): 2950, 1598, 1581, 1495, 1475, 1452, 1438, 1024, 740, and 695 cm^{-1} . 1H NMR (CCl_4): δ =0.93 (6H, d, J =6 Hz), 1.43–2.28 (3H, m), 3.47 (2H, s), 5.88 (1H, t, J =7 Hz), and 6.81–7.38 (10H, m). Found: C, 80.94; H, 7.98; S, 11.19%. Calcd for $C_{19}H_{22}S$: C, 80.80; H, 7.85; S, 11.35%. 7-Methyl-4-phenylthio-1,4-octadiene (**10f-4**); an oil. IR (neat): 2900, 1647, 1593, 1490, 1037, 922, 752, and 702 cm^{-1} . 1H NMR (CCl_4): δ =0.92 (6H, d, J =6 Hz), 1.43–2.25 (3H, m), 2.93 (2H, d, J =6 Hz), 4.76–5.22 (2H, m), 6.13–5.45 (2H, m), and 7.05–7.47 (5H, m). Found: C, 77.50; H, 8.80; S, 13.67%. Calcd for $C_{15}H_{20}S$: C, 77.52; H, 8.68; S, 13.80%. 4-Methyl-1-phenylthio-1-trimethylsilyl-1-pentene (**10f-5**); an oil. IR (neat): 2960, 1582, 1477, 1440, 1249, 841, 740, and 692 cm^{-1} . 1H NMR (CCl_4): δ =0.11 (9H, s), 0.93 (6H, d, J =6 Hz), 1.35–1.89 (1H, m), 2.16 (2H, t, J =7 Hz), 6.42 (1H, t, J =7 Hz), and 6.93–7.42 (5H, m). Found: C, 68.46; H, 9.21; S, 12.32%. Calcd for $C_{15}H_{24}SSi$: C, 68.11; H, 9.15; S, 12.12%. 2-Phenylthio-2-octene (**10g-1**); an oil. IR (neat): 2960, 1593, 1487, 1449, 1035, 750, and 701 cm^{-1} . 1H NMR (CCl_4): δ =0.60–1.72 (9H, m), 1.82–2.01 (3H, m), 2.01–2.60 (2H, m), 5.63–6.02 (1H, m), and 7.01–7.62 (5H, m). Found: C, 76.25; H, 9.25; S, 14.34%. Calcd for $C_{14}H_{20}S$: C, 76.30; H, 9.15; S, 14.55%. 3-Phenylthio-3-nonene (**10g-2**); an oil. IR (neat): 2980, 1593, 1489, 1474, 1449, 1036, 748, and 701 cm^{-1} . 1H NMR (CCl_4): δ =0.67–1.70 (9H, m), 1.04 (3H, t, J =7 Hz), 1.88–2.45 (4H, m), 5.81 (1H, t, J =7 Hz), and 6.92–7.53 (5H, m). Found: C, 76.83; H, 9.65; S, 13.39%. Calcd for $C_{15}H_{22}S$: C, 76.86; H, 9.46; S, 13.68%. 7-Phenylthio-6-pentadecene (**10g-3**); an oil. IR (neat): 2930, 1583, 1480, 1468, 1441, 1027, 762, 740, and 692 cm^{-1} . 1H NMR (CCl_4): δ =0.50–1.75 (24H, m), 1.85–2.48 (4H, m), 5.78 (1H, t, J =7 Hz), and 6.95–7.42 (5H, m). Found: C, 79.33; H, 10.81; S, 10.06%. Calcd for $C_{21}H_{34}S$: C, 79.18; H, 10.76; S, 10.06%. 1-Phenyl-2-phenylthio-2-octene (**10g-4**); an oil. IR (neat): 3030, 2930, 1600, 1582, 1498, 1476, 1453, 1440, 1026, 742, and 695 cm^{-1} . 1H NMR (CCl_4): δ =0.68–1.64 (9H, m), 1.96–2.48 (2H, m), 3.52 (2H, s), 5.93 (1H, t, J =7 Hz), and 7.16 and 7.25 (10H, 2s). Found: C, 81.07; H, 8.20; S, 10.76%. Calcd for $C_{20}H_{24}S$: C, 81.03; H, 8.16; S, 10.81%.

The Reaction of 1-Phenylthio-1-heptynyllithium (3g) with 1,2-Epoxybutane. To a THF solution of **3g** prepared from **1g** (477 mg, 2 mmol) was added an HMPA (0.6 ml) solution of

1,2-epoxybutane (216 mg, 3 mmol) at $-78^\circ C$. After stirring for 30 min, the reaction mixture was warmed up to r.t. The reaction was quenched by the addition of a phosphate buffer solution (pH 7). The usual work up gave 5-phenylthio-5-undecen-3-ol (**11g-2**) (301 mg, 54%). **11g-2**; a viscous oil. IR (neat): 3420, 3070, 2930, 1584, 1477, 1440, 1105, 744, and 692 cm^{-1} . 1H NMR (CCl_4): δ =0.62–1.70 (14H, m), 1.90–2.43 (5H, m), 3.53–3.90 (1H, m), 5.96 (1H, t, J =7 Hz), and 6.94–7.45 (5H, m). Found: C, 73.02; H, 9.43; S, 11.36%. Calcd for $C_{17}H_{26}OS$: C, 73.33; H, 9.41; S, 11.51%. In a similar manner, the following γ -phenylthio γ , δ -unsaturated alcohols (**11**) were obtained. 3-Methylthio-1-phenyl-3-buten-1-ol (**11a-1**); a viscous oil. IR (neat): 3400, 1600, 1582, 1053, 854, 757, and 700 cm^{-1} . 1H NMR (CCl_4): δ =2.16 (3H, s), 2.52 (2, d, J =6 Hz), 2.64–2.87 (1H, br s), 4.53 (1H, s), 4.80 (1H, t, J =6 Hz), 5.01 (1H, s), and 7.28 (5H, s). Found: C, 68.10; H, 7.20; S, 16.49%. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26; S, 16.50%. 6-Methyl-1-phenyl-3-phenylthio-3-hepten-1-ol (**11f-1**); a viscous oil. IR (neat): 3400, 1600, 1582, 1053, 854, 757, and 700 cm^{-1} . 1H NMR (CCl_4): δ =0.80 and 0.85 (6H, 2d, J =6 Hz), 1.24–2.09 (4H, m), 2.43 and 2.53 (2H, 2d, J =5 and 7 Hz), 4.90 (1H, dd, J =5 and 7 Hz), 5.94 (1H, t, J =7 Hz), and 6.93–7.45 (10H, m). Found: C, 76.86; H, 7.79; S, 10.14%. Calcd for $C_{20}H_{24}OS$: C, 76.88; H, 7.74; S, 10.26%. 8-Methyl-5-phenylthio-5-nonen-3-ol (**11f-2**); a viscous oil. IR (neat): 3390, 2950, 1584, 1480, 1072, 1028, 743, and 696 cm^{-1} . 1H NMR (CCl_4): δ =0.60–1.08 (3H, m), 0.93 (6H, d, J =6 Hz), 1.13–1.77 (3H, m), 1.86–2.63 (5H, m), 3.48–3.97 (1H, m), 5.96 (1H, t, J =7 Hz), and 7.29 (5H, s). Found: C, 72.46; H, 9.12; S, 12.15%. Calcd for $C_{16}H_{24}OS$: C, 72.68; H, 9.15; S, 12.12%. 1-Phenyl-3-phenylthio-3-nonen-1-ol (**11g-1**); a viscous oil. IR (neat): 3410, 3050, 3020, 2920, 1582, 1478, 1050, 1024, 742, and 699 cm^{-1} . 1H NMR (CCl_4): δ =0.66–1.53 (9H, m), 1.60–2.34 (3H, m), 2.46 and 2.56 (2H, 2d, J =5 and 8 Hz), 4.94 (1H, dd, J =5 and 8 Hz), 5.97 (1H, t, J =8 Hz), and 7.23 and 7.28 (10H, 2s). Found: C, 76.64; H, 8.02; S, 9.68%. Calcd for $C_{21}H_{26}OS$: C, 77.25; H, 8.03; S, 9.80%.

Preparation of (E)-4-Methyl-1-phenylthio-1-pentene (2f) and (Z)-2f. A hexane (4 ml) solution of **2f** (364 mg, 1.9 mmol) prepared by the reaction of **1f** with an equimolar amount of butyllithium was irradiated by high pressure mercury lamp (400 W) for 40 min. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 (6 ml) and was added to a CH_2Cl_2 (6 ml) solution of MCPBA (327 mg, 1.9 mmol) at $-23^\circ C$. The reaction mixture was stirred for 1 h. Then, the reaction was quenched by the addition of 5% aqueous $NaHCO_3$ and the crude sulfoxides were extracted with CH_2Cl_2 . The extract was dried over Na_2SO_4 and condensed under reduced pressure. The residue was chromatographed on silica gel (AcOEt–hexane) and (*E*)-4-methyl-1-phenylsulfanyl-1-pentene (**12-1**) (136 mg, 34%) and (*Z*)-**12-1** (96 mg, 24%) were obtained. The reduction of the sulfoxides were carried out by the method reported by Posner and Tang.⁸ To a suspension of CuI (37 mg, 0.19 mmol) in ether (0.7 ml) was added an ethereal solution of ethylmagnesium bromide (1.9 mmol) at $0^\circ C$. After stirring for 1 h, (*E*)-**12-1** (135 mg, 0.65 mmol) in ether (0.7 ml) was added to the solution and the reaction mixture was stirred for 1 h. The reaction was quenched by the addition of aqueous NH_4Cl and the organic substance was extracted with ether. The extract was dried over Na_2SO_4 and condensed under reduced pressure. The crude sulfide was purified by TLC (hexane) and (*E*)-**2f** (61 mg) was isolated in 49% yield. In a similar manner, (*Z*)-**2f** was also obtained by the reduction of (*Z*)-**12-1** in 33% yield. (*E*)-**12-1**; a viscous oil. IR (neat): 2950, 1623, 1580, 1466, 1444, 1086, 1047, 968, 746, and 690 cm^{-1} . 1H NMR (CCl_4): δ =0.90 (6H, d, J =6 Hz), 1.43–2.28 (3H, m), 6.18 (1H, d, J =15 Hz), 6.57 (1H, dt, J =15 and 7 Hz), and 7.37–7.82 (5H, m). (*Z*)-**12-1**; a viscous oil. IR (neat): 2950, 1614, 1580, 1465, 1443, 1083,

1040, 745, 715, and 690 cm^{-1} . ^1H NMR (CCl_4): $\delta=1.00$ (6H, d, $J=6$ Hz), 1.47–2.07 (1H, m), 2.36–2.68 (2H, m), 5.86–6.42 (2H, m), and 7.35–7.73 (5H, m). (*E*)-**2f**; an oil. IR (neat): 2950, 1582, 1480, 1440, 1080, 1025, 953, 738, and 689 cm^{-1} . ^1H NMR (CCl_4): $\delta=0.93$ (6H, d, $J=6$ Hz), 1.07–1.93 (1H, m), 1.93–2.20 (2H, m), 5.83 (1H, dt, $J=14$ and 6 Hz), 6.15 (1H, d, $J=14$ Hz), and 7.21 (5H, s). (*Z*)-**2f**; an oil. IR (neat): 2940, 1584, 1479, 1438, 1080, 1023, 762, 733, and 685 cm^{-1} . ^1H NMR (CCl_4): $\delta=0.97$ (6H, d, $J=6$ Hz), 1.37–2.02 (1H, m), 2.16 (2H, t, $J=7$ Hz), 5.77 (1H, dt, $J=10$ and 7 Hz), 6.20 (1H, d, $J=10$ Hz), and 7.23 (5H, s).

Photoisomerization of 5-Methyl-2-phenylthio-2-hexene (10f-1). A hexane (2.8 ml) solution of **10f-1** (305 mg, 1.47 mmol) was irradiated with high pressure mercury lamp (400 W) for 2 h. After evaporation of the solvent, the residue was chromatographed on silica gel (hexane) and (*E*)-**10f-1** (100 mg) and (*Z*)-**10f-1** (164 mg) were obtained in 33% and 54% yields, respectively. (*Z*)-**10f-1**; an oil. IR (neat): 2960, 1583, 1479, 1441, 1026, 739, and 690 cm^{-1} . ^1H NMR (CCl_4): $\delta=0.93$ (6H, d, $J=7$ Hz), 1.09–2.42 (3H, m), 1.86 (3H, br s), 5.83 (1H, br t, $J=7$ Hz), and 7.25 (5H, s). In a similar manner, the photoisomerization of **7f-1** (0.7 h, *E*; 16%, *Z*; 33%), **7f-4** (0.7 h, 78%, *E*:*Z*=40:60), and **10f-2** (2 h, *E*; 35%, *Z*; 38%) were carried out and the following *Z*-isomers were obtained. (*Z*)-5-Methyl-1-phenyl-2-phenylthio-2-hexene-1-ol (**7f-1**); a viscous oil. IR (neat): 3380, 2950, 1582, 1479, 1025, 740, and 698 cm^{-1} . ^1H NMR (CCl_4): $\delta=0.91$ (6H, d, $J=7$ Hz), 1.20–1.98 (1H, m), 2.26 (3H, br t, $J=7$ Hz), 5.08 (1H, br s), 6.33 (1H, t, $J=7$ Hz), 7.21 and 7.27 (10H, 2s) (*E* and *Z*)-7-methyl-4-phenylthio-4-octen-3-ol (**7f-4**); a viscous oil. IR (neat): 3400, 2960, 1583, 1480, 1024, 739, and 690 cm^{-1} . ^1H NMR (CCl_4): $\delta=0.91$ (6H, d, $J=7$ Hz), 0.68–1.12 (3H, m), 1.12–2.46 (6H, m), 3.99 and 4.44 (1H, 2t, $J=7$ Hz), 5.81 and 6.33 (1H, 2t, $J=7$ Hz), and 6.99–7.56 (5H, m). (*Z*)-2-Methyl-5-phenylthio-4-tridecene (**10f-2**); an oil. IR (neat): 2920, 1582, 1479, 1438, 1027, 739, and 690 cm^{-1} . ^1H NMR (CCl_4): $\delta=0.64$ –2.48 (20H, m), 0.93 (6H, d, $J=6$ Hz), 5.85 (1H, t, $J=7$ Hz), and 7.22 (5H, s).

Preparation of (Z)-5-Methyl-2-phenylsulfinyl-2-hexene (12-2). To a CH_2Cl_2 (3 ml) solution of MCPBA (134 mg, 0.78 mmol) was added a CH_2Cl_2 (3 ml) solution of (*Z*)-5-methyl-2-phenylthio-2-hexene (**10f-1**) (160 mg, 0.78 mmol) at -23°C . After stirring for 1 h, 5% aqueous NaHCO_3 was added to the reaction mixture and the usual work up gave (*Z*)-**12-2** (102 mg) in 59% yield. (*Z*)-**12-2**; a viscous oil. IR (neat): 2950, 1580, 1464, 1443, 1083, 1041, 748, and 693 cm^{-1} . ^1H NMR (CCl_4): $\delta=1.03$ (6H, d, $J=5$ Hz), 1.45–2.86 (3H, m), 1.64 (3H,

br s), 5.94 (1H, br t, $J=8$ Hz), and 7.49 (5H, m). In a similar manner, (*E*)-**12-2** was obtained by the oxidation of (*E*)-**10f-1**. (*E*)-5-Methyl-2-phenylsulfinyl-2-hexene (**12-2**) (55%); a viscous oil. IR (neat): 2950, 1580, 1466, 1443, 1086, 1043, 749, and 692 cm^{-1} . ^1H NMR (CCl_4): $\delta=0.97$ (6H, d, $J=5$ Hz), 1.16–2.28 (3H, m), 1.56 (3H, br s), 6.40 (1H, br t, $J=8$ Hz), and 7.25–7.72 (5H, m).

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