Bull. Chem. Soc. Jpn., *57, 1863—1869 (1984)*

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

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(Received August 6, 1983)

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]

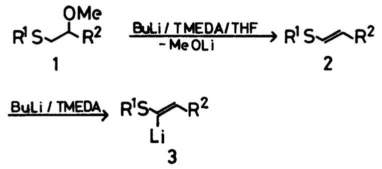
Since **3** is generally prepared by the treatment of alkenlyl sulfide (**2**) with strong base, such as *s*-butyllithium, *t*-butyllithium, or lithium diisopropylamide (LDA), the preparation of alkenyl sulfides (**2**) is required at the first step of the aforementioned synthesis. However, the synthesis 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 vinyllithium (**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.

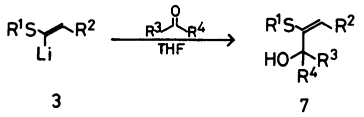
Results and Discussion

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 butyllitium at −30 °C or higher for 1 to 3 h in the presence of TMEDA. At −78 °C, the yield of **3a**



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

(1)



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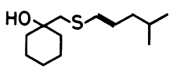

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Table 1. The reaction of **3** with benzaldehyde

Run	2-Methoxy-alkyl sulfide	Temp / °C	Time / h	Product	(Yield/%)
1	**1a**	−78	1	**7a-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_3CH_2	H	**7e-2** (64)
1a	$Ph(CH_2)_2$	H	**7a-2** (81)	**1e**	$(CH_3)_2CHCH_2$	H	**7e-3** (58)
1a	PhCH=CH	H	**7a-3** (88)	**1e**	Ph	CH_3	**7e-4** (44)
1a	CH_3CH_2	H	**7a-4** (65)	**1f**	Ph	H	**7f-1** (74)
1a	$(CH_3)_2CHCH_2$	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_3CH_2	H	**7f-4** (72)
1d	Ph	H	**7d-1** (55)	**1f**	$(CH_3)_2CHCH_2$	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_3CH_2	H	**7d-4** (28)	**1g**	Ph	H	**7g-1** (61)
1d	$(CH_3)_2CHCH_2$	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.

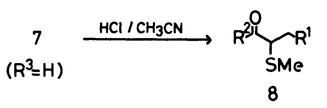

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Table 3. The reaction of **3b** and **3c** with aldehydes

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_3CH_2	**8b-3**	(27)
$(CH_3)_2CHCH_2$	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 methl 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 CH_3CN,[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.

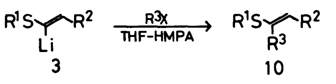

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Table 4. The reaction of **3** with alkyl halides

2-Methoxy-alkyl sulfide	RX	Product	(Yield/%)
1a	$CH_3(CH_2)_7I$	**10a-1**	(77)
1e	CH_3I	**10e-1**	(76)
1e	$CH_3(CH_2)_7I$	**10e-2**	(64)
1e	$PhCH_2Br$	**10e-3**	(34)
1f	CH_3I	**10f-1**	(92)[a]
1f	$CH_3(CH_2)_7I$	**10f-2**	(82)
1f	$PhCH_2Br$	**10f-3**	(32)
1f	$CH_2=CHCH_2Br$	**10f-4**	(43)
1f	$(CH_3)_3SiCl$	**10f-5**	(84)
1g	CH_3I	**10g-1**	(84)
1g	CH_3CH_2I	**10g-2**	(85)
1g	$CH_3(CH_2)_7I$	**10g-3**	(67)
1g	$PhCH_2Br$	**10g-4**	(31)

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

The alkylation of 1-(pheylthio)vinyllithium (**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-

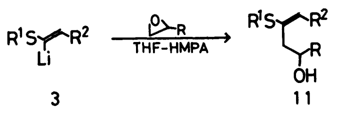
TABLE 5. THE REACTION OF **3** WITH OXIRANES

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_3CH_2	**11f-2**	(64)
1g	Ph	**11g-1**	(58)
1g	CH_3CH_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.

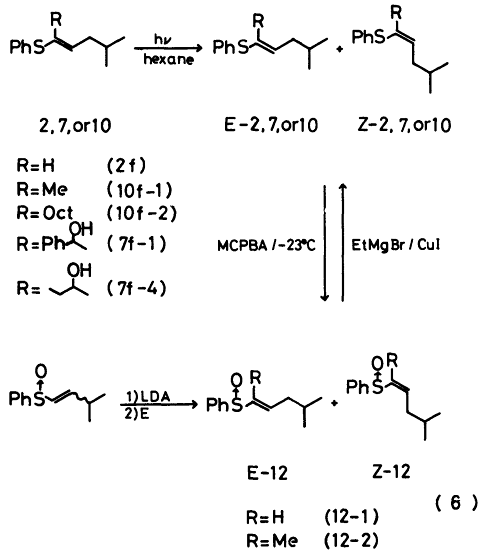
The reaction of **3** with oxiranes also took place smoothly and γ-alkylthio γ,δ-unsaturated alcohols (**11**) were obtained in good yields (Table 5). In this reaction, the addition of HMPA markedly increased the yield of **11** as well.



(5)

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 CH_2Cl_2 at −23 °C. The stereochemically pure alkenyl sulfoxides ((*E*)- and (*Z*)-**12-1**) were reduced with ethylmagnesium bromide in the presence of CuI[8] 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 several 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 δ=6.40 and that of (*Z*)-**12-2** appeared at δ=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 δ=6.40.



(6)

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)vinyllithium 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}. ^{1}H NMR (CCl_4): 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}. ^{1}H NMR (CCl_4): 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}. ^{1}H NMR (CCl_4): 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}. ^{1}H NMR (CCl_4): 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}. ^{1}H NMR (CCl_4): 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}. ^{1}H NMR (CCl_4): 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)vinyllithium (3). 1-(Methylthio)vinyllithium (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-phenylvinyllithium (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-butenyllithium (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 vinyllithiums (**3b** and **c**; 0 °C, 30 min, **3f** and **g**; −23 °C, 3 h) were prepared.

The Reaction of 1-(Methylthio)vinyllithium (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 Na_2SO_4. 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}. ^{1}H NMR (CCl_4): 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 $C_{10}H_{12}OS$: 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}. ^{1}H NMR (CCl_4): 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 $C_{12}H_{16}OS$: 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}. ^{1}H NMR (CCl_4): 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 $C_{12}H_{14}OS$: 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}. ^{1}H NMR (CCl_4): 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 $C_6H_{12}OS$: 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}. ^{1}H NMR (CCl_4): 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 $C_8H_{16}OS$: 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}. ^{1}H NMR (CCl_4): 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 $C_{11}H_{14}OS$: 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}. ^{1}H NMR (CCl_4): 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 $C_{13}H_{24}OS$: 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}. ^{1}H NMR (CCl_4): 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 $C_{13}H_{24}OS$: 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}. ^{1}H NMR (CCl_4): 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 $C_{16}H_{16}OS$: 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}. ^{1}H NMR (CCl_4): 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 $C_{18}H_{20}OS$: 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}. ^{1}H NMR (CCl_4): 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}H NMR (CCl_4): δ=0.85 (3H, t, J=7 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}H NMR (CCl_4): δ=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}H NMR (CCl_4): δ=2.19—2.97 (4H, m), 2.78 (1H, s), 5.52 (1H, s), 5.76 (1H, t, J=7 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}H NMR (CCl_4): δ=0.84 (3H, t, J=7 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 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}H NMR (CCl_4): δ=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 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}H NMR (CCl_4): δ=1.64 (3H, s), 2.08 (1H, s), 2.15—2.38 (4H, m), 5.64 (1H, t, J=7 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}H NMR (CCl_4): δ=0.91 (6H, d, J=7 Hz), 1.17—1.92 (1H, m), 2.16 (2H, t, J=8 Hz), 2.59 (1H, d, J=7 Hz), 5.54 (1H, d, J=7 Hz), 5.79 (1H, t, J=8 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}H NMR (CCl_4): δ=0.85 (6H, d, J=7 Hz), 1.11—2.12 (6H, m), 2.60 (2H, t, J=7 Hz), 4.14—4.56 (1H, m), 5.69 (1H, t, J=8 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}H NMR (CCl_4): δ=0.95 (6H, d, J=6 Hz), 1.20—1.92 (1H, m), 2.19 (2H, t, J=7 Hz), 4.93—5.27 (1H, m), 5.88 (1H, t, J=7 Hz), 5.97 (1H, dd, J=16 and 5 Hz), 6.48 (1H, d, J=16 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}H NMR (CCl_4): δ=0.68—1.11 (3H, m), 0.91 (6H, d, J=7 Hz), 1.11—2.30 (6H, m), 4.18—4.66 (1H, m), 5.81 (1H, t, J=8 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}H NMR (CCl_4): δ=0.93 (12H, d, J=7 Hz), 1.16—2.25 (7H, m), 4.28—4.62 (1H, m), 5.69 (1H, t, J=8 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}H NMR (CCl_4): δ=0.93 (6H, d, J=7 Hz), 1.06—2.03 (12H, m), 2.39 (2H, t, J=7 Hz), 5.81 (1H, t, J=7 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}H NMR (CCl_4): δ=0.65 and 0.70 (6H, 2d, J=7 Hz), 1.10—2.00 (3H, m), 1.70 (3H, s), 2.31 (1H, s), 5.70 (1H, t, J=8 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}H NMR (CCl_4): δ=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 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}H NMR (CCl_4): δ=0.70—2.03 (20H, m), 2.25—2.73 (2H, m), 5.84 (1H, t, J=7 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}H NMR (CCl_4): δ=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 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 followded 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}H NMR (CCl_4): δ=1.41—2.06 (4H, m), 1.81 (3H, s), 2.41—2.78 (2H, m), 3.94 (1H, t, J=7 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}H NMR (CCl_4): δ=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}H NMR (CCl_4): δ=1.04 (3H, t, J=8 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}H NMR (CCl_4): δ=0.92 (6H, d, J=6 Hz), 1.03—2.13 (5H, m), 1.85 (3H, s), 3.92 (1H, t, J=7 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}H NMR (CCl_4): δ=0.60—1.67 (15H, m), 1.82—2.90 (6H, m), 5.77 (1H, t, J=7 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}H NMR (CCl_4): δ=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**)[10]; an oil. IR (neat): 2920, 1601, 1582, 1496, 1478, 1453, 1439, 1026, 745, and 697 cm^{-1}. ^{1}H 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}. ^{1}H 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}. ^{1}H 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}. ^{1}H 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}. ^{1}H 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}. ^{1}H 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}. ^{1}H 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}. ^{1}H 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}. ^{1}H 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}. ^{1}H 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}. ^{1}H 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-heptenyllithium (**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 °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}. ^{1}H 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}. ^{1}H NMR (CCl_4): δ=2.16 (3H, s), 252 (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}. ^{1}H 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}. ^{1}H 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}. ^{1}H 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=8Hz), 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 °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-phenylsulfinyl-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 °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}. ^{1}H 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}. ^{1}H NMR (CCl_4): δ=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}. ^{1}H NMR (CCl_4): δ=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}. ^{1}H NMR (CCl_4): δ=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}. ^{1}H NMR (CCl_4): δ=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}. ^{1}H NMR (CCl_4): δ=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}. ^{1}H NMR (CCl_4): δ=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}. ^{1}H NMR (CCl_4): δ=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}. ^{1}H NMR (CCl_4): δ=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}. ^{1}H NMR (CCl_4): δ=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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