Reactions of 1,2-Propadienyl Sulfides with Aldehydes and Acetals Catalyzed by $BF_3 \cdot OEt_2$

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Ene reaction proceeds between 1-alkyl-1,2-propadienyl sulfides and aldehydes in the presence of $BF_3 \cdot OEt_2$ to afford 1,3-dienes possessing an alkylthio group. On the other hand, the reactions of 1-silyl-1,2-propadienyl sulfides with aldehydes or their dimethylacetals give aldol-type addition products, α-methylene acylsilanes.

In organic synthesis, allene compounds[1] have been used for the introduction of three carbon units. For example, various kinds of 1,2-propadienyl metals have been devised for the introduction of propargyl or 1,2-propadienyl groups.[2] 1,2-Propadienyl ethers are also used as a dienophile in intramolecular [4+2] cycloaddition[3] and 1,2-propadienyl silanes react with aldehydes and α,β-unsaturated ketones to give [3+2] cycloadducts.[4]

In the previous paper,[5] we have reported the Lewis acid-catalyzed [2+2] cycloaddition reactions between electron-deficient olefins and 1,2-propadienyl sulfides, while oxygen analogue, 1,2-propadienyl ether, fails to react under the same reaction conditions. These results indicate the reactivity of allenes is increased by the introduction of an alkylthio group.[6] 1,2-Propadienyl sulfides are expected to react with other electrophiles, and the reactions of 1,2-propadienyl sulfides with aldehydes or acetals were examined in the presence of Lewis acid, and the full details of these results are described in this paper.[7]

Results and Discussion

Reaction between 1-Alkyl-1,2-propadienyl Sulfides and Aldehydes. When a mixture of 3-methylthio-4-phenyl-1,2-butadiene (**1a**) and benzaldehyde was treated with Et_2AlCl at −78 °C in dichloromethane, ene reaction proceeded to give 2-methylene-3-methylthio-1,4-diphenyl-3-buten-1-ol (**2a**) in 34% yield (Table 1, Entry 1). After screening several Lewis acids, it was found that $BF_3 \cdot OEt_2$ catalyzes the reaction effectively, giving the 1,3-diene **2a** in 83% yield (Entry 3).

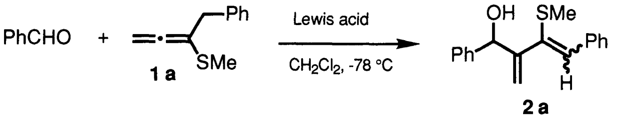
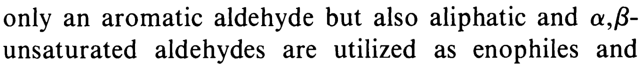


Table 1. Effect of Lewis Acid in the Ene Reaction of **1a**

Entry	Lewis acid	Yield/%
1	Et_2AlCl	34
2	$EtAlCl_2$	50
3	$BF_3 \cdot OEt_2$	83
4	$SnCl_4$	43
5	$TiCl_4$	0
6	$ZrCl_4$	48

On the other hand, when the alkoxy analogue of **1a**, 3-methoxy-4-phenyl-1,2-butadiene (**3**), was employed, no reaction proceeded with benzaldehyde. As expected, an alkylthio substituent effectively increases the reactivity of allene compounds as an ene component.[8] In fact, there is no precedent in which Lewis acid-catalyzed ene reaction proceeds at such low temperature except for the reactions using highly reactive aldehydes such as glyoxylate derivatives,[9] or polyhalogenated aldehydes.[10]



By employing $BF_3 \cdot OEt_2$ in dichloromethane, 1-alkyl-1,2-propadienyl sulfides **1a**—**c** reacted with various aldehydes and the results are shown in Table 2.

The present reaction has the wide generality both in aldehydes and 1,2-propadienyl sulfides. That is, not only an aromatic aldehyde but also aliphatic and α,β-unsaturated aldehydes are utilized as enophiles and various 1-alkyl-1,2-propadienyl sulfides can be employed as ene components to afford the corresponding 2-methylthio-1,3-butadienes. When 1,2-propadienyl sulfide **1a** was employed, *Z* isomers of the ene products were preferentially generated (Entries 1—4). 2-Methylthio-1,3-dienes bearing no substituent on the terminal positions, which are relatively unstable in acidic conditions, were prepared in good yields from **1c**, owing to the mild reaction conditions (Entries 10—13).

Allene derivatives have been used as an ene component only in the intramolecular ene reaction[11] or in the reaction with the reactive enophiles such as hexafluoroacetone and acetylene dicarboxylate.[12] The present study disclosed that the intermolecular ene reaction proceeds with various aldehydes by employing 1,2-propadienyl sulfides and synthetically useful 1,3-dienes possessing an alkylthio group[13] are prepared in good yields.

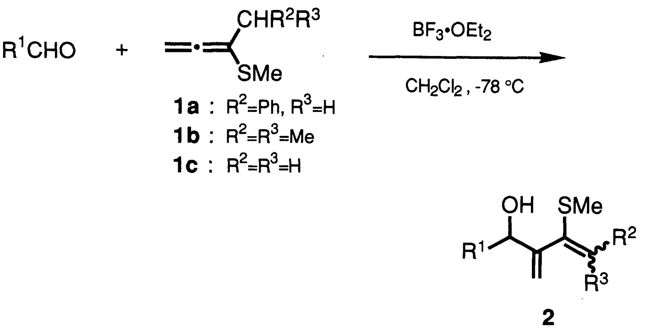


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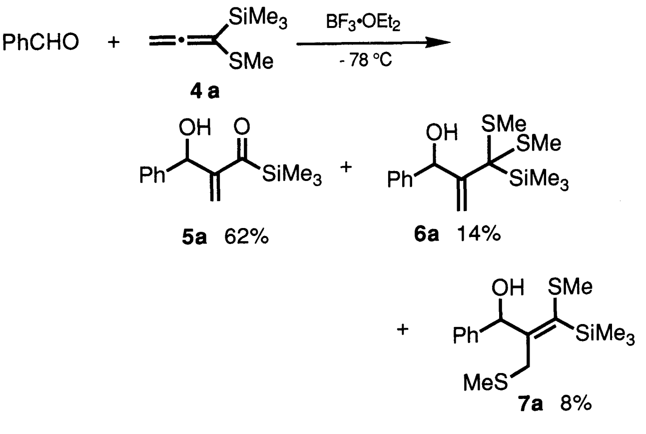
Table 2. The Ene Reaction between Aldehydes and 1,2-Propadienyl Sulfides

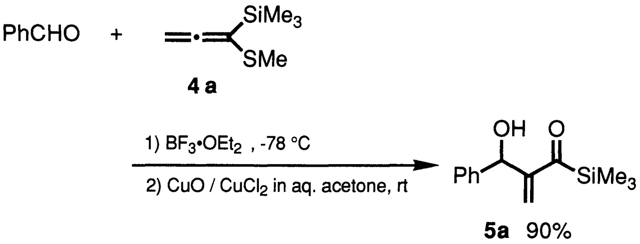
Entry	R¹	Allene	Yield/% (*Z*:*E*)
1	Ph	**1a**	83 (15:1) (**2a**)
2	PhCH$_2$CH$_2$	**1a**	73 (10:1) (**2b**)
3	Pr^i	**1a**	62 (6:1) (**2c**)
4	*cyclo*-C$_6$H$_{11}$	**1a**	67 (6:1) (**2d**)
5	Ph	**1b**	75 (**2e**)
6	PhCH$_2$CH$_2$	**1b**	88 (**2f**)
7	Pr^i	**1b**	83 (**2g**)
8	*cyclo*-C$_6$H$_{11}$	**1b**	68 (**2h**)
9	CH$_3$(CH$_2$)$_2$CH=CH	**1b**	64 (**2i**)
10	Ph	**1c**	80 (**2j**)
11	PhCH$_2$CH$_2$	**1c**	55 (**2k**)
12	Pr^i	**1c**	57 (**2l**)
13	*cyclo*-C$_6$H$_{11}$	**1c**	61 (**2m**)

Reaction between 1-Silyl-1,2-propadienyl Sulfides and Aldehydes or Acetals. The ene reaction proceeded between 1-alkyl-1,2-propadienyl sulfides and aldehydes, then, 1-silyl-1,2-propadienyl sulfide, which cannot act as an ene component, was submitted to the reaction with aldehydes.

When a mixture of benzaldehyde and 1-methylthio-1-trimethylsilyl-1,2-propadiene (**4a**) was treated with BF$_3$·OEt$_2$, the aldol-type addition reaction proceeded to afford an α-methylene acylsilane[14] **5a** in 62% yield along with the bis(methylthio) derivatives, **6a** and **7a**, in 14 and 8% yield, respectively.



The formation of these bis(methylthio) adducts **6a** and **7a** was due to the presence of methanethiol, which was generated in quenching the reaction. To scavenge methanethiol, the reaction was quenched with copper(II) chloride and copper(II) oxide in wet acetone.[15] As a result, the desired α-methylene acylsilane **5a** was obtained in good yield (90%) without the formation of **6a** and **7a**.



Both of aryl and aliphatic aldehydes provide the corresponding β-hydoxy-α-methylene acylsilanes in high yields without the formation of bis(methylthio) adducts **6** and **7** (Table 3, Entries 1—4). Only in the reaction of cinnamaldehyde, the yield was low because of the instability of the adduct **5e** under acidic conditions. By quenching the reaction with saturated aq NaHCO$_3$ solution, however, **5e** was obtained in moderate yield along with the formation of bis(methylthio) adducts (**6e** and **7e**).

Another notable feature of the present aldol-type reaction is as follows. Danheiser et al. reported the [3+2] cycloaddition between 1-alkyl-1,2-propadienylsilane (**8**) and aldehydes catalyzed by TiCl$_4$, where the γ-position of 1,2-propadienylsilane reacts with aldehydes

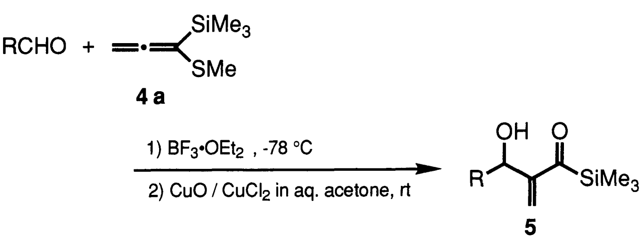
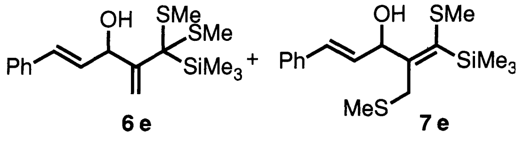


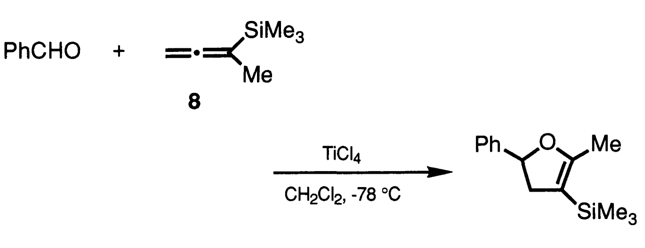
Table 3. The Reaction between Aldehydes and 1,2-Propadienyl Sulfides **4a**

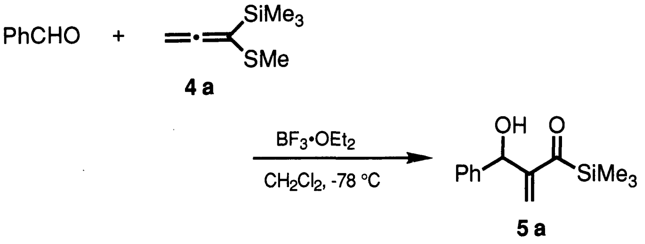
Entry	R	Temp/°C	Yield/%
1	Ph	−78	90 (**5a**)
2	PhCH$_2$CH$_2$	−45	77 (**5b**)
3	*n*-C$_9$H$_{19}$	−45	77 (**5c**)
4	*cyclo*-C$_6$H$_{11}$	−45	78 (**5d**)
5	PhCH=CH	−78	17 (**5e**)
6[a)]	PhCH=CH	−78	50 (**5e**)[16]

a) The reaction was quenched with saturated aq NaHCO$_3$ solution, and the following bis(methylthio) adducts **6e** and **7e** were also generated (18% in total).



to give dihydrofurans with 1,2-migration of silyl substituent.[4] But in the present reaction of the 1,2-propadienyl sulfide **4a**, no [3+2] cycloaddition product was obtained and β-hydroxy-α-methylene acylsilane **5a** was afforded in good yield.





Next, acetals[17] were submitted to the reaction with 1-silyl-1,2-propadienyl sulfides **4**. Various acetals reacted with 1-silyl-1,2-propadienyl sulfides in the presence of $BF_3 \cdot OEt_2$ (Table 4). The reactions of dimethylacetals of benzaldehyde and cinnamaldehyde gave the corresponding β-alkoxy-α-methylene acylsilanes (**9a,b**) in good yields accompanied with the formation of desilylated products (**10a,b**) (Entries 1, 2). By employing dimethylacetals of aliphatic aldehydes, the reaction of **4a** gave a complex mixture and the yields of acylsilanes were low (Entries 3, 4). On the contrary, when 1-*t*-butyldimethylsilyl-1-methylthio-1,2-propadiene (**4b**) having more bulky silyl group was employed, the yields of the reaction with dimethylacetals of aliphatic aldehydes were improved, and moreover, the formation of desilylated product was suppressed (Entries 5—7).

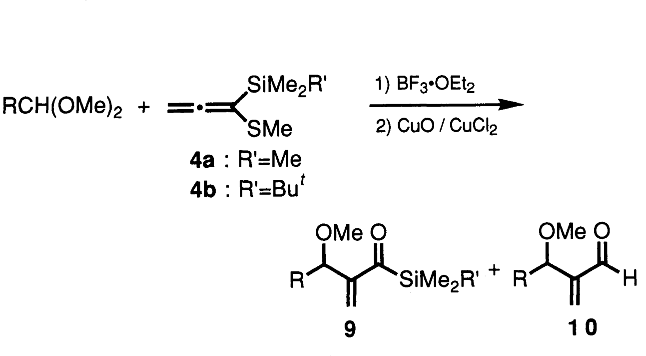


Table 4. The Reaction between Acetals with 1,2-Propadienyl Sulfide **4a**, **b**

Entry	R	Allene	Temp/°C	Yield/%
1	Ph	**4a**	−78	68 (**9a**) 16 (**10a**)
2	PhCH=CH	**4a**	−78	70 (**9b**) 16 (**10b**)
3	$PhCH_2CH_2$	**4a**	−45	<30 (**9c**)
4	*cyclo*-C_6H_{11}	**4a**	−45	<30 (**9d**)
5	Ph	**4b**	−78	81 (**9e**)
6	$PhCH_2CH_2$	**4b**	−45	62 (**9f**)
7	*cyclo*-C_6H_{11}	**4b**	−45	62 (**9g**)

This paper disclosed that ene and aldol-type addition reactions proceed between 1,2-propadienyl sulfides and aldehydes or acetals. In the case of 1-alkyl-1,2-propadienyl sulfides, ene reaction proceeds to provide 1,3-dienes possessing an alkylthio group (Table 2). 1-Trialkylsilyl-1,2-propadienyl sulfides react with aldehydes or their dimethylacetals to give various α-methylene acylsilanes (Tables 3 and 4). Thus, allene derivatives are employed effectively for carbon–carbon bond formation reactions by the introduction of an alkylthio group.

Experimental

General. ^{1}H NMR spectra (500 MHz) and ^{13}C NMR spectra (125 MHz) were measured with Bruker AM500 spectrometer, using tetramethylsilane as the internal standard. $CDCl_3$ was used as solvent. IR spectra were recorded with Horiba FT 300-S spectrophotometer. High-resolution mass spectra (HRMS) were obtained with JEOL JMS-D300 mass spectrometer at ionization energy of 70 eV.

Preparative thin-layer chromatography (TLC) was performed on a silica gel (Wakogel B-5F). Dichloromethane was distilled from P_2O_5, then from CaH_2, and dried over Molecular Sieves 4A (MS 4A). $BF_3 \cdot OEt_2$ was distilled from CaH_2. Copper(II) chloride and copper(II) oxide were reagent grade and were used without further purification. Aldehydes were used after distillation.

3-Methylthio-4-phenyl-1,2-butadiene (**1a**),[18] 4-methyl-3-methylthio-1,2-pentadiene (**1b**),[6] and 3-methylthio-1,2-butadiene (**1c**)[6] were prepared according to the literature procedures.

All the operations were carried out under an argon atmosphere.

Typical Procedure for the Ene Reaction between Aldehyde and 1,2-Propadienyl Sulfide 1. (Table 2). To a dichloromethane solution (3.0 ml) of aldehyde (0.40 mmol) and 1,2-propadienyl sulfide **1** (0.60 mmol) was added a dichloromethane solution (2.0 ml) of $BF_3 \cdot OEt_2$ (68.1 mg, 0.48 mmol) at −78 °C. After being stirred for 10 h, the reaction mixture was quenched with saturated aqueous sodium hydrogencarbonate. Organic materials were extracted with dichloromethane and the combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by TLC to afford the product.

Spectral data and physical properties of the ene products are as follows.

(*Z*)-2-Methylene-3-methylthio-1,4-diphenyl-3-buten-1-ol (2a-*Z*). IR (neat) 3434, 1598, 1444 cm^{-1}; ^{1}H NMR δ=2.12 (s, 3H), 2.37 (bs, 1H), 5.38 (s, 1H), 5.46 (s, 1H), 5.60 (s, 1H), 6.51 (s, 1H), 7.20—7.34 (m, 10H); ^{13}C NMR δ=16.3, 75.3, 115.3, 126.7, 127.2, 127.6, 127.9, 128.3, 129.4, 131.3, 136.3, 136.4, 141.7, 150.7. Anal. Calcd for $C_{18}H_{18}OS$: C, 76.56; H, 6.42; S, 11.35%. Found: C, 76.26; H, 6.41; S, 11.47%.

(*E*)-2-Methylene-3-methylthio-1,4-diphenyl-3-buten-1-ol (2a-*E*). Mp 75 °C; IR (KBr) 3419, 1592, 1446 cm^{-1}; ^{1}H NMR δ=2.13 (s, 3H), 2.20 (bs, 1H), 5.23 (s, 1H), 5.41 (d, 1H, *J*=1.2

Hz), 5.54 (d, 1H, J=1.2 Hz), 6.35 (s, 1H), 7.24—7.34 (m, 10H); ^{13}C NMR δ=15.6, 74.7, 117.9, 124.1, 126.6, 126.7, 127.7, 128.1, 128.2, 128.3, 136.9, 137.6, 141.4, 148.6. Anal. Calcd for $C_{18}H_{18}OS$: C, 76.56; H, 6.42; S, 11.35%. Found: C, 76.27; H, 6.42; S, 11.26%.

(*Z*)-4-Methylene-5-methylthio-1,6-diphenyl-5-hexen-3-ol (2b-*Z*). IR (neat) 3600, 1600, 1452 cm^{-1}; ^{1}H NMR δ=1.85—2.10 (m, 2H) 2.0 (bs, 1H), 2.15 (s, 3H), 2.70—2.88 (m, 2H), 4.52 (bs, 1H), 5.31 (d, 1H, J=1.1 Hz), 5.40 (dd, 1H, J=1.1, 1.1 Hz), 6.69 (s, 1H), 7.17—7.58 (m, 10H); ^{13}C NMR δ=16.5, 32.0, 37.6, 72.3, 114.4, 125.6, 127.3, 128.3, 128.4, 128.4, 129.5, 130.4, 136.2, 137.1, 141.6, 151.6. HRMS Found: m/z 310.1379. Calcd for $C_{20}H_{22}OS$: M, 310.1393.

(*E*)-4-Methylene-5-methylthio-1,6-diphenyl-5-hexen-3-ol (2b-*E*). IR (neat) 3598, 1596, 1448 cm^{-1}; ^{1}H NMR δ=1.72 (bs, 1H), 1.75—2.00 (m, 2H), 2.31 (s, 3H), 2.56—2.81 (m, 2H), 4.13 (bs, 1H), 5.43 (d, 1H, J=1.1 Hz), 5.60 (dd, 1H, J=1.1, 1.1 Hz), 6.21 (s, 1H), 7.12—7.34 (m, 10H); ^{13}C NMR δ=15.9, 31.9, 37.7, 72.2, 117.0, 122.3, 125.7, 126.7, 128.1, 128.3, 128.3, 128.4, 137.0, 138.1, 141.9, 149.9. HRMS Found: m/z 310.1379. Calcd for $C_{20}H_{22}OS$: M, 310.1393.

(*Z*)-2-Methyl-4-methylene-5-methylthio-6-phenyl-5-hexen-3-ol (2c-*Z*). IR (neat) 3608, 1600, 1448 cm^{-1}; ^{1}H NMR δ=0.88 (d, 3H, J=6.8 Hz), 1.02 (d, 3H, J=6.9 Hz), 1.83 (bs, 1H), 1.92—1.98 (m, 1H), 2.18 (s, 3H), 4.34 (bs, 1H), 5.33 (s, 1H), 5.34 (s, 1H), 6.70 (s, 1H), 7.22—7.57 (m, 5H); ^{13}C NMR δ=15.4, 16.5, 20.0, 31.4, 77.4, 114.9, 127.3, 128.0, 129.5, 130.3, 136.4, 137.6, 151.0. HRMS Found: m/z 248.1232. Calcd for $C_{15}H_{20}OS$: M, 248.1236.

(*E*)-2-Methyl-4-methylene-5-methylthio-6-phenyl-5-hexen-3-ol (2c-*E*). IR (neat) 3604, 1599, 1454 cm^{-1}; ^{1}H NMR δ=0.82 (d, 3H, J=6.8 Hz), 0.89 (d, 3H, J=6.8 Hz), 1.45 (bs, 1H), 1.81—1.90 (m, 1H), 2.34 (s, 3H), 3.93 (bs, 1H), 5.51 (s, 1H), 5.56 (s, 1H), 6.11 (s, 1H), 7.14—7.49 (m, 5H). HRMS Found: m/z 248.1212. Calcd for $C_{15}H_{20}OS$: M, 248.1236.

(*Z*)-1-Cyclohexyl-2-methylene-3-methylthio-4-phenyl-3-buten-1-ol (2d-*Z*). IR (neat) 3452, 1599, 1442 cm^{-1}; ^{1}H NMR δ=0.99—1.76 (m, 11H), 1.93 (bs, 1H), 2.16 (s, 3H), 4.30 (d, 1H, J=4.4 Hz), 5.30 (d, 1H, J=1.4 Hz), 5.32 (d, 1H, J=1.4 Hz), 6.68 (s, 1H), 7.16—7.57 (m, 5H); ^{13}C NMR δ=16.4, 26.1, 26.1, 26.3, 26.4, 30.4, 41.4, 77.1, 115.0, 127.2, 127.9, 129.5, 130.2, 136.4, 137.6, 150.6. HRMS Found: m/z 288.1559. Calcd for $C_{18}H_{24}OS$: M, 288.1549.

(*E*)-1-Cyclohexyl-2-methylene-3-methylthio-4-phenyl-3-buten-1-ol (2d-*E*). IR (neat) 3489, 1593, 1446 cm^{-1}; ^{1}H NMR δ=0.86—1.77 (m, 12H), 2.33 (s, 3H), 3.90 (d, 1H J=2.5 Hz), 5.48 (s, 1H), 5.51 (s, 1H), 6.11 (s, 1H), 7.14—7.56 (m, 5H); ^{13}C NMR δ=15.9, 25.8, 26.0, 26.4, 26.5, 30.7, 41.4, 76.9, 117.8, 121.1, 126.6, 128.0, 128.3, 136.8, 137.2, 146.8. HRMS Found: m/z 288.1552. Calcd for $C_{18}H_{24}OS$: M, 288.1549.

4-Methyl-2-methylene-3-methylthio-1-phenyl-3-penten-1-ol (2e). IR (neat) 3432, 1635, 1444 cm^{-1}; ^{1}H NMR δ=1.36 (s, 3H), 1.86 (s, 3H), 2.08 (s, 3H), 2.80 (bs, 1H), 4.82 (d, 1H, J=1.7 Hz), 5.40 (d 1H J=1.7 Hz), 5.44 (s, 1H), 7.22—7.35 (m, 5H); ^{13}C NMR δ=16.4, 21.7, 22.1, 75.7, 115.2, 126.5, 126.8, 127.4, 128.0, 137.6, 141.7, 147.5. HRMS Found: m/z 234.1086. Calcd for $C_{14}H_{18}OS$: M, 234.1079.

6-Methyl-4-methylene-5-methylthio-1-phenyl-5-hepten-3-ol (2f). IR (neat) 3411, 1633, 1444 cm^{-1}; ^{1}H NMR δ=1.74—2.01 (m, 2H), 1.79 (s, 3H), 1.96 (s, 3H), 2.03 (s, 3H), 2.19 (d, 1H, J=4.8 Hz), 2.65—2.89 (m, 2H), 4.32—4.34 (m, 1H), 4.81 (d, 1H, J=1.8 Hz), 5.41 (dd, 1H, J=1.8, 1.8 Hz), 7.15—7.28 (m, 5H); ^{13}C NMR δ=16.5, 22.0, 23.0, 32.4, 37.5, 73.5, 115.0, 125.8, 127.7, 128.4, 128.5, 137.3, 142.2, 148.0. HRMS Found: m/z 262.1370. Calcd for $C_{16}H_{22}OS$: M, 262.1393.

2,6-Dimethyl-4-methylene-5-methylthio-5-hepten-3-ol (2g). IR (neat) 3475, 1623, 1459 cm^{-1}; ^{1}H NMR δ=0.88 (d, 3H, J=6.8 Hz), 0.98 (d, 3H, J=6.8 Hz), 1.76—1.85 (m, 1H), 1.80 (s, 3H), 1.89 (bs, 1H), 1.96 (s, 3H), 2.03 (s, 3H), 4.15—4.17 (m, 1H), 4.87 (d, 1H, J=1.8 Hz), 5.38 (dd, 1H, J=1.8, 1.8 Hz). Anal. Calcd for $C_{11}H_{20}OS$: C, 69.94; H, 10.06; S, 13.34%. Found: C, 69.83; H, 9.98; S, 13.16%.

1-Cyclohexyl-4-methyl-2-methylene-3-methylthio-3-penten-1-ol (2h). IR (neat) 3464, 1628, 1446 cm^{-1}; ^{1}H NMR δ=1.02—1.77 (m, 11H), 1.79 (s, 3H), 1.92 (d, 1H, J=4.3 Hz), 1.96 (s, 3H), 2.02 (s, 3H), 4.14 (bs, 1H), 4.86 (d, 1H, J=1.9 Hz), 5.33 (s, 1H). HRMS Found: m/z 240.1534. Calcd for $C_{14}H_{24}OS$: M, 240.1548.

2-Methyl-4-methylene-3-methylthio-2,6-decadien-5-ol (2i). IR (neat) 3428, 1668, 1635, 1438 cm^{-1}; ^{1}H NMR δ=0.84 (t, 3H, J=7.4 Hz), 1.35 (tq, 2H, J_t=7.2 Hz, J_q=7.4 Hz), 1.72 (s, 3H), 1.92 (s, 3H), 1.94—1.99 (m, 2H), 2.01 (s, 3H), 2.32 (bs, 1H), 4.72 (d, 1H, J=7.0 Hz), 4.77 (s, 1H), 5.38 (s, 1H), 5.43 (dd, 1H, J=7.0, 15.3 Hz), 5.65 (dt, 1H, J_d=15.3 Hz, J_t=7.2 Hz); ^{13}C NMR δ=13.6, 16.3, 21.7, 22.2, 22.6, 34.2, 74.7, 115.0, 127.5, 130.5, 132.5, 136.5, 147.2. HRMS Found: m/z 226.1396. Calcd for $C_{13}H_{22}OS$: M, 226.1393.

2-Methylene-3-methylthio-1-phenyl-3-buten-1-ol (2j). IR (neat) 3402, 1697, 1576, 1444 cm^{-1}; ^{1}H NMR δ=1.75 (bs, 1H), 2.16 (s, 3H), 4.82 (s, 1H), 5.19 (s, 1H), 5.43 (s, 1H), 5.52 (s, 1H), 5.58 (s, 1H), 7.20—7.40 (m, 5H). HRMS Found: m/z 206.0773. Calcd for $C_{12}H_{14}OS$: M, 206.0766.

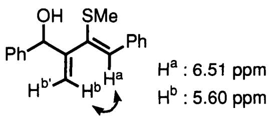
4-Methylene-5-methylthio-1-phenyl-5-hexen-3-ol (2k). IR (neat) 3411, 1726, 1676, 1444 cm^{-1}; ^{1}H NMR δ=1.85 (dddd, 1H, J=3.9, 5.1, 7.6, 10.0 Hz), 2.10 (dddd, 1H, J=3.9, 6.6, 7.6, 10.0 Hz), 1.98 (bs, 1H), 2.24 (s, 3H), 2.69 (ddd, 1H, J=6.6, 10.0, 13.8 Hz), 2.80 (ddd, 1H, J=5.1, 10.0, 13.8 Hz), 4.45 (dd, 1H, J=3.9, 7.6 Hz), 4.85 (s, 1H), 5.22 (s, 1H), 5.34 (s, 1H), 5.42 (s, 1H), 7.16—7.29 (m, 5H); ^{13}C NMR δ=15.1, 31.9, 37.5, 72.1, 107.5, 113.8, 125.7, 128.3, 128.4, 141.9, 144.6, 150.2. HRMS Found: m/z 234.1064. Calcd for $C_{14}H_{18}OS$: M, 234.1079.

2-Methyl-4-methylene-5-methylthio-5-hexen-3-ol (2l). IR (neat) 3457, 1703, 1628, 1442 cm^{-1}; ^{1}H NMR δ=0.83 (d, 3H, J=6.8 Hz), 0.92 (d, 3H, J=6.8 Hz), 1.82—1.91 (m, 1H), 1.84 (bs, 1H), 2.20 (s, 3H), 4.17 (bs 1H), 4.80 (s, 1H), 5.22 (s, 1H), 5.25 (s, 1H), 5.38 (s, 1H); ^{13}C NMR δ=15.1, 16.0, 19.8, 31.4, 77.9, 107.3, 114.5, 145.0, 149.5. HRMS Found: m/z 172.0951. Calcd for $C_9H_{16}OS$: M, 172.0923.

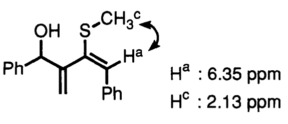
1-Cyclohexyl-2-methylene-3-methylthio-3-buten-1-ol (2m). IR (neat) 3431, 1674, 1620, 1444 cm^{-1}; ^{1}H NMR δ=0.92—1.77 (m, 12H), 2.22 (s, 3H), 4.15 (bs, 1H), 4.82 (s, 1H), 5.20 (s, 1H), 5.27 (s, 1H), 5.39 (s, 1H); ^{13}C NMR δ=15.2, 26.0, 26.3, 26.4, 26.8, 30.2, 41.3, 77.6, 107.6, 114.7, 144.9, 149.1. HRMS Found: m/z 212.1240. Calcd for $C_{12}H_{20}OS$: M, 212.1236.

Assignment of the Stereochemistry of the Ene Products 2a—d. The relative stereochemistry of the ene product **2a** was determined by the NOESY spectra. In the major isomer, the NOE was observed between H^a and H^b, as shown in the following figure and it was assigned as *Z* isomer. On the other hand, in the minor isomer, the NOE was observed between and H^a and H^c, and it was assigned as *E* isomer. The singlet signal of H^a proton appeared at 6.73 ppm in *Z* isomer and it appeared at 6.12 ppm in *E* isomer.

The relative stereochemistry of the other ene products **2b**—**d** was assigned from the chemical shift of the proton corresponding to H^a. The major isomer, where the singlet signal of H^a appeared at lower field, was determined to be *Z* isomer and the minor isomer, where it appeared at higher field, was assigned as *E* isomer.



the major isomer of **2a**
(assigned as *Z* isomer)



the minor isomer of **2a**
(assigned as *E* isomer)

Preparation of 1,2-Propadienyl Sulfides 4a and 4b. **4a** was prepared according to the literature procedures.[18] **4b** was prepared by the same method for the preparation of **4a** except that *t*-butyldimethylsilyl chloride was employed in place of trimethylsilyl chloride.

1-*t*-Butyldimethylsilyl-1-methylthio-1,2-propadiene (4b). To a THF solution (20 ml) of diisopropylamine (2.22 g, 21.9 mmol) was added BuLi (22.2 mmol, 1.62 M hexane solution, 1 M=1 mol dm^{-3}) dropwise at 0 °C and the mixture was stirred for 10 min. To this reaction mixture was added a THF solution (10 ml) of 1-methylthio-1-propyne (1.83 g, 21.2 mmol) at −78 °C, and after being stirred for 30 min, a THF solution (10 ml) of *t*-butyldimethylsilyl chloride (3.24 g, 21.5 mmol) was added. After being stirred at −78 °C for 1 h, then at 0 °C for 2 h, the reaction was quenched with pH 7 phosphate buffer, and the organic materials were extracted with Et_2O and the extracts were washed with brine and dried over Na_2SO_4. After evaporation of the solvent, the crude materials were purified by distillation. Yield 80%. Bp 62 °C/0.8 mmHg (1 mmHg=133.322 Pa). IR (neat) 1921, 1466, 833 cm^{-1}; ^{1}H NMR δ=0.12 (s, 6H), 0.96 (s, 9H), 2.16 (s, 3H), 4.89 (s, 2H); ^{13}C NMR δ=−6.1, 15.2, 18.0, 26.6, 75.6, 93.0, 204.8. HRMS Found: *m*/*z* 200.1068. Calcd for $C_{10}H_{20}SSi$: M, 200.1056.

Typical Procedure for the Aldol-Type Reaction between Aldehyde and 1,2-Propadienyl Sulfide 4a. (Table 3). To a dichloromethane solution (3.0 ml) of aldehyde (0.40 mmol) and 1,2-propadienyl sulfide **4a** (190.0—316.8 mg, 1.2—2.0 mmol) was added a dichloromethane solution (2.0 ml) of $BF_3 \cdot OEt_2$ (141.9 mg, 1.0 mmol) at the temperature indicated in Table 3. After being stirred for 8 h, the reaction mixture was poured into acetone–water (300/1) solution (10 ml) of copper(II) chloride (268.7 mg, 2.0 mmol) and copper(II) oxide (318.2 mg, 4.0 mmol) and stirred for 5 min, then water (10 ml) was added into the mixture. Inorganic materials were filtered off and organic materials were extracted with dichloromethane and the combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by TLC to provide the product.

Spectral data and physical properties of the products are as follows.

3-Hydroxy-2-methylene-3-phenyl-1-trimethylsilyl-1-propanone (5a). Mp 34 °C; IR (neat) 3464, 1691, 1591 cm^{-1}; ^{1}H NMR δ=0.23 (s, 9H), 3.12 (bs, 1H), 5.52 (s, 1H), 6.10 (s, 1H), 6.63 (s, 1H), 7.22—7.40 (m, 5H); ^{13}C NMR δ=−1.5, 72.5, 126.5, 127.6, 128.3, 129.1, 141.4, 154.1, 239.5. Anal. Calcd for $C_{13}H_{18}O_2Si$: C, 66.62; H, 7.74%. Found: C, 66.53; H, 7.74%.

3-Hydroxy-2-methylene-5-phenyl-1-trimethylsilyl-1-pentanone (5b). IR (neat) 3462, 1687, 1595 cm^{-1}; ^{1}H NMR δ=0.26 (s, 9H), 1.85—2.02 (m, 2H), 2.62—2.87 (m, 2H), 2.69 (bs, 1H), 4.38 (bs, 1H), 6.07 (s, 1H), 6.19 (d, 1H, *J*=0.8 Hz), 7.15—7.27 (m, 5H). HRMS Found: *m*/*z* 262.1339. Calcd for $C_{15}H_{22}O_2Si$: M, 262.1390.

3-Cyclohexyl-3-hydroxy-2-methylene-1-trimethylsilyl-1-propanone (5c). IR (neat) 3448, 1689, 1595 cm^{-1}; ^{1}H NMR δ=0.25 (s, 9H), 0.89—1.74 (m, 11H), 1.88 (bs, 1H), 4.02 (d, 1H, *J*=6.9 Hz), 6.06 (s, 1H), 6.08 (s, 1H); ^{13}C NMR δ=−1.4, 25.9, 26.1, 26.4, 28.3, 30.0, 42.4, 129.4, 153.0, 240.2. HRMS Found: *m*/*z* 240.1559. Calcd for $C_{13}H_{24}O_2Si$: M, 240.1559.

3-Hydroxy-2-methylene-1-trimethylsilyl-1-dodecanone. (5d). IR (neat) 3442, 1689, 1594 cm^{-1}; ^{1}H NMR δ=0.26 (s, 9H), 0.85 (t, 3H, *J*=7.0 Hz), 1.23—1.54 (m, 17H), 4.34 (t, 1H, *J*=6.5 Hz), 6.05 (s, 1H), 6.16 (s, 1H); ^{13}C NMR δ=−1.4, 14.1, 22.7, 25.9, 29.2, 29.4, 29.5, 29.6, 31.9, 36.2, 71.2, 128.2, 154.6, 240.0. HRMS Found: *m*/*z* 284.2174. Calcd for $C_{16}H_{32}O_2Si$: M, 284.2173.

(*E*)-3-Hydroxy-2-methylene-5-phenyl-1-trimethylsilyl-4-penten-1-one (5e). IR (neat) 3433, 1707, 1595 cm^{-1}; ^{1}H NMR δ=0.28 (s, 9H), 3.05 (bs, 1H), 5.11—5.14 (m, 1H), 6.14 (s, 1H), 6.24 (dd, 1H, *J*=6.2, 15.7 Hz), 6.28 (d, 1H *J*=0.8 Hz), 6.61 (d, 1H, *J*=15.7 Hz), 7.20—7.36 (m, 5H); ^{13}C NMR δ=−1.4, 71.3, 126.5, 127.7, 128.6, 129.0, 129.4, 130.9, 136.6, 153.0, 239.3. HRMS Found: *m*/*z* 260.1218. Calcd for $C_{15}H_{20}O_2Si$: M, 260.1233.

Typical Procedure for the Aldol-Type Reaction between Acetal and 1,2-Propadienyl Sulfide 4. (Table 4). The procedure was the same as that of the reaction between aldehyde and 1,2-propadienyl sulfide **4a**, except that acetal was employed in place of aldehyde.

3-Methoxy-2-methylene-3-phenyl-1-trimethylsilyl-1-propanone (9a). IR (neat) 1697, 1603, 1099 cm^{-1}; ^{1}H NMR δ=0.19 (s, 9H), 3.26 (s, 3H), 5.13 (s, 1H), 6.11 (s, 1H), 6.29 (s, 1H), 7.20—7.33 (m, 5H). HRMS Found: *m*/*z* 248.1259. Calcd for $C_{14}H_{20}O_2Si$: M, 248.1233.

(*E*)-3-Methoxy-2-methylene-5-phenyl-1-trimethysilyl-4-penten-1-one (9b). IR (neat) 1680, 1600, 1093 cm^{-1}; ^{1}H NMR δ=0.28 (s, 9H), 3.34 (s, 3H), 4.77 (d, 1H, *J*=6.9 Hz), 6.03 (dd, 1H, *J*=6.9, 15.9 Hz), 6.16 (s, 1H), 6.34 (d, 1H, *J*=0.6 Hz), 6.60 (d, 1H, *J*=15.9 Hz), 7.21—7.37 (m, 5H); ^{13}C NMR δ=−1.4, 56.6, 77.3, 126.4, 127.5, 127.6, 128.2, 128.4, 131.7, 136.6, 152.5, 236.4. HRMS Found: *m*/*z* 274.1375. Calcd for $C_{16}H_{22}O_2Si$: M, 274.1390.

1-*t*-Butyldimethylsilyl-3-methoxy-2-methylene-3-phenyl-1-propanone (9e). IR (neat) 1693, 1597, 1101 cm^{-1}; ^{1}H NMR δ=0.18 (s, 6H), 0.78 (s, 9H), 3.24 (s, 3H), 5.15 (s, 1H), 6.06 (s, 1H), 6.27 (d, 1H, *J*=0.9 Hz), 7.18—7.29 (m, 5H); ^{13}C NMR δ=−5.1, −4.7, 16.6, 26.4, 56.8, 78.0, 126.6, 127.3, 127.5, 128.1, 140.0, 155.5, 236.7. HRMS Found: *m*/*z* 290.1708. Calcd for $C_{17}H_{26}O_2Si$: M, 290.1703.

1-*t*-Butyldimethylsilyl-3-methoxy-2-methylene-5-phenyl-1-pentanone (9f). IR (neat) 1741, 1593, 1109 cm^{-1}; ^{1}H NMR δ=0.27 (s, 3H), 0.28 (s, 3H), 0.93 (s, 9H), 1.67 (dddd, 1H, *J*=3.2, 4.9, 8.2, 11.0 Hz), 1.82 (dddd, 1H, *J*=3.2, 6.1, 8.2, 11.0 Hz), 2.61 (ddd, 1H, *J*=6.0, 11.0, 13.7 Hz), 2.75 (ddd, 1H, *J*=4.8, 11.0, 13.7 Hz), 3.23 (s, 3H), 4.15 (dd, 1H, *J*=3.2, 8.2 Hz), 6.15 (s, 1H), 6.27 (s, 1H), 7.14—7.27 (m, 5H); ^{13}C NMR δ=−4.7, −4.5, 16.7, 26.7, 31.9, 37.8, 56.9, 77.0, 125.7, 128.3, 128.3, 128.4, 142.1, 154.6, 237.3. HRMS Found: *m*/*z* 318.1988. Calcd for $C_{19}H_{30}O_2Si$: M, 318.2016.

1-*t*-Butyldimethylsilyl-3-cyclohexyl-3-methoxy-2-meth-

ylene-1-propanone (9g). IR (neat) 1701, 1595, 1111 cm^{-1}; ^{1}H NMR δ=0.24 (s, 3H), 0.25 (s, 3H), 0.91 (s, 9H), 1.04—1.69 (m, 11H), 3.13 (s, 3H), 3.93 (d, 1H, J=5.4 Hz), 6.11 (s, 1H), 6.12 (s, 1H); ^{13}C NMR δ=−4.5, −4.4, 16.7, 26.2, 26.3, 26.5, 26.7, 27.8, 29.5, 42.7, 57.2, 81.4, 128.7, 153.4, 237.5. Anal. Calcd for $C_{17}H_{32}O_2Si$: C, 68.86; H, 10.88%. Found: C, 68.57; H, 10.75%.

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