2794 © 1992 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 65, 2794—2799 (1992) [Vol. 65, No. 10

A New Synthesis of 5-Substituted 3-Methyl-2-phenylthio-2-penten-5-olides

Huiwen Su, Kozo Shirai, and Takanobu Kumamoto*
Department of Chemistry, Faculty of Science, Tokai University,
1117, Kitakaname, Hiratsuka, Kanagawa 259-12

(Received April 2, 1992)

Dienolate **11**, which was produced from 3-methyl-2-phenylthio-2-butenoic acid (**1**) and two equivalents of LDA, reacted with aldehydes or ketones to give 5-alkyl-3-methyl-2-phenylthio-2-penten-5-olides (**12**) in good yields.

A number of investigations on the regioselective reactions of dienolate of conjugated acids have been reported.[1] We recently described the highly regioselective side-chain lithiation of 2-methyl-3-thiophenecarboxylic acid.[2] Further extention of this reaction, we report herein the convenient method for the preparation of 3-methyl-2-phenylthio-2-penten-5-olide derivatives by the regioselective addition of ε-position on the *s-cis* lithium dienolate, which was produced from 3-methyl-2-phenylthio-2-butenoic acid (**1**) and two equivalents of lithium diisopropylamide (LDA), followed by the intramolecular cyclization reaction.

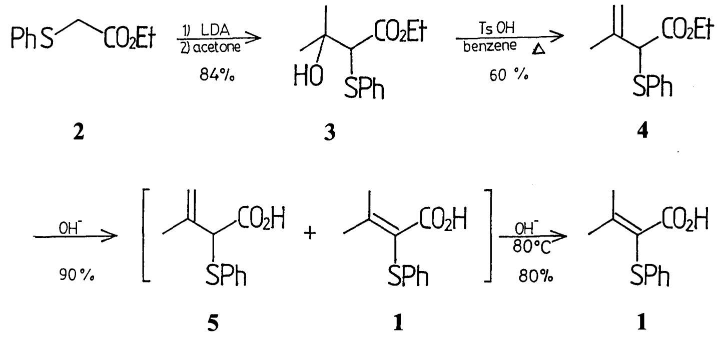
Results and Discussion

Preparation of 3-Methyl-2-phenylthio-2-butenoic Acid (1). Dehydration of ethyl 3-hydroxy-3-methyl-2-(phenylthio)butanoate (**3**), which was prepared from the lithium enolate of ethyl (phenylthio)acetate (**2**) and acetone, in the presence of *p*-toluenesulfonic acid in refluxing benzene gave the nonconjugated ester, ethyl 3-methyl-2-phenylthio-3-butenoate (**4**) in good yield. On the other hand, hydrolysis of **4** with aqueous sodium hydroxide resulted in the formation of desired conjugated acid, 3-methyl-2-phenylthio-2-butenoic acid (**1**).

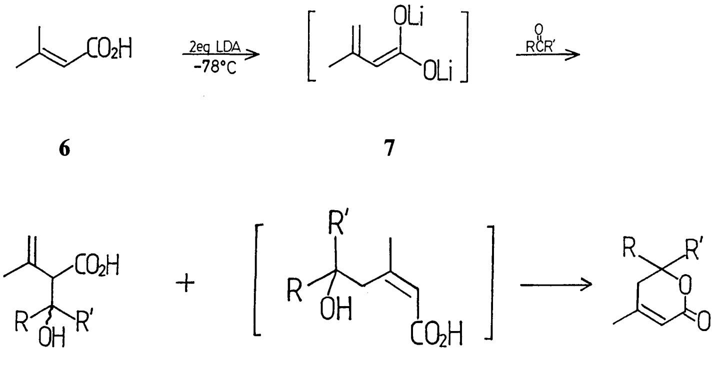
The isomerization of nonconjugated acid **5** to conjugated acid **1** needed rather long time, that is, conjugated acid **1** and nonconjugated acid **5** were obtained in a ratio of 20 : 80, when **4** was hydrolyzed with 1 : 1 mixture of 10% aqueous sodium hydroxide and ethanol at room temperature for 6 h. This mixture was heated at 80 °C with 20% aqueous sodium hydroxide for 6 h, **5** became undetectable and **1** was obtained as the pure form in good yield. However, when **4** was heated at 80 °C with 1 : 1 mixture of 10% aqueous sodium hydroxide and ethanol for 10 h, the yield of **1** became very low because of the formation of by-products.

The Reaction of Lithium Dienolate of 3-Methyl-2-butenoic Acid Derivatives with Carbonyl Compounds. The regioselectivity of the reaction of dienolate of 3-methyl-2-butenoic acid (**6**) with carbonyl compounds was shown by some reports[1] that the addition products of γ-position on dienolate of **6** were obtained predominantly with the addition compounds of ε-position on the *s-cis*-dienolate (**7**). Further, the ratio of the two types of the products changes by the reaction temperature. In these reports, the addition compounds of the ε-position on the **7** were obtained as the methyl ester by the treatment of diazomethane with pentenolide derivatives. From the interest in the preparation of pentenolide derivatives, these reactions were reinvestigated at −78 °C.

The reaction of dienolate **7**, which was prepared from two equivalents of LDA and **6** with benzaldehyde at −78 °C resulted in the formation of two types of addition compounds in 97% yield. The separation of these compounds gave the diastereomeric mixture of γ-adduct **8** and 3-methyl-5-phenyl-2-penten-5-olide (**10a**) in the ratio of 71 : 29. The pentenolide **10a** was formed by the cyclization of intermediate **9** which produced by the addition of ε-position of **7** with benzaldehyde. The results proved that the main product is γ-addition compounds on **7** at low temperature as illustrated in the literature.[1a] Further, the results of the reactions of dienolate **7** with carbonyl compounds are summarized in Table 1.



Scheme 1.



6 7

8 9 10

a: R=Ph, R′=H; **b**: R=$PhCH_2CH_2$, R′=H;
c: R=CH_3CH_2, R′=CH_3CH_2

Scheme 2.

Table 1. Condensation of Dienolate **7** with Carbonyl Compounds

	R	R′	Yield/%	**8**:**10**
a	Ph	H	97	71:29
b	$PhCH_2CH_2$	H	93	74:26
c	CH_3CH_2	CH_2CH_3	65	87:13

Table 2. Condensation of Dienolate **11** with Carbonyl Compounds

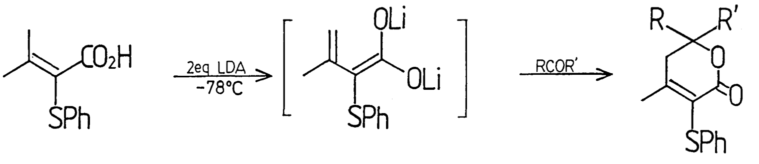
	R	R′	**12**/%	Recovered **1**/%
a	Ph	H	71	18
b	$PhCH_2CH_2$	H	70	25
c	$CH_3CH_2CH_2$	H	91	8
d	$CH_3CH_2CH_2CH_2$	H	71	5
e	CH_3CH_2	CH_3	65	10
f	CH_3CH_2	CH_2CH_3	75	15

Then, the reactions of dienolate **11**, which was prepared from two equivalents of LDA and **1**, with carbonyl compounds were examined. It was found that the reaction of dienolate **11** with benzaldehyde gave 3-methyl-5-phenyl-2-phenylthio-2-penten-5-olide (**12a**) at −78 °C in 71% yield. The careful separation of the carboxylic acid part after the treatment with diazomethane gave only methyl ester of starting **1**.

Further, the reactions of dienolate **11** with various carbonyl compounds were examined and the results are summarized in Table 2. From the results shown in the Table 2, aldehydes or ketones react smoothly with **11** to give pentenolide derivatives even at −78 °C in good yields.

Although it is highly speculative, the regioselectivity of the present reaction may be explained as follows: If dienolate **11** has a lithium enolate structure, it will have the same chance to react at ε-position on the *s-trans* form and *s-cis* form with carbonyl compounds. Therefore, it is reasonably considered that dienolate **11** is in equilibrium with the structure **13**[3] which is stabilized by the intramolecular chelation of the carbonyl group to the lithium as shown below. Further, the reactivity of the γ-position decreases by the steric effect of phenylthio group to give pentenolide derivatives as the main products (See Scheme 4).

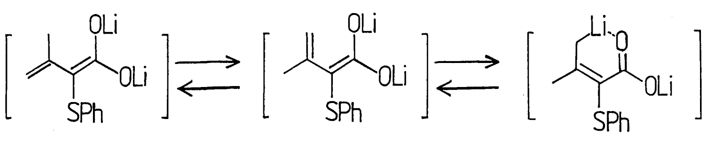
The Migration Reaction of Phenylthio Group in Dienolate 11. The reactions of alkyl halides or alkyl cyanides with dienolate **11** were examined. When dienol-



1 11 12

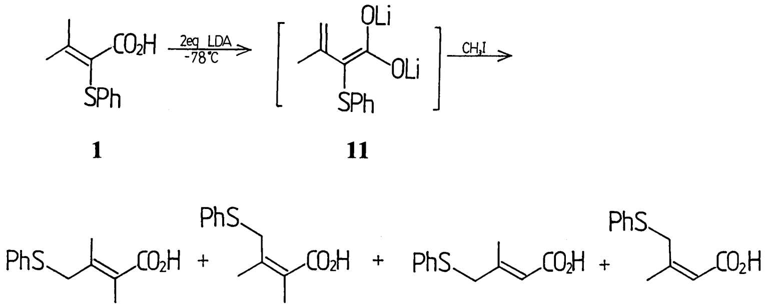
a: R=Ph, R′=H; **b**: R=$PhCH_2CH_2$, R′=H;
c: R=$CH_3CH_2CH_2$, R′=H; **d**: R=$CH_3CH_2CH_2CH_2$, R′=H; **e**: R=CH_3CH_2, R′=CH_3; **f**: R=CH_3CH_2, R′=CH_3CH_2

Scheme 3.



trans-**11** *cis*-**11** **13**

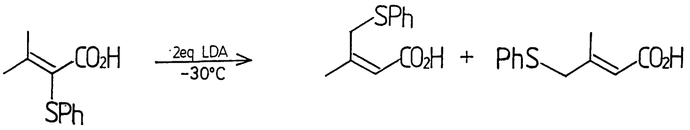
Scheme 4.



1 **11**

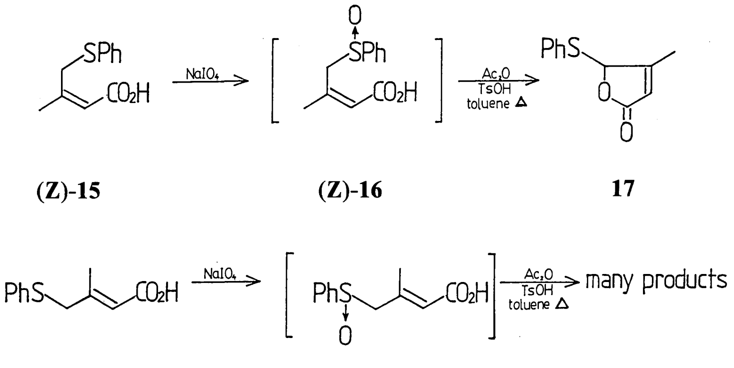
(E)-14 **(Z)-14** **(E)-15** **(Z)-15**

Scheme 5.



1 **(Z)-15** **(E)-15**

Scheme 6.



(Z)-15 **(Z)-16** **17**

(E)-15 **(E)-16**

Scheme 7.

ate **11** was allowed to react with methyl iodide at −78 °C, a mixture of four products, (*E*),(*Z*)-2,3-dimethyl-4-phenylthio-2-butenoic acids (**14**) and (*E*), (*Z*)-3-methyl-4-phenylthio-2-butenoic acids (**15**), was obtained (See Scheme 5).

Further, the reactions of butyl bromide or butyronitrile with dienolate **11** at −78 °C gave only phenylthio-migrated compounds (**15**) in 43 or 70% yield. To confirm these results, the reaction of dienolate **11** in the absence of electrophile was examined. A THF solution of dienolate **11** was stirred at −78 °C for 3 h and was quenched with 10% hydrochloric acid to give geometric isomers **15** in 15% yield. The same reaction was examined again at −30 °C, the geometric isomers (*Z*)-**15** and (*E*)-**15** were formed in the ratio of 37 : 63 in 85% yield (See Scheme 6). It is interesting that the yield of phenylthio-migrated compounds was increased in the presence of electrophile at −78 °C as mentioned above. This result shows that the rearrangement of phenylthio group was promoted by electrophilic reagents. However, the mechanism is not clear.

The geometry of **15** was confirmed as follows: (*Z*)-**15** and (*E*)-**15** isolated by column chromatography were converted to the sulfoxides (*Z*)-**16** and (*E*)-**16**, respectively. Both of these sulfoxides were treated with acetic anhydride to give Pummerer rearrangement products. From the spectral data, it was clarified that the product drived from (*Z*)-**16** is the butenolide **17**[4] and the product drived from (*E*)-**16** is a complex mixture. From these results, geometry of (*Z*)-**15** was assigned (See Scheme 7).

Experimental

IR spectra were determined with a Hitachi 215 infracord spectrophotometer. NMR spectra were recorded on Hitachi R-22 90 MHz instruments. Mass spectra were measured on GCMS-QP1000EX Shimadzu spectrometer. Element analysis were measured with Yanaco CHN-CORDER MT-5.

Preparation of Ethyl 3-Hydroxy-3-methyl-2-(phenylthio)-butanoate (3). Into a solution of lithium diisopropylamide (LDA) in 20 cm^3 of THF, prepared from diisopropylamine (1.01 g, 10.0 mmol) and butyllithium (10 mmol), a solution of ethyl (phenylthio)acetate (1.96 g, 10.0 mmol) in 10 cm^3 of THF was added at −78 °C under nitrogen. After the reaction mixture was stirred for 1 h at −78 °C, a solution of acetone (0.87 g, 15.0 mmol) in 10 cm^3 of THF was added and the mixture was stirred for 3 h at −78 °C. Then, the reaction temperature was raised to room temperature. After the addition of 10% hydrochloric acid, the mixture was extracted with ether and the ethereal layer was dried over magnesium sulfate. After removal of the ether, the residue was chromatographed on a silica gel and **3** was obtained as oily product, from the elution with benzene–petroleum ether (1 : 1): 2.13 g, yield 84%; IR (NaCl) 3500 (OH), 1740 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.11 (3H, t, J=8.0 Hz), 1.34 (3H, s), 1.40 (3H, s), 3.29 (1H, s), 3.62 (1H, s), 4.12 (2H, q, J=8.0 Hz), 7.20—7.60 (5H, m); MS m/z 254 (M^+). Found: C, 61.34; H, 7.29%. Calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13%.

Preparation of Ethyl 3-Methyl-2-phenylthio-3-butenoate (4). A mixture of **3** (2.54 g, 10.0 mmol) and catalytic amounts of *p*-toluenesulfonic acid in 30 cm^3 of dry benzene was refluxed 6 h under the water separating apparatus. After the removal of benzene, the resulting residue was chromatographed on silica gel. From the elution with petroleum ether, **4** was obtained: 1.58 g yield 67%. IR (NaCl) 1750 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.14 (3H, t, J=8.0 Hz), 1.84 (3H, s), 4.12 (2H, q, J=8.0 Hz), 4.31 (1H, s), 4.92 (2H, s), 7.14—7.46 (5H, m); MS m/z 236 (M^+). Found: C, 65.96; H, 6.86%. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82%.

Preparation of 3-Methyl-2-phenylthio-2-butenoic Acid (1). Into a solution of 10% sodium hydroxide solution (10 cm^3), a solution of **4** in 10 cm^3 of ethanol was added. After the mixture was stirred at room temperature for 6 h, the mixture was evaporated under the reduced pressure. The residue was acidified with 10% hydrochloric acid, and was extracted with ether. The ethereal layer was dried over magnesium sulfate. After removal of the ether, the residue was chromatographed on silica gel and the mixture of 3-methyl-2-phenylthio-3-butenoic acid (**5**) and **1** was obtained from the elution with benzene in the ratio of 80 : 20, 1.96 g yield 94%. The mixture was dissolved into the 20% sodium hydroxide solution and the solution was stirred at 80 °C for 6 h. Then, the reaction mixture was acidified with 10% hydrochloric acid and was extracted with ether. The ethereal layer was dried over magnesium sulfate. After removal of the ether, the residue was chromatographed on silica gel column. From the elution with benzene, **1** was obtained: 1.37 g yield 70%. Mp 85—85.5 °C (from petroleum ether); IR (KBr) 3500—2600 (COOH), 1700 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=2.14 (3H, s), 2.20 (3H, s), 7.20 (5H, s), 10.9 (1H, brs); MS m/z 208 (M^+). Found: C, 63.41; H, 6.02%. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.80%. The ^{1}H NMR spectrum of **5** δ=1.96 (3H, s), 4.38 (1H, s), 5.02 (2H, s), 7.14—7.47 (5H, m).

The Reaction of Dienolate 7 of 3-Methyl-2-butenoic Acid (6). Into a solution of LDA in 20 cm^3 of THF, prepared from diisopropylamine (2.02 g, 20.0 mmol) and butyllithium (20 mmol), was added a solution of 3-methyl-2-butenoic acid (**6**) (1.00 g, 10.0 mmol) in 10 cm^3 of THF at −78 °C under nitrogen. After the reaction mixture was stirred for 1 h at −78 °C, a solution of benzaldehyde (1.27 g, 12.0 mmol) in 10 cm^3 of THF was added and stirring was continued for 3 h at −78 °C. After the reaction temperature was raised to 0 °C, 10% hydrochloric acid was added and the mixture was extracted with ether. The ethereal layer was dried over magnesium sulfate. After removal of the ether, the residue was chromatographed on a silica gel column to give *threo* and *erythro*-2-(α-hydroxybenzyl)-3-methyl-3-butenoic acid (**8a**) in the ratio of 60 : 40 (1.42 g, 69%) from the elution with benzene and 3-methyl-5-phenyl-2-penten-5-olide (**10a**) in the yield of 0.53 g (28%) from the elution with benzene–petroleum ether (3 : 1). The spectral and analytical data of **8a** and **10a** are as follows:

Threo-**8a**: Mp 147—148 °C (from benzene–petroleum ether). IR (KBr) 3500 (OH), 3200—2800 (COOH), 1705 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.58 (3H, s), 3.35 (1H, d, J=8.0 Hz), 4.82 (2H, s), 4.97 (1H, d, J=8.0 Hz), 6.3 (1H, brs), 7.20 (5H, s); MS m/z 206 (M^+).[1a]

Erythro-**8a**: Mp 132—133 °C (from benzene–petroleum ether). ^{1}H NMR ($CDCl_3$) δ=1.80 (3H, s), 3.32 (1H, d, J=8.0 Hz), 4.95 (2H, s), 5.05 (1H, d, J=8.0 Hz), 7.10—7.50 (5H, m).[1a]

10a: Yield 28%, mp 59—60 °C (from petroleum ether) IR (KBr) 1740 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=2.01 (3H, s), 2.43 (1H, dd, J=3.6, 18.0 Hz), 2.63 (1H, dd, J=12.0, 18.0 Hz), 5.39 (1H, dd, J=3.6, 12.0 Hz), 5.89 (1H, s), 7.31—7.41 (5H, m); MS m/z 188 (M^+).[1a] Similarly, 2-(1-hydroxy-3-phenylpropyl)-3-methyl-3-butenoic acid (**8b**), 3-methyl-7-phenyl-2-hepten-5-olide (**10b**), 3-methyl-2-(1-ethyl-1-hydroxypropyl)-3-butenoic acid (**8c**), and 5-ethyl-3-methyl-2-hepten-5-olide (**10c**) were obtained by the reactions of dienolate **7** with 3-phenylpropanal or 3-pentanone. The spectral and analytical data of **8b**, **10b**, **8c**, and **10c** are as follows:

8b: Yield 69%, *threo*-**8b**: *erythro*-**8b**=74 : 26.

Threo-**8b**: Mp 107—108 °C (from petroleum ether-benzene); IR (KBr) 3600—2400 (COOH), 3300 (OH), 1700 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.72 (3H, s), 1.63-1.75 (1H, m), 1.80—1.91 (1H, m), 2.69 (1H, oct), 2.91 (1H, oct), 3.15 (1H, d, J=9.3 Hz), 4.03 (1H, dt, J=2.7, 9.3 Hz), 4.98 (1H, s), 5.00 (1H, s), 5.9 (1H, brs), 7.17—7.33 (5H, m); MS m/z 234 (M^+). Found: C, 71.77; H, 7.98%. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74%.

Erythro-**8b** could not be purified by column chromatography.

10b: Yield 24%, oily product. IR (NaCl) 1705 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ=1.86 (3H, s), 2.15 (2H, ABq), 3.64—3.95 (4H, m), 4.11—4.49 (1H, m), 5.75 (1H, s), 7.20 (5H,s); MS *m/z* 216 (M$^+$). Found: C, 77.45; H, 7.59%. Calcd for $C_{14}H_{16}O_2$: C, 77.73; H, 7.46%.

8c: Yield 55%, mp 77—77.5 °C (from petroleum ether–benzene). IR (KBr) 3600 (OH), 3500—2400 (COOH), 1695 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ=0.89 (6H, t, *J*=6.0 Hz), 1.44—1.70 (4H, m), 1.90 (3H, s), 3.22 (1H, s), 5.07 (2H, s), 6.8 (1H, brs). MS *m/z* 186 (M$^+$). Found: C, 64.73; H, 10.09%. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74%.

10c: Yield 9%, oily product. IR (NaCl) 1710 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ=0.92 (6H, t, *J*=7.2 Hz), 1.65—1.81 (4H, m), 1.96 (3H, s), 2.30 (2H, s), 5.80 (1H, s). MS *m/z* 168 (M$^+$). Found: C, 71.34; N, 9.87%. Calcd for $C_{10}H_{16}O_2$: C, 71.38; H, 9.59%.

The Reaction of Dienolate 11 with Benzaldehyde. A solution of **1** (2.08 g, 10.0 mmol) in 10 cm^3 of THF was added to a solution of LDA (20 mmol) in 20 cm^3 of THF, prepared from diisopropylamine (2.02 g, 20.0 mmol) and butyllithium (20 mmol), at −78 °C under nitrogen. After the reaction mixture had been stirred for 1 h at −78 °C, a solution of benzaldehyde (1.27 g, 12.0 mmol) in 10 cm^3 of THF was added and the solution was stirred for 3 h at −78 °C. Then, the reaction temperature was raised to 0 °C. The reaction mixture was acidified with 10% hydrochloric acid and extracted with ether. The ethereal layer was dried over magnesium sulfate. After removal of the ether, the residue was chromatographed on silica gel. From the elution with benzene–petroleum ether (3 : 1), 2.10 g (71%) of 3-methyl-5-phenyl-2-phenylthio-2-penten-5-olide (**12a**) was obtained and 0.37 g (18%) of starting **1** was recovered from the elution with benzene. The **12a** was further purified by recrystallization from petroleum ether. Mp 101—102 °C; IR (KBr) 1710 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ=2.31 (3H, s), 2.77 (1H, dd, *J*=3.9, 18.0 Hz), 2.97 (1H, dd, *J*=11.3, 18.0 Hz), 5.50 (1H, dd, *J*=3.9, 11.3 Hz), 7.20 (5H, s), 7.35 (5H, s); MS *m/z* 296 (M$^+$). Found: C, 72.79: H, 5.39%. Calcd for $C_{18}H_{16}O_2S$: C, 72.94; H, 5.44%.

By a similar procedure 3-methyl-7-phenyl-2-phenylthio-2-hepten-5-olide (**12b**), 3-methyl-2-phenylthio-2-octen-5-olide (**12c**), 3-methyl-2-phenylthio-2-nonen-5-olide (**12d**), 3,5-dimethyl-2-phenylthio-2-hepten-5-olide (**12e**), and 5-ethyl-3-methyl-2-phenylthio-2-hepten-5-olide (**12f**) were obtained from **1** and corresponding aldehydes or ketones. The yields, spectral and analytical data of **12b**, **12c**, **12d**, **12e**, and **12f** are as follows.

12b: Yield 70%, mp 81—82 °C (from petroleum ether). IR (KBr) 1705 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ=1.66—2.88 (6H, m), 2.11 (3H, s), 4.15—4.44 (1H, m), 7.15 (5H, s), 7.30 (5H, s); MS *m/z* 324 (M$^+$). Found: C, 73.90; H, 6.20%. Calcd for $C_{20}H_{20}O_2S$: C, 74.04; H, 6.21%.

12c: Yield 91%, oily product. IR (NaCl) 1710 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ=0.90 (3H, t, *J*=6.8 Hz), 1.29—1.78 (4H, m), 2.22 (3H, s), 2.45 (1H, dd, *J*=4.2, 18.0 Hz), 2.58 (1H, dd, *J*=11.7, 18.0 Hz), 4.36—4.45 (1H, m), 7.10—7.26 (5H, m); MS *m/z* 262 (M$^+$). Found: C, 68.68; H, 7.26%. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.91%.

12d: Yield 71%, oily product. IR (NaCl) 1740 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ=0.94 (3H, t, *J*=6.9 Hz), 1.25—1.81 (6H, m), 2.22 (3H, s), 2.45 (1H, dd, *J*=3.9, 18.0 Hz), 2.58 (1H, dd, *J*=11.4, 18.0 Hz), 4.38—4.47 (1H, m), 7.10—7.27 (5H, m); MS *m/z* 276 (M$^+$). Found: C, 69.36; H, 7.40%. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29%.

12e: Yield 65%, mp 85—86 °C (from petroleum ether). IR (KBr) 1700 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ=0.94 (3H, t, *J*=7.0 Hz), 1.35 (3H, s), 1.63 (2H, q, *J*=7.0 Hz), 2.20 (3H, s), 2.50 (1H, s), 2.60 (1H, s), 7.20 (5H, s); MS *m/z* 262 (M$^+$). Found C, 68.60; H, 6.94%. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.91%.

12f: Yield 75%, oily product. IR (NaCl) 1710 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ=0.89 (6H, t, *J*=8.0 Hz), 1.71 (4H, q, *J*=8.0 Hz), 2.18 (3H, s), 2.51 (2H, s), 7.07—7.39 (5H, m); MS *m/z* 276 (M$^+$). Found: C, 69.64; H, 7.45%. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29%.

The Phenylthio-migration Reaction of 1. To a solution of LDA, prepared from diisopropylamine (2.02 g, 20.0 mmol) and butyllithium (20 mmol), was added a solution of **1** (2.08 g, 10.0 mmol) in 10 cm^3 of THF at −30 °C under nitrogen. The mixture was stirred at −30 °C for 3 h and was quenched with 10% hydrochloric acid. The mixture was extracted with ether and ethereal layer was dried over magnesium sulfate. After removal of the solvent, the residue was chromatographed on silica gel. From the elution with petroleum ether–benzene (3 : 1), a mixture of geometrical isomers of 3-methyl-4-phenylthio-2-butenoic acids (**15**) was obtained. Yield 1.77 g (85%). IR (NaCl) 3600—2500 (COOH), 1705 cm^{-1} (C=O); MS *m/z* 208 (M$^+$). Found: C, 63.38; H, 6.02%. Calcd for $C_{12}H_{12}O_2S$: C, 63.43; H, 5.81%. Further, the mixture was chromatographed on silica gel again. From the elution with petroleum ether–benzene (4 : 1), (*E*)-**15** (1.12 g) and (*Z*)-**15** (0.65 g) were obtained. The ^{1}H NMR data of (*E*)-**15** and (*Z*)-**15** are as follows:

(*E*)-**15**, oily product. ^{1}H NMR (CDCl$_3$) δ=2.29 (3H, s), 3.56 (2H, s), 5.60 (1H, s), 7.11—7.48 (5H, m), 10.8 (1H, brs).

(*Z*)-**15**, oily product. ^{1}H NMR (CDCl$_3$) δ=2.03 (3H, s), 4.18 (2H, s), 5.71 (1H, s), 7.18—7.44 (5H, m), 11.3 (1H, brs).

Preparation of 3-Methyl-4-phenylthio-2-buten-4-olide (17). A solution of (*Z*)-**15** in 10 cm^3 of ethanol was added to a solution of 20 cm^3 of sodium periodate (2.57 g, 12.0 mmol) in 20 cm^3 of water at 0 °C and stirring was continued for 12 h at the same temperature. The reaction mixture was extracted with chloroform and the chloroform layer was washed with a solution of sodium sulfite. The chloroform layer was dried over magnesium sulfate. After removal of the chloroform, the residue was used as the sulfoxide **16** for the next reaction without further purification. A solution of **16**, acetic anhydride (1.33 g, 13.0 mmol) and catalyic amounts of *p*-toluenesulfonic acid in 50 cm^3 of toluene was refluxed for 3 h. After the removal of the solvent under the reduced pressure, the resulting residue was chromatographed on silica gel. From the elution with mixted solvent of petroleum ether and benzene (6 : 1), the **17** was obtained as the oily product: 1.96 g yield 95%; IR (NaCl) 1795 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ=2.10 (3H, s), 5.70 (1H, s), 6.00 (1H, s), 7.20—7.60 (5H, m); MS *m/z* 206 (M$^+$). Found : C, 64.09; H, 4.89%. Calcd for $C_{11}H_{10}O_2S$:, C, 64.05; H, 4.89%.

References

1) I. Casinos and R. Mestres, *An. Quim., Ser. C,* **78**, 364 (1982); *C. A.*, **98**, 160333n (1983); b) P. E. Pfeffer, L. S. Silbert, and E. Kinsel, *Tetrahedron Lett.*, **1973**, 1163; c) G. Cainelli, G. Cardillo, M. Contento, G. Trapani, and A. Umani Ronchi, *J. Chem. Soc., Perkin Trans. 1,* **1973**, 400; d) I. Casinos and R. Mestres, *J. Chem. Soc., Perkin Trans. 1,* **1978**,

1651; e) C. J. Kowalski and K. W. Fields, *J. Am. Chem. Soc.*, **104**, 1777 (1982); f) H. Okamura, Y. Mitsuhira, M. Miura, and H. Taki, *Chem. Lett.*, **1978**, 517; g) M. Kitaoka, Y. Takahashi, H. Kosugi, and H. Uda, *Chem. Lett.*, **1983**, 1065.

2) Su Hui-wen, K. Hirose, K. Shirai, and T. Kumamoto, *Bull. Chem. Soc. Jpn.*, **62**, 2725 (1989).

3) a) T. Fujisawa, K. Tajima, M. Ito, and T. Sato, *Chem. Lett.*, **1984**, 1169; b) C. S. Shiner, A. H. Berks, and A. M. Fisher, *J. Am. Chem. Soc.*, **110**, 957 (1988).

4) M. Watanabe, S. Nakamori, H. Hasegawa, K. Shirai, and T. Kumamoto, *Bull. Chem. Soc. Jpn.*, **54**, 817 (1981).