  Bull. Chem. Soc. Jpn., 57, 729—733 (1984)

Conversion of 2-Sulfinylated 2-Alkenoate Esters to (2*E*,4*E*)-2,4-Alkadienoate Esters by Pyrolysis

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(Received July 1, 1983)

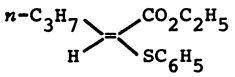
Thermal reaction of ethyl (2*E*)-2-phenylsulfinyl-2-alkenoates (*E*-**2**) prepared from aldehydes and ethyl 2-phenylsulfinylacetate have been investigated. Refluxing of *E*-**2** or their *Z*-isomers in xylene resulted in the formation of ethyl (2*E*,4*E*)-2,4-alkadienoates accompanied by ethyl (2*E*)-4-hydroxy-2-alkenoates. Ethyl 2-cycloalkylidene-2-phenylsulfinylacetates were found to be more susceptible to pyrolysis. The enoate esters (**2**) undergo migration of their carbon-carbon double bond and then [2,3]sigmatropic rearrangement to benzenesulfenate esters, followed by thermolytic extrusion of a benzenesulfenic acid probably *via* ethyl (2*E*)-4-phenylsulfinyl-2-alkenoates to afford ethyl (2*E*,4*E*)-2,4-alkadienoates.

(2*E*,4*E*)-2,4-Alkadienoate esters (**1**) are versatile synthetic intermediates for naturally occurring compounds.[1-3] A number of syntheses of (2*E*,4*E*)-*N*-isobutyl-2,4-decadienamide (pellitorine) have been accomplished by the pathway *via* decadienoic acid or its esters,[1,4,5] which in turn were prepared by a number of routes.[6-11] We previously reported that pyrolysis of 2-phenylsulfinyl-2-alkenoate esters (**2**) led to the formation of **1**.[7]

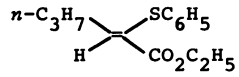
Saturatd sulfoxides with one or more β-hydrogen atoms are known to undergo readily syn elimination on pyrolysis to form olefins by way of a concerted five-membered cyclic pathway.[12,13] This reaction is of great value for making carbon-carbon double bonds and introducing unsaturation at the α-position of esters, ketones and aldehydes,[14] but the corresponding thermal reaction of α,β- and β,γ-unsaturated sulfoxides had scarecely been investigated.[15] Cookson and Parsons reported the formation of 2-methyl-1,3-nonadien-5-one from 2-methyl-4-phenylsulfinyl-2-nonen-5-one, but no explanation of this observation was given.[16] Recently Nokami *et al.* prepared butyl 2,4-decadienoate by pyrolysis of butyl 2-phenylsulfinyl-2-decenoate and proposed an attractive mechanism involving a flexible seven-membered cyclic transition state.[9] It seems interesting to clarify whether this mechanism is operative or not. The present report aims at elucidating the mechanism of this novel conversion of **2** to **1**.

Results and Discussion

Ethyl (2*E*)-2-phenylsulfinyl-2-alkenoates (*E*-**2**) were easily prepared by treatment of aldehydes with ethyl 2-phenylsulfinylacetate and a catalytic amount of piperidine.[17] Their configurations were assigned by the comparison of δ values for olefinic protons (-CH=) in ^{1}H-NMR spectra of the corresponding sulfides (**3**). For example, the olefinic proton of ethyl (2*E*)-2-phenylthio-2-hexenoate (*E*-**3a**) appeared at δ 6.41, whereas that of its *Z*-isomer (*Z*-**3a**) at δ 7.36. It seems reasonable to conclude that the chemical shift of the proton cis to the carbonyl group must show up at a lower field than that cis to the sulfenyl group.



E-3a



Z-3a

When ethyl (2*E*)-2-phenylsulfinyl-2-hexenoate (*E*-**2a**) was refluxed for 4 h in xylene containing anhydrous potassium carbonate ethyl (2*E*,4*E*)-2,4-hexadienoate (**1a**) and ethyl (2*E*)-4-hydroxy-2-hexenoate (**4a**) were formed, but (2*E*,4*Z*)-, (2*Z*,4*E*)-, and (2*Z*,4*Z*)-2,4-hexadienoate esters were scarecely found (GLPC).

The results obtained in the thermolysis of *E*-**2a—g** are summarized in Table 1.

The carbon-carbon double bonds of α,β-unsaturated sulfoxides and sulfilimines are known to migrate under basic conditions.[18,19] O'Connor established that base-catalyzed equilibriation between α,β- and β,γ-unsaturated sulfoxides greatly favored the latter ones.[18] Therefore, **2** may at first undergo migration of their double bonds to yield ethyl 2-phenylsulfinyl-3-alkenoates (**5**), which may produce **1** and **4** with loss of the sulfenic acid group. This assumption appears to be consistent with the findings that both *E*-**2a** and *Z*-**2a** gave **1a** and **4a** in the same ratio.

In order to study the validity of the seven-membered transition state for the diene formation (Ei mechanism; Fig. 1),[9] pyrolysis of ethyl 2-cyclopentylidene-2-

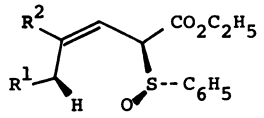
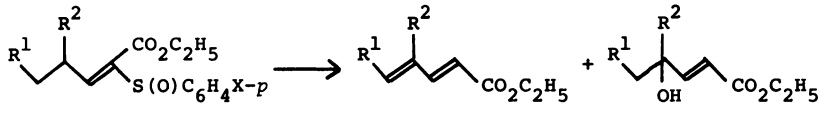


Fig. 1.

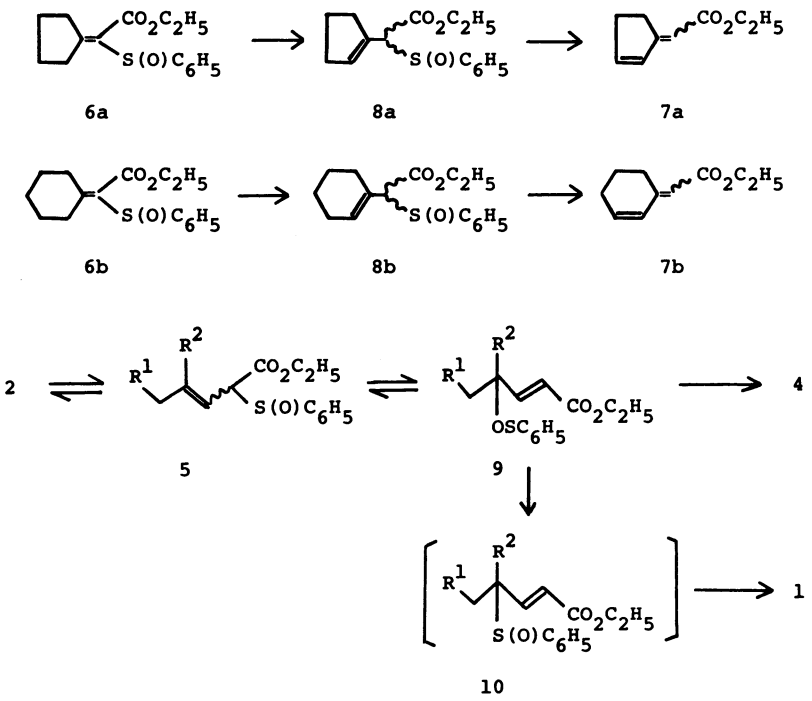


E-2 1 4

TABLE 1. PYROLYSIS OF ETHYL (2*E*)-2-PHENYLSULFINYL-2-ALKENOATES (*E*-**2**)

	R^1	R^2	X	Reaction time/h	Yield[a] of **1**/%	(2*E*, 4*E*)/ other isomers[b]	Yield[a] of **4**/%
a	CH_3	H	H	4	59	91/9	12
b	CH_3	H	Cl	4	30	92/8	27
c	*n*-C_3H_7	H	H	4	55	93/7	10
d	*n*-C_5H_{11}	H	H	4	60	94/6	8
e	*n*-C_5H_{11}	H	Cl	4	25	93/7	25
f	*n*-C_7H_{15}	H	H	4	58	93/7	9
g	$-(CH_2)_4-$		H	15	46 (68[c])	97/3	5

a) Isolated yield. b) Determined by GLPC with a 30 m glass capillary column. c) Yield was based on the consumed **2g**.



Scheme 1.

phenylsulfinylacetate (**6a**) and ethyl 2-cyclohexylidene-2-phenylsulfinylacetate (**6b**) was then investigated. Refluxing of **6a** and **6b** in xylene afforded ethyl 2-(2-cyclopentenylidene)acetate (**7a**) and ethyl 2-(2-cyclohexenylidene)acetate (**7b**) in 59 and 51% yields, respectively. The yields were moderate because **7** were somewhat unstable at high temperature. The α,β-unsaturated sulfoxides **6a**, **6b**, and **2a** were found to be labile to pyrolysis in that order. If the seven-membered transition state were operative, neither **6a** nor **6b** might show high reactivities because the hydrogen atom at δ position is located too far (3.5—4.0 Å) from the sulfinyl oxygen atom in the intermediary β,γ-unsaturated sulfoxides **8a** and **8b**.[20]

On the basis of these findings, the mechanism shown in Scheme 1 seems to be more reasonable than the Ei mechanism.

In the present transformation, it is assumed that the [2,3]sigmatropic rearrangement of **5** would take place in the first step to yield the sulfenate esters **9**, which produce **1** probably *via* the sulfoxides **10**. The rapid [2,3]sigmatropic rearrangement of **5** may be supported by the observations that the treatment of **2** with an equimolar amount of piperidine in acetonitrile resulted in the formation of **4**, the hydrolysis products of **9**, in high yields,[21] and in the attempted preparation of **8a** the oxidation of the corresponding sulfide, ethyl 2-(1-cyclopentenyl)-2-(phenylthio)acetate, with *m*-chloroperbenzoic acid at 0 °C gave ethyl (2*E*)-2-(2-hydroxycyclopentylidene)acetate, but did not allow the isolation of **8a**. Since it is known that the introduction of an electron-withdrawing group at the phenyl group of sulfoxides brings about the acceleration of thermolysis,[22] the *p*-chloro derivatives, **2b** and **2e**, were examined. The yields of **1** were rather low, however, probably owing to the ready hydrolysis of **9**.

Although the thermal rearrangement of sulfenates to sulfoxides is known to occur in benzylic derivatives,[23] we could not rigorously prove, at the present time, that the thermal reaction of **2** proceeds through ethyl (2*E*)-4-

phenylsulfinyl-2-alkenoates (**10**). However, it shoud be pointed out that **10a**, prepared from the corresponding sulfide by oxidation, produced **1a** upon heating in xylene.[24] In addition it was observed that the attempted isolation of **9a** from the reaction mixture of benzenesulfenyl chloride with sodium salt of **4a** was unsuccessful, but **1a** was detected in the pyrolysis product of that mixture. The predominant formation of the (2*E*,4*E*)-isomers of **1** might also be in accordance with the mechanism shown in Scheme 1.

Experimental

NMR spectra were recorded with a JEOL JNM-PS-100 or a Hitachi R-24B spectrometer in $CDCl_3$ using TMS as an internal standard. IR spectra were taken on a Hitachi 215 spectrometer. Mass spectra were determined with a Hitachi M-52 spectrometer. GLPC analysis was performed with a Varian 920 using a glass column (1 m×6 mm) packed with 20% silicone DC-550 or a Shimadzu GC-6AM using a SS-4 glass capillary column (30 m×0.3 mm). Column chromatography was performed using Wakogel 200 silica gel.

Materials. All aldehydes were commercially available and purified by distillation before use. Commercial acetonitrile and piperidine were used without purification. Xylene and tetrahydrofuran (THF) were distilled over CaH_2 prior to use.

*Ethyl 2-(Phenylthio)acetate (**11a**).* To a solution of sodium ethoxide prepared by dissolving Na (11.5 g, 0.5 mol) in ethanol (300 ml), benzenethiol (55.1 g, 0.5 mol) was added at room temperature. To the stirred solution was added dropwise a solution of ethyl bromoacetate (83.5 g, 0.5 mol) in ethanol (50 ml) at 0 °C. The reaction mixture was refluxed for 1 h, diluted with water (500 ml), and extracted with chloroform (300 ml). The chloroform solution was washed with water and dried over anhydrous Na_2SO_4. After removal of chloroform **11a** was obtained as a colorless liquid by distillation *in vacuo*: yield 88.0 g (90%); bp 101—104 °C/0.4 mmHg (1 mmHg≈133.322 Pa).[25]

Ethyl 2-(*p*-chlorophenylthio)acetate (**11b**) was obtained as a colorless liquid by the similar method: yield 85%; bp 130—133 °C/1.8 mmHg.[26]

*Ethyl 2-Phenylsulfinylacetate (**12a**).* A solution of **11a** (88.0 g, 0.45 mol) and $NaIO_4$ (115 g, 0.54 mol) in water (400 ml) and methanol (100 ml) was kept stirring at room temperature for 1 d, and filtered. The filtrate was extracted with chloroform (300 ml). The chloroform layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated to afford **12a** as a colorless liquid: yield 94.2 g (99%); NMR ($CDCl_3$) δ=1.19 (3H, t), 3.62 (1H, d), 3.82 (1H, d), 4.09 (2H, q), and 7.4—7.8 (5H, m).[27]

Ethyl 2-(*p*-chlorophenylsulfinyl)acetate (**12b**) was similarly prepared by oxidation of **11b**: yield 96%; colorless solid; mp 43 °C; NMR ($CDCl_3$) δ=1.20 (3H t, J=7 Hz), 3.64 (1H, d, J=12 Hz), 3.82 (1H, d, J=12 Hz), 4.10 (2H, q, J=7 Hz), 7.44 (2H, d, J=8 Hz), and 7.60 (2H, d, J=8 Hz); IR (Nujol) 1725, 1270, and 1050 cm^{-1}. Found: C, 48.70; H, 4.55%. Calcd for $C_{10}H_{11}ClO_3S$: C, 48.67; H, 4.50%.

*Ethyl (2E)-2-Phenylsulfinyl-2-hexenoate (E-**2a**).* A solution of **12a** (2.12 g, 10 mmol), butanal (1.08 g, 15 mmol), and piperidine (0.08 g, 1 mmol) in acetonitrile (30 ml) was allowed to stand at 0 °C for 2 d. After removal of acetonitrile the residue was chromatographed on a silica-gel column with a chloroform eluent to give *E*-**2a** (1.46 g, 55%) and **12a** (0.7 g, recovery 33%). *E*-**2a**: viscous colorless oil; NMR ($CDCl_3$) δ=0.98 (3H, t, J=7 Hz), 1.14 (3H, t, J=7 Hz), 1.4—1.8 (2H, m), 2.73 (2H, q, J=7 Hz), 4.06 (2H, q, J=7 Hz), 7.12 (1H, t, J=7 Hz), and 7.3—7.7 (5H, m); IR (neat) 1720, 1200, and 1050 cm^{-1}; MS m/z 266 (M^+). Found: C, 63.34; H, 6.91%. Calcd for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81%.

Other ethyl (2*E*)-2-phenylsulfinyl-2-alkenoates (*E*-**2b—g**) were obtained by similar treatment of **12a** or **12b** (10 mmol) with aldehydes (15 mmol) and piperidine (1 mmol).

*Ethyl (2E)-2-(p-Chlorophenylsulfinyl)-2-hexenoate (E-**2b**)*: Viscous colorless oil; yield 68%, NMR ($CDCl_3$) δ=0.96 (3H, t, J=7 Hz), 1.14 (3H, t, J=7 Hz), 1.4—1.8 (2H, m), 2.70 (2H, q, J=7 Hz), 4.06 (2H, q, J=7 Hz), 7.11 (1H, t, J=7 Hz), 7.34 (2H, d, J=8 Hz), and 7.53 (2H, d, J=8 Hz); IR (neat) 1725, 1210, and 1055 cm^{-1}; MS m/z 301 (M^+). Found: C, 56.10; H, 5.89%. Calcd for $C_{14}H_{17}ClO_3S$: C, 55.89; H, 5.70%.

*Ethyl (2E)-2-Phenylsulfinyl-2-octenoate (E-**2c**)*: Viscous colorless oil; yield 51%; NMR ($CDCl_3$) δ=0.90 (3H, t, J=7 Hz), 1.15 (3H, t, J=7 Hz), 1.0—1.8 (8H, br), 4.06(2H, q, J=7 Hz), 7.13 (1H, t, J=7 Hz), and 7.3—7.7 (5H, m); IR (neat) 1720, 1210, and 1050 cm^{-1}: MS m/z 294 (M^+). Found: C, 65.50: H, 7.59%. Calcd for $C_{16}H_{22}O_3S$: C, 65.27; H, 7.53%.

*Ethyl (2E)-2-Phenylsulfinyl-2-decenoate (E-**2d**)*: Viscous colorless oil; yield 50%; NMR ($CDCl_3$) δ=0.87 (3H, t, J=7 Hz), 1.14 (3H, t, J=7 Hz), 1.0—1.8 (12H, br), 4.06 (2H, q, J=7 Hz), 7.14 (1H, t, J=7 Hz), and 7.3—7.7 (5H, m); IR (neat) 1720, 1210, and 1050 cm^{-1}; MS m/z 322 (M^+). Found: C, 67.31; H, 8.02%. Calcd for $C_{18}H_{26}O_3S$: C, 67.04; H, 8.13%.

*Ethyl (2E)-2-(p-Chlorophenylsulfinyl)-2-decenoate (E-**2e**)*: Viscous colorless oil; yield 77%; NMR ($CDCl_3$) δ=0.87 (3H, t, J=7 Hz), 1.14 (3H, t, J=7 Hz), 1.0—1.8 (12H, br), 4.06 (2H, q, J=7 Hz), 7.10 (1H, t, J=7 Hz), 7.34 (2H, d, J=8 Hz), and 7.54 (2H, d, J=8 Hz); IR (neat) 1725, 1210, and 1055 cm^{-1}; MS m/z 357 (M^+). Found: C, 60.62; H, 7.34%. Calcd for $C_{18}H_{25}ClO_3S$: C, 60.62: H, 7.06%.

*Ethyl (2E)-2-Phenylsulfinyl-2-dodecenoate (E-**2f**)*: Viscous colorless oil; yield 53%; NMR ($CDCl_3$) δ=0.87 (3H, t, J=7 Hz), 1.14 (3H, t, J=7 Hz), 1.0—1.8 (16H, br), 4.06 (2H, q, J=7 Hz), 7.13 (1H, t, J=7 Hz), and 7.3—7.7 (5H, m); IR (neat) 1720, 1210, and 1050 cm^{-1}; MS m/z 350 (M^+). Found; C, 68.50; H, 8.75%. Calcd for $C_{20}H_{30}O_3S$: C, 68.53; H, 8.63%.

*Ethyl (2E)-2-Phenylsulfinyl-3-cyclohexyl-2-propenoate (E-**2g**)*: Viscous colorless oil; yield 71%; NMR ($CDCl_3$) δ=1.14 (3H, t, J=7 Hz), 1.0—1.9 (10H, br), 3.0—3.4 (1H, m), 4.06 (2H, q, J=7 Hz), 6.98 (1H, d, J=9 Hz), and 7.3—7.7 (5H, m); IR (neat) 1720, 1210, and 1050 cm^{-1}; MS m/z 306 (M^+). Found: C, 66.91; H, 7.41%. Calcd for $C_{17}H_{22}O_3S$: C, 66.63; H, 7.24%.

*Ethyl (2E)-2-Phenylthio-2-hexenoate (E-**3a**).* Trifluoroacetic anhydride (0.63 g, 3 mmol) was added to a stirred solution of *E*-**2a** (0.53 g, 2 mmol) and NaI (0.75 g, 5 mmol) in acetone (30 ml) at 0 °C.[28] The mixture was stirred for 2 min, diluted with benzene (100 ml), and washed with water, aq $NaHCO_3$, aq $Na_2S_2O_3$, and then water. After drying over anhydrous Na_2SO_4 the solvent was evaporated to give *E*-**3a** in a quantitative yield; yellowish liquid; NMR ($CDCl_3$) δ=0.96 (3H, t, J=7 Hz), 1.09 (3H, t, J=7 Hz), 1.4—1.7 (2H, m), 2.53 (2H, q, J=7 Hz), 4.11 (2H, q, J=7 Hz), 6.41 (1H, t, J=7 Hz), and 7.2—7.5 (5H, m); IR (neat) 1720 cm^{-1}; MS m/z 250 (M^+). Found: C, 67.06; H, 7.23%. Calcd for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.25%.

*Ethyl (2Z)-2-Phenylthio-2-hexenoate (Z-**3a**).* Similar reduction of ethyl (2*Z*)-2-phenylsulfinyl-2-hexenoate (*Z*-**2a**)[7] gave *Z*-**3a** in a quantitative yield; yellowish liquid; NMR ($CDCl_3$) δ=0.98 (3H, t, J=7 Hz), 1.09 (3H, t, J=7 Hz), 1.4—1.7 (2H, m), 2.54 (2H, q, J=7 Hz), 4.11 (2H, q, J=7 Hz), 7.36 (1H, t, J=7 Hz), and 7.2—7.5 (5H, m); IR (neat) 1720 cm^{-1}; MS m/z 250 (M^+). Found: C, 67.03; H, 7.21%. Calcd for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.25%.

*Ethyl 2-(1-Hydroxycyclopentyl)-2-phenylsulfinylacetate (**13a**).* A solution of ethyl 2-phenylsulfinylacetate (7.29 g, 44 mmol) in anhydrous THF (15 ml) was added under argon

atomosphere at −78 °C to a stirred solution of lithium diisopropylamide (44 mmol) prepared from diisopropylamine (6.16 ml) and butyllithium (29.0 ml, 1.55 M solution in hexane) in anhydrous THF (30 ml), and stirring was continued for 1 h at −60 °C. A solution of cyclopentanone (3.80 ml, 43 mmol) in anhydrous THF (10 ml) was added dropwise. The resultant solution was stirred for 1.5 h at −60 °C, quenched with aq NH_4Cl, and diluted with ether (300 ml). The ethereal solution was washed with 10% HCl and aq saturated NaCl, dried over anhydrous Na_2SO_4, and evaporated. The residue was chromatographed on silica gel with a benzene eluent to give **13a** (8.75 g, 78%) as a yellowish liquid; NMR (CCl_4) δ=1.22 (3H, t, J=7 Hz), 0.9-2.3 (10H, m) 3.00 (1H, s), 3.52 (1H, s), 4.01 (2H, q, J=7 Hz), and 7.0—7.4 (5H, m).[29]

Ethyl 2-Cyclopentylidene-2-(phenylthio)acetate (14a). A solution of **13a** (3.65 g, 13 mmol) in acetic anhydride (10 ml) was refluxed for 3 h, cooled to room temperature, neutralized with 30% aq NaOH, and diluted with ether (200 ml). The ethereal solution was washed with water, dried over anhydrous Na_2SO_4 and evaporated. The residue was dissolved in anhydrous THF (5 ml), and the resultant solution was added to a solution of lithium diisopropylamide (14.4 mmol) in anhydrous THF (30 ml) at −10 °C. The mixture was stirred at room temperature for 2 h, quenched with aq NH_4Cl, and extracted with ether (200 ml). The ethereal extract was washed with 10% HCl and aq saturated NaCl, dried over anhydrous Na_2SO_4, and evaporated. The product **14a** was separated by chromatography on a silica-gel column using a hexane-benzene mixture (v/v=1/1); yellowish liquid; yield 1.17 g (50%); NMR (CCl_4) δ=1.00 (3H, t, J=7 Hz), 1.5—2.0 (4H, m), 2.4—2.9 (4H, m), 3.95 (2H, q, J=7 Hz), and 6.9—7.4 (5H, m); IR (neat) 1705 cm^{-1}; MS m/z 262 (M^+).[29]

Ethyl 2-Cyclopentylidene-2-phenylsulfinylacetate (6a). To a solution of **14a** (4.07 g, 15.5 mmol) in dichloromethane (100 ml) was added a solution of *m*-chloroperbenzoic acid (3.68 g, 17 mmol) in dichloromethane (50 ml) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and neutralized with aq $NaHCO_3$. The organic layer was washed with aq saturated NaCl, dried over anhydrous Na_2SO_4, and evaporated. The residual crude **6a** was purified by chromatography on silica gel using chloroform; colorless liquid; yield 2.74 g (64%); NMR ($CDCl_3$) δ=1.03 (3H, t, J=7 Hz), 1.7—2.0 (4H, m), 2.8—3.1 (4H, m), 3.98 (2H, q, J=7 Hz), and 7.3—7.7 (5H, m); IR (neat) 1710 and 1045 cm^{-1}; MS m/z 278 (M^+). Found: C, 64.92; H, 6.61%. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52%.

Ethyl 2-Cyclohexylidene-2-phenylsulfinylacetate (6b). Similar treatment of cyclohexanone with lithium enolate of **12a**, followed by elimination and oxidation procedures as described above, yielded **6b** as a colorless liquid; overall yield 27%; NMR ($CDCl_3$) δ=1.02 (3H, t, J=7 Hz), 1.5—2.0 (6H, m), 2.3—2.9 (4H, m), 3.92 (2H, q, J=7 Hz), and 7.3—7.7 (5H, m); IR (neat) 1720 and 1047 cm^{-1}; MS m/z 292 (M^+). Found: C, 65.93; H, 6.91%. Calcd for $C_{16}H_{20}O_3S$: C, 65.72; H, 6.89%.

General Pyrolysis of Ethyl 2-Phenylsulfinyl-2-alkenoates (2). A mixture of **2** (10 mmol) and anhydrous K_2CO_3 (12 mmol) in xylene was refluxed while the reaction was monitored by TLC and GLPC. The reaction completed after 4 h in the cases of *E*-**2a—f** and *Z*-**2a**, but *E*-**2g** remained unreacted after 15 h. After cooling K_2CO_3 and xylene were removed by filtration and evaporation. The residue was separated through silica-gel column chromatography with a hexane-benzene mixture (v/v=1/1) and then chloroform to afforded **1** and **4**.[21] The ratio of (2*E*,4*E*)/(2*E*,4*Z*)+(2*Z*,4*E*)+(2*Z*,4*Z*) was determined by GLPC analysis using a capillary column. The configuration of **1** was determined by comparison of NMR spectra of authentic **1a** (=**1b**), **1c**[30], and **1d** (=**1e**).[31,32] Physical data of **1e** and **1g** are as follows.

Ethyl (2E,4E)-2,4-Dodecadienoate (1f): Colorless liquid; NMR(CCl_4) δ=0.88 (3H, t, J=7 Hz), 1.25 (3H, t, J=7 Hz), 1.0—1.7 (10H, m) 2.0—2.4 (2H, m), 4.07 (2H, q, J=7 Hz), 5.64 (1H, d, J=15 Hz), 5.8—6.3 (2H, m), and 7.0—7.4 (1H, m); IR (neat) 1720, 1640, and 1620 cm^{-1}; MS m/z 224 (M^+). Found: C, 74.90; H, 10.71%; Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78%.

Ethyl (2E)-3-(1-Cyclohexenyl)-2-propenoate (1g): Colorless liquid; NMR (CCl_4) δ=1.25 (3H, t, J=7 Hz), 1.4—2.4 (8H, br), 4.07 (2H, q, J=7 Hz), 5.58 (1H, d, J=15 Hz), 5.23 (1H, m), and 7.1—7.6 (1H, m); IR (neat) 1720 and 1630 cm^{-1}; MS m/z 180 (M^+). Found: C, 73.35; H, 9.03%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

Pyrolysis of Ethyl 2-Cyclopentylidene-2-phenylsulfinylacetate (6a). A mixture of **6a** (1.39 g, 5 mmol) and anhydrous K_2CO_3 (0.83 g, 6 mmol) in xylene (6 ml) was refluxed monitoring with TLC and GLPC. The reaction was completed within 20 min. After removal of K_2CO_3 and xylene chromatograpy on silica gel with hexane-benzene (v/v=1/1) as an eluent gave ethyl 2-(2-cyclopentenylidene)acetate (**7a**) as a colorless liquid; yield 0.45 g (59%); *E*/*Z*=54/46; NMR ($CDCl_3$) δ=1.27 (3H, t, J=7 Hz), 2.4—3.1 (4H, m), 4.13 (2H, t, J=7 Hz), 5.56 (s, =CHCO, *Z*-isomer), 5.70 (s, =CHCO, *E*-isomer), and 6.1—6.7 (2H, m); IR (neat) 1700 cm^{-1}; MS m/z 152 (M^+). Found: C, 71.23; H, 7.92%. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95%.

Pyrolysis of Ethyl 2-Cyclohexylidene-2-phenylsulfinylacetate (6b). A mixture of **6b** and anhydrous K_2CO_3 was similarly refluxed for 1 h. Chromatography on silica gel with hexane-benzene as an eluent afforded ethyl 2-(2-cyclohexenylidene)acetate (**7b**) as a colorless liquid; yield 51%; *E*/*Z*=51/49; NMR ($CDCl_3$) δ=1.24 (3H, t, J=7 Hz), 1.5—1.9 (2H, m), 2.1—2.5 (3H, m), 2.8—3.0 (1H, m), 4.11 (2H, q, J=7 Hz), 5.41 (s, =CHCO, *Z*-isomer), 5.50 (s, =CHCO, *E*-isomer), and 5.9—6.3 (2H, m); IR (neat) 1705 cm^{-1}; MS m/z 166 (M^+). Found: C, 72.45; H, 8.51%. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%.

Oxidation of Ethyl 2-(1-Cyclopentenyl)-2-(phenylthio)acetate (15a). To a stirred solution of **15a**[20] (2.62 g, 10 mmol) in dichloromethane (100 ml) was added dropwise a solution of *m*-chloroperbenzoic acid (2.37 g, 11 mmol) in dichloromethane (50 ml) at 0 °C, and the resultant mixture was stirred for 30 min at 0 °C. During the oxidation ethyl (2*E*)-2-(2-hydroxycyclopentylidene)acetate (**16a**) and diphenyldisulfide were gradually formed (TLC and GLPC). The reaction mixture was neutralized with aq $NaHCO_3$, washed with aq saturated NaCl, and dried over anhydrous Na_2SO_4. After evaporation of the solvent the residue was chromatographed on a silica-gel column successively using hexane-benzene (v/v=2/1), benzene and chloroform to give diphenyldisulfide (0.32 g), *S*-phenyl benzenethiosulfonate (*ca.* 0.1 g), **15a** (1.23 g, 47% recovery), **16a** (0.76 g, 45%), and some unidentified compounds. **16a**: colorless liquid; NMR ($CDCl_3$) δ=1.1—2.2 (4H, m), 1.24 (3H, t), 2.6—3.0 (2H, m), 3.8 (1H, s), 4.10 (2H, q), 4.51 (1H, m), and 5.93 (1H, q, J=2 Hz).[20]

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