Oxidation of 2,4-Alkadienoic Esters with Selenium Dioxide. A New Synthesis of Furans and Selenophenes

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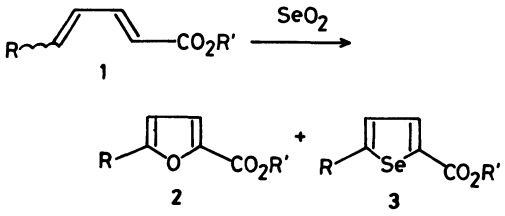
Direct oxidation of 2,4-alkadienoic esters with selenium dioxide gave 5-alkyl-2-furancarboxylic esters along with 5-alkyl-2-selenophenecarboxylic esters. Ethyl 5-methylfurancarboxylate was converted to 5-hydroxymethyl-2-furancarbaldehyde, a component of honey, via ethyl 5-bromomethyl-2-furancarboxylate (**5**) in good yield. The compound **5** was converted to (5-ethoxycarbonyl-2-furyl)methyl dimethyldithiocarbamate possessing fungicidal activity. Reaction of triphenylphosphonium salt of **5** with nonanal gave ethyl 5-(1-decenyl)-2-furancarboxylate (E/Z=88:12) in 86% yield. Ethyl 5-methyl-2-selenophenecarboxylate was also converted to ethyl 5-(1-decenyl)-2-selenophenecarboxylate (E/Z=7:3) in 30% total yield.

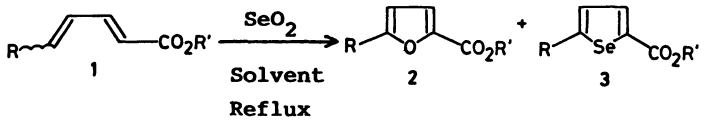
Selenium dioxide is a conventional and useful reagent for the oxidation of olefins to α,β-unsaturated ketones and allylic alcohols.[1] As our continuing interest in the chemistry of 2,4-alkadienoic esters **1**,[2] we carried out the oxidation of **1** with selenium dioxide.[3] Here we describe a novel synthesis of furans **2** and selenophenes **3** via the oxidation of **1** with selenium dioxide, as summarized below.



Oxidation of α,β-unsaturated carboxylic acids with SeO_2 gave a γ-acetoxy derivative[4] and an α,β-unsaturated γ-butyrolactone derivative.[5] However, oxidation of conjugated dienoic esters with SeO_2 is little known. Only the oxidation of methyl 3-(2,6,6-trimethyl-2-cyclohexenyl)-1-methyl-2-propenylideneacetate with SeO_2 in ethanol to give the corresponding 1- and 4-hydroxy-cyclohexenyl derivatives is reported.[6] Recently we reported a convenient synthesis of (2*E*,4*Z*)-alkadienoic esters.[2a,b] For its application to the syntheses of natural products, we oxidized some 2,4-alkadienoic esters **1** with SeO_2.

Oxidation of commercially available methyl (2*E*,4*E*)-2,4-hexadienoate (sorbate) (**1a**) with SeO_2 gave unexpectedly a mixture of methyl 5-methyl-2-furancarboxylate (**2a**) (56%) and methyl 5-methyl-2-selenophenecarboxylate (**3a**) (29%). Any trace amount of 6-hydroxy- or 6-oxosorbates which were expected to be produced could not be detected. To generalize the present synthesis, various kinds of 2,4-alkadienoic esters were oxidized with SeO_2 and the results are summarized in Table 1. Methyl (2*E*,4*Z*)-hexadienoate (**1b**) was also oxidized with SeO_2, giving an 1:1

Table 1. Oxidation of **1** with SeO_2



Run	1[a]			SeO_2 (equiv)	Solvent	Reaction Time	Yield/%[b] of Products			
							2		3	
	No.	R	R′			h	No.	Yield	No.	Yield
(1)	**1a**	CH_3	CH_3	1.1	Benzene	5	**2a**	56	**3a**	29
(2)	**1b**	CH_3	CH_3	1.1	Benzene	0.5	**2a**	46	**3a**	48
(3)	**1c**	CH_3	C_2H_5	1.5	Bromobenzene	2	**2b**	37	**3b**	5
(4)	**1d**	n-C_3H_7	CH_3	1.0	Xylene	6	**2c**	57	**3c**	29
(5)	**1e**	n-C_3H_7	C_2H_5	1.5	Xylene	2	**2d**	58	**3d**	15
(6)	**1e**	n-C_3H_7	C_2H_5	2.2	DME	6.5	**2d**	22[c]	**3d**	9[c]
(7)	**1f**	$(CH_3)_2CH$	C_2H_5	1.1	Xylene	1.5	**2e**	45	**3e**	2
(8)	**1g**	n-C_5H_{11}	C_2H_5	3.0	Xylene	26	**2f**	17[c]	**3f**	6[c]

a) Geometries of **1a** and **1c** are (2*E*,4*E*), and those of others are (2*E*,4*Z*). b) Unless otherwise indicated, determined by ^1H NMR analysis after removal of polymerized products by short-path distillation or short column chromatography. c) Isolated yield.

mixture of **2a** and **3a** in good yields. Although the oxidation of ethyl (2*E*,4*Z*)-octadienoate (**1d**) with SeO_2 afforded furan **2c** (57%) and selenophene **3c** (29%), the yield in that of alkadienoates bearing a longer chain such as **1g** decreased.

Oxidations of **1a** with SeO_2 under various reaction conditions were conducted to optimize the yields, and the results were tabulated in Tables 2 and 3. Oxidation with 1—2 equiv of SeO_2 gave the best result. Most of the reaction gave the furan **2a** as a major product. However, the reaction in acetic acid afforded an 1:1 mixture of **2a** and **3a**.

Table 2. Oxidation of **1a** with a Various Amount of SeO_2[a]

Run	SeO_2 (equiv)	Yield/%[b] of Product	
		2a	**3a**
1	0.5	3[c]	0
2	1	60	20
3	2	52	30
4	5	13[d]	3[d]

a) Conducted in benzene at the reflux temperature for 6.5 h. b) Calculated by GLC analysis after purification by flash column chromatography. c) Starting material (**1a**) was recovered. d) Resinous materials were produced.

Table 3. Oxidation of **1a** with SeO_2 in Various Solvents[a]

Solvents	Reaction Time/h	Yield/%[b] of Products	
		2a	**3a**
Xylene	2.5	62	15
Toluene	4	56	8
Dioxane	4	50	25
Ethanol	1	66	2.4
Acetic Acid	4	32	32

a) SeO_2 (1.1 equiv) was used. b) Calculated by ^1H NMR analysis of a reaction mixture.

Structural determination was carried out on the basis of IR, NMR, and elemental analysis which were tabulated in Tables 4 and 5. IR spectra of furancarboxylates **2** showed characteristic absorptions at 1520, 1536, and 1600 cm^{-1}. On the other hand, IR spectra of selenophenecarboxylates **3** exhibited signals due to a selenophene ring at 1550, 1616, and 1640 cm^{-1}. Proton NMR spectra of **2a** showed two singlets at δ 2.36 and 3.78 and two doublets (J=3.2 Hz) at δ 6.00 and 6.92. Signals due to ring protons of selenophene **3** appeared at ca. δ 6.8 and 7.7 as two doublets (J= 3.7 Hz). Mass spectrum of **3a** showed characteristic signals of a selenium compound at m/z 204, 202, and 200.

To examine the synthetic utility of the product obtained by the present method, some chemical conversions of **2b** and **3b** were conducted representatively. Many natural products possessing 2,5-disubstituted furan rings have been reported.[7] The present synthesis will be useful for these compounds. For example, **2b** was successfully converted to 5-hydroxymethyl-2-furancarbaldehyde (**4**), a component of honey.[7a] The synthetic sequence are shown in Scheme 1. Furan **2b** was brominated with NBS to give ethyl 5-bromomethyl-2-furancarboxylate (**5**) in 85% yield which was subsequently hydrolyzed with aqueous $AgNO_3$ to ethyl 5-hydroxymethyl-2-furancarboxylate (**6**). After the alcohol **6** was converted to tetrahydropyranyl (THP) ether **7**, reduction of the latter with $LiAlH_4$ followed by oxidation with MnO_2 gave aldehyde **9** in good yield. Deprotection of THP

Table 4. Spectral Data of **2**

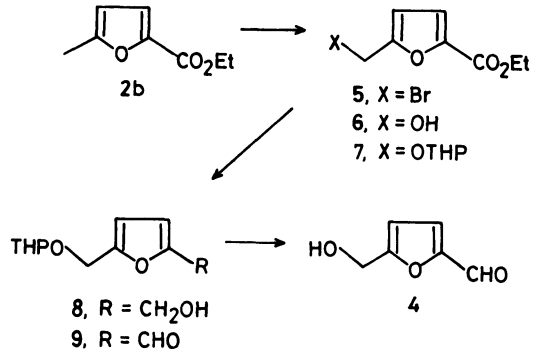
Compd	IR/cm^{-1}	^1H NMR (δ, CCl_4)
2a[a]	1730, 1600, 1520, 1536	2.35(s, 3H), 3.77(s, 3H), 6.0(d, 3H, J=4 Hz), 6.90(d, 1H, J=4 Hz)
2b[a]	1720, 1600, 1539, 1521, 1020, 760	1.32(t, 3H, J=7 Hz), 2.35(s, 3H), 4.23(q, 2H, J=7 Hz), 6.02(d, 1H, J=3.2 Hz), 6.92(d, 1H, J=3.2 Hz)
2c[b]	1720, 1596, 1530, 1519, 1018, 756	0.98(t, 3H, J=7 Hz), 1.38—2.05(m, 2H), 2.66(t, 2H, J=7 Hz), 3.77 (s, 3H), 6.02(d, 1H, J=3.2 Hz), 6.92(d, 1H, J=3.2 Hz)
2d[b]	1720, 1600, 1535, 1520, 1018, 760	1.00(t, 3H, J=7 Hz), 1.35(t, 3H, J=7 Hz), 1.3—2.1(m, 2H), 2.65 (t, 2H, J=7 Hz), 4.28(q, 2H, J=7 Hz), 6.0(d, 1H, J=3.2 Hz), 6.92 (d, 1H, J=3.2 Hz)
2e[b]	1720, 1601, 1535, 1520, 1300, 1140	1.34(d, 6H, J=6.5 Hz), 1.37(t, 3H, J=6.5 Hz), 1.9—2.5(m, 1H), 4.25(q, 2H, J=6.5 Hz), 5.96(d, 1H, J=3.2 Hz), 6.90(d, 1H, J= 3.2 Hz)
2f[c]	1720, 1595, 1520, 1300, 1015, 760	0.93(t, 3H, J=6 Hz), 1.36(t, 3H, J=6.5 Hz), 1.2—2.1(m, 6H), 2.67 (t, 2H, J=7 Hz), 4.26(q, 2H, J=6.5 Hz), 6.00(d, 1H, J=3.2 Hz), 6.90(d, 1H, J=3.2 Hz)

a) Known compound; see Ref. 13. b) The corresponding acid is known; see Ref. 14. c) The corresponding methyl ester is known; see Ref. 15.

Table 5. Spectral and Analytical Data of **3**

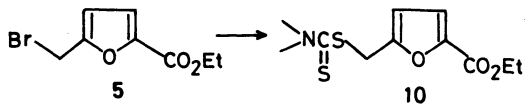
Compd	IR/cm^{-1}	^{1}H NMR (δ, CCl_4)	Formula	Found (Required) C	H
3a[a]	1705, 1555, 1280, 1260, 1080, 740	2.58(s, 3H), 3.78(s, 3H), 6.83(d, 1H, J=3.7 Hz), 7.69(d, 1H, J=3.7 Hz)			
3b[a]	1720, 1560, 1280, 1265, 1080, 760	1.32(t, 3H, J=7 Hz), 2.55(s, 3H), 4.22(q, 2H, J=7 Hz), 6.81(d, 1H, J=3.7 Hz), 7.63 (d, 1H, J=3.7 Hz)			
3c	1710, 1550, 1275, 1260, 1082, 740	1.00(t, 3H, J=7 Hz), 1.3—2.0(m, 2H), 2.83(t, 2H, J=7 Hz), 3.77(s, 3H), 6.86(d, 1H, J=3.7 Hz), 7.74(d, 1H, J=3.7 Hz)	$C_9H_{12}O_2Se$	46.83 (46.77	5.45 5.23)
3d	1705, 1550, 1260, 1470, 1080, 740	1.00(t, 3H, J=6.5 Hz), 1.32(t, 3H, J=7 Hz), 1.4—2.1(m, 2H), 2.82(t, 2H, J=7 Hz), 3.63(s, 3H), 4.20(q, 2H, J=7 Hz), 6.82(d, 1H, J=3.7 Hz), 7.66(d, 1H, J=3.7 Hz)	$C_{10}H_{14}O_2Se$	49.03 (48.99	5.96 5.75)
3f	1705, 1550, 1270, 1270, 1080, 740	0.90(br t, 3H, J=6.5 Hz), 1.32(t, 3H, J=7 Hz), 1.1—2.0(m, 6H), 2.80(t, 2H, J=6 Hz), 4.20(q, 2H, J=6.5 Hz), 6.82(d, 1H, J=3.7 Hz), 7.65(d, 1H, J=3.7 Hz)	$C_{12}H_{18}O_2Se$	52.58 (52.75	6.79 6.64)

a) Known compound although spectral data are not reported; see Ref. 11.

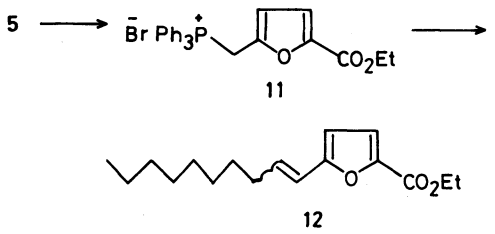


Scheme 1.

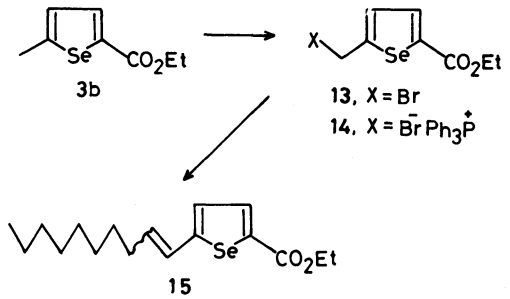
ether **9** with pyridinium *p*-toluenesufonate (PPTS) provided **4**[7a] in 21% yield from **7**. Pianka[8] has reported (5-ethoxycarbonyl-2-furyl)methyl dimethyldithiocarbamate (**10**) showed fungicidal activity. We prepared **10** in 65% yield by the reaction of **5** with sodium dimethyldithiocarbamate.



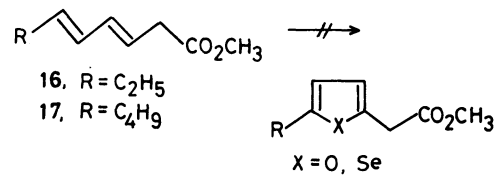
Furthermore, the bromide **5** was treated with triphenylphosphine to afford phosphonium salt **11**. The Wittig reaction of **11** with nonanal in the presence of butyllithium gave ethyl 5-(1-decenyl)-2-furancarboxylate (**12**) in 86% yield with the geometry of E/Z (88:12). Similarly, selenophenecarboxylate **3b** was also brominated with NBS to give bromide **13** in 71% yield. Reaction of **13** with triphenylphosphine



yielded triphenyl phosphonium salt **14**. Reaction of **14** with nonanal in the presence of butyllithium gave ethyl 5-(1-decenyl)-2-selenophenecarboxylate (**15**) in 85% yield with the geometry of E/Z (7:3).

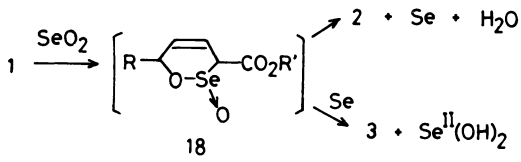


On the other hand, similar treatment of 3,5-alkadienoates such as methyl (3*E*,5*E*)-3,5-octadienoate (**16**) and methyl (3*E*,5*E*)-3,5-decadienoate (**17**) with



SeO_2 resulted in the recovery of the starting material. This fact shows that conjugated system between a diene and an ester group is required for the formation of furan and selenophene rings.

Although the accurate mechanism of the present reaction can not be clarified, the formation of **2** and **3** can be explained by the assumption of an intermediate **18** which is similar to the adduct of butadiene derivatives with SeO_2.[9] Thermal decomposition of **18** will give **2** along with selenium and water, and the reduction of **18** with selenium will give **3** and selenium(II) dihydroxide.



To our knowledge, syntheses of furans via the oxidation of alkadienes are quite few. Parthasarathy and Hort[10] reported the oxidative dehydrogenation of butadiene in the presence of silver ion to yield furan. But their methods required drastic conditions (258 °C[10a], 483 °C[10b]) and special techniques to control the reaction (4 second reaction[10a]). In particular, no reference was found on the use of selenium dioxide for furan synthesis from 2,4-alkadienoates **1**. The present method provides straightforwardly furans and selenophenes under comparatively mild conditions, and the simplicity makes it considerably attractive. Noteworthy is that this procedure for the synthesis of 5-methyl-2-selenophenecarboxylate is simpler than the previously reported one.[11]

Experimental

The melting and boiling points are uncorrected. Infrared (IR) spectra were obtained with a JASCO Model A-102 infrared spectrophotometer. ^1H NMR spectra (60 MHz) were recorded with a JEOL JNM-PMX60SI apparatus. ^1H NMR (100 MHz) and ^{13}C NMR spectra (25 MHz) were obtained with a JEOL JNM-FX100 apparatus using $CDCl_3$ as a solvent. All chemical shifts are reported in δ units downfield from internal Me_4Si, and J values are given in herz. Mass spectra were obtained with an ESCO EMD-05B apparatus. Column chromatography was accomplished using 100—200 mesh Wakogel C-200. Analytical determinations by GLC were performed on a Hitachi Model 163 gas chromatograph fitted with 10% Silicone SE-30 on Chromosorb W column (3 mm o.d.×1 m). Preparative GLC was performed on a Yanagimoto Model G-80 gas chromatogaph fitted with 10% Apiezone Grease L on Chromosorb W column (3 mm o.d.×1 m). High-performance liquid chromatography (HPLC) was obtained with a Yanagimoto liquid chromatograph L-2000.

All solvents and reagents were reagent grade, and solvents were dried according to the literature procedures.[12] Methyl sorbate and ethyl sorbate were distilled prior to use. Methyl (or ethyl) (2*E*,4*Z*)-2,4-alkadienoates (**1b** and **1d—g**) were prepared by the procedure reported previously.[2a,b]

Oxidation of 1 with SeO_2. The reaction was carried out under nitrogen at the reflux temperature of the solvent as shown in Table 1 until the starting material was consumed. The crude product was purified by column chromatography or preparative TLC. Spectral data and elemental analyses of **2**[13-15] and **3** are shown in Tables **4** and **5**. Representative procedures are detailed below.

Methyl 5-Methy-2-furancarboxylate (2a) and Methyl 5-Methyl-2-selenophenecarboxylate (3a). A mixture of **1a** (2 g, 15.9 mmol), SeO_2 (1.94 g, 17.5 mmol), and benzene (1 ml) was heated under reflux for 5 h with stirring. After filtration, the solvent was removed in vacuo. The residual oil was chromatographed on SiO_2 (hexane–ethyl acetate, 20:1) to give 2.18 g of a mixture of **2a**[13] (56% yield) and **3a** (29% yield) as an oil; **2a**/**3a** =57:43 by ^1H NMR analysis. Preparative TLC (SiO_2, hexane–ethyl acetate (4:1)) gave analytical samples, **2a** (R_f=0.52) and **3a** (R_f=0.61). Spectral and analytical data were shown in Tables 4 and 5.

Ethyl 5-Propyl-2-furancarboxylate (2d) and Ethyl 5-Propyl-2-selenophenecarboxylate (3d). A mixture of **1e** (0.10 g, 0.60 mmol), SeO_2 (0.1 g, 0.9 mmol), and xylene (0.5 ml) was heated under reflux for 2 h. The mixture was filtered off, and the solvent was removed in vacuo to give a brown oil. Flash column chromatography [SiO_2, hexane–ethyl acetate (4:1)] gave 85.3 mg of a mixture of **2d** (58%) and **3d** (15%) as an oil; **2d**/**3d**=74/26 by ^1H NMR analysis. Medium pressure liquid chromatography [SiO_2, hexane–ethyl acetate (4:1)] gave pure **2d** and **3d**: TLC analysis (SiO_2, hexane–ethyl acetate=4:1), **2d** (R_f=0.55) and **3d** (R_f=0.60).

Ethyl 5-Pentyl-2-furancarboxylate (2f) and Ethyl 5-Pentyl-2-selenophenecarboxylate (3f). A mixture of **1g** (1.0 g, 5.1 mmol), SeO_2 (0.85 g, 7.6 mmol), and xylene (10 ml) was heated under reflux for 20 h. After being mixed with celite, the mixture was filtered and the filtrate was concentrated in vacuo. The crude products were purified by column chromatography [SiO_2, hexane–ethyl acetate (30:1—0:1)] to give 0.179 g (17%) of **2f** and 43 mg (6.0%) of **3f**. Spectral and analytical data are shown in Tables 4 and 5.

Ethyl 5-Bromomethyl-2-furancarboxylate (5).[16] A mixture of **2b** (1.2 g, 7.8 mmol), NBS (1.52 g, 8.6 mmol), carbon tetrachloride (12 ml), and benzoyl peroxide (50 mg) was heated at the reflux temperature for 2 h. After filtration, the filtrate was concentrated to give 1.9 g of crude **5** which was distilled with a bulb-to-bulb distillation apparatus to afford 1.70 g (94%) of **5**:[16] Bp 120—140 °C (bath temp)/2 Torr (1 Torr=133.322 Pa); IR (neat)1720, 1590, 1535, 1520, 1300, 1221, 1145, 1020, 760 cm^{-}; ^1H NMR data were consistent with those reported.[16]

Ethyl 5-Hydroxymethyl-2-furancarboxylate (6).[17] To a mixture of **5** (0.15 g, 0.65 mmol), acetone (2.5 ml), and water (2.5 ml) was added $AgNO_3$ (0.267 g, 1.7 mmol). The mixture was stirred for 6 h at 22 °C, and then organic materials were extracted with ether. The combined extracts were washed with water, dried over $MgSO_4$ and concentrated. The crude product (111 mg) was purified by preparative TLC [SiO_2, hexane–ethyl acetate (2:1)] to give 33 mg (30%) of **6**:[17] R_f=0.13; IR (neat) 3500, 1730, 1600, 1550, 1540, 1320, 1225, 1160, 1038, 780 cm^{-1}; ^1H NMR (CCl_4) δ=1.35 (t, 3H, $CO_2CH_2C\underline{H}_3$), 3.50 (br s, 1H, OH), 4.25 (q, 2H, J=7 Hz, $CO_2C\underline{H}_2CH_3$), 4.55 (s, 2H, $C\underline{H}_2OH$), 6.30 (d, 1H, J=3.2 Hz,

=CHCH=CCO$_2$Et), 7.00 (d, 1H, J=3.2 Hz, CH=CCO$_2$Et).

Ethyl 5-Hydroxymethyl-2-furancarboxylate THP Ether (7). To a solution of **6** (64 mg, 0.38 mmol) and 3,4-dihydro-2*H*-pyran (34 mg, 0.4 mmol) in 0.2 ml of ether was added a catalytic amount of *p*-toluenesulfonic acid. The mixture was stirred for 90 min at room temperature, and then neutralized with NaHCO$_3$. After the mixture was filtered, washed with ether, and the filtrate was concentrated to give 74 mg (84%) of **7:** IR (neat) 1730, 1600, 1535, 1520, 1300, 1205, 1130, 1020 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.37 (t, 3H, J=7 Hz $CO_2CH_2CH_3$), 1.65 (br s, 6H, $3CH_3$), 3.55 (m, 2H, OCH_2), 4.28 (q, 2H, J=7 Hz, $CO_2CH_2CH_3$), 4.53 (d, 2H, J=3.5 Hz, THPOCH$_2$), 4.68 (m, 1H, >CHO), 6.33 (d, 2H, J=3.2 Hz, CHCH=C-CO$_2$Et), 7.00 (d, 2H, J=3.2 Hz, CH=C-CO$_2$Et).

2,5-Bis(hydroxymethyl)furan MonoTHP Ether (8). To a mixture of $LiAlH_4$ (11.4 mg, 0.30 mmol) and dry ether (2 ml) was added at −40 °C a solution of **7** (73 mg, 0.29 mmol) in 0.5 ml of dry ether. The mixture was stirred for 1 h at −40 °C. The mixture was worked up as shown in **6**, giving 52.8 mg (93%) of **8:** IR (neat) 3450, 1560, 1260, 1120, 1020, 800 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.0—2.0 (m, 6H, $3CH_2$), 3.0 (br s, 1H, OH), 3.5 (m, 2H, OCH_2CH_2), 4.38 (s, 2H, OCH_2), 4.45 (s, 2H, OCH_2C=), 4.61 (s, 1H, OCHO), 6.10 (s, 2H, 2CH=).

5-Hydroxymethyl-2-furancarbaldehyde THP Ether (9). To a mixture of activated MnO_2 (226 mg, 2.6 mmol), petroleum ether (2 ml), and diethyl ether (1 ml) was added a solution of **8** (50 mg, 0.26 mmol) in 1 ml of ether at room temperature. The mixture was stirred for 7d at room temperature and the organic materials were extracted with ether. The combined extract was washed with water, dried over $MgSO_4$. Removal of the solvent gave 70 mg of crude **9:** IR (neat) 1680, 1660, 1530, 1260, 1155, 1020, 965, 900, 815 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.6 (br s, 6H, $3CH_2$), 3.55 (m, 2H, CH_2O), 4.56 (d, 2H, J=3.5 Hz, OCH_2C=), 4.65 (m, 1H, OCHO), 6.41 (d, 2H, J=3.2 Hz, =CHCH=C-CHO), 7.10 (d, 2H, J=3.2 Hz, CH=C-CHO), 9.64 (s, 1H, CHO). Crude **9** was used for the next step without further purification.

5-Hydroxymethyl-2-furancarbaldehyde (4).[7a] To a solution of pyridinium *p*-toluenesulfonate[18] (6.6 mg, 0.03 mmol) in ethanol (1 ml) was added 70 mg (0.33 mmol) of crude **9**, and the mixture was stirred for 12 h at 55 °C. After removing the solvent, the residual oil (57 mg) was purified by preparative TLC [SiO_2, hexane–ethyl acetate (2:1)] to give 10 mg (21% yield from **6**) of **4:**[7a] IR (neat) 3440, 1680, 1530, 1195, 1020, 810, 780 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.66 (br s, 1H, OH), 4.77 (s, 2H, CH_2OH), 6.55 (d, 1H, J=3.2 Hz, CHCH=CCHO), 7.25 (d, 1H, J=3.2 Hz), 9.60 (s, 1H, CHO).

(5-Ethoxycarbonyl-2-furyl)methyl Dimethyldithiocarbamate (10).[8] To a solution of sodium dimethyldithiocarbamate (170 mg, 1.2 mmol) in methanol (2 ml) was added **5** (200 mg, 1.08 mol) at 0 °C with stirring. The mixture was stirred for 20 h at room temperature, and then poured into water. The organic materials were extracted with water, and dried over $MgSO_4$. Removal of the solvent gave 250 mg of crude **10**, which was purified by preparative TLC [SiO_2, hexane–ethyl acetate (4:1)] to yield 192 mg (65%) of **10:**[8] R_f=0.23; IR (neat) 1720, 1595, 1520, 1380, 1300, 1150, 1020, 980, 760 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.35 (t, 3H, J=7 Hz, $CO_2CH_2CH_3$), 3.43 (s, 6H, $N(CH_3)_2$), 4.26 (q, 2H, J=7 Hz, $CO_2CH_2CH_3$), 4.58 (s, 2H, SCH_2), 6.39 (d, 1H, J=3.2 Hz, =CHCH=C-CO$_2$Et), 6.96 (d, 1H, J=3.2 Hz, CH=CO$_2$Et).

(5-Ethoxycarbonyl-2-furylmethyl)triphenylphosphonium Bromide (11). A mixture of triphenylphosphine (310 mg, 1.18 mmol), **5** (200 mg, 1.08 mmol), and benzene (2 ml) was stirred for 25 h at room temperature, and then filtered, washed with benzene, and dried in vacuo, giving 370 mg (74%) of **11**: Mp 194.5—195 °C; IR (KBr) 3450, 2900—2800, 1710, 1590, 1530, 1340, 1240, 1140, 760 cm^{-1}.

Ethyl 5-(1-Decenyl-2-furancarboxylate (12). To a solution of **11** (120 mg, 0.242 mmol) in dry THF (2 ml) was added dropwise 1.5 M† *n*-BuLi (0.162 ml, 0.242 mmol) at 0 °C with stirring under an atmosphere of nitrogen. After 30 min, nonanal (35 mg, 0.242 mmol) was added dropwise over 10 min, and the mixture was stirred for 30 min at 0 °C and for 4 h at room temperature. After being poured into ice water, the mixture was neutralized with dil HCl. The organic materials were extracted with ether, and the ethereal layer was washed with water, dried over $MgSO_4$, and concentrated. The residual oil (180 mg) was chromatographed on SiO_2 (hexane–ethyl acetate=40:1—0:1) to give 58 mg (86%) of **12:** IR (neat) 1730, 1650, 1580, 1500, 1380, 1300, 1200, 1010, 960, 760 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.7—1.6 (m, 18H, $CH_3(CH_2)_6$ and $CO_2CH_2CH_3$), 2.20 (m, 2H, CH_2CH=CH), 4.28 (q, 2H, J=7 Hz, $CO_2CH_2CH_3$), 6.12 (d, 1H, J=3.2 Hz, CHCH=C-CO$_2$Et), 6.97 (d, 1H, J=3.2 Hz, CH=C-CO$_2$Et). Found: C, 73.43; H, 9.56%. Calcd for $C_{17}H_{26}O_3$: C, 73.35; H, 9.41%. HPLC analysis [column, Unisil Q (10.7 mm o.d.×250 mm); eluent, hexane–ethyl acetate (20:1), 2.0 ml min^{-1}] showed two peaks at R_t17.6 and 20.2 min in an intensity ratio of 12:88. Each component was separated by preparative HPLC. The first fraction gave 5 mg of (*Z*)-**12:** IR (neat) 1730, 1720, 1640, 1502, 1300, 1020, 760 cm^1; ^{1}H NMR (CCl_4) δ=0.86 (t, 3H, J=5.5 Hz, CH_3), 1.28 (br s, 14H, $(CH_2)_7$), 1.32 (t, 3H, J=7 Hz, $CO_2CH_2CH_3$), 2.45 (m, 2H, CH_2CH=CH), 4.22 (q, 2H, J=7 Hz, $CO_2CH_2CH_3$), 5.61 (td, 1H, J=6.3 and 11.0 Hz, CH_2CH=CH), 6.12 (d, 1H, J=11.0 Hz, CH=CH-furyl) 6.14 (d, 1H, J=3 Hz, CH=C-CO$_2$Et), 6.98 (d, 1H, J=3 Hz, =CH=C-CO$_2$Et), 6.98 (d, 1H, J=3 Hz, =CH-CH=C-CO$_2$Et). The second fraction gave 35 mg of (*E*)-**12:** IR (neat) 1730, 1720, 1660, 1580, 1505, 1300, 1022, 1110, 968, 770 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.89 (t, 3H, J=5 Hz, CH_3), 1.30 (br s, 14H, $(CH_2)_7$), 1.32 (t, 3H, J=6 Hz, $CO_2CH_2CH_3$), 2.15 (m 2H, CH_2CH=CH), 4.22 (q, 2H, J=8 Hz, $CO_2CH_2CH_3$), 6.03 (d, 1H, J=15 Hz, CH=C-CO$_2$Et), 6.42 (dt, 1H, J=5 and 15 Hz, CH_2CH=CH-), 6.08 (d, 1H, J=3 Hz, =CH-CH=C-CO$_2$Et), 6.93 (d, 1H, J=3 Hz, CH=C-CO$_2$Et).

Ethyl 5-Bromomethyl-2-selenophenecarboxylate (13). A mixed solution of **3b** (300 mg, 1.4 mmol), NBS (274 mg, 1.5 mmol), a catalytic amount of benzoyl peroxide and CCl_4 (3 ml) was heated under reflux for 10 h. The mixture was cooled and the precipitates were filtered off. Concentration of the filtrate gave 510 mg of crude products, which were purified by preparative TLC [SiO_2, hexane–ethyl acetate (4:1)] giving 90 mg of **3b** (R_f=0.59) and 290 mg (71%) of **13:** R_f=0.53; IR (neat) 1710, 1550, 1470, 1330, 1220, 1100, 1030, 1000, 750 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.35 (t, 3H, J=7 Hz, $CO_2CH_2CH_3$), 4.27 (q, 2H, J=7 Hz, $CO_2CH_2CH_3$), 4.67 (s, 2H, CH_2Br), 7.18 (d, 1H, J=3.7 Hz, =CHCH=C-CO$_2$Et), 7.74 (d, 1H, J=3.7 Hz, CH=C-CO$_2$Et). Found: C, 32.55; H, 3.18%. Calcd for $C_8H_9BrO_2Se$: C, 32.46; H, 3.06%.

† 1 M=1 mol dm^{-3}.

(5-Ethoxycarbonyl-2-selenophenylmethyl)triphenylphosphonium Bromide (14). A mixture of **13** (200 mg, 0.86 mmol), triphenylphosphine (247 mg, 0.95 mmol), and benzene (2 ml) was heated at the reflux temperature for 20 h. The mixture was cooled and then filtered to afford 230 mg (50%) of **14** as white crystals: Mp 211—213 °C; IR (KBr) 1710, 1695, 1585, 1545, 1460, 1270, 1115, 1080, 745, 725 cm^{-1}.

Ethyl 5-(1-Decenyl)-2-selenophenecarboxylate (15). To a solution of **14** (190 mg, 0.34 mmol) in THF (2 ml), 1.5 M *n*-BuLi in hexane (0.20 ml, 0.34 mmol) was added at 0 °C. After 30 min nonanal (48 mg, 0.34 mmol) was added dropwise over 10 min, and the mixture was stirred for 30 min at 0 °C and for 6 h at room temperature and then worked up as shown in **12**, giving 180 mg of an oil. Preparative TLC [SiO_2, hexane–ethyl acetate(4:11)] gave 98 mg (85%) of **15:** R_f=0.62; E/Z=7:3; IR (neat) 1710, 1530, 1360, 1270, 1080, 945, 740 cm^{-1}; ^1H NMR (CCl_4) δ=0.7—0.8 (m, 18 Hz, (CH_2)$_6$$CH_3$ and $CO_2CH_2CH_3$), 2.20 (m, 2H, CH_2CH=CH), 4.24 (q, 2H, J=7 Hz, $CO_2CH_2CH_3$); 5.60 (dt, 0.3H, J=10 and 7Hz, CH_2CH=CH), 5.95 (dt, 0.7H,J=7 and 15 Hz, CH_2CH=CH), 6.42 (d, 0.7H, J=15 Hz, CH_2CH=CH), 6.48(d, 0.3H, J=10 Hz, CH_2CH=CH), 6.86 (d, 0.7 H, J=3.5 Hz CHCH=CCO_2Et), 6.98 (d, 0.3H, J=3.5 Hz, CHCH=C-CO_2), 7.68 (d, 0.7 H, J=3.5 Hz, CH=C-CO_2Et), 7.75 (d, 0.3H, J=3.5 Hz, CH=C-CO_2Me). Found: C, 59.61; H, 7.69%. Calcd for $C_{17}H_{26}O_2Se$: C, 59.82; H, 7.68%.

Treatment of Methyl (3*E*, 5*E*)-3,5-Octadienoate (16) with SeO_2. A mixture of **16** (49 mg, 0.32 mmol), SeO_2 (71 mg, 0.64 mmol), and xylene (2 ml) was heated under reflux for 3 h with stirring. After column chromatography [SiO_2, hexane–ethyl acetate(10:1)], the starting material **16** (30 mg) was recovered.

Treatment of Methyl (3*E*,5*E*)-3,5-Decadienoate (17) with SeO_2. A mixture of **17** (84 mg, 0.46 mmol), SeO_2 (102 mg, 0.92 mmol), and benzene (3 ml) was heated under reflux for 12 h with stirring. Column chromatography [SiO_2, hexane–ethyl acetate(10:1)] gave 52mg of the starting material **17**.

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