A New 1-Alkoxy-2-(chalcogeno)allylic or 1-Alkoxy-2,4-bis(chalcogeno)penta-2,4-dienyl Cation: Highly-Regioselective Allylating or Penta-2,4-dienylating Electrophiles and Their Reactions

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2-(Chalcogeno)-1-ethoxyallylic cations **4A** are easily generated from the reactions of 2-(chalcogeno)-1-ethoxyprop-1-en-3-ols **2a**−**e** or 2-(chalcogeno)prop-2-enal acetals **3a**−**c** and TMSOTf and reacted with various nucleophiles to give the adducts **5a**−**8a**, **5b**−**11b**, and **5c**−**e** regio and stereoselectively. 2,4-Bis(chalcogeno)penta-2,4-dienal acetals **16a**,**c** and the 2,4,6-tris(phenylthio)hepta-2,4,6-trienal acetal **20c** also gave the dienones **17a**,**c** and **21c** in good yields. Furthermore, the intramolecular cyclization of the alkenyl alcohols **25a**,**b** and the 2,4-dienal 2,4-dinitrophenyl hydrazones **29a**−**c** afforded the tetrahydrofurans **26a**,**b** and 3,5-bis(chalcogeno)pyridines **30a**−**c**, respectively.

Much attention has been paid to β-heteroatom-substituted allylic cations from both the synthetic and mechanistic points of view. In particular, β-oxyallylic cations are among the most practical of the allylic cations and are used for cycloaddition with alkenes or conjugate dienes, providing an important route to five- or seven-membered ring systems.[1] On the other hand, β-sulfur-[2] or β-selenium-stabilized allylic cations were investigated using the propenal diselenoacetals,[3] 2-selenopropenyl bromide, or the corresponding alcohols;[4] however, the regio- and stereoselectivities of their electrophilic addition reactions were not satisfactory. Furthermore, the product allylic selenides were obtained as a mixture of the [1,3] sigmatropic isomers.[5] It is very difficult to control the regioselectivity because it depends on the electrophilicity of the allylic cations and the substituent (α- and β-postion) on the electrophile. To control the regioselectivity, we planned to introduce an alkoxy group at the 1-position of the 2-chalcogene (2-sulfur or 2-selenium)-substituted allylic cations. Although 2-(chalcogeno)allylic cations are reported to be important for the contribution of the cyclic intermediate **4B**,[4a] high regioselectivities in the nucleophilic substitution reactions of 1-alkoxy-2-(chalcogeno) allylic cations **4A** would be expected for the reason that the reactivity of the α-alkoxy carbenium ion is higher than that of the sulfur or selenium analogue.[6] We selected the 1-ethoxy-2-(chalcogeno)prop-1-en-3-ols **2** and the 2-(chalcogeno)prop-2-enal acetals **3** as precursors for the allylic cations **4A**. Since the acid-promoted reactions of 1-alkoxy-2-(chalcogene)-substituted allylic cations with soft nucleophiles have not been reported, herein we wish to report their reactions with various nucleophiles and their application to the 2,4-bis(chalcogeno)penta-2,4-dienylation reactions.

The allylic alcohols **2** and prop-2-enal *O*,*O*-acetals **3** were prepared by our original method as shown in Scheme 1.[7] 2-Ethoxy-1-(phenylchalcogeno)ethenes **1** were treated with BuLi at −70 °C, and successive treatment with the corresponding aldehydes or ketones gave the allylic alcohols **2**. The reactions of the alcohols with CH(OEt)$_3$/*p*-toluenesulfonic acid (TsOH) afforded the acetals **3** in high yields.

First, we examined the acid-promoted allylation of **4A** from 1-ethoxy-2-(seleno)prop-1-en-3-ols **2** in the presence of *O*-trimethylsilyl trifluoromethanesulfonate (TMSOTf), and the results are shown in Table 1. The reaction of 1-ethoxy-4,4-dimethyl-2-(phenylseleno)prop-1-en-3-ol (**2a**) and allyltrimethylsilane at −78 °C afforded *(Z)*-4-ethoxy-7,7-dimethyl-5-(phenylseleno)octa-1,4-diene (**5a**) (entry 1). From observation of the ^{1}H NMR spectral data, which shows a ddd (J = 1, 4, 7 Hz) at δ 3.54 due to the α-proton of the ethoxy group and a doublet at δ 6.39 (J = 1 Hz) due to the olefinic proton, it was found that allylation occurred at the α-position of the ethoxy group. The stereochemistry of **5a** was determined as *Z* by the NOE experiment. Irradiation of the olefinic proton at δ 6.39 ppm increased the intensity of the methine proton at δ 3.54 ppm. Phenyl-**2b** and phenylethynyl-substituted prop-1-en-3-ol **2e** also gave the 1,4-diene **5b** and **5e** in good yields (entries 2 and 5); however, **5d** ($R^1 = R^2$ = Me) was obtained in low yield (entry 4). The corresponding sulfur analogue **2c** regioselectively gave the adduct **5c** (entry 3).

Next, we examined the reactions of 2-(seleno)prop-2-enal diethyl acetals **3a**−**c** with various soft nucleophiles, and the results are shown in Table 2. The reaction of **3a** with allyltrimethylsilane in the presence of TMSOTf gave *(Z)*-4-ethoxy-5-(phenylseleno)octa-1,5-diene (**5a**) in 80% yield (Table 2, entry 1). The reaction of **3a** with the

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(3) Renard, M.; Hevesi, L. *Tetrahedron Lett.* **1983**, *24*, 3911.

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(6) Hevesi, L. *Phosphorous, Sulfur, Silicon* **1992**, *67*, 155.

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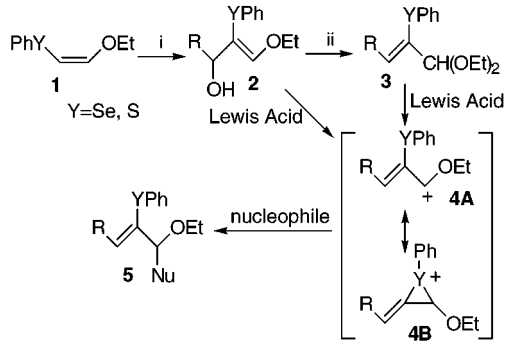
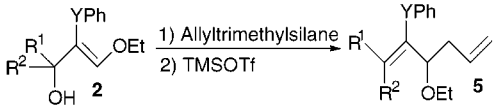
Scheme 1[a]



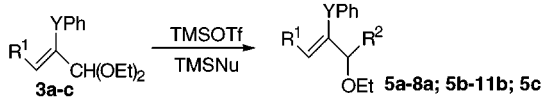
[a] Reagents: (i) ^{n}BuLi/−70 °C/RCHO; (ii) $CH(OEt)_3$/cat. TsOH.

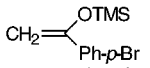
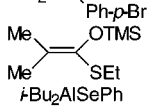
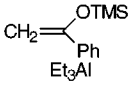
Table 1. Reaction of 3-Ethoxy-2-(phenylseleno)-2-propen-1-ol with Allyltrimethylsilane

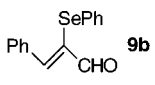


entry	alcohol **2**	product (% yield)
1	**2a** (R^1 = *t*-Bu; R^2 = H; Y = Se)	**5a** (71)
2	**2b** (R^1 = Ph; R^2 = H; Y = Se)	**5b** (60)
3	**2c** (R^1 = *t*-Bu; R^2 = H; Y = Se)	**5c** (69)
4	**2d** (R^1 = R^2 = Me; Y = Se)	**5d** (30)
5	**2e** (R^1 = phenylethynyl; R^2 = H; Y = Se)	**5e** (52)

Table 2. Reaction of 2-(Chalcogeno)prop-2-enal Acetals with Soft Nucleophiles



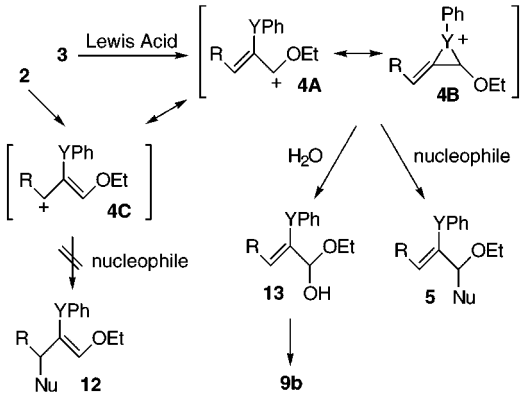
Entry	Acetal (R^1;Y)	Nucleophile	R^2	Product (%yield)
1	**3a** (^{t}Bu;Se)	allyltrimethylsilane	allyl	**5a** (80)
2	**3a**		CH_2COPh-*p*-Br	**6a** (85)
3	**3a**		CMe_2COSEt	**7a** (90)
4	**3a**	*i*-$Bu_2AlSePh$	SePh	**8a** (47)
5	**3b** (Ph;Se)	allyltrimethylsilane	allyl	**5b** (90)
6	**3b**		CH_2COPh	**6b** (70)
7	**3b**	Et_3Al	Et	**7b** (45)
8	**3b**	TMSCN	CN	**8b** (71)
9	**3b**	vinyltrimethylsilane	–	**9b** (72)*1
10	**3b**	Et_2Al—≡—Ph	≡—Ph	**10b** (66)
11	**3b**	Et_2Al—≡—Bu^t	≡—Bu^t	**11b** (63)
12	**3c** (^{t}Bu;S)	allyltrimethylsilane	allyl	**5c** (86)

*1  **9b**

trimethylsilyl enol ether gave the allylated ketone **6a** in high yield (Table 2, entry 2). *S*-Ethyl *O*-trimethylsilyl ketene acetal afforded the thio ester **7a** (Table 2, entry 3). We also examined the addition reaction of the heteroatom nucleophile using *i*-$Bu_2AlSePh$. Treatment of **3a** with 2 equiv of *i*-$Bu_2AlSePh$/TMSOTf gave the *O*,*Se*-acetal **8a** in 47% yield (Table 2, entry 4).

The reactions of the 3-phenylallylic cation generated from the acetal **3b** were then examined. Allyltrimethylsilane also regioselectively afforded the same type of product (**5b**) as that of the *t*-Bu analogue **3a** (Table 2, entry 5). The silyl enol ether and triethylaluminum gave the addition products **6b** and **7b**, respectively (Table 2, entries 6 and 7). The reaction of **3b** with (trimethylsilyl)-nitrile (TMSCN) gave the α-ethoxyallyl cyanide **8b** in good yield; however, vinyltrimethylsilane gave not the addition products, but *(Z)*-3-phenyl-2-(phenylseleno)prop-2-enal **9b** predominantly (Table 2, entries 8 and 9). Although the γ-(chalcogeno)prop-2-ynyl cations reacted with the alkynyldiethylaluminum, the products were obtained in low yield and accompanied with an ethylated product.[8] The prop-2-enal diethyl acetal **3b** was reacted with alkynyl nucleophlies to give the alkynylated products **10b** and **11b** as sole products, respectively (Table 2, entries 10 and 11). Sulfur analogue **3c** gave the product **5c** in high yield (Table 2, entry 12). Plausible mechanisms for formations of the products are shown in Scheme 2. The treatment of the allylic alcohol **2** with TMSOTf provides an allylic cation **4C**, which easily isomerizes to the more stable **4A** and **4B**. The reaction of the nucleophile affords the adduct **5**; however, the hydrolysis of **4A**,**B** gives the aldehyde **9b** via a hemiacetal **13**. We could not detect the adduct **12** through the direct attack of the nucleophile to the intermediate **4C** in the reaction of the alcohol **2** or the acetal **3**.

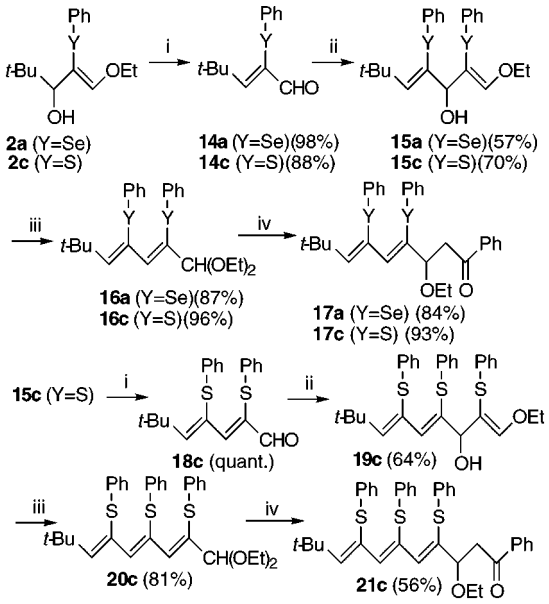
Scheme 2



Furthermore, we performed the acid-promoted nucleophilic substitution reaction of 2,4-bis(chalcogeno)penta-2,4-dienal acetals or 2,4,6-tris(chalcogeno)hepta-2,4,6-trienal acetal. Penta-2,4-dienal acetals **16a**,**c** were prepared from the tandem addition of PhYCH=CHOEt/BuLi to the prop-2-enals **14a**,**c** and the successive treatment with $CH(OEt)_3$/TsOH. Trienal acetal **20c** was also obtained by the same route. Since the reaction of dienal acetals **16a**,**c** with the nucleophiles using TMSOTf gave the aldehyde **18c**, not the adduct, we examined the reaction using other Lewis acids. Lanthanide metals were found to be a very suitable Lewis acid for these addition reactions. The dienal acetal **16a** (Y = Se) reacted with the silyl enol ether in the presence of Yb-$(OTf)_3$ to give the α-adduct of the alkoxide **17a** in moderate yield. The structure of the dienone **17a** was determined by the IR, ^{1}H and ^{13}C NMR, and mass spectral data. The IR spectrum showed the absorption of the carbonyl group at ν 1690 cm^{-1}. The ^{1}H NMR spectrum exhibits two singlets at δ 5.94 (brs) and 6.64 (brs) ppm due to the characteristic olefinic protons. Mass

(8) Yoshimatsu, M.; Shimizu, H.; Kataoka, T. *J. Chem. Soc., Chem. Commun.* **1995**, 149.

Scheme 3[a]



[a] Reagents: (i) $TMSOTf/CH_2Cl_2$; (ii) PhYCH=CHOEt/*n*-BuLi; (iii) $CH(OEt)_3$/TsOH/EtOH; (iv) $Yb(OTf)_3/CH_2$=C(OTMS)Ph.

spectra show the molecular formula ($C_{31}H_{34}O_2Se_2$) at *m*/*z* 598. The stereochemistry of **17a** was determined by the NOE experiments. Irradiation of the 5-olefinic proton at δ 6.64 ppm increased the intensities of the 7-olefinic proton (8%) at δ 5.94 ppm and that of the α-proton of the alkoxide (6%) at δ 4.05 ppm. The reaction of the trienal acetal **20c** with the silyl enol ether proceeded stereoselectively to give the nona-4,6,8-trienone **21c** in good yield. High regioselectivities of the addition reactions are explained as shown in Scheme 4. 2,4-Bis(chalcogeno)pentadienyl cation **22A**, which easily forms from the reactions of **16a**,**c** and $Yb(OTf)_3$, exclusively affords the adducts **17a**,**c** because of the high reactivity of the α-oxy carbenium ions (Scheme 4).[6] The cation **22C** is a stable intermediate by the contribution to the cyclic **22D** and **22E**; however, the adduct **23** was not obtained in the reactions of **16a**,**c**. An adduct such as **24** derived from **22F** or **22G** also was not given.

To demonstrate more useful utilization of the adducts, the cyclization reactions of the 2-(phenylseleno)pent-1-en-5-ols **25a** and **25b**, which were easily obtained from

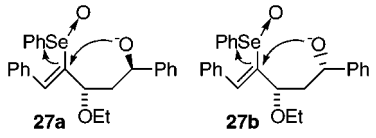
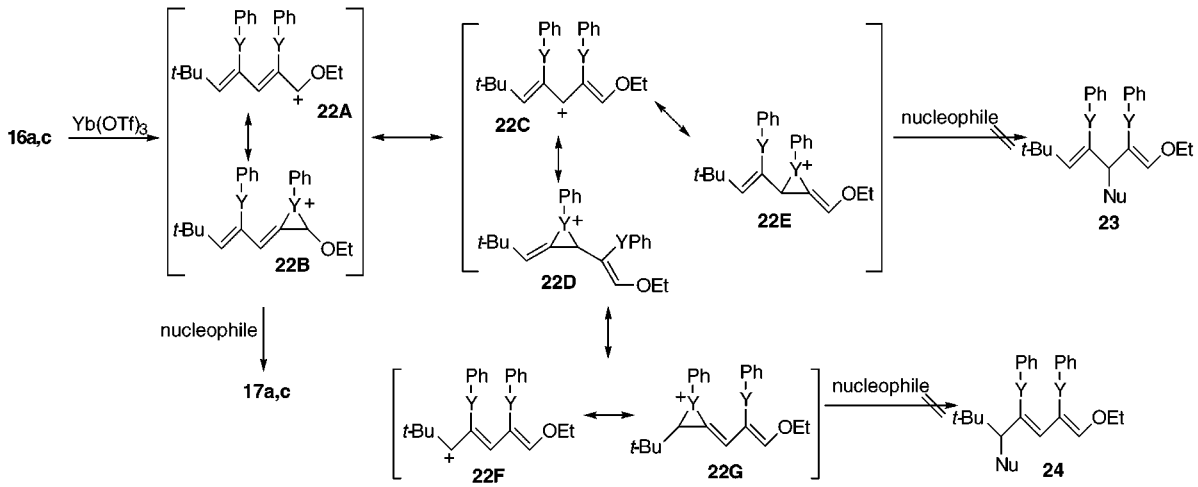


Figure 1.

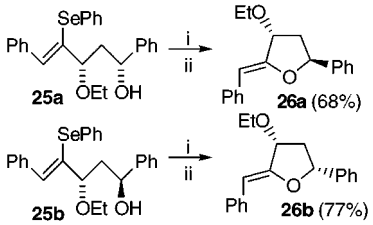
the reduction of the 4-(phenylseleno)pent-4-enone (Scheme 5), were carried out. First, the pent-1-en-5-ol **25a** was oxidized by *m*-chloroperbenzoic acid (*m*-CPBA), and the successive treatment of *t*-BuOK/THF/18-crown-6 gave 2-(benzylidene)-3-ethoxy-5-phenyltetrahydrofuran (**26a**) in 68% yield as the sole product. The *anti* alcohol **25b** afforded the *cis*-substituted tetrahydrofuran **26b** (77%) predominantly. Structure assignment of **26a** was performed by ^{1}H NMR spectral data, which exhibited a characteristic olefinic proton at δ 5.48 (brs) and a pair of doublets at δ 5.71 (J = 5, 10 Hz) due to 5-H and δ 4.43 (J = 4, 5 Hz) due to 3-H, respectively. The *trans*-configuration between the phenyl and ethoxy groups was determined by reference to our previous report on the chemical shift method of the 3,5-disubstituted tetrahydrofurans, which was supported by a single X-ray analysis.[9] The chemical shift difference of 4-methylene protons for 3,5-*syn*-**26b** was observed to be larger at 0.24 ppm than that for 3,5-*anti*-**26a**. The stereostructure of the benzylidene part of **26a** was determined as *Z* by NOE experiments. Irradiation of the olefinic proton at δ 5.48 ppm increased the intensities of the methylene protons of the ethoxy group (3%) and the 3-methine proton (3%), respectively. This result shows that the intramolecular cycloaddition reaction of vinylselenoxide and the alkoxide would proceed with retention of the configuration of the vinylselenoxide.[10] In the *syn* isomer **25a**, this cyclization proceeds through the addition−elimination of the alkoxy vinylselenoxide **27a**, which provides a 3,5-*trans*-tetrahydrofuran exclusively, while the anti isomer **25b** gives 3,5-*cis*-tetrahydrofuran through the intermediate **27b** (Figure 1).

Furthermore, we also examined the reactions of 2,4-bis(chalcogeno)penta-2,4-dienal derivatives with a radical species (Scheme 6). 2,4-Bis(seleno)pentadienal acetal **16a** underwent deselenylation by the normal reduction of Bu_3SnH/2,2′-azobis(isobutyronitrile) (AIBN) to give the dienal **28** in 81% yield; however, the reduction of pentadienal hydrazones gave complex mixtures. Further investigation of the reduction of hydrazones revealed that

Scheme 4

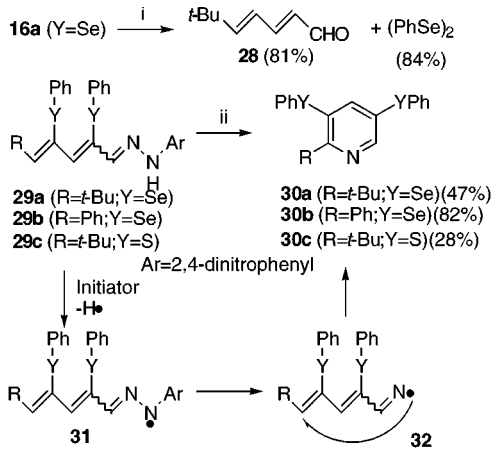


Scheme 5[a]



[a] Reagents: (i) *m*-CPBA; (ii) *t*-BuOK/THF/18-crown-6.

Scheme 6[a]



[a] Reagents: (i) Bu_3SnH/AIBN; (ii) AIBN/benzene/reflux.

the product is 3,5-bis(chalcogeno)pyridine **30** and AIBN acts as an effective reagent for formation of the 3,5-bis(chalcogeno)pyridines. 2,4-Bis(phenylseleno)penta-2,4-dienal hydrazones **29b** (R = Ph) gave the pyridine **30b** in good yield; however, the sulfur analogue **29c** was obtained in low yield. The cyclization of the penta-2,4-dienal hydrazones would proceed in the 6-endo-mode via the iminyl radical **32**. Recently, the 5-exo-mode cyclization of the alkylidene iminyl radicals derived from the *O*-carboxymethyl oximes has been reported.[11] Our cyclization of the dienal hydrazones would proceed by the same route, which is the hydride abstraction[12] of **29** and the following formation of the iminyl radical **32**,[13] and finally, the iminyl radical **32** cyclizes in the 6-endo-mode. Moreover, the vinyl-, dienyl-, and trienylchalcogenides moiety can be converted into other functional groups;[14] work is under way to clarify their fundamental reactivities, which are of potential interest. The results of our further investigation will be reported elsewhere.

Experimental Section[9c]

NOE experiments were run on a Varian Inova-400 (400 MHz) spectrometer at the Center of Instrumentation of Gifu University. The starting materials, *(Z)*-2-ethoxyvinyl phenyl sulfide and the selenium analogue, were quantitatively prepared according to our previous work.[7] Purities of the products were assessed by the elemental analysis; however, the compounds, satisfactory elemental analysis of which could not be achieved because of their labilities, were determined as the almost pure form by ^1H and ^{13}C NMR and mass spectrometric data.

Syntheses of 1-Ethoxy-2-(chalcogeno)prop-1-en-3-ols 2a−e, 1-Ethoxy-2-(chalcogeno)penta-1,4-dien-3-ol 15a,c, and Hepta-1,4,6-trien-3-ol 19c. Typical Procedure. Under an Ar atmosphere, BuLi (28.0 mL, 42.2 mmol) was added to a THF (50 mL) solution of 2-ethoxyvinyl phenyl selenide (8.00 g, 35.2 mmol). After the mixture was stirred for 5 min, a THF (10 mL) solution of *tert*-butyl aldehyde (6.60 g, 70.4 mmol) was added dropwise to the mixture. The whole was poured into water (150 mL), and the organic layer was separated. The aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel eluting with AcOEt/hexane (1:20). *(Z)*-1-Ethoxy-4,4-dimethyl-2-(phenylseleno)pent-1-en-3-ol (**2a**) (7.60 g, 69%) was obtained as a yellow oil.

2a: IR (film, cm^{-1}) 3600−3400 (OH); ^1H NMR δ 0.93 (9H, s), 1.29 (3H, t, J = 7 Hz), 2.59 (1H, brd, J = 10 Hz), 3.92 (2H, q, J = 7 Hz), 4.32 (1H, brd, J = 10 Hz), 6.76 (1H, s), 7.14−7.27 (3H, m), 7.43−7.48 (2H, m); ^{13}C NMR δ 15.37 (q), 26.30 (q × 3), 37.41 (s), 68.99 (t), 79.92 (d), 108.57 (s), 125.97 (d), 128.85 (d × 2), 129.08 (d × 2), 134.30 (s), 155.67 (d); MS *m/z* 314 (M^+). Anal. Calcd for $C_{15}H_{22}O_2Se$: C, 57.51; H, 7.08. Found: C, 57.46; H, 7.09.

(1*Z*,4*Z*)-1-Ethoxy-6,6-dimethyl-2,4-bis(phenylseleno)-hepta-1,4-dien-3-ol (15a): IR (film, cm^{-1}) 3600−3200 (OH); ^1H NMR δ 1.08 (9H, s), 1.21 (3H, t, J = 7 Hz), 2.69 (1H, d, J = 8 Hz), 3.86−3.92 (2H, m), 5.12 (1H, d, J = 8 Hz), 6.46 (1H, s), 6.74 (1H, s), 7.15−7.19 (6H, m), 7.39−7.44 (4H, m); ^{13}C NMR δ 15.28 (q), 30.64 (q × 3), 33.82 (s), 69.05 (t), 73.05 (d), 109.32 (s), 125.98 (d), 126.12 (d), 128.60 (s), 128.88 (d × 2), 129.00 (d × 2), 129.31 (d × 2), 130.55 (d × 2), 132.47 (s), 133.27 (s), 147.68 (d), 156.51 (d); MS *m/z* 496 (M^+). Anal. Calcd for $C_{23}H_{28}O_2Se_2$: C, 55.88; H, 5.71. Found: C, 55.74; H, 5.71.

(1*Z*,4*Z*)-1-Ethoxy-6,6-dimethyl-2,4-bis(phenylthio)hepta-1,4-dien-3-ol (15c): IR (film, cm^{-1}) 3600−3400 (OH); ^1H NMR δ 1.04 (9H, s), 1.17 (3H, t, J = 7 Hz), 2.78 (1H, brd, J = 8 Hz), 3.82−3.89 (2H, m), 5.08 (1H, brd, J = 8 Hz), 6.39 (1H, s), 6.71 (1H, s), 7.06−7.11 (2H, m), 7.18−7.32 (8H, m); ^{13}C NMR δ 15.10 (q), 30.27 (q × 3), 33.32 (s), 69.20 (t), 71.11 (d), 109.22 (s), 125.11 (d), 125.31 (d), 126.48 (d × 2), 127.73 (d × 2), 128.56 (d × 2), 128.64 (d × 2), 129.64 (s), 136.88 (s), 138.51 (s), 148.21 (d), 156.95 (d); high-resolution mass calcd for $C_{23}H_{28}O_2S_2$ 400.1531, found *m/z* 400.1539.

(1*Z*,4*Z*,6*Z*)-1-Ethoxy-8,8-dimethyl-2,4,6-tris(phenylthio)nona-1,4,6-trien-3-ol (19c): IR (film, cm^{-1}) 3600−3400 (OH); ^1H NMR δ 1.11 (3H, t, J = 7 Hz), 1.20 (9H, s), 2.05 (1H, brs), 3.79 (2H, q, J = 7 Hz), 5.07 (1H, brs), 5.60 (1H, s), 6.51 (1H, s), 6.66 (1H, s), 7.07−7.27 (15H, m); ^{13}C NMR δ 15.03 (q), 30.42 (q × 3), 34.07 (s), 69.22 (t), 69.56 (d), 109.12 (s), 125.15 (s), 125.59 (d), 125.63 (d), 126.05 (d), 126.82 (d × 2), 128.52 (d × 2), 128.61 (d × 2), 128.71 (d × 2), 129.34 (d × 2), 129.76 (d × 2), 135.27 (s), 135.30 (s), 135.48 (d), 136.18 (s), 138.18 (s), 152.84 (d), 156.61 (d); MS *m/z* 534 (M^+). Anal. Calcd for $C_{31}H_{34}O_2S_3$: C, 69.62; H, 6.41. Found: C, 69.10; H, 6.48.

Reaction of Prop-1-en-3-ols 2a−e with the Soft Nucleophiles. Typical Procedure. TMSOTf (0.29 mL, 1.50 mmol) was added dropwise to a CH_2Cl_2 (2 mL) solution of *(Z)*-1-ethoxy-4,4-dimethylpent-1-en-3-ol (**2a**) (0.16 g, 0.50 mmol) and allyltrimethylsilane (0.29 g, 2.50 mmol) at −78 °C under an Ar atmosphere. The reaction mixture was poured into a saturated $NaHCO_3$ solution (100 mL), and then the organic layer was separated. The aqueous layer was extracted with

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$CHCl_3$. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with CH_2Cl_2−hexane (1:5).

(Z)-4-Ethoxy-7,7-dimethyl-5-(phenylseleno)oct-1,5-diene (**5a**) (0.12 g, 71%) was obtained as a pale yellow oil. The stereostructure of **5a** was determined as *Z* by the observation of the NOE enhancement between the olefinic proton at δ 6.39 and the methine proton at δ 3.54 (8%).

5a: a pale yellow oil; IR (film, cm^{-1}) 1090 (ether); ^1H NMR δ 1.04 (3H, t, $J = 7$ Hz), 1.26 (9H, s), 2.22−2.29 (1H, m), 2.46−2.53 (1H, m), 3.03−3.11 (1H, m), 3.40−3.56 (1H, m), 3.54 (1H, ddd, $J = 1, 4, 7$ Hz), 4.95−5.01 (2H, m), 5.71−5.78 (1H, m), 6.39 (1H, s), 7.23−7.25 (3H, m), 7.46−7.47 (2H, m); ^{13}C NMR δ 15.18 (q), 30.99 (q × 3), 33.74 (s), 40.29 (t), 63.88 (t), 83.33 (d), 116.25 (t), 126.89 (d), 129.01 (d × 2), 130.69 (s), 132.54 (d × 2), 135.36 (d), 145.39 (d); MS *m/z* 338 (M^+). Anal. Calcd for $C_{18}H_{26}OSe$: C, 64.08; H, 7.77. Found: C, 63.85; H, 7.76.

Syntheses of the Prop-2-enal Acetals 3a−c, Penta-2,4-dienal Acetals 16a,c, and Hepta-2,4,6-trienal Acetal 20c. The experimental procedure was performed according to the general method.

***(Z)*-4,4-Dimethyl-2-(phenylseleno)pent-2-enal diethyl acetal (3a)**: a pale yellow oil; IR (film, cm^{-1}) 1050, 1110 (acetals); ^1H NMR δ 1.13 (6H, t, $J = 7$ Hz), 1.26 (9H, s), 3.31−3.39 (2H, m), 3.47−3.54 (2H, m), 4.58 (1H, s), 6.66 (1H, s), 7.20−7.26 (3H, m), 7.45−7.48 (2H, m); ^{13}C NMR δ 15.06 (q × 2), 30.67 (q × 3), 33.37 (s), 61.97 (t × 2), 103.38 (d), 125.48 (s), 126.54 (d), 128.86 (d × 2), 129.19 (s), 132.05 (d × 2), 147.92 (d); MS *m/z* 342 (M^+). Anal. Calcd for $C_{17}H_{26}O_2Se$: C, 59.82; H, 7.68. Found: C, 59.42; H, 7.41.

(2*Z*,4*Z*)-6,6-Dimethyl-2,4-bis(phenylseleno)hepta-2,4-dienal diethyl acetal (16a): IR (film, cm^{-1}) 1120, 1050 (acetal); ^1H NMR δ 0.97 (6H, t, $J = 7$ Hz), 1.31 (9H, s), 2.85−2.91 (2H, m), 3.15−3.21 (2H, m), 4.31 (1H, s), 6.06 (1H, s), 6.69 (1H, s), 7.21−7.31 (6H, m), 7.41−7.44 (2H, m), 7.52−7.54 (2H, m); ^{13}C NMR δ 14.94 (q × 2), 30.67 (q × 3), 34.48 (s), 61.95 (t × 2), 101.08 (d), 124.97 (s), 126.97 (d), 127.59 (d), 128.70 (d × 2), 128.74 (d × 2), 128.97 (s), 130.53 (s), 131.65 (s), 133.88 (d × 2), 134.49 (d × 2), 135.69 (d), 149.06 (d); MS *m/z* 524 (M^+). Anal. Calcd for $C_{25}H_{32}O_2Se_2$: C, 57.47; H, 6.17. Found: C, 57.39; H, 6.17.

(2*Z*,4*Z*)-6,6-Dimethyl-2,4-bis(phenylthio)hepta-2,4-dienal diethyl acetal (16c): IR (film, cm^{-1}) 1120, 1060 (acetal); ^1H NMR δ 1.15 (6H, t, $J = 7$ Hz), 1.27 (9H, s), 3.37−3.42 (2H, m), 3.49−3.54 (2H, m), 4.58 (1H, s), 6.62 (1H, s), 7.14−7.27 (9H, m), 7.30−7.32 (2H, m). The EI mass spectrum of **16c** did not show the M^+ (*m/z* 428) but showed many peaks because of its lability. The elemental analysis also did not give satisfactory results.

(2*Z*,4*Z*,6*Z*)-8,8-Dimethyl-2,4,6-tris(phenylthio)nona-2,4,6-trienal diethyl acetal (20c): IR (film, cm^{-1}) 1180−1000 (acetal); ^1H NMR δ 0.91 (6H, t, $J = 7$ Hz), 1.33 (9H, s), 2.83−2.89 (2H, m), 3.07−3.13 (2H, m), 4.33 (1H, s), 6.03 (1H, s), 6.30 (1H, s), 6.44 (1H, s), 7.00−7.04 (1H, m), 7.13−7.28 (12H, m), 7.31−7.33 (2H, m); ^{13}C NMR δ 14.89 (q × 2), 30.66 (q × 3), 34.28 (s), 61.61 (t × 2), 100.16 (d), 110.69 (s), 125.91 (d), 126.84 (d), 126.88 (d), 128.48 (d × 2), 128.52 (d × 2), 128.65 (d × 2), 130.03 (d × 2), 131.50 (d × 2), 131.69 (s), 131.92 (d × 2), 132.19 (d), 133.76 (s), 133.86 (s), 134.82 (s), 135.93 (s), 137.32 (d), 152.00 (d); MS *m/z* 517 (M^+ − OEt). Anal. Calcd for $C_{33}H_{38}O_2S_3$: C, 70.42; H, 6.81. Found: C, 70.18; H, 6.85.

Reactions of Prop-2-enal Acetals 3a−c, Penta-2,4-dienal Acetals 16a,c, and Hepta-2,4,6-trienal Acetal 20c with Soft Nucleophiles. The experiments were performed by the same procedure as described above for the reaction of **2a** with allyltrimethylsilane.

***(Z)*-4′-Bromo-3-ethoxy-6,6-dimethyl-4-(phenylseleno)-hept-4-enophenone (6a)**: a yellow oil; IR (film, cm^{-1}) 1690 (CO), 1110 (ether); ^1H NMR δ 0.96 (3H, t, $J = 7$ Hz), 1.29 (9H, s), 3.06−3.13 (2H, m), 3.28 (1H, dd, $J = 3, 7$ Hz), 3.43 (1H, dd, $J = 7, 9$ Hz), 4.18 (1H, dd, $J = 3, 9$ Hz), 6.55 (1H, s), 7.22−7.26 (3H, m), 7.44−7.55 (4H, m), 7.57−7.69 (2H, m); ^{13}C NMR δ 14.99 (q), 30.93 (q × 3), 33.78 (s), 45.62 (t), 64.06 (t), 80.23 (d), 127.03 (d), 127.83 (s), 128.29 (s), 129.14 (d × 2), 129.72 (d × 2), 130.36 (s), 131.59 (d × 2), 132.20 (d × 2), 135.90 (s), 146.61 (d), 197.08 (s); MS *m/z* 450 (M^+ − OEt). Anal. Calcd for $C_{23}H_{27}BrO_2Se$: C, 55.88; H, 5.51. Found: C, 55.69; H, 5.48.

***(Z)*-3-Ethoxy-5-phenyl-4-(phenylseleno)pent-4-enophenone (6b)**: a yellow oil; IR (film, cm^{-1}) 1690 (CO), 1100 (ether); ^1H NMR δ 1.05 (3H, t, $J = 7$ Hz), 3.24−3.33 (3H, m), 3.54−3.60 (1H, m), 4.49−4.52 (1H, m), 7.16−7.53 (12H, m), 7.58−7.59 (2H, m), 7.85−7.87 (2H, m); ^{13}C NMR δ 15.12 (q), 45.31 (t), 64.61 (t), 80.07 (d), 127.35 (d), 127.82 (s), 128.01 (d × 2), 128.18 (d × 2), 128.42 (d × 2), 129.18 (d × 2), 129.31 (s), 129.37 (d × 2), 132.72 (d × 2), 132.86 (d), 133.41 (s), 133.91 (d), 136.42 (d), 137.16 (s), 197.70 (s); MS *m/z* 390 (M^+ − EtOH). Anal. Calcd for $C_{25}H_{24}O_2Se$: C, 68.96; H, 5.56. Found: C, 68.79; H, 5.54.

(4*Z*,6*Z*)-3-Ethoxy-8,8-dimethyl-4,6-bis(phenylseleno)-nona-4,6-dienophenone (17a): IR (film, cm^{-1}) 1690 (CO), 1040 (ether); ^1H NMR δ 0.71 (3H, t, $J = 7$ Hz), 1.35 (9H, s), 2.68 (2H, q, $J = 7$ Hz), 2.93 (1H, dd, $J = 10, 16$ Hz), 3.07 (1H, dd, $J = 3, 16$ Hz), 4.05 (1H, dd, $J = 2, 9$ Hz), 5.94 (1H, s), 6.64 (1H, s), 7.22−7.41 (10H, m), 7.46−7.48 (1H, m), 7.55−7.57 (2H, m), 7.71−7.74 (2H, m); ^{13}C NMR δ 14.96 (q), 30.80 (q × 3), 34.46 (s), 45.79 (t), 64.02 (t), 77.34 (d), 125.93 (s), 127.17 (d), 127.99 (d), 128.15 (d × 2), 128.30 (d × 2), 128.63 (s), 128.83 (d × 2), 129.07 (d × 2), 130.49 (s), 132.70 (d), 133.92 (d), 134.32 (d × 2), 134.42 (d × 2), 135.92 (s), 137.10 (s), 148.19 (d), 197.47 (s); MS *m/z* 598 (M^+). Anal. Calcd for $C_{31}H_{34}O_2Se_2$: C, 62.42; H, 5.75. Found: C, 62.01; H, 5.85. The stereostructure of **17a** was determined as 4*Z*,6*Z* by the observation of the NOE enhancements as described above.

(4*Z*,6*Z*)-3-Ethoxy-8,8-dimethyl-4,6-bis(phenylthio)nona-4,6-dienophenone (17c): IR (film, cm^{-1}) 1690 (CO), 1100 (ether); ^1H NMR δ 1.01 (3H, t, $J = 7$ Hz), 1.29 (9H, s), 3.12−3.23 (2H, m), 3.34 (1H, dd, $J = 3, 16$ Hz), 3.46−3.53 (1H, m), 4.18 (1H, dd, $J = 3, 9$ Hz), 6.51 (1H, s), 7.14−7.39 (13H, m), 7.46−7.50 (1H, m), 7.85 (2H, d, $J = 8$ Hz); ^{13}C NMR δ 15.07 (q), 30.72 (q × 3), 33.40 (s), 45.68 (t), 64.22 (t), 78.56 (d), 126.25 (d × 2), 128.13 (d × 4), 128.30 (d × 4), 128.90 (d × 2), 129.26 (d × 2), 130.09 (s × 2), 132.71 (d), 135.23 (s), 137.13 (s × 2), 146.97 (d × 2), 198.06 (s); MS *m/z* 368 (M^+ − (PhCO + Et)). Anal. Calcd for $C_{31}H_{34}O_2S_2$: C, 74.06; H, 6.82. Found: C, 74.23; H, 7.67.

(4*Z*,6*Z*,8*Z*)-3-Ethoxy-10,10-dimethyl-4,6,8-tris(phenylthio)undeca-4,6,8-trienophenone (21c): IR (film, cm^{-1}) 1690 (CO), 1100 (ether); ^1H NMR δ 0.73 (3H, t, $J = 7$ Hz), 1.34 (9H, s), 2.73−2.78 (2H, m), 2.98 (1H, dd, $J = 9, 16$ Hz), 3.12 (1H, dd, $J = 2, 16$ Hz), 4.08 (1H, dd, $J = 2, 9$ Hz), 6.02 (1H, s), 6.49 (1H, s), 7.20−7.30 (10H, m), 7.34−7.39 (8H, m), 7.47−7.50 (1H, m), 7.75−7.77 (2H, m); ^{13}C NMR δ 14.95 (q), 30.67 (q × 3), 34.10 (s), 45.71 (t), 64.05 (t), 76.18 (d), 126.45 (d), 127.06 (s), 127.46 (d), 128.17 (d × 3), 128.34 (d × 3), 128.67 (d × 3), 128.97 (d × 3), 131.20 (d × 3), 131.59 (d × 3), 132.70 (d), 132.78 (d), 133.45 (s), 135.69 (s × 2), 136.41 (s × 2), 137.06 (s), 150.16 (d), 197.56 (s); EI MS *m/z* 502 ((M^+ − (PhCO + Et)). Anal. Calcd for $C_{39}H_{40}O_2S_3$: C, 73.55; H, 6.33. Found: C, 73.42; H, 6.28.

Syntheses of the Prop-2-enal 14a,c and Penta-2,4-dienal 18c. Typical Procedure.[7] TMSOTf (4.70 mL, 24.3 mmol) was added dropwise to a CH_2Cl_2 (80 mL) solution of *(Z)*-1-ethoxy-4,4-dimethyl-2-(phenylseleno)pent-1-en-3-ol (**2a**) (7.60 g, 24.3 mmol) at −78 °C under an Ar atmosphere. After being stirred for 10 min, the reaction mixture was poured into a saturated $NaHCO_3$ (150 mL) solution. The workup procedure afforded *(Z)*-4,4-dimethyl-2-(phenylseleno)pent-2-enal (**14a**) (6.34 g, 98%) as a yellow oil.

14a: IR (film, cm^{-1}) 1680 (CO); ^1H NMR δ 1.37 (9H, s), 7.20−7.24 (3H, m), 7.35−7.38 (2H, m), 7.36 (1H, s), 9.23 (1H, s); ^{13}C NMR δ 29.96 (q × 3), 35.35 (s), 126.92 (d), 129.18 (d × 2), 131.05 (s), 131.43 (d × 2), 132.49 (s), 170.02 (d), 191.64 (d); MS *m/z* 268 (M^+). Anal. Calcd for $C_{13}H_{16}OSe$: C, 58.43; H, 6.04. Found: C, 58.34; H, 6.01.

Syntheses of *syn*- and *anti*-Pent-4-en-1-ols 25a,b. The reduction of **6b** was performed according to our previous paper.[9c]

(1*R,3*R**)-*(Z)*-3-Ethoxy-1,5-diphenyl-4-(phenylseleno)-pent-4-en-1-ol (25a)**: IR (film, cm^{-1}) 3700−3150 (OH), 1050

(ether); ^{1}H NMR δ 1.15 (3H, t, J = 7 Hz), 2.15−2.28 (2H, m), 3.06−3.13 (1H, m), 3.53−3.61 (1H, m), 3.61 (1H, d, J = 5 Hz), 3.94 (1H, dd, J = 3, 8 Hz), 4.98 (1H, s), 7.11−7.35 (14H, m), 7.53 (2H, d, J = 7 Hz); ^{13}C NMR δ 15.34 (q), 43.49 (t), 64.41 (t), 71.21 (d), 80.96 (d), 125.39 (d × 2), 126.83 (d), 127.54 (d), 127.67 (d), 127.98 (d × 2), 128.21 (d × 2), 128.71 (s), 129.05 (d × 2), 129.31 (d × 2), 132.16 (d), 133.34 (s), 133.64 (d × 2), 136.53 (s), 144.32 (s); high-resolution mass calcd for $C_{25}H_{26}O_2Se$ 438.1118, found m/z 438.1083.

(1*S,3*R**)-*(Z)*-3-Ethoxy-1,5-diphenyl-4-(phenylseleno)-pent-4-en-1-ol (25b)**: IR (film, cm^{-1}) 3700−3200 (OH), 1040 (ether); ^{1}H NMR δ1.17 (3H, t, J = 7 Hz), 1.96−2.04 (1H, m), 2.12−2.23 (1H, m), 3.18−3.25 (1H, m), 3.62−3.70 (1H, m), 4.00 (1H, dd, J = 3, 10 Hz), 4.06 (1H, s), 4.70 (1H, dd, J = 3, 9 Hz), 7.17−7.33 (12H, m), 7.41 (2H, dd, J = 2, 7 Hz), 7.50 (2H, d, J = 7 Hz); high-resolution mass calcd for $C_{25}H_{26}O_2Se$ 438.1089, found m/z 438.1110.

Cyclization Reactions of Pent-5-en-1-ols 25a,b by *m*-CPBA/*t*-BuOK. Typical Procedure. *m*-CPBA (0.10 g, 0.46 mmol) was added to a $ClCH_2CH_2Cl$ (30 mL) solution of syn alcohol **25a** (0.20 g, 0.46 mmol) at 0 °C. After 10 min of stirring, the mixture was washed with saturated $NaHCO_3$ solution (100 × 3 mL). The organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The almost pure selenoxide thus obtained was used without further purification because of its lability. A THF (2 mL) solution of the residue was added dropwise to a THF (3 mL) solution of *t*-BuOK (0.08 g, 0.72 mmol) and 18-crown-6 (10 mg, 0.04 mmol) at −78 °C under an Ar atmosphere. After 10 min of stirring, the mixture was poured into water (100 mL). The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel, eluting with AcOEt−hexane (1:30) to give (3*R**,5*S**)-*(Z)*-2-(benzylidene)-3-ethoxy-5-phenyltetrahydrofuran (**26**) (0.09 g, 68%) as a colorless oil. The stereostructure of the 2-benzylidene group of **26a** was determined as *Z* by the observation of NOE enhancement as described above.

26a: IR (film, cm^{-1}) 1120 (ether); ^{1}H NMR δ 1.26 (3H, t, J = 7 Hz), 2.00−2.06 (1H, m), 2.73−2.78 (1H, m), 3.59−3.69 (2H, m), 4.68−4.72 (1H, m), 5.40 (1H, dd, J = 6, 9 Hz), 5.51 (1H, s), 7.09−7.13 (1H, m), 7.25−7.45 (7H, m), 7.62−7.64 (2H, m); ^{13}C NMR δ 15.45 (q), 39.70 (t), 65.01 (t), 79.55 (d), 81.93 (d), 98.94 (d), 125.25 (d), 125.85 (d × 2), 127.82 (d × 2), 128.00 (d), 128.19 (d × 2), 128.52 (d × 2), 136.22 (s), 141.06 (s), 155.82 (s); high-resolution mass calcd for $C_{19}H_{20}O_2$ 280.1474, found m/z 280.1459.

(3*R,5*R**)-*(Z)*-2-(Benzylidene)-3-ethoxy-5-phenyltetrahydrofuran (26b)**: IR (film, cm^{-1}) 1090 (ether); ^{1}H NMR δ 1.27 (3H, t, J = 7 Hz), 2.05 (1H, ddd, J = 3, 5, 13 Hz), 2.51 (1H, dd, J = 5, 13 Hz), 3.49−3.53 (1H, m), 3.76−3.82 (1H, m), 4.44 (1H, d, J = 4 Hz), 5.48 (1H, s), 5.71 (1H, dd, J = 5, 10 Hz), 7.12−7.16 (1H, m), 7.25−7.42 (7H, m), 7.63−7.67 (2H, m); ^{13}C NMR δ 15.28 (q), 41.42 (t), 63.81 (t), 80.78 (d), 83.73 (d), 101.53 (d), 125.61 (d), 125.68 (d × 2), 127.97 (d), 128.00 (d × 2), 128.28 (d × 2), 128.59 (d × 2), 135.99 (s), 141.04 (s), 155.51 (s); high-resolution mass calcd for $C_{19}H_{20}O_2$ 280.1450, found m/z 280.1469.

Reaction of Penta-2,4-dienal Acetal 16a with Bu_3SnH/AIBN. A benzene (2 mL) solution of penta-2,4-dienal acetal **16a** (0.15 g, 0.28 mmol), tributyltin hydride (0.26 g, 0.86 mmol), and AIBN (10 mg) was refluxed for 0.3 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with CH_2Cl_2−hexane (1:5), to afford (2*E*,4*E*)-6,6-dimethylhepta-2,4-dienal (**28**) (31 mg, 81%) and $(PhSe)_2$ (73 mg, 84%). The structure of **28** was determined by comparison with the literature data.[15]

(2*E*,4*E*)-6,6-Dimethylhepta-2,4-dienal (28): ^{1}H NMR δ 1.10 (9H, s), 6.11 (1H, dd, J = 8, 15 Hz), 6.25 (1H, ddd, J = 1, 9, 15 Hz), 6.30 (1H, dd, J = 1, 15 Hz), 7.08 (1H, ddd, J = 1, 9, 15 Hz), 9.53 (1H, d, J = 8 Hz).

Syntheses of Penta-2,4-dienal 2,4-Dinitrophenylhydrazones 29a−c. Typical Procedure. A benzene (30 mL) solution of (2*Z*,4*Z*)- and (2*E*,4*Z*)-6,6-dimethyl-2,4-bis(phenylseleno)hepta-2,4-dienal (1.00 g, 2.23 mmol), 2,4-dinitrophenylhydrazine (0.88 g, 4.46 mmol), and TsOH (40 mg, 0.20 mmol) was refluxed for 0.25 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel, eluting with AcOEt−hexane (1:10) to afford (2*Z*,4*Z*)- and (2*E*,4*Z*)-6,6-dimethyl-2,4-bis(phenylseleno)hepta-2,4-dien-al 2,4-dinitrophenyl hydrazone (**29a**) (1.38 g, quant) as orange prisms (mp 131−133 °C).

29a: IR (film, cm^{-1}) 1510, 1340, 850 (NO_2); ^{1}H NMR δ 1.15 (s), 1.38 (s), 6.15 (d, J = 1 Hz), 6.25 (d, J = 1 Hz), 6.83 (brs), 6.85 (brs), 6.96−6.97 (m), 7.13−7.41 (m), 7.50−7.52 (m), 8.00 (dd, J = 2, 10 Hz), 8.04 (dd, J = 2, 10 Hz), 8.97 (d, J = 3 Hz), 9.00 (d, J = 2 Hz), 10.86 (s), 10.97 (s); ^{13}C NMR δ 30.12 (*2E*-q), 30.70 (*2Z*-q), 35.07 (*2Z*-s), 36.23 (*2E*-s), 116.78 (*2Z*-d), 116.90 (*2E*-d), 122.48 (*2E*-s), 123.04 (d), 124.61 (*2Z*-s), 126.90 (d), 127.04 (d), 127.27 (d), 127.45 (d), 128.45 (s), 128.76 (d), 128.93 (d), 129.06 (d), 129.12 (d), 129.16 (d), 129.22 (d), 129.25 (d), 129.42 (d), 129.51 (d), 130.34 (s), 133.09 (d), 133.26 (d), 133.63 (d), 138.22 (*2Z*-s), 138.24 (*2E*-s), 143.87 (*2E*-s), 144.33 (*2Z*-s), 144.40 (d), 147.36 (*2Z*-d), 148.06 (*2E*-d), 151.94 (*2E*-d), 153.07 (*2Z*-d); MS m/z 447 (M^+ − NH-2,4-dinitrophenyl). Anal. Calcd for $C_{27}H_{26}N_4O_2Se_2$: C, 51.68; H, 4.17; N, 8.92. Found: C, 51.61; H, 4.21; N, 8.98.

Reactions of Penta-2,4-dienal 2,4-Dinitrophenylhydrazones 29a−c with AIBN. Typical Procedure. A benzene (2 mL) solution of AIBN (0.08 g, 0.50 mmol) and penta-2,4-dienal 2,4-dinitrophenyl hydrazone (**29a**) (0.10 g, 0.16 mmol) was refluxed for 0.5 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel, eluting with AcOEt−hexane (1:20) to afford 2-*tert*-butyl-3,5-bis(phenylseleno)pyridine (**30a**) (0.04 g, 47%) as a colorless oil.

30a: IR (film, cm^{-1}) 3050, 1570, 1470, 1420, 1360, 1140, 1030, 1020, 770, 730; ^{1}H NMR δ 1.53 (9H, s), 7.17−7.39 (10H, m), 7.51 (1H, brd, J = 2 Hz), 8.36 (1H, brd, J = 2 Hz); ^{13}C NMR δ 29.51 (q × 3), 39.73 (s), 126.28 (s), 127.84 (d), 128.20 (d), 128.96 (s), 129.12 (s), 129.45 (d × 2), 129.71 (d × 2), 130.79 (s), 133.64 (d × 2), 134.35 (d × 2), 145.56 (d), 148.18 (d), 165.26 (s); EI-MS m/z 370 (M^+ − Ph); FAB-high-resolution mass calcd for $C_{21}H_{21}NSe$ 448.0090, found m/z 448.0076.

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Supporting Information Available: Characterization data for the products **2b−e**, **3b**,**c**, **5b−e**, **7a**,**b**, **8a**,**b**, **9b−11b**, **14c**, **18c**, **29b**,**c**, and **30b**,**c** and NMR spectra, complete with peak assignments of other products (34 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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