Reactions of Diphenyl(phenylethynyl)selenonium Salts with Active Methylene Compounds and Amides: First Isolation of Oxyselenuranes [10-Se-4(C3O)] as a Reaction Intermediate

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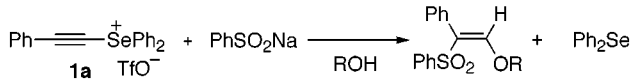
The reaction of the diphenyl(phenylethynyl)selenonium triflate **1a** with active methylene compounds **5** and *t*-BuOK in THF gave furan derivatives **6**. The [10-Se-4(C3O)] selenuranes **8a** and **8b** could be isolated from the reactions with benzoylacetonitrile **5f** and with 1,3-indandione **5g**, respectively, as reaction intermediates. The structures of the selenuranes **8** were elucidated by X-ray crystallography and ^{77}Se high-resolution solid-state NMR spectroscopy. The selenuranes **8** underwent ligand coupling on standing at room temperature or refluxing in chloroform and gave the furan derivatives **6** and the ring-opened product **9**. Similarly, the reaction of **1a** with benzamide **13a** and pivalamide **13d** in the presence of NaH in THF afforded oxazole derivatives **14**.

Introduction

Many kinds of hypervalent organoselenium compounds have been synthesized, and their detailed structures and reactivities have been reported.[1] In particular, the haloselenuranes [10-Se-4(C2OHal)][2] and the alkoxyselenuranes [10-Se-4(O4)][3] and [10-Se-4(C2O2)][4] were widely studied because they bear electronegative ligands and are stable. The σ-selenuranes with four carbon−selenium bonds [10-Se-4(C4)] have been extensively studied by Furukawa's group.[5] Generation of the selenuranes bearing three carbon−selenium bonds and an oxygen−selenium bond [10-Se-4(C3O)] has been investigated by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy of the reaction of bis-(2,2′-biphenylene)selenurane with various alcohols or phenol; however, isolation of the σ-selenurane has been unsuccessful.[6]

Scheme 1



We reported the synthesis of diphenyl(phenylethynyl)-selenonium triflate **1a** and its reactions with sodium benzenesulfinate (Scheme 1).[7] Very recently, the oxyselenuranes [10-Se-4(C3O)] were fortunately obtained from the reactions of the selenonium salt **1a** with active methylene compounds. Therefore, this paper reports the reactions of the alkynylselenonium salts with active methylene compounds and amides and the first isolation of the [10-Se-4(C3O)] σ-selenuranes.

Results and Discussion

We investigated the reaction of trimethyl(phenylethynyl)silane and diphenyl selenoxide **2a** with a Lewis acid in CH_2Cl_2 to prepare the alkynyldiarylselenonium salts. When BF_3·Et_2O was used as a Lewis acid, an alkynylselenonium salt was not obtained at all. In contrast, the reaction with trifluoromethanesulfonic anhydride (Tf_2O), which is extremely strong Lewis acid, afforded diphenyl-(phenylethynyl)selenonium triflate **1a** in 89% yield (Table 1). The reaction with a milder Lewis acid, trimethylsilyl trifluoromethanesulfonate, in comparison with Tf_2O gave **1a** in only 20% yield. The structure of **1a** was determined from its spectral data. The ^{13}C NMR spectrum indicated the presence of the alkynylic carbons at δ 64.7 and 110.9 and the quaternary carbon of $CF_3SO_3^-$ at δ 120.9 (q, J_{C-F} = 319.8 Hz). An absorption band of the alkynyl group showed at 2181 cm^{-1} in the IR spectrum. The FABMS

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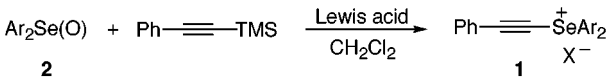
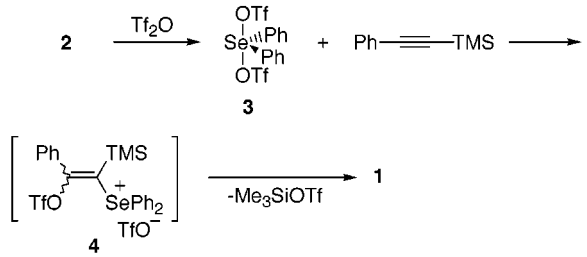
Table 1. Reactions of Diaryl Selenoxide and Trimethyl(phenylethynyl)silane with Lewis Acid



entry	2	Lewis acid	time	products (% yield)
1[a]	**2a**: Ar = Ph	$BF_3{\cdot}Et_2O$	17 h	no reaction
2	**2a**	Tf_2O	12 h	**1a**: X = TfO (89)
3	**2a**	TMSOTf	4 d	**1a** (20)
4	**2b**: Ar = *p*-tolyl	Tf_2O	12 h	**1b**: X = TfO (69)

[a] Treatment with aqueous $NaBF_4$.

Scheme 2



spectrum showed fragment ion peaks arising from the cation moiety of **1a**. Di-*p*-tolyl(phenylethynyl)selenonium triflate**1b** was prepared (69%) in a manner similar to that for **1a**. A plausible reaction mechanism for formation of **1** is shown in Scheme 2. The reaction of diaryl selenoxide **2** with Tf_2O forms bis(trifluoromethanesulfonyl)selenurane **3** (or their ionic form),[4d,8] and then the selenurane **3** reacts with (trimethylsilyl)alkyne to afford an evidently unstable intermediate **4**, which rapidly decomposes to form **1** and trimethylsilyl triflate.

The reaction of **1a** with 2,4-pentanedione **5a** and *t*-BuOK in THF gave a furan derivative **6a**[9] (40%) and diphenyl selenide **7a** (62%). The yield of this reaction was much improved by refluxing the reaction mixture. The reactions with other active methylene compounds under the refluxing conditions similarly gave the corresponding furan derivatives in high yields except the reaction with 1,3-indandione **5g** affording **6g** (2%), **7a** (24%), **8b** (30%), and **9a** (8%). In sharp contrast, the reactions with benzoylacetonitrile **5f** and 1,3-indandione **5g** at room temperature only gave the products **8a** and **8b** in yields of 70% and 39%, respectively. Similarly the reaction of **1b** with **5g** afforded the compound **8c** in good yield (Scheme 3, Table 2). Judging from thermal reactions of the compounds **8a**−**c** as described below, it was assumed that these products would be the reaction intermediates to form the furan derivatives **6f** and **6g** or a ring-opened coupling product **9a**. The structures of **8a**−**c** were characterized by NMR (^1H, ^{13}C, ^{77}Se) spectroscopy, mass spectrometry, and elemental analysis. In particular, the olefinic protons of **8a**, **8b**, and **8c** were observed at δ 5.45, 5.55, and 5.54, respectively, at higher field than that of the (*Z*)-(*β*-phenylsulfonyl)vinylselenonium triflate (δ 7.22).[7] This result implied that the structure of **8** might not be the ionic form. To solve the question of whether the intermediate is a hypervalent compound A or a betaine B, we measured the solid-state

Scheme 3

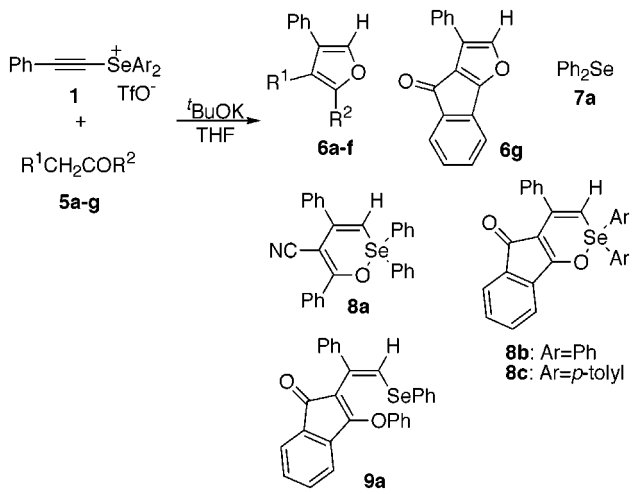


Table 2. Reactions of 1 with Active Methylene Compounds 5

entry	1	5	*T* (°C)	time	products (% yield)	
1	**1a**	**5a** (R^1: MeCO, R^2: Me)	rt	1 d	**6a** (40)	**7a** (62)
2	**1a**	**5a**	reflux	1 h	**6a** (58)	**7a** (88)
3	**1a**	**5b** (R^1: PhCO, R^2: Me)	reflux	1 h	**6b** (80)	**7a** (86)
4	**1a**	**5c** (R^1: PhCO, R^2: Ph)	reflux	2 h	**6c** (53)	**7a** (97)
5	**1a**	**5d** (R^1: MeOCO, R^2: Me)	reflux	1 h	**6d** (83)	**7a** (97)
6	**1a**	**5e** (R^1: EtOCO, R^2: Ph)	reflux	1 h	**6e** (58)	**7a** (97)
7	**1a**	**5f** (R^1: CN, R^2: Ph)	rt	1 d	**8a** (70)	
8	**1a**	**5f**	reflux	1 h	**6f** (63)	**7a** (77)
9	**1a**	**5g** (1,3-indandione)	rt	1 d	**8b** (39)	
10	**1a**	**5g**	reflux	1 h	**6 g** (2)	**7a** (24)
					8b (30)	**9a** (8)
11	**1b**	**5g**	rt	3 h	**8c** (63)	

NMR spectroscopy[10] and compared the ^{77}Se NMR chemical shifts with those in the solutions. Although the cross-polarization magic-angle spinning (CP/MAS) ^{77}Se NMR experiment[11] of the selenonium salt **1a** showed a chemical shift (δ 467.7) almost similar to that in a $CDCl_3$ solution (δ 469.6), the chemical shifts of **8a** and **8b** in the solid state (**8a**, δ 454.1; **8b**, δ 451.3) were different from those monitored in $CDCl_3$ solutions (**8a**, δ 462.2; **8b**, δ 476.2) and shifted to higher field at about 8.1 and 24.9 ppm, respectively. These high-field shifts in the solid state might be attributable to the different structure in each state. Thus, the results suggested that the intermediate **8** in the solid state might be the selenurane form A.[12]

The crystal structure of the intermediate **8a** was established more clearly by X-ray diffraction analysis (Figure 1).[13] The apical-bond distance of Se−O (2.553 Å) is shorter than the sum of the van der Waals radii (3.40 Å). The O−Se−C_{ap} bond angle of 173.5° is approximately collinear and close to those of other selenuranes.[2,4] The quadruple average angle of **8a** (111.3°) coincided with the mean values (ca. 112°) in the

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(13) Crystallographic data for **8a**: $C_{29}H_{21}NOSe$, MW = 478.451, triclinic, space group $P\bar{1}$ (#2), a = 10.867 (2) Å, b = 11.553(2) Å, c = 9.634(1) Å, α = 91.70(1)°, β = 102.68(1)°, γ = 103.46(1)°, V = 1143.4-(3) Å^3, Z = 2, D_{calcd} = 1.390 g/cm^3, μ(Mo Kα) = 16.43 cm^{-1}, R = 3.8%, R_w = 4.2%. Full details of the crystallographic analysis of **8a** are described in the Supporting Information.

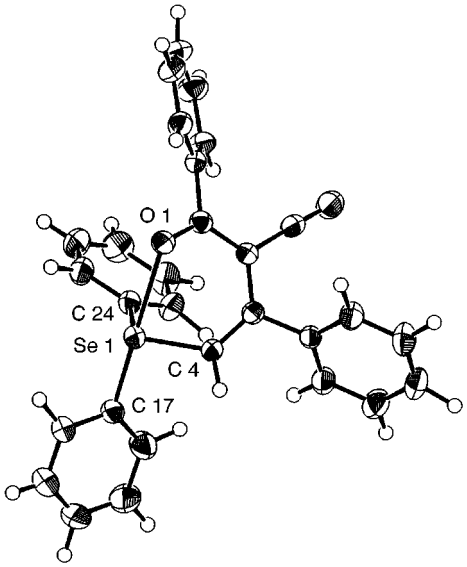


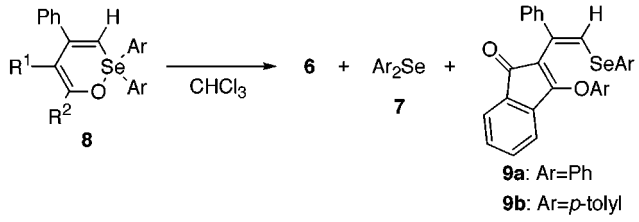
Figure 1. ORTEP drawing of **8a**.

Table 3. Decomposition of Selenuranes 8

entry	**8**	*T* (°C)	time	products (%yield)		
1	**8a**	rt	3 d	**6f** (77)	**7a**: Ar = Ph (81)	
2	**8a**	reflux	8 h	**6f** (87)	**7a** (85)	
3[a]	**8a**	rt	3 d	**6f** (75)	**7a** (90)	
4	**8b**	reflux	3 d	**6g** (13)	**7a** (60)	**9a** (29)
5	**8c**	reflux	3 d	**6g** (52)	**7b**: Ar = *p*-tolyl (87)[b]	**9b** (4)

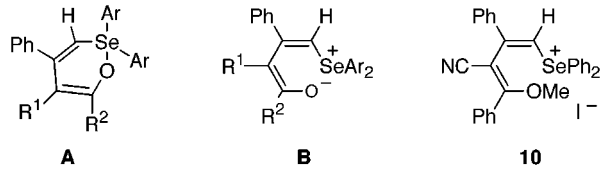
[a] Addition of 10 equiv of CH_3I. [b] A mixture of (*E*)- and (*Z*)-**9b**.

Scheme 4



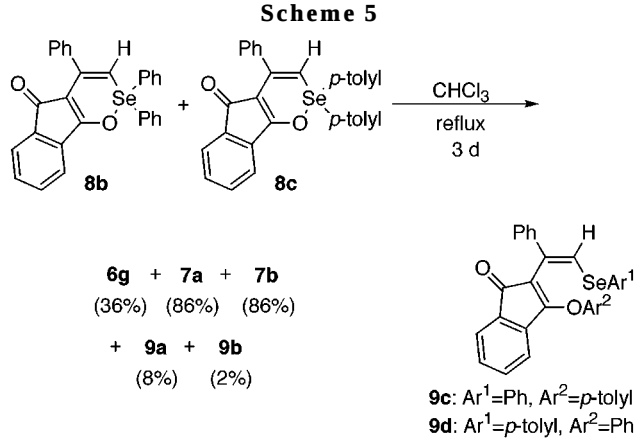
literature.[1b] The configuration about the selenium atom is a slightly distorted trigonal bipyramid with two apical Se−O and Se−Ph bonds and two equatorial Se−C= and Se−Ph bonds, and the lone-pair electrons occupy the third equatorial position. These structural features are consistent with a σ-selenurane structure.

If the compound **8a** has a betaine structure B, the *O*-methylation would occur by treatment of **8a** with iodomethane and a methoxy selenonium salt **10** would be formed. However, the reaction did not give the

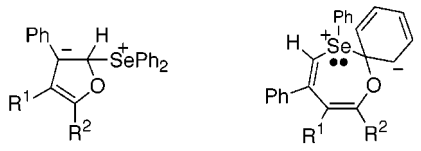


selenonium salt **10** but gave the furan derivative **6f** (75%) and the selenide **7a** (90%) (entry 3 in Table 3). Furthermore, we chemically observed that the compounds **8a** and **8b** underwent the ligand-coupling reactions to form **6f**, **6g**, and **7a** (Scheme 4). When a solution of **8a** in chloroform was allowed to stand at room temperature for 3 days, a furan derivative **6f** (77%) and **7a** (81%) were

Scheme 5



obtained. The reaction was completed in 8 h under reflux in chloroform. The reaction of **8b** proceeded slowly to give a furan derivative **6g** (13%), **7a** (60%), and a ring-opened product **9a** (29%). The structure of the selenide **9a** was determined from the result of spectral data. The ^{1}H NMR spectrum of **9a** showed a singlet at δ 6.93 assignable to a vinyl proton. The electron impact MS showed the molecular ion peak at *m*/*z* 480 and the base peak at *m*/*z* 323 due to a fragment ion peak of [M − PhSe]$^+$. The reaction of **8c** similarly afforded **6g** (52%), **7b** (87%), and a small amount of a mixture of (*E*)- and (*Z*)-**9b** (4%). Two reaction pathways can be considered for the formation of the furan derivative. If the reactions proceed via the betaine **11**, which is formed by addition of an alkoxide ion to the vinylselenonium ion and the subsequent elimination of diphenyl selenide, the selenide **9a** cannot be formed. Thus, the addition−elimination



mechanism is not feasible for this reaction. The second route to **6** and **9a** is a pathway going through the selenurane intermediate **8**. The ligand coupling reaction of **8** between the alkoxy group and the alkenyl carbon and between the alkoxy group and the phenyl group gives **6** and **9a**, respectively. We conducted the crossover reaction of **8b** and **8c** to examine the possibility that **9a** might be formed via the intermolecular ipso attack of the alkoxide ion on the phenyl group (Scheme 5). A thermal reaction of the mixture of **8b** and **8c** in chloroform gave **6g** (36%), **7a** (86%), **7b** (86%), and a mixture of **9a** (8%) and **9b** (2%). If the crossover reaction proceeded, the crossed products **9c** or **9d** should be formed. Since the MS spectra of the concentrated reaction mixture did not show the molecular ion peaks of **9c** and **9d**, this reaction route was ruled out. The intramolecular ipso substitution must go through a seven-membered cyclic intermediate **12**, and therefore, the ligand coupling reaction via the hypervalent intermediate **8** mentioned above is more favorable for formation of **6** and **9a**. It has been reported that reactions of alkynyliodonium salts with β-ketosulfone and β-ketonitrile gave furan derivatives via alky-

Scheme 6

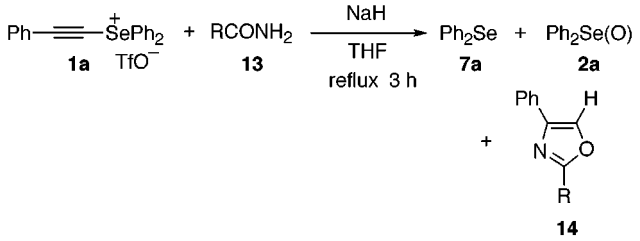
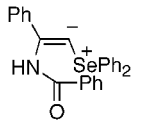


Table 4. Reactions of 1a with Amides 13

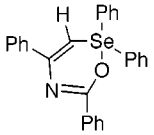
entry	13	products (%yield)		
1	**13a** (R = Ph)	**14a** (50)	**7** (56)	**2a** (40)
2	**13b** (R = H)		**7** (19)	**2a** (44)
3	**13c** (R = Me)		**7** (6)	**2a** (78)
4	**13d** (R = *t*-Bu)	**14b** (27)	**7** (43)	**2a** (44)

lidene carbene intermediates.[14] Our findings were much different from these and particularly interesting in terms of the formation of the hypervalent intermediates.

If amides are used instead of the active methylene compounds, formation of oxazole derivatives can be expected. We conducted the reaction of **1a** with benzamide **13a** and NaH in THF and obtained 2,4-diphenyloxazole **14a** (50%), **7a** (56%), and **2a** (40%) (Scheme 6, Table 4). The structure of the compound **14a** was determined by comparing its ^{1}H and ^{13}C NMR spectral data with those of an authentic sample in the literature.[15] The reactions with formamide **13b** and acetamide **13c** did not afford any oxazole derivatives but the complex mixtures. The selenonium salt **1a** reacted with pivalamide **13d** to give **14b**[16] in low yield. The oxazole derivatives would be formed by the ligand-coupling reaction of the hypervalent intermediate similar to formation of furans. The amide ion adds to the C_β to the selenonio group of **1a** and produces the Michael adduct C. The subsequent protonation of the C_α and the attack of the resulting lactim anion −N=C−O$^-$ on the selenium atom form the selenurane intermediate D. The ligand coupling between the oxygen atom and the alkenyl carbon affords an oxazole derivative. Diphenyl selenoxide **2a** would be produced by hydrolysis of **1a**, probably because the reactions were slow.



C



D

In conclusion, the reactions of alkynylselenonium salts **1** with active methylene compounds and amides gave furan and oxazole derivatives, respectively, and we have isolated the first selenuranes with three carbon−selenium bonds and an oxygen−selenium bond [10-Se-4(C3O)] as reaction intermediates. Their selenurane structures were established by the ^{77}Se NMR spectroscopy and X-ray crystallography as well as their chemical behavior giving the ligand coupling products.

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Expermental Section

General Procedures. Uncorrected melting points were determined with a micro melting point apparatus. ^{1}H (270 or 400 MHz), ^{13}C (100 MHz), and ^{77}Se (76.1 MHz) NMR spectra were determined with solutions in $CDCl_3$. Mass spectra (MS and HRMS) were obtained with electron impact (EI, 70 eV) or fast atom bombardment (FAB, glycerol or 3-nitrobenzyl alcohol) techniques. IR spectra were recorded as solids (KBr) and liquids (NaCl). Organic solvents used were dried by standard methods. All chromatographic isolations were accomplished with Kieselgel 60 PF_{254} containing gypsum for preparative TLC.

Diphenyl(phenylethynyl)selenonium Trifluoromethanesulfonate (1a). Trifluoromethanesulfonic anhydride (1.5 mL, 8.9 mmol) was added dropwise to a stirred solution of diphenyl selenoxide (1.0 g, 4.0 mmol) and 1-phenyl-2-(trimethylsilyl)ethyne (1.5 g, 8.6 mmol) in dichloromethane (30 mL) at 0 °C. The mixture was stirred at room temperature for 12 h. After the solvent was evaporated under reduced pressure, the precipitate was filtered off and washed several times with ether and benzene. Recrystallization from CH_2Cl_2/Et_2O afforded 1.72 g (89%) of **1a** as white prisms: mp 117 °C; IR (KBr) 2181, 1270, 1154, 1029 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.06 (d, 4H), 7.77−7.57 (m, 9H), 7.48 (t, 1H); ^{13}C NMR ($CDCl_3$) δ 133.8, 133.4, 132.7, 131.8, 130.8, 130.2, 129.3, 120.9 (q, J = 319.8 Hz), 118.1, 110.9, 64.7; ^{77}Se NMR ($CDCl_3$) δ 469.6; ^{77}Se CP-MAS NMR δ 467.7; FAB MS *m*/*z* 335 [(M − TfO)$^+$]. Anal. Calcd for $C_{21}H_{15}F_3O_3SSe$: C, 52.18; H, 3.13. Found: C, 52.08; H, 3.24.

Di-*p*-tolyl(phenylethynyl)selenonium Trifluoromethanesulfonate (1b). Trifluoromethanesulfonic anhydride (0.75 mL, 4.5 mmol) was added dropwise to a stirred solution of di-*p*-tolyl selenoxide (554 mg, 2.0 mmol) and 1-phenyl-2-(trimethylsilyl)ethyne (750 mg, 4.3 mmol) in dichloromethane (15 mL) at 0 °C. The mixture was stirred at room temperature for 12 h. After the solvent was evaporated under reduced pressure, the precipitate was filtered off and washed several times with ether and benzene. Recrystallization from CH_2Cl_2/Et_2O afforded 703 mg (69%) of **1b** as white prisms: mp 116−118 °C; IR (KBr) 2175, 1270, 1155, 1029 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.90 (d, 4H), 7.66 (d, 2H), 7.56 (t, 1H), 7.46 (t, 2H), 7.41 (d, 4H), 2.43 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 144.7, 133.1, 132.3, 132.1, 129.9, 129.1, 127.2, 120.7 (q, J = 319.8 Hz), 118.0, 109.9, 64.8, 21.5; FAB MS *m*/*z* 363 [(M − TfO)$^+$]. Anal. Calcd for $C_{23}H_{19}F_3O_3SSe$: C, 54.02; H, 3.74. Found: C, 54.02; H, 3.67.

General Procedure for Reactions of Alkynylselenonium Salts 1 with Active Methylene Compounds 5. A Typical Example (Table 2, Entry 1): 3-Acetyl-2-methyl-4-phenylfuran (6a). To a stirred solution of 2,4-pentanedione **5a** (20 mg, 0.20 mmol) in THF (3 mL) was added 90% *t*-BuOK (25 mg, 0.20 mmol) at room temperature under argon. After the mixture was stirred for 30 min, the selenonium triflate **1a** (97 mg, 0.20 mmol) was added, and the mixture was stirred for 1 d at room temperature. The mixture was quenched with water and extracted with chloroform. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. Preparative TLC (10:1 hexanes−ethyl acetate) of the crude product gave **7a** (29 mg, 62%) and **6a** (16 mg, 40%). **6a**: colorless oil; IR (neat) 1674 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.42−7.35 (m, 3H), 7.32 (d, 2H), 7.23 (s, 1H), 2.56 (s, 3H), 2.05 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 195.1, 158.6, 138.0, 132.4, 129.2, 128.4, 127.7, 126.7, 122.2, 30.9, 14.3; MS *m*/*z* (relative intensity) 200 (71, M$^+$), 185 (100); HRMS calcd for $C_{13}H_{12}O_2$ (M$^+$) 200.0837, found 200.0840.

The mixture of 2,4-pentanedione **5a** (20 mg, 0.20 mmol), 90% *t*-BuOK (25 mg, 0.20 mmol), and the selenonium triflate **1a** (97 mg, 0.20 mmol) in THF (3 mL) was refluxed for 1 h in a manner similar to that of the above experiment. Preparative TLC (5:1 hexanes−ethyl acetate) of the crude products gave **7a** (41 mg, 88%) and **6a** (23 mg, 58%).

The products and their yields are listed in Table 2.

3-Benzoyl-2-methyl-4-phenylfuran (6b): colorless oil; IR (neat) 1652 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.72 (d, 2H), 7.44 (s, 1H), 7.39 (t, 1H), 7.26 (t, 2H), 7.16−7.12 (m, 5H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 192.5, 157.2, 138.1, 137.6, 132.7, 131.4, 129.5,

128.2, 128.1, 128.0, 127.5, 126.9, 120.5, 31.8; MS *m/z* (relative intensity) 262 (100, M^+), 261 (95), 185 (14); HRMS calcd for $C_{18}H_{14}O_2$ (M^+) 262.0994, found 262.1001.

3-Benzoyl-2,4-diphenylfuran (6c): colorless oil; IR (neat) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85 (d, 2H), 7.67 (s, 1H), 7.58 (d, 2H), 7.42 (t, 1H), 7.28−7.17 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 193.8, 153.4, 138.6, 137.4, 133.5, 131.1, 129.8, 129.7, 128.9, 128.5, 128.4, 127.8, 127.4, 126.4, 120.3; MS *m/z* (relative intensity) 324 (100, M^+), 247 (25), 105 (67); HRMS calcd for $C_{23}H_{16}O_2$ (M^+) 324.1150, found 324.1160.

Methyl 2-methyl-4-phenyl-3-furancarboxylate (6d): colorless oil; IR (neat) 1716 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36−7.30 (m, 5H), 7.26 (s, 1H), 3.71 (s, 3H), 2.60 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 164.5, 160.3, 138.3, 131.9, 129.1, 127.8, 127.4, 127.3, 112.5, 51.0, 14.3; MS *m/z* (relative intensity) 216 (100, M^+), 185 (64), 184 (60), 128 (47), 127 (33). Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.28; H, 5.78.

Ethyl 2,4-diphenyl-3-furancarboxylate (6e): colorless oil; IR (neat) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82 (d, 2H), 7.49 (s, 1H), 7.46−7.32 (m, 8H), 4.18 (q, 2H), 1.07 (t, 3H); ^{13}C NMR ($CDCl_3$) δ 164.6, 156.5, 139.0, 131.7, 129.9, 129.1, 128.7, 128.5, 128.2, 128.1, 127.7, 127.5, 113.9, 60.8, 13.7; MS *m/z* (relative intensity) 292 (100, M^+), 247 (53), 105 (83); HRMS calcd for $C_{19}H_{16}O_3$ (M^+) 292.1099, found 292.1107.

5-Cyano-2,2,4,6-tetraphenyl-1,2-oxaselenin (8a) was obtained as a pale yellow powder. This compound was pure enough to use its analysis and reactions: mp 139−141 °C dec; IR (KBr) 2185 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.64 (d, 4H), 7.58−7.49 (m, 7H), 7.43−7.36 (m, 5H), 7.28−7.24 (m, 4H), 5.45 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 186.0, 157.0, 141.01, 140.97, 132.7, 131.8, 130.5, 129.7, 129.5, 129.30, 129.27, 129.0, 128.4, 127.6, 127.5, 124.7, 95.6, 79.7; ^{77}Se NMR ($CDCl_3$) δ 462.2; ^{77}Se CP-MAS NMR δ 454.1; FAB MS *m/z* 480 $(M + 1)^+$. Anal. Calcd for $C_{29}H_{21}NOSe$: C, 72.80; H, 4.42; N, 2.93. Found: C, 72.67; H, 4.42; N, 2.84.

3-Cyano-2,4-diphenylfuran (6f): white powder; mp 89 °C; IR (neat) 2231 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.03 (d, 2H), 7.63 (d, 2H), 7.62 (s, 1H), 7.51−7.43 (m, 5H), 7.38 (t, 1H); ^{13}C NMR ($CDCl_3$) δ 161.0, 138.3, 130.2, 129.2, 129.0, 128.7, 128.5, 128.0, 126.9, 125.5, 115.2, 91.5; MS *m/z* (relative intensity) 245 (100, M^+), 216 (35), 189 (15); HRMS calcd for $C_{17}H_{11}NO$ (M^+) 245.0841, found 245.0848.

2,2,4-Triphenyl-5*H*-indeno[1,2-*e*]-1,2-oxaselenin (8b): yellow powder; mp 146−148 °C dec; IR (KBr) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.67 (d, 4H), 7.60−7.51 (m, 6H), 7.50−7.46 (m, 2H), 7.43−7.31 (m, 7H), 5.55 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 190.4, 156.3, 139.9, 139.4, 133.3, 131.8, 130.9, 130.5, 130.0, 129.3, 129.2, 128.8, 127.9, 119.4, 104.4, 96.2; ^{77}Se NMR ($CDCl_3$) δ 476.2; ^{77}Se CP-MAS NMR δ 451.3; MS *m/z* 480 (M^+). Anal. Calcd for $C_{29}H_{20}O_2Se \cdot 1/2H_2O$: C, 71.31; H, 4.33. Found: C, 71.06; H, 4.54.

4-Phenyl-2,2-di-*p*-tolyl-5*H*-indeno[1,2-*e*]-1,2-oxaselenin (8c): yellow powder: mp 119−123 °C dec; IR (neat) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53 (d, 4H), 7.49−7.46 (m, 2H), 7.41 (d, 2H), 7.39−7.36 (m, 2H), 7.35−7.31 (m, 7H) 5.54 (s, 1H), 2.42 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 190.4, 155.7, 142.5, 140.0, 139.9, 139.4, 131.2, 130.9, 122.9, 129.8, 129.2, 128.7, 127.9, 119.3, 104.3, 97.3, 21.3; MS *m/z* 508 (M^+). Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.28; H, 5.78.

3-Phenyl-4*H*-indeno[1,2-*b*]furan-4-one (6g): yellow powder; mp 129−130 °C; IR (neat) 1706 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88 (d, 2H), 7.78 (s, 1H), 7.51 (d, 1H), 7.43 (t, 2H), 7.33 (t, 2H), 7.22 (t, 1H), 7.16 (d, 1H); ^{13}C NMR ($CDCl_3$) δ 184.9, 176.0, 143.6, 138.4, 133.7, 133.0, 129.9, 129.2, 128.9, 128.2, 126.8, 126.0, 123.9, 121.6, 117.2; MS *m/z* (relative intensity) 246 (100, M^+), 189 (50); HRMS calcd for $C_{17}H_{10}O_2$ (M^+) 246.0681, found 246.0686.

3-Phenoxy-2-[1-phenyl-2-(phenylseleno)ethenyl]inden-1-one (9a): pale yellow oil: IR (neat) 1707 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.01 (m, 2H), 7.82 (m, 2H), 7.37−7.31 (m, 4H), 7.21−7.07 (m, 11H), 6.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 198.4, 143.2, 142.4, 135.7, 135.5, 132.2, 131.8, 129.4, 129.2, 128.5, 128.4, 127.9, 127.7, 127.6, 127.5, 127.3, 126.7, 123.9, 70.5; ^{77}Se NMR ($CDCl_3$) δ 395.4; MS *m/z* (relative intensity) 480 (37, M^+), 323 (100), 247 (40); HRMS calcd for $C_{29}H_{20}O_2Se$ (M^+) 480.0628, found 480.0622.

Decomposition of 8a. (a) A solution of compound **8a** (96 mg, 0.20 mmol) in chloroform (3 mL) was stirred at room temperature for 3 d. After the solution was concentrated, the residue was purified by preparative TLC (5:1 hexanes−ethyl acetate) to give **7a** (38 mg, 81%) and **6f** (38 mg, 77%). (b) A solution of compound **8a** (128 mg, 0.27 mmol) in chloroform (10 mL) was refluxed for 8 h and similarly worked up as above to give **7a** (53 mg, 85%) and **6f** (57 mg, 87%).

Treatment of 8a with Iodomethane. Compound **8a** (96 mg, 0.20 mmol) was stirred with 95% iodomethane (300 mg, 2.0 mmol) in chloroform (3 mL) at room temperature for 3 d. After the solution was concentrated, the residue was purified by preparative TLC (5:1 hexanes−ethyl acetate) to give **7a** (42 mg, 90%) and **6f** (37 mg, 75%).

Decomposition of 8b. A solution of compound **8b** (62 mg, 0.13 mmol) in chloroform (10 mL) was treated in a manner similar to that for **8a** and gave **7a** (18 mg, 60%), **6g** (4 mg, 13%), and **9a** (18 mg, 29%).

Decomposition of 8c. A solution of compound **8c** (92 mg, 0.18 mmol) in chloroform (10 mL) was treated in a manner similar to that for **8a** and gave **7b** (41 mg, 87%), **6g** (23 mg, 52%), and a mixture of (*E*)- and (*Z*)-3-*p*-methylphenoxy-2-[1-phenyl-2-(*p*-tolylseleno)ethenyl]inden-1-one **9b** (4 mg, 4%). **9b**: pale yellow oil; IR (neat) 1707 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.99 (m, 0.5H), 7.90 (m, 2H), 7.81 (m, 0.5H), 7.74 (m, 2H), 7.49 (d, 2H), 7.28−7.01 (m, 17H), 6.95 (d, 0.5H), 6.88 (s, 0.25H), 6.57 (s, 1H), 2.29 (s, 6H), 2.27 (s, 0.75H), 2.19 (s, 0.75H); MS *m/z* (relative intensity) 508 (35, M^+), 506 (18), 337 (100), 309 (20), 265 (45); HRMS calcd for $C_{31}H_{24}O_2Se$ (M^+) 508.0941, found 508.0936.

Crossover Reaction of 8b and 8c. A solution of the mixture of **8b** (73 mg, 0.15 mmol) and **8c** (77 mg, 0.15 mmol) in chloroform (10 mL) was refluxed for 3 d. After the solution was concentrated, the residue was purified by preparative TLC (5:1 hexanes−ethyl acetate) to give a mixture of **7a** (31 mg, 87%) and **7b** (34 mg, 86%), **6g** (27 mg, 36%), a mixture of **9a** (7 mg, 8%) and **9b** (1 mg, 2%), and an unidentified product (27 mg). The ratio of the products in a mixture was determined by ^1H NMR.

General Procedure for Reactions of Alkynylselenonium Salts 1a with Amides 13. A Typical Example (Table 4, Entry 1). To a stirred solution of benzamide **13a** (24 mg, 0.20 mmol) in THF (3 mL) was added 60% NaH (8 mg, 0.20 mmol) at room temperature under argon. After the mixture was stirred for 30 min, the selenonium triflate **1a** (97 mg, 0.20 mmol) was added, and then the mixture was refluxed for 3 h. The mixture was quenched with NH_4Cl (aq) and extracted with chloroform. The organic phase was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. Preparative TLC (5:1 hexanes−ethyl acetate and 10:1 chloroform−methanol) of the crude product gave 2,4-diphenyloxazole **14a** (22 mg, 50%), **7a** (26 mg, 56%), and **2a** (20 mg, 40%). **14a**: a white powder; mp 101−102 °C; ^1H NMR ($CDCl_3$) δ 8.15−8.11 (m, 2H), 7.97 (s, 1H), 7.83 (d, 2H), 7.51−7.46 (m, 3H), 7.43 (t, 2H), 7.34 (t, 1H); ^{13}C NMR ($CDCl_3$) δ 161.9, 142.0, 133.4, 133.4, 131.1, 130.4, 128.7, 128.1, 127.5, 126.5, 125.6; MS *m/z* (relative intensity) 221 (100, M^+), 193 (83). The melting point and spectral data were identical with those of an authentic sample in the literature.[15]

2-*tert*-Butyl-4-phenyloxazole (14b):[16] colorless oil; IR (neat) 1566 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.79 (s, 1H), 7.73 (d, 2H), 7.38 (t, 2H), 7.28 (t, 1H), 1.43 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 171.5, 140.2, 132.7, 131.5, 128.6, 127.7, 125.6, 33.8, 28.6; MS *m/z* (relative intensity) 201 (100, M^+), 186 (73); HRMS calcd for $C_{13}H_{15}NO$ (M^+) 201.1154, found 201.1150.

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Supporting Information Available: Details of the crystallographic analysis of **8a** (10 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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