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Oxidative Cleavage of Diselenide by *m*-Nitrobenzenesulfonyl Peroxide. Novel Method for the Electrophilic Benzeneselenenylations of Olefins and Aromatic Rings

Masato Yoshida,* Shuichi Sasage, Kyoko Kawamura, Takashi Suzuki, and Nobumasa Kamigata
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158

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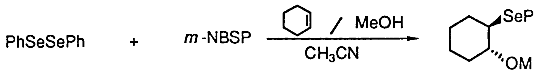
Diphenyl diselenide was found to be readily converted into benzeneselenenyl *m*-nitrobenzenesulfonate ($PhSeOSO_2C_6H_4NO_2$-*m*) by treating with *m*-nitrobenzenesulfonyl peroxide. When the selenenyl sulfonate thus formed was allowed to react in situ with olefins, such as cyclohexene, 1-octene, or styrene, in the presence of various nucleophiles, the adducts of benzeneselenenyl group and a nucleophile were obtained. As the nucleophiles water, methanol, acetic acid, phenol, and anisole could be employed; oxyselenenylated ($\mathrm{PhSe{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}OR}$: R=H, Me, Ac, and Ph) and arylselenenylated ($\mathrm{PhSe{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}C_6H_4OR}$: R=H and Me) adducts were afforded. Phenol gave oxyselenenylated products in cyclohexene or 1-octene and arylselenenylated products in styrene. Efficient intramolecular cyclizations of unsaturated alcohols and carboxylic acids were similarly performed by the selenenyl sulfonate to afford corresponding benzeneselenenylated cyclic ethers and lactones. The selenenyl sulfonate was also found to be a highly reactive benzeneselenenylating reagent for aromatic rings, such as anisole, phenol, acetanilide, toluene, and benzene.

Organoselenium reagents can be used as nucleophiles, electrophiles, and radicals according to the conditions. Electrophilic selenenylating reagents are usually prepared from oxidative cleavage of diselenide, which is stable and easy to prepare and handle, by halogens,¹⁾ metal ions,²⁾ electrolytic oxidation,³⁾ and photoelectron transfer.⁴⁾ We are currently interested in the conversion of stable substrates into electrophilic reagents using nitrobenzenesulfonyl peroxides (NBSP).⁵⁾ In the course of the study, we found that diphenyl diselenide could be readily converted into electrophilic selenenylating reagent by treating with *m*-nitrobenzenesulfonyl peroxide (*m*-NBSP), and a preliminary communication has appeared.⁶⁾ Since we further investigated the electrophilic selenenylations of olefins and aromatic rings using a combination of diphenyl diselenide with *m*-NBSP in detail under various conditions, we report the results as full account.

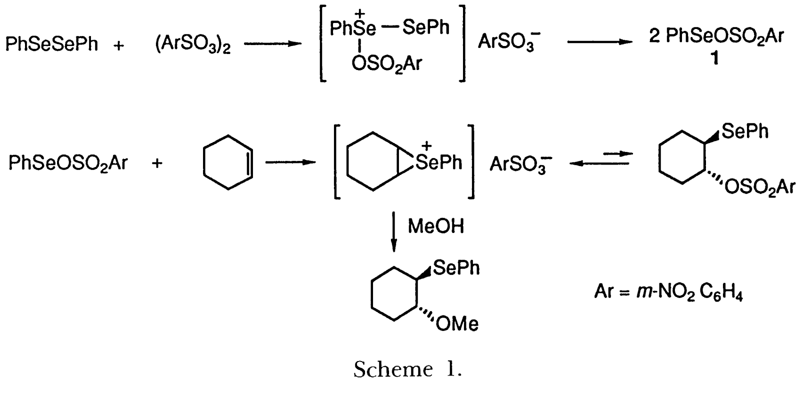
Results and Discussion

Diphenyl diselenide (0.5 mmol) was treated with *m*-NBSP (0.5 mmol) in 20 ml acetonitrile at 0 °C, and then to the resulting solution cyclohexene (1.1 mmol) in 5 ml methanol was added. The anti-adduct of benzeneselenenyl and methoxyl groups to cyclohexene was obtained in 92% yield.



(1)

A plausible mechanism is shown in Scheme 1. Methoxyselenenylations are well-known to occur by the reactions of electrophilic selenenylating reagents with olefins in the presence of methanol,⁷⁾ so the formation of cationic benzeneselenenyl species is suggested in the reaction of diphenyl diselenide with *m*-NBSP. We propose benzeneselenenyl *m*-nitrobenzenesulfonate (**1**) as the electrophilic intermediate as shown in Scheme 1. The lone pair on the selenium atom of the diselenide attacks the O-O bond of *m*-NBSP to produce the selenonium salt, and then the cleavage of Se-Se bond gives two moles of benzenesele-



Scheme 1.

nenyl sulfonate.[8] *m*-NBSP is known to behave as a good electrophile in the presence of π- and n-electron donors.[9]

The formation of selenenyl sulfonate **1** was confirmed by ^{13}C NMR studies. Diphenyl diselenide was treated with *m*-NBSP or *p*-NBSP in chloroform-*d*, and ^{13}C NMR was measured to compare with those of benzeneselenenyl trifluoromethanesulfonate. The chemical shifts of the benzeneselenenyl group in benzeneselenenyl *m*-nitrobenzenesulfonate were 130.7, 130.7, 132.5, and 135.8 ppm from internal TMS, and those of bezeneselenenyl *p*-nitrobenzenesulfonate were 130.8, 130.8, 133.2, and 135.6 ppm. The observed chemical shifts were quite similar to those in benzeneselenenyl trifluoromethanesulfonate reported in the literature.[10] Benzeneselenenyl trifluoromethanesulfonate has been prepared from benzeneselenenyl chloride with silver trifluoromethanesulfonate[10,11] or trifluoromethanesulfonic acid.[11]

Electrophilic benzeneselenenylating reagents are known to react with olefins to give episelenonium salts.[7] Although episelenonium salts usually exists in equilibrium with their adducts,[7] the episelenonium nitrobenzenesulfonate did not give adduct, probably because the counter anion, *m*-nitrobenzenesulfonate, is a very stable and weak nucleophile. Therefore, when methanol exists in the reaction system of olefin with **1**, the episelenonium salt thus formed reacts with the methanol to give the adduct of benzeneselenenyl and methoxyl groups (Scheme 1). The anti addition observed in methoxyselenenylation of cyclohexene supports the formation of episelenonium ion. Selenenyl chlorides and bromides have been most widely used for electrophilic selenenylation, however the halide anions act as nucleophiles and often cause an addition of halogen.[7] If it is desired to favor introduction of methanol, the counter anion of episelenonium salt is preferable to be as weak nucleophile as possible. For this purpose it was attempted that selenenyl halides were converted into other selenenylating reagents possessing weak nucleophilic counter anions, such as *N*-phenylselenophthalimide or succinimide.[12] Benzeneselenenyl sulfonates are also expected to be good reagents for oxyselenenylations due to the weak nucleophilicity of sulfonate.[13]

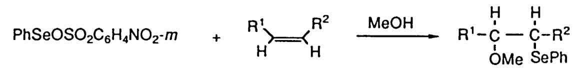
So we investigated the various benzeneselenenylations of styrene, cyclohexene, and 1-octene with **1** in the presence of oxygen nucleophile such as methanol, acetic acid, water, or phenol. Diphenyl diselenide (0.5 mmol) was reacted with *m*-NBSP (0.5 mmol) in a freshly distilled solvent (20 ml), such as dichloromethane, acetonitrile, or nitromethane, and olefin and then nucleophile were added. The results are sum-

Table 1. Reactions of Selenenyl Sulfonate **1** with Olefins in the Presence of Oxygen Nucleophiles

Olefin	Nucleophile		Solvent	Products (Yield/%)[a]
Styrene	MeOH	(5 ml)	CH_3CN	**2** (98)[b]
Cyclohexene	MeOH	(5 ml)	CH_3CN	**3** (92)[b]
1-Octene	MeOH	(5 ml)	CH_3CN	**4a**+**4b** (83)[b,c]
Cyclohexene	MeOH	(5 ml)	CH_2Cl_2	**3** (81)
Cyclohexene	AcOH	(5 ml)	CH_2Cl_2	**6** (trace)
Cyclohexene	AcOH	(5 ml)	CH_3CN	**6** (25)
Cyclohexene	AcOH	(5 ml)	CH_3NO_2	**6** (70)
Styrene	AcOH	(5 ml)	CH_3NO_2	**5** (11)
1-Octene	AcOH	(5 ml)	CH_3NO_2	**7** (73)
Styrene	H_2O	(5 ml)	CH_3CN	**8** (99)
Cyclohexene	H_2O	(5 ml)	CH_3CN	**9** (77), **12** (16)
1-Octene	H_2O	(5 ml)	CH_3CN	**13a**+**13b** (22)[d]
Styrene	H_2O	(5 mmol)	CH_3CN	**8** (61), **11** (Trace)
Cyclohexene	H_2O	(5 mmol)	CH_3CN	**9** (33), **12** (64)
1-Octene	H_2O	(5 mmol)	CH_3CN	**10a** (43),[e] **13a**+**13b** (54)[f]
Styrene	H_2O	(5 ml)	CH_3NO_2	**8** (77)
Cyclohexene	H_2O	(5 ml)	CH_3NO_2	**9** (72)
1-Octene	H_2O	(5 ml)	CH_3NO_2	None
Styrene	PhOH	(10 mmol)	CH_3CN	**16** (78)[b]
Cyclohexene	PhOH	(10 mmol)	CH_3CN	**14** (38)[b]
1-Octene	PhOH	(10 mmol)	CH_3CN	**15** (25)[b]
Styrene	PhOH	(10 mmol)	CH_3NO_2	**16** (82)
Cyclohexene	PhOH	(10 mmol)	CH_3NO_2	**14** (64)
1-Octene	PhOH	(10 mmol)	CH_3NO_2	**15** (62)

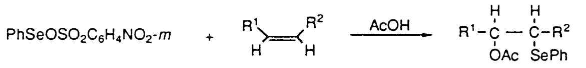
a) Products were isolated and the yields were determined based on **1** evaluated from diselenide. b) Data from Ref. 6. c) The products were obtained as a mixture of **4a** and **4b** (80:20 by NMR). d) The products were obtained as a mixture of **13a** and **13b** (88:12 by NMR). e) A small amount of regioisomer **10b** was contained. f) The products were obtained as a mixture of **16a** and **16b** (84:16 by NMR).

marized in Table 1. Methoxyselenenylation (Eq. 2) proceeded in good to excellent yields regardless of olefins and solvents employed.


(2)

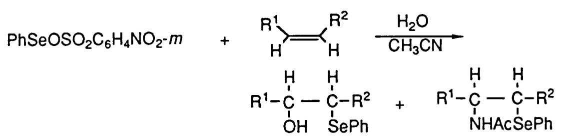
2 (R^1 = Ph, R^2 = H)
3 (R^1 = R^2 = -$(CH_2)_4$-)
4a (R^1 = C_6H_{13}, R^2 = H)
4b (R^1 = H, R^2 = C_6H_{13})

On the other hand, the yields of acetoxyselenenylation (Eq. 3) depended on both solvents and olefins employed. Acetoxyselenenylation of cyclohexene proceeded in nitromethane in good yield, however, in dichloromethane the reaction proceeded only to a small extent. The results mean that selenenyl sulfonate **1** is formed in dichloromethane, acetonitrile, and nitromethane, but the acetoxyselenenylation with **1** is extremely influenced by solvents. Thus, acetoxyselenenylations of styrene and 1-octene were examined in nitromethane; although 1-octene afforded **7** in good yield, the yield of acetoxyselnenylated product of styrene (**5**) was only 11%.


(3)

5 (R^1 = Ph, R^2 = H)
6 (R^1 = R^2 = -$(CH_2)_4$-)
7 (R^1 = C_6H_{13}, R^2 = H)

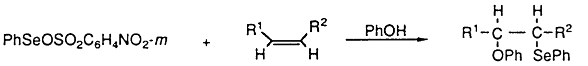
When excess of water (5 ml) was added in acetonitrile, hydroxyselenenylation occurred in good to excellent yields in styrene and cyclohexene to afford **8** and **9**. Hydroxyselenenylation of 1-octene did not occur under similar conditions, but amidoselenenylated product (**13**) was obtained in 22% yield. On the other hand, when small amount of water (5 mmol) was used in acetonitrile, amidoselenenylation of cyclohexene and 1-octene occurred prior to hydroxyselenenylation, but amidoselenenylation of styrene proceeded only in a small yield.


(4)

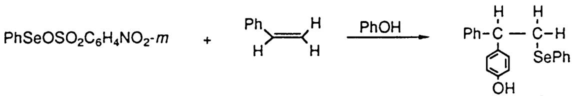
8	11 (R^1 = Ph, R^2 = H)
9	12 (R^1 = R^2 = -$(CH_2)_4$-)
10a	13a (R^1 = C_6H_{13}, R^2 = H)
10b	13b (R^1 = H, R^2 = C_6H_{13})

The amidoselenenylation is explained by the reaction of episelenonium ion with acetonitrile as shown in Scheme 2. Amidoselenenylations of olefins have been known to proceed in the reaction of electrophilic benzeneselenenylating reagents with olefin in acetonitrile in the presence of trifluoromethanesulfonic acid and water.[14,15] By the use of nitromethane as a solvent hydroxyselenenylated products of styrene **8** and cyclohexene **9** could be obtained selectively in good yields, however, hydroxyselenenylation of 1-octene did not occur.

Since the nucleophilicity of nitrobenzenesulfonate is very weak, the oxyselenenylation is expected to occur even in the presence of weak oxygen nucleophiles, which are inapplicable with benzeneselenenyl halides. Thus, we investigated the reaction of **1** with olefins in the presence of phenol. Phenoxyselenenylation of cyclohexene and 1-octene occurred in moderate yields in acetonitrile and in good yields in nitromethane (Eq. 5). An unexpected product (**16**) was obtained in the reaction of styrene as shown in Eq. 6. The episelenonium ion produced from the reaction of styrene with **1** electrophilically attacked on the aromatic ring of phenol, whereas those from cyclohexene and 1-octene reacted at oxygen atom of phenol.

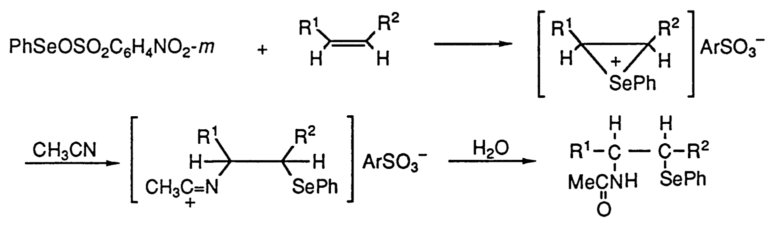

(5)

14 (R^1 = R^2 = -$(CH_2)_4$-)
15 (R^1 = C_6H_{13}, R^2 = H)


(6)

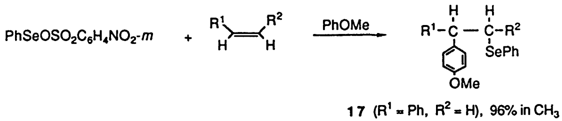
16

The arylselenenylation is interesting as Friedel-Crafts type C-C bond formation. The electrophilic aromatic substitutions of the episelenonium ion with



Scheme 2.

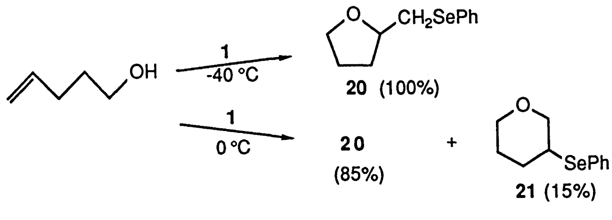
anisole were also observed.[6] When anisole was added to the reaction mixture of diselenide with *m*-NBSP and olefin, the adduct of benzeneselenenyl group and anisole to styrene was obtained in excellent yield in acetonitrile (Eq. 7). *p*-Methoxyphenylselenenylations of cyclohexene and 1-octene also occurred in moderate yields in nitromethane (Eq. 7), but not in acetonitrile. Acetonitrile reacted as nucleophile prior to anisole to give amidoselenenylated products **12** and **13** in 51% and 43% yields, respectively. The aromatic substitutions of the episelenonium ion did not occur in benzene and toluene under similar conditions.



(7)

17 (R^1 = Ph, R^2 = H), 96% in CH_3CN
18 (R^1 = R^2 = -$(CH_2)_4$-), 33% in CH_3NO_2
19 (R^1 = C_6H_{13}, R^2 = H), 53% in CH_3NO_2

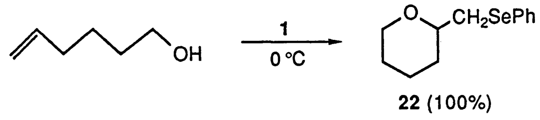
Intramolecular ring closure by electrophilic activation of an unsaturated alcohol or carboxylic acid is a useful synthetic methodology for the synthesis of complex natural products. The reagents composed of reactive electrophiles and weak nucleophiles are expected to have the particular advantage of being applicable for cyclofunctionalization, and benzeneselenenyl sulfonates were shown to be good reagents for cycloselenenylations.[10,16,17] We have also examined cyclizations of 4-penten-1-ol, 5-hexen-1-ol, 4-pentenoic acid, and 5-hexenoic acid using our method for preparation of selenenyl sulfonate. To the resulting solution of diphenyl diselenide (0.5 mmol) with *m*-NBSP (0.5 mmol) in acetonitrile (20 ml) 4-penten-1-ol was added at −40 °C, and the solution was further allowed to react at −40 °C for 2 h to give cyclic ether **20** almost quantitatively. When the reaction was carried out at 0 °C, small amoumt of the isomer **21** was obtained in addition to **20**. On the other hand, the cyclic ether **22** was obtained as a sole product at 0 °C from 5-hexen-1-ol.



20 (100%)

20 (85%) + **21** (15%)

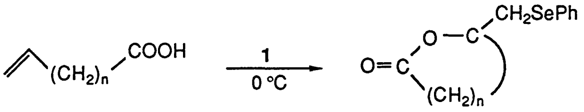
(8)



22 (100%)

(9)

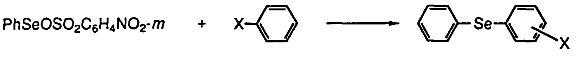
Similary, lactones **23** and **24** were obtained from 4-pentenoic acid and 5-hexenoic acid in excellent yields, respectively (Eq. 10).



(10)

23 : n = 2 (93%)
24 : n = 3 (96%)

Although electrophilic selenenylating reagents easily react with olefins, electrophilic aromatic substitutions by benzeneselenenyl group have been scarecely reported in the literature. Most methods for the introduction of areneselenenyl group into aromatic rings were nucleophilic displacement of selenium reagents on halobenzenes bearing an electron-withdrawing group.[18–20] Benzeneselenenyl chloride reacted with electron-rich benzenes as a reagent for chlorination rather than selenenylation.[21] Benzeneselenenyl chloride was converted in situ into benzeneselenenyl hexafluorophosphate, which reacted with anisole to give *p*-methoxyphenyl phenyl selenide and bis(*p*-methoxyphenyl)phenylselenonium hexafluorophosphate.[22] Dimethyl(phenylseleno)sulfonium tetrafluoroborate formed from benzeneselenenyl bromide was reported to be a highly reactive selenenylating reagent for electron-rich aromatic compounds, however, aromatic rings were limited to aromatic amines, phenols, and aromatic ethers.[23] Selenenyl sulfonate **1** also electrophilically reacted with aromatic rings to afford aryl phenyl selenides. To the resulting solution of diphenyl diselenide (0.5 mmol) with *m*-NBSP (0.5 mmol) in dichloromethane or acetonitrile, substituted benzene was added, and the solution was allowed to react at room temperature for 1 h and then refluxed for 2 h. Benzeneselenenyl group was introduced into aromatic rings, and the results are summarized in Table 2.



(11)

The electrophilic aromatic substitutions with **1** described herein proceeded in good to excellent yields for electron-rich benzenes such as anisole, phenol, and acetanilide, selectively at the *p*-position, and also could be applied to even toluene and benzene. Thus, benzeneselenenyl group in **1** was found to act as very reactive electrophile to react not only with olefins but also with aromatic rings.

In conclusion, diphenyl diselenide could be readily converted into very reactive electrophilic selenenylating reagents, benzeneselenenyl arenesulfonate, by the oxidative cleavage of Se-Se bond with *m*-NBSP.

Table 2. Benzeneselenenylation of Aromatic Rings with Selenenyl Sulfonate **1**

ArH/mmol		Solvent	Yield[a)]	Isomer ratio para/ortho[a)]
PhOMe	1.1	CH_2Cl_2	94	98/ 2
PhOMe	1.1	CH_3CN	75	99/ 1
PhOH	1.1	CH_2Cl_2	51	88/12
PhOH	1.1	CH_3CN	53	94/ 6
$PhNHCOCH_3$	5.0	CH_2Cl_2	84	100/ 0
$PhNHCOCH_3$	1.1	CH_2Cl_2	18	100/ 0
$PhNHCOCH_3$	5.0	CH_3CN	83	100/ 0
$PhNHCOCH_3$	1.1	CH_3CN	60	100/ 0
$PhCH_3$	5.0	CH_2Cl_2	50	72/28
$PhCH_3$	5.0	CH_3CN	45	68/32
PhH	5.0	CH_2Cl_2	21	
PhH	5.0	CH_3CN	12	
PhCl	5.0	CH_2Cl_2	0	
PhCl	5.0	CH_3CN	0	

a) Yields and isomer ratio were determined by GC.

m-NBSP is readily synthesized from *m*-nitrobenzenesulfonyl chloride with 30% hydrogen peroxide and relatively stable for handling and storage.[24)] Thus, the method for electophilic benzeneselenenylation described in this paper is expected to be very attractive and potentially useful in general organic synthesis.

Experimental

^{1}H NMR spectra were taken with a JEOL JNM PMX 60SI (60 MHz) spectrometer. ^{13}C NMR spectra were taken with a JEOL JNM FX90Q FTNMR spectrometer. IR spectra were recorded on a Hitachi 260-10 spectrometer. Gas chromatography was performed by a Hitachi 263-30 gas chromatograph with SE-30 (10%) 2-m stainless steel column. Gel-permeation chromatography was performed by means of a JAI Model LC-08 liquid chromatograph equipped with two JAIGEL-1H columns (20ϕ×600 mm) with chloroform as eluent. Mass spectra were obtained with a JEOL JMS DX-300 spectrometer by an electron-impact (EI) ionization technique at 70 eV.

Materials. Diphenyl diselenide was obtained from Nacalai Tesque and recrystallized prior to use. *m*-Nitrobenzenesulfonyl peroxide was synthesized from *m*-nitrobenzenesulfonyl chloride and 30% hydrogen peroxide according to the method described in the literature[24)] (mp 107 °C (decomp) lit, 112 °C (decomp)). Dichloromethane and acetonitrile were refluxed over calcium hydride and distilled prior to use. Nitromethane was dried over phosphorus pentaoxide and distilled prior to use.

General Procedure for the Preparation of Selenenyl Sulfonate 1. Diphenyl diselenide (0.5 mmol) was dissolved in freshly distilled solvent (20 ml), and solid *m*-NBSP (0.5 mmol) was added to the solution in small portions at 0 °C. The color of the solution turned reddish brown at once, and the resulting solution was further allowed to stir for 10 min at 0 °C and used for reactions in situ.

The Reactions of 1 with Olefins in the Presence of Methanol. Olefin (1.1 mmol) dissolved in methanol (5 ml) was added to the solution of **1** prepared in acetonitrile, and the reaction mixture was allowed to stir at room temperature for 3 h. Ether (20 ml) was added to the reaction mixture, and the solution was washed twice with 20 ml of water, 5% aqueous solution of sodium hydrogencarbonate (20 ml) and then water (20 ml). The separated organic layer from aqueous layer was dried over anhydrous magnesium sulfate, and the solvent was evaporated to give yellow oil, which was subjected to column chromatography on silica gel (Wakogel C-60) to give methoxyselenenylated products (hexane-ethyl acetate 5 : 1 as eluent). 2-Methoxy-2-phenylethyl phenyl selenide (**2**), 2-methoxycyclohexyl phenyl selenide (**3**) was isolated as pure forms, but 2-methoxyoctyl phenyl selenide (**4a**) could not be separated from a small amount of its regioisomer (**4b**), and these products were identified by comparison of the spectral data with those described in the literature.[25)]

The Reaction of 1 with Olefins in the Presence of Acetic Acid. Olefin (1.1 mmol) dissolved in nitromethane and then acetic acid (1 ml) was added to the solution of **1** prepared in nitromethane, and the reaction mixture was allowed to stir for 3 h at room temperature. Ether (20 ml) was added to the reaction mixture, and the solution was washed with 5% aqueous solution of sodium hydrogencarbonate (100 ml) and water (100 ml) twice in order to remove acetic acid and *m*-nitrobenzenesulfonic acid. The organic layer was separated from the aqueous layer and dried over anhydrous magnesium sulfate. The reactions in acetonitrile were similarly performed. When dichloromethane was used as solvent, the reaction mixture was washed with aqueous solution of sodium hydrogencarbonate and water without addition of ether. The evaporation of the solvent left a yellow oil which was subjected column chromatography on Wakogel C-60 to give diphenyl diselenide (hexane as eluent) and acetoxyselenenylated product (hexane-ethyl acetate 5 :1). 2-Acetoxy-2-phenylethyl phenyl selenide (**5**), 2-acetoxycyclohexyl phenyl selenide (**6**), and 2-acetoxyoctyl phenyl selenide (**7**) were isolated as almost pure forms and identified by comparison of the spectral data with those described in the literature.[2)]

Reactions of 1 with Olefins in the Presence of Water. To the solution of **1** prepared in acetonitrile, olefin (1.1 mmol) and then water (5 mmol) dissolved in acetonitrile was added, and the solution was allowed to react at room temperature for 3 h. After working up the products were separated by column chromatography on Wakogel C-60 using hexane and hexane-ethyl acetate (5 : 1) as eluent. Amidoselenenylated products (**11**, **12**, **13**)[14)] and hydroxyselenenylated products (**8**, **9**, **10**)[26)] were identified by comparison of the spectral data with those described in literatures. The reactions in the presence of water (5 ml) in nitromethane and acetonitrile were similarly performed.

The Reaction of 1 with Olefins in the Presence of Phenol. To the solution of **1** prepared in nitromethane or acetonitrile, olefin (1.1 mmol) and then phenol (10 mmol) were added. The reaction mixture was allowed to stir for 3 h at room temperature and worked up as in the case of acetoxyselenenylations. Column chromatography on Wakogel C-60 afforded pure products (hexane-ethyl acetate 5 : 1 as eluent).

2-(4-Hydroxyphenyl)-2-phenylethyl phenyl selenide (**16**): Yellow oil; ^{1}H NMR ($CDCl_3$) δ=3.40 (d, J=7.9 Hz, 2H), 4.25 (t, J=7.9 Hz, 1H), 4.63 (s, 1H), 6.44 and 6.88 (ABq, J=9.6 Hz, 4H), and 6.9—7.3 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=34.1, 50.8, 115.5, 126.7, 126.9, 127.8, 128.6, 129.1, 129.1, 129.2, 132.8, 136.0, 144.0, and 154.2; IR (neat) 3340 cm^{-1} (OH); MS *m/z* 354 (M$^+$); Exact MS 354.0523 (Calcd for $C_{29}H_{18}OSe$: 354.0570).

2-Phenoxycyclohexyl phenyl selenide (**14**): Yellow oil; ^{1}H NMR ($CDCl_3$) δ=1.0—2.5 (m, 8H), 3.3 (m, 1H), 4.2 (m, 1H), and 6.6—7.7 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=22.9, 25.3, 30.2, 31.2, 46.4, 78.4, 116.3, 121.0, 127.6, 128.4, 128.9, 129.5, 135.4, and 157.7; MS *m/z* 332 (M$^+$); Exact MS 332.0671 (Calcd for $C_{18}H_{20}OSe$: 332.0678).

2-Phenoxyoctyl phenyl selenide (**15**): Yellow oil; ^{1}H NMR ($CDCl_3$) δ=0.6—2.3 (m, 13H), 3.05 (d, *J*=6.0 Hz, 1H), 3.10 (d, *J*=3.6 Hz, 1H), 4.27 (m, 1H), and 6.5—7.6 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=14.0, 22.5, 25.3, 29.2, 31.7, 31.8, 34.0, 77.5, 116.1, 120.9, 127.2, 129.0, 129.4, 130.0, 133.3, and 158.0; MS *m/z* 362 (M$^+$), Exact MS 362.1159 (Calcd for $C_{20}H_{26}OSe$: 362.1158).

The Reaction of 1 with Olefins in the Presence of Anisole. To the solution of **1** prepared in acetonitrile, styrene (1.1 mol) dissolved in anisole (5 ml) was added. The reaction mixture was allowed to stir at room temperature for 3 h, and worked up according to the same procedure described in the case of methoxyselenenylations. The solvent and excess anisole was distilled off in vacuo, and the residue was almost pure 2-(*p*-methoxyphenyl)-2-phenylethyl phenyl selenide (**17**), which was further purified by column chromatography on Wakogel C-60; yellow oil; ^{1}H NMR ($CDCl_3$) δ=3.49 (d, *J*=7.9 Hz, 2H), 3.70 (s, 3H), 4.25 (t, *J*=7.9 Hz, 1H), 6.74 and 7.05 (ABq, *J*=7.8 Hz, 4H), and 7.1 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=34.1, 50.8, 55.3, 113.9, 126.6, 126.9, 127.7, 128.6, 128.8, 129.1, 130.9, 132.8, 133.0, 135.7, 144.0, and 158.4; MS *m/z* 368 (M$^+$); Exact MS 368.0679 (Calcd for $C_{21}H_{20}OSe$: 368.0694). Cyclohexene or 1-octene was also allowed to react in nitromethane and worked up as in the case of styrene. The products were separated by preparative layer chromatography (Merck Silica Gel 60 PF) using hexane–chloroform (5 : 1) as eluent. 2-(*p*-Methoxyphenyl)cyclohexyl phenyl selenide (**18**) and 2-(*p*-methoxyphenyl)octyl phenyl selenide (**19**) were further purified by medium-pressure column chromatography (Kusano Kagakukikai Co. CIG Pre-Packed Column CPS-HS-221-05).

2-(*p*-Methoxyphenyl)cyclohexyl phenyl selenide: Mp 136—138 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ=1.0—2.5 (m, 8H), 2.8 (m, 1H), 3.3 (m, 1H), 3.76 (s, 3H), and 6.8—7.6 (m, 9H), coupling constant between H^1 and H^2 of cyclohexyl group was determined to be 10.0 Hz by spin decoupling technique; ^{13}C NMR ($CDCl_3$) δ=26.5, 27.6, 35.7, 37.1, 49.1, 50.4, 55.2, 113.8, 127.3, 128.2, 128.6, 129.2, 135.7, 137.6, and 158.2; MS *m/z* 346 (M$^+$); Exact MS 346.0801 (Calcd for $C_{19}H_{22}SeO$: 346.0836).

2-(*p*-Methoxyphenyl)octyl phenyl selenide: Yellow oil; ^{1}H NMR ($CDCl_3$) δ=0.7—2.1 (m, 13H), 2.5—3.5 (m, 3H), 3.76 (s, 3H), 6.7—7.7 (m, 9H); ^{13}C NMR ($CDCl_3$) δ=14.0, 22.6, 27.5, 29.2, 31.7, 35.9, 36.4, 45.5, 55.2, 113.9, 126.6, 128.4, 128.9, 132.5, 132.7, 136.5, and 158.3; MS *m/z* 376 (M$^+$); Exact MS 376.1333 (Calcd for $C_{21}H_{28}OSe$: 376.1306).

Reactions of 1 with Unsaturated Alcohols or Carboxylic Acids. To the solution of **1** prepared in acetonitrile 4-penten-1-ol (1.1 mmol) was added at 0 °C or −40 °C. The reaction mixture was allowed to stir at 0 °C for 2 h or −40 °C for 2.5 h and worked up as in the case of methoxyselenenylations. The separated organic layer was dried over anhydrous magnesium sulfate, and the solvent was evaporated. Almost pure tetrahydro-2-(phenylselenomethyl)furan (**20**) was obtained from the reaction mixture at −40 °C. The furan (**20**)(27) was further purified by GPC and identified on the basis of the spectral data. Tetrahydro-3-(phenylseleno)-pyran (**21**),(28) which was obtained from the reaction at 0 °C, could not be separated as pure form. Similarly, the reactions of 5-hexen-1-ol, 4-pentenoic acid, and 5-hexenoic acid were carried out. Tetrahydro-2-(phenylselenomethyl)-pyran (**22**),(27) dihydro-5-(phenylselenomethyl)-2-furanone (**23**),(29) and tetrahydro-6-(phenylselenomethyl)-2-pyranone (**24**)(29) were identified on the basis of spectral data.

Reactions of 1 with Substituted Benzenes. Substituted benzene dissolved in dichloromethane was added to the solution of **1** prepared in dichloromethane, and the solution was allowed to stir at room temperature for 1 h and then refluxed for 2 h. The reaction mixture was washed with 5% aqueous solution of sodium hydrogencarbonate and water, and the organic layer was dried over magnesium sulfate. The products were analyzed by GC-MS and the yields were determined by GC using diphenyl sulfide as an internal standard. The aryl phenyl selenides were isolated by column chromatograpy on Wakogel C-60 and Gel-permeation chromatography. 4-Methoxyphenyl phenylselenide,(17) 4-hydroxyphenyl phenyl selenide,(23) 2-hydroxyphenyl phenyl selenide,(23) 4-acetamidophenyl phenyl selenide,(21) 4-methylphenyl phenyl selenide,(20) and diphenyl selenide(30) were identified by their ^{1}H NMR, ^{13}C NMR, and MS.

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