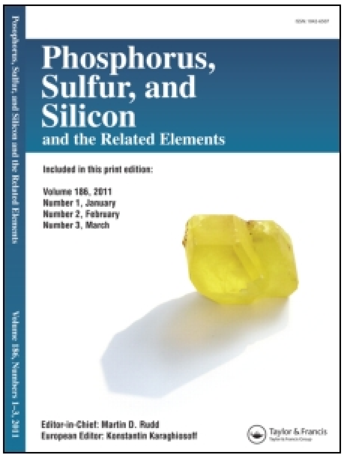

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A MECHANISM ON GENERATION AND RECYCLE OF THE SELENENYLATING REAGENTS IN ELECTROCHEMICAL OXYSELENENYLATION–DESELENENYLATION OF OLEFINS

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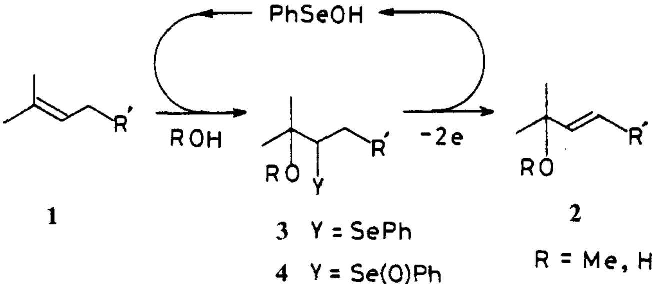
The transformation of olefins **1** into allylic ethers and alcohols **2** (R = Me or H) was performed in 70–90% yields, using a catalytic amount of diphenyl diselenide, by an electrochemical oxyselenenylation–deselenenylation sequence. The electrooxidation of diphenyl diselenide in methanol or aqueous acetonitrile generates selenenylating reagents (PhSeOMe or PhSeOH), which subsequently react with **1** to produce the corresponding oxyselenide **3**. The selenide **3** suffers further oxidation, providing **2** via selenoxide **4**. Phenylselenenic acid produced in the step (**4** → **2**) was recycled *in situ* for oxyselenenylation (**1** → **3**) in the presence of inorganic salts such as alkaline or alkaline earth metal sulfates. A strong ionic media resulting from adsorption of these inorganic anions on the electrode surface would induce a fast diffusion of phenylselenenic acid from the proximity of the electrode into a bulk solution in which oxyselenenylation occurs. Cyclic voltammetry of diphenyl diselenide and oxyselenide **3** suggests that the electrochemical reaction is initiated by electron transfer from diphenyl diselenide.

INTRODUCTION

Because of the potential utility of selenium compounds for selective organic functionalization, a variety of organoseleno reagents have been devised.[1] Most of the conventional selenenylating reagents PhSeX (X = Cl, Br, I, OH, AcO, CN, CF_3CO_2, NR_2 etc) have been prepared by the action of diphenyl diselenide with halogenating

$$\mathrm{PhSeSePh} \xrightarrow[2\ \mathrm{ROH}]{-2e} 2\ \mathrm{PhSeOR} + 2\ \mathrm{H}^+$$



SCHEME 1

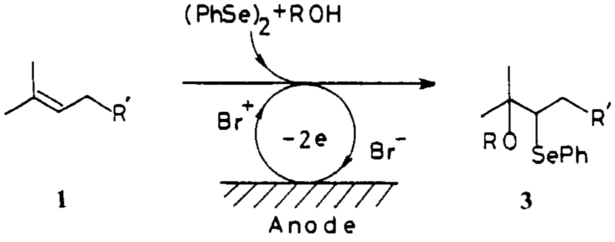
or oxidizing reagents and some must be handled under carefully controlled reaction conditions because of their instability. Furthermore, the toxicity and the high cost of the selenium reagents posed another problem in manufacturing organic materials with these reagents. From this point of view, recycling of selenium reagents has attracted much attention. Some studies on the selenium-mediated carbonylation,[2] epoxidation,[3] oxidation of alcohols,[4] and allylic oxidation[5] and chlorination[6] of olefins have been attempted. We recently showed an electrochemical transformation of olefins **1** into allylic ethers **2** (R = Me) and alcohols **2** (R = H) by the selenenylating reagents generated by anodic oxidation of diphenyl diselenide (Scheme 1). We describe here a study on the mechanism of generation and recycling of selenenylating reagents in the electrochemical reaction.

RESULTS AND DISCUSSION

The electrochemical oxyselenenylation of olefins (**1** → **3**) has been performed by the bromonium ion-mediated indirect oxidation of diphenyl diselenide in protic solvents (R = H, Me, Ac). The reaction proceeds *via* electrooxidation of bromide ion followed by oxidation of diphenyl diselenide by the active bromo species to generate the selenenylating reagent and then oxyselenenylation occurs as shown in Scheme 2.[8]

On the other hand, in the absence of sulfuric acid, the oxyselenide **3** suffers further electrochemical oxidation producing allylic alcohols or ethers **2** *via* the corresponding selenoxide **4**.[9] The phenylselenenic acid produced in the step (**4** → **2**) must be an effective hydroxy selenenylating reagent.[10] However, under the usual conditions **3** decomposes spontaneously into phenylseleninic acid both by disproportionation[11] and electrooxidation, and therefore, is not recycled for the transformation (**1** → **2**).[12] Recently, it was found that recyclization of the selenenylating reagent occurred when the reagent was generated by direct electrochemical oxidation of diphenyl diselenide (not by bromonium ion-mediated indirect oxidation) and stabilized in the presence of certain inorganic salts.[7]

In a typical case, the electrochemical reaction is carried out by electrolyzing a mixture of olefins, 10 mole% of diphenyl diselenide, and 1.5 mole-equivalent of magnesium sulfate in methanol or aqueous acetonitrile. Platinum foils were employed as electrodes in an undivided cell and constant current (10–20 mA) was passed at 60–70°C until **1** was completely consumed. Allyl ether (**2**, R = Me) and allyl alcohol (**2**, R = H) were obtained in 70–90% yields in methanol and aqueous acetonitrile, respectively.[7]



SCHEME 2

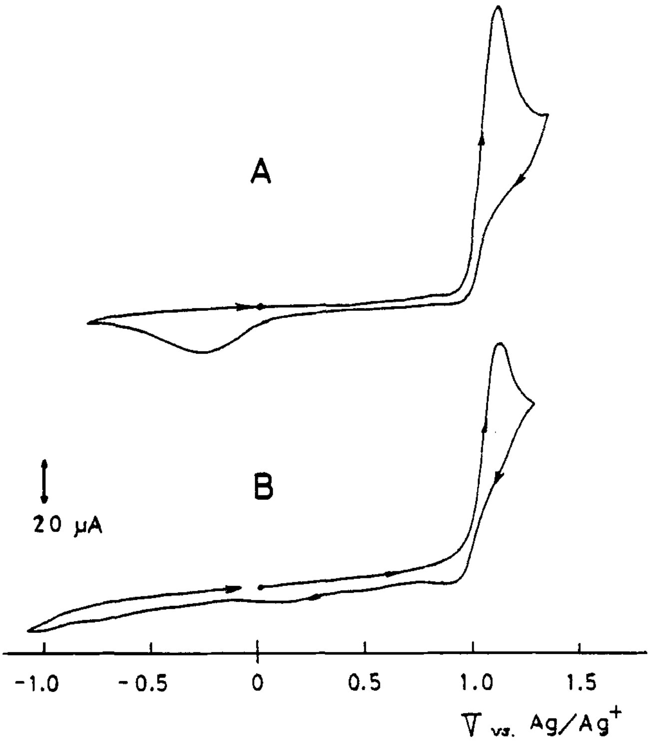


FIGURE 1 Cyclic voltammetry of diphenyl diselenide and oxyselenide [3, R = H, R′ = $CH_2CMe(OAc)C{\equiv}CH$] in acetonitrile containing 0.1 M of Et_4NClO_4 and 10^{-3} M of substrate. A; $(PhSe)_2$, B; 3. Sweep rate; 10 sec/V.

In order to elucidate the mechanism of the initiation process of the electrochemical reaction, cyclic voltammetry of diphenyl diselenide and oxyselenide 3 [R′ = $CH_2CMe(OAc)C{\equiv}CH$, R = H] was examined in acetonitrile-tetraethylammonium perchlorate system. Diphenyl diselenide exhibits an irreversible oxidation peak at Ep = 1.10 V *vs* Ag/Ag^+. The reaction at this potential would be electron transfer from diphenyl diselenide followed by attack of water, resulting in the formation of phenylselenenic acid.[13] Since the substrate **1** is not electrochemically oxidized at 1.10 V *vs* Ag/Ag^+,[14] the cyclic voltammetry of diphenyl diselenide suggests that the oxyselenenylation is initiated by an anodically generated selenenylating reagent (R = Me or H).

The electrophilic attack of the senenenylating reagent on the double bond of olefin **1** followed by solvolysis produces oxyselenides **3**. Methoxyselenide **3** (R = Me) and hydroxyselenide **3** (R = H) are obtained in methanol and aqueous acetonitrile, respectively. Likewise, the corresponding amideselenides were obtained in dry acetonitrile by Bewick.[15] When **1** is oxidized in a mixed solvent of methanol and water, both methoxy and hydroxyolefins **2** are produced in a ratio proportional to the mole ratio of the solvent (Figure 2). Interestingly, the combined yield of methoxy and hydroxyolefins **2** are approximately constant.

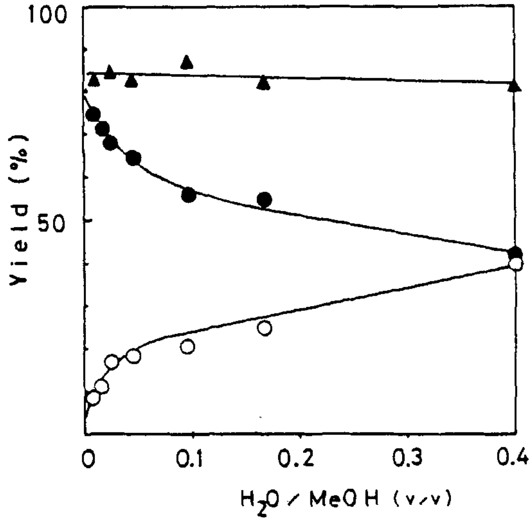
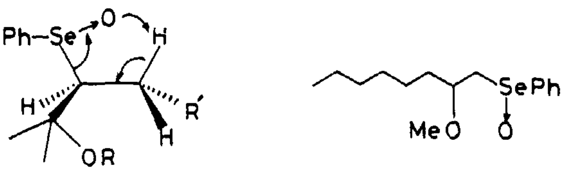


FIGURE 2 Relationship between ratio of product **2** (R = Me and H) and ratio of solvent (methanol and water) in the transformation of dehydrolinalyl acetate into **2** [R′ = $CH_2CMe(OAc)C{\equiv}CH$] at room temperature in the presence of 10 mol% of $(PhSe)_2$. -●- (R = Me), -○- (R = H), -▲- (total yield).

The oxyselenide **3** thus formed *in situ* is subsequently electrooxidized at the same potential (1.10 V, Figure 1, B) as that of diphenyl diselenide affording **4** which instantaneously undergoes syn elimination[16] to give **2** as a final product along with phenylselenenic acid. Although the selenoxide **4** could not be isolated because of its fast syn elimination, some evidence supports the existence of **4** as an intermediate; (1) the geometry of the newly formed double bond in **2** is trans,[7] suggesting that **2** should be derived through the most sterically favorable conformation at the transition state as illustrated in **5**; and (2) 2-methoxy-1-phenylseleninyloctane **6** was isolated from the electrolysis of 1-octene in methanol.[17]

The relationship between the ratio of product and the amount of electricity is shown in Figures 3 and 4. When 50 mole% of diphenyl diselenide was used (Figure 3), the yield of **3** was optimal at 2 F/mol where more than 95% of **1** was consumed and only 5% of **2** was isolated. On electrolyzing further, the amount of **2** increased progressively as **3** disappeared. This result indicates the conversion of **1** into **2** proceeds stepwise *via* **3**. Figure 4 shows a similar relationship when 10 mole% of diphenyl diselenide was used. Oxyselenide **3** increased gradually, reached the optimum yield (17%) at around 1 F/mol, and completely disappeared at 3.7 F/mol.



SCHEME 3

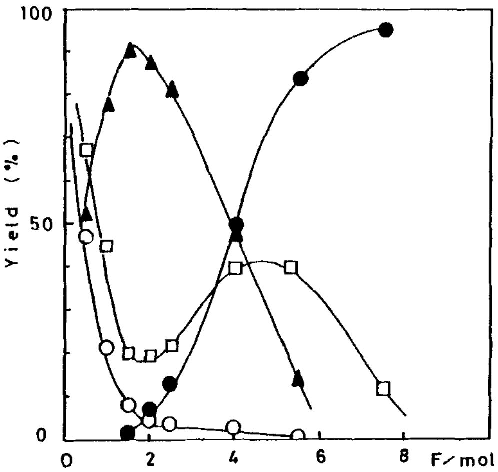


FIGURE 3 Relationship between yield of product and electricity in 50 mol% of $(PhSe)_2$—10 mol% of Et_4NBr-methanol system. **1**; [R′ = $CH_2CMe(OAc)C{\equiv}CH$] **2**,**3**; (R = Me).

Diphenyl diselenide was consumed at 1 F/mol where the starting material **1** (52%) remained in excess and the final product **2** was produced in 23% yield, in sharp contrast to the result shown in Figure 3 in which no **2** was detected. On continuing the electrolysis, **2** increased sharply and reached a maximum at 3.7 F/mol. These results clearly show that a selenenylating reagent is generated even after diphenyl diselenide is consumed and it promotes the catalytic transformation of **1** into **2**. In fact, electrooxidation of a mixture (84% of **1** and 16% of **3**, R′ = $CH_2CMe(OAc)C{\equiv}CH$, R = Me) in the absence of diphenyl diselenide in methanol

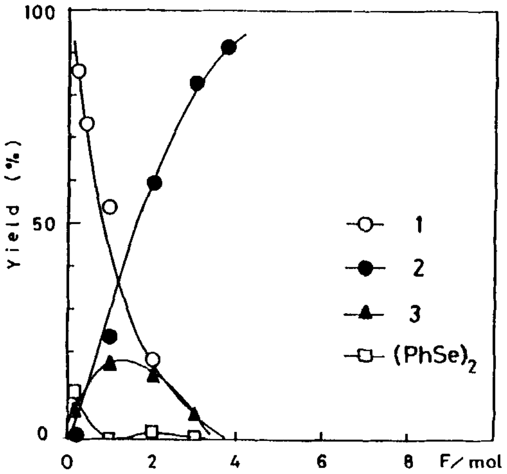


FIGURE 4 Relationship between yield of product and electricity in 10 mol% of $(PhSe)_2$-methanol system. **1**; [R′ = $CH_2CMe(OAc)C{\equiv}CH$], **2**,**3**; (R = Me).

provided **2** in 63% yield, demonstrating the generation of phenylselenenic acid from **3**.

Since phenylselenenic acid is unstable and converted both by disproportionation and electrooxidation into phenylseleninic acid, which is not an oxyselenenylating reagent, suitable protection of phenylselenenic acid from the two undesirable reactions is required to obtain an effective recycle of the reagent. The presence of inorganic salts extensively affects the recycle as shown in Table I. In the absence of any salts, the yield of **2** was only 26%. In contrast, sulfate, perchlorate, nitrate, hydrogensulfate, tosylate, and carbonate were effective, although the recycle efficiency of the sulfates is variable, depending on the counterion. The use of sodium acetate was unsuccessful presumably because it is electrooxidized under the electrolysis conditions.

The concentration of these salts also affects the yield of **2**. In methanol the yield of **2** increased linearly with the concentration of magnesium sulfate up to 0.1 M and then stayed constant at the higher concentration (Figure 5). In an aqueous acetonitrile, a similar result was observed. Since the concentration of **1** was kept at 0.07–0.14 M, this saturation phenomenon suggests that the interaction of phenylselenenic acid with these salts does not occur in the bulk solution but may occur in close proximity to the electrode surface where anions of these salts are adsorbed. The adsorbed anion would provide a strong ionic medium on the electrode surface which would prevent organic substances from being adsorbed.[18] This means that phenylselenenic acid produced from oxidation of diphenyl diselenide or elimination of the selenoxide **4** in close proximity to the electrode would be desorbed quickly and saved from inactivation by disproportionation and electrooxidation. On this basis, it is quite reasonable that the efficiency for the recycle of phenylselenenic acid increased markedly as the electrolysis temperature was raised. In general, both the rate of diffusion and desorption of substrate increase with rise of temperature. Therefore,

TABLE I

Effect of inorganic salts in the electrochemical transformation of **1** into **2**[a]

Inorganic Salt	eq[b]	F/mol	Yield of **2** (%)[c]
—	—	3.6	26
$MgSO_4$	1.7	3.7	89
$CaSO_4$	2.9	5.7	82
Na_2SO_4	1.5	6.0	86
K_2SO_4	2.7	6.8	62
$(NH_4)_2SO_4$	3.0	8.4	65
n-Bu_4NHSO_4	1.9	4.7	65
$SrSO_4$	1.9	5.8	51
$BaSO_4$	1.5	8.3	54
$Mg(ClO_4)_2$	1.5	4.0	63
$Mg(NO_3)_2$	1.3	4.0	45
$CaCO_3$	4.0	5.6	42
Et_4NOTs	1.7	12.0	57

[a] Dehydrolinalyl acetate **1** [R′ = $CH_2CMe(OAc)C{\equiv}CH$] was used as substrate in the presence of 10 mole% of $(PhSe)_2$ in methanol.

[b] Mole equivalent to substrate **1**.

[c] **2** (R = Me)

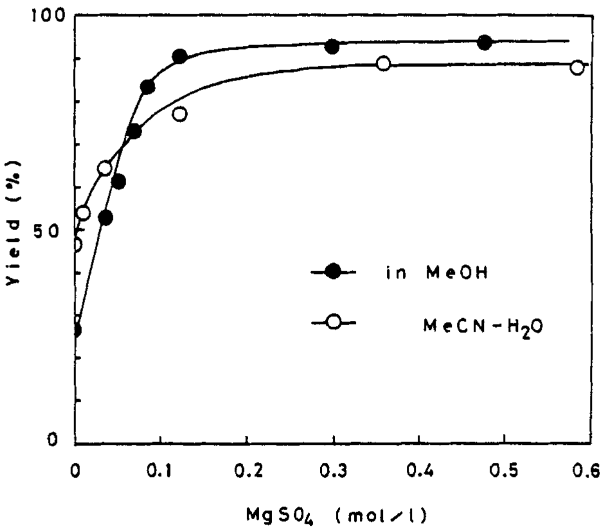


FIGURE 5 Effect of the concentration of $MgSO_4$ in oxyselenenylation–deselenenylation of dehydrolinalyl acetate (**1** → **2**) in the presence of 10 mol% of $(PhSe)_2$ at 65°C.

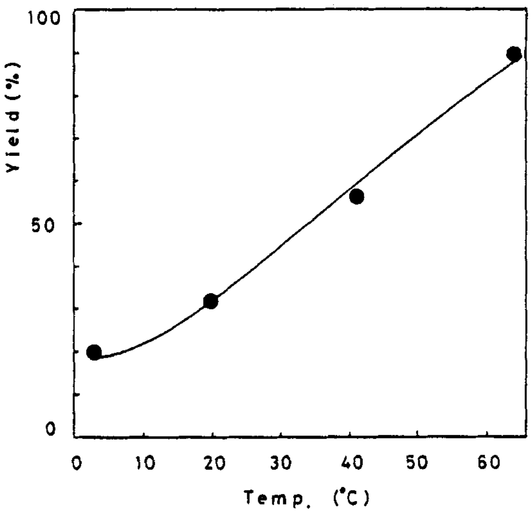


FIGURE 6 Effect of temperature in oxyselenenylation–deselenenylation of dehydrolinalyl acetate in the presence of 10 mol% of $(PhSe)_2$ and 1.7 eq of $MgSO_4$ in MeOH.

electrolysis at the higher temperature enhances the efficiency of the recycle of phenylselenenic acid as shown in Figure 6.

EXPERIMENTAL

Boiling points were measured by an air-bath temperature without correction. The IR spectra were obtained with a JASCO IRA-1 spetrometer. ^{1}H NMR spectra were measured with a JEOL FX-100 Fourier-Transform spectrometer at 100 MHz in $CDCl_3$ using Me_4Si as an internal standard.

Electrolysis of dehydrolinalyl acetate; Preparation of 1-ethynyl-5-methoxy-1,5-dimethyl-3-hexenyl acetate [**2**, *R* = *Me*, *R′* = $CH_2CMe(OAc)C{\equiv}CH$]. Two platinum-foil electrodes (1.5 × 2 cm^2) were placed in a glass tube cell (3 cm in diameter and 10 cm in height) and a mixture of dehydrolinalyl acetate (93 mg, 0.45 mmol), $(PhSe)_2$ (15 mg, 0.048 mmol), Et_4NClO_4 (5 mg, 0.02 mmol), and $MgSO_4$ (200 mg, 1.66 mmol) was added. The solution was electrolyzed at constant current (20 mA) at 61–63°C for 2.4 h (3.7 F/mol) using a regulated D-C power supply (Metronix Co., Tokyo, Japan). After evaporation of MeOH under reduced pressure, water was added to the residue and the organic substances were extracted with ethyl acetate. The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed over silica gel (Wako-gel C-200, *n*-hexane–ethyl acetate = 10 : 1) to give **2** (89%) as a colorless oil; b.p. 81–83°C/2.5 mmHg; IR (neat) 3300 (≡CH), 2120 (C≡C), 1750 (AcO), 1230 cm^{-1}; ^{1}H NMR δ 5.66–5.52 (m, 2 H, =CH), 3.17 (s, 3 H, OCH_3), 2.72–2.60 (m, 2 H, CH_2), 2.57 (s, 1 H, ≡CH), 2.04 (s, 3 H, Ac), 1.66 (s, 3 H, CH_3), 1.28 (s, 6 H, CH_3). Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.59; H, 9.21.

1-Ethynyl-5-hydroxy-1,5-dimethyl-3-hexenyl acetate (**2**, *R* = *H*). A similar electrolysis to that of dehydrolinalyl acetate **1** in a mixture of water (2 ml)–acetonitrile (5 ml) at 66–68°C (20 mA, 4.2 F/mol) provided **2** [R = H, R′ = $CH_2CMe(OAc)C{\equiv}CH$], in 89% yield; colorless oil, b.p. 85–86°C/2.3 mmHg; IR (neat) 3430 (OH), 3290 (≡CH), 2110 (C≡C), 1745 (AcO), 1230 cm^{-1}; ^{1}H NMR δ 5.87–5.46 (m, 2 H, =CH), 2.70–2.60 (m, 2 H, CH_2), 2.57 (s, 1 H, ≡CH), 2.02 (s, 3 H, Ac), 1.62 (s, 3 H, CH_3), 1.76–1.40 (m, 1 H, OH), 1.30 (s, 6 H, CH_3). Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.48; H, 8.88.

1-Ethynyl-5-methoxy-1,5-dimethyl-4-phenylselenenylhexyl acetate [**3**, *R* = *Me*, *R′* = $CH_2CMe(OAc)C{\equiv}CH$]. A mixture of dehydrolinalyl acetate (50 mg, 0.26 mmol), $(PhSe)_2$ (40 mg, 0.13 mmol), Et_4NBr (16 mg, 0.08 mmol), and conc. H_2SO_4 (3 mg, 0.03 mmol) in distilled methanol (8 ml) was electrolyzed in a similar manner as described above (20 mA for 30 min, 1.5 F/mol). Usual workup and chromatography (SiO_2, *n*-hexane–ethyl acetate = 10 : 1) provided **3** as a colorless oil in 91% yield: b.p. 130–133°C/0.01 mmHg; IR (neat) 3310 (≡CH), 2840 (CH_3O), 2120 (C≡C), 1745 (AcO), 1580, 1235 cm^{-1}; ^{1}H NMR δ 7.62–7.10 (m, 5 H, Ph), 3.16 (s, 3 H, CH_3O), 3.24–2.90 (m, 1 H, CHSe), 2.50 (d, J = 1 Hz, 1 H, ≡CH), 2.60–1.40 (m, 4 H, CH_2), 2.01 (d, J = 1 Hz, 3 H, Ac), 1.66 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3). Anal. Calcd. for $C_{19}H_{26}O_3Se$: C, 59.84; H, 6.87. Found: C, 59.83; H, 6.83.

1-Ethynyl-5-hydroxy-1,5-dimethyl-4-phenylselenenylhexyl acetate **3** [*R* = *H*, *R′* = $CH_2CMe(OAc)C{\equiv}CH$]. A similar electrolysis of dehydrolinalyl acetate in a mixed solvent [water–acetonitrile = 2 ml–6 ml, **1**; 50 mg, $(PhSe)_2$; 80 mg, Et_4NBr; 14 mg, conc. H_2SO_4; 30 mg] provided **3** as a slightly yellow colored oil in 93% yield: b.p. 132–134°C/0.01 mmHg; IR (neat) 3480 (OH), 3300 (≡CH), 2120 (C≡C), 1745 (AcO), 1580, 1230 cm^{-1}; ^{1}H NMR δ 7.10–7.70 (m, 5 H, Ph), 3.10 (d, J = 12 Hz, CHSe), 2.56 (d, J = 2 Hz, 1 H, ≡CH), 1.80–2.44 (m, 4 H, CH_2), 2.02 (d, J = 3 Hz, 3 H, Ac), 1.68 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3). Anal. Calcd. for $C_{18}H_{24}O_3Se$: C, 58.85; H, 6.59. Found: C, 58.71; H, 6.33.

Methyl 1-phenylseleninyl-2-octyl ether (**6**). A mixture of 1-octene (30 mg, 0.267 mmol), $(PhSe)_2$ (41 mg, 0.133 mmol), Et_4NBr (17 mg, 0.08 mmol) in methanol (8 ml) was electrolyzed at room temperature in the manner described above (30 mA, 9 F/mol). After evaporation of methanol under reduced pressure, the residue was taken up into water (2 ml) and the organic substances were extracted with ethyl acetate. The usual workup and chromatography (SiO_2, *n*-hexane–ethyl acetate–methanol = 2 : 2 : 1) provided **6** as an oil (28 mg, 37%). The Rf value of TLC and spectral data (IR and ^{1}H NMR) were consistent with those of authentic sample prepared by oxidation of methyl 1-phenylselenenyl-2-octyl ether with $NaIO_4$.[17]

Cyclic voltammetry. Cyclic voltammetry of diphenyl diselenide and oxyselenide **3** [R = H, R′ = $CH_2CMe(OAc)C{\equiv}CH$] was measured with a Kowa Electronics Model PGS-1550 potentio-galvanostat. Platinum wire (0.1 cm in diameter and 0.5 cm in length) was placed in a dry acetonitrile solution containing 0.1 M of Et_4NClO_4 and 0.001 M of substrate, and nitrogen gas was bubbled through for 5 min before starting. Potentials were measured using a Ag/Ag$^+$ (0.1 M of Et_4NClO_4 and 0.01 M of $AgNO_3$ in acetonitrile) reference electrode. Sweep rates were changed in the range of 5–40 sec/V.

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REFERENCES AND NOTES

1. (a) D. L. J. Clive, *Tetrahedron*, **34**, 1049 (1978); (b) H. J. Reich, *Acc. Chem. Res.*, **12**, 22 (1979).
2. (a) N. Sonoda, T. Yasuhara, K. Kondo, T. Ikeda and S. Tsutsumi, *J. Am. Chem. Soc.*, **93**, 6344 (1971); (b) P. Koch and E. Perrotti, *Tetrahedron Lett.*, **15**, 2899 (1974); (c) N. Sonoda, G. Yamamoto, K. Natsukawa, K. Kondo and S. Murai, *Tetrahedron Lett.*, **16**, 1969 (1975) and references cited therein.
3. H. J. Reich, F. Chow and S. L. Peake, *Synthesis*, 299 (1978).
4. (a) M. Shimizu and I. Kuwajima, *Tetrahedron Lett.*, **20**, 2801 (1979); (b) D. H. J. Barton, A. G. Brewster, R. A. H. F. Hui, D. J. Lester and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 952 (1978).
5. (a) M. A. Umbreit and K. B. Sharpless, *J. Am. Chem. Soc.*, **99**, 5526 (1977); (b) F. Camps, J. Coll and A. Parente, *Synthesis*, 215 (1978). (c) B. Chabaud and K. B. Sharpless, *J. Org. Chem.*, **44**, 4202 (1979).
6. (a) T. Hori and K. B. Sharpless, *J. Org. Chem.*, **44**, 4204 (1979); (b) T. Hori and K. B. Sharpless, *ibid.*, **44**, 4208 (1979).
7. S. Torii, K. Uneyama, M. Ono and T. Bannou, *J. Am. Chem. Soc.*, **103**, 4606 (1981).
8. A mixture of olefin, 1 eq. of $(PhSe)_2$, 0.2 eq. of Et_4NBr, and 1 eq. of conc. H_2SO_4 in MeOH was electrolized in an undivided cell using platinum electrodes. The yields of the oxyselenides are 80–95%. S. Torii, K. Uneyama and M. Ono, *Tetrahedron Lett.*, **21**, 2741 (1980).
9. S. Torii, K. Uneyama and M. Ono, *Tetrahedron Lett.*, **21**, 2653 (1980).
10. Phenylselenenic acid adds to carbon-carbon double bond to form hydroxyselenide. (a) G. Holzle and W. Jenny, *Helv. Chim. Acta*, **41**, 593 (1958); (b) H. J. Reich, *J. Org. Chem.*, **39**, 428 (1974); (c) D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, 100 (1974); (d) T. Hori and K. B. Sharpless, *J. Org. Chem.*, **43**, 1689 (1978).
11. (a) O. Behaghel and H. Seibert, *Chem. Ber.*, **66**, 708 (1933); (b) H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow and D. F. Wendelborn, *J. Org. Chem.*, **43**, 1697 (1978).
12. After electrolysis phenylseleninic acid was extracted with aqueous Na_2CO_3 and converted into diphenyl diselenide by reduction with $NaHSO_3$ as reported by Sharpless.[10d]
13. A similar electron transfer from diphenyl selenide leading to the corresponding cation radical is suggested. R. Seeber, A. Cinquantini, P. Zanello and G. A. Mazzocchin, *J. Electroanal. Chem.*, **88**, 137 (1978).
14. Carbon–carbon double bonds of aliphatic olefins are electrooxidized usually at the higher voltage than 2.0 V vs. Ag/Ag^+. (a) M. M. Baizer, "Organic Electrochemistry," Marcel Dekker, Inc., N.Y. (1973); (b) C. K. Mann and K. K. Barnes, "Electrochemical reaction in nonaqueous system," Marcel Dekker, Inc., N.Y. (1970).
15. A. Bewick, D. E. Coe, G. B. Fuller and J. M. Mellor, *Tetrahedron Lett.*, **21**, 3827 (1980).
16. (a) H. J. Reich, J. M. Renga and I. L. Reich, *J. Am. Chem. Soc.*, **97**, 5434 (1975); (b) reference 11b.
17. 2-Ethoxy-1-phenylseleninyloctane was isolated and could be converted into 1-phenylselenenyl-2-octanone in refluxing toluene. T. Takahashi, H. Nagashima and J. Tsuji, *Tetrahedron Lett.*, **19**, 799 (1978).
18. J. H. P. Utley, "Technique of Electroorganic Synthesis" Part I. Ed. by N. L. Weinberg, John Wiley and Sons, New York (1974).