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A HALIDE ION PROMOTED ELECTROCHEMICAL OXYSELENENYLATION OF OLEFINS

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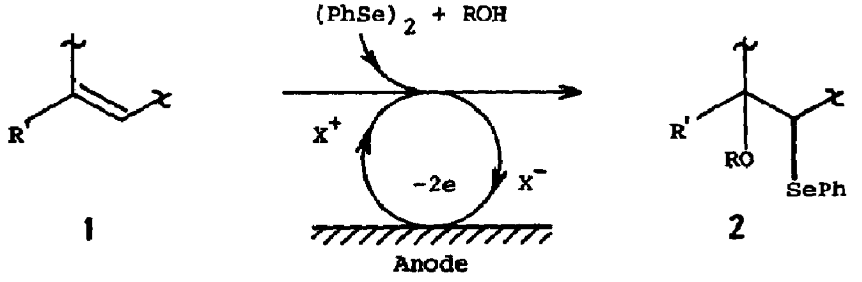
Summary A novel electrolytic transformation of olefins **1** into oxyselenides **2** has been performed in high yields and high regioselectivities by elctrolyzing olefins in protic solvents (MeOH, AcOH, H_2O-MeCN) containing Et_4NX (X = Cl, Br, I) and diphenyl diselenide using platinum foils.

Oxyselenenylation has been recognized as a powerful tool for functionalization in synthetic organic chemistry.[1) The most important strategy is how to introduce the seleno group into the target molecules. Phenylselenenyl halides PhSeX (X=Cl, Br) most widely used for alkoxy and acyloxyselenenylation are prepared by use of stoichiometric amount of bromine, chlorine, and sulfuryl chloride. Meanwhile, phenylselenenamides,[2) phenylselenocyanate,[3) and phneylselenenic acid,[4,5) are useful reagents for hydroxyselenenylation,[6) however, preparation of these reagents are not straightforward. Reported here is a first example on electrolytic oxyselenenylation of olefins which is characterized by the facts; (1) The reaction is promoted electrochemically with a trace amount of halide ion; (2) A direct hydroxyselenenylation can be performed without use of PhSeX (X=OH, NR_2, CN); (3) high regioselectivity and yield in mild conditions.



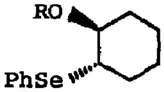
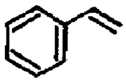
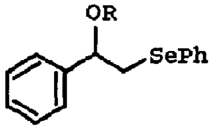
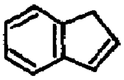
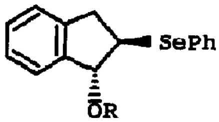
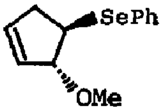
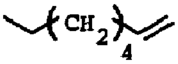
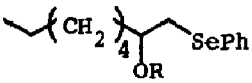
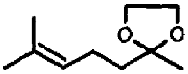
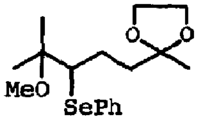
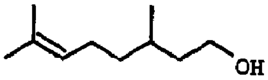
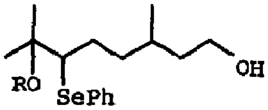
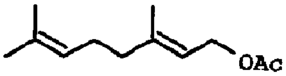
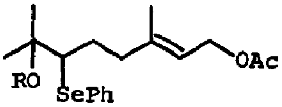
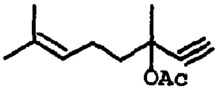
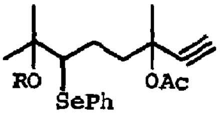
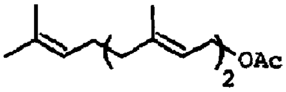
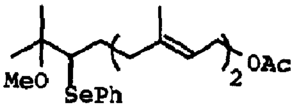
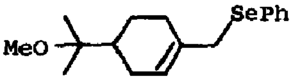
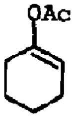
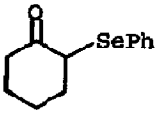
X = Cl, Br, I R = Me, H, Ac

The oxyselenenylations were furnished by generating a halonium ion in situ in the electrolysis system, thus dehydrolinalyl acetate (1.57 mmol), diphenyl diselenide (0.78 mmol), tetraethylammonium bromide (TEAB) (0.05 mmol), and H_2SO_4 7) (0.03 mmol) in MeOH (30 ml) were electrolyzed at room temperature under a constant current (20 mA, 2.0 F/mol) using Pt foils (2x1.5 cm^2) in an undivided cell (entry i). The ratio of regio isomers was determined by HPLC 8) and the result obtained by use of TEAB are summarized in Table 1. Most of olefins provided the corresponding methoxy, hydroxy, and acetoxyselenides in high yields along with high regioselectivities (Markownikoff type adduct). In particular, the electrolysis provides a very simple access to hydroxyselenides since the desired products can be prepared by merely electrolyzing a mixture of olefin, $(PhSe)_2$, (0.5 mol eq), NaBr or TEAB (0.05 mol eq) in H_2O-MeCN (2:6) at room temperature. In contrast, the reported hydroxyselenenylation using phenylselenenamides 9) and phenylselenenic acid 4,5,10) requires rather carefully controlled reaction conditions along with costly reagents.

Besides bromide ion, both chloride and iodide ions are effective for the reaction although in the latter case the current efficiency was somewhat poor [for cyclohexene in MeOH, Cl = 95% (1.4 F/mol), Br = 96% (1.4 F/mol), and I = 97% (4.5 F/mol)]. A half equimolar amount of $(PhSe)_2$ is enough to complete of the reaction. No change was observed in ethylene ketalyl, acetoxyl, hydroxyl, and ethynyl groups after the electrolysis. ω-Double bond of diene and triene (entry h and j) is affected preferentially.11) The electrolysis of β-pinene afforded terpineol moiety by accompanying with ring opening of the cyclobutane system (entry k). The oxyselenenylation of enol acetate resulted in α-phenylselenocarbonyl compound by spontaneous hydrolysis (entry m). 12)

A reasonable mechanism can be envisioned for the oxyselenenylation. Bromonium ion or bromine electrochemically generated by two electron discharge can react immediately with $(PhSe)_2$ producing PhSeBr. Attack of PhSeBr to the olefins followed by solvolysis would provide selenides **2** and bromide ion. The voltammetric study revealed that initial oxidative discharge arises from bromide ion and neither from $(PhSe)_2$ nor olefins. 13) The electrolysis in the absence of bromide ion was unsuccessful. 14)

Table 1. Electrolytic Oxyselenenylation of Olefins

Entry	Olefin 1	Electricity F/mol	Selenide 2	Yield[a] %	Isomer[b] ratio
a		1.4 1.6 1.7		R = Me 96 Ac 98 H 96 [e]	--
b		1.2 1.5 1.5		Me 91 Ac 96 H 92 [f]	100/0 100/0 100/0
c		1.5 2.9		Me 91 H 91 [e]	98/2 100/0
d		5.1[c]		89	99.6/0.4
e		1.7 3.2		Me 92 H 94 [e]	83/17 86/14
f		4.2[d]		80	100/0
g		2.5 3.0		Me 90 H 91[e]	99.5/0.5 98/2
h		2.3 2.6		Me 83 H 80 [e]	100/0 98/2
i		2.0 3.0		Me 91 H 93 [e]	99/1 99/1
j		1.7		56	98/2
k		2.0[c]		63	100/0
m		11.0[c]		95	100/0

a) Isolated yield. b) (Markownikoff)/(anti-Markownikoff adduct). c) Sulfuri acid was not used. d) Pyridine (0.14 mol eq) was used. e) MeCN-H_2O = 6 ml-2 ml. f) MeCN-H_2O = 8 ml-0.5 ml.

References and Notes

1) D. L. J. Clive, Tetrahedron, 34, 1049 (1978); H. J. Reich, Acc. Chem. Rec. 12, 22 (1979).

2) K. C. Nicolaou, D. A. Claremon, W. E. Barnette, and S. P. Seitz, J. Am. Chem. Soc., 101, 3704 (1979); H. J. Reich and J. M. Renga, J. Org. Chem., 40, 3313 (1975).

3) A. Toshimitsu, S. Uemura, M. Okano, J. Chem. Soc., Chem. Commun., 166 (1977

4) T. Hori and K. B. Sharpless, J. Org. Chem., 43, 1689 (1978); H. J. Reich, Wollowitz, J. E. Trend, F. Chow, and D. F. Wendelborn, ibid., 43, 1697(197

5) D. Labar, A. Krief, and L. Hevesi, Tetrahedron Lett., 3967 (1978).

6) As an indirect method, hydrolysis of β-trifluoroacetoxyalkylselenide has been reported. H. J. Reich, J. Org. Chem., 39, 428 (1974); D. L. J. Cliv J. Chem. Soc., Chem. Commun., 100 (1974).

7) The presence of small amount of sulfuric acid improved the current efficiency due to its nature to suppress oxidation of methanol.

8) All new compounds showed satisfactory IR, PMR, and elemetal analyses. HPLC; μ-porasil, n-hexane-AcOEt.

9) The selenenamides are relatively unstable at room temperature and thus mus be handled in dry solvent under argon atmosphere. ref. 2.

10) Excess amount (3 molar eq) of PhSeOH is necessary to terminate the reaction. 4)

11) Less than 10% of 7,11-dimethoxy-6,10-diphenylselenofarnesyl acetate was ob tained. Similar regioselectivity was observed in electrolytic ω-epoxidation of polyisoprenoids. S. Torii, K. Uneyama, M. Ono, H. Tazawa, and S. Matsunami, Tetrahedron Lett., 4661 (1979).

12) Reaction of 1-acetoxycyclohexene with $PhSeOCOCF_3$ in ether at 0 °C followed by hydrolysis gave α-phenylselenocyclohexanone in 70% yield. D. L. J. Clive, J. Chem. Soc., Chem. Commun., 695 (1973).

13) Oxidation of Br^- in MeOH occurs at around 0.6-0.7 volt vs. Ag/Ag^+, while $(PhSe)_2$ did not show any clear-cut oxidation curves below 1.0 volt vs. Ag/A

14) In the absence of bromide ion the current efficiency was one half or less, and product selectivity and yield were poor. For instance electrolysis of dehydrolinalyl acetate (entry i) in the absence of bromide ion in MeOH provided only 50% of the desired methoxyselenide along with 20-30% 6-aceto -2-methoxy-2,6-dimethyl-7-octyn-3-ene after 4 F/mol of electricity was passed.

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