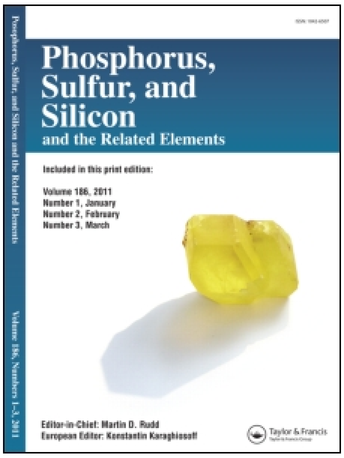


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Indirect Electroreduction of α,β-Epoxy Carbonyl Compounds and Their Analogues by Use of A $(PhSe)_2$/Sacrificial Anode System

Tsutomu Inokuchi[a]; Masahiko Kusumoto[a]; Tatsya Sugimoto[a]; Hideo Tanaka[a]; Sigeru Torii[a]
[a] Department of Applied Chemistry, Faculty of Engineering, Okayama University, Okayama, Japan

To cite this Article Inokuchi, Tsutomu , Kusumoto, Masahiko , Sugimoto, Tatsya , Tanaka, Hideo and Torii, Sigeru(1992) 'Indirect Electroreduction of α,β-Epoxy Carbonyl Compounds and Their Analogues by Use of A $(PhSe)_2$/Sacrificial Anode System', Phosphorus, Sulfur, and Silicon and the Related Elements, 67: 1, 271 — 276

To link to this Article: DOI: 10.1080/10426509208045848

URL: http://dx.doi.org/10.1080/10426509208045848

Phosphorus, Sulfur, and Silicon, 1992, Vol. 67, pp. 271–276
Reprints available directly from the publisher
Photocopying permitted by license only

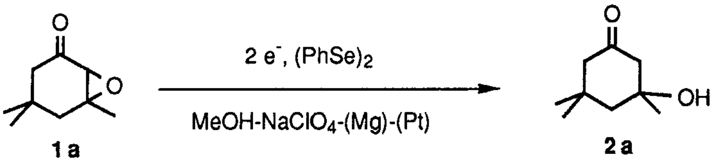
INDIRECT ELECTROREDUCTION OF α,β-EPOXY CARBONYL COMPOUNDS AND THEIR ANALOGUES BY USE OF A $(PhSe)_2$/SACRIFICIAL ANODE SYSTEM

TSUTOMU INOKUCHI, MASAHIKO KUSUMOTO, TATSUYA SUGIMOTO, HIDEO TANAKA, and SIGERU TORII*
Department of Applied Chemistry, Faculty of Engineering, Okayama University, Okayama, Japan 700

Abstract Indirect electroreductive transformations of α,β-epoxy carbonyl compounds **1** mediated by diphenyl diselenide ($(PhSe)_2$) as a recyclable reagent to their β-hydroxy derivatives **2** in 80-90% yields were achieved in an undivided cell by use of a sacrificial anode. The procedure can be applicable to the selenation of the haloalkane **4**, the epoxide **6**, and the α,β-enone **8** with an equimolar amount of $(PhSe)_2$.

INTRODUCTION

Usability of diaryl diselenides as a recyclable mediator in the indirect electroorganic synthesis stems from facile their conversions to the corresponding anionic and cationic species, respectively.[1,2] However, reductive transformations, in contrast to oxidative ones, with arylselenide anions have only been realized by use of a divided cell with a diaphragm.[3,4] We report here a new procedure for generation of phenylselenide anion from diphenyl diselenide ($(PhSe)_2$) in an undivided cell in combination with a sacrificial anode.[5] This $(PhSe)_2$/sacrificial anode system[6] provides a new method for the indirect electroreductive transformations of α,β-epoxy carbonyl compounds **1** to their β-hydroxy derivatives **2** as depicted in Figure 1.[7]



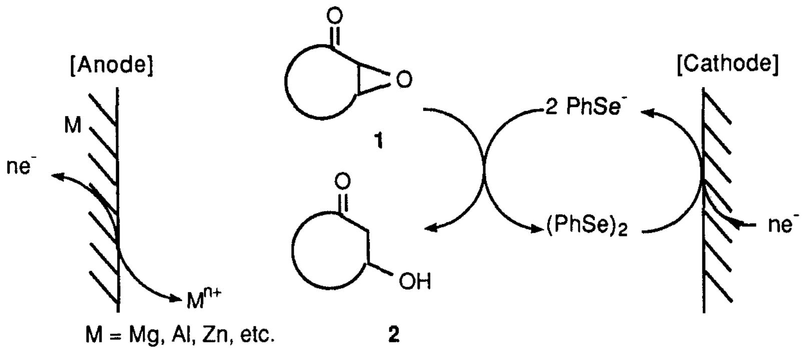
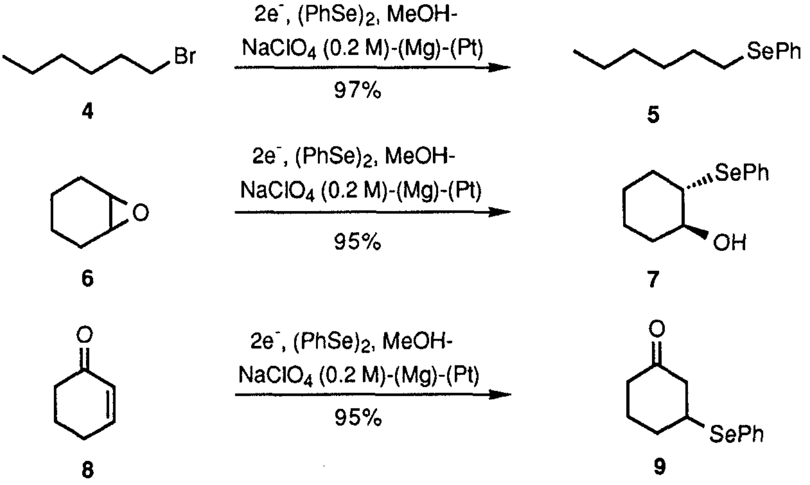


Figure 1. A composite mediatory system by using $(PhSe)_2$ as a recyclable reagent and a sacrificial anode.

RESULTS AND DISCUSSION

Prior to the electroreduction of α, β-epoxy carbonyl compounds **1**, a direct phenylselenation of haloalkane **4** by S_N-2 replacement[8] was attempted by using an equimolar amount of $(PhSe)_2$. Thus, the electrolysis of **4** and $(PhSe)_2$ under an applied voltage of 1 V for 2.7 F/mol of electricity in an MeOH-$NaClO_4$ (0.2 M) with a magnesium anode and a platinum cathode afforded the phenylselenide **5** in 97% yield. The electrochemical selenation in an undivided cell was successful in the conversions of the epoxide **6** to β-phenylseleno alcohol **7** and the enone **8** to the β-phenylseleno ketone **9**, respectively.



Subsequently, the procedure was extended to the transformation of α,β-epoxy ketones **1** to the corresponding β-hydroxy ketones **2** in the presence of a catalytic amount of diphenyl diselenide as a recyclable mediator.[7] As a result of survey on optimization of the solvent/electrode/additive factor in the conversion of **1a** to **2a** (Table I), the best yield was obtained in the run with magnesium anode in an MeOH-$NaClO_4$ (0.2 M) system and with 10~15 equimolar of dimethyl malonate as a proton donor (entry 1). Aprotic solvent such as DMF was not useful in this case (entry 2). The consumption of magnesium anode amounted to 3.5 mmol for the conversion of 1 mmol of **1a**.[9] Aluminum and zinc were also effective as a sacrificial anode, but the electrolyses required more electricity than the run with magnesium anode (entries 3 and 4). No selenation could be realized by using a platinum foil as an anode in this undivided system (entry 5). The electrolysis under the above conditions without adding $(PhSe)_2$ resulted in the recovery of **1a** (98%). The reaction did not proceed without charging the electricity. In these experiments, addition of malonic ester was essential for survival of the aldol structure of **2a**, otherwise the compound **2a** underwent quick dehydration leading to isophorone (**3a**).

Table I. Indirect Electroreduction of 1a in a Composite System of $(PhSe)_2$/Sacrificial Anode[a]

entry	anode	electricity (F/mol)	product, yield[b]	
			2a	**3a**[c]
1	Mg	3.0	86	0
2[d]	Mg	3.0	22	5
3	Al	15.0	76	0
4	Zn	25.0	65	10
5[e]	Pt	6.0	0	0

[a]Unless otherwise noted the electrolyses were carried out by using **1a** (1 mmol) and $(PhSe)_2$ (0.02 mmol) in an 0.2 M $NaClO_4$-MeOH (10 mL) system in the presence of dimethyl malonate (10-15 mmol) under an applied voltage of 1V. [b] Yield of isolated products based on **1a**. [c] **3a** is isophorone due to the dehydration of **2a**. [d] A 0.2 M $NaClO_4$-DMF (10 mL) solution in the presence of dimethyl malonate (15 mmol) was used. The starting **1a** was recovered (68%). [e] The starting **1a** was recovered (35%).

As shown in Table II, a variety of epoxy carbonyl compounds **1b**-**1e** including α,β-epoxy ester **1f** and α,β-epoxy nitrile **1g** are converted to the corresponding β-hydroxy carbonyl compounds **2b-2g**.[10] The yields of **2** are generally higher than those obtained by the indirect procedure mediated by $(PhSe)_2$ with the platinum-platinum electrodes system in a divided cell.[7]

The easy operation in a large scale is one of the merits of the procedure. For example, the electrolyses of 20-50 mmol of **1a** were achieved in a simple beaker type flask (200 mL) by using 0.2-0.5 mmol of $(PhSe)_2$, producing **2a** in 70-81% yields. After completion of the conversion, the mediator ($(PhSe)_2$) and the additive (dimethyl malonate) were recovered, quantitatively.

In conclusion, the employment of a sacrificial anode even in a protic solvent is useful for the indirect electroreduction with a mediator ($(PhSe)_2$), susceptible to oxidation on the counter electrode when handled in an undivided cell.[11]

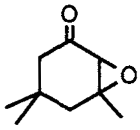
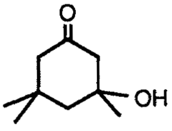
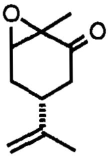
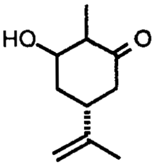
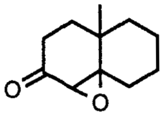
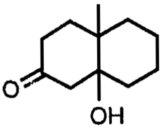
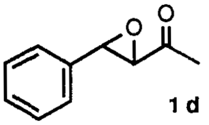
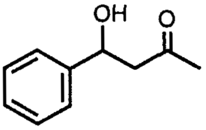
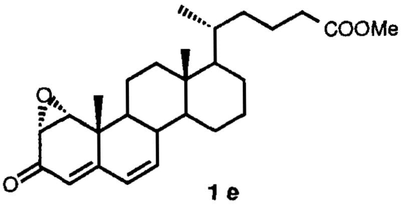
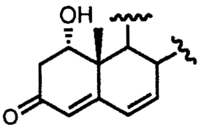
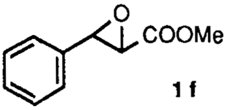
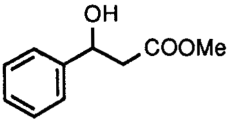
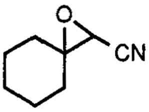
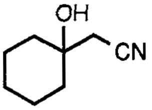
EXPERIMENTAL

Indirect Electroreduction of Isophorone Oxide (1a) with Diphenyl Diselenide and a Magnesium Anode: General Procedure. A mixture of **1a** (154 mg, 1 mmol), dimethyl malonate (1.92 g, 15 mmol), and $(PhSe)_2$ (6 mg, 0.02 mmol) dissolved in a 0.2 M $NaClO_4$-MeOH solution (10 mL) was charged in an undivided cell. A magnesium foil (1 x 3 cm^2) and a platinum foil (2 x 1.5 cm^2) were immersed in the electrolyte solution. Prior to the electrolysis, the electrolyte solution was bubbled with argon for 30 min and the resulting mixture was electrolyzed at 15-20 °C under a constant applied voltage of 1 V, during which an electric current decreased from 50 to 25 mA/cm^2. The electrolysis was interrupted when 3.0 F/mol of electricity had been passed (reaction time: 2.0 h). The solution was bubbled with air for 10 min, and then concentrated to a half of the original volume. The mixture was poured into water and taken up in ethyl acetate. The extracts were washed with brine (30 mL x 2), dried (Na_2SO_4), and concentrated. Column chromatography (SiO_2, hexane-AcOEt = 5:1) of the residue gave 6 mg (100%) of $(PhSe)_2$, 1.52 g (79%) of dimethyl malonate, and 145 mg (83%) of **2a**[7]: mp 79-80 °C (from hexane) (lit.[12] mp 79-79.5 °C). Amount of the consumed Mg anode was 86 mg (3.5 mmol). Large scale operation: A similar electrolysis of 3.08 g (20 mmol) of **1a** was carried out by using 31 mg (0.1 mmol) of $(PhSe)_2$ in an MeOH-0.2 M $NaClO_4$ system (100 mL) with a platinum foil (12 cm^2) and a magnesium foil (12 cm^2) in the presence of dimethyl malonate (200 mmol) at an applied voltage of 1-1.5 V (100-50 mA/cm^2) for 4.0 F/mol of electricity, giving the desired **2a** in 81% yield after column chromatography (SiO_2).

ACKNOWLEDGEMENT.

The present work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 01649512) from the Ministry of Education, Science and Culture of Japan. We are grateful to the SC-NMR laboratory of Okayama University for experiments with Varian VXR-500 and -200 instruments.

Table 2. Indirect electroreduction of α,β-epoxy carbonyl compounds 1 in an undivided cell.[a]

entry	compound, 1	β-hydroxy carbonyls 2	yield, %[b, c]
1	 1 a		86 (79)
2	 1 b		85 (85)
3	 1 c		88 (85)
4	 1 d		80 (75)
5	 1 e		85 (72)
6	 1 f		82 (75)
7	 1 g		90 (82)

[a] Carried out in an undivided cell by using 1 (1 mmol), $(PhSe)_2$ (0.02 mmol), and dimethyl malonate (15 mmol) in a MeOH-0.2 M $NaClO_4$-(Mg)-(Pt) system under an applied voltage of 1 V (100-25 mA/cm^2) for 3.0 F/mol of electricity. [b] Based on isolated product. [c] Numbers in parenthese are yields of 2 carried out in a divided cell with 1 (1 mmol), $(PhSe)_2$ (0.02 mmol), and dimethyl malonate (5 mmol) in a MeOH-0.2 M $NaClO_4$-(Pt)-(Pt) system under an applied voltage of 3 V (30-5 mA/cm2) for 4.5 F/mol of electricity.

REFERENCES

1. (a) J. R. Bradbury, A. F. Masters, A. C. McDonell, A. A. Brunette, A. M. Bond and A. G. Wedd, *J. Am. Chem. Soc.*, **103**, 1959 (1981). (b) F. Fagioli, F. Pulidori, C. Gighi and A. De Battisti, *Gazz. Chim. Ital.*, **104**, 639 (1974). (c) G. Paliani and M. L. Cataliotti, Z. *Naturforsch.*, **29B**, 376 (1974).

Oxidation and reduction potentials of $(PhSe)_2$ are as follows:[1a]

$$\mathrm{PhSeSePh} + 2e^- \longrightarrow 2\,[\mathrm{PhSe}]^- : -1.20\ \mathrm{V}\ \mathit{vs.}\ \mathrm{SCE\ (in\ DMF)}$$

$$\mathrm{PhSeSePh} \longrightarrow [\mathrm{PhSeSePh}]^{+\cdot} + e^- : 1.60\ \mathrm{V}\ \mathit{vs.}\ \mathrm{SCE\ (in\ DMF)}$$

2. (a) S. Torii, K. Uneyama, M. Ono and T. Bannou, *J. Am. Chem. Soc.*, **103**, 4606 (1981). (b) A. Bewick, D. E. Coe, G. B. Fuller and J. M. Mellor, *Tetrahedron Lett.*, **21**, 3827 (1980).

3. (a) C. Degrand, C. Gautier and M. Kharroubi, *Tetrahedron*, **44**, 6071 (1988). (b) C. Degrand, *J. Org. Chem.*, **52**, 1421 (1987). (c) B. Gautheron, G. Tainturier and C. Degrand, *J. Am. Chem. Soc.*, **107**, 5579 (1985).

4. (a) S. Torii, T. Inokuchi and N. Hasegawa, *Chem. Lett.*, 639 (1980). (b) S. Torii, T. Inokuchi, G. Asanuma, N. Sayo and H. Tanaka, *Chem. Lett.*, 867 (1980).

5. (a) G. Silvestri, S. Gambino and G. Filardo, *Stud. Org. Chem.* (Amsterdam), **30**, 1987, p287. (b) M. Heintz, O. Sock, C. Saboureau and J. Perichon, *Tetrahedron*, **44**, 1631 (1988). (c) H. Tanaka, T. Nakahara, H. Dhimane and S. Torii, *Tetrahedron Lett.*, **30**, 4164 (1989). (d) C. Saboureau, M. Troupel, S. Sibille and J. Perichon, *J. Chem. Soc., Chem. Commun.*, 1138 (1989).

6. D. Perez, N. Greenspoon and E. Keinan, *J. Org. Chem.*, **52**, 5570 (1987).

7. T. Inokuchi, M. Kusumoto and S. Torii, *J. Org. Chem.*, **55**, 1548 (1990).

8. (a) J. D. L. Clive, *Tetrahedron*, **34**, 1049 (1978). (b) H. J. Reich, *Acc. Chem. Res.*, **12**, 22 (1979). (c) K. C. Nicolau, *Tetrahedron*, **37**, 4097 (1981). (d) D. Liota, *Acc. Chem. Res.*, **17**, 28 (1984).

9. An overconsumption of the Mg anode was observed: C. Saboureau, M. Troupel and J. Perichon, *J. Appl. Electrochem.*, **20**, 97 (1990).

10. Reductive transformation of α,β-epoxy carbonyl compounds with selenium reagents: M. Miyashita, M. Hoshino, T. Suzuki and A. Yoshikoshi, *Chem. Lett.*, 507 (1988) and *Tetrahedron Lett.*, **28**, 4293 (1987).

11. (a) S. Torii, *Synthesis*, 873 (1986). (b) E. Steckhan, *Angew. Chem. Int., Ed. Engl.*, **25**, 683 (1986).

12. A. Osuka, K. Taka-Oka and H. Suzuki, *Chem. Lett.*, 271 (1984).