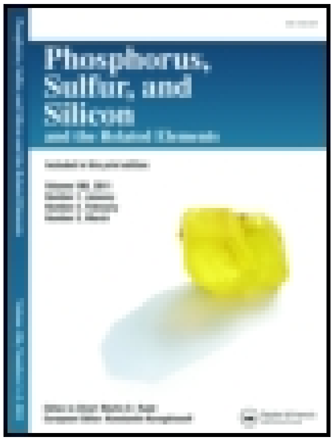
This article was downloaded by: [Akdeniz Universitesi]
On: 19 December 2014, At: 20:34
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

A Novel Synthesis of Selenides and Selenol Esters Using Liquid-Liquid Phase-Transfer Catalysis

Toshio Takido [a] , Masaharu Toriyama [a] , Kentaro Yamashita [a] , Tomoyuki Suwa [a] & Manabu Seno [a]

[a] Nihon University , Tokyo, Japan

Published online: 27 Oct 2010.

To cite this article: Toshio Takido , Masaharu Toriyama , Kentaro Yamashita , Tomoyuki Suwa & Manabu Seno (2003) A Novel Synthesis of Selenides and Selenol Esters Using Liquid-Liquid Phase-Transfer Catalysis, Phosphorus, Sulfur, and Silicon and the Related Elements, 178:2, 319-326, DOI: 10.1080/10426500307940

To link to this article: http://dx.doi.org/10.1080/10426500307940

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Phosphorus, Sulfur and Silicon, 2003, Vol. 178:319–326
Copyright © 2003 Taylor & Francis
1042-6507/03 $12.00 + .00
DOI: 10.1080/10426500390170444

Taylor & Francis
Taylor & Francis Group

A NOVEL SYNTHESIS OF SELENIDES AND SELENOL ESTERS USING LIQUID-LIQUID PHASE-TRANSFER CATALYSIS

Toshio Takido, Masaharu Toriyama, Kentaro Yamashita,
Tomoyuki Suwa, and Manabu Seno
Nihon University, Tokyo, Japan

(Received March 22, 2002; accepted May 30, 2002)

This article describes the first attempt to synthesize selenides and selenol esters prepared from the reaction of 1-benzyl or 1-acylselenophenylmethaniminium halides and organic halides under liquid-liquid phase-transfer conditions. This method also can be applied to the synthesis of diseleno tweezers-like molecules as metalloreceptors.

Keywords: Phase-transfer catalysis; selenides; selenium; selenobenzamide; selenol esters

Downloaded by [Akdeniz Universitesi] at 20:34 19 December 2014

Many different methods[1–12] for preparing selenides and selenol esters have been reported because functionalized organic selenium compounds show wide applicability in synthetic organic chemistry. Selenides are able to afford ylide derivatives[13] which are important intermediates in organic synthesis, and selenol esters are used not only as useful acylating agents,[14–16] but afford carboxylic acids,[17] ester,[17] aldehydes,[18] ketones,[19,20] and amides[21] as well. However, conventional methods for the preparation of selenides and selenol esters often have suffered from cumbersome manipulations and have sometimes involved the use of toxic and malodorous compounds such as hydrogen selenide.

We previously have reported[22,23] an efficient method of synthesizing sulfides and thiol esters using 1-alkyl or 1-acylthioethaniminium halides as a source of alkanethiolate or thiocarboxylate ions. In an extension of this work, this article describes the novel synthesis of selenides and selenol esters from the reaction of 1-benzyl or 1-acylselenophenylmethaniminium halides prepared by alkylation or

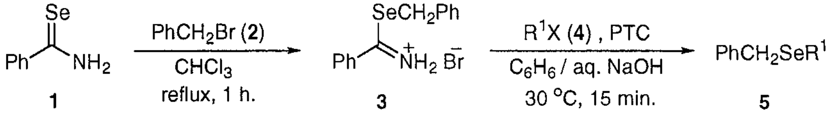
Address correspondence to Toshio Takido, Department of Mechanical and Applied Chemistry, College of Science and Technology, Nihon University, Kanda Surugadai, Chiyoda-Ku, Tokyo 101-8308, Japan. E-mail: takido@chem.cst.nihon-jp

Downloaded by [Akdeniz Universitesi] at 20:34 19 December 2014

acylation of selenobenzamide used as a source of selenolate ions and organic halides under liquid-liquid phase-transfer conditions.

RESULTS AND DISCUSSION

In our present method, 1-benzylselenophenylmethaniminium bromide, **3**, prepared from selenobenzamide,[24] **1**, and benzyl bromide, **2**, reacted with corresponding organic halides, **4**, to give an asymmetrical benzyl selenide, **5**, in a liquid-liquid two phase system consisting of benzene, a sodium hydroxide aqueous solution, and a catalytic amount of a quarternary ammonium salt as a phase transfer catalyst.



5	R^1	5	R^1
a	n-$C_{18}H_{37}$	g	2-$NO_2C_6H_4$
b	n-$C_{12}H_{25}$	h	4-$NO_2C_6H_4$
c	n-C_8H_{17}	i	$2,4$-$(NO_2)_2C_6H_3$
d	n-C_4H_9	j	C_6H_5CO
e	$(CH_3)_2CHCH_2$	k	n-$C_{17}H_{35}CO$
f	$CH_2{=}CH(CH_2)_4$	l	n-$C_5H_{11}CO$

SCHEME 1

The reactions were carried out under mild conditions (30°C, 15 min), and benzyl selenides and selenol esters, **5**, were obtained in 59–94% yields and the results are summarized in Table I. The reaction did not proceed in the absence of a phase transfer catalyst under otherwise identical conditions. These results were in complete contrast to the synthesis of thiol esters. As reported before, 1-alkylthioethaniminium bromides reacted with acyl halides to form the corresponding thiol esters under similar conditions, however, the corresponding reaction afforded no thiol esters but rather *N*-acylthioimino esters as the main products.[22] This result suggests that the iminium carbon-selenium likage of **3** is weaker than the iminium carbon-sulfur linkage of 1-alkylthioethaniminium bromides in alkaline solution. The attempts to apply various kinds of alkyl and aryl halides in this reaction were examined. It was found that primary alkyl, secondary alkyl, allyl, and aryl halides having electron withdrawing groups such as *o*- or *p*-substituted nitrophenyl halides could be prepared, as opposed to tertiary alkyl and other aryl halides.

Downloaded by [Akdeniz Universitesi] at 20:34 19 December 2014

TABLE I Benzyl Selenides **5** Prepared

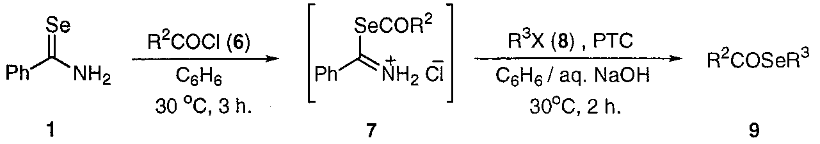
Product[a] **5**	X in **4**	Yield[b] (%)	m.p. (°C) or b.p. (°C/torr)	Mol. form.	HR-MS m/z (M^+)	^{13}C-NMR: ($CDCl_3$/TMS) δ
a	Br	94	43–44	$C_{25}H_{44}Se$	424.2588	14.1, 22.6, 24.1, 26.9, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 29.9, 30.3, 31.9, 126.5, 128.4, 128.8, 139.6
b	Br	94	Oil	$C_{19}H_{32}Se$	340.1624	14.1, 22.7, 24.1, 26.9, 29.1, 29.3, 29.4, 29.5, 29.6, 29.9, 30.2, 31.9, 126.5, 128.4, 128.8, 139.6
c	Br	79	136–137/10	$C_{15}H_{24}Se$	284.1066	14.0, 22.6, 24.1, 26.9, 29.0, 29.1, 29.9, 30.2, 31.8, 126.5, 128.3, 128.7, 139.6
d	Br	84	124–125/10	$C_{11}H_{16}Se$	228.0445	13.6, 23.0, 23.8, 126.5, 128.3, 128.7, 139.6
e	Br	82	47–48/10	$C_{11}H_{16}Se$	228.0406	22.7, 27.5, 29.1, 34.0, 126.6, 128.4, 128.8, 139.9
f	Br	80	72–73/10	$C_{13}H_{18}Se$	254.0581	23.9, 27.0, 29.2, 29.7, 33.3, 114.7, 126.7, 128.5, 128.9, 138.6, 139.6
g	Cl	61	98–99	$C_{13}H_{11}NO_2Se$	292.9932	31.4, 125.9, 126.7, 127.8, 129.1, 129.3, 129.6, 134.1, 135.1, 138.8, 146.5
h	Cl	69	97–98	$C_{13}H_{11}NO_2Se$	293.0001	31.5, 123.7, 127.5, 128.7, 128.9, 131.1, 136.7, 141.7, 146.4
i	Cl	94	123–124	$C_{13}H_{10}N_2O_4Se$	337.9808	29.1, 127.0, 127.2, 128.6, 128.8, 129.0, 133.7, 138.8, 139.0
j	Cl	75	133–134/10	$C_{14}H_{12}OSe$	276.0093	29.1, 127.0, 127.2, 128.6, 128.8, 129.0, 133.7, 138.8, 139.0, 194.5
k	Cl	75	55–56	$C_{25}H_{42}OSe$	438.2362	14.1, 22.7, 28.8, 28.9, 29.4, 29.5, 29.6, 29.7, 31.9, 47.9, 126.9, 128.6, 128.9, 201.0
l	Cl	59	116–117/10	$C_{13}H_{18}OSe$	270.0516	13.8, 22.3, 25.1, 28.7, 31.0, 47.8, 126.8, 128.5, 128.8, 139.3, 201.6

[a] All products were characterized by ^{1}H-NMR, IR spectra.

[b] Yield of pure isolated **9** based on selenobenzamide **1**.

Downloaded by [Akdeniz Universitesi] at 20:34 19 December 2014

The attempts to isolate the 1-alkyl or 1-acylselenophenylmethaniminium halides were unsuccessful due to their instability in air while 1-benzylselenophenylmethaniminium bromide, **3**, was successfully prepared. It is therefore reasonable to assume that the preparation of selenol esters by means of a one-pot reaction would be effective as a synthetic strategy.



9	R^2	R^3	**9**	R^2	R^3
a	C_6H_5	$C_6H_5CH_2$	f	n-C_7H_{15}	n-C_8H_{17}
b	C_6H_5	n-$C_{18}H_{37}$	g	n-C_7H_{15}	n-C_6H_{13}
c	C_6H_5	n-$C_{12}H_{25}$	h	n-C_7H_{15}	n-C_4H_9
d	C_6H_5	$CH_2{=}CH(CH_2)_4$	i	n-C_5H_{11}	$C_6H_5CH_2$
e	n-$C_{17}H_{35}$	$C_6H_5CH_2$			

SCHEME 2

1-Acylselenophenylmethaniminium halides **7** prepared by the reaction of **1** and acyl chlorides **6** in benzene were allowed to react with corresponding alkyl bromides **8** in a phase transfer system without isolation, the results of which are summarized in Table II. Furthermore, the comparative reaction of 1-octanoylselenophenylmethaniminium chloride with octyl bromide, and 1-octylselenophenylmethaniminium bromide with octanoyl chloride under similar conditions were examined; it was found that the former reaction gave 1-octanoyl octaneselenoate **9f** as the main product in 71% yield and the latter gave it in 57% yield respectively. This result would suggest that the rate of formation of 1-acylselenophenylmethaniminium halides are faster than that of 1-alkylselenophenylmethaniminium halides. In spite of the fact that selenol esters are easily hydrolyzed in alkaline media, the products were not hydrolyzed as seen in the case of thiol ester synthesis,[23] which produced selenol esters **9** in 52–88% yields.

We also have attempted to prepare 1,3-bis[(selenobenzyl)methyl]-benzene **11** by the reaction of m-xylenebis[(selenophenyl)methan]-iminium bromide **10** and benzyl bromide **2**. The synthesis of diseleno tweezers-like ligands such as **11** recently have begun to attract notice because they have the ability of cyclometalation with a metal such

Downloaded by [Akdeniz Universitesi] at 20:34 19 December 2014

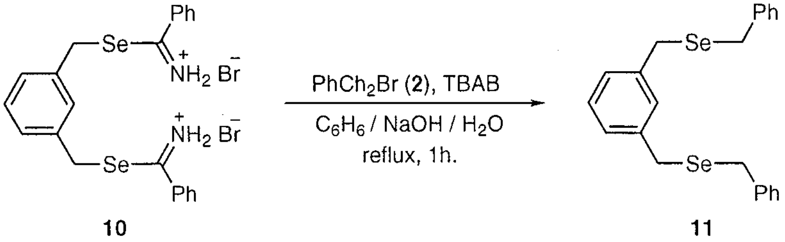
TABLE II Selenol Esters **9** Prepared

Product[a] **9**	Yield[b] (%)	m.p. (°C) or b.p. (°C/torr)	Mol. form.	HR-MS m/z (M^+)	^{13}C-NMR: ($CDCl_3$/TMS) δ
a	88	133–134/10	$C_{14}H_{12}OSe$	See 5j	
b	88	40–41	$C_{25}H_{42}OSe$	438.2425	14.1, 22.7, 25.8, 29.1, 29.4, 29.6, 29.7, 30.0, 30.5, 31.9, 127.1, 128.7, 133.4, 139.2, 195.1
c	78	Oil	$C_{19}H_{30}OSe$	354.1489	14.1, 22.7, 25.8, 29.1, 29.3, 29.5, 29.6, 30.0, 30.5, 31.9, 127.1, 128.7, 133.4, 139.2, 195.1
d	78	93–94/10	$C_{13}H_{16}OSe$	268.0407	25.5, 29.2, 29.9, 33.2, 114.7, 127.1, 128.7, 133.5, 138.4, 139.1, 194.9
e	78	55–56	$C_{25}H_{42}OSe$	See 5k	
f	71	125–126/10	$C_{16}H_{32}OSe$	320.1589	14.0, 14.1, 22.5, 22.6, 25.5, 28.7, 28.8, 29.4, 30.5, 31.2, 31.6, 48.2, 202.1
g	61	84–85/10	$C_{14}H_{28}OSe$	292.1313	13.9, 14.0, 22.4, 22.5, 25.5, 28.7, 29.4, 30.5, 31.2, 31.6, 48.2, 202.1
h	52	73–74/10	$C_{12}H_{24}OSe$	264.0982	13.5, 14.0, 22.6, 23.0, 25.2, 25.5, 28.8, 28.9, 31.6, 32.6, 48.3, 202.3
i	75	116–117/10	$C_{13}H_{18}OSe$	See 5l	

[a] All products were characterized by ^1H-NMR, IR spectra.

[b] Yield of pure isolated **9** based on selenobenzamide **1**.

as Pt(II) as functionalized metalloreceptors.[25] Our present method afforded a good yield (88%) of pure **11**, using very little purification.



SCHEME 3

As far as we know, this is the first example of the syntheses of selenides and selenol esters in selenium chemistry using selenoiminium salt. This method does not use harmful or malodorous compounds and can be widely applied to the synthesis of selenides and selenol esters.

EXPERIMENTAL

Selenobenzamide[24] **1** used for the synthesis of **3**, **7**, and **10** was prepared by the procedure reported previously. The other reagents were commercially available chemicals. Melting points were determined on Yanako Micro melting point apparatus and are uncorrected. Boiling points are uncorrected. Mass spectra were recorded on a HITACHI M-80B spectrometer. NMR spectra were recorded on JEOL GX-400.

1-Benzylselenophenylmethaniminium Bromide 3: Typical Procedure

A mixture of selenobenzamide **1** (2.76 g, 15 mmol) and benzyl bromide **2** (2.565 g, 15 mmol) in chloroform (25 mL) was heated under reflux for 30 min. After cooling, the precipitate was collected by filtration and washed with diethyl ether to give **3** (5.01 g, 94%) as a colorless solid of m.p. 144–145°C. IR (KBr) cm^{-1}: 2894, 1607, 754. Anal. Calcd for $C_{14}H_{14}BrNSe$: C, 47.34; H, 3.85; N, 3.95. Found: C, 47.10; H, 3.86; N, 4.00.

Benzyl Selenides and Selenol Esters 5: General Procedure

A mixture of 1-benzylselenophenylmethaniminium bromide **3** (3.55 g, 10 mmol), organic halides **4** (10 mmol), tetrabutylammonium bromide

Downloaded by [Akdeniz Universitesi] at 20:34 19 December 2014

Downloaded by [Akdeniz Universitesi] at 20:34 19 December 2014

(TBAB; 0.10 g, 0.3 mmol), benzene (50 mL) and sodium hydroxide aqueous solution (30 wt% 50 g) were vigorously stirred at 30°C for 15 min. The organic layer was separated, washed with water, dried over Na_2SO_4, and evaporated to dryness in vacuo to give a residue, which was distilled under reduced pressure or recrystallized to give pure unsymmetrical selenides **5**.

Selenol Esters 9 by One-Pot Reaction; General Procedure

A mixture of selenobenzamide **1** (1.84 g, 10 mmol) and acyl halides **6** (10 mmol) in benzene (50 mL) was stirred at 30°C for 2 h under nitrogen atmosphere. Then, alkyl halides **8** (10 mmol), TBAB (0.10 g, 0.3 mmol) and sodium hydroxide aqueous solution (30 wt% 50 g) were added successively to the reaction mixture, and the whole was stirred at 30°C for 3 h. The organic layer was separated, washed with water, dried over Na_2SO_4, and evaporated to dryness in vacuo to give a residue, which was distilled under reduced pressure or recrystallized to give pure selenol esters **9**.

Synthesis of 1,3-Bis[(selenobenzyl)methyl]benzene 11

A mixture of freshly prepared m-xylenebis[(selenophenyl)methan] iminium bromide **10** (4.43 g, 7 mmol), benzyl bromide **2** (2.39 g, 14 mmol), TBAB (0.20 g, 0.6 mmol), benzene (40 mL), and sodium hydroxide aqueous solution (20 wt% 30 g) were heated under reflux for 1 h. The organic layer was separated, washed with water, dried over Mg_2SO_4, and evaporated to dryness in vacuo to give a residue, which was dried by heating under reduced pressure due to the removal of remaining benzyl bromide, and **11** was obtained as a pale yellow solid of mp 37–39°C in 88% yield. This sample was sufficiently pure without further purification. ^{1}H-NMR δ (ppm): 3.66 (4H, s, $CH_2 \times 2$), 3.70 (4H, s, $CH_2 \times 2$), 7.00–7.33 (14H, m, aromatic H). ^{13}C-NMR δ (ppm): 27.40, 27.54, 126.56, 127.22, 128.34, 128.46, 128.84, 129.45, 138.96, 139.24. HR-MS m/z: 447.0130(M^+) (Calcd for $C_{22}H_{23}Se_2$: 447.0125).

REFERENCES

[1] D. P. Thompson and P. Boudjouk, *J. Org. Chem.*, **53,** 2109 (1988).

[2] C. Chen, M. Qiu, and X. Zhou, *J. Synth. Commun.*, **21,** 1729 (1991).

[3] Y. Nishiyama, A. Katsuura, A. Negoro, S. Hamanaka, N. Miyoshi, Y. Yamana, A. Ogawa, and N. Sonoda, *J. Org. Chem.*, **56,** 3776 (1991).

[4] J. A. Gladysz, J. L. Hornby, and J. E. Garbe, *J. Org. Chem.*, **43,** 1204 (1978).

[5] Y. Kojima, K. Ibi, T. Kanda, H. Ishihara, T. Murai, and S. Kato, *Bull. Chem. Soc. Jpn.*, **66,** 990 (1993).

[6] H. Kageyama, H. Tsutsumi, T. Murai, and S. Z. Kato, *Naturforsch.*, **B**(44b), 1050 (1989).
[7] T. Inoue, T. Takeda, N. Kambe, A. Ogawa, and N. Sonoda, *J. Org. Chem.*, **59,** 5824 (1994).
[8] L. Syper and J. Mlochowski, *Synthesis*, 439 (1984).
[9] M. Sakakibara, K. Katsumata, Y. Watanabe, T. Toru, and Y. Ueno, *Synthesis*, 377 (1992).
[10] J. Bergman and L. Engman, *Synthesis*, 569 (1980).
[11] K. Bhasin, V. Gupta, S. Bari, and R. Sharma, *Indian Journal of Chemistry*, **30A,** 635 (1988).
[12] S. Fujiwara, A. Asai, T. Shin-ike, N. Kambe, and N. Sonoda, *J. Org. Chem.*, **63,** 1724 (1998).
[13] P. G. Gassman, T. Miura, and A. Mossman, *J. Org. Chem.*, **47,** 954 (1982).
[14] D. L. Boger and R. J. Mathvink, *J. Org. Chem.*, **53,** 3377 (1988).
[15] D. L. Boger and R. J. Mathvink, *J. Org. Chem.*, **54,** 1777 (1989).
[25] D. L. Boger and R. J. Mathvink, *J. Org. Chem.*, **57,** 1429 (1992).
[17] M. J. Dabdoub and L. H. Viana, *Synth. Commun.*, **22,** 1619 (1992).
[18] H. Kuniyasu, A. Ogawa, K. Higaki, and N. Sonoda, *Organometallics*, **11,** 3937 (1992).
[19] T. G. Back and R. G. Kerr, *Tetrahedron Lett.*, **23,** 3241 (1982).
[20] T. G. Back and R. G. Kerr, *Tetrahedron*, **41,** 4759 (1985).
[21] A. P. Kozikowski and A. Ames, *J. Org. Chem.*, **43,** 2735 (1978).
[22] T. Takido and K. Itabashi, *Synthesis*, 817 (1987).
[23] T. Takido, M. Toriyama, and K. Itabashi, *Synthesis*, 404 (1988).
[24] L.-L. Lai and D. H. Reid, *Synthesis*, 870 (1993).
[26] M. A. El Amiri, P. Meunier, R. Louis, N. Pirio, and H. Ossor, *Phosphorus, Sulfur and Silicon*, **150,** 1 (2000).

Downloaded by [Akdeniz Universitesi] at 20:34 19 December 2014