



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lcyc20>

Samarium Diiodide-Induced Reduction of Elemental Selenium Leading to a Selenolate Anion Species. A Selective Synthesis of Diacyl Diselenides

Xueshun Jia^a, Yongmin Zhang^a & Xunjun Zhou^a

^a Department of Chemistry, Hangzhou University, Hangzhou, 310028 P.R., China

Published online: 23 Sep 2006.

To cite this article: Xueshun Jia, Yongmin Zhang & Xunjun Zhou (1993) Samarium Diiodide-Induced Reduction of Elemental Selenium Leading to a Selenolate Anion Species. A Selective Synthesis of Diacyl Diselenides, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 23:10, 1403-1408, DOI: [10.1080/00397919308011229](https://doi.org/10.1080/00397919308011229)

To link to this article: <http://dx.doi.org/10.1080/00397919308011229>

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>

SAMARIUM DIIODIDE-INDUCED REDUCTION OF ELEMENTAL
SELENIUM LEADING TO A SELENOLATE ANION SPECIES.
A SELECTIVE SYNTHESIS OF DIACYL DISELENIDES

Xueshun Jia, Yongmin Zhang* and Xunjun Zhou

Department of Chemistry, Hangzhou University,
Hangzhou 310028 P.R. China

ABSTRACT: Elemental selenium was reduced by samarium diiodide in THF to produce selenolate anion species which reacted with acyl chlorides to give diacyl diselenides in good yields under mild and neutral conditions.

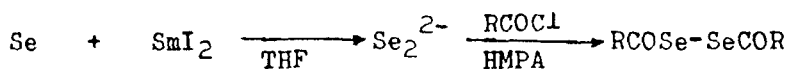
Samarium diiodide is a strong one-electron transfer reducing reagent and much attention has recently been paid to its utilization in organic synthesis¹. We have previously reported some deoxygenation and reduction of organic substrates with SmI_2 and aldol-

*To whom correspondence should be addressed.

like reaction between α -haloketone and aldehydes mediated by $\text{SmI}_2^{2,3}$. To our knowledge, most conventional methods for the preparation of diacyl diselenides made use of unstable and toxic reagents or alkali metal salts.⁴ Here we wish to report that SmI_2 reduces elemental selenium to Se_2^{2-} species which reacts with acyl chlorides to give diacyl diselenides in good yields under mild and neutral conditions.

Samarium diiodide reduces amorphous selenium to Se_2^{2-} species with an excellent selectivity in THF⁵. We found that addition of amorphous selenium to a deep blue solution of SmI_2 in THF resulted in a rapid change of colour of the solution to brown, indicating that the amorphous selenium had been reduced by SmI_2 . On the other hand, it was very difficult to reduce metallic selenium to Se_2^{2-} species with SmI_2 ; the THF solution was still deep blue after the mixture of metallic selenium and the solution of SmI_2 in THF was stirred for 12h, showing that the rate of reduction of metallic selenium by SmI_2 was very slow. The acylation of Se_2^{2-} species with acyl chlorides at room temperature in the presence of HMPA gave the exclusive diacyl diselenides in good yields. The advantages of the reaction are excellent selectivity, mild and neutral conditions, and simple operation. The reaction is shown in scheme and the results are summarized in Table 1.

Scheme

(a): $\text{R}=\text{C}_6\text{H}_5$ (e): $\text{R}=4\text{-BrC}_6\text{H}_4$ (b): $\text{R}=4\text{-MeC}_6\text{H}_4$ (f): $\text{R}=2\text{-BrC}_6\text{H}_4$ (c): $\text{R}=3\text{-ClC}_6\text{H}_4$ (g): $\text{R}=4\text{-MeOC}_6\text{H}_4$ (d): $\text{R}=4\text{-ClC}_6\text{H}_4$ (h): $\text{R}=\text{CH}_3(\text{CH}_2)_{10}$

Experimental

Mps were uncorrected. IR spectra were recorded with a PE-683 spectrometer. NMR spectra were recorded with a PMX-60 spectrometer, using TMS as internal standard.

General procedure:

The amorphous selenium(2mmol) was added to a stirred deep blue solution of SmI_2 (2.2mmol) in THF(22ml) at room temperature under nitrogen. After 2-3minutes, the deep blue colour of the solution disappeared and the solution became brown. The resulting solution was stirred at room temperature under nitrogen for 0.5h. The HMPA(1ml) and acyl chloride(3mmol) in THF(2ml) were then added successively to the solution with syringe, and the mixture was stirred at room temperature under nitrogen for 5h. Then the reaction mixture was

Table 1. Physical properties of diacyl Diselenides^a

Entry	mp(lit.) °C ^c	Yield % ^b	IR(KBr) (cm ⁻¹)	¹ H NMR(CDCl ₃), δ
(a)	130-131 (131-132)	87	1733 1680	7.40-8.02(10H, m)
(b)	109-110 (110-111.5)	86	1755 1710	2.40(6H, s) 7.18-7.94(8H, q, J=4.2Hz)
(c)	98-99	83	1722 1684	7.20-7.94(8H, m)
(d)	121-122 (122-124)	85	1730 1690	7.34-7.95(8H, q, J=4.5Hz)
(e)	152-153 (150-151)	82	1736 1702	7.56-7.97(8H, q, J=5.1Hz)
(f)	97-98 (94-95)	76	1737 1696	7.20-7.82(8H, m)
(g)	105-106 (106-107)	91	1721 1703	3.87(6H, s) 6.87-8.17(8H, q, J=4.8Hz)
(h)	60-61 (62-63)	94	1726	0.87(6H, t) 1.17-1.80(36H, m) 2.80(4H, t)

a. All products gave satisfactory elemental analyses;

b. Isolated yields; c. Ref. 4;

diluted with ether(40ml) and filtered. The ethereal solution was washed with water(40mlx3), dried over $MgSO_4$, and the solvent was removed by evaporation under reduced pressure. The crude product was purified by recrystallization from cyclohexane. The product was identified by elemental analysis, IR and NMR.

Acknowledgement: We are grateful to the National Natural science foundation of China for financial support.

References

1. (a) Kamochi, Y. and Kudo, T., *Tetrahedron Lett.*, 1991, 29, 3511. (b) Kende, A.S. and Mendoza, J.S., *ibid*, 1991, 14, 1699. (c) Walborsky, and Topolski, M., *J. Org. Chem.*, 1992, 57, 570. (d) John, A.S., *Aldrichimica Acta.*, 1991, 1, 15.
2. Zhang, Y.M. and Lin, R.H., *Synth. Commun.*, 1987, 17, 329.
3. Zhang, Y.M., Liu, T.C. and Lin, R.H., *ibid*, 1988, 18, 2003.
4. (a) Wang, J.X., Cui, W.F., Hu, Y.L. and Zang, S.S., *J. Chem. Res.*, 1990, 230. (b) Lewis, D., *J. Chem. Soc.*, 1940, 831. (c) Ishihara, H., Sato, S. and Hirabayashi, Y., *Bull. Chem. Soc. Jpn.*, 1977, 50, 3007. (d) Jensen, K.A., Boje, L. and Henriksen, L., *Acta Chem. Scand.*, 1972, 26, 1465.

5. Sekiguchi, M., Tanaka, H., Takami, N., Ogawa, A.,
Ryu, I. and Sonoda, N., *Heteroatom Chem.*, 1991, 2,
427.

(Received in UK 01 December 1992)