



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>

Synthesis of Organic Diselenide Using Zinc Powder

Lue Ping^a & Zhou Xunjun^a

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

Published online: 23 Sep 2006.

To cite this article: Lue Ping & Zhou Xunjun (1993) Synthesis of Organic Diselenide Using Zinc Powder, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 23:12, 1721-1725, DOI: [10.1080/00397919308011270](https://doi.org/10.1080/00397919308011270)

To link to this article: <http://dx.doi.org/10.1080/00397919308011270>

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>

SYNTHESIS OF ORGANIC DISELENIDE USING ZINC POWDER

Lue Ping Zhou Xunjun*

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

Abstract: A new synthetic method of diselenide by reducing element selenium with zinc powder in basic environment, and then reacting with electrophiles is described. Nine diselenides are synthesized with yields between 52-90%.

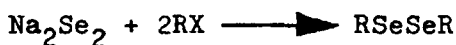
With the development of organoselenium chemistry, much attention has been paid to the synthesis of selenium reagents in recent years¹. Both arylseleno cation and anion produced by reduction of diselenides are predecessors of many organo-selenium compounds². Several synthetic methods for diselenides have been reported: reaction of M_2Se_2 ($M:Li, Na, K$) with various electrophiles³⁻¹⁰; hydrolysis of $RSeMgX$ ¹¹⁻¹⁴ or $ArSeCN$ ^{15,16}; reduction of carbonyl compounds with H_2Se and combination of sodium selenophosphoric diethyl ester with

* To whom correspondence should be addressed.

diazo fluoroborate¹⁰. However, most of the existing methods of preparation of diselenides are generally troublesome and toxic.

We shall now report a very simple synthetic method for diselenide. Element selenium is reduced by zinc powder in sodium hydroxide to produce disodium diselenide, followed by treatment of various electrophiles (Scheme I).

Scheme I



The reaction time for aryl halide system (12hrs) is longer than for alkyl halides (2hrs). This rule is in accordance with the activity of alkyl or aryl halide. The characteristic of this synthetic method is one-pot reaction, easy to perform, easy to obtain raw material and to avoid using toxic selenoreagents. The reaction is under room temperature with good yields between 52-90%. It is a useful synthetic method both for aromatic and for aliphatic diselenide.

EXPERIMENTAL SECTION

A mixture of selenium (0.8g, 10mmol), zinc powder (90%, 0.4g 5.5mmol) (washed by acid, base, water and dried in vacuo) and aqueous sodium hydroxide (2.5N, 8ml) was

Table I. The Results of Na_2Se_2 with Various RX

No. RX	Reaction times(hr)	M. P. obs. Ref.	Extract Solvents	Yield (%)	^1H NMR (ppm, CDCl_3)
1a $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br}$	2	oil	CH_2Br_2	60	3.90(m, 2H) 4.35(m, 4H)
1b $\text{O}_2\text{H}_5\text{Br}$	2	oil	Et_2O	78	2.90(q, 4H, J=7Hz) 1.50(t, 6H, J=7Hz)
1c $\text{n-C}_4\text{H}_9\text{Br}$	2	oil	Et_2O	82	2.87(t, 4H, J=7Hz) 1.30-1.90(m, 8H) 0.95(t, 6H, J=Hz)
1d PhCH_2Cl	2	90-92 91-92(21) (EtOH)	Et_2O	87	3.92(s, 4H) 7.25(s, 10H)
1e $\text{p-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$	2	93-94 a (EtOH)	Et_2O	90	3.97(s, 4H) 7.30-7.48(d, 4H, J=8Hz) 8.12-8.30(d, 4H, J=8Hz)
1f PhCOCH_2Br	2	85-87 a (EtOH)	CH_2Cl_2	52	2.50(s, 4H) 7.30-8.00(m, 10H)
1g $\text{p-NO}_2\text{C}_6\text{H}_4\text{I}$	12	175-177(Decomp.) (PhCl) 180(4)	CH_2Cl_2	80	7.54-8.30(m, 8H)
1h $\text{o-NO}_2\text{C}_6\text{H}_4\text{Cl}$	12	209-210 21-213 (4)	CH_2Cl_2	85	7.35-8.50(m, 8H)
1i $2,4\text{-2NO}_2\text{C}_6\text{H}_3\text{Cl}$	12	260(Decomp.) (DMF/ H_2O) 263(4)	CH_2Cl_2	70	7.40-8.30(m, 6H)

a: No data is available, the product is checked by E. A..

stirred at 80°C for 2hrs under nitrogen. A deep brown solution was obtained, cooled to room temperature and then added alkyl or aryl halide (10mmol). The reaction time was listed in Table I. After filtration, the residue was washed by solvent (10mlx3) (See Table I), the organic layer was separated, washed by water and dried by anhydrous MgSO_4 . Concentration the dried solution with Rotavapor to give crude diselenide. We can purify the solid product by recrystallization and chromatography the liquid product on silica gel (pet ether or CH_2Cl_2). The product was examined by $^1\text{HNMR}$, M.p., and E.A..

Project Supported by the National Science Fund, P. R. China

REFERENCES

1. Reich, H. J., Acc. Chem. Res., 1979, 12, 22.
2. Inayama, S., Harimaga, K., Shimitzu, N., Hari, H., Ohkura, T., Litake, Y., Kawamata, T., Heterocycles, 1985, 23, 377.
3. Bergstorm, F. W., J. Am. Chem. Soc., 1926, 146.
4. Syper, L., Mlochowski, J., Tetrahedron, 1988, 6119.
5. Brid, M. L., Challenger, F., J. Chem. Soc., 1942, 570.
6. Klayman, D.L., Griffin, T.S., J. Am. Chem. Soc., 1973, 197.

7. Clive, D. L. J., Menchen, S. M., J. Org. Chem., 1979, 4279.
8. Gladdysz, J. A., Hornby, J. L., Garbe, J. E., J. Org. Chem., 1984, 1204.
9. Syper, L., Mlochowski, J., Synthesis, 1984, 439.
10. Li, J., Zhou, X., unpublished.
11. Reich, H. J., Renga, J. M., Reich, I. L., J. Am. Chem. Soc., 1975, 97, 5434.
12. Foster, D. G., Organic Synthesis, Coll. Vol. 3 p. 771, 1955.
13. Jen, K.-Y., Cava, M. P., J. Org. Chem., 1983, 1449.
14. Gruuther, W. H. H., J. Org. Chem., 1967, 32, 3929.
15. Waitkins, G. R., Shutt, R., Inorg. Synth., 1946, 2, 186.
16. Hori, T., Sharpless, K. B., J. Org. Chem., 1978, 1689.
17. Margolis, D. S., Pittman, R. W., J. Chem. Soc., 1957, 799.
18. Cohen, V. I., J. Org. Chem., 1977, 2510.
19. Lewicki, J. W., Gruuther, W. H. H., Chu, J. Y. C., J. Chem. Soc., Chem. Commun., 1976, 552.

(Received in UK 31 December 1992)