This article was downloaded by: [The University of British Columbia] On: 12 March 2013, At: 01:59 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



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

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

HYPERVALENT IODINE IN SYNTHESIS. 49. A NEW EFFECTIVE SYNTHESIS OF Se-PHENYL O,O-DIALKYL PHOSPHOROSELENOATES WITH POLYMER-SUPPORTED PHENYLIODINE DIACETATE

Da-Jun Chen<sup>a</sup> & Zhen-Chu Chen<sup>b</sup>

<sup>a</sup> Department of Chemistry, Zhejiang University at Xixi Campus, Hangzhou, 310028, People's Republic of China

<sup>b</sup> Department of Chemistry, Zhejiang University at Xixi Campus, Hangzhou, 310028, People's Republic of China

Version of record first published: 09 Nov 2006.

To cite this article: Da-Jun Chen & Zhen-Chu Chen (2001): HYPERVALENT IODINE IN SYNTHESIS. 49. A NEW EFFECTIVE SYNTHESIS OF Se-PHENYL O, O-DIALKYL PHOSPHOROSELENOATES WITH POLYMER-SUPPORTED PHENYLIODINE DIACETATE, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:3, 421-424

To link to this article: http://dx.doi.org/10.1081/SCC-100000533

## PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <u>http://www.tandfonline.com/page/terms-and-conditions</u>

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.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## SYNTHETIC COMMUNICATIONS, 31(3), 421-424 (2001)

# HYPERVALENT IODINE IN SYNTHESIS. 49. A NEW EFFECTIVE SYNTHESIS OF Se-PHENYL *0,0*-DIALKYL PHOSPHOROSELENOATES WITH POLYMER-SUPPORTED PHENYLIODINE DIACETATE

Da-Jun Chen and Zhen-Chu Chen\*

Department of Chemistry, Zhejiang University at Xixi Campus, Hangzhou, 310028, People's Republic of China

## ABSTRACT

Se-phenyl *O*,*O*-dialkyl phosphoroselenoates have been prepared by the one-pot reaction of sodium *O*,*O*-dialkyl phosphorates, diphenyl diselenide, and polymer-supported phenyliodine diacetate (PPID).

Esters of O,O-dialkyl phosphoroselenoic acids are of particular importance in the synthesis of selenium dependent enzymes and seleno-t-RNAs (1). Besides, they also serve as selenophosphorylating reagents of alkynes (2). The literature methods of preparing Se-phenyl O,O-dialkyl phosphoroselenoates include the Arbuzove-type reaction of trialkyl phosphites with benzeneselenenyl bromide or chloride (3,4), the benzeneselenation of mercury O,O-dialkyl phosphorates with benzeneselenenyl bromide (3), or the action of lithium selenophenolate on

421

Copyright © 2001 by Marcel Dekker, Inc.

www.dekker.com

<sup>\*</sup>Corresponding author.

ORDER		REPRINTS
-------	--	----------

### CHEN AND CHEN

*O*,*O*-dialkyl phosphoryl chlorides (2). However, they generally implicate tedious procedures, and sometimes involve toxic reagents or require strict reaction conditions. Therefore, there is a need to develop an efficient method for their preparation.

Recently, we found that phenyliodine dicarboxylates can oxidatively cleave the Se–Se bond in diaryl diselenides to form arylselenyl carboxylates, which can be used as an electrophilic phenylselenating reagent. On the basis of this reaction, we developed a convenient one-pot synthesis of selenosulfonates (5). In connection with our studies on the synthetic application of polymer-supported phenyliodine diacetate (PPID) (6), this previous find led us to extend the phenylselenation reaction to sodium *O*,*O*-dialkyl phosphorates by utilizing the combinative reagent of diphenyl diselenide and PPID. Such a reaction would provide a new one-pot procedure for the synthesis of Se-phenyl *O*,*O*-dialkyl phosphoroselenoates.

In fact, simply stirring a mixture of PPID, diphenyl diselenide, and sodium *O*,*O*-dialkyl phosphorate in methylene chloride at room temperature gave the desired product, Se-phenyl *O*,*O*-dialkyl phosphoroselenoates, after workup and isolation. The reaction is efficient and high-yielding, while variation of the alkyl groups does not affect the readiness of this conversion.



As usual, we also examined the regeneration and recycling of the polymer reagent. The spent resin was collected by filtration and reoxidized with peracetic acid. The regenerated resin was used to repeat the reaction with no loss of activity (see Table 1, entry 3).

In summary, this reaction represents a new efficient method for the synthesis of Se-phenyl *O*,*O*-dialkyl phosphoroselenoates. It has some advantages over existing ones, such as accessible starting materials, mild reaction conditions, simple procedure, and better yields. Furthermore, the range of useful application of polymer-supported phenyliodine diacetate in organic synthesis has been extended.

## **EXPERIMENTAL**

IR spectra were recorded on PE-683 Spectrophotometer. <sup>1</sup>H NMR spectra were recorded on PMX-60 Spectrometer, using CCl<sub>4</sub> as the solvent with TMS as an internal standard.

# Copyright @ Marcel Dekker, Inc. All rights reserved



ORDER		REPRINTS
-------	--	----------

## **HYPERVALENT IODINE. 49**

Table 1. Preparation of Se-phenyl O, O-dialkyl Phosphoroselenoates

Entry	R	Time (h)	Yield (%) <sup>a</sup>
1	Me	1	86
2	Et	1	93
3	Et	1.5	91 <sup>b</sup>
4	<i>n</i> -Pr	1	88
5	<i>i</i> -Pr	1	85
6	<i>n</i> -Bu	1.5	85
7	s-Bu	1.5	83

<sup>a</sup> Yield of isolated product based on diphenyl diselenide.

<sup>b</sup> Regenerated PPID was employed in this case.

**Materials.** PPID were prepared by our previous reported method with the same functional capacity 2.96 mmol/g (6).

General Procedure for the Synthesis of Se-phenyl *O,O*-dialkyl Phosphoroselenoates. A mixture of sodium *O,O*-dialkyl phosphorate (4.0 mmol), diphenyl diselenide (0.5 mmol) and PPID (0.3 g) was stirred for the appropriate time at room temperature. When the reaction was complete as detected by TLC, ether was then introduced to remove the polymer for recovery. The filtrate was washed with H<sub>2</sub>O, dried with MgSO<sub>4</sub>, and concentrated. The desired product was seperated by preparative TLC (petroleum ether:EtOAc = 8:1).

- *Entry 1*: oil. IR (film): 1585, 1490, 1450, 1260, 1185, 1020, 785, 740 cm<sup>-1</sup>. <sup>1</sup>H NMR: 7.83–7.17 (m, 5H), 3.67 (d, 6H, J = 12 Hz).
- *Entry 2*: oil. IR (film): 1585, 1490, 1440, 1255, 1165, 1020, 970, 790, 745 cm<sup>-1</sup>. <sup>1</sup>H NMR: 7.80–7.17 (m, 5H), 4.50–3.80 (m, H), 1.28 (t, 6H, J = 6 Hz).
- *Entry 4*: oil. IR (film): 1590, 1490, 1453, 1400, 1255, 1000, 740 cm<sup>-1</sup>. <sup>1</sup>H NMR: 7.75–7.12 (m, 5H), 4.20–3.71 (m, 4H), 1.92–1.35 (m, 4H), 0.95 (t, 6H, J = 6 Hz).
- *Entry 5*: oil. IR (film): 1580, 1490, 1445, 1390, 1380, 1252, 975, 740 cm<sup>-1</sup>. <sup>1</sup>H NMR: 7.83–7.12 (m, 5H), 5.00–4.35 (m, 2H), 1.25 (t, 12H, J = 6 Hz).
- *Entry* 6: oil. IR (film): 1585, 1490, 1450, 1390, 1255, 1150, 1125, 1000, 740 cm<sup>-1</sup>. <sup>1</sup>H NMR: 7.70–7.06 (m, 5H), 4.26–3.65 (m, 4H), 1.90–0.60 (m, 14H).
- *Entry* 7: oil. IR (film): 1580, 1475, 1440, 1380, 1250, 1170, 1125, 1110, 1090, 1025, 975, 740 cm<sup>-1</sup>. <sup>1</sup>H NMR: 7.80–7.05 (m, 5H), 4.75–4.11 (m, 2H), 1.90–0.65 (m, 16H).

Marcel Dekker, Inc.

270 Madison Avenue, New York, New York 10016

ORDER		REPRINTS
-------	--	----------

## CHEN AND CHEN

## REFERENCES

- Glass, R.S.; Singh, W.P.; Jung, W.; Veres, Z.; Scholoz, T.D.; Stadtman, T. Monoselenophosphate: Synthesis, Characterization, and Identity with the Prokaryotic Biological Selenium Donor, Compound SePX. Biochemistry 1993, 32, 12555.
- Han, L.B.; Choi, N.; Tanaka, M. Facil Oxidative Addition of the Phosphorous-Selenium Bond to Pd(0) and Pt(0) Complexes and Development of Pd-Catalyzed Regio-and Stereoselective Selenophosphorylation of Alkynes. J. Am. Chem. Soc. 1996, 118, 7000.
- Petragnani, N.; Toscano, V.; Moura Campos, M. Selenophosphororganische Verbindungen, II. Chem. Ber. 1986, 101, 3070.
- Kataev, E.G.; Mannafov, T.G. Phenylselenochloride in Arbuzov Rearrangement, Zh. Obsh. Khim. J. Allg. Chem. 1966, 36, 254 (Russ), (CA 1966, 64, 15784).
- Chen, D.W.; Chen, Z.C. Hypervalent Iodine in Synthesis XIII: Synthesis of Selenosulfonates Using A One Pot Reaction of Diaryl Diselenides Sodium Sulfinates and [Bis(trifluoroacetoxy)iodo]benzene. Tetrahedron Lett. 1994, 35, 7637.
- 6. Wang, G.P.; Chen, Z.C. Hypervalent Iodine in Synthesis XVIII: The Preparation and Utility of Polymer-Supported Phenyliodine(III)diacetate. Synth. Commun. **1999**, *29*, 2859.

Received in Japan January 11, 2000



# **Request Permission or Order Reprints Instantly!**

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the <u>U.S. Copyright Office</u> for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on <u>Fair Use in the Classroom</u>.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our <u>Website</u> <u>User Agreement</u> for more details.

# **Order now!**

Reprints of this article can also be ordered at http://www.dekker.com/servlet/product/DOI/101081SCC100000533