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## New synthesis of trimethylsilyl diphenylphosphinite

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## Treatment of (2-hydroxyprop-2-yl)diphenylphosphine oxide<br/>with silylating agents affords trimethylsilyl diphenylphos-<br/>phinite in high yield.O<br/>Me<br/>OH $Me_3SiX \longrightarrow Ph_2P-O-SiMe_3$

The Arbuzov reaction is a principal methodology to access organophosphorus compounds.<sup>1,2</sup> However, the synthesis of the required alkyl and silyl esters of trivalent phosphorus acids is time-consuming and proceeds under strictly controlled conditions, while the precursors are sometimes poorly accessible. Among the initial compounds, trimethylsilyl diphenylphosphinite **1** has a special synthetic significance.<sup>3</sup> Its subjection to the Arbuzov reaction provides better yield of products compared with the structurally related ethyl diphenylphosphinites.<sup>3(d)</sup> However, the use of compound **1** is limited because the known synthetic procedures are based on diphenylphosphine oxide [Ph<sub>2</sub>P(O)H] which would oxidize in air and readily undergo disproportionation.<sup>4</sup>

We studied the reaction of (2-hydroxyprop-2-yl)diphenylphosphine oxide **2** with a number of silylating reagents and showed that it proceeds in an unexpected manner to afford trimethylsilyl diphenylphosphinite **1** (Scheme 1).<sup>†</sup>

$Me \xrightarrow{Me}_{OH} OH$	+ Me <sub>3</sub> SiX ·	→ Ph <sub>2</sub> P–O	-SiMe <sub>3</sub> + Me <sub>2</sub> C=O + HX
2	3a-d	1	l
	<b>a</b> $X = Me_3SiN$	Η	$\mathbf{c}  \mathbf{X} = \mathbf{E}\mathbf{t}_2\mathbf{N}$
	<b>b</b> $X = MeC(=1)$	NSiMe <sub>3</sub> )O	$\mathbf{d} \mathbf{X} = \mathbf{Cl}$
Scheme 1			

<sup>&</sup>lt;sup>†</sup> Syntheses were carried out in argon atmosphere. NMR spectra were recorded on a Bruker AV-400 spectrometer with working frequencies of 400.13 MHz (<sup>1</sup>H) and 161.98 MHz (<sup>31</sup>P) in CDCl<sub>3</sub>, using the signal of residual protons from the solvent as internal standard (<sup>1</sup>H) and 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) as external standard. Initial (1-hydroxy-1-methylethyl)diphenyl-phosphine oxide **2** was obtained according to the previously described procedures.<sup>9</sup> The accuracy of carbon, hydrogen, nitrogen and silicon determination in the synthesized compounds was ±0.5%; and that of phosphorus, ±0.2%.

© 2016 Mendeleev Communications. Published by ELSEVIER B.V. – 3 on behalf of the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences. The transformation of compound **2** was processed with silylating reagents taken in 1:1.1 ratio in refluxing 1,4-dioxane. Instead of the expected (2-trimethylsilyloxyprop-2-yl)diphenyl-phosphine oxide **4**, compound **1** was obtained as a final product in 71–80% yields. If hexamethyldisilazane **3a** and bis(trimethyl-silyl)acetamide **3b** were used as silylating agents, <sup>1</sup>H NMR spectra of low-boiling fraction showed the proton signals of acetone, and for diethyl(trimethylsilyl)amine **3c** proton signals of solvent were observed.

Since the silvl ethers of  $\alpha$ -phosphorylated alcohols are stable,<sup>5</sup> it seems probable that the first stage of the reaction is silvlation of the phosphoryl group of compound 2 rather than its hydroxy group to give O-silyl derivative 4. The resultant zwitterion 5 immediately decomposes under the reaction conditions with the cleavage of the P-C bond to form phosphinite 1 and acetone (Scheme 2). This scheme is also evidenced by the fact that the attempted preparation of silyl ether 4 by the reaction of compound 2 with trimethylchlorosilane 3d at 20 °C in CHCl<sub>3</sub> in the presence of Et<sub>3</sub>N failed giving phosphinite 1 in 75% yield. Also, rapid formation of compound 1 at 20 °C can evidence that Ph<sub>2</sub>P(O)H is not the intermediate in the process [Ph2P(O)H is formed on the base-promoted retro-Abramov decomposition of  $2^6$ ]. In all cases no signal of compound 4 and Ph<sub>2</sub>P(O)H was detected in the <sup>31</sup>P NMR spectra of reaction mixtures in the expected region 17-35 ppm.<sup>7</sup> This allows us to represent the general pathway of the reaction as shown in Scheme 2.

For more details, see Online Supplementary Materials.

*Trimethylsilyl diphenylphosphinite* **1**. Hexamethyldisilazane **3a** (1.36 g, 8.4 mmol) and two drops of trimethylchlorosilane **3d** were added to a suspension of (2-hydroxyprop-2-yl)diphenylphosphine oxide **2** (2 g, 7.8 mmol) in 4 ml of 1,4-dioxane, the mixture was heated to reflux and low-boiling fraction with bp 50–80 °C was distilled off. Compound **2** completely dissolved within 20 min. The volatiles were removed under reduced pressure (12 Torr) and the residue was distilled twice at 12 Torr using collar adapter to give 1.65 g (79%) of product **1**. <sup>1</sup>H NMR, δ: 7.56–7.51 (m, 4 H, *o*-H<sub>ph</sub>), 7.38–7.30 (m, 6H, *m,p*-H<sub>ph</sub>), 0.27 (s, 9H, 3Me).<sup>3(a),4(b),(c),(e)</sup> {<sup>1</sup>H} <sup>31</sup>P NMR, δ: 94.90.

The reactions of compound **2** with bis(trimethylsilyl)acetamide **3b** and diethyl(trimethylsilyl)amine **3c** were performed similarly, the yields of **1** were 1.49 g (71%) and 1.69 g (80%), respectively.

On using trimethylchlorosilane **3d** (0.96 g, 8.4 mmol), it was added for 2 min under stirring to a solution of compound **2** (2 g, 7.8 mmol) and triethylamine (0.85 g, 8.4 mmol) in 10 ml of chloroform at 20 °C. After 2 h, 30 ml of benzene–hexane (1:1) mixture was added. The mixture was cooled to 0 °C, the resultant precipitate was filtered off after 1 h and washed with benzene–hexane mixture (1:1,  $2 \times 20$  ml). The filtrate was concentrated, the residue was distilled twice at 12 Torr using collar adapter to give 1.58 g (75%) of compound **1**.

All four samples of trimethylsilyl diphenylphosphinite **1** were combined. Distillation afforded 6.23 g of **1**, bp 110–112 °C (1 Torr).<sup>4(*b*)</sup> Colorless needle-like crystals, mp 24–26 °C.<sup>4(*b*),(*c*)</sup> Found (%): C, 65.67; H, 6.98; P, 11.47; Si, 9.02. Calc. for  $C_{15}H_{19}OPSi$  (%): C, 65.66; H, 6.98; P, 11.29; Si, 9.24.



Scheme 2

The prepared trimethylsilyl diphenylphosphinite **1** was subjected to Arbuzov reaction with ethyl bromoacetate **6** and (chloromethyl)diphenylphosphine oxide **7**. The reactions led in high yields to ethyl (diphenylphosphoryl)acetate **8** ( $\delta_P$  26.74 ppm, lit.,<sup>8</sup> 28.9 ppm), a precursor for the synthesis of extractants for actinides and lanthanides,<sup>9</sup> and bis(diphenylphosphoryl)methane **9** ( $\delta_P$  24.64 ppm, lit.,<sup>10(a)</sup> 25.47 ppm), one of the most efficient extractants for *f*-block elements (Scheme 3).<sup>10(b)</sup>



In conslusion, we have developed a quick convenient and high-yield synthesis of trimethylsilyl diphenylphosphinite 1 a valuable reactant for the preparation of functionalized diphenylphosphine oxides by Arbuzov reaction. It is also important that initial (2-hydroxyprop-2-yl)diphenylphosphine oxide  $2^{4(a)}$  is stable, available, and easy for handling. The starting compound 2 can be rapidly and in high yield synthesized from Ph<sub>2</sub>PCl<sup>11(a)</sup> or Ph<sub>2</sub>P(O)H.<sup>11(b)</sup> Reactivity of compound 2 allows us to consider it as a synthetic equivalent of diphenyl phosphine oxide (or diphenylphosphinite) anion Ph<sub>2</sub>PO<sup>-,11(a)</sup> while 2-hydroxyprop-2-yl moiety being a temporary protective group.

## **Online Supplementary Materials**

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.09.010.

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