# Synthesis and Reactivity of Alkoxy(trimethylsiloxy)phosphines and Their Derivatives

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ABSTRACT: Convenient procedures for the synthesis of new alkoxy(trimethylsiloxy)phosphines and their derivatives starting from the available alkyl hypophosphites and N-trimethylsilyl succinimide are proposed. Some properties of these new phosphines such as nucleophilic substitution of the trimethylsiloxy group at trivalent phosphorus, the Arbuzov reaction, and addition of PH and POSi fragments to multiple carboncarbon bonds are presented. © 2011 Wiley Periodicals, Inc. Heteroatom Chem 23:138–145, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20762

# INTRODUCTION

Various esters of hypophosphorous acid are widely used as unique organophosphorus synthons for preparation of numerous types of organophosphorus compounds [1]. Some properties of alkyl or trimethylsilyl hypophosphites [2–4], bis(alkoxy)phosphines [5,6], and bis(trialkylsiloxy) phosphines [7–13] are investigated in detail. The new highly reactive alkoxy(trimethylsiloxy)phosphines, which were synthesized by us, are of great interest as the key substances for the synthesis of functional-

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ized organophosphorus compounds with promising useful properties.

# **RESULTS AND DISCUSSION**

It is known that hypophosphorous acid is slowly esterified by orthocarbonyl compounds [2]. So the starting alkyl hypophosphites **A** are prepared as intermediates by mixing crystalline hypophosphorous acid and trialkyl orthoformates at room temperature (cf. [2]), and treatment of the reaction mixture with an excess of the mild silylating reagent—N-trimethylsilyl succinimide—leads to alkoxy(trimethylsiloxy)phosphines **1–4** with good yields (Eq. (1)):



It should be noted that the phosphines **1–4** are stable compounds, which may be distilled in vacuum in contrast to bismethoxy-, bisethoxy-, and bispropoxyphosphines that are easily destroyed after heating [5,14]. The obtained phosphines **1–4** are used by us as convenient synthons to form new types of organophosphorus compounds. So

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the interaction of phosphines **1–4** with disubstituted lithium or sodium amides proceeds only as nucleophilic substitution of the trimethylsiloxy group at trivalent phosphorus, but not as metalation of the PH fragment. This reaction takes place at  $0^{\circ}$ C, and after treatment of the reaction mixture with chlorotrimethylsilane to neutralize the formed lithium or sodium, trimethylsilanolates yields alkoxy(amino)phosphines **5–10** (Eq. (2); cf. [15]).

$$1-4 \xrightarrow{1. X_2 \text{NM } 2. \text{ Me}_3 \text{SiCl}}_{-\text{MCl}, -(\text{Me}_3 \text{Si})_2 \text{O}} \xrightarrow{\text{RO}}_{X_2 \text{N}} \text{PH}$$

$$5-10$$

$$M = Li, Na; R = Me (5,9), Et (6,10), Bu (7,8);$$
  
X = Et (7), Bu (5,6,8), Me<sub>3</sub>Si (9,10). (2)

A similar reaction of bis(trimethylsiloxy)phosphine **B** with lithium dialkylamides or sodium bis (trimethylsilyl)amide proceeds under the same conditions to give trimethylsiloxy(amino)phosphines **11–14** (Eq. (3))

$$(Me_{3}SiO)_{2}PH \xrightarrow{1. X_{2}NM 2. Me_{3}SiCl} -MCl, -(Me_{3}Si)_{2}O \xrightarrow{Me_{3}SiO} PH$$

$$X_{2}N$$

$$B \xrightarrow{11-14}$$

$$M = Li, Na; X = Et (11), i-Pr (12), Bu (13), Me_3Si (14).$$
 (3)

The new bisphosphine **15** of unsymmetrical structure is obtained similarly via the reaction of phosphine **B** and lithium bis(tert-butyl)phosphide (Eq. (4))

$$(Me_{3}SiO)_{2}PH \xrightarrow{1. t-Bu_{2}PLi 2. Me_{3}SiCl}_{-LiCl, -(Me_{3}Si)_{2}O} t-Bu_{2}P-P H$$

$$B \qquad 15 \qquad (4)$$

It should be noted that in all cases there are no products of double replacement of alkoxy or trimethylsiloxy groups at trivalent phosphorus. In contrast, the interaction of phosphine **B** with highly nucleophilic butyllithium in a ratio of 1:1 even under cooling to  $-70^{\circ}$ C leads to an equimolar mixture of phosphines **16** and **17** in low yields (15%; Eq. (5))

$$B \xrightarrow{1. \text{ BuLi } 2. \text{ Me}_3 \text{SiO}}_{-\text{LiCl}, -(\text{Me}_3 \text{Si})_2 \text{O}} \xrightarrow{\text{Me}_3 \text{SiO}}_{\text{Bu}} PH + \text{Bu}_2 PH$$

$$Bu \xrightarrow{16} 17$$

**16**:  $\delta_P 88.1$  d,  ${}^{I}J_{PH} 17.7$ ; **17**:  $\delta_P - 70.5$  d,  ${}^{I}J_{PH} 184$ . (5)

The synthesized phosphines **1–17** are readily oxidized and hydrolyzed in air sometimes with burning. The slow oxidation of phosphine **2** in a solution of benzene by dry air current results in formation of phosphite **18** with high yield, and addition of sulfur to phosphines **1–4** and aminophosphines **10** and **14** proceeds under similar conditions to give thiophosphites **19–24** (Eq. (6))





 $X = Et (10,23), Me_3Si (14,24)$  (6)

In contrast, the similar oxidation of aminophosphine **10** under the same conditions gives amidophosphate **25** with high yield. The formation of phosphate **25** includes an irreversible rearrangement of the primary oxidation product amidophosphite **C**—via N,O-migration of the trimethylsilyl group into a mixture of two tautomers, **D** and **E** (the last one **E** is oxidized), yielding amidophosphate 25 (Eq. (7); cf. [16,17])



For the first time, we have realized the successful Arbuzov reaction for esters of hypophosphorous acid (cf. [8–10,18]). So, the most reactive methoxyphosphine **1** reacts with allyl iodide under refluxing in benzene via a classic scheme of the Arbuzov reaction, yielding phosphonite **26** (Eq. (8))



The less reactive methyl and benzyl iodides react with phosphine 1 under the same conditions to give a mixture of corresponding phosphonites 27, 28, bis(trimethylsilyl)phosphite  $\mathbf{F}$ , methyl(trimethylsilyl)phosphite  $\mathbf{G}$ , and yellow polymer (Eq. (9))



Yet the more nucleophilic aminophosphine **9** reacts with methyl iodide exothermically, but this reaction leads to an unusual product—crystalline phosphonium iodide **29**—whose structure was confirmed by its transformation into imidophosphinate **30** using sodium bis(trimethylsilyl)amide as a strong base. The scheme of formation of product **29** is similar to the scheme of oxidation of aminophosphine **10** (Eq. (7)). The primary phosphonite **H** transforms via N,O-migration of the trimethylsilyl group into a mixture of two tautomers, **I** and **J**, and the last one, **J**, adds methyl iodide to give phosphonium **29** (Eq. (10))



As alkoxy(trimethylsiloxy)phosphines **1–4** include two highly reactive PH and POSi fragments, it is possible to realize the double addition of these phosphines to several multiple carbon–carbon bonds (cf. [19,20]). So, phosphine **2** easily adds methylacrylate step by step under mild conditions to yield functionalized phosphonite **31** or corresponding phosphinate **32** (Eq. (11); cf. [20])



In contrast, the interaction of phosphine **2** with ethoxyacetylene in the ratio 1:1 under the same conditions gives a mixture of three adducts **33**, **34**, and **36**; however, using an excess of alkoxyacetylenes leads to substituted bisvinylphosphinates **35–38** (Eq. (12))



 $\mathrm{X}=\mathrm{Y}=\mathrm{Et}\;(\textbf{33,34,36});\;\mathrm{X}=\mathrm{Et}\;(\textbf{2,35}),\;\mathrm{Bu}\;(\textbf{4,37,38});\;\mathrm{Y}=\mathrm{Me}\;(\textbf{35,37}),\;\mathrm{Et}\;(\textbf{38});$ 

**33**:  $\delta_P$  132 s; **34**:  $\delta_P$  21.2 d,  ${}^I J_{\text{PH}}$  543

(12)

TABLE 1 Yields, Product Constants, and NMR Spectral Data for the PH Fragments<sup>a</sup> (δ, ppm; J, Hz) of Compounds 1–30

| No. | Yield (%) | bp (° C) (p, mmHg) | n_D^{20} | δ <b>(H) PH, d</b> | δ <b>(P), d</b>           | <sup>1</sup> JPH |
|-----|-----------|--------------------|----------|--------------------|---------------------------|------------------|
| 1   | 59        | 48 (55)            | _        | 6.23               | 160.91                    | 182.2            |
| 2   | 67        | 57 (40)            | _        | 6.23               | 154.43                    | 184.1            |
| 3   | 66        | 61 (20)            | _        | 6.23               | 153.74                    | 186.0            |
| 4   | 68        | 30 (1)             | _        | 6.30               | 155.21                    | 189.3            |
| 5   | 82        | 46 (1)             | _        | 6.63               | 130.92                    | 231.2            |
| 6   | 76        | 66 (2)             | _        | 6.67               | 124.72                    | 232.3            |
| 7   | 75        | 44 (1)             | _        | 6.72               | 124.07                    | 232.1            |
| 8   | 78        | 71 (1)             | _        | 6.61               | 124.34                    | 231.5            |
| 9   | 69        | 42 (1)             | -        | 6.95               | 122.21                    | 215.4            |
| 10  | 78        | 46 (1)             | _        | 6.97               | 116.45                    | 218.7            |
| 11  | 58        | 69 (16)            | -        | 6.83               | 109.52                    | 225.3            |
| 12  | 31        | 43 (1)             | -        | 6.88               | 87.04                     | 229.2            |
| 13  | 59        | 56 (1)             | -        | 6.97               | 111.73                    | 224.0            |
| 14  | 52        | 49 (1)             | -        | 7.12               | 105.08                    | 203.9            |
| 15  | 46        | 61 (1)             | _        | 7.07 <sup>b</sup>  | 67.81 <sup><i>c</i></sup> | 182.4            |
| 18  | 85        | 33 (1)             | 1.4102   | 6.73               | -3.30                     | 684.3            |
| 19  | 79        | 65 (8)             | 1.4590   | 7.67               | 58.07                     | 645.7            |
| 20  | 81        | 49 (1)             | 1.4560   | 7.73               | 54.43                     | 644.2            |
| 21  | 86        | 59 (1)             | 1.4565   | 7.73               | 56.67                     | 643.1            |
| 22  | 84        | 68 (1)             | 1.4545   | 7.80               | 56.26                     | 643.0            |
| 23  | 82        | 86 (2)             | 1.4788   | 8.12               | 60.58                     | 581.5            |
| 24  | 85        | 80 (1)             | 1.4700   | 8.23               | 45.74                     | 589.3            |
| 25  | 85        | 71 (1)             | 1.4255   | _                  | -1.81                     | _                |
| 26  | 63        | 78 (8)             | 1.4355   | 6.50               | 22.12                     | 549.2            |
| 29  | 100       | a                  | _        | _                  | 62.11                     | _                |
| 30  | 73        | 29 (1)             | 1.4280   | -                  | 14.52                     | -                |

<sup>a</sup>For compounds **1–15**,  $n_D^{20}$  was not measured because of their extreme reactivity. The salt **29** consists of very hygroscopic crystals; therefore, its melting point was not measured. In the <sup>1</sup>H NMR spectra, all signals of alkyl and trimethylsilyl fragments are in the standard area. In the <sup>1</sup>H NMR spectra, fragment MeOP for compounds,  $\delta_H$ , d,  ${}^{3}J_{PH}$ : **1**:3.62, 8.1; **5**:3.45, 11.2; **9**:3.33, 13.1; **19**:3.43, 16.1. The supplementary data on the <sup>1</sup>H NMR spectra for compounds: **15**: 0.20 s (Me<sub>3</sub>Si, 9 H), 1.13 d and 1.23 d,  ${}^{3}J_{PH}$  **11**.2 (2*t*-Bu, 18 H); **25**: 0.28 s (2Me<sub>3</sub>Si, 18 H), 1.17 t,  ${}^{3}J_{HH}$  7 (CH<sub>3</sub>C, 3 H), 3.7–4.2 m (CH<sub>2</sub>O, 2 H), 5.57 s (NH, 1 H); **26**: 0.15 s (Me<sub>3</sub>Si, 9H), 2.03 dd,  ${}^{2}J_{PH}$  **19**.1,  ${}^{3}J_{HH}$  7.2 (CH<sub>2</sub>P, 2H), 4.3–5.6 m (CH<sub>2</sub>=CH, 3 H); **29**: 0.25 s (Me<sub>3</sub>SiN, 9H), 0.32 s (Me<sub>3</sub>SiO, 9H), 2.05 d,  ${}^{2}J_{PH}$  **15**.2 (Me<sub>2</sub>P, 6H), rapid proton exchange for NH; **30**: 0.22 s (Me<sub>3</sub>SiN and Me<sub>3</sub>SiO, 18 H), 1.15 d,  ${}^{2}J_{PH}$  **13**.1 (Me<sub>2</sub>P, 6 H).

<sup>b</sup>dd, <sup>2</sup>J<sub>PH</sub> 17.3.

<sup>c</sup>dd, <sup>1</sup> $J_{PP}$  289.2;  $\delta_P(t-Bu_2P)$  39.9 d, <sup>1</sup> $J_{PP}$  289.2.

| No. | Yield (%) | bp (° C) (p, mmHg) | $n_{D}^{20}$ | Ratio (%) | $\delta$ (C <sup>1</sup> ), d | $^{1}J_{PC}$ | $\delta$ (C <sup>2</sup> ), d | <sup>2</sup> J <sub>PC</sub> | δ <b>(Ρ),s<sup>b</sup></b> |
|-----|-----------|--------------------|--------------|-----------|-------------------------------|--------------|-------------------------------|------------------------------|----------------------------|
| 31  | 65        | 64 (1)             | _            | 100       | 35.89                         | 23.5         | 27.68                         | 12.5                         | 169.72                     |
| 32  | 100       | Oìl                | 1.4610       | 100       | 24.98                         | 93.7         | 28.73                         | <1                           | 51.86                      |
|     |           |                    |              |           | 24.03 <sup>c</sup>            | 92.4         | 71.97                         | 9.0                          |                            |
| 35  | 49        | 94 (1)             | 1.4729       | 60        | 163.04 <sup><i>d</i></sup>    | 104.4        | 98.38                         | 22.1                         | 13.22                      |
|     |           |                    |              |           | 156.75 <sup>e</sup>           | 126.4        | 124.66                        | 18.9                         |                            |
|     |           |                    |              | 40        | 163.70 <sup>d</sup>           | 117.8        | 97.63                         | 22.6                         | 13.03                      |
|     |           |                    |              |           | 157.83 <sup>e</sup>           | 138.6        | 124.55                        | 18.3                         |                            |
| 36  | 55        | 103 (1)            | 1.4655       | 60        | 162.74 <sup>d</sup>           | 117.2        | 98.62                         | 22.0                         | 13.76                      |
|     |           |                    |              |           | 157.07 <sup>e</sup>           | 139.8        | 124.37                        | 18.9                         |                            |
|     |           |                    |              | 40        | 162.05 <sup>d</sup>           | 109.3        | 97.85                         | 22.6                         | 13.37                      |
|     |           |                    |              |           | 156.01 <sup><i>e</i></sup>    | 123.3        | 124.14                        | 18.3                         |                            |
| 37  | 47        | 104 (1)            | 1.4670       | 70        | 162.94 <sup><i>d</i></sup>    | 106.8        | 98.40                         | 22.0                         | 13.03                      |
|     |           |                    |              |           | 156.67 <sup>e</sup>           | 129.4        | 124.41                        | 18.9                         |                            |
|     |           |                    |              | 30        | 163.62 <sup>d</sup>           | 119.0        | 97.59                         | 22.2                         | 12.78                      |
|     |           |                    |              |           | 157.73 <sup>e</sup>           | 141.0        | 124.39                        | 17.7                         |                            |
| 38  | 49        | 115 (1)            | 1.4625       | 70        | 163.76 <sup>d</sup>           | 91.7         | 98.58                         | 22.0                         | 13.60                      |
|     |           |                    |              |           | 156.49 <sup>e</sup>           | 113.9        | 124.41                        | 19.0                         |                            |
|     |           |                    |              | 30        | 163.14 <sup>d</sup>           | 76.7         | 97.87                         | 22.4                         | 13.09                      |
|     |           |                    |              |           | 155.35 <sup>e</sup>           | 100.3        | 124.17                        | 18.3                         |                            |

**TABLE 2** Yields, Product Constants, and NMR Spectral Data for the PC<sup>1</sup>H<sub>0</sub>C<sup>2</sup>H<sub>m</sub>C<sup>3</sup> Fragments<sup>*a*</sup> ( $\delta$ , ppm; J, Hz) of Functionalized Compounds 31-38

<sup>a</sup>All signals of alkyl and trimethylsilyl groups are in the standard area. The <sup>1</sup>H NMR signals of the protons of the fragments PC<sup>1</sup>H<sub>n</sub>C<sup>2</sup>H<sub>m</sub>C<sup>3</sup> of compounds **31** and **32** are multiplets. In the <sup>13</sup>C NMR spectra, fragments,  $\delta_C(C^3=O)$  for compounds: **31**, 173.71 d,  ${}^{3}J_{PC}$  9.1; **32**, 172.59 d,  ${}^{3}J_{PC}$ 14.4;  $\delta_C(C^3=)$  for compound **32**: 152.26 d,  ${}^{3}J_{PC}$  11.2. According to the NMR spectra, compounds **35–38** are mixtures of two stereoisomers, and their ratio was determined from <sup>1</sup>H and <sup>31</sup>P NMR spectra. In the <sup>1</sup>H NMR spectra, fragments C<sup>2</sup>H<sub>2</sub>=C of compounds **35–38** are observed as two overlapping characteristic ABX multiplets of the diastereotopic protons of the methylene groups C<sup>2</sup>H<sub>2</sub> for two stereoisomers in the range 4.5–5.6 ppm; fragments =  $C^2HSi$  for compounds, d,  ${}^{3}J_{PH}$ : 35: 6.19, 14.0 and 6.13, 14.0; 36: 6.08, 14.3 and 6.12, 14.3; 37: 6.16, 14.2 and 6.21, 14.2; 38: 6.10, 14.4 and 6.16, 14.4.

<sup>b</sup>Data of <sup>31</sup>P-{<sup>1</sup>H} spectra. <sup>c</sup>Fragment PC<sup>1</sup>H<sub>2</sub>C<sup>2</sup>H=C<sup>3</sup>.

<sup>d</sup>Fragment PC<sup>1</sup>=C<sup>2</sup>H<sub>2</sub>.

<sup>e</sup>Fragment PC<sup>1</sup>=C<sup>2</sup>HSi.

The structures of compounds 1-38 were confirmed by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra, which show the characteristic signals of P-H fragments or other fragments of tri- or tetracoordinated phosphorus (see Tables 1 and 2). According to the NMR spectra, the compounds 35-38 are a mixture of two stereoisomers. Their ratio was determined from the <sup>1</sup>H and <sup>31</sup>P NMR spectra. The elemental analysis data of synthesized compounds are presented in Table 3.

# EXPERIMENTAL

The <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were registered on a Bruker Avance-400 spectrometer (400, 100, and 162 MHz, respectively) in  $CDCl_3$  or  $C_6D_6$  (1-38) against TMS (<sup>1</sup>H and <sup>13</sup>C) and 85%  $H_3PO_4$  in  $D_2O$  (<sup>31</sup>P). All reactions were performed under dry argon in anhydrous solvents. Starting crystalline hypophosphorous acid was prepared according to the procedure described by Fitch [2].

#### N-Trimethylsilyl Succinimide

A mixture of 99 g of succinimide, 101 g of triethylamine, and 109 g of chlorotrimethylsilane in 1 L of dioxane was heated under reflux with stirring for 2 h. Then 300 mL of pentane was added to the mixture; triethylamine hydrochloride was filtered off and washed with 300 mL of pentane. The combined organic solutions were distilled off; the residue was distilled to obtain 137 g of N-trimethylsilyl succinimide. Yield 80%, bp 119°C (13 mmHg), n<sub>D</sub><sup>20</sup> 1.4735 (cf. [21]).

#### *Bis(trimethylsiloxy)phosphine* (**B**)

A mixture of 41 g of ammonium hypophosphite and 100 g of bis(trimethylsilyl)amine was refluxed under 130°C until ammonia no longer evolved, and then it was distilled to obtain 90 g of phosphine B. Yield 85%, bp 42°C (9 mmHg),  $\delta_P$  140 d, <sup>1</sup> $J_{PH}$  176 (cf. [7]).

| No. |   | Formula Weight | Calc  | ed. (%) | Found (%) |       |
|-----|---|----------------|-------|---------|-----------|-------|
|     | Empirical Formula   |                | С     | Н       | С         | Н     |
| 1   | C <sub>4</sub> H <sub>13</sub> O <sub>2</sub> PSi               | 152.20         | 31.56 | 8.61    | 31.71     | 8.67  |
| 2   | C <sub>5</sub> H <sub>15</sub> O <sub>2</sub> PSi               | 166.23         | 36.13 | 9.10    | 35.93     | 9.34  |
| 3   | C <sub>6</sub> H <sub>17</sub> O <sub>2</sub> PSi               | 180.25         | 39.98 | 9.51    | 40.23     | 9.40  |
| 4   | C <sub>7</sub> H <sub>19</sub> O <sub>2</sub> PSi               | 194.28         | 43.27 | 9.86    | 43.40     | 9.94  |
| 5   | C <sub>9</sub> H <sub>22</sub> NOP                              | 191.25         | 56.52 | 11.59   | 56.45     | 11.69 |
| 6   | C <sub>10</sub> H <sub>24</sub> NOP                             | 205.28         | 58.51 | 11.78   | 58.39     | 11.63 |
| 7   | C <sub>8</sub> H <sub>20</sub> NOP                              | 177.23         | 54.22 | 11.38   | 54.40     | 11.31 |
| 8   | C <sub>12</sub> H <sub>28</sub> NOP                             | 233.33         | 61.77 | 12.09   | 61.68     | 12.01 |
| 9   | C7H22NOPSi2   | 223.40         | 37.63 | 9.93    | 37.23     | 10.17 |
| 10  | C <sub>8</sub> H <sub>24</sub> NOPSi <sub>2</sub>               | 237.43         | 40.47 | 10.19   | 40.11     | 10.32 |
| 11  | C <sub>7</sub> H <sub>20</sub> NOPSi                            | 193.31         | 43.49 | 10.43   | 43.84     | 10.37 |
| 12  | C <sub>9</sub> H <sub>24</sub> NOPSi                            | 221.36         | 48.83 | 10.93   | 48.57     | 11.08 |
| 13  | C <sub>11</sub> H <sub>28</sub> NOPSi                           | 249.41         | 52.97 | 11.32   | 53.28     | 11.20 |
| 14  | C <sub>9</sub> H <sub>28</sub> NOPSi <sub>3</sub>               | 281.56         | 38.39 | 10.02   | 38.21     | 10.13 |
| 15  | C <sub>11</sub> H <sub>28</sub> OP <sub>2</sub> Si              | 266.37         | 49.60 | 10.60   | 49.21     | 10.45 |
| 18  | C <sub>5</sub> H <sub>15</sub> O <sub>3</sub> PSi               | 182.23         | 32.95 | 8.30    | 32.70     | 8.43  |
| 19  | C <sub>4</sub> H <sub>13</sub> O <sub>2</sub> PSSi              | 184.27         | 26.08 | 7.11    | 26.20     | 7.33  |
| 20  | C <sub>5</sub> H <sub>15</sub> O <sub>2</sub> PSSi              | 198.30         | 30.29 | 7.63    | 30.12     | 7.82  |
| 21  | C <sub>6</sub> H <sub>17</sub> O <sub>2</sub> PSSi              | 212.33         | 33.94 | 8.07    | 34.30     | 7.89  |
| 22  | C <sub>7</sub> H <sub>19</sub> O <sub>2</sub> PSSi              | 226.36         | 37.14 | 8.46    | 37.41     | 8.30  |
| 23  | C <sub>8</sub> H <sub>24</sub> NOPSSi <sub>2</sub>              | 269.50         | 35.66 | 8.98    | 35.29     | 8.71  |
| 24  | C <sub>9</sub> H <sub>28</sub> NOPSSi <sub>3</sub>              | 313.63         | 34.47 | 9.00    | 34.65     | 8.89  |
| 25  | C <sub>8</sub> H <sub>24</sub> NO <sub>3</sub> PSi <sub>2</sub> | 269.43         | 35.66 | 8.98    | 35.98     | 8.70  |
| 26  | C <sub>6</sub> H <sub>15</sub> O <sub>2</sub> PSi               | 178.23         | 40.43 | 8.48    | 40.19     | 8.31  |
| 30  | C <sub>8</sub> H <sub>24</sub> NOPSi <sub>2</sub>               | 237.43         | 40.47 | 10.19   | 40.12     | 10.08 |
| 31  | C <sub>9</sub> H <sub>21</sub> O <sub>4</sub> PSi               | 252.32         | 42.84 | 8.39    | 43.15     | 8.22  |
| 32  | C <sub>13</sub> H <sub>27</sub> O <sub>6</sub> PSi              | 338.41         | 46.14 | 8.04    | 45.89     | 8.17  |
| 35  | C <sub>11</sub> H <sub>23</sub> O <sub>4</sub> PSi              | 278.36         | 47.46 | 8.33    | 47.15     | 8.20  |
| 36  | C <sub>13</sub> H <sub>27</sub> O <sub>4</sub> PSi              | 306.42         | 50.96 | 8.88    | 50.68     | 8.71  |
| 37  | C <sub>13</sub> H <sub>27</sub> O <sub>4</sub> PSi              | 306.42         | 50.96 | 8.88    | 50.72     | 8.65  |
| 38  | C <sub>15</sub> H <sub>31</sub> O <sub>4</sub> PSi              | 334.47         | 53.87 | 9.34    | 53.59     | 9.11  |

TABLE 3 Elemental Analyses Data of Synthesized Compounds<sup>a</sup>

<sup>a</sup>The compounds 16, 17, 27, 28, 33, and 34 were obtained as mixtures. The very hygroscopic compound 29 was analyzed in its stable derivative 30.

# *Methoxy(trimethylsiloxy)phosphine* (1)

A mixture of 6.6 g of hypophosphorous acid and 12.7 g of trimethyl orthoformate was stirred for 0.5 h at 20°C; then this mixture was added dropwise to a solution of 38 g of *N*-trimethylsilyl succinimide in 100 mL of diethyl ether. The mixture was stirred for 1.5 h, and 100 mL of pentane was added. The precipitate of succinimide was filtered off, the solvent was removed, and the residue was distilled in vacuum to obtain 9 g of phosphine **1**.

The phosphines 2–4 were prepared similarly.

## *Methoxy(dibutylamino)phosphine* (5)

A solution of lithium dibutylamide obtained from 6.3 g of dibutylamine in 30 mL of diethyl ether and 0.05 mol of butyllithium in pentane was added under stirring and cooled to  $0^{\circ}$ C to a solution of 7.4 g of phosphine **1** in 25 mL of diethyl ether. The mixture

was stirred for 2 h under  $20^{\circ}$ C and was then cooled to  $0^{\circ}$ C. A solution of 5.3 g of chlorotrimethylsilane in 20 mL of diethyl ether was added to the mixture and then 100 mL of pentane was also added. The precipitate was separated, the solvent was removed, and the residue was distilled to yield 7.6 g of aminophosphine **5**.

Aminophosphines **6–14**, bisphosphine **15**, and a mixture of phosphines **16** and **17** were prepared similarly.

# Ethyl Trimethylsilyl Phosphite (18)

Dry air was bubbled through a solution of 7.3 g of phosphine 2 in 5 mL of benzene until the exothermic reaction was completed. The solvent was removed, and the residue was distilled to obtain 6.8 g of phosphite **18**.

Amidophosphate 25 was prepared similarly.

#### O-Methyl O-Trimethylsilyl Thiophosphite (19)

A mixture of 6.6 g of phosphine **1** and 1.7 g of sulfur in 25 mL of diethyl ether was refluxed for 0.5 h and then 25 mL of pentane was added. An excess of sulfur was separated, the solvents were removed, and the residue was distilled in vacuum to give 6.2 g of thiophosphite **19**.

Thiophosphites **20–24** were prepared similarly.

### O-Trimethylsilyl Allylphosphonite (26)

A solution of 8.1 g of phosphine **1** in 10 mL of benzene was added dropwise under stirring to a mixture of 30 g of allyl iodide and 50 mL of benzene, and the mixture was refluxed for 1 h. A small amount of polymer was separated, the solvent was removed, and the residue was distilled in vacuum to give 6 g of phosphonite **26**.

The reactions of phosphine **1** with methyl and benzyl iodides were carried out similarly.

# *Dimethyl(trimethylsiloxy)trimethylsilylaminophosphonium Iodide* (**29**)

A solution of 5.5 g of methyl iodide in 5 mL of benzene was added under stirring to a solution of 8 g of phosphine **9** in 20 mL of benzene, and the mixture was refluxed for 1 h. The solvent was removed and white crystals that were formed were kept in vacuum (1 mmHg) for 1 h to obtain 13 g of phosphonium **29**.

## *Dimethyl O,N-Bis(trimethylsilyl) imidophosphinate* (**30**)

A solution of sodium bis(trimethylsilyl)amide, 0.036 mol, in 30 mL of diethyl ether was added with stirring and cooled to 0°C to a mixture of 13 g of phosphonium **29** in 30 mL of diethyl ether, and the mixture was stirred for 2 h under 20°C. The precipitate was separated, the solvent was removed, and the residue was distilled in vacuum to give 6.2 g of imidophosphinate **30**.

# *O-Ethyl O-trimethylsilyl 2-(methoxycarbonyl) ethylphosphonite* (**31**)

A solution of 4 g of methyl acrylate in 10 mL of methylene chloride was added with stirring and cooled to  $-10^{\circ}$ C to a solution of 7.7 g of phosphine **2** in 20 mL of methylene chloride. The reaction mixture was kept for 24 h at 20°C, the solvent was then

removed, and the residue was distilled in vacuum to obtain 6.4 g of phosphonite **31**.

Bis(vinyl)phosphinates **35–38** were prepared similarly.

# *O-Ethyl 2-(methoxycarbonyl)ethyl 3-methoxy-3-(trimethylsiloxy)prop-2-yl-phosphinate* (**32**)

A solution of 2 g of methyl acrylate in 10 mL of methylene chloride was added dropwise with stirring and cooled to  $10^{\circ}$ C to a solution of 4 g of phosphonite **31** in 20 mL of methylene chloride. The reaction mixture was kept for 24 h at 20°C, the solvent was then removed, and the residue was kept in vacuum (0.5 mmHg) for 1 h to obtain 5.4 g of phosphinate **32** as a thick oil.

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