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Regioselective addition of secondary phosphine oxides to 3-(trialkylsilyl)- and 3-(trialkylgermyl)-2-propynals

Nina K. Gusarova *, Aelita M. Reutskaya, Nina I. Ivanova, Alevtina S. Medvedeva, Maria M. Demina, Peter S. Novopashin, Andrei V. Afonin, Alexander I. Albanov, Boris A. Trofimov

Institute of Chemistry, Russian Academy of Sciences, Siberian Branch, 1 Favorsky Street, 664033 Irkutsk, Russia

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Abstract

3-(Trialkylsilyl)- and 3-(trialkylgermyl)-2-propynals as well as 2-propynal react with secondary phosphine oxides by carbonyl group under mild conditions (−10 to 22 °C) to give corresponding tertiary phosphine oxides with acetylenic and hydroxyl moieties in quantitative yield. The reactivity of the aldehydes in this reaction drops in the following order: $HC{\equiv}CC(O)H > Me_3SiC{\equiv}CC(O)H > Et_3GeC{\equiv}CC(O)H$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 3-(Trimethylsilyl)-2-propynal; 3-(Triethylgermyl)-2-propynal; Secondary phosphine oxides; Nucleophilic addition; Competitive reactions; 1-(Diorganylphosphoryl)-3-[trialkylsilyl(or germyl)]-2-propyn-1-ols

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1. Introduction

Reaction of α,β-acetylenic aldehydes with nucleophilic reagents (e.g. amines, thiols, etc.) follows the scheme of 1,4-addition to afford the corresponding Michael adducts [1,2] or products of their subsequent cyclization [3,4]. 3-(Trialkylsilyl)- and 3-(trialkylgermyl)-2-propynals react with NH- and SH-acids as ambident electrophiles with participation of carbonyl group and (or) acetylenic moiety depending on both reaction conditions and the nature of heteroatom in the initial reagents [5]. At the same time there is no data on the reactivity of PH-acids in this reaction, although it would contribute to the theoretical aspects of chemistry of element substituted acetylenic aldehydes and lead to new convenient routes to the synthesis of new polyfunctional Si-, Ge- and P-containing compounds, prospective polydentate amphiphilic ligands for design of new metal complex catalysts (including the chiral ones) [6–11]. In the present paper, taking available 3-(trimethylsilyl)- and 3-(triethylgermyl)-2-propynals (**1**, **2**) [5] and bis(2-phenethyl)- and bis[2-(2-pyridyl)ethyl]phosphine oxides (**3**, **4**) [12] as an example, the data on the reaction of acetylenic aldehydes with secondary phosphine oxides are presented for the first time.

2. Results and discussion

2.1. Synthesis

Secondary phosphine oxides **3**, **4** readily add to propynals **1**, **2** under mild conditions (−10 to 22 °C, THF or methanol) regioselectively at C=O group to give tertiary phosphine oxides **5**–**7** in almost quantitative yield.

The asymmetric carbon atom in phosphine oxides **5**–**7** gives rise to non-equivalence of signals of carbon atoms in phenethyl and pyridylethyl groups. Moreover, in ^{1}H-NMR spectrum of compound **7** the signals of protons in pyridylethyl groups are also non-equivalent.

2-Propynal **8** reacts with phosphine oxide **3** in the same way to form 1-(diphenethylphosphoryl)-2-propyn-1-ol (**9**).

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* Corresponding author. Tel.: +7-3952-466436; fax: +7-3952-396046

E-mail address: gusarova@irioch.irk.ru (N.K. Gusarova).

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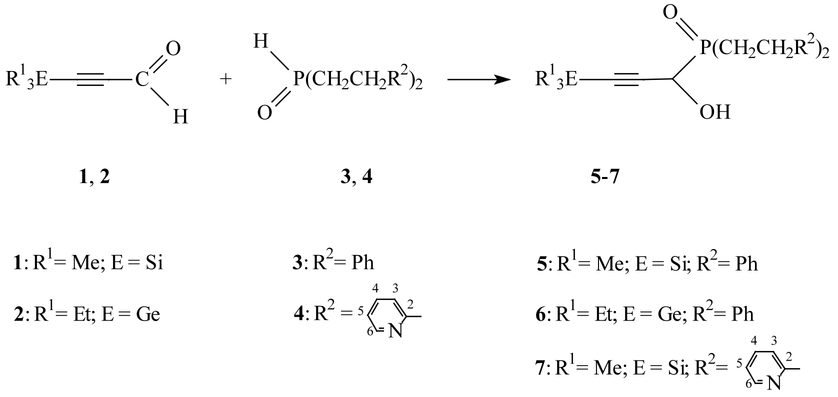


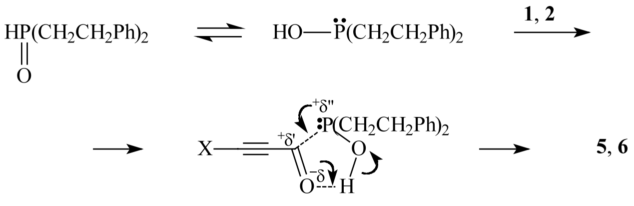
2.2. Reactivity

The reactivity of propynals **1** and **2** towards phosphine oxide **3** was evaluated using the method of competitive reactions. According to the literature data [5], the basicities of triethylgermylpropynal is higher than that of triethylsilylpropynal. At the same time the basicities of trimethyl- and triethylsilylpropynals are comparable [5].

The dynamics of conversion of aldehydes **1**, **2** and formation of the corresponding phosphine oxides **5**, **6** was monitored by the ^{1}H-NMR spectra. For this purpose, a THF solution of propynals **1**, **2** and phosphine oxide **3** in 1:1:2.2 molar ratio, respectively, was used; the reaction was carried out in an NMR tube at room temperature.

The process of formation of hydroxyphosphine oxides **5**, **6** in the reaction mixture was resulting in an increase of the intensity of trimethylsilyl protons (0.10 ppm, s) for **5** and CH_2-protons of triethylgermyl group (0.81 ppm, s) in the case of **6**. The intensities of the corresponding peaks of protons from propynals **1** (0.20 ppm, s) and **2** (0.94 ppm, q) have been synchronously decreasing.

The data obtained prove that in the reaction with phosphine oxide **3** trimethylsilylpropynal **1** is more active than triethylgermylpropynal **2**. Thus, in the first 10 min of the reaction the concentration of formed phosphine oxide **5** is almost three times higher than that of phosphine oxide **6**. After 20 min this ratio decreases to 2 and after 40 min to 1.5. Then the formation rates for compounds **5** and **6** become relatively equal and after 3.5 h the ratio of trimethylsilyl (**5**) and triethylgermyl (**6**) products reaches 1.2. Relative rate constants for the formation of hydroxyphosphine oxides **5** and **6** become 10.7 and 4.1 mol l min^{-1}, respectively. A higher reactivity of trimethylsilylpropynal **1** in the studied reaction is caused by a stronger electron withdrawing effect of trimethylsilylethynyl group as compared with triethylgermylethynyl group. As a result, transition state **A** in the case of propynal **1** is more stable.



A

In order to qualitatively estimate the relative reactivity of propynal **8**, an experiment was carried out in an NMR tube for a mixture of propynals **8** and **1**, in the reaction with phosphine oxide **3**. Comparison and analysis of the ^{1}H- and ^{31}P-NMR spectra have shown that the rate of the formation of phosphine oxide **9** is higher than that for phosphine oxide **5**. Thus, 10 min after mixing the reagents **1**, **3**, **8** in THF at −10 °C, the signal at δ_P 49.42 ppm resultant from phosphine oxide **9** was first to appear whereas the signals of protons of phosphine oxide **5** in the ^{1}H-NMR spectrum were absent.

3. Conclusions

Reaction of acetylenic aldehydes with secondary phosphine oxides represents a new convenient approach for the synthesis of previously unknown polyfunctional chiral tertiary phosphine oxides. The reactivity of the ambident electrophiles **1**, **2**, **8** in this process follows the order: $HC{\equiv}CC(O)H > Me_3SiC{\equiv}CC(O)H > Et_3GeC{\equiv}CC(O)H$, which is in accordance with the literature data on the activity of these aldehydes towards the N- and S-nucleophiles [5].

4. Experimental

4.1. General

The ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were taken on Bruker DPX 400 and DPX 250 spectrometers in $CDCl_3$ solutions; HMDS as an internal standard, 85% H_3PO_4 as an external one, respectively. All chemical shifts are presented relative to HMDS. In ^{13}C-NMR spectra of compounds **5**–**7** (the signals were attributed using 2D (^{1}H and ^{13}C) experiment techniques HSQC [13] and HMBC [14]) the signals of two quarternary carbon atoms of the C≡C fragment appear at 90–100 ppm region. IR spectra were recorded on a Bruker IFS 25 instrument in KBr pellets and in thin film. Investigation of the formation dynamics for hydroxyphosphine oxides **5**, **6** was performed using a 3% molar solutions of aldehydes **1**, **2** and phosphine oxide **3** in THF (molar ratio **1**:**2**:**3** = 1:1:2.2) were used. These solutions were mixed and placed in an NMR tube at −15 °C. ^{1}H-NMR spectra were recorded at a temperature of 22 °C (proton chemical shifts were registered relative to THF).

4.2. 1-(Diphenethylphosphoryl)-3-(trimethylsilyl)-2-propyn-1-ol (5)

To a solution of 0.20 g (0.77 mmol) of phosphine oxide **3** in 1 ml of THF, a solution of 0.10 g (0.77 mmol) of 3-(trimethylsilyl)-2-propynal in 1 ml of THF was added during 10 min at −10 °C. After removal of cooling, the solution was stirred at room temperature (r.t.) for 1 h and 20 min. THF was removed in vacuum, the residue was washed with ether. Yield 98%, m.p. 124–125 °C (hexane). Anal. Calc. for $C_{22}H_{29}O_2PSi$: C, 68.72; H, 7.60; P, 8.05; Si 7.30. Found: C, 68.63; H, 7.41; P, 7.94; Si, 7.02%. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 0.23 (s, 9H, $3CH_3$), 2.23 (m, 4H, $2PCH_2$), 3.04 (m, 4H, $2PhC\mathit{H}_2$), 4.85 (d, $^{2}J_{PH} = 10.2$ Hz, 1H, CH), 5.82 (br s, 1H, OH), 7.32 (m, 10H, 2Ph). $^{13}C\{^{1}H\}$-NMR (250 MHz, $CDCl_3$): δ 0.26 (s, $Si(CH_3)_3$), 26.28; 27.90 (d, $^{1}J_{PC} = 60.0$ Hz, PCH_2), 27.60 (d, $^{2}J_{PC} = 4.1$ Hz, $PhC\mathit{H}_2$), 61.70 (d, $^{1}J_{PC} = 77.2$ Hz, CH), 94.76 (d, $^{3}J_{PC} = 6.9$ Hz, $\equiv\mathit{C}-Si(CH_3)_3$), 100.77 (s, $CH-\mathit{C}\equiv$), 126.44; 126.59 (s, C_p, Ph), 128.17 (s, C_o, Ph), 128.69; 128.76 (s, C_m, Ph), 140.89; 141.24 (d, $^{3}J_{PC} = 13.3$ Hz, C_i, Ph).^{31}P-NMR (400 MHz, $CDCl_3$): δ 48.70 (s). IR (KBr, cm^{-1}): 3108–3027 (OH), 2172 (C≡C), 1149 (P=O), 1250, 842, 757 (Si–C).

4.3. 1-(Diphenethylphosphoryl)-3-(triethylgermyl)-2-propyn-1-ol (6)

Obtained analogously to **5** from 0.12 g (0.46 mmol) of phosphine oxide **3** and 0.10 g (0.46 mmol) of 3-(triethylgermyl)-2-propynal in 2 ml of THF at a temperature of −10 to 22 °C (2.5 h). Yield 98%, m.p. 88–90 °C (hexane). Anal. Calc. for $C_{25}H_{35}GeO_2P$: C, 63.73; H, 7.49; Ge, 15.41; P, 6.57. Found: C, 63.80; H, 7.50; Ge, 15.25; P, 6.03%. ^{1}H-NMR (250 MHz, $CDCl_3$): 0.92 (m, 6H, $3CH_2$), 1.12 (m, 9H, $3CH_3$), 2.20 (m, 4H, $2PCH_2$), 3.03 (m, 4H, $2PhC\mathit{H}_2$), 4.91 (d, $^{2}J_{PH} = 10.7$ Hz, 1H, CH), 6.15 (br s, 1H, OH), 7.32 (m, 10H, 2Ph). $^{13}C\{^{1}H\}$-NMR (250 MHz, $CDCl_3$): δ 5.86 (s, $GeCH_2$), 9.29 (s, CH_3), 27.32; 28.36 (d, $^{1}J_{PC} = 60.0$ Hz, PCH_2), 27.76 (d, $^{2}J_{PC} = 4.0$ Hz, $Ph\mathit{C}H_2$), 61.92 (d, $^{1}J_{PC} = 77.2$ Hz, CH), 92.64 (d, $^{3}J_{PC} = 7.8$ Hz, $\equiv\mathit{C}-Ge(C_2H_5)_3$), 101.49 (s, $CH-\mathit{C}\equiv$), 126.48; 126.64 (s, C_p, Ph), 128.27 (s, C_o, Ph), 128.73; 128.80 (s, C_m, Ph), 141.06; 141.46 (d, $^{3}J_{PC} = 13.3$ Hz, C_i, Ph).^{31}P-NMR (400 MHz, $CDCl_3$): δ 49.18 (s). IR (KBr, cm^{-1}): 3118–3018 (OH), 2165 (C≡C), 1147 (P=O), 1202, 700, 580 (Ge–C).

4.4. 1-bis[2-(2-Pyridinyl)ethyl]phosphoryl-3-(trimethylsilyl)-2-propyn-1-ol (7)

Obtained analogously to **5** from 0.18 g (0.69 mmol) of phosphine oxide **4** and 0.09 g (0.69 mmol) of 3-(trimethylsilyl)-2-propynal in 2 ml of methanol at a temperature of 22 °C (10 h). Yield 98%, viscous liquid. Anal. Calc. for $C_{20}H_{27}N_2O_2PSi$: C, 62.15; H, 7.04; N, 7.25; P, 8.01; Si, 7.27. Found: C, 62.21; H, 7.07; N, 7.24; P, 7.98; Si, 7.22%. ^{1}H-NMR (250 MHz, $CDCl_3$): 0.12 (s, 9H, $3CH_3$), 2.30; 2.36 (m, 4H, $2PCH_2$), 3.18; 3.31 (m, 4H, $2CH_2$), 3.82 (br s, 1H, OH), 4.69 (d, $^{2}J_{PH} = 10.8$ Hz, 1H, CH), 7.11 (m, 2H, H5–Py), 7.23 (m, 2H, H3–Py), 7.61 (m, 2H, H4–Py), 8.48 (m, 2H, H6–Py). $^{13}C\{^{1}H\}$-NMR (250 MHz, $CDCl_3$): −0.54 (s, $Si(CH_3)_3$), 23.67; 24.61 (d, $^{1}J_{PC} = 64.8$ Hz, PCH_2), 28.43; 29.34 (d, $^{2}J_{PC} = 4.2$ Hz, $Py\mathit{C}H_2$), 60.51 (d, $^{1}J_{PC} = 76.9$ Hz, CH), 94.43 (d, $^{3}J_{PC} = 6.9$ Hz, $\equiv\mathit{C}-Si(CH_3)_3$), 100.26 (s, $CH-\mathit{C}\equiv$), 121.76; 121.97 (s, C5–Py), 123.17; 123.58 (s, C3–Py), 136.99; 137.39 (s, C4–Py), 148.70; 149.05 (s, C6–Py), 160.08; 160.24 (d, $^{3}J_{PC} = 13.0$ Hz, C2–Py). ^{31}P-NMR (400 MHz, $CDCl_3$): δ 49.27 (s). IR (film, cm^{-1}): 3175–3010 (OH), 2169 (C≡C), 1150 (P=O), 1250, 846, 762 (Si–C).

4.5. 1-(Diphenethylphosphoryl)-2-propyn-1-ol (9)

Obtained analogously from 0.10 g (0.39 mmol) of phosphine oxide **3** (in 1 ml of THF) and 0.05 g (0.9 mmol) of 2-propynal (in 1.5 ml of THF) at −10 to 22 °C during 30 min. Yield 100%, viscous liquid of dark-red color. Anal. Calc. for $C_{19}H_{21}O_2P$: C, 73.06; H, 6.78; P, 9.92. Found: C, 73.16; H, 6.78; P, 9.95%. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.19 (m, 4H, $2PCH_2$), 2.61 (s, 1H, ≡CH), 2.97 (m, 4H, $2PhC\mathit{H}_2$), 4.82 (d, $^{2}J_{PH} = 10.4$ Hz, 1H, CH), 6.35 (br s, 1H, OH), 7.21 (m, 10H, 2Ph). ^{31}P-NMR (400 MHz, $CDCl_3$): δ 49.42 (s).

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