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LETTERS TO THE EDITOR

Reaction of Bis(trimethylsiloxy)phosphine with Ethoxymethyleneimines Hydrochlorides

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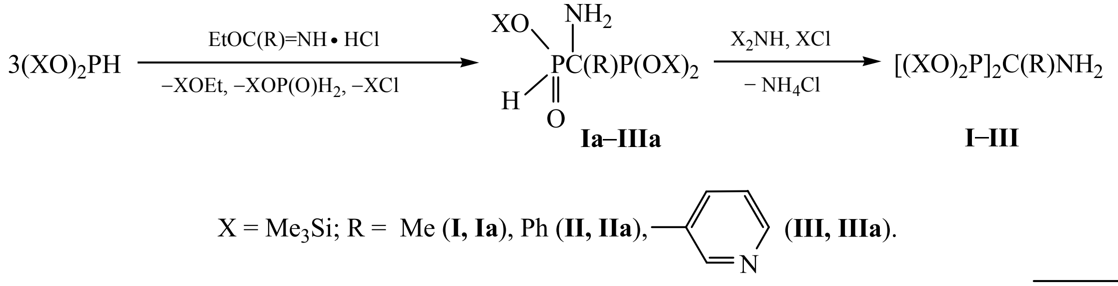
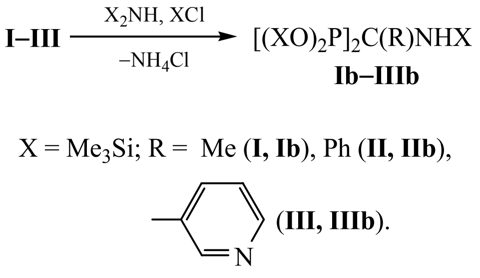
Aminomethylenediphosphonites containing unsubstituted amino group are of interest as key synthons in the preparation of a variety of aminomethylenediphosphorus-containing compounds, promising ligands and biologically active substances [1]. Recently, we obtained some *N*-substituted aminomethylenediphosponites by reacting bis(trimethylsiloxy)phosphine with *N*-substituted formamides and ethoxymethyleneimines [2]. In this work we studied the reaction of bis(trimethylsiloxy)phosphine with easily accessible ethoxymethyleneimines hydrochlorides [3]. Thus, the reaction of an excess of highly active bis(trimethylsiloxy)phosphine with hydrochlorides of substituted ethoxyimines proceeded in methylene chloride to form diphosponite intermediates **Ia**–**IIIa**. Refluxing the latter with a mixture of bis(trimethylsilyl)amine and trimethylchlorosilane afforded diphosponites **I**–**III** in high yields.



Note that the intermediate diphosponite **Ia** was isolated in good yield by distillation. The initial formation of diphosponites **IIa**, **IIIa** was detected in the reaction mixture by ^{31}P NMR spectroscopy. Further trimethylsilylation of diphosponites **I**–**III** with a mixture of bis(trimethylsilyl)amine and trimethylchlorosilane proceeded slowly to afford the target diphosponites **Ib**–**IIIb** only in trace amounts (5–15%) (Scheme 1).

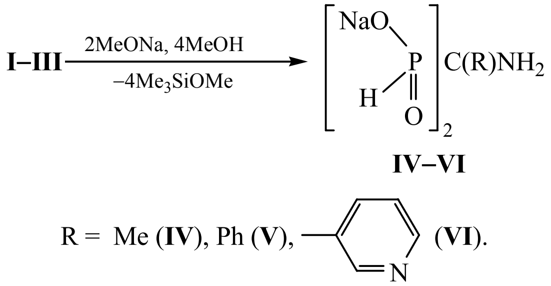
Treating the diphosponites **I**–**III** with a diluted solution of sodium methoxide in methanol yielded diphosphonous acids salts **IV**–**VI** as white hygroscopic crystalline substances (Scheme 2).

Scheme 1.

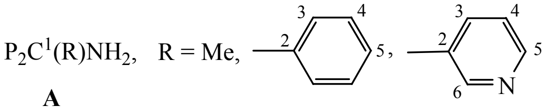


Compounds **I**–**VI** contain reactive fragments (NH, POSi, PH) and are convenient synthons for obtaining new functionalized aminomethylenediphosphorus-containing substances. NMR spectra of **I**–**VI** contain

Scheme 2.



characteristic signals of the fragment **A**, whose structure is shown below.



A

According to NMR spectra, compound **Ia** is a mixture of four stereoisomers and compounds **IIa**, **IIIa** are mixtures of two stereoisomers, whose ratio was determined by ^{31}P NMR. Instead of readily oxidizable compounds **I**–**III** elemental analysis was carried out for their stable derivatives **IV**–**VI**.

***O*,*O*,*O*-Tris(trimethylsilyl)-1-aminoethylidenediphosphonite (Ia).** A solution of 13 g of bis(trimethylsiloxy)phosphine in 10 mL of methylene chloride was added to a suspension of 2.5 g of 1-ethoxyethylideneimine hydrochloride in 25 mL of methylene chloride with stirring. The mixture was stirred for 1 h, and then the solvent was removed in a vacuum. To the residue was added 20 mL of bis(trimethylsilyl)amine. The mixture was heated until the evolution of ammonia ceased. Excess of bis(trimethylsilyl)amine was distilled off, and the residue was distilled. Yield 5.4 g, 68%, bp 121°C (1 mm Hg). First isomer (content 35%). ^{1}H NMR spectrum, δ, ppm: –0.03–0.05 m (2Me$_3$Si), 0.03–0.05 m (Me$_3$Si), 0.88 d.d (Me, $^3J_{PH}$ 13.2, $^3J_{PH}$ 17.4 Hz), 6.58 d (2PH, $^1J_{PH}$ 550.8 Hz), 1.12–1.32 m (NH$_2$). ^{13}C NMR spectrum, δ$_C$, ppm: 55.81 d.d (C^1, $^1J_{PC}$ 34.3, $^1J_{PC}$ 67 Hz), 15.18 d (Me, $^2J_{PC}$ 19.1 Hz), 0.8–1.2 m (3Me$_3$Si). ^{31}P NMR spectrum, δ$_P$, ppm: 145.83 d (P), 30.74 d (PH), $^2J_{PP}$ 53.6 Hz. Second isomer (content 30%). ^{1}H NMR spectrum, δ, ppm: –0.03–0.05 m (2Me$_3$Si), 0.03–0.05 m (Me$_3$Si), 0.9–1.1 m (Me), 6.64 d (2PH, $^1J_{PH}$ 551.2 Hz), 1.12–1.32 m (NH$_2$). ^{13}C NMR spectrum, δ$_C$, ppm: 56.15 d.d (C^1, $^1J_{PC}$ 34.4, $^1J_{PC}$ 68.7 Hz), 15.29 d (Me, $^2J_{PC}$ 18.3 Hz), 0.8–1.2 m (3Me$_3$Si). ^{31}P NMR spectrum, δ$_P$, ppm: 146.34 d (P, $^2J_{PP}$ 51.5 Hz), 29.05 d (PH, $^2J_{PP}$ 51.5 Hz). Third isomer (content 20%). ^{1}H NMR spectrum, δ, ppm: –0.03–0.05 m (2Me$_3$Si), 0.03–0.05 m (Me$_3$Si), 0.9–1.1 m (Me), 6.57 d (2PH, $^1J_{PH}$ 545.2 Hz), 1.12–1.32 m (NH$_2$). ^{13}C NMR spectrum, δ$_C$, ppm: 55.47 d.d (C^1, $^1J_{PC}$ 32.7, $^1J_{PC}$ 66.3 Hz), 14.04 d (Me, $^2J_{PC}$ 22.4 Hz), 0.8–1.2 m (3Me$_3$Si). ^{31}P NMR spectrum, δ$_P$, ppm: 145.39 d (P, $^2J_{PP}$ 41.6 Hz), 28.14 d (PH, $^2J_{PP}$ 41.6 Hz). Fourth isomer (content 15%). ^{1}H NMR spectrum, δ, ppm: from –0.03 to 0.05 m (2Me$_3$Si), 0.03–0.05 m (Me$_3$Si), 0.9–1.1 m (Me), 6.54 d (2PH, $^1J_{PH}$ 546.8 Hz), 1.12–1.32 m (NH$_2$). ^{13}C NMR spectrum, δ$_C$, ppm: 54.73 d.d (C^1, $^1J_{PC}$ 34.3, $^1J_{PC}$ 71.1 Hz), 13.61 d (Me, $^2J_{PC}$ 20.8 Hz), 0.8–1.2 m (3Me$_3$Si). ^{31}P NMR spectrum, δ$_P$, ppm: 144.97 d (P, $^2J_{PP}$ 55.4 Hz), 31.91 d (PH, $^2J_{PP}$ 55.4 Hz).

According to NMR data, diphosphonite **Ia** contains 10% of diphosphonite **I**.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)-1-aminoethylidenediphosphonite (I).** A mixture of 5.4 g diphosphonite **Ia**, 20 g of bis(trimethylsilyl)amine, and 5 g of trimethylchlorosilane was refluxed until sublimation of ammonium chloride ceased, and then the reaction mixture was distilled. Yield 5.6 g, 88%, bp 124°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 0.92 t (NH$_2$, $^3J_{PH}$ 13.2 Hz), 0.76 t (Me, $^3J_{PH}$ 12.4 Hz), 0.01 br.s (4Me$_3$Si). ^{13}C NMR spectrum, δ$_C$, ppm: 60.30 t (C^1, $^1J_{PC}$ 32.8 Hz), 14.55 t (Me, $^2J_{PC}$ 17.6 Hz), 1.24 (4Me$_3$Si). ^{31}P NMR spectrum: δ$_P$ 154.54 ppm.

According to NMR data, diphosphonite **I** contains 15% of diphosphonite **Ib**. ^{13}C NMR spectrum, δ$_C$, ppm: 62.36 t (C^1, $^1J_{PC}$ 33.5 Hz), 13.09 t (Me, $^2J_{PC}$ 19.2 Hz). ^{31}P NMR spectrum: δ$_P$ 151.21 ppm.

Diphosphonites **II**, **III** were prepared similarly.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)-1-aminobenzylidenediphosphonite (II).** Yield 74%, bp 144°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: –0.16 s (2Me$_3$Si), 0.04 s (2Me$_3$Si), 1.60 t (NH$_2$, $^3J_{PH}$ 7.6 Hz), 6.9–7.4 m (C$_6$H$_5$). ^{13}C NMR spectrum, δ$_C$, ppm: 70.35 t (C^1, $^1J_{PC}$ 41.5 Hz), 138.75 t (C^2, $^2J_{PC}$ 10.4 Hz), 126.73 t (C^3, $^3J_{PC}$ 8.8 Hz), 127.43 (C^4), 125.26 (C^5), 0.92 (2Me$_3$Si), 1.35 (2Me$_3$Si). ^{31}P NMR spectrum: δ$_P$ 149.74 ppm. According to ^{31}P NMR diphosphonite **II** contains 5% of diphosphonite **IIb** (δ$_P$ 141.14 ppm).

In the spectrum of the reaction mixture there were the signals of diphosphonite **IIa**. First isomer (content 80%). ^{31}P NMR spectrum, δ$_P$, ppm: 142.45 d (P, $^2J_{PP}$ 65.4 Hz), 28.88 d (PH, $^2J_{PP}$ 65.4 Hz). Second isomer (content 20%). ^{31}P NMR spectrum, δ$_P$, ppm: 141.04 d (P, $^2J_{PP}$ 71.4 Hz), 24.96 d (PH, $^2J_{PP}$ 71.4 Hz).

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)-1-amino-1-(pyrid-**

3-yl)methylenediphosphonite (III). Yield 72%, bp 145°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: –0.13 s (2Me$_3$Si), –0.28 s (2Me$_3$Si), 1.42 t (NH$_2$, $^3J_{PH}$ 9.6 Hz), 6.92 d.d (C^{4}H, $^3J_{HH}$ 4.8, 8 Hz), 7.52 d (C^{3}H, $^3J_{HH}$ 8 Hz), 8.10 d (C^{5}H, $^3J_{HH}$ 4.8 Hz), 8.48 s (C^{6}H). ^{13}C NMR spectrum, δ$_C$, ppm: 69.16 t (C^1, $^1J_{PC}$ 41.5 Hz), 151.61 (C^2), 134.05 t (C^3, $^3J_{PC}$ 7.2 Hz), 135.03 (C^4), 146.07 (C^5), 148.28 t (C^6, $^3J_{PC}$ 9.6 Hz), 0.80 (2Me$_3$Si), 1.14 (2Me$_3$Si). ^{31}P NMR spectrum, δ$_P$: 148.07 ppm. According to ^{31}P NMR data, diphosphonite **III** contains 5% of diphosphonite **IIIb** (δ$_P$ 141.18 ppm).

In the spectrum of the reaction mixture there were the signals of diphosphonite **IIIa**. First isomer (content 70%). ^{31}P NMR spectrum, δ$_P$, ppm: 142.15 d (P, $^2J_{PP}$ 61.4 Hz), 27.51 d (PH, $^2J_{PP}$ 61.4 Hz). Second isomer (content 30%). ^{31}P NMR spectrum, δ$_P$, ppm: 141.24 d (P, $^2J_{PP}$ 65.4 Hz), 23.61 d (PH, $^2J_{PP}$ 65.4 Hz).

1-Aminoethylidenediphosphonous acid disodium salt (IV). To a solution of 1.3 g of sodium methylate in 30 mL of methanol was added 5.6 g diphosphonite **I** in 20 mL of diethyl ether with stirring under cooling to 10°C. Then the solvent was removed. White crystals were kept in a vacuum (1 mm Hg) for 1 h. Yield 2.5 g, 97%. ^{1}H NMR spectrum, δ, ppm: 1.07 t (Me, $^3J_{PH}$ 16 Hz), 6.67 d (2 PH, $^1J_{PH}$ 524 Hz). ^{13}C NMR spectrum, δ$_C$, ppm: 51.99 t (C^1, $^1J_{PC}$ 89.4 Hz), 15.26 (Me). ^{31}P NMR spectrum: δ$_P$ 29.45 ppm. Found, %: C 10.88; H 3.13. $C_2H_7NNa_2O_4P_2$. Calculated, %: C 11.07; H 3.25.

Salts **V**, **VI** was prepared similarly.

1-Aminobenzylidenediphosphonous acid disodium salt (V). Yield 96%. ^{1}H NMR spectrum, δ, ppm: 6.92 d (2PH, $^1J_{PH}$ 538.4 Hz), 7.2–7.5 m (C$_6$H$_5$). ^{13}C NMR spectrum, δ$_C$, ppm: 60.62 t (C^1, $^1J_{PC}$ 85.4 Hz), 135.93 (C^2), 126.15 (C^3), 128.55 (C^4), 127.04 (C^5). ^{31}P NMR spectrum: δ$_P$ 27.10 ppm. Found, %: C 29.98; H 3.28. $C_7H_9NNa_2O_4P_2$. Calculated, %: C 30.13; H 3.25.

1-Amino-1-(pyrid-3-yl)methylenediphosphonousacid disodium salt (VI). Yield 94 %. ^{1}H NMR spectrum, δ, ppm: 6.82 d (2PH, $^1J_{PH}$ 541.2 Hz), 7.2–8.5 m (C$_5$H$_4$N). ^{13}C NMR spectrum, δ$_C$, ppm: 60.34 t (C^1, $^1J_{PC}$ 75.9 Hz), 151.59 (C^2), 135.90 (C^3), 136.14 (C^4), 146.30 (C^5), 147.43 (C^6). ^{31}P NMR spectrum: δ$_P$ 27.84 ppm. Found, %: C 25.59; H 2.97. $C_6H_8N_2Na_2O_4P_2$. Cal-culated, %: C 25.73; H 2.88.

NMR spectra were recorded on a Bruker Avance-400 spectrometer in CDCl$_3$ (**I–III**) or D$_2$O (**IV–VI**), internal reference TMS (^{1}H, ^{13}C) or external reference 85% phosphoric acid solution in D$_2$O (^{31}P).

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