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*To the 80th Anniversary of B.I. Ionin*

# Synthesis of New Types of Aminomethylenediphosphorus-Containing Acids and Their Derivatives

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**Abstract**—Convenient methods for synthesis of various aminomethylenediphosphorus-containing acids and their derivatives starting from available trimethylsilyl esters of hypophosphorous and phosphorous acids, ethoxymethyleneimine hydrochlorides, and *N*-substituted formamides have been proposed. Selected properties of the obtained compounds have been examined.

**Keywords:** aminomethylenediphosphonite, diphosphonate, imine, diphosphonic acid, silylation, trimethylsilyl triflate

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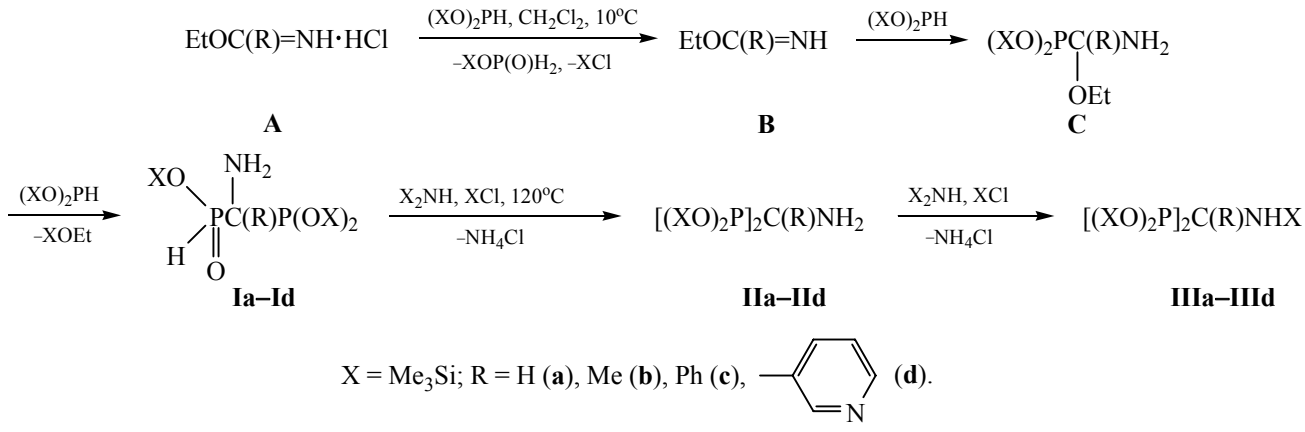
Functionalized aminomethylenediphosphorus-containing compounds are organophosphorus analogs of natural pyrophosphates and are of interest as promising ligands and biologically active substances with different properties [1–5]. Previously, convenient synthesis methods using dialkylformamide dialkylacetals [6] and *N*-phenyl-substituted derivatives of formamidine [7] have been proposed for some compounds of this class. In order to prepare new types of trimethylsilyl-substituted derivatives of aminomethylenediphosphorus-containing acids we studied the interaction of a number of trimethylsilyl esters of phosphorous and hypophosphorous acids with available substituted ethoxymethyleneimines hydrochlorides (the Pinner adducts) [8] and various *N*-substituted formamides; the present contribution discusses those methods in detail.

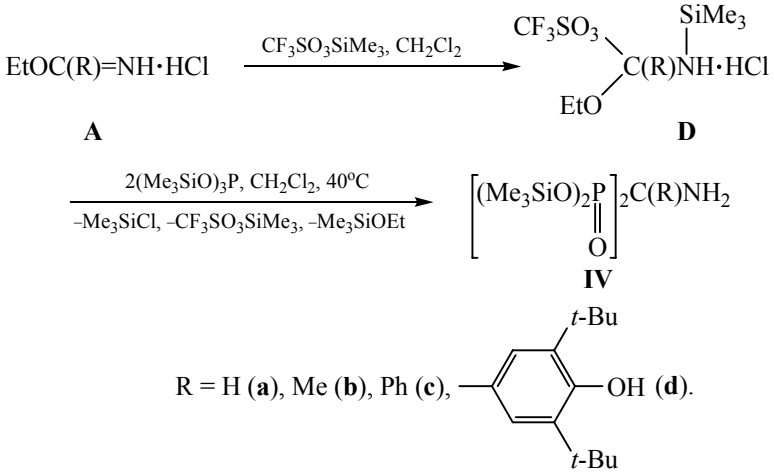
Reaction of highly reactive bis(trimethylsiloxy)phosphine (taken in excess) with substituted ethoxymethyleneimine hydrochlorides in methylene chloride medium led to intermediate diphosphonites **I**; those

**Scheme 1.**

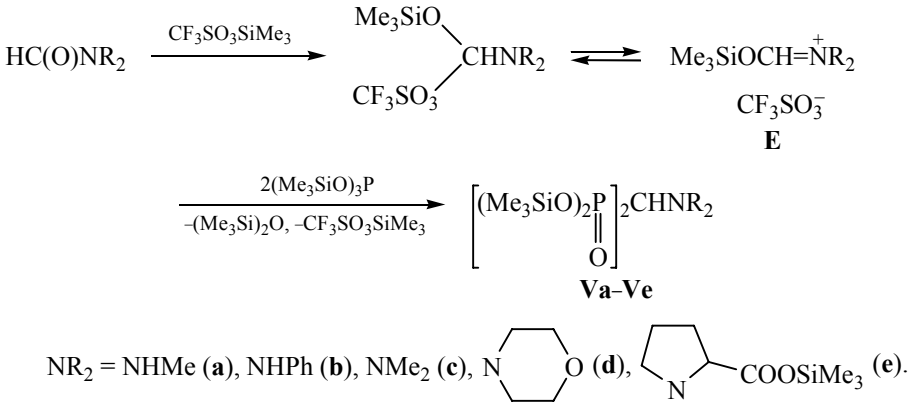



X = $Me_3Si$; R = H (**a**), Me (**b**), Ph (**c**),  (**d**).

**Scheme 2.**




**Scheme 3.**




compounds gave diphosphonites **II** in high yield upon refluxing with a mixture of bis(trimethylsilyl)amine and trimethylchlorosilane. Obviously, formation of diphosphonites **I** resulted from of a series of three reactions: dehydrochlorination of the adduct **A**, addition of bis(trimethylsiloxy)phosphine to imine **B**, and substitution of ethoxy function in aminal **C**; the mechanism was consistent with the known data [6, 7] (Scheme 1).

Note that the intermediate diphosphonites **Ia** and **Ib** were purposefully isolated in good yields by distillation. Original formation of diphosphonites **Ic** and **Id** was detected by $^{31}$P NMR study of the reaction mixture. Further trimethylsilylation of diphosphonites **II** using a mixture of bis(trimethylsilyl)amine and trimethylchlorosilane proceeded slowly; as a result, no more that 5–15% of the *N*-trimethylsilylaminomethylenediphosphonites **III** was isolated.

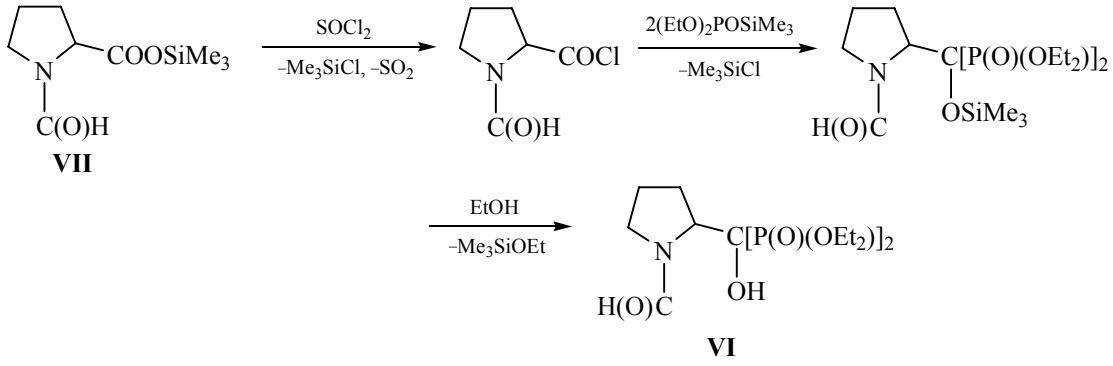
Similarly, the reaction of excess of tris(trimethylsilyl)phosphite with hydrochlorides of substituted ethoxymethyleneimines **A** proceeded under catalysis with trimethylsilyl trifluoromethanesulfonate (trimethylsilyl triflate) to afford diphosphonates **IV** in good yields (Scheme 2).

Obviously, the mild reaction conditions were possible due to catalytic activation of the starting imines with trimethylsilyl triflate capable of forming highly reactive intermediate adducts **D** (cf. [9]).

We successfully used trimethylsilyl triflate for activation of *N*-substituted formamides in the reactions with trimethylsilyl esters of phosphorous and hypophosphorous acids; the latter being known to readily add at carbonyl group of various aldehydes and ketones, but the analogous reaction with formamide has been unknown so far [10].

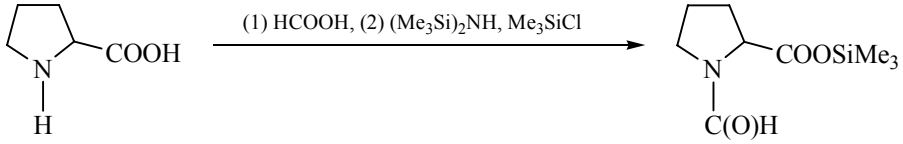
We found that *N*-substituted formamides reacted exothermally with excess of tris(trimethylsilyl) phosphite in methylene chloride medium in the presence of trimethylsilyl triflate to form bisphosphonates **V** in high yields (Scheme 3).

**Scheme 4.**



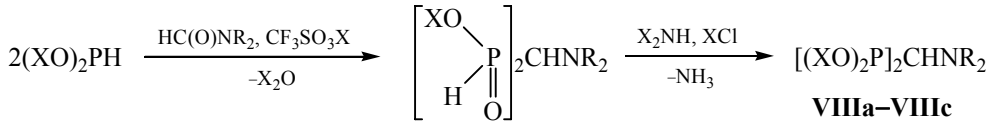

**VII** **VI**

**Scheme 5.**




**VII**

**Scheme 6.**




**F** **VIIIa–VIIIc**

X = $Me_3Si$, $NR_2$ = NHPh (**a**), $NMe_2$ (**b**), N O (**c**).

Undoubtedly, the catalytic effect of trimethylsilyl triflate was associated with formation of highly reactive immonium salts **E** during the reaction.

Note that a structural analog of aminomethylenediphosphonate **Vd** containing pyrrolidine fragment, hydroxymetylenediphosphonate **VI**, was generated with high yield via sequential interaction of functionalized formamide **VII** with thionyl chloride, excess of diethyl(trimethylsilyl)phosphate, and ethanol (cf. [11]) (Scheme 4).

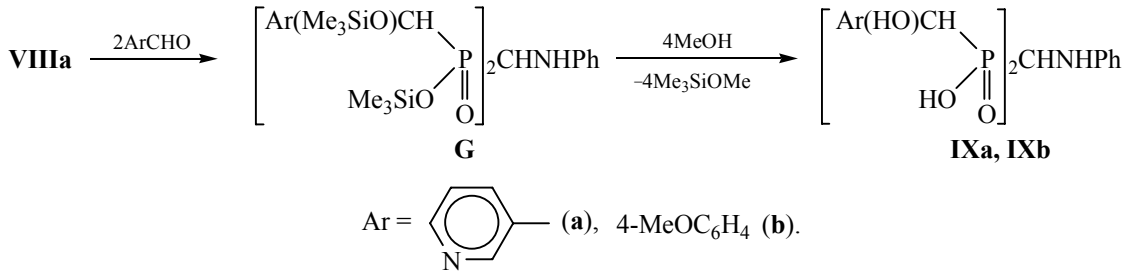
We purposefully prepared the previously described formamide **VII** via proline formylation followed by treating the reaction mixture with bis(trimethylsilyl) amine and trimethylchlorosilane as silylating agents under heating at 130°C (Scheme 5).

Reaction of excess of bis(trimethylsiloxy)phosphine with *N*-substituted formamides also occurred readily in methylene chloride only in the presence of trimethylsilyl triflate as a catalyst forming intermediate diphosphonites **F**. Refluxing of the latter with bis-(trimethylsilyl)amine in the presence of trimethylchlorosilane resulted in formation of diphosphonites **VIII** in good yields (Scheme 6).

The obtained aminomethylenediphosphonites are key parent compounds for preparation of new aminomethylenediphosphorus-containing species. In particular, diphosphonite **VIIIa** containing highly reactive fragment POSi was readily attached at the carbonyl group of aromatic aldehydes (the latter being taken in excess) in methylene chloride to form intermediate diphosphinates **G**. After treating the reaction mixture with methanol, new functionalized aminomethylenediphosphinic acids **IX** were isolated in high yields (Scheme 7).

The readily oxidized diphosphonites **II** and **VIII** were treated with a diluted solution of sodium

**Scheme 7.**




methoxide in methanol to form stable disodium salts of diphosphonous acids **X** and **XI** in the form of white hygroscopic crystals (Scheme 8).

Similarly, trimethylsilyl-containing diphosphonates **IV** and **V** reacted under mild conditions with excess of methanol to form diphosphonic acids **XII** and **XIII** in high yields (Scheme 9).

Crystal hydrates of the previously obtained aminomethylenediphosphonic acids **XIIIc** and **XIIId** have been described in [12].

NMR spectra of compounds **I–XIII** contained characteristic signals of the fragments **H** (see Experimental, Scheme 10).

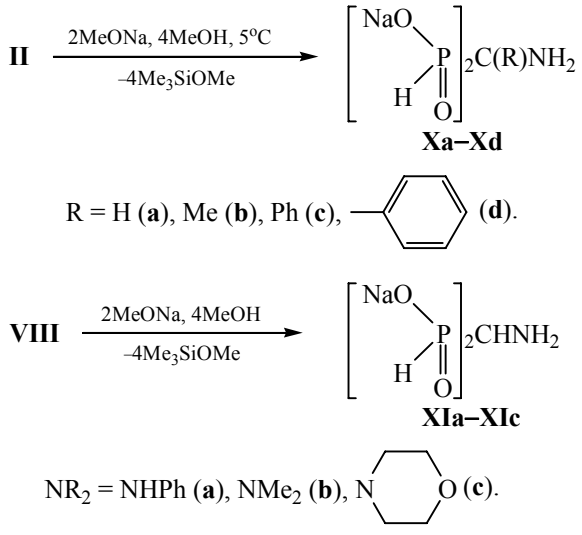
According to NMR data, the compounds containing asymmetric atoms were obtained as stereoisomers mixtures; their compositions were determined by $^{1}H$ and $^{31}P$ NMR. Noteworthily, in $^{31}P$ NMR spectrum the two diastereotopic phosphoryl groups of the major isomers of **VI** and **IX** resonated as characteristic AB-system.

To conclude, we elaborated convenient approaches towards synthesis of new types of aminomethylenediphosphorus-containing acids and their derivatives, promising ligands and biologically active substances. The resulting compounds contained active fragments (NH, POSi, or PH) and are suitable synthons for preparation of novel functionalized aminomethylenediphosphorus-containing substances such as diphosphorus-containing peptides.

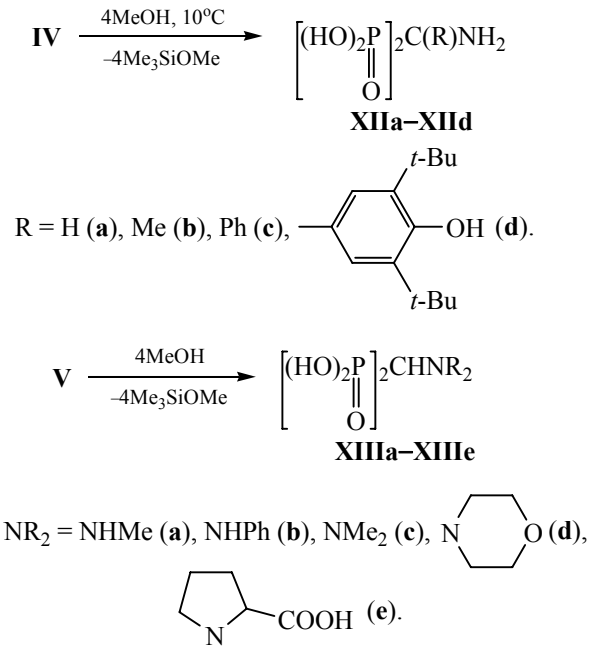
## EXPERIMENTAL

$^{1}H$ (400 MHz), $^{13}C$ (100 MHZ), and $^{31}P$ (162 MHz) NMR spectra were registered with a Bruker Avance 400 spectrometer relative to internal TMS ($^{1}H$ and $^{13}C$)

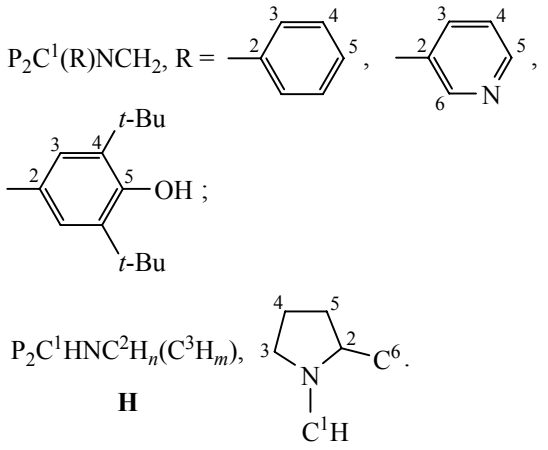
**Scheme 8.**




**Scheme 9.**



**Scheme 10.**



or external 85% $H_3PO_4$ in $D_2O$ ($^{31}P$) references, using $CDCl_3$ (**I**–**VIII**), $D_2O$ (**IX**–**XI**), or mixtures of $D_2O$, $CD_3OD$, and $C_5D_5N$ (**XII**, **XIII**) as solvents. All the reactions were carried out under argon atmosphere using anhydrous solvents. Elemental analysis of easily oxidized diphosphonites **I**–**III** and **VIII** was performed using their stable derivatives **X**, **XI**, and **XIIa**.

***O*,*O*,*O*-Tris(trimethylsilyl)aminomethylenediphosphonite (Ia).** A solution of 24 g of bis(trimethylsiloxy)phosphine in 10 mL of methylene chloride was added upon stirring to a suspension of 2.5 g of ethoxymethyleneimine hydrochloride in 25 mL of methylene chloride. After stirring the mixture during 1 h, the solvent was evaporated. 20 mL of bis(trimethylsilyl)amine was added to the residue, and the mixture was stirred until ammonia evolution ceased. Excess of bis(trimethylsilyl)amine was removed, and the residue was distilled. Yield 7.9 g (78%), bp 122°C (1 mmHg). The first isomer, content 60%. $^1$H NMR spectrum, δ, ppm: 2.4–2.7 m ($C^1H$), 0.7–0.8 m ($NH_2$), 6.91 d (PH, $^1J_{PH}$ 551.2 Hz), 0.02–0.06 m (Me). $^{13}$C NMR spectrum, $\delta_C$, ppm: 59.24 d.d ($C^1$, $^1J_{PC}$ 91.0, $^1J_{PC}$ 38.0 Hz), 0.35–1.13 m (Me). $^{31}$P NMR spectrum, $\delta_P$, ppm: 23.88 d and 147.25 d ($^2J_{PP}$ 39.7 Hz). The second isomer, content 40%. $^1$H NMR spectrum, δ, ppm: 2.4–2.7 m ($C^1H$), 0.7–0.8 m ($NH_2$), 6.92 d (PH, $^1J_{PH}$ 551.2 Hz), 0.02–0.06 m (Me). $^{13}$C NMR spectrum, $\delta_C$, ppm: 59.90 d.d ($C^1$, $^1J_{PC}$ 94.0, $^1J_{PC}$ 40.0 Hz), 0.35–1.13 m (Me). $^{31}$P NMR spectrum, $\delta_P$, ppm: 25.58 d and 146.32 d ($^2J_{PP}$ 50.2 Hz). From NMR data, diphosphonite **Ia** contained 10% of diphosphonite **IIa**.

***O*,*O*,*O*-Tris(trimethylsilyl)-1-aminoethylidenediphosphonite Ib** was obtained similarly. Yield 68%, bp 121°C (1 mmHg). The first isomer, content 35%. $^1$H NMR spectrum, δ, ppm: from –0.03 to –0.05 m ($2Me_3Si$), 0.03–0.05 m ($Me_3Si$), 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, $\delta_C$, ppm: 55.81 d.d ($C^1$, $^1J_{PC}$ 34.3, $^1J_{PC}$ 67.0 Hz), 15.18 d (Me, $^2J_{PC}$ 19.1 Hz), 0.8–1.2 m ($3Me_3Si$). $^{31}$P NMR spectrum, $\delta_P$, ppm: 145.83 d (P, $^2J_{PP}$ 53.6 Hz), 30.74 d (PH, $^2J_{PP}$ 53.6 Hz). The second isomer, content 30%. $^1$H NMR spectrum, δ, ppm: from –0.03 to –0.05 m ($2Me_3Si$), 0.03–0.05 m ($Me_3Si$), 0.90–1.10 m (Me), 6.64 d (2PH, $^1J_{PH}$ 551.2 Hz), 1.12–1.32 m ($NH_2$). $^{13}$C NMR spectrum, $\delta_C$, 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 ($3Me_3Si$). $^{31}$P NMR spectrum, $\delta_P$, ppm: 146.34 d (P, $^2J_{PP}$ 51.5 Hz), 29.05 d (PH, $^2J_{PP}$ 51.5 Hz). The third isomer, content 20%. $^1$H NMR spectrum, δ, ppm: from –0.03 to –0.05 m ($2Me_3Si$), 0.03–0.05 m ($Me_3Si$), 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 spec-trum, $\delta_C$, 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 ($3Me_3Si$). $^{31}$P NMR spectrum, $\delta_P$, ppm: 145.39 d (P, $^2J_{PP}$ 41.6 Hz), 28.14 d (PH, $^2J_{PP}$ 41.6 Hz). The fourth isomer, content 15%. $^1$H NMR spectrum, δ, ppm: from –0.03 to –0.05 m ($2Me_3Si$), 0.03–0.05 m ($Me_3Si$), 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, $\delta_C$, 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 ($3Me_3Si$). $^{31}$P NMR spectrum, $\delta_P$, ppm: 144.97 d (P, $^2J_{PP}$ 55.4 Hz), 31.91 d (PH, $^2J_{PP}$ 55.4 Hz). From NMR data, diphosphonite **Ib** contained 10% of diphosphonite **IIb**.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)aminomethylenediphosphonite (IIa).** A mixture of 7.9 g of diphosphonite **Ia**, 20 g of bis(trimethylsilyl)amine, and 7 g of trimethylchlorosilane was refluxed until ammonium chloride sublimation ceased. The residue was distilled. Yield 7.7 g (84%), bp 126°C (1 mmHg). $^1$H NMR spectrum, δ, ppm: 2.6–2.7 m ($C^1H$), 2.21 d. t ($NH_2$, $^3J_{PH}$ 6.4, $^3J_{HH}$ 12 Hz), 0.10 s, and 0.11 s ($4Me_3SiO$). $^{13}$C NMR spectrum, $\delta_C$, ppm: 68.98 t ($C^1$, $^1J_{PC}$ 38.0 Hz), 1.37 ($4Me_3SiO$). $^{31}$P NMR spectrum: $\delta_P$ 153.83 ppm. From NMR data, diphosphonite **IIa** contained 5% of diphosphonite **IIIa**, $\delta_P$ 151.33 ppm.

Diphosphonites **IIb**–**IId** were prepared similarly.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)-1-aminoethylidenediphosphonite (IIb).** Yield 88%, bp 124°C (1 mmHg). $^1$H NMR spectrum, δ, ppm: 0.92 t ($NH_2$, $^3J_{PH}$ 10.2 Hz), 0.76 t (Me, $^3J_{PH}$ 12.4 Hz), 0.01 br.s (4 $Me_3Si$). $^{13}$C NMR spectrum, $\delta_C$, ppm: 60.30 t ($C^1$, $^1J_{PC}$ 32.8 Hz),

14.55 t (Me, $^2J_{PC}$ 17.6 Hz), 1.24 s (4$Me_3Si$). $^{31}P$ NMR spectrum: $\delta_P$ 154.54 ppm. From NMR data, diphosphonite **IIb** contained 15% of diphosphonite **IIIb**. $^{31}C$ NMR spectrum, $\delta_C$, ppm: 62.36 t ($C^1$, $^1J_{PC}$ 33.5 Hz), 13.09 t (Me, $^2J_{PC}$ 19.2 Hz). $^{31}P$ NMR spectrum: $\delta_P$ 151.21 ppm.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)-1-aminobenzylidenediphosphonite (IIc).** Yield 74%, bp 144°C (1 mmHg). $^1H$ NMR spectrum, δ, ppm: –0.16 s (2$Me_3Si$), 0.04 s (2$Me_3Si$), 1.60 t ($NH_2$, $^3J_{PH}$ 7.6 Hz), 6.9–7.4 m ($C_6H_5$). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 138.75 t ($C^2$, $^2J_{PC}$ 10.4 Hz), 127.43 ($C^4$), 126.73 t ($C^3$, $^3J_{PC}$ 8.8 Hz), 125.26 ($C^5$), 70.35 t ($C^1$, $^1J_{PC}$ 41.5 Hz), 1.35 (2$Me_3Si$), 0.92 (2$Me_3Si$). $^{31}P$ NMR spectrum: $\delta_P$ 149.74 ppm. From NMR data, diphosphonite **IIc** contained 5% of diphosphonite **IIIc**, $\delta_P$ 141.14 ppm. In the spectrum of the reaction mixture, the signals of **Ic** were observed, $\delta_P$, ppm: the first isomer (content 80%), 142.45 d (P, $^2J_{PP}$ 65.4 Hz), 28.88 d (PH, $^2J_{PP}$ 65.4 Hz); the second isomer (content 20%), 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 (IId).** Yield 72%, bp 145°C (1 mmHg). $^1H$ NMR spectrum, δ, ppm: –0.28 s (2$Me_3Si$), –0.13 s (2$Me_3Si$), 1.42 t ($NH_2$, $^3J_{PH}$ 9.6 Hz), 6.92 d.d ($C^4H$, $^3J_{HH}$ 4.8, 8.0 Hz), 7.52 d ($C^3H$, $^3J_{HH}$ 8.0 Hz), 8.10 d ($C^5H$, $^3J_{HH}$ 4.8 Hz), 8.48 s ($C^6H$). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 151.61 ($C^2$), 148.28 t ($C^6$, $^3J_{PC}$ 9.6 Hz), 146.07 ($C^5$), 135.03 ($C^4$), 134.05 t ($C^3$, $^3J_{PC}$ 7.2 Hz), 69.16 t ($C^1$, $^1J_{PC}$ 41.5 Hz), 1.14 (2$Me_3Si$), 0.80 (2$Me_3Si$). $^{31}P$ NMR spectrum: $\delta_P$ 148.07 ppm. From NMR data, diphosphonite **IId** contained 5% of diphosphonite **IIId**, $\delta_P$ 141.18 ppm. In the spectrum of the reaction mixture, the signals of **Id** were observed, $\delta_P$, ppm: the first isomer (content 70%), 142.15 d (P, $^2J_{PP}$ 61.4 Hz), 27.51 d (PH, $^2J_{PP}$ 61.4 Hz); the second isomer (content 30%), 141.24 d (P, $^2J_{PP}$ 65.4 Hz), 23.61 d (PH, $^2J_{PP}$ 65.4 Hz).

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)aminomethylenediphosphonate (IVa).** Ethoxymethyleneimine hydrochloride (2.4 g) and trimethylsilyl triflate (0.2 mL) were added to a solution of 15 g of tris(trimethylsilyl) phosphite in 10 mL of methylene chloride. The mixture was refluxed during 1 h, then the solvent was removed. Bis(trimethylsilyl)amine (15 g) was added to the residue, and the mixture was refluxed during 1 h. The solvent was removed, and the residue was distilled. Yield 8.4 g (69%), bp 139°C (0.5 mmHg). $^1H$ NMR spectrum, δ, ppm: 2.6–2.9 m ($C^1H$), 1.19 d. t ($NH_2$, $^3J_{PH}$ 13.6, $^3J_{HH}$ 8.0 Hz), 0.01 s and –0.02 s (4$Me_3Si$). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 50.66 t ($C^1$, $^1J_{PC}$ 155.0 Hz), 0.72 and 0.87 ($Me_3Si$). $^{31}P$ NMR spectrum: $\delta_P$ 3.43 ppm. Found, %: C 34.64; H 8.49. $C_{16}H_{47}NO_6P_2Si_5$. Calculated, %: C 34.82; H 8.58.

Diphosphonates **IVb**–**IVd** were prepared similarly.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)-1-aminoethylidenediphosphonate (IVb).** Yield 73%, bp 127°C (1 mmHg). $^1H$ NMR spectrum, δ, ppm: –0.09 d (2$Me_3Si$, $^4J_{PH}$ 2.0 Hz), –0.08 d (2$Me_3Si$, $^4J_{PH}$ 1.6 Hz), 0.99 t ($CH_3$, $^3J_{PH}$ 16.8 Hz), 1.13 t ($NH_2$, $^3J_{PH}$ 12.8 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 51.58 t ($C^1$, $^1J_{PC}$ 152.5 Hz), 20.03 (Me), 0.73 (2$Me_3Si$), 0.78 (2$Me_3Si$). $^{31}P$ NMR spectrum: $\delta_P$ 6.65 ppm. Found, %: C 33.78; H 8.23. $C_{14}H_{41}NO_6P_2Si_4$. Calculated, %: C 34.05; H 8.37.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)-1-aminobenzylidenephosphonate (IVc).** Yield 72%, bp 152°C (1 mmHg). $^1H$ NMR spectrum, δ, ppm: –0.24 d (2$Me_3Si$, $^4J_{PH}$ 2.8 Hz), –0.20 d (2$Me_3Si$, $^4J_{PH}$ 2.8 Hz), 1.72 t ($NH_2$, $^3J_{PH}$ 13.0 Hz), 6.8–7.6 m ($C_6H_5$). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 135.77 br.s ($C^2$), 127.18 and 127.25 ($C^3$, $C^4$), 126.79 ($C^5$), 59.63 t ($C^1$, $^1J_{PC}$ 147.7 Hz), 0.52 (2$Me_3Si$), 0.45 (2$Me_3Si$). $^{31}P$ NMR spectrum: $\delta_P$ 2.23 ppm. Found, %: C 40.74; H 7.72. $C_{19}H_{43}NO_6P_2Si_4$. Calculated, %: C 41.06; H 7.80.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)-1-amino-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)methylenephosphonate (IVd).** Yield 89%, mp 52°C. $^1H$ NMR spectrum, δ, ppm: 0.06 s (2$Me_3Si$), 0.07 s (2$Me_3Si$), 1.19 br.s ($NH_2$), 1.34 s ($Me_3C$), 5.08 br.s (OH), 7.63 s ($C_6H_2$). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 152.31 ($C^5$), 139.46 ($C^4$), 126.42 ($C^2$), 125.03 ($C^3$), 59.65 t ($C^1$, $^1J_{PC}$ 149.3 Hz), 35.12 ($Me_3\underline{C}$), 30.98 ($\underline{Me}_3C$), 0.68 (2$Me_3Si$), 0.77 (2$Me_3Si$). $^{31}P$ NMR spectrum: $\delta_P$ 3.27 ppm. Found, %: C 47.26; H 8.61. $C_{27}H_{59}NO_7P_2Si_4$. Calculated, %: C 47.41; H 8.69.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)dimethylaminomethylenediphosphonate (Vc).** Trimethylsilyl triflate (3 mL) was added upon stirring to a solution of 15 g of tris(trimethylsilyl)phosphite and 1.5 g of DMF in 8 mL of methylene chloride. The mixture was incubated at 20°C during 24 h, and then the solvent was evaporated. 3 mL of hexane was added to the residue. After cooling to 5°C, the solvent was decanted. White crystals were kept in vacuum at 0.5 mmHg. Yield 8.8 g (87%), mp 42°C. $^1H$ NMR spectrum, δ, ppm: –0.08 s ($Me_3Si$), 2.40 s ($2C^2H_3N$), 3.05 t ($C^1H$, $^2J_{PH}$ 24.4 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 62.77 t ($C^1$, $^1J_{PC}$

147.7 Hz), 43.53 t ($C^2$, $^3J_{PC}$ 4.3 Hz), 0.48 ($Me_3Si$). $^{31}P$ NMR spectrum: $\delta_P$ –2.87 ppm. Found, %: C 35.26; H 8.49. $C_{15}H_{43}NO_6P_2Si_4$. Calculated, %: C 35.48; H 8.53.

Diphosphonates **Va**, **Vb**, **Vd**, and **Ve** were prepared similarly; diphosphonates **Va** and **Vb** were isolated by distillation.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)methylaminomethylenediphosphonate (Va).** Yield 78%, bp 139°C (1 mmHg). $^1H$ NMR spectrum, δ, ppm: –0.06 s ($Me_3Si$), 2.35 s ($C^2H_3N$), 2.57 t ($C^1H$, $^2J_{PH}$ 21.6 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 58.25 t ($C^1$, $^1J_{PC}$ 151.3 Hz), 37.20 t ($C^2$, $^3J_{PC}$ 6.4 Hz), 0.35 ($Me_3Si$). $^{31}P$ NMR spectrum: $\delta_P$ 1.77 ppm. Found, %: C 33.89; H 8.26. $C_{14}H_{41}NO_6P_2Si_4$. Calculated, %: C 34.05; H 8.37.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)-*N*-anilinomethylenediphosphonate (Vb).** Yield 84%, bp 157°C (0.5 mmHg). $^1H$ NMR spectrum, δ, ppm: 0.04 s and 0.06 s ($Me_3Si$), 3.70–3.85 m (NH), 4.21 t ($C^1H$, $^2J_{PH}$ 27.2 Hz), 6.41 d ($2C^3H$, $^3J_{HH}$ 8.0 Hz), 6.51 t ($2C^4H$, $^3J_{HH}$ 8.0 Hz), 6.96 t ($2C^4H$, $^3J_{HH}$ 8.0 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 149.39 ($C^2$); 129.08, 118.15 and 112.96 ($C^3$, $C^4$, $C^5$), 58.16 t ($C^1$, $^1J_{PC}$ 153.3 Hz), 0.74 s and 0.86 s ($Me_3Si$). $^{31}P$ NMR spectrum: $\delta_P$ –1.67 ppm. Found, %: C 40.94; H 7.74. $C_{19}H_{43}NO_6P_2Si_4$. Calculated, %: C 41.06; H 7.80.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)-*N*-morpholinomethylenediphosphonate (Vd).** Yield 85%, oil. $^1H$ NMR spectrum, δ, ppm: 0.07 s ($4Me_3Si$), 2.76 t ($C^1H$, $^2J_{PH}$ 25.6 Hz), 2.7–2.8 m ($2C^2H_2$), 3.3–3.4 m ($2C^3H_2$). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 63.82 t ($C^1$, $^1J_{PC}$ 148.9 Hz), 51.33 t ($C^2$, $^3J_{PC}$ 4.4 Hz), 67.11 ($C^3$), 0.75 ($Me_3Si$). $^{31}P$ NMR spectrum: $\delta_P$ –0.62 ppm. Found, %: C 36.94; H 8.16. $C_{17}H_{45}NO_7P_2Si_4$. Calculated, %: C 37.14; H 8.25.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)-*N*-(*O*-trimethylsilylprolino)methylenediphosphonate (Ve).** Yield 89%, oil. The first isomer, content 60%. $^1H$ NMR spectrum, δ, ppm: : –0.17 s ($4Me_3Si$), 2.6–2.8 m ($C^3H_2$), 1.3–1.7 m ($C^4H_2$, $C^5H_2$), 3.42 br.t ($C^1H$, $^2J_{PH}$ 26.2 Hz), 3.6–3.8 m ($C^2H$). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 171.82 ($C^6$), 63.8–64.5 m ($C^2$), 58.41 t ($C^1$, $^1J_{PC}$ 155.7 Hz), 48.9–49.6 m ($C^3$), 22.97 ($C^4$), 27.98 ($C^5$), 0.43 ($Me_3Si$). $^{31}P$ NMR spectrum: $\delta_P$ –0.42 ppm. The second isomer. $^1H$ NMR spectrum, δ, ppm: –0.17 s ($4Me_3Si$), 1.3–1.7 m ($C^4H_2$, $C^5H_2$), 2.6–2.8 m ($C^3H_2$), 3.42 br.t ($C^1H$, $^2J_{PH}$ 26.2 Hz), 3.6–3.8 m ($C^2H$). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 171.54 ($C^6$), 63.8–64.5 m ($C^2$), 58.16 t ($C^1$, $^1J_{PC}$ 156.5 Hz), 48.9–49.6 m ($C^3$), 27.98 ($C^5$), 22.97 ($C^4$), 0.43 ($Me_3Si$). $^{31}P$ NMR spectrum: $\delta_P$ 3.16 ppm. Found, %: C 38.72; H 8.14. $C_{21}H_{53}NO_8P_2Si_5$. Calculated, %: C 38.96; H 8.22.

***O*,*O*,*O*,*O*-Tetraethyl-(*N*-formylpyrrolidin-2-yl)-hydroxymethylenediphosphonate (VI).** A solution of 3.6 g of thionyl chloride in 5 mL of methylene chloride was added upon stirring at 5°C to a solution of 6.1 g of ester **VII** in 10 mL of methylene chloride. The mixture was heated to reflux, and then evaporated. The residue was kept in vacuum at 1 mmHg during 0.5 h and dissolved in 15 mL of methylene chloride. After cooling to 5°C, a solution of 18 g of diethyl(trimethylsilyl)phosphite in 15 mL of methylene chloride was added. Next, the solvent was removed, the residue was dissolved in 30 mL of ethanol, and the mixture was heated to 40°C. Trimethyl(ethoxy)silane and ethanol were distilled off; the residue was dissolved in 15 mL of diethyl ether and mixed with 10 mL of hexane and 10 mL of water. The formed oily substance was separated and incubated in vacuum at 1 mmHg during 0.5 h. Yield 10.3 g (91%). $^1H$ NMR spectrum, δ, ppm: 0.9–1.0 m ($4CH_3$), 1.3–1.6 m ($C^4H_2$), 1.9–2.3 m ($C^5H_2$), 3.15–3.65 m ($C^3H_2$), 3.6–4.0 m ($C^2H$, $4CH_2OP$), 7.84 s ($C^1H$). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 164.22 ($C^1$), 62.7–64.3 m ($C^2$, $CH_2OP$), 77.90 t ($C^6H$, $^2J_{PC}$ 154.9 Hz), 48.50 ($C^3$), 24.18 ($C^4$), 27.71 ($C^5$), 15.9–16.2 m (Me). $^{31}P$ NMR spectrum: 15.87 and 16.22 (AB-system, $^2J_{PP}$ 28.7 Hz). Found, %: C 41.71; H 7.22. $C_{14}H_{29}NO_8P_2$. Calculated, %: C 41.90; H 7.28.

**Trimethylsilyl ester of *N*-formylproline (VII).** A mixture of 20 g of proline and 50 g of formic acid was heated upon stirring in boiling water bath during 5 h, and then evaporated in vacuum at 7 mmHg. A mixture of 56 g of bis(trimethylsilyl)amine and 8 g of trimethylchlorosilane was added to the residue; the mixture was refluxed until ammonium chloride sublimation ceased and then distilled. Yield 27 g (72%), bp 133°C (2 mmHg). The first isomer, content 60%. $^1H$ NMR spectrum, δ, ppm: –0.06 s ($Me_3Si$), 1.5–2.0 m ($C^4H_2$, $C^5H_2$,), 3.25–3.35 m ($C^3H_2$), 4.08 d.d ($C^2H$, $^3J_{HH^A}$ 8.4, $^3J_{HH^B}$ 3.6Hz), 7.91 s ($C^1H$). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 171.43 ($C^6$), 160.18 ($C^1$), 57.17 ($C^2$), 45.90 ($C^3$), 29.03 ($C^5$), 23.63 ($C^4$). The second isomer (content 40%). $^1H$ NMR spectrum, δ, ppm: –0.06 s ($Me_3Si$), 1.5–2.0 m ($C^4H_2$, $C^5H_2$,), 3.08–3.19 m ($C^3H_2$), 3.99 d.d ($C^2H$, $^3J_{HH^A}$ 8.4, $^3J_{HH^B}$ 4 Hz), 7.86 s ($C^1H$). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 171.82 ($C^6$), 161.21 ($C^1$), 59.27 ($C^2$), 43.43 ($C^3$), 29.31 ($C^5$), 22.43 ($C^4$). Found, %: C 49.97; H 7.82. $C_9H_{17}NO_3Si$. Calculated, %: C 50.20; H 7.96.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)-*N*-anilinomethylenediphosphonite (VIIIa).** Trimethylsilyl triflate (1 mL) was added upon stirring to a solution of 18 g of bis(trimethylsiloxy)phosphine and 2.4 g of formanilide in 10 mL of methylene chloride. The mixture was incubated at 20°C during 4 h, and then evaporated. 20 g bis(trimethylsilyl)amine and 2 mL of trimethylchlorosilane were added to the residue. The mixture was refluxed during 1 h and distilled. Yield 7.7 g (74%), bp 152°C (1 mmHg). $^1$H NMR spectrum, δ, ppm: 0.1–0.2 m (12$CH_3$), 3.2–3.3 m ($C^1H$), 4.44 d (NH, $^3J_{HH}$ 8.0 Hz), 6.60 t (2$CH_{Ph}$, $^3J_{HH}$ 8.0 Hz), 6.68 d (2$CH_{Ph}$, $^3J_{HH}$ 8.0 Hz), 7.07 t (2$CH_{Ph}$, $^3J_{HH}$ 8.0 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 151.03 ($C^2$); 128.53, 115.67 and 112.56 ($C_{Ph}$), 71.78 t ($C^1$, $^1J_{PC}$ 38.5 Hz), 1.31 ($CH_3$). $^{31}$P NMR spectrum: $\delta_P$ 155.78 ppm.

Diphosphonites **VIIIb** and **VIIc** were prepared similarly.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)dimethylaminomethylenediphosphonite (VIIIb).** Yield 52%, bp 119°C (1 mmHg). $^1$H NMR spectrum, δ, ppm: 0.15 s (4$Me_3Si$), 2.11 t ($C^1H$, $^2J_{PH}$ 5.6 Hz), 2.67 s (2$C^2H_3N$). $^{13}$C NMR spectrum, $\delta_C$, ppm: 82.37 t ($C^1$, $^1J_{PC}$ 41.6 Hz), 45.19 t ($C^2$, $^3J_{PC}$ 7.2 Hz), 1.39 ($Me_3Si$). $^{31}$P NMR spectrum: $\delta_P$ 166.82 ppm.

***O*,*O*,*O*,*O*-Tetra(trimethylsilyl)-*N*-morpholinomethylenediphosphonite (VIIIc).** Yield 72%, bp 144°C (1 mmHg). $^1$H NMR spectrum, δ, ppm: 0.17 s (4$Me_3Si$), 2.08 t ($C^1H$, $^2J_{PH}$ 6.2 Hz), 3.0–3.1 m (2$C^2H_2$), 3.4–3.5 m (2$CH_2O$). $^{13}$C NMR spectrum, $\delta_C$, ppm: 82.34 t ($C^1$, $^1J_{PC}$ 42.8 Hz), 53.11 t ($C^2$, $^3J_{PC}$ 6.8 Hz), 67.73 ($CH_2O$), 1.35 ($Me_3Si$). $^{31}$P NMR spectrum: $\delta_P$ 165.33 ppm.

***N*-Anilinomethylenebis[hydroxy(pyrid-3-yl)methyphosphinic] acid (IXb).** A solution of 1.6 g of 3-pyridinylcarbaldehyde in 10 mL of methylene chloride was added upon stirring to a solution of 3.5 g of diphosphonite **VIIIa** in 10 mL of methylene chloride under cooling to 10°C. Then the solvent was removed, and a mixture of 10 mL of methanol and 20 mL of diethyl ether was added to the residue. The mixture was heated to reflux. After cooling, the formed crystals were filtered off, washed with diethyl ether, and kept in vacuum at 1 mmHg during 1 h. Yield 2.7 g (89%), mp >150°C (decomp.). The first isomer, content 50%. $^1$H NMR spectrum, δ, ppm: 4.14 t ($C^1H$, $^2J_{PH}$ 16.4 Hz), 4.95 d ($C^3H$, $^2J_{PH}$ 12.4 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 69.74 d ($C^3$, $^1J_{PC}$ 104.2 Hz), 50.24 t ($C^1$, $^1J_{PC}$ 84.8 Hz). $^{31}$P NMR spectrum: 29.98 d ($^2J_{PP}$ 20.3 Hz), 31.19 d ($^2J_{PP}$ 20.3 Hz). The second isomer, content 30%. $^1$H NMR spectrum, δ, ppm: 4.31 t ($C^1H$, $^2J_{PH}$ 16 Hz), 4.97 d ($C^3H$, $^2J_{PH}$ 12.4 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 69.97 d ($C^3$, $^1J_{PC}$ 106.4 Hz), 48.51 t ($C^1$, $^1J_{PC}$ 86.9 Hz). $^{31}$P NMR spectrum: $\delta_P$ 30.22 ppm. The third isomer, content 20%. $^1$H NMR spectrum, δ, ppm: 3.92 t ($C^1H$, $^2J_{PH}$ 16.3 Hz), 5.05 d ($C^3H$, $^2J_{PH}$ 12.4 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 69.13 d ($C^3$, $^1J_{PC}$ 97.8 Hz), 51.89 t ($C^1$, $^1J_{PC}$ 87.6 Hz). $^{31}$P NMR spectrum: $\delta_P$ 30.67 ppm. The signals of aromatic moieties of all the stereoisomers in the $^1$H and $^{13}$C NMR spectra were overlapped being located in characteristic spectral regions. Found, %: C 50.57; H 4.78. $C_{19}H_{21}N_3O_6P_2$. Calculated, %: C 50.79; H 4.71.

***N*-Anilinomethylenebis[hydroxy(anisyl)methylphosphinic] acid (IXa)** was obtained similarly. Yield 87%, mp >150°C (decomp.). The first isomer, content 50%. $^1$H NMR spectrum, δ, ppm: 4.71 t ($C^1H$, $^2J_{PH}$ 16.2 Hz), 4.89 d ($C^3H$, $^2J_{PH}$ 16.1 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 70.27 d ($C^3$, $^1J_{PC}$ 103.3 Hz), 48.39 t ($C^1$, $^1J_{PC}$ 78.7 Hz). $^{31}$P NMR spectrum, $\delta_P$, ppm: 38.17 d ($^2J_{PP}$ 24.3 Hz), 39.07 d ($^2J_{PP}$ 24.3 Hz). the second isomer, content 30%. $^1$H NMR spectrum, δ, ppm: 4.78 t ($C^1H$, $^2J_{PH}$ 16 Hz), 4.89 d ($C^3H$, $^2J_{PH}$ 16.1 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 70.96 d ($C^3$, $^1J_{PC}$ 105.2 Hz), 48.59 t ($C^1$, $^1J_{PC}$ 81.2 Hz). $^{31}$P NMR spectrum: $\delta_P$ 39.80 ppm. The third isomer, content 20%. $^1$H NMR spectrum, δ, ppm: 4.41 t ($C^1H$, $^2J_{PH}$ 16.2 Hz), 4.89 d ($C^3H$, $^2J_{PH}$ 16.1 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 69.20 d ($C^3$, $^1J_{PC}$ 106.4 Hz), 49.64 t ($C^1$, $^1J_{PC}$ 79.8 Hz). $^{31}$P NMR spectrum: $\delta_P$ 39.08 ppm. The signals of methoxyl and aromatic moieties of all the stereoisomers in the $^1$H and $^{13}$C NMR spectra were overlapped being located in characteristic spectral regions. Found, %: C 54.26; H 5.28. $C_{23}H_{27}NO_8P_2$. Calculated, %: C 54.44; H 5.36.

**Disodium salt of aminomethylenediphosphonous acid (Xa).** A solution of 6.5 g of diphosphonite **IIa** in 20 mL of diethyl ether was added upon stirring at 10°C to a solution of 1.57 g of sodium methoxide in 30 mL of methanol. After the solvent removal, white crystals were kept in vacuum at 1 mmHg during 1 h. Yield 2.8 g (95%). $^1$H NMR spectrum, δ, ppm: 2.67 t ($C^1H$, $^2J_{PH}$ 15.6 Hz), 6.90 d (2PH, $^1J_{PH}$ 528.8 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 53.20 t ($C^1$, $^1J_{PC}$ 84.6 Hz). $^{31}$P NMR spectrum: $\delta_P$ 22.40 ppm. Found, %: C 5.79; H 2.52. $CH_5NNa_2O_4P_2$. Calculated, %: C 5.91; H 2.48.

The salts **Xb**–**Xd**, **XIa**–**XIc** were obtained similarly. Sodium salts **X** and **XI** decomposed upon heating above 100°C.

**Disodium salt of 1-aminoethylidenediphosphonous acid (Xb).** Yield 97%. $^1$H NMR spectrum, δ, ppm: 1.07 t (Me, $^3J_{PH}$ 16 Hz), 6.67 d (2PH, $^1J_{PH}$ 524 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 51.99 t (C$^1$, $^1J_{PC}$ 89.4 Hz), 15.26 (Me). $^{31}$P NMR spectrum: $\delta_P$ 29.45 ppm. Found, %: C 10.88; H 3.13. $C_2H_7NNa_2O_4P_2$. Calculated, %: C 11.07; H 3.25.

**Disodium salt of 1-aminobenzylidenediphosphonous acid (Xc).** Yield 96%. $^1$H NMR spectrum, δ, ppm: 6.92 d (2PH, $^1J_{PH}$ 538.4 Hz), 7.2–7.5 m ($C_6H_5$). $^{13}$C NMR spectrum, $\delta_C$, ppm: 135.93 (C$^2$), 128.55 (C$^4$), 127.04 (C$^5$), 126.15 (C$^3$), 60.62 t (C$^1$, $^1J_{PC}$ 85.4 Hz). $^{31}$P NMR spectrum: $\delta_P$ 27.10 ppm. Found, %: C 29.98; H 3.28. $C_7H_9NNa_2O_4P_2$. Calculated, %: C 30.13; H 3.25.

**Disodium salt of 1-amino-1-(pyrid-3-yl)methylenediphosphonous acid (Xd).** Yield 94%. $^1$H NMR spectrum, δ, ppm: 6.82 d (2PH, $^1J_{PH}$ 541.2 Hz), 7.2–8.5 m ($C_5H_4N$). $^{13}$C NMR spectrum, $\delta_C$, ppm: 151.59 (C$^2$), 147.43 (C$^6$), 146.30 (C$^5$), 136.14 (C$^4$), 135.90 (C$^3$), 60.34 t (C$^1$, $^1J_{PC}$ 75.9 Hz). $^{31}$P NMR spectrum: $\delta_P$ 27.84 ppm. Found, %: C 25.59; H 2.97. $C_6H_8N_2Na_2O_4P_2$. Calculated, %: C 25.73; H 2.88.

**Disodium salt of *N*-anilinomethylenediphosphonous acid (XIa).** Yield 95%. $^1$H NMR spectrum, δ, ppm: 3.64 t (C$^1$H, $^2J_{PH}$ 16.0 Hz), 6.70 t (C$^1H_{Ph}$, $^3J_{HH}$ 8.0 Hz), 6.77 d (2C$^1H_{Ph}$, $^3J_{HH}$ 8.0 Hz), 7.04 d (2PH, $^1J_{PH}$ 532.0 Hz), 7.16 t (2C$H_{Ph}$, $^3J_{HH}$ 8.0 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 147.80 (C$^2$); 129.52, 118.13 and 113.72 (C$_{Ph}$), 56.24 t (C$^1$, $^1J_{PC}$ 85.7 Hz). $^{31}$P NMR spectrum: $\delta_P$ 20.10 ppm. Found, %: C 29.90; H 3.26. $C_7H_9NNa_2O_4P_2$. Calculated, %: C 30.13; H 3.25.

**Disodium salt of dimethylaminomethylenediphosphonous acid (XIb)**. Yield 95%. $^1$H NMR spectrum, δ, ppm: 2.59 t (C$^1$H, $^2J_{PH}$ 15.2 Hz), 7.16 d (PH, $^1J_{PH}$ 563 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 65.16 t (C$^1$, $^1J_{PC}$ 70.2 Hz), 44.21 (C$^2$). $^{31}$P NMR spectrum: $\delta_P$ 9.78 ppm. Found, %: C 15.46; H 3.98. $C_3H_9NNa_2O_4P_2$. Calculated, %: C 15.59; H 3.93.

**Disodium salt of *N*-morpholinomethylenediphosphonous acid (XIc).** Yield 94%. $^1$H NMR spectrum, δ, ppm: 2.55 t (C$^1$H, $^2J_{PH}$ 15.8 Hz), 7.09 d (PH, $^1J_{PH}$ 557.0 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 64.98 t (C$^1$, $^1J_{PC}$ 72.4 Hz), 52.83 (C$^2$). $^{31}$P NMR spectrum: $\delta_P$ 12.05 ppm. Found, %: C 21.73; H 4.11. $C_5H_{11}NNa_2O_5P_2$. Calculated, %: C 21.99; H 4.06.

**Aminomethylenediphosphonic acid (XIIa).** Diphosphonate **IVa** (7.7 g) was added upon stirring at 10°C to 30 mL of methanol. The mixture was heated to reflux, and then evaporated. White crystals were filtered off and kept in vacuum at 1 mmHg during 1 h. Yield 2.5 g (96%), mp 159°C. $^1$H NMR spectrum, δ, ppm: 3.82 t (C$^1$H, $^2J_{PH}$ 19.2 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 54.89 t (C$^1$, $^1J_{PC}$ 147.4 Hz). $^{31}$P NMR spectrum: $\delta_P$ 15.83 ppm. Found, %: C 6.12; H 3.74. $CH_7NO_6P_2$. Calculated, %: C 6.29; H 3.70.

The acids **XIIb–XIId** and **XIIIa–XIIIe** were prepared similarly.

**1-Aminoethylidenediposphonic acid (XIIb).** Yield 96%, mp 252°C. $^1$H NMR spectrum, δ, ppm: 1.12 t (Me, $^3J_{PH}$ 13.2 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 51.69 t (C$^1$, $^1J_{PC}$ 122.2 Hz), 15.64 (Me). $^{31}$P NMR spectrum: $\delta_P$ 11.15 ppm. Found, %: C 11.58; H 4.47. $C_2H_9NO_6P_2$. Calculated, %: C 11.71; H 4.42.

**1-Aminobenzylidenediphosphonic acid (XIIc).** Yield 97%, mp 223°C. $^1$H NMR spectrum, δ, ppm: 6.8–7.6 m ($C_6H_5$). $^{13}$C NMR spectrum, $\delta_C$, ppm: 131.22 (C$^2$), 126.20 (C$^4$), 125.52 (C$^3$), 124.27 (C$^5$), 60.26 t (C$^1$, $^1J_{PC}$ 120.5 Hz). $^{31}$P NMR spectrum: $\delta_P$ 8.54 ppm. Found, %: C 31.32; H 4.19. $C_7H_{11}NO_6P_2$. Calculated, %: C 31.48; H 4.15.

**1-Amino-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-methylenediphosphonic acid (XIId).** Yield 98%, mp 183–184°C. $^1$H NMR spectrum, δ, ppm: 1.30 s ($Me_3C$), 5.29 br.s (OH), 7.50 s ($C_6H_2$). $^{13}$C NMR spectrum, $\delta_C$, ppm: 151.09 (C$^5$), 138.65 (C$^4$), 126.89 (C$^2$), 124.43 (C$^3$), 62.84 t (C$^1$, $^1J_{PC}$ 118.2 Hz), 34.35 ($Me_3\underline{C}$), 30.08 ($\underline{Me}_3C$). $^{31}$P NMR spectrum: $\delta_P$ 11.06 ppm. Found, %: C 45.43; H 6.94. $C_{15}H_{27}NO_7P_2$. Calculated, %: C 45.57; H 6.88.

**Methylaminomethylenediphosphonic acid (XIIIa).** Yield 96%, mp 178°C. $^1$H NMR spectrum, δ, ppm: 2.50 s (C$^2H_3$), 2.94 t (C$^1$H, $^2J_{PH}$ 17.2 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 55.95 t (C$^1$, $^1J_{PC}$ 117.4 Hz), 34.07 (C$^2$). $^{31}$P NMR spectrum: $\delta_P$ 7.78 ppm. Found, %: C 11.57; H 4.51. $C_2H_9NO_6P_2$. Calculated, %: C 11.71; H 4.42.

***N*-Anilinomethylenediphosphonic acid (XIIIb).** Yield 97%, mp 182°C. $^1$H NMR spectrum, δ, ppm: 4.20 t (C$^1$H, $^2J_{PH}$ 22.0 Hz), 6.69 t (C$^5$H, $^3J_{HH}$ 8.0 Hz), 6.81 d (2C$^3$H, $^3J_{HH}$ 8.0 Hz), 7.15 t (2C$^4$H, $^3J_{HH}$ 8.0 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 147.03 (C$^2$); 128.63, 117.75 and 113.41 (C$^3$, C$^4$, C$^5$), 50.95 t (C$^1$, $^1J_{PC}$ 142 Hz). $^{31}$P NMR spectrum: $\delta_P$ 16.99 ppm. Found, %: C 31.37; H 4.19. $C_7H_{11}NO_6P_2$. Calculated, %: C 31.48; H 4.15.

**Dimethylaminomethylenediphosphonic acid (XIIIc).** Yield 97%, mp 212°C. $^1$H NMR spectrum, δ, ppm: 2.57 s ($2C^2H_3$), 3.05 t ($C^1H$, $^2J_{PH}$ 18.4 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 62.24 t ($C^1$, $^1J_{PC}$ 115.8 Hz), 43.67 ($C^2$). $^{31}$P NMR spectrum: $\delta_P$ 6.29 ppm. Found, %: C 16.23; H 4.92. $C_3H_{11}NO_6P_2$. Calculated, %: C 16.45; H 5.06.

***N*-Morpholinomethylenediphosphonic acid (XIIId).** Yield 96%, mp 202°C. $^1$H NMR spectrum, δ, ppm: 2.54 s ($2C^2H_2$), 3.08 t ($C^1H$, $^2J_{PH}$ 17.6 Hz), 3.2–3.3 m ($2C^3H_2$). $^{13}$C NMR spectrum, $\delta_C$, ppm: 62.99 t ($C^1$, $^1J_{PC}$ 111.0 Hz), 64.07 ($C^3$), 51.74 ($C^2$). $^{31}$P NMR spectrum: $\delta_P$ 6.22 ppm. Found, %: C 22.83; H 4.92. $C_5H_{13}NO_7P_2$. Calculated, %: C 23.00; H 5.02.

***N*-Prolinomethylenediphosphonic acid (XIIIe).** Yield 95%, mp 187°C. The first isomer, content 55%. $^1$H NMR spectrum, δ, ppm: 2.0–2.5 m ($C^4H_2$, $C^5H_2$), 3.95–4.05 m ($C^3H_2$), 4.29 t ($C^1H$, $^2J_{PH}$ 20.0 Hz), 5.1–5.2 m ($C^2H$). $^{13}$C NMR spectrum, $\delta_C$, ppm: 170.20 ($C^6$), 67.54 t ($C^2$, $^3J_{PC}$ 5.6 Hz), 58.31 t ($C^1$, $^1J_{PC}$ 127.7 Hz), 54.09 ($C^3$), 28.06 ($C^5$), 22.84 ($C^4$). $^{31}$P NMR spectrum: $\delta_P$ 7.04 ppm. The second isomer, content 45%. $^1$H NMR spectrum, δ, ppm: 2.0–2.5 m ($C^4H_2$, $C^5H_2$), 4.1–4.2 m ($C^3H_2$), 4.32 t ($C^1H$, $^2J_{PH}$ 20 Hz), 5.1–5.2 m ($C^2H$). $^{13}$C NMR spectrum, $\delta_C$, ppm: 168.97 ($C^6$), 67.21 t ($C^2$, $^3J_{PC}$ 5.4 Hz), 58.39 t ($C^1$, $^1J_{PC}$ 128.5 Hz), 54.21 ($C^3$), 27.78 ($C^5$), 22.64 ($C^4$). $^{31}$P NMR spectrum: $\delta_P$ 7.89 ppm. Found, %: C 24.69; H 4.42. $C_6H_{13}NO_8P_2$. Calculated, %: C 24.93; H 4.53.

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