New functionalized derivatives of mono- and diphosphonic acids substituted with five-membered nitrogen heterocycles

A. A. Prishchenko, M. V. Livantsov, O. P. Novikova, L. I. Livantsova, R. S. Alekseyev, V. I. Terenin, and V. S. Petrosyan*

Department of Chemistry, M. V. Lomonosov Moscow State University, 3 Build., 1 Leninskie Gory, 119991 Moscow, Russian Federation. E-mail: aprishchenko@yandex.ru

New types of (hydroxymethyl)phosphonic and (methylene)diphosphonic acids bearing heterocyclic fragments were synthesized by addition of tris(trimethylsilyl) phosphite to *N*-formyl derivatives of five-membered nitrogen heterocycles.

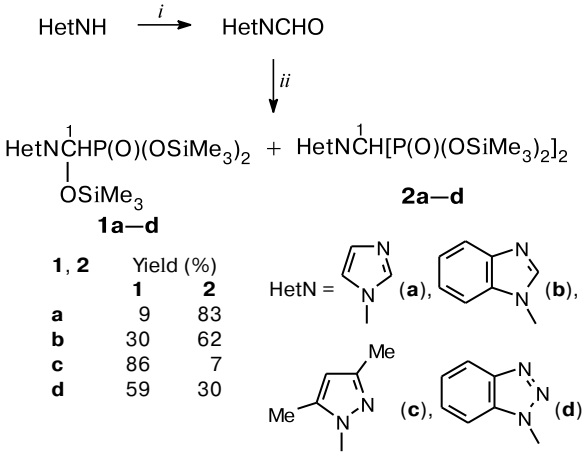
Key words: tris(trimethylsilyl) phosphite, five-membered nitrogen heterocycles, *N*-formyl-substituted heterocycles, trimethylsilyl triflate.

Functionalized phosphonic and (methylene)diphosphonic acids and their derivatives bearing fragments of nitrogen heterocycles are well known biomimetics of hydroxy(amino) acids and natural pyrophosphates. Some of these compounds, for instance, zoledronic, risedronic, and minodronic acids, are widely applied in medicine as the therapeutic agents for disorders of bone and calcium metabolism. They are also of interest as promising plant growth regulators and efficient polydentate ligands.[1—3] Earlier, we have described convenient synthetic procedures to access a series of aminomethylenediphosphoric acids and their derivatives from highly reactive synthones, *i.e.*, trimethylsilyl esters of trivalent phosphorus acids.[4—7] The aim of the present work is to study the addition of excess tris(trimethylsilyl) phosphite to readily available *N*-formyl-substituted five-membered rings with two or three nitrogen heteroatoms. The heterocyclic compounds were generated *in situ* using formic acid and *N*,*N*′-dicyclohexylcarbodiimide as earlier described.[8] It was found that phosphite adds to the carbonyl group of *N*-formyl heterocycle only in the presence of the catalyst, trimethylsilyl triflate (*cf.* Refs 5 and 9). The reaction proceeds under mild conditions and produces mixtures of phosphonates **1** and diphosphonates **2** in the ratios depending on the structure of the starting *N*-formyl heterocycle. For instance, *N*-formyl-3,5-dimethyl-1*H*-pyrazole gives predominantly phosphonate **1c** and *N*-formylimidazole produces diphosphonate **2a** in high yield (Scheme 1). Owing to unusual variability, this reaction allows simultaneous synthesis of two types of the target products and, therefore, advantageously differs from the similar reaction between formamides and tris(trimethylsilyl) phosphite always giving only aminomethylene diphosphonates.[5]

Thus, the addition of *N*-formyl derivatives of five-membered nitrogen heterocycles to tris(trimethylesilyl) phosphite proceeds similarly to the reactions of formamides of simple structure.[5] The role of trimethylsilyl triflate as a catalyst is to favor the formation of highly reactive intermediate iminium salts (Scheme 2). The absence of further conversion of substituted trimethylsilyloxymethyl phosphonates **1** during the reaction is apparently can be rationalized in terms of the bulkiness of the heterocyclic fragment impeding substitution of the C(1) trimethylsilyloxy group of phosphonates **1**.

Trimethylsilyl esters **1** and **2** readily react with excess methanol under mild conditions to give functionalized mono- and diphosphonic acids **3** and **4**, respectively (Scheme 3).

Scheme 1



Reagents and conditions: *i.* HCOOH, (*cyclo*-$C_6H_{11}N{=})_2C$, —(*cyclo*-$C_6H_{11}NH)_2CO$, 20 °C; *ii.* $P(OSiMe_3)_3$ (3 equiv.), $CF_3SO_3SiMe_3$ (0.26 equiv.), 40 °C.

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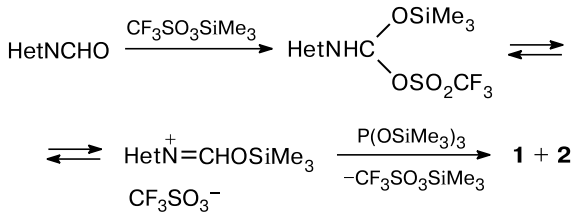
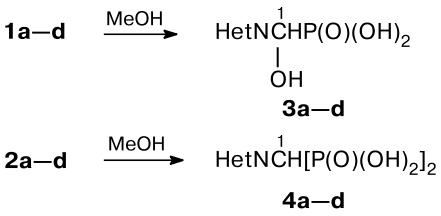
Scheme 2



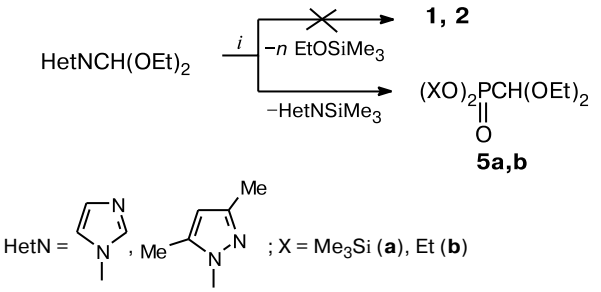
Scheme 3



The synthesized compounds **1**—**4** can found applications in the synthesis of new types of organophosphorus compounds bearing both heterocyclic and phosphonic moieties. These compounds are promising precursors for pharmaceuticals for multifunctional targeted therapy, plant growth regulating agents, and efficient polydentate ligands to access new complexes of different (including biogenic) metals with mono- and diphosphorus-containing ligands.

It should be emphasized that in contrast to formamide diethyl acetals reacting with esters of phosphorous acids to give aminomethylene diphosphonates,[10] reactions of readily available *N*-diethoxymethyl derivatives of five-membered nitrogen heterocycles[11—13] with tris(trimethylsilyl) phosphite involve the nitrogen—carbon bond cleavage and produce diethoxymethyl phosphonates **5** in high yields (Scheme 4).

Scheme 4



Reagents and conditions: *i*. $(XO)_2POSiMe_3$, Me_3SiCl, CH_2Cl_2, 40 °C.

In summary, we elaborated convenient procedures to synthesize new functional derivatives of mono- and diphosphonic acids bearing fragments of five-membered nitrogen heterocycles *via* the unique reaction of tris(trimethylsilyl) phosphite with *N*-formyl-substituted heterocycles.

Experimental

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker Avance 400 spectrometer at working frequencies of 400, 100, and 162 MHz, respectively. The chemical shifts are given in the δ scale relative to Me_4Si (^1H, $^{13}C\{^1H\}$) and a 85% solution of H_3PO_4 in D_2O ($^{31}P\{^1H\}$). All reactions were carried out in anhydrous solvents under dry argon. The starting trimethylsilyl esters of trivalent phosphorus acids[14,15] were synthesized by the known procedures.

Bis(trimethylsilyl) (1*H*-imidazol-1-yl)(trimethylsilyloxy)methylphosphonate (1a) and tetrakis(trimethylsilyl) (1*H*-imidazol-1-yl)methylenediphosphonate (2a). To a stirred mixture of imidazole (3.4 g, 0.05 mol) and formic acid (2.8 g, 0.06 mol) in dichloromethane (50 mL), a solution of *N*,*N*′-dicyclohexylcarbodiimide (14.4 g, 0.07 mol) in dichloromethane (20 mL) was added. The mixture was stirred for 6 h and then kept for 12 h. The precipitate was filtered off and the filtrate was successively treated with tris(trimethylsilyl) phosphite (44.8 g, 0.15 mol) and a solution of trimethylsilyl triflate (2.9 g, 0.013 mol) in dichloromethane (10 mL). The mixture was heated in a boiling water bath with simultaneous distillation off of the low-boiling components. Vacuum distillation of the residue afforded 1.8 g (9%) of phosphonate **1a**, b.p. 102 °C (1 Torr), and 22.0 g (83%) of diphosphonate **2a**, b.p. 126 °C (1 Torr).

Phosphonate 1a. Found (%): C, 39.42; H, 7.83. $C_{13}H_{31}N_2O_4PSi_3$. Calculated (%): C, 39.57; H, 7.92. ^1H NMR ($CDCl_3$), δ: –0.38 (s, Me_3SiO); –0.24 (s, 2 Me_3Si); 5.22 (d, C(1)H, $^2J_{P,H}$ = 4.8 Hz); 6.57 and 7.15 (both s, CH_{Het}). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 1.62 (s, Me_3Si); –0.25 and 0.05 (both s, 2 Me_3Si); 76.47 (d, C(1), $^1J_{P,C}$ = 213.2 Hz); 106.61, 139.80, 146.52 (all s, C_{Het}). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: –4.02 (s).

Diphosphonate 2a. Found (%): C, 36.12; H, 7.52. $C_{16}H_{40}N_2O_6P_2Si_4$. Calculated (%): C, 36.21; H, 7.60. ^1H NMR ($CDCl_3$), δ: –0.15 (s, 2 Me_3Si); –0.14 (s, 2 Me_3Si); 3.55 (t, C(1)H, $^2J_{P,H}$ = 17.2 Hz); 6.57 and 7.15 (both s, CH_{Het}). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 0.47 (s, 4 Me_3Si); 67.80 (t, C(1), $^1J_{P,C}$ = = 168.2 Hz); 121.00 and 134.69 (both s, C_{Het}). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: –0.32 (s).

Phosphonates **1b**—**d** and diphosphonates **2b**—**d** were synthesized similarly.

Bis(trimethylsilyl) (1*H*-benzimidazol-1-yl)(trimethylsilyloxy)methylphosphonate (1b). Yield 30%, b.p. 110 °C (1 Torr). Found (%): C, 45.81; H, 7.40. $C_{17}H_{33}N_2O_4PSi_3$. Calculated (%): C, 45.92; H, 7.48. ^1H NMR ($CDCl_3$), δ: –0.44 (s, Me_3Si); –0.25 (s, 2 Me_3Si); 5.58 (d, C(1)H, $^2J_{P,H}$ = 4.4 Hz); 6.70—7.45 (m, CH_{Het}). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: –0.22 (s, Me_3Si); 1.11 (s, 2 Me_3Si); 75.50 (d, C(1), $^1J_{P,C}$ = 214.1 Hz); 110.40, 120.23, 122.51, 123.19, 139.62, 143.28, 145.74 (all s, C_{Het}). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: –3.47 (s).

Tetra(trimethylsilyl) (1*H*-benzimidazol-1-yl)methylenediphosponate (2b). Yield 62%, b.p. 139 °C (1 Torr). Found (%): C, 41.26; H, 7.20. $C_{20}H_{42}N_2O_6P_2Si_4$. Calculated (%): C, 41.36; H, 7.29. ^1H NMR ($CDCl_3$), δ: –0.38 and –0.31 (both s, 2 Me_3Si); –0.16 (s, Me_3Si); 3.55 (t, C(1)H, $^2J_{P,H}$ = 16.8 Hz); 6.65—7.55

(m, CH_{Het}). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 1.10 (s, 4 Me_3Si); 68.11 (d, C(1), $^1J_{P,C}$ = 167.3 Hz); 112.46, 119.92, 122.13, 122.75, 139.71, 141.75, 145.46 (all s, C_{Het}). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: –0.58 (s).

Bis(trimethylsilyl) (3,5-dimethyl-1*H*-pyrazol-1-yl)(trimethylsilyloxy)methylphosphonate (1c). Yield 86%, b.p. 106 °C (1 Torr). Found (%): C, 42.49; H, 8.28. $C_{15}H_{35}N_2O_4PSi_3$. Calculated (%): C, 42.62; H, 8.35. ^1H NMR ($CDCl_3$), δ: –0.38 and –0.31 (both s, 2 Me_3Si); –0.16 (s, Me_3Si); 1.71 and 1.99 (both s, 2 Me); 5.36 (s, CH_{Het}); 5.40 (d, C(1)H, $^2J_{P,H}$ = 7.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: –1.62 (s, Me_3Si); –0.25 and 0.05 (both s, 2 Me_3Si); 10.77 and 12.36 (both s, 2 Me); 81.19 (d, C(1), $^1J_{P,C}$ = 214.1 Hz); 106.61, 139.80, 146.52 (all s, C_{Het}). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: –3.35 (s).

Tetrakis(trimethylsilyl) (3,5-dimethyl-1*H*-pyrazol-1-yl)methylenediphosphonate (2c). Yield 7%, b.p. 129 °C (1 Torr). Found (%): C, 38.52; H, 7.86. $C_{18}H_{44}N_2O_6P_2Si_4$. Calculated (%): C, 38.69; H, 7.94. ^1H NMR ($CDCl_3$), δ: –0.12 and –0.16 (both s, 4 Me_3Si); 1.80 and 2.01 (both s, 2 Me); 3.58 (t, C(1)H, $^2J_{P,H}$ = = 17.2 Hz); 5.36 (s, CH_{Het}). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 0.35 (s, 4 Me_3Si); 10.80 and 12.40 (both s, 2 Me); 68.09 (t, C(1), $^1J_{P,C}$ = 168.2 Hz); 106.68, 139.86, 146.57 (all s, C_{Het}). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: –0.30 (s).

Bis(trimethylsilyl) (1*H*-benzotriazol-1-yl)(trimethylsilyloxy)-methylphosphonate (1d). Yield 59%, b.p. 108 °C (1 Torr). Found (%): C, 43.03; H, 7.16. $C_{16}H_{32}N_3O_4PSi_3$. Calculated (%): C, 43.12; H, 7.24. ^1H NMR ($CDCl_3$), δ: –0.36 (s, Me_3Si); –0.05 (s, 2 Me_3Si); 6.26 (d, C(1)H, $^2J_{P,H}$ = 6.4 Hz); 6.99—7.76 (m, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: –0.93 (s, Me_3Si); –0.75 (s, Me_3Si); –0.43 (s, Me_3Si); 80.73 (d, C(1), $^1J_{P,C}$ = 13.2 Hz); 113.37, 119.20, 124.17, 127.30, 131.84, 146.45 (all s, C_{Het}). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: –4.81 (s).

Tetrakis(trimethylsilyl) (1*H*-benzotriazol-1-yl)methylenediphosphonate (2d). Yield 30%, b.p. 133 °C (1 Torr). Found (%): C, 39.03; H, 7.01. $C_{19}H_{41}N_3O_6P_2Si_4$. Calculated (%): C, 39.22; H, 7.10. ^1H NMR ($CDCl_3$), δ: –0.11 (s, 4 Me_3Si); 3.75 (t, C(1)H, $^2J_{P,H}$ = 16.8 Hz); 7.17—7.83 (m, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 0.01 (s, 4 Me_3Si); 67.71 (t, C(1), $^1J_{P,C}$ = 168.2 Hz); 110.50, 114.55, 119.44, 126.22, 129.93, 140.27 (all s, C_{Het}). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: –0.47 (s).

(1*H*-Imidazol-1-yl)methylenediphosphonic acid (4a). A solution of diphosphonate **2a** (10.6 g, 0.02 mol) in diethyl ether (15 mL) was added to methanol (40 mL) at 10 °C under continuous stirring. The mixture was heated to reflux and concentrated. The white crystals were dried *in vacuo* (1 Torr) for 1 h to give 4.7 g (98%) of acid **4a**, m.p. 174—176 °C. Found (%): C, 19.69; H, 3.28. $C_4H_8N_2O_6P_2$. Calculated (%): C, 19.85; H, 3.33. ^1H NMR (D_2O—C_5D_5N), δ: 3.33 (t, C(1)H, $^2J_{P,H}$ = 16.0 Hz); 6.55 and 7.85 (both s, CH_{Het}). $^{13}C\{^1H\}$ NMR (D_2O—C_5D_5N), δ: 66.26 (t, C(1), $^1J_{P,C}$ = 139.9 Hz); 117.83 and 132.43 (both s, C_{Het}). $^{31}P\{^1H\}$ NMR (D_2O—C_5D_5N), δ: 14.66 (s).

Acids **3a**—**d** and **4b**—**d** were synthesized similarly.

1*H*-Imidazol-1-yl(hydroxy)methylphosphonic acid (3a). Yield 96%, m.p. 144—145 °C (decomp.). Found (%): C, 26.86; H, 3.88. $C_4H_7N_2O_4P$. Calculated (%): C, 26.98; H, 3.96. ^1H NMR (D_2O—C_5D_5N), δ: 6.81 (d, C(1)H, $^2J_{P,H}$ = 4.2 Hz); 6.57 and 7.92 (both s, CH_{Het}). $^{13}C\{^1H\}$ NMR (D_2O—C_5D_5N), δ: 78.81 (d, C(1), $^1J_{P,C}$ = 180.4 Hz); 117.96 and 132.86 (both s, C_{Het}). $^{31}P\{^1H\}$ NMR (D_2O—C_5D_5N), δ: 7.47 (s).

1*H*-Benzimidazol-1-yl(hydroxy)methylphosphonic acid (3b). Yield 94%, m.p. 157—159 °C (decomp.). Found (%): C, 41.97; H, 3.91. $C_8H_9N_2O_4P$. Calculated (%): C, 42.12; H, 3.98. ^1H NMR (D_2O—C_5D_5N), δ: 5.15 (d, C(1)H, $^2J_{P,H}$ = 6.4 Hz); 7.17 (dd, $^3J_{H,H}$ = 16.0 Hz, $^4J_{H,H}$ = 3.2 Hz); 7.47 (dd, $^3J_{H,H}$ = = 16.0 Hz, $^4J_{H,H}$ = 3.2 Hz); 7.57 (s) (CH_{Het}). $^{13}C\{^1H\}$ NMR (D_2O—C_5D_5N), δ: 78.85 (d, C(1), $^1J_{P,C}$ = 170.0 Hz); 114.16, 125.86, 129.74, 138.52 (all s, C_{Het}). $^{31}P\{^1H\}$ NMR (D_2O—C_5D_5N), δ: 6.88 (s).

3,5-Dimethyl-1*H*-pyrazol-1-yl(hydroxy)methylphosphonic acid (3c). Yield 97%, m.p. 357—359 °C (decomp.). Found (%): C, 34.78; H, 5.30. $C_6H_{11}N_2O_4P$. Calculated (%): C, 34.96; H, 5.38. ^1H NMR (($CD_3)_2SO$—C_5D_5N), δ: 1.86 and 2.20 (both s, 2 Me); 4.92 (d, C(1)H, $^2J_{P,H}$ = 6.0 Hz); 5.64 (s, CH_{Het}). $^{13}C\{^1H\}$ NMR (($CD_3)_2SO$—C_5D_5N), δ: 10.47 and 12.44 (both s, 2 Me); 88.18 (d, C(1), $^1J_{P,C}$ = 191.4 Hz); 103.71, 144.05 (both s, C_{Het}). $^{31}P\{^1H\}$ NMR (($CD_3)_2SO$—C_5D_5N), δ: 10.42 (s).

1*H*-Benzotriazol-1-yl(hydroxy)methylphosphonic acid (3d). Yield 95%. m.p. 105—107 °C (decomp.). Found (%): C, 36.55; H, 3.48. $C_7H_8N_3O_4P$. Calculated (%): C, 36.70; H, 3.52. ^1H NMR ($(CD_3)_2SO$), δ: 6.43 (d, C(1)H, $^2J_{P,H}$ = 7.2 Hz); 7.41 (dd, $^3J_{H,H}$ = 6.4 Hz, $^4J_{H,H}$ = 3.2 Hz); 7.89 (dd, $^3J_{H,H}$ = 6.4 Hz, $^4J_{H,H}$ = 3.2 Hz) (CH_{Het}). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$), δ: 79.96 (d, C(1), $^1J_{P,C}$ = 187.7 Hz); 114.92, 118.84, 125.42, 126.86, 131.87, 145.86 (all s, C_{Het}). $^{31}P\{^1H\}$ NMR ($(CD_3)_2SO$), δ: 10.62 (s).

1*H*-Benzimidazol-1-ylmethylenediphosphonic acid (4b). Yield 98%. m.p. 348—350 °C (decomp.). Found (%): C, 32.74; H, 3.40. $C_8H_{10}N_2O_6P_2$. Calculated (%): C, 32.89; H, 3.45. ^1H NMR ($(CD_3)_2SO$), δ: 4.18 (t, C(1)H, $^2J_{P,H}$ = 16.0 Hz); 7.18 (dd, $^3J_{H,H}$ = 6.0 Hz, $^4J_{H,H}$ = 3.2 Hz); 7.46 (dd, $^3J_{H,H}$ = 6.0 Hz, $^4J_{H,H}$ = 3.2 Hz); 7.56 (s) (CH_{Het}). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$), δ: 66.86 (d, C(1), $^1J_{P,C}$ = 142.1 Hz); 113.79, 125.73, 129.59, 138.88 (all s, C_{Het}). $^{31}P\{^1H\}$ NMR ($(CD_3)_2SO$), δ: 15.63 (s).

3,5-Dimethyl-1*H*-pyrazol-1-ylmethylenediphosphonic acid (4c). Yield 98%. m.p. 357—359 °C (decomp.). Found (%): C, 26.49; H, 4.52. $C_6H_{12}N_2O_6P_2$. Calculated (%): C, 26.68; H, 4.48. ^1H NMR (($CD_3)_2SO$—C_5D_5N), δ: 1.82 and 2.14 (both s, 2 Me); 3.97 (t, C(1)H, $^2J_{P,H}$ = 15.6 Hz); 5.60 (s, CH_{Het}). $^{13}C\{^1H\}$ NMR (($CD_3)_2SO$—C_5D_5N), δ: 10.44 and 12.34 (both s, 2 Me); 55.57 (t, C(1), $^1J_{P,C}$ = 181.7 Hz); 105.63, 140.83 (both s, C_{Het}). $^{31}P\{^1H\}$ NMR (($CD_3)_2SO$—C_5D_5N), δ: 15.03 (s).

1*H*-Benzotriazol-1-ylmethylenediphosphonic acid (4d). Yield 96%. m.p. 355—357 °C (decomp.). Found (%): C, 28.56; H, 3.14. $C_7H_9N_3O_6P_2$. Calculated (%): C, 28.68; H, 3.09. ^1H NMR (($CD_3)_2SO$—C_5D_5N), δ: 3.88 (t, C(1)H, $^2J_{P,H}$ = 17.2 Hz); 8.01 (d, $^3J_{H,H}$ = 8.2 Hz); 8.95 (d, $^3J_{H,H}$ = 8.2 Hz). $^{13}C\{^1H\}$ NMR (($CD_3)_2SO$—C_5D_5N), δ: 65.28 (t, C(1), $^1J_{P,C}$ = 150.2 Hz); 113.61, 118.64, 124.03, 125.42, 126.86, 138.69 (all s, C_{Het}). $^{31}P\{^1H\}$ NMR (($CD_3)_2SO$—C_5D_5N), δ: 16.41 (s).

Bis(trimethylsilyl) diethoxymethylphosphonate (5a). A solution of *N*-diethoxymethylimidazole (4 g, 0.024 mol), tris(trimethylsilyl) phosphite (18 g, 0.06 mol), and chlorotrimethylsilane (5 g, 0.046 mol) in dichloromethane (20 mL) was refluxed for 1 h and then the solvent was carefully distilled off upon heating in a boiling water bath. Vacuum distillation of the residue afforded 5.8 g (74%) of compound **5a**, b.p. 104 °C (2 Torr). ^1H NMR ($CDCl_3$), δ: 0.03 (s, Me_3Si); 0.97 (t, 2 CH_3, $^3J_{H,H}$ = = 6.8 Hz); 3.38—3.55 (m, 2 CH_2O); 4.34 (d, C(1)H, $^2J_{P,H}$ = 5.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 0.67 (s, 2 Me_3Si); 14.85 (s, 2 Me); 63.97 and 64.08 (both s, 2 CH_2O); 98.97 (d, C(1)H, $^1J_{P,C}$ = = 216.0 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: –3.58 (s) (*cf.* Ref. 16).

Phosphonate **5b** was synthesized similarly.

Diethyl (diethoxymethyl)phosphonate (5b). Yield 78%, b.p. 93 °C (2 Torr). ^1H NMR ($CDCl_3$), δ: 0.81 (t, 2 CH_3, $^3J_{H,H}$ = = 6.8 Hz); 0.91 (t, 2 CH_3, $^3J_{H,H}$ = 7.2 Hz); 3.10—3.50

(m, 2 CH_2O); 3.60—3.80 (m, 2 CH_2O); 4.32 (d, C(1)H, $^2J_{P,H}$ = = 4.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 14.62 (s, 2 Me); 15.93 (d, Me, $^3J_{P,C}$ = 5.5 Hz); 62.41 (d, CH_2O, $^3J_{P,C}$ = 6.5 Hz); 63.99 (d, CH_2O, $^2J_{P,C}$ = 10.1 Hz); 98.59 (d, C(1)H, $^1J_{P,C}$ = 207.7 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 13.63 (s) (*cf.* Ref. 17).

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