Chemistry of Heterocyclic Compounds, Vol. 41, No. 3, 2005

ATOM-ECONOMIC SYNTHESIS OF NEW IMIDAZOLES AND BENZIMIDAZOLES WITH THIOPHOSPHORYL AND HYDROXYL GROUPS*

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Nucleophilic addition of secondary phosphine sulfides to an aldehyde of the azole series occurs under noncatalytic conditions in THF at room temperature and enables the preparation in high yield of imidazoles and benzimidazoles with thiophosphoryl and hydroxyl groups, which are promising building blocks for organic synthesis and polydentate ligands for metal complexes.

Keywords: bis(2-phenylethyl)phosphine sulfide, 2-[bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-ethyl(vinyl)imidazoles, hydrochlorides of 2-[bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-ethyl(vinyl)imidazoles, 2-formyl-1-organylimidazoles, 2-formyl-1-organylbenzimidazoles, hydrothiophosphorylation.

The reaction of accessible aldehydes of the azole series [1] with PH acids has been accomplished for the first time in the example of secondary phosphine oxides, which add under mild conditions to 2-formyl-1-organylimidazole and 2-formyl-1-organylbenzimidazole giving 2-(diorganylphosphorylhydroxymethyl)-1-organylimidazoles in practically quantitative yield [2-4]. The latter readily form biomimetic complexes with transition metal salts [5, 6].

The aim of the present work is the study of the principles of the processes of interaction of functional aldehydes with PH acids, and also the development of a convenient general approach to the synthesis of new chiral azoles with hydroxyl and phosphorus-containing groups. Therefore the reaction of 1-organyl-2-formylimidazoles **1a,b** and 2-formyl-1-organylbenzimidazoles **1c,d** with bis(2-phenylethyl)phosphine sulfide has been carried out and investigated. The phosphine sulfide is readily obtained from the available bis(2-phenylethyl)phosphine [7] and elementary sulfur.

Information on the interaction of aldehydes with secondary phosphine sulfides is limited to studies on the addition of dialkyl- and diarylphosphine sulfides to aliphatic and aromatic aldehydes in the presence of bases [8, 9], and also to formaldehyde and chloral under noncatalytic conditions [8, 10].

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* Dedicated to Academician V. I. Minkin on his 70th birthday.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 365-371, March, 2005. Original article submitted September 30, 2004.

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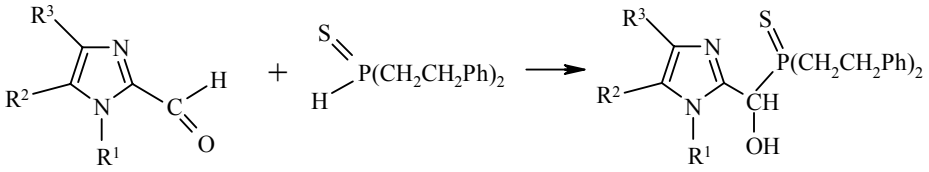
It turned out that the hydrothiophosphorylation of aldehydes **1a-d** by bis(2-phenylethyl)phosphine sulfide proceeds readily at room temperature in THF with the formation of 2-[bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-ethyl(vinyl)imidazoles and the corresponding benzimidazoles **2a-d**, the yield of which was 65-82%.



1a–d **2a–d**

1, **2 a** R^1 = Et, $R^2 = R^3$ = H, **b** R^1 = Vin, $R^2 = R^3$ = H; **c** R^1 = Et, $R^2 = R^3 = (CH)_4$;
d R^1 = Vin, $R^2 + R^3 = (CH)_4$

In the ^{1}H and ^{13}C NMR spectra of compounds **2a-d** the most characteristic signals were of the CH group of the OCHP=S fragment. The vicinal coupling constant of ^{31}P–C–^{1}H in the α-hydroxyphosphine sulfides was small [10], consequently the splitting of the resonance signal of the proton, present as a narrow singlet at 4.9-5.2 ppm, was not always observed. Other characteristic signals were the broadened singlet of the hydroxyl group proton at 4.5-5.8 ppm (^{1}H NMR) and the doublet at ~68 ppm ($^1J_{PC}$ ~58 Hz) (^{13}C NMR). The nonequivalence of the signals of the two phenylethyl groups in the ^{1}H and ^{13}C NMR spectra of thiophosphorylazoles **2a-d** is caused by the presence of the chiral carbon atom in the OCHP=S fragment. The resonance of the protons of each of the CH_2 groups of the two phenylethyl fragments of $PhCH_2CH_2P(S)$ in the ^{1}H NMR spectrum gives four multiplets, two of which are superimposed (high field multiplets for the CH_2P protons and low field for the CH_2Ph protons), which was confirmed by C–H correlation spectroscopy. In the benzimidazole derivative **2c** the difference of the chemical shifts of the two anisotropic protons of the $NC\underline{H}_2CH_3$ group was significantly greater than in the imidazole derivative **2a**, consequently the resonance of these protons for **2c** is displayed as two doublets of quartets.

The absorption band at 3130-3150 cm^{-1} in the IR spectra (KBr, nujol) of thiophosphorylazoles **2a-d** belongs to the stretching vibration of the associated OH group. An intense ν_{OH} band at 3420-3442 cm^{-1} was observed in the spectra of solutions in low polarity CCl_4 (conc. ~10^{-1}-10^{-4} M). However at higher dilution (to 10^{-4} M) in $CHCl_3$ and CH_2Cl_2 this band disappears, which indicates its belonging to the vibrations of an OH group participating in a simple intermolecular hydrogen bond, probably OH···N.

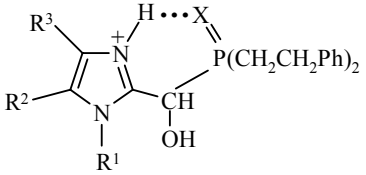
Disappearance of the indicated band is accompanied by the appearance in the IR spectra of solutions of compounds **2a-d** of a band for free OH groups (3607 cm^{-1}) and a band for ν_{OH} at ~3530 cm^{-1}, probably characterizing an intramolecular OH···S bond.

The ionization constants of compounds **2a-c**, and the ionization constants of some of their oxygen analogs, *viz*. 2-[bis(2-phenylethyl)phosphorylhydroxymethyl]-1-ethylimidazole (**3a**) and 2-[bis(2-phenylethyl)-phosphorylhydroxymethyl]-1-vinylimidazole (**3b**) were determined by potentiometric titration with perchloric acid in acetonitrile to assess the electron-donating ability of compounds **2a-c**.

The data obtained indicate that the azoles with thiophosphoryl functions **2a-c**, like their analogs with phosphine oxide fragments **3a,b**, are "monoacidic" bases in acetonitrile with a center of protonation at the N-3 atom of the azole ring [11]. The increased basicity (by ~2 pK_a units) of phosphorylazoles **3a,b** compared with the thiophosphorylazoles **2a-c** is possibly linked with the higher stabilization of the cation formed on titration of phosphorylazoles **3a,b** with perchloric acid. This is the result of an intramolecular hydrogen bond with the oxygen atom which is more electronegative than the sulfur atom in the corresponding thiophosphorylazoles **2a-c**.

TABLE 1. Values of pK_a of Thiophosphorylazoles **2a-c** and Phosphorylazoles **3a,b** (in Acetonitrile)

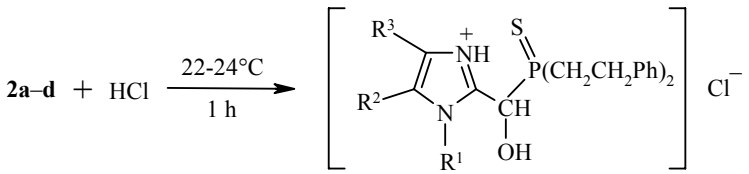
Compound	pK_a
2a	13.21
2b	11.95
2c	11.63
3a	15.41
3b	14.56



X = O, S

We note that the secondary phosphine sulfides are less reactive than their oxygen analogs in reactions with aldehydes of the azole series. The hydrophosphorylation of formylimidazole **1a** with bis(2-phenylethyl)phosphine oxide proceeds quantitatively in 1 h [3], while complete reaction of this aldehyde with bis(2-phenylethyl)phosphine sulfide requires 24 h. These data are in agreement with the data of [10] on the lower reactivity of dimethylphosphine sulfide in comparison with dimethylphosphine oxide in reactions with carbonyl compounds.

The functional thiophosphorylimidazoles **2a,b** and thiophosphorylbenzimidazoles **2c,d** interact readily with gaseous hydrogen chloride (diethyl ether, room temperature) forming the corresponding stable hydrochlorides **4a-d** of composition 1:1 in yields up to 99%.



4a–d

A comparative analysis of the ^{1}H NMR spectra of the initial compounds **2a-d** and the salts **4a-d** synthesized from them showed the presence of a low field displacement of the signals of the protons in radical R^1: up to δ 0.40 ppm for the CH_2 protons of the ethyl substituent and up to δ 0.57 ppm for the protons of $=CH_2$ of the vinyl fragment. These data, and also the significant low-field displacement of the proton signal of the (S)PCHO (up to δ 0.72 ppm), indicate the protonation of the N-3 atom of the imidazole ring, similar to that observed for hydrochlorides obtained from functionally substituted 1-vinyl(ethyl) imidazoles [12].

The data of the IR spectra of hydrochlorides **4a-d** (KBr, nujol), particularly the presence of a broad intense band for the stretching vibrations of the ammonium cation $^+$NH at 2400-3100 cm^{-1} and the high frequency displacement of the absorption bands of the heterocycle (1523→1581, 1496→1518 cm^{-1}), also indicates that the reaction of thiophosphorylazoles **2a-d** with HCl proceeds with the participation of only the pyridine-type nitrogen atom of the azole ring.

A low frequency displacement is observed for the doublet absorption band in the IR spectra of hydrochlorides **4a-d** characterizing the stretching vibrations of the S=P fragment [13] participating in H bonds at 556, 566 (**2a**), 550, 556 (**4a**); 558, 568 (**2b**), 550, 556 (**4b**); 550, 568 (**2c**), 547, 557 (**4c**); 540, 565 (**2d**), 539, 560 (**4d**). In addition, a broad low intensity absorption band was present in the spectra of hydrochlorides **4a-d** for an associated OH group with two maxima at ~3450 and ~3530 cm^{-1}. The doublet disappears in $CHCl_3$ solution at high dilution and a band for a free OH group appears at a frequency of ~3610 cm^{-1}. These data indicate that the hydrochlorides **4** being investigated form associates through intermolecular hydrogen bonds involving the sulfur and chlorine heteroatoms (NH···Cl and OH···S).

The hydrothiophosphorylation of aldehydes of the azole series is therefore a simple atom-economic method of synthesizing new polyfunctional chiral heterocyclic compounds. These are highly reactive building blocks for organic synthesis, precursors of optically active amphiphilic ligands for enantioselective processes, and also convenient models for solving fundamental problems of coordination chemistry.

EXPERIMENTAL

The ^1H, ^{13}C, and ^{31}P NMR spectra were obtained on a Bruker DPX 400 (400, 101, and 161 MHz respectively), internal standard was HMDS (^1H NMR), and deuterochloroform (^{13}C NMR), and external standard 85% H_3PO_4 (^{31}P NMR). The IR spectra were recorded on a Bruker IFS 25 spectrometer in KBr disks and in nujol.

The pK_a values were determined by potentiometric titration in absolute acetonitrile with a precision of ±0.03 by the method described in [14], the standard base was diphenylguanidine of pK_a = 17.90 [15]. The titration was carried out at 20°C in an EV-74 universal ionomer with glass and silver chloride electrodes. The titrant was 0.1 N $HClO_4$.

The synthesis of 2-[bis(2-phenylethyl)phosphorylhydroxymethyl]-1-ethylimidazole (**3a**) from bis(2-phenylethyl)phosphine oxide and 1-ethyl-2-formylimidazole was described in [3], 2-[bis(2-phenylethyl)phosphorylhydroxymethyl]-1-vinylimidazole (**3b**) was obtained analogously from bis(2-phenylethyl)phosphine oxide and 2-formyl-1-vinylimidazole.

Preparation of 2-[Bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-ethyl(vinyl)imidazoles and -benzimidazoles (2a-d) (General Procedure). A mixture of one of the aldehydes **1a-d** (1.6 mmol) and bis(2-phenylethyl)phosphine sulfide (1.5 mmol) in THF (9 ml) was purged with argon and stirred at room temperature for 24 h. The solvent was evaporated in vacuum, the viscous residue was kept for 72-80 h at room temperature to crystallize, then washed with small portions of ethanol (7 × 1 ml), and recrystallized from hexane. A light yellow to light brown powder was obtained, soluble in chloroform, acetone, and DMSO.

2-[Bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-ethylimidazole (2a). Yield 80%; mp 127-128°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.38 (3H, t, $^3J_{HH}$ = 7.1, CH_3); 2.14, 2.34, 2.52 (4H, m, CH_2P); 2.53, 2.74, 2.98 (4H, m, $PhC\underline{H}_2$); 4.13, 4.19 (2H, qq, $^2J_{AB}$ = 13.9, $^3J_{HH}$ = 7.1, NCH_2); 4.94 (1H, s, PCH); 6.93, 6.98 (2H, both s, H-4, H-4); 7.13-7.25 (10H, m, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 15.90 (CH_3); 27.91 (d, $^1J_{PC}$ = 45.4, CH_2P); 28.20 (d, $^2J_{PC}$ = 2.3, $PhCH_2$); 28.01 (d, $^2J_{PC}$ = 2.3, CH_2Ph); 30.47 (d, $^1J_{PC}$ = 45.4, CH_2P); 42.13 (NCH_2); 67.89 (d, $^1J_{PC}$ = 58.7, PCH); 120.42 (C-5), 126.25, 126.42 (C-*p*), 127.69 (C-4), 128.31, 128.47, 128.53, 128.56 (C-*m*, C-*o*), 141.01 (d, $^3J_{PC}$ = 14.9, C_{ipso}), 140.14 (d, $^3J_{PC}$ = 14.9, C_{ipso}), 142.79 (C-2). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 57.01. IR spectrum (KBr and nujol, cm^{-1}): 3150 (ν_{OH}); 3134, 3107, 3060, 3024 ($\nu_{=CH}$ phenyl, imidazole rings); 2976, 2930, 2907, 2840 (ν_{C-H}); 1600, 1581, 1523, 1496, 1487, 1452 ($\nu_{C=C,C=N}$ phenyl, imidazole rings); 1073 (δ_{COH}); 566, 556 ($\nu_{P=S}$). Found, %: C 65.99; H 6.88; N 7.08; P 7.84; S 8.21. $C_{22}H_{27}N_2OPS$. Calculated, %: C 66.31; H 6.83; N 7.03; P 7.77; S 8.05.

2-[Bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-vinylimidazole (2b). Yield 63%; mp 118-119°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.16, 2.36, 2.51 (4H, m, CH_2P); 2.65, 2.79, 2.98 (4H, m, $PhCH_2$); 4.57 (1H, br. s, OH); 4.95 (1H, d, $^3J_{HH}$ = 8.9, $=CH_2$, *cis*); 4.97 (1H, s, PCH); 5.23 (1H, d,

$^3J_{HH}$ = 15.7, =CH_2, *trans*); 7.02 (1H, s, H-5); 7.22 (1H, s, H-4); 7.11-7.29 (10H, m, Ph); 7.39 (1H, dd, $^3J_{HH}$ = 8.9, $^3J_{HH}$ = 15.7, =CH, *cis, trans*). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 28.25 (d, $^2J_{PC}$ = 2.3, $PhCH_2$); 28.19 (d, $^2J_{PC}$ = 2.3, $PhCH_2$); 28.57 (d, $^1J_{PC}$ = 45.0, CH_2P); 30.53 (d, $^1J_{PC}$ = 45.0, CH_2P); 67.85 (d, $^1J_{PC}$ = 57.0, PCH); 103.59 (=CH_2); 117.74 (C-5); 126.47, 126.56 (C-*p*); 128.39, 128.34 (C-4); 128.53, 128.61, 128.68 (C-*m*, C-*o*), 130.16 (=CH), 140.78 (d, $^3J_{PC}$ = 14.1, C_{ipso}), 141.64 (d, $^3J_{PC}$ = 14.1, C_{ipso}), 142.87 (C-2). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 59.40. IR spectrum (KBr and nujol, cm^{-1}): 3150 (ν_{OH}); 3140, 3106, 3085, 3058, 3021 ($\nu_{=CH_2}$, $\nu_{=CH}$, phenyl, imidazole rings); 2943, 2907, 2843 (ν_{C-H}); 1641 ($\nu_{C=C}$ vinyl group); 1601, 1582, 1524, 1496, 1483, 1452 ($\nu_{C=C,\ C=N}$ phenyl, imidazole rings); 1079 (δ_{COH}); 568, 558 ($\nu_{P=S}$). Found, %: C 67.04; H 6.49; N 7.17; P 7.61; S 8.21. $C_{22}H_{25}N_2OPS$. Calculated, %: C 66.64; H 6.36; N 7.07; P 7.81; S 8.08.

2-[Bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-ethylbenzimidazole (2c). Yield 82%; mp 131-132°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.24 (3H, t, CH_3, $^3J_{HH}$ = 7.1); 2.22, 2.46, 2.56 (4H, m, CH_2P); 2.67, 2.77, 3.09 (4H, m, $PhCH_2$); 4.19 (1H, dq, NCH_2, $^3J_{HH}$ = 7.1, $^2J_{AB}$ = 13.9); 4.58 (1H, dq, NCH_2); 5.08 (1H, d, $^2J_{PH}$ = 4.2, PCH); 5.73 (1H, br. s, OH); 7.09-7.33 (13H, m, H-7, H-8, H-9, Ph); 7.67 (d, $^3J_{HH}$ = 7.2, H-6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 14.62 (CH_3), 28.14 (d, $^2J_{PC}$ = 2.3, $PhCH_2$), 28.17 (d, $^2J_{PC}$ = 2.3, $PhCH_2$), 28.10 ($^1J_{PC}$ = 45.0, CH_2P), 30.40 (d, $^1J_{PC}$ = 45.0, CH_2P), 40.08 (NCH_2), 68.14 (d, $^1J_{PC}$ = 57.0, PCH), 110.25 (C-6), 119.31 (C-9), 122.57 (C-7), 123.17 (C-8), 126.25, 126.49 (C-*p*), 128.32, 128.46, 128.60, 128.62 (C-*m*, C-*o*), 135.09 (C-5), 140.66 (d, $^3J_{PC}$ = 13.8, C_{ipso}), 140.90 (d, $^3J_{PC}$ = 13.8, C_{ipso}), 141.71 (C-4), 149.57 (C-2). ^{31}P NMR ($CDCl_3$), δ, ppm: 58.83. IR spectrum (KBr and nujol, cm^{-1}): 3100 (ν_{OH}); 3103, 3082, 3061, 3025 ($\nu_{=CH}$ phenyl, benzimidazole rings); 2982, 2900, 2870, 2849 (ν_{C-H}), 1602, 1496, 1454 ($\nu_{C=C,\ C=N}$ phenyl, benzimidazole rings); 1073 (δ_{COH}); 568, 550 ($\nu_{P=S}$). Found, %: C 69.87; H 6.62; N 6.68; P 6.81; S 7.04. $C_{26}H_{29}N_2OPS$. Calculated, %: C 69.62; H 6.52; N 6.25; P 6.91; S 7.13.

2-[Bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-vinylbenzimidazole (2d). Yield 65%; mp 97-98°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.24, 2.46, 2.64 (4H, m, CH_2P); 2.69, 2.79, 3.04 (4H, m, $PhCH_2$); 4.70 (1H, br. s, OH); 5.16 (1H, s, PCH); 5.33 (1H, d, $^3J_{HH}$ = 8.6, =CH_2, *cis*); 5.33 (1H, d, $^3J_{HH}$ = 15.6, =CH_2, *trans*); 7.10-7.35 (12H, m, H-7, H-8, Ph); 7.46 (1H, dd, =CH), 7.56 (1H, d, $^3J_{HH}$ = 7.3, H-9); 7.69 (1H, d, $^3J_{HH}$ = 7.3, H-6). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 28.08 (d, $^2J_{PC}$ = 2.3, $PhCH_2$); 27.95 (d, $^2J_{PC}$ = 2.3, $PhCH_2$); 28.31 (d, $^1J_{PC}$ = 45.0, CH_2P); 30.45 (d, $^1J_{PC}$ = 45.0, CH_2P); 67.79 (d, $^1J_{PC}$ = 55.8, PCH); 109.74 (=CH_2); 111.68 (C-6); 119.62 (C-9); 123.24 (C-7); 123.98 (C-8); 126.23, 126.37 (C-*p*); 128.19, 128.35 (C-*o*); 128.37, 128.49 (C-*m*), 129.79 (=CH); 134.23 (C-5); 140.45 (d, $^3J_{PC}$ = 13.7, C_{ipso}), 140.59 (d, $^3J_{PC}$ = 13.7, C_{ipso}); 141.91 (C-4); 149.40 (C-2). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 59.23. IR spectrum (KBr and nujol, cm^{-1}): 3100 (ν_{OH}); 3085, 3057, 3025 ($\nu_{=CH_2}$, $\nu_{=CH}$ phenyl, imidazole rings; 2946, 2927, 2900, 2864 (ν_{C-H}); 1641 ($\nu_{C=C}$ vinyl group); 1602, 1582, 1497, 1483, 1454 ($\nu_{C=C,C=N}$ phenyl, benzimidazole rings; 1074 (δ_{COH}); 555, 540 ($\nu_{P=S}$). Found, %: C 69.83; H 6.81; N 6.24; P 6.83; S 7.06. $C_{26}H_{27}N_2OPS$. Calculated, %: C 69.93; H 6.09; N 6.27; P 6.94; S 7.19.

Preparation of Hydrochlorides of 2-[Bis(2-phenylethyl)thiophosphoryl-hydroxymethyl]-1-ethyl-(vinyl)imidazoles and -benzimidazoles (4a-d) (General Procedure). A mixture of one of the thiophosphorylazoles **2a-d** (0.5 mmol) and absolute ether (25 ml) was saturated with dry hydrogen chloride gas and stirred at room temperature for 1 h, continuously passing dry HCl through the reaction mixture. Hydrochlorides **4a,b** were isolated by rubbing the obtained oil in fresh portions of absolute ether (3 × 25 ml) until a powder formed, which was dried in vacuum. Hydrochlorides **4c,d** were separated by filtration at once, then dried in vacuum.

Hydrochloride of 2-[Bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-ethylimidazole (4a). Yield 81%; mp 106-109°C. Found, %: C60.32; H 6.46; Cl 8.31; N 6.55; P 6.91; S 7.74. $C_{22}H_{28}ClN_2OPS$. Calculated, %: C 60.76; H 6.44; Cl 8.17; N 6.44; P 7.13; S 7.36.

Hydrochloride of 2-[Bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-vinylimidazole (4b). Yield 93%; mp 124-126°C. Found, %: C 60.79; H 5.80; Cl 8.23; N 6.51; P 6.96; S 7.63. $C_{22}H_{26}ClN_2OPS$. Calculated, %: C 61.04; H 6.01; Cl 8.21; N 6.47; P 7.17; S 7.40.

Hydrochloride of 2-[Bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-ethylbenzimidazole (4c). Yield 99%; mp 157-159°C. Found, %: C 64.39; H 6.09; Cl 7.45; N 5.89; P 6.07; S 7.01. $C_{26}H_{39}ClN_2OPS$. Calculated, %: C 64.40; H 6.19; Cl 7.33; N 5.78; P 6.40; S 6.60.

Hydrochloride of 2-[Bis(2-phenylethyl)thiophosphorylhydroxymethyl]-1-vinylbenzimidazole (4d). Yield 94%; mp 120-122°C. Found, %: C 64.55; H 6.02; Cl 7.71; N 5.88; P 5.99; S 6.25. $C_{26}H_{28}ClN_2OPS$. Calculated, %: C 64.66; H 5.80; Cl 7.36; N 5.80; P 6.42; S 6.63.

The work was carried out with financial support by the President of the Russian Federation of Advanced Scientific Schools (grant No. NSh-2241.2003.3), and also within the framework of the Program for Fundamental Investigations of the Russian Academy of Sciences 2004 (state contract No. 21-3 from 01.04.2004).

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