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LETTERS TO THE EDITOR

Reaction of 2-[2-(Benzylideneamino)phenoxy]- and 2-[2-(Benzylideneamino)ethoxy]-1,3,2-benzodioxaphospholes with Hexafluoroacetone. Formation of Spirophosphoranes with Phosphorus–Carbon and Phosphorus–Nitrogen Bonds

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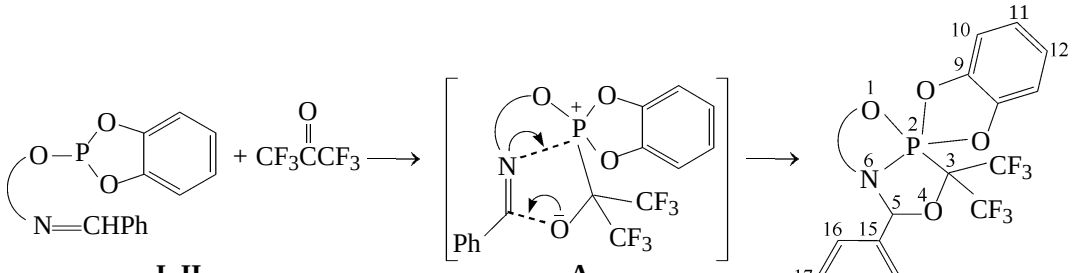
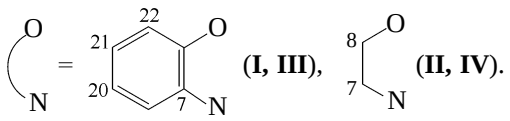
It is known that trivalent phosphorus derivatives containing NCO, NCS, C≡CR, or $RC{=}CR_2$ groups directly attached to phosphorus easily react with carbonyl compounds to form various P-heterocyclic systems [1, 2]. These reactions are postulated to involve intermediate dipolar ions with $P–C–O^-$ or $P–O–C^-$ fragments, that convert into the final products via intramolecular attack of the anionic part on the unsaturated substituent on phosphorus.

In the present work we made an attempt to extend this approach on trivalent phosphorus derivatives containing an unsaturated fragment that is not directly bound with phosphorus. 2-[2-(Benzylideneamino)-phenoxy]- and 2-[2-(benzylideneamino)ethoxy]-1,3,2-benzodioxaphospholes (**I, II**) were chosen as representatives of such compounds. They are fairly stable and do not tend to cyclize in the absence of hydrogen chloride. The behavior of analogous acyclic phosphites has been described by in [3]. Phospholes **I, II** easily react with hexafluoroacetone to give 1:1 adducts. Their $^{31}P–\{^1H\}$ NMR spectrum contains broadened singlets at δ_P –3.1 and –3.5 ppm, respectively. Based of ^{13}C and ^{19}F NMR and mass spectral data, we assigned to the adducts the structure of spirophosphoranes **III, IV** with phosphorus–carbon and phosphorus–nitrogen bonds. The electron impact mass spectra of these compounds contain molecular ion peaks $[M]^{+\cdot}$ at *m/z* 501 and 453. The common fragmentation pathway of these molecules under electron impact is the formation of $[M – F]^+$ ions (*m/z* 482 and 434, respectively).



I, II **A** **III, IV**



(**I, III**), (**II, IV**).

The reaction evidently begins with nucleophilic attack of phosphorus on the carbonyl carbon atom with initial formation of dipolar ion **A**. Further stabilization includes intramolecular attack of the alkoxide anion on the C=N bond to form a P–N bond.

2-[2-(Benzylideneamino)phenoxy]-1,3,2-benzodioxaphosphole (I). To a mixture of 1.8 g of 2-(benzylideneamino)phenol, 1 g of triethylamine, and 300 ml of ether, a solution of 1.6 g of 2-chloro-1,3,2-benzodioxaphosphole in 30 ml of ether was added dropwise with stirring under argon at –20°C. The reaction mixture was stirred for 5 h until it warmed up to 20°C and for 7 h at this temperature. The precipitate that formed was filtered off and washed with ether. The solvent was removed from the filtrate, and the residue was dried in a vacuum (0.1 mm Hg) to obtain 2.9 g (97%) of compound **I** as a yellowish colorless oil. $^{31}P–\{^1H\}$ NMR spectrum (CH_2Cl_2): δ_P 126.4 ppm. Found, %: C 68.11; H 4.33; N 3.95; P 9.41. $C_{19}H_{14}NO_3P$. Calculated, %: C 68.06; H 4.18; N 4.18; P 9.25.

2-[2-(Benzylideneamino)ethoxy]-1,3,2-benzodioxaphosphole (II) was prepared by an analogous procedure as a light yellow oil, yield 97%. $^{31}P–\{^1H\}$ NMR spectrum (CH_2Cl_2): δ_P 129.8 ppm. Found, %: C 62.51; H 5.17; N 4.64; P 10.42. $C_{15}H_{14}NO_3P$. Calculated, %: C 62.72; H 4.88;N 4.88; P 10.80.

1-Phenyl-3,3-bis(trifluoromethyl)-2λ^5,4′λ^5-spiro-[1,3,2-benzodioxaphosphole-2,4′-[1,3,4]oxazaphospholo[4,3-*b*][1,3,2]benzoxazaphosphole] (III). Hexafluoroacetone, 1.5 g, was condensed at –40°C to a solution of 2.9 g of 2-[2-(benzylideneamino)phenoxy]-1,3,2-benzodioxaphosphole (**I**) in 20 ml of CH_2Cl_2 and 20 ml of $CHCl_3$. The mixture was kept for 6 h until it warmed up to 20°C and then for 7 days at this temperature. Crystals of compound **III** (0.9 g) formed and were filtered off, washed with cold CH_2Cl_2, and dried in a vacuum. The filtrate was reduced by half and let to stand to obtain an additional 1.22 g of compound **III**. Total yield 47%, mp 139–140°C. IR spectrum, ν, cm^{-1}: 2030, 1966, 1934, 1895, 1820, 1775, 1674, 1621, 1595, 1534, 1494, 1483, 1419, 1368, 1355, 1337, 1302, 1275, 1220, 1183, 1172, 1149, 1101, 1090, 1017, 1000, 975, 937, 923, 896, 872, 813, 783, 772, 757, 742, 718, 701, 692, 671, 654, 642, 619, 605, 596, 560, 525, 499, 471, 446, 431. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.10 d (1H, H^5, $^3J_{PNCH}$ 4.2); 6.51 br.d (1H, H^{19}, $^3J_{HCCH}$ 7.6); 7.02 br.d (1H, H^{22}, $^3J_{HCCH}$ 7.3); 6.96 d.d.d (1H, $^3J_{HCCCH}$ 1.4, $^4J_{POCCH}$ 1.2) and 7.14 d.d.d (1H, $^3J_{HCCH}$ 7.6, $^4J_{HCCCH}$ 1.5, $^4J_{POCCH}$ 1.3) (H^{10}, H^{13}); 7.04–7.05 m (2H, H^{11}, H^{12}, *AB* part of *ABMX* spectrum); 6.97 m and 6.93 m (2H, H^{21}. H^{20}, *AB* part of *ABMX* spectrum, $^3J_{AB}$ 7.3). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz) (here and hereinafter, the shape of the signal in the $^{13}C–\{^1H\}$ NMR spectrum is given in parentheses): 78.75 br.d.septet (br.d.septet) (C^3, $^1J_{PC}$ 125.0–130.0, $^2J_{FCC}$ 31.9–32.5); 88.67 d.d.t.d (d) (C^5, $^1J_{HC}$ 162.8, $^2J_{PNC}$ 17.4, $^3J_{HCCC}$ 4.8, $^2J_{HCC}$ 4.8); 137.64 br.m (d) (C^7, $^2J_{PNC}$ 2.3); 141.47 m (br.s) (C^8); 146.54 d.d(s) (C^9, $^3J_{HCCC}$ 7.2, $^3J_{HCCC}$ 7.2); 111.03 d.m (d) (C^{10}, $^1J_{HC}$ 161.6, $^3J_{POCC}$ 12.0); 121.68 d.d (s) (C^{11}, $^1J_{HC}$ 161.6, $^3J_{HCCC}$ 6.6); 124.02 d.d (s) ($^1J_{HC}$ 162.5, $^3J_{HCCC}$ 7.8) and 123.98 d.d (s) ($^1J_{HC}$ 162.5, $^3J_{HCCC}$ 7.8) (C^{12}, C^{20}); 111.71 br.d.d.d (d) (C^{13}, $^1J_{HC}$ 165.8, $^3J_{POCC}$ 15.6, $^3J_{HCCC}$ 6.6); 142.46 d.d (s) (C^{14}, $^3J_{HCCC}$ 10.5, $^3J_{HCCC}$ 10.5); 133.77 d.t (d) (C^{15}, $^3J_{PNCC}$ 18.6, $^3J_{HCCC}$ 7.5); 127.28 br.d.m (s) (C^{16}, $^1J_{HC}$ 158.0, $^3J_{HCCC}$ 6.6, $^3J_{HCCC}$ 6.6–6.8), 128.86 d.d (s) (C^{17}, $^1J_{HC}$ 161.0, $^3J_{HCCC}$ 7.8); 129.89 d.t(s) (C^{18}, $^1J_{HC}$ 161.0, $^3J_{HCCC}$ 7.2); 121.02 br.q (CF_3, $^1J_{FC}$ 282.2); 120.56 br.q.d (br.q.d) (CF_3, $^1J_{CF}$ 285.0–286.0. $^2J_{PCC}$ 4.5); 110.97 d.m (d) (C^{19}, $^1J_{CH}$ 164.6, $^3J_{PNCC}$ 9.6); 121.42 d.d (s) (C^{21}, $^1J_{HC}$ 163.4, $^3J_{HCCC}$ 7.8); 112.00 d.d.d.d (d) (C^{22}, $^1J_{HC}$ 164.4, $^3J_{POCC}$ 12.6, $^3J_{HCCC}$ 6.8, $^2J_{HCC}$ 2.4. ^{19}F NMR spectrum ($CDCl_3$) δ_F: –70.37 q.d ($^4J_{FCCCF}$ 8.7–9.0, $^3J_{PCCF}$ 1.7–2.0); –71.41 q.d ($^4J_{FCCCF}$ 8.7–9.0, $^3J_{PCCF}$ 4.4). Found, %: C 52.23; H 3.11; P 6.13. $C_{22}H_{14}F_6NO_4P$. Calculated, %: C 52.69; H 2.79; P 6.19.

5′-Phenyl-7′,7′-bis(trifluoromethyl)-2′,3′-dihydro-2λ^5,8′λ^5-spiro[1,3,2-benzodioxaphosphole-2,8′-[1,3,4]oxazaphospholo[4,3-*b*][1,3,2]oxazaphosphole] (IV) was obtained by a similar procedure, yield 89%, light yellow viscous oil. ^1H NMR spectrum ($CDCl_3$ + 20% CCl_4), δ, ppm, *J*, Hz: 7.62 br.d (H^{16}, $^3J_{HCCH}$ 7.4); 7.46 d.d (H^{17}, $^3J_{HCCH}$ 7.3, $^3J_{HCCH}$ 7.4); 7.43 m (H^{18}, $^3J_{HCCH}$ 7.3); 7.44 m, 7.09 m, 6.92–7.01 m (H^{10}–H^{13}); 5.90 br.s (H^5); 4.12–4.19 m (OCH_2); 2.78 m (NCH, $^2J_{HCH}$ 8.7, $^3J_{HCCH}$ 10.0, $^3J_{PNCH}$ 10.0); 3.12 m (NCH, $^2J_{HCH}$ 8.7, $^3J_{HCCH}$ 8.0, $^3J_{PNCH}$ 25.3). ^{13}C NMR spectrum ($CDCl_3$ + 20% CCl_4), δ_C, ppm, *J*, Hz: 77.85 br.d.septet (br.d.septet) (C^3, $^1J_{PC}$ 127.0–129.0, $^2J_{FCC}$ 32.0); 88.63 br.d.d.m (d) (C^5, $^1J_{HC}$ 163.8, $^2J_{PNC}$ 13.4); 42.46 t.d.m (d) (C^7, $^1J_{HC}$ 144.5, $^2J_{PNC}$ 13.5); 63.79 br.t (br.s) (C^8, $^1J_{HC}$ 153.2); 145.57 br.m (br.s) (C^9); 111.18 br.d.d.m (d) (C^{10}, $^1J_{HC}$ 164.0, $^3J_{POCC}$ 14.6, $^3J_{HCCC}$ 4.7); 123.36 br.d.d (s) (C^{11}, $^1J_{HC}$ 161.4, $^3J_{HCCC}$ 6.8); 121.50 br.d.d (s) (C^{12}, $^1J_{HC}$ 158.7, $^3J_{HCCC}$ 4.3); 110.70 br.d.d.d (d) (C^{13}, $^1J_{HC}$ 164.6, $^3J_{POCC}$ 13.2, $^3J_{HCCC}$ 9.2); 142.62 br.m (br.s)

(C^{14}); 135.92 d (m) (C^{15}, $^{3}J_{PNCC}$ 6.0–6.3); 126.72 br.d.d.d (s) (C^{16}, $^{1}J_{HC}$ 159.6, $^{3}J_{HCCC}$ 5.9–6.0, $^{3}J_{HCCC}$ 5.9–6.0); 128.68 d.d (s) (C^{17}, $^{1}J_{HC}$ 160.0, $^{3}J_{HCCC}$ 7.7); 129.22 d.t (s) (C^{18}, $^{1}J_{HC}$ 160.5, $^{3}J_{HCCC}$ 7.4); 122.82 br.q.d (br.q.d) (CF_3, $^{2}J_{FC}$ 282.2, $^{2}J_{PCC}$ 4.6–4.8); 122.37 br.q (br.q) (CF_3, $^{1}J_{FC}$ 285.0); 110.97 d.m (d) (C^{19}, $^{1}J_{HC}$ 164.6, $^{3}J_{PNCC}$ 9.6); 121.42 d.d (s) (C^{21}, $^{1}J_{HC}$ 163.4, $^{3}J_{HCCC}$ 7.8); 112.00 d.d.d.d (d) (C^{22}, $^{1}J_{HC}$ 164.4, $^{3}J_{POCC}$ 12.6, $^{3}J_{HCCC}$ 6.8, $^{2}J_{HCC}$ 2.4). ^{19}F NMR spectrum (CCl_4): δ_F –73.91 br.q.m ($^{4}J_{FCCCF}$ 8.6–9.0); δ_F –74.52 br.q.m ($^{4}J_{FCCCF}$ 8.6–9.0. $^{4}J_{PCCF}$ 3.0). Found, %: C 47.44; H 3.47; P 7.01. $C_{18}H_{14}F_6NO_4P$. Calculated, %: C 47.68; H 3.09; P 6.84.

The IR spectrum was recorded on a Bruker Vector 22 spectrometer for suspensions in mineral oil. The NMR spectra were recorded on Bruker Avance-600 (^{1}H, 600 MHz; ^{13}C, 150.8 MHz) and Varian Unity-300 (^{19}F, 282.2 MHz, ^{31}P, 121.4 MHz) spectrometers. The mass spectra were measured on a Finnigan MAT TRACE MS spectrometer, ionizing energy 70 eV, ion source temperature 200°C. Direct sample injection into the ion source was applied. The injector ampule was heated from 35 to 150°C at a step of 35 deg min^{-1}. The mass spectra were treated using the Xcalibur program.

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