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Reactions of 2-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-1,3,2-benzodioxaphosphinin-4-one with chloral and hexafluoroacetone

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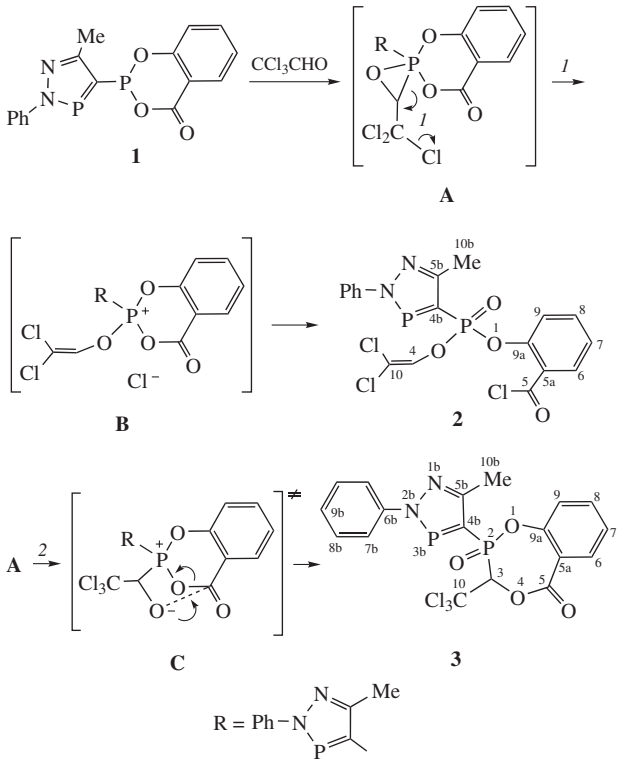
Reaction of 2-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-1,3,2-benzodioxaphosphinin-4-one with chloral occurs at P^{III} atom of the 1,3,2-dioxaphosphinine cycle giving mostly 2-chlorocarbonylphenyl 2,2-dichlorovinyl (5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)phosphonate, whereas hexafluoroacetone incorporates into the 1,3,2-dioxaphosphorine cycle affording the corresponding 1,3,2-benzodioxaphosphepine.

Coupled bis-heterocycles are of considerable interest both theoretically and in practice.[1–7] Representatives containing phosphorus atoms in various coordination states, such as biphospholes or biphosphinines,[8–12] are less studied than their nitrogen analogues. Bis-heterocycles based on systems with P^{II} and P^{III} atoms can serve as ligands with coordination sites of different degrees of hardness[13] and as possible substrates for cascade reactions.

On treatment with highly electrophilic chloral or hexafluoroacetone, 1,2,3-diazaphospholes having P^{II} atom react at C(4b) atom of the heterocyclic system,[14,15] whereas 2-R-4*H*-1,3,2-benzodioxaphosphinin-4-ones being P^{III} derivatives afford seven-membered benzo-1,4,2- or benzo-1,3,2-dioxaphosphepines.[16,17]

Herein, we studied reaction of 2-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-1,3,2-benzodioxaphosphinin-4-one **1**,† containing two different phosphorus atoms in each heterocyclic moiety, with chloral and hexafluoroacetone. In fact, the reaction occurred exclusively at P^{III} atom of 1,3,2-dioxaphosphorine cycle (Schemes 1 and 2). The fact that the reaction



Scheme 1

† NMR spectra were recorded on Bruker MSL-400 (^{31}P, 162.0 MHz) and Bruker Avance-400 (^{1}H, 400 MHz; ^{13}C, 100.6 MHz) instruments in $CDCl_3$ with the use of HMDS (^{1}H) or the signals of the solvent (^{13}C) as the internal standard and H_3PO_4 (^{31}P) as the external standard. The IR spectra were measured on a Bruker Vector-22 instrument in KBr pellets. The EI mass spectra were obtained on a DFS Thermo Electron Corporation instrument (USA); the ionizing electron energy was 70 eV; the ion source temperature was 290 °C. A direct inlet system was used. The evaporator tube temperature was programmed from 100 to 350 °C. The processing of mass spectral data was performed using the Xcalibur software.

*2-(5-Methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-1,3,2-benzodioxaphosphinin-4-one* **1**. At first, 4-dichlorophosphino-5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphole was synthesized analogously to 4-dichlorophosphino-2,5-dimethyl-2*H*-1,2,3-diazaphosphole,[18,19] bp 125–127 °C/0.02 Torr, yield 60%. ^{31}P NMR, δ: 241.8 (br. d, P^{II}, $^{2}J_{P^{III}CP^{II}}$ 78.0 Hz), 157.0 (d, P^{III}, $^{2}J_{P^{II}CP^{III}}$ 78.0 Hz). Then, a mixture of thus obtained 4-dichlorophosphino-5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphole (2.77 g, 0.010 mol) and trimethylsilyl 2-trimethylsiloxybenzoate (2.82 g, 0.013 mol) was kept under argon for 6 days. The reaction mixture was then evaporated (1.5 Torr) to afford a light-yellow powder of compound **1**, mp 97–98 °C, yield 73%. MS, *m*/*z*: 342 $[M]^{+\cdot}$. IR (ν/cm^{-1}): 1206, 1153, 1129, 1070, 1043, 1014, 960, 930, 904, 880, 869, 787, 767, 754, 748, 686, 656, 632, 586, 543, 527, 496, 473. ^{1}H NMR, δ: 8.05 (dd, 1H, H^5, $^{3}J_{HCCH}$ 8.0 Hz, $^{4}J_{HCCCH}$ 1.9 Hz), 7.66 (dd, 1H, H^{7b}, $^{3}J_{HCCH}$ 8.5 Hz, $^{4}J_{PNCCH}$ 1.6 Hz), 7.59 (ddd, 1H, H^7, $^{3}J_{HCCH}$ 7.6 Hz, $^{3}J_{HCCH}$ 8.3 Hz, $^{4}J_{HCCCH}$ 1.6 Hz), 7.38 (dd, 1H, H^{8b}, $^{3}J_{HCCH}$ 8.6 Hz, $^{3}J_{HCCH}$ 6.7 Hz), 7.30 (dd, 1H, H^6, $^{3}J_{HCCH}$ 7.6 Hz, $^{3}J_{HCCH}$ 6.6 Hz), 7.20 (td, 1H, H^{9b}, $^{3}J_{HCCH}$ 7.6 Hz, $^{4}J_{HCCCH}$ 2.0 Hz), 7.10 (d, 1H, H^8, $^{3}J_{HCCH}$ 8.2 Hz), 2.69 (s, 1H, H^{10b}). ^{13}C NMR, δ: 162.28 [dd (br. s), C^4, $^{2}J_{POC}$ 8.5 Hz, $^{3}J_{HCCC}$ 8.4 Hz], 158.38 [ddq (dd), C^{5b}, $^{2}J_{PCC}$ 23.8 Hz, $^{2}J_{PCC}$ 5.5 Hz, $^{2}J_{HCC}$ 6.4 Hz], 157.68 [m (d), C^{8a}, $^{2}J_{POC}$ 8.0 Hz], 155.43 [m (d), C^{6b}, $^{2}J_{PNC}$ 7.3 Hz], 148.48 [ddq (dd), C^{4b}, $^{1}J_{PC}$ 63.5 Hz, $^{1}J_{PC}$ 56.1 Hz, $^{3}J_{HCCC}$ 2.5 Hz], 136.87 [ddd (s), C^8, $^{1}J_{HC}$ 161.8 Hz, $^{3}J_{HCCC}$ 9.1 Hz, $^{2}J_{HCC}$ 1.9 Hz], 131.53 [ddd (br. s), C^6, $^{1}J_{HC}$ 166.4 Hz, $^{3}J_{HCCC}$ 8.4 Hz, $^{2}J_{HCC}$ 2.1 Hz], 129.55 [dd (s), C^{8b}, $^{1}J_{HC}$ 161.0 Hz, $^{3}J_{HCCC}$ 8.0 Hz]. 127.78 [dt (s), C^{9b}, $^{1}J_{HC}$ 162.5 Hz, $^{3}J_{HCCC}$ 7.3 Hz], 124.58 [dd (s), C^5, $^{1}J_{HC}$ 164.7 Hz, $^{3}J_{HCCC}$ 7.7 Hz], 120.55 [ddd (d), C^{7b}, $^{1}J_{HC}$ 161.8 Hz, $^{3}J_{PNCC}$ 9.5 Hz, $^{3}J_{HCCC}$ 7.3 Hz], 120.27 [ddd (s), C^7, $^{1}J_{HC}$ 159.0 Hz, $^{3}J_{HCCC}$ 7.7 Hz, $^{2}J_{HCC}$ 1.4 Hz], 116.10 [dd (m), C^{4a}, $^{3}J_{POCC}$ 11.7 Hz, $^{5}J_{PCPOCC}$ 3.3 Hz], 15.41 [qd (d), C^{10b}, $^{1}J_{HC}$ 128.8 Hz, $^{3}J_{PCCC}$ 8.4 Hz]. ^{31}P NMR, δ: 238.5 (br. d, P^{II}, $^{2}J_{P^{III}CP^{II}}$ 16.6 Hz), 156.3 (d, P^{III}, $^{2}J_{P^{II}CP^{III}}$ 16.6 Hz).

between 1,2,3-diazaphosphole cycle of compound **1** and these electrophiles does not proceed can be simply explained by the presence of substituents at C(4b) in this moiety. Additionally, steric hindrance at P^{II} prevents any type of cycloaddition leading to compounds with tetra- and hexacoordinated phosphorus, which are usually inherent in heterophospholes.[20–22]

In the reaction with chloral (20 °C), two products **2** and **3** (9:1) were obtained (Scheme 1).‡ Product **2** is of dichlorovinyl phosphonate chemotype and results from the Perkow reaction. The minor cycloexpansion product **3** is 1,4,2-benzodioxaphosphepine derivative [a 2:1 mixture of two diastereoisomers, δ_P 246.1 (br. d), 26.0 (d, $^2J_{P^{II}CP^{IV}}$ 65.7 Hz); 246.1 (br. d), 29.6 (d, $^2J_{P^{II}CP^{IV}}$ 68.1 Hz)]. Note that previously studied 2-R-4*H*-1,3,2-benzodioxaphosphinin-4-ones in reactions with chloral gave exclusively 1,4,2-dioxaphosphepines.[16]

Apparently, the reaction starts with [1+2] cycloaddition of P^{III} atom at carbonyl group of chloral, leading to the intermediate spirophosphorane **A** (*cf.* ref. 23). It undergoes three-membered ring opening and chloride elimination in line with the Perkow reaction mechanism (see Scheme 1, pathway *1*), giving thus quasiphosphonium salt **B**, the nearest precursor to the final product **2**. The second direction (pathway *2*) involves the conversion of intermediate **A** through a betaine-like transition state **C** into the cycloexpansion product **3**.

Benzodioxaphosphepine **3** gradually crystallizes from the reaction mixture and thus can be isolated. Compound **2** containing reactive functional groups was obtained as a non-distilled oil after separation from compound **3**. Its ^{31}P NMR spectrum manifests signals at δ_P 251.86 (br. d) and 11.3 (d, $^2J_{P^{II}CP^{IV}}$ 84.5 Hz), which confirms that 1,2,3-diazaphosphole fragment remained intact in the product.

The major diastereoisomer of 1,4,2-benzodioxaphosphepine **3** was obtained individual by crystallization and its structure was established by NMR and XRD.§ An asymmetric part of the unit cell contains one independent molecule of compound **3** (space group $P2_1/n$, monoclinic). The geometry of the molecule in a crystal is shown in Figure 1. Conformation of its 1,4,2-dioxaphosphepine ring is distorted asymmetrical boat. Diazaphosphole substituent occupies pseudoaxial position while trichloromethyl group and the phosphoryl oxygen are in pseudoequatorial sets. Atoms P(2), C(3) and O(4) are deviated from the plane O(1)–C(5a)–C(9a)–C(5) [which is planar within 0.010 (2) Å] on one side with various distances [–1.1531(5), –1.853(2) and –0.744(2) Å, respectively]. The O(5) atom of the carbonyl group noticeably deviates from the plane O(1)–C(9a)–C(5a)–C(5) [O(5)–C(5)–C(5a)–C(6) torsion angle is 37.4(4)°]. 1,2,3-Diazaphosphole heterocycle of the molecule **3** is planar within 0.000(2) Å, its phenyl substituent is slightly turned relatively to this plane [N(1b)–N(2b)–C(6b)–C(11b) torsion angle is 14.8(2)°]. Phosphorus atom has a distorted tetrahedral configuration. Relative configurations of the P(2) and C(3) atoms are *R**,*S**.

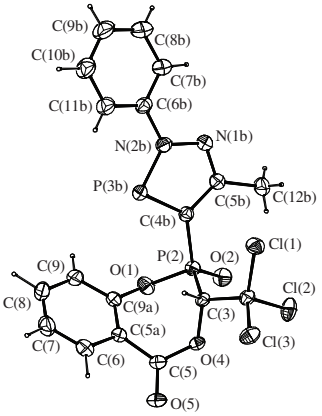


Figure 1 Molecular structure for compound **3** (30% thermal ellipsoids). Selected bond lengths (Å), bond and torsion angles (°): P(2)–O(1) 1.598(2), P(2)–O(2) 1.464(2), P(2)–C(3) 1.853(2), P(2)–C(4b) 1.764(2), P(3b)–N(2b) 1.682(2), P(3b)–C(4b) 1.714(2), O(4)–C(5) 1.196(3), N(1b)–N(2b) 1.358(3), C(4b)–C(5b) 1.423(3), C(5a)–C(9a) 1.380(4), C(5)–C(5a) 1.483(4), O(1)–P(2)–O(2) 110.6(1), O(1)–P(2)–C(3) 98.2(1), O(1)–P(2)–C(4b) 105.8(1), O(2)–P(2)–C(3) 114.7(1), O(2)–P(2)–C(4b) 115.7(1), C(3)–P(2)–C(4b) 110.0(1), N(2b)–P(3b)–C(4b) 88.7(1), N(2b)–N(1b)–C(5b) 109.3(2), P(3b)–N(2b)–N(1b) 117.1(2), P(3b)–N(2b)–C(6b) 125.3(2), N(1b)– N(2b)–C(6b) 117.6(2), P(3b)–C(4b)–C(5b) 109.9(2), O(2)–P(2)–O(1)–C(9a) 152.3(2), O(1)–P(2)–C(3)–O(4) 56.0(2), O(2)–P(2)–C(3)–O(4) –61.3(2), C(7b)–C(6b)–N(2b)–P(3b) 15.7(4), O(2)–P(2)–C(4b)–P(3b) 149.5(2), O(2)– P(2)–C(3)–C(10) 56.9(2).

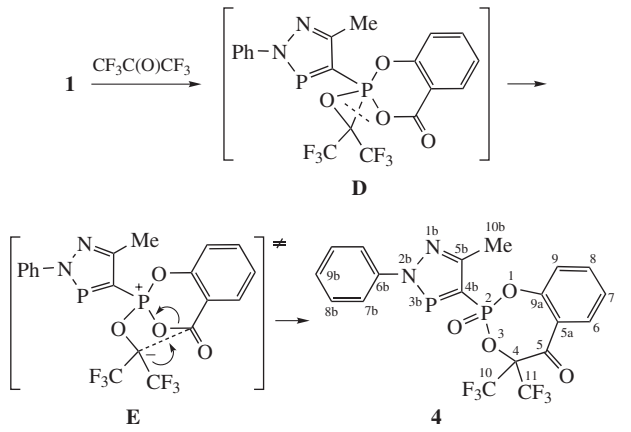
Reaction of compound **1** with hexafluoroacetone leads to 1,3,2-benzodioxaphosphepine derivative **4** (Scheme 2). In this

‡ *2-(5-Methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-2,5-dioxo-3-trichloromethyl-2,3-dihydro-5*H*-1,4,2-benzodioxaphosphepine* **3**. A mixture of compound **1** (2.58 g, 0.008 mol), CH_2Cl_2 (10 ml), diethyl ether (10 ml), and chloral (1.11 g, 0.008 mol) was kept for 5 days, during which a crystalline precipitate gradually formed. The precipitate was filtered off, washed with hexane and dried *in vacuo* (0.1 Torr) to afford compound **3** as colourless crystals, mp 169–170 °C, yield 9%. MS, *m/z*: 488 ($C_{18}H_{13}{}^{35}Cl_3N_2O_4P_2$) $[M]^{+\cdot}$, 372 [M – CCl_3], 330 [M – CCl_3 – N=CCH_2], 295 [M – CCl_3 – C_6H_4]. IR (ν/cm^{-1}): 3421, 3411, 3397, 2884, 1741, 1602, 1591, 1578, 1490, 1478, 1454, 1430, 1382, 1343, 1288, 1266, 1254, 1236, 1214, 1158, 1133, 1112, 1080, 1057, 1040, 1015, 953, 931, 911, 872, 846, 808, 783, 772, 755, 743, 706, 689, 666, 639, 606, 585, 549, 521, 509. ^{1}H NMR, δ: 8.02 (dd, H^6, $^3J_{H^7CCH^6}$ 7.8 Hz, $^4J_{H^8CCCH^6}$ 1.8 Hz), 7.75 (m, H^{7b}), 7.68 (dddd, H^8, $^3J_{H^9CCH^8}$ 8.3 Hz, $^3J_{H^7CCH^8}$ 7.4–7.5 Hz, $^4J_{H^6CCCH^8}$ 1.8 Hz, $^5J_{POCCCH^8}$ 1.0 Hz), 7.48 (m, H^{8b}), 7.40 (m, H^7, overlapped with H^{9b}), 7.40 (m, H^{9b}, overlapped with H^7), 7.07 (ddd, H^9, $^3J_{H^8CCH^9}$ 8.3 Hz, $^4J_{H^7CCCH^9}$ 1.2 Hz, $^4J_{POCCH^9}$ 1.0 Hz), 5.11 (d, H^3, $^2J_{PMe}$ 2.8 Hz), 2.82 (s, H^{10b}). ^{13}C NMR, δ: 163.66 [br. d (d), C^5, $^3J_{HC^6CC^5}$ 6.0 Hz], 159.67 [m (dd), C^{5b}, $^2J_{P^{II}CC^{5b}}$ 7.8 Hz, $^3J_{P^{IV}CC^{5b}}$ 4.3 Hz], 142.59 [m (d), C^{6b}, $^1J_{P^{II}NC^{6b}}$ 11.1 Hz], 136.13 [ddd (s), C^8, $^1J_{HC^8}$ 165.6 Hz, $^3J_{HC^6CC^8}$ 8.4 Hz, $^2J_{HC^9C^8}$ 1.3 Hz], 133.88 [br. dd (d), C^6, $^1J_{HC^6}$ 166.3 Hz, $^3J_{HC^8CC^6}$ 8.7 Hz], 132.97 [ddq (dd), C^{4b}, $^1J_{P^{II}C^{4b}}$ 201.6 Hz, $^1J_{P^{IV}C^{4b}}$ 48.6 Hz, $^3J_{HC^{10}CC^{4b}}$ 3.0–4.0 Hz], 129.89 [dd (s), C^{8b}, $^1J_{HC^{8b}}$ 161.8 Hz, $^3J_{HC^{8b}CC^{8b}}$ 8.0 Hz], 128.77 [br. dt (d), C^{9b}, $^1J_{HC^{9b}}$ 162.6 Hz, $^3J_{HC^{7b}CC^{9b}}$ 7.8 Hz, $^5J_{P^{II}NCCCC^{9b}}$ 1.2 Hz], 127.62 [br. dd (d), C^7, $^1J_{HC^7}$ 166.0 Hz, $^3J_{HC^9CC^7}$ 7.8 Hz], 126.33 [m (d), C^{5a}, $^3J_{POCC^{5a}}$ 6.2 Hz], 123.66 [br. ddd (d), C^9, $^1J_{HC^9}$ 165.0–166.0 Hz, $^3J_{HC^7CC^9}$ 8.5 Hz, $^3J_{POCC^9}$ 3.9 Hz], 120.76 [ddm (d), C^{7b}, $^1J_{HC^{7b}}$ 161.1 Hz, $^3J_{P^{II}NCC^{7b}}$ 9.8 Hz], 93.53 [dd (d), C^{10}, $^2J_{PC^3C^{10}}$ 6.5 Hz, $^2J_{HC^3C^{10}}$ 6.5 Hz], 85.95 [ddd (dd), C^3, $^1J_{HC^3}$ 146.2 Hz, $^1J_{PC^3}$ 104.5 Hz, $^3J_{P^{II}CPC^3}$ 2.9 Hz], 16.59 [q (s), C^{10b}, $^1J_{HC^{10b}}$ 130.0 Hz].

*2-Chlorocarbonylphenyl 2,2-dichlorovinyl (5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)phosphonate* **2** was obtained after filtering precipitate **3** off, the filtrate was evaporated (0.1 Torr) affording a colourless oil, yield 88%. For spectral characteristics of compound **2**, see Online Supplementary Materials.

§ *X-ray diffraction analysis*. Crystals of **3** ($C_{18}H_{13}Cl_3N_2O_4P_2$, M = 489.59) are monoclinic, space group $P2_1/n$. At 293 K: a = 5.5566(9), b = 26.838 (4) and c = 13.963(2) Å, β = 98.674(2)°, V = 2058.5(6) Å^3, Z = 4, d_{calc} = = 1.580 g cm^{-3}, μ = 6.29 cm^{-1}, F(000) = 992. Data were collected on a Bruker Smart APEX II CCD automatic diffractometer [graphite monochromator, λ(MoKα) = 0.71073 Å, ω-scanning], $2\theta < 54°$, R_{int} = 0.0243. 16584 reflections were measured, 4475 of them were independent, the number of observed reflections with $I > 2\sigma(I)$ were 3513, R = 0.0395, R_w = 0.0924, GOF = 1.055, the number of refined parameters is 303. An absorption correction was performed using SADABS program.[24] The structure was solved by direct method using SIR program[25] and refined by the full matrix least-squares using SHELXL-97 program.[26] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except H(121), H(122) and H(123) were located from the difference Fourier synthesis and refined isotropically. The atoms H(121), H(122) and H(123) were placed into the geometrically calculated positions and refined as riding atoms. All calculations were performed using WinGX[27] and APEX2[28] programs. All the figures and analysis of intermolecular interactions were performed using PLATON[29] and ORTEP[30] programs.

CCDC 837574 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2011.



Scheme 2

case, contrary to chloral, a possible oxaphosphirane intermediate **D**, being the product of the cheletropic reaction of P^{III} atom with carbonyl group, turns into 1,3,2-dioxaphosphepine **4** *via* a betaine-like transition state **E**. The structure of compound **4** was confirmed by the NMR and IR spectra.¶ The ^{13}C-{^1H} NMR spectrum contains characteristic signals of carbon atoms C(4) and C(5) (δ_C 83.63 and 185.45 ppm), relating to the seven-membered cycle, which unambiguously confirm the 1,3,2-dioxaphosphepine structure. The appearance of characteristic doublet at δ_P 252.9 ppm ($^2J_{P^{II}CP^{IV}}$ 82.8 Hz) in the ^{31}P-{^1H} NMR spectrum indicates that P^{II}-containing fragment of the molecule remained unaffected in spite of hexafluoroacetone excess and a long reaction duration.

¶ *2-(5-Methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-2,5-dioxo-4,4-bis(trifluoromethyl)-4,5-dihydro-1,3,2-benzodioxaphosphepine* **4**. Hexafluoroacetone (1.99 g, 0.012 mol) was condensed into a solution of compound **1** (4.0 g, 0.012 mol) in CCl_4 (10 ml) and CH_2Cl_2 (10 ml) at –40 °C. The reaction mixture was slowly (8–10 h) warmed to 20 °C and kept at this temperature for one day, during which crystals of compound **4** were formed. The crystals were filtered off, washed with CCl_4/CH_2Cl_2 mixture and dried *in vacuo* to give colourless crystals, mp 173–175 °C, yield 91%. MS, *m*/*z*: 481 $[MH - CO]^+$. IR (ν/cm^{-1}): 3436, 3103, 3035, 2998, 2926, 2853, 1708, 1693, 1602, 1573, 1493, 1481, 1448, 1427, 1383, 1357, 1277, 1247, 1234, 1210, 1173, 1151, 1124, 1066, 1036, 1020, 980, 945, 931, 891, 878, 849, 786, 767, 754, 739, 712, 677, 651, 602, 579, 565, 543, 517, 500, 481, 457. ^1H NMR, δ: 7.82 (dd, H^6, 1H, $^3J_{H^7CCH^6}$ 7.9 Hz, $^4J_{H^8CCCH^6}$ 1.6 Hz), 7.77 (m, 2H, H^{7b}, $^3J_{H^{8b}CCH^{7b}}$ 7.7–8.0 Hz), 7.64 (dddd, 1H, H^8, $^3J_{H^9CCH^8}$ 8.2 Hz, $^3J_{H^7CCH^8}$ 7.4 Hz, $^4J_{H^6CCCH^8}$ 1.6 Hz, $^5J_{POCCCH^8}$ 1.1 Hz), 7.47 (m, 2H, H^{8b}, $^3J_{H^{7b}CCH^{8b}}$ 7.7 Hz, $^3J_{H^{9b}CCH^{8b}}$ 7.4 Hz), 7.40 (br. m, H^{9b}, 1H, $^3J_{H^{8b}CCH^{9b}}$ 7.4 Hz), 7.38 (br. m, 1H, H^7, $^3J_{H^6CCH^7}$ 7.9–8.0 Hz, $^3J_{H^8CCH^7}$ 7.4 Hz), 7.08 (br. d, H^9, 1H, $^3J_{H^8CCH^9}$ 8.2 Hz), 2.76 (s, 3H, H^{10b}). ^{13}C NMR, δ: 185.45 [ddd (d), C^5, $^3J_{HC^6CC^5}$ 4.3 Hz, $^3J_{POCC^5}$ 1.9 Hz, $^4J_{HCCCC^5}$ 1.7 Hz], 159.15 [ddq (dd), C^{5b}, $^2J_{P^{II}CC^{5b}}$ 10.5 Hz, $^2J_{P^{IV}CC^{5b}}$ 4.4 Hz, $^2J_{HC^{10b}C^{5b}}$ 4.2 Hz], 147.95 [ddddd (d), C^{9a}, $^3J_{HC^8CC^{9a}}$ 10.4 Hz, $^3J_{HC^6CC^{9a}}$ 9.0 Hz, $^2J_{POC^{9a}}$ 8.2 Hz, $^2J_{HC^9C^{9a}}$ 4.1 Hz, $^4J_{HC^7CCC^{9a}}$ 1.7 Hz], 142.69 [dtt (d), C^{6b}, $^2J_{P^{II}NC^{6b}}$ 11.1 Hz, $^3J_{HC^{8b}CC^{6b}}$ 8.5–9.0 Hz, $^2J_{HC^{7b}C^{6b}}$ 2.7 Hz], 136.81 [ddd (s), C^8, $^1J_{HC^8}$ 163.3 Hz, $^3J_{HC^6CC^8}$ 9.0 Hz, $^2J_{HC^9C^8}$ 2.1 Hz], 132.36 [ddddd (d), C^6, $^1J_{HC^6}$ 166.4 Hz, $^3J_{HC^8CC^6}$ 8.3 Hz, $^2J_{HC^7C^6}$ 2.6 Hz, $^4J_{POCCCC^6}$ 1.2 Hz, $^4J_{HC^9CCC^6}$ 1.2 Hz], 130.07 [ddq (dd), C^{4b}, $^1J_{P^{II}C^{4b}}$ 204.9 Hz, $^1J_{P^{IV}C^{4b}}$ 49.0 Hz, $^3J_{HC^{10b}CC^{4b}}$ 2.8 Hz], 129.82 [ddd (s), C^{8b}, $^1J_{HC^{8b}}$ 162.6 Hz, $^3J_{HC^{8b}CC^{8b}}$ 7.5 Hz, $^2J_{HCC^{8b}}$ 1.2 Hz], 128.65 [dtd (d), C^{9b}, $^1J_{HC^{9b}}$ 162.5 Hz, $^3J_{HC^{7b}CC^{9b}}$ 7.6 Hz, $^5J_{P^{II}NCCCC^{9b}}$ 1.6 Hz], 127.99 [br. m (br. s), C^{5a}], 126.52 [dddd (d), C^7, $^1J_{HC^7}$ 165.2 Hz, $^3J_{HC^9CC^7}$ 8.1 Hz, $^2J_{HC^8C^7}$ 1.1 Hz, $^4J_{POCCC^7}$ 1.1 Hz], 121.65 [ddddd (d), C^9, $^1J_{HC^9}$ 165.8 Hz, $^3J_{POCC^9}$ 8.1 Hz, $^3J_{HC^7CC^9}$ 8.0 Hz, $^2J_{HC^8C^9}$ 1.2 Hz, $^4J_{HC^6CCC^9}$ 1.2 Hz], 120.91 [dm (d), C^{7b}, $^1J_{HC^{7b}}$ 162.2 Hz, $^3J_{P^{II}NCC^{7b}}$ 9.6 Hz, $^3J_{HC^{7b}CC^{7b}}$ 6.5–7.5 Hz, $^3J_{HC^{9b}CC^{7b}}$ 6.5–7.5 Hz], 120.13 [qdq (qdq), C^{10}, $^1J_{FC^{10}}$ 288.3 Hz, $^3J_{POCC^{10}}$ 3.0 Hz, $^4J_{FC^{11}CC^{10}}$ 1.1 Hz], 120.05 [qdq (qdq), C^{11}, $^1J_{FC^{11}}$ 290.0 Hz, $^3J_{POCC^{11}}$ 10.0 Hz, $^4J_{FC^{10}CC^{11}}$ 1.3 Hz], 83.63 [sept. d (sept. d), C^4, $^2J_{FCC^4}$ 30.3 Hz, $^2J_{POC^4}$ 7.6 Hz], 15.56 [q (s), C^{10b}, $^1J_{HC}$ 129.6 Hz]. ^{31}P NMR (36.46 MHz, $CDCl_3$) δ: 253.20 (br. d, $^2J_{P^{II}CP^{IV}}$ 82.8 Hz), 15.8 (d, $^2J_{P^{II}CP^{IV}}$ 82.8 Hz).

In summary, 2-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-1,3,2-benzodioxaphosphinin-4-one reacts with only one molecule of carbonyl compound at more active P^{III} atom of dioxaphosphinine cycle, while atom P^{II} of diazaphosphole fragment remains unaffected.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2011.09.018.

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