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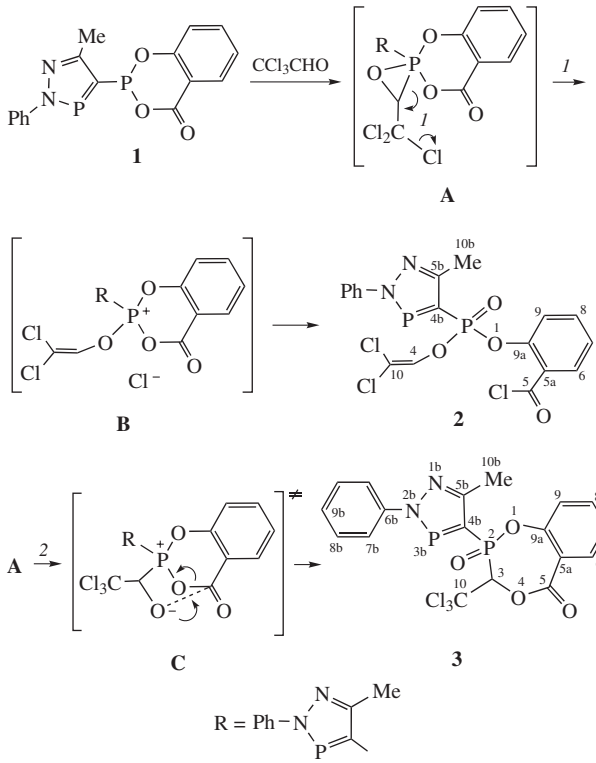
Reaction of 2-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-1,3,2-benzodioxaphosphinin-4-one with chloral occurs at P^{III} atom of the 1,3,2-dioxaphosphinine cycle giving mostly 2-chlorocarbonylphenyl 2,2-dichlorovinyl (5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)phosphonate, whereas hexafluoroacetone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