ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 2, pp. 306–308. © Pleiades Publishing, Ltd., 2012.
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SHORT COMMUNICATIONS

Special Features of Reaction of 2-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-benzo[*d*]-1,3,2-dioxaphosphorin-4-one with Diethyl Mesoxalate

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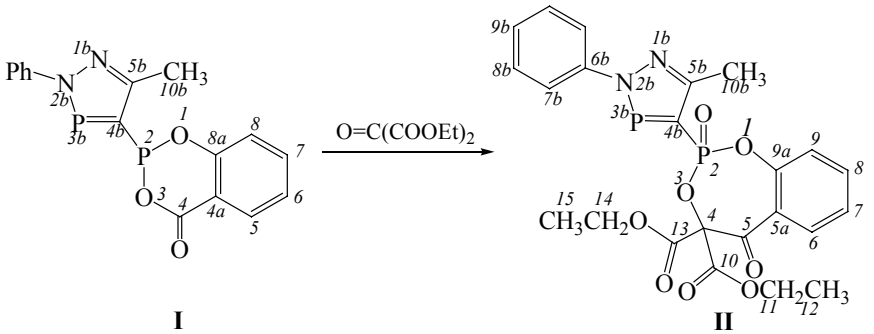
Received June, 2010

DOI: 10.1134/S1070428012020261

Mixed anhydrides of salicylic and phosphoric (phosphonic) acids, salicylphosphites (phosphonites), are convenient and available reagents for the synthesis of derivatives of tetra- and pentacoordinate phosphorus owing to the presence of the energy-rich P–O bond [1]. Introducing to the atom of the tricoordinate phosphorus an additional diazaphosphol fragment containing a bicoordinate phosphorus could have both affected the regiochemistry of reactions of the salicylphosphites with activated carbonyl compounds and led to the formation of new reaction products.

In this study by the reaction of previously described [2] 4-(dichlorophosphino)-5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol with bis(O-trimethylsilyl) derivative of salicylic acid we prepared for the first time 2-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-benzo[*d*]-1,3,2-dioxaphosphorin-4-one (**I**) containing two phosphorus atoms of different coordination at a carbon atom (P=C–P) and investigated its reaction with diethyl mesoxalate. Common phosphorus derivatives of hydroxycarboxylic acids react with this compound forming phosphoranes and leaving intact the anhydride P–O bond [3]; the introduction to the atom of the tricoordinate phosphorus of an isocyanate group leads to the formation of products of bicyclononane structure [4]. Although the molecule of compound **I** contains a reactive bicoordinate P atom, the reaction occurs exclusively at the tricoordinate P atom resulting in the formation of 2-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-2,5-dioxo-4,4-bis(diethyldicarbonyl)benzo[2,3-*f*]-1,3,2-dioxaphosphepine (**II**). Thus 5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl substituent apparently owing to its electronic and steric effects directed the reaction to the path uncharacteristic of the diethyl mesoxalate involving



I **II**

expansion of the six-membered ring to a seven-membered with a high regioselectivity (only 1,3,2-dioxaphosphepine was obtained).

2-(5-Methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-benzo[*d*]-1,3,2-dioxaphosphorin-4-one (I). To 2.82 g (0.010 mol) of trimethylsilyl 2-trimethylsiloxybenzoate [5] under an inert atmosphere was slowly added 2.77 g (0.010 mol) of 4-(dichlorophosphino)-5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol. Trimethylchlorosilane was removed in a vacuum (165–200 mm Hg) in an argon flow. The residue was dried in a vacuum (0.1 mm Hg) and was further used without additional purification. Yield 73%, mp 97–98°C. IR spectrum, ν, cm^{-1}: 3440, 3100, 3066, 3027, 3012, 2958, 2914, 1734, 1664, 1606, 1579, 1492, 1475, 1457, 1424, 1383, 1346, 1286, 1227, 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 spectrum, δ, ppm (*J*, Hz): 8.05 d. d (H^5, 1H, $^3J_{HCCH}$ 8.0, $^4J_{HCCCH}$ 1.9), 7.30 d.d (H^6, 1H, $^3J_{HCCH}$ 7.6, $^3J_{HCCH}$ 6.6), 7.59 d.d.d (H^7, 1H, $^3J_{HCCH}$ 7.6, $^3J_{HCCH}$ 8.3, $^4J_{HCCCH}$ 1.6), 7.10 d (H^8, 1H, $^3J_{HCCH}$ 8.2), 7.66 d.d (H^{7b}, 1H, $^3J_{HCCH}$ 8.5, $^4J_{PNCCH}$ 1.6), 7.38 d.d (H^{8b}, 1H, $^3J_{HCCH}$ 8.6, $^3J_{HCCH}$ 6.7), 7.20 t.d (H^{9b}, 1H, $^3J_{HCCH}$ 7.6, $^4J_{HCCCH}$ 2.0), 2.69 c (H^{10b}, 1H). ^{13}C NMR spectrum (the appearance of the signal in the spectrum ^{13}C-{^{1}H} is given in parentheses), δ, ppm (*J*, Hz): 162.28 d.d (br.s) (C^4, $^2J_{POC}$ 8.5, $^3J_{HCCC}$ 8.4); 116.10 d.d (m) (C^{4a}, $^3J_{POCC}$ 11.7, $^5J_{PCPOCC}$ 3.3); 124.58 d.d (s) (C^5, $^1J_{HC}$ 164.7, $^3J_{HCCC}$ 7.7); 131.53 d.d.d (br.s) (C^6, $^1J_{HC}$ 166.4, $^3J_{HCCC}$ 8.4, $^2J_{HCC}$ 2.1); 120.27 d.d.d (s) (C^7, $^1J_{HC}$ 159.0, $^3J_{HCCC}$ 7.7, $^2J_{HCC}$ 1.4); 136.87 d.d.d (s) (C^8, $^1J_{HC}$ 161.8, $^3J_{HCCC}$ 9.1, $^2J_{HCC}$ 1.9); 157.68 m (d) (C^{8a}, $^2J_{POC}$ 8.0); 148.48 d.d.q (d.d) (C^{4b}, $^1J_{PC}$ 63.5, $^1J_{PC}$ 56.1, $^3J_{HCCC}$ 2.5); 158.38 d.d.q (d.d) (C^{5b}, $^2J_{PCC}$ 23.8, $^2J_{PCC}$ 5.5, $^2J_{HCC}$ 6.4); 155.43 m (d) (C^{6b}, $^2J_{PNC}$ 7.3); 120.55 d.d.d (d) (C^{7b}, $^1J_{HC}$ 161.8, $^3J_{PNCC}$ 9.5, $^3J_{HCCC}$ 7.3); 129.55 d.d (s) (C^{8b}, $^1J_{HC}$ 161.0, $^3J_{HCCC}$ 8.0); 127.78 d.t (s) (C^{9b}, $^1J_{HC}$ 162.5, $^3J_{HCCC}$ 7.3); 15.41 q.d (d) (C^{10b}, $^1J_{HC}$ 128.8, $^3J_{PCCC}$ 8.4). ^{31}P-{^{1}H} NMR spectrum, δ, ppm (*J*, Hz): 238.5 br.d ($^2J_{PCP}$ 16.6), 156.3 d ($^2J_{PCP}$ 16.6). Mass spectrum, *m*/*z*: 342 [*M*]$^{+\cdot}$.

2-(5-Methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-2,5-dioxo-4,4-bis(diethyldicarbonyl)benzo[2,3-*f*]-1,3,2-dioxaphosphepine (II). To 1.71 g (0.005 mol) of compound **I** in 10 ml of dichloromethane under an inert atmosphere at cooling to –10°C was added 0.87 g (0.005 mol) of diethyl mesoxalate. On removing the solvent light-yellow oily substance was obtained that was washed with a mixture of hexane and dichloromethane and dried in a vacuum. Yield 89%. IR spectrum, ν, cm^{-1}: 3412, 3119, 3058, 2985, 2940, 2874, 2696, 1752, 1690, 1603, 1562, 1545, 1494, 1477, 1452, 1388, 1370, 1268, 1239, 1207, 1156, 1113, 1076, 1056, 1021, 925, 851, 831, 781, 738, 703, 628, 584, 557, 512. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.06 d. d (H^6, 1H, $^3J_{HCCH}$ 7.9, $^4J_{HCCCH}$ 1.7), 7.68 d (H^{7b}, 1H, $^3J_{HCCH}$ 8.2), 7.59 d.d.d (H^8, 1H, $^3J_{HCCH}$ 7.4, $^3J_{HCCH}$ 8.0, $^4J_{HCCCH}$ 0.8), 7.38 d.d (H^{8b}, 1H, $^3J_{HCCH}$ 8.1, $^3J_{HCCH}$ 7.3), 7.27–7.32 m (H^{9b}, H^{7b}, 2H), 7.10 d (H^9, 1H, $^3J_{HCCH}$ 8.2), 4.41 q (part *B* of *AB* system, $^3J_{HAHB}$ 7.1), 4.27 q (part *A* of *AB* system, $^3J_{HAHB}$ 7.1), 2.71 s (H^{10b}, 1H), 1.33 t (H^{12}, 3H, $^3J_{HCCH}$ 7.1), 1.18 t (H^{15}, 3H, $^3J_{HCCH}$ 7.1). ^{13}C NMR spectrum (the appearance of the signal in the spectrum ^{13}C-{^{1}H} is given in parentheses), δ, ppm (*J*, Hz): 88.62 d (d) (C^4, $^2J_{POC}$ 8.3); 185.34 d (s) (C^5, $^3J_{HCCC}$ 3.3); 125.88 m (d) (C^{5a}, $^3J_{POCC}$ 1.8); 131.81 br. d.d.d (d) (C^6, $^1J_{HC}$ 166.3, $^3J_{HCCC}$ 8.4, $^5J_{POCCCC}$ 1.4); 126.63 d.d.d (d) (C^7, $^1J_{HC}$ 164.4, $^3J_{HCCC}$ 8.2, $^5J_{POCCCC}$ 1.0); 137.00 d.d.d.d (s) (C^8, $^1J_{HC}$ 164.1, $^3J_{HCCC}$ 8.9, $^2J_{HCC}$ 2.0, $^2J_{HCC}$ 1.2); 122.25 d.d.d.d (d) (C^9, $^1J_{HC}$ 159.8, $^3J_{POCC}$ 5.7, $^2J_{HCC}$ 2.3, $^2J_{HCC}$ 1.0); 149.20 d.d.d.d (s) (C^{9a}, $^2J_{POC}$ 8.4, $^3J_{HCCC}$ 7.0, $^3J_{HCCC}$ 5.2, $^2J_{HCC}$ 2.3); 163.00 d.t (d) (C^{10}, $^3J_{POCC}$ 7.4, $^3J_{HCCC}$ 3.4); 162.04 d.t (d) (C^{13}, $^3J_{POCC}$ 8.3, $^3J_{HCCC}$ 3.4); 63.73 t.q (s) (C^{11}, $^1J_{HC}$ 149.5, $^2J_{HCC}$ 4.4); 63.52 t.q (s) (C^{14}, $^1J_{HC}$ 149.5, $^2J_{HCC}$ 4.4); 13.80 q.t (c) (C^{12}, $^1J_{HC}$ 127.4, $^2J_{HCC}$ 2.6); 13.71 q.t (c) (C^{15}, $^1J_{HC}$ 127.7, $^2J_{HCC}$ 2.6); 132.13 d.d.q (d.d) (C^{4b}, $^1J_{PC}$ 199.2, $^1J_{PC}$ 50.3, $^3J_{HCCC}$ 2.8, $^3J_{HCCC}$ 2.8); 158.90 d.d.q (d.d) (C^{5b}, $^2J_{PCC}$ 11.0, $^2J_{PCC}$ 5.0, $^2J_{HCC}$ 6.6); 142.60 t.d (d) (C^{6b}, $^2J_{PNC}$ 9.0, $^2J_{HCC}$ 2.8); 120.57 d.d.d.d (d) (C^{7b}, $^1J_{HC}$ 162.2, $^3J_{PNCC}$ 9.7, $^3J_{HCCC}$ 7.9, $^2J_{HCC}$ 1.4); 129.54 d.d.d (s) (C^{8b}, $^1J_{HC}$ 162.3, $^3J_{HCCC}$ 8.1, $^2J_{HCC}$ 1.1); 128.13 d.t (s) (C^{9b}, $^1J_{HC}$ 161,4, $^3J_{HCCC}$ 7.5); 15.63 q (s) (C^{10b}, $^1J_{HC}$ 129.6). ^{31}P-{^{1}H} NMR spectrum, δ, ppm (*J*, Hz): 251.30 br.d ($^2J_{PCP}$ 76.3), 14.9 d ($^2J_{PCP}$ 76.3). Mass spectrum, *m*/*z*: 516 [*M*]$^{+\cdot}$, 487 [*M* – C_2H_4], 470 [*M* – OEt + H], 424 [*M* – 2 C_2H_4], 398 [*M* –C(C(O)OEt)$_2$], 313 [*M* – C(C(O)OEt)$_2$ – C(O)], 121 [$C_6H_4OHC(O)$], 92 [C_6H_4O], 77 [C_6H_5].

NMR spectra were registered on spectrometers Bruker MSL-400 (^{31}P, 162.0 MHz), Bruker Avance-600 (^{1}H, 600 MHz; ^{13}C, ^{13}C-{^{1}H}, DEPT, 150.9 MHz) in $CDCl_3$. As internal reference served HMDS (^{1}H) or solvent (^{13}C); H_3PO_4 was used as external reference (^{31}P). IR spectra were recorded on a spectrophotometer Bruker Vector-22 from mulls of the samples in mineral oil. Mass spectra were measured on an instrument DFS Thermo Electron Corporation (ionizing electrons energy 70 eV, ion source

temperature 290°C, direct admission, vaporizer temperature in the range from 100 to 350°C).

ACKNOWLEDGMENTS

The study was performed under the financial support of the Russian Foundation for Basic Research (grant no. 10-03-00525).

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