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LETTERS TO THE EDITOR

Reaction of Ethyl Trifluoropyruvate with 2-(5-Methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-benzo[*d*]-1,3,2-dioxaphosphorin-4-one. Effect of Exocyclic Substituent on Chemoselectivity

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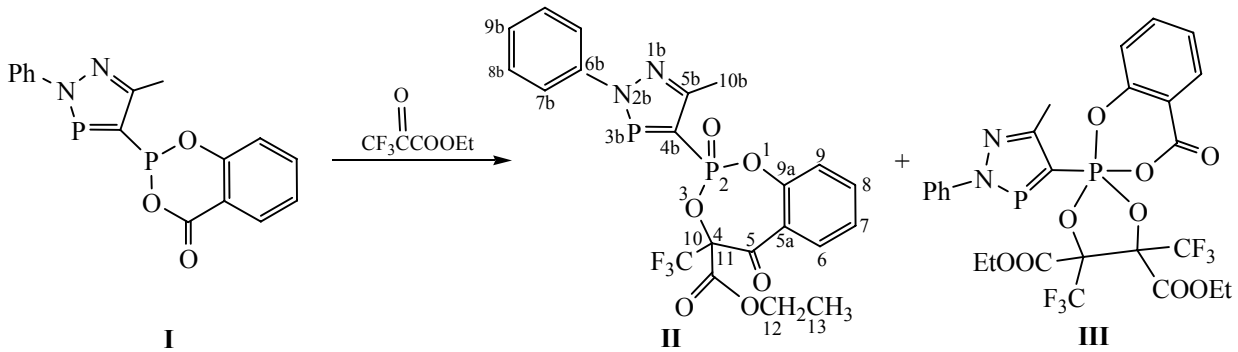
Benzo[*d*]-1,3,2-dioxaphosphorin-4-ones (P^{III}-phosphorrylated cyclic derivatives of salicylic acid), containing a nucleophilic phosphorus atom and electrophilic endocyclic carbonyl group, exhibit a specific reactivity. They react readily to increase the ring to seven-membered one by the action of activated systems with multiple bonds [1–6]. Introduction to the phosphorus atom of the benzo[*d*]-1,3,2-dioxaphosphorin-4-one an exocyclic substituent, the $\lambda^3\sigma^2$-diazaphosphol fragment containing the P^{II} atom, could change the direction of the interaction with such activated unsaturated systems as carbonyl compounds. Indeed, it appears that the weak-acceptor and bulky diazaphosphol moiety in the compound **I** leads to a change of the reaction direction with ethyl trifluoropyruvate. In contrast to the ordinary derivatives of benzo[*d*]1,3,2-dioxaphosphorin-4-one [7], here predominates (>90%) the formation of a (P–C → P–OC)-regrouping product, the 1,3,2-dioxaphosphepin derivative **II** involving a dioxaphosphorine fragment only. The trifluoropyruvate ester contains a prochiral carbonyl group, which is the source of the second chiral center (C^4), causing the formation of two diastereomers (55:45) of the reaction product **II**, whose structure was established by the NMR and mass spectrometry. The ^1H, $^{13}C–\{^1H\}$, $^{31}P–\{^1H\}$ NMR spectra of the compound **II** purified from the volatile impurities contain a double set of signals that can not be attributed to one or other diastereomers due to their close arrangement. The minor reaction direction (<8%) is the formation of a pentacoordinated phosphorus atom derivative **III**, whose signals in the $^{31}P–\{^1H\}$ NMR spectrum are: –32.3 d, –34.1 d (5:1) (P^{IV}), 254.0 br.d (P^{II}) ($^2J_{PCP}$ 87.2–87.3 Hz).

Thus, the exocyclic 1,2,3-diazaphosphol-4-yl substituent affects the chemoselectivity of the reaction



I **II** **III**

of benzo[*d*]-1,3,2-dioxaphosphorin-4-one with ethyl trifluoropyruvate, directing mainly the process to expand the 1,3,2-dioxaphosphorinone ring to 1,3,2-dioxaphosphepin.

Ethyl-[2-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-1,3-dioxa-4-trifluoromethylbenzo[*f*]-1,3,2-dioxaphosphepin-4-yl]carboxylate (II). A mixture of compound **I** (3.42 g, 0.01 mol) and ethyl trifloropyruvate (2.21 g, 0.013 mol), obtained in 15 ml of diethyl ether at –5°C in an inert atmosphere, was kept for 30 min to reach 20°C and 1 day at 20°C. The solvent was distilled off, the residue was washed with hexane. The resulting pale yellow oily substance containing compound **II** (>94%) was dried in a vacuum of 12 mm Hg. Yield 80%. IR spectrum, ν, cm^{-1}: 3056, 2986, 2941, 2835, 2694, 1770, 1705, 1603, 1493, 1428, 1451, 1387, 1371, 1282, 1224, 1156, 1141, 1069, 1025, 925, 846, 739, 704, 691, 673, 652, 640, 618. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.02 d.d (H^6, 1H, $^3J_{HCCH}$ 7.9, $^4J_{HCCCH}$ 1.7), 7.91 d.d (H^6, 1H, $^3J_{HCCH}$ 7.9, $^4J_{HCCCH}$ 1.7), 7.71 br.d (H^7, 1H, $^3J_{HCCH}$ 8.2), 7.56 br.d (H^7, 1H, $^3J_{HCCH}$ 8.2), 7.62 br.d.d.d (H^8, 1H, $^3J_{HCCH}$ 8.2, $^3J_{HCCH}$ 7.9, $^4J_{HCCCH}$ 1.4), 7.51 br.d.d.d (H^8, 1H, $^3J_{HCCH}$ 8.2, $^3J_{HCCH}$ 7.9, $^4J_{HCCCH}$ 1.7), 7.36 and 7.34 two m (H^{8b}), 7.30–7.35 m ($H^{7b,9b}$), 7.02 and 7.28 two br.d (H^9, $^3J_{HCCH}$ 8.2), 4.43 m (OCH_2, 2H, AB-part of ABX_3 system, $^2J_{AB}$ 10.7), 4.19 and 4.06 two m (OCH_2, 2H, AB-part of ABX_3 system, $^2J_{AB}$ 10.7), 2.76 s (H^{10b}, 3H), 2.63 s (H^{10b}, 3H), 1.32 t ($OCCH_3$, 3H, $^3J_{HCCH}$ 7.2), 1.11 t ($OCCH_3$, 3H, $^3J_{HCCH}$ 7.2). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz) (signals multiplicity in the $^{13}C–\{^1H\}$ NMR spectrum is given in brackets): 84.57 q.d (q.d) (C^4, $^2J_{POC}$ 7.2, $^2J_{FCC}$ 28.9), 84.86 q.d (q.d) (C^4, $^2J_{POC}$ 7.3, $^2J_{FCC}$ 28.9), 185.60 d.d (s) (C^5, $^3J_{HC^6CC^5}$ 4.3, $^4J_{HC^7CCC^5}$ 1.5), 182.35 br.d (s) (C^5, $^3J_{HC^6CC^5}$ 4.0), 125.86 br.m (br.s) (C^{5a}), 126.70 br.m (br.s) (C^{5a}), 131.75 d.d (c) (C^6, $^1J_{HC^6}$ 166.4, $^3J_{HC^8CC^6}$ 8.6), 131.61 d.d (s) (C^6, $^1J_{HC^6}$ 166.8, $^3J_{HC^8CC^6}$ 8.2), 126.70 d.d (s) (C^7, $^1J_{HC^7}$ 165.4, $^3J_{HC^9CC^7}$ 7.7), 126.61 d.d (s) (C^7, $^1J_{HC^7}$ 164.9, $^3J_{HC^9CC^7}$ 7.6), 137.87 d.d (s) (C^8, $^1J_{HC^8}$ 163.5, $^3J_{HC^6CC^8}$ 8.8, $^2J_{HCC^8}$ 1.3), 136.76 br.d.d.d (s) (C^8, $^1J_{HC^8}$ 161.6, $^3J_{HC^6CC^8}$ 8.8, $^2J_{HCC^8}$ 2.3), 121.92 d.m (d) (C^9, $^1J_{HC^9}$ 160.0–162.0, $^3J_{POCC^9}$ 6.1), 121.88 d.m (d) (C^9, $^1J_{HC^9}$ 160.0–162.0, $^3J_{POCC^9}$ 6.3), 148.60 d.d.d.d. d (d) (C^{9a}, $^3J_{HCCC^{9a}}$ 10.5, $^3J_{HCCC^{9a}}$ 9.0, $^2J_{POC^{9a}}$ 8.4, $^2J_{HC^9C^{9a}}$ 3.9, $^4J_{HC^7CCC^{9a}}$ 1.7), 147.86 d.d.d.d.d (d) (C^{9a}, $^3J_{HCCC^{9a}}$ 10.5, $^3J_{HCCC^{9a}}$ 9.1, $^2J_{POC^{9a}}$ 8.4, $^2J_{HC^9C^{9a}}$ 4.0, $^4J_{HC^7CCC^{9a}}$ 1.7), 120.65 q.d (q.d) (C^{10}, $^1J_{FC^{10}}$ 286.5, $^2J_{POC^{10}}$ 13.1), 121.25 br.q (br.q) (C^{10}, $^1J_{FC^{10}}$ 284.0–287.0), 161.06 d.t (d) (C^{11}, $^3J_{HC^{12}OC^{11}}$ 3.4–3.5, $^3J_{POCC^{11}}$ 1.4), 160.67 d.t (d) (C^{11}, $^3J_{POCC^{11}}$ 3.5, $^3J_{HC^{12}OC^{11}}$ 3.5), 64.58 t.q (s) (C^{12}, $^1J_{HC^{12}}$ 150.1, $^2J_{HC^{13}C^{12}}$ 4.5), 64.24 t.q (s) (C^{12}, $^1J_{HC^{12}}$ 150.2, $^2J_{HC^{13}C^{12}}$ 4.5), 13.39 q.t (s) (C^{13}, $^1J_{HC^{13}}$ 127.9, $^2J_{HC^{12}C^{13}}$ 2.6), 13.18 q. t (s) (C^{13}, $^1J_{HC^{13}}$ 127.9, $^2J_{HC^{12}C^{13}}$ 2.6), 131.83 d.d.q (d.d) (C^{4b}, $^1J_{P^3bC^{4b}}$ 67.2, $^1J_{P^2C^{4b}}$ 49.5, $^3J_{HC^{10b}CC^{4b}}$ 3.0–3.1), 158.95 d.q.d (d.d) (C^{5b}, $^2J_{P^3bCC^{5b}}$ 11.2, $^2J_{HC^{10b}C^{5b}}$ 6.5–6.6, $^2J_{P^2CC^{5b}}$ 4.5), 158.51 d.q.d (d.d) (C^{5b}, $^2J_{P^3bCC^{5b}}$ 10.8, $^2J_{HC^{10b}C^{5b}}$ 6.4–6.5, $^2J_{P^2CC^{5b}}$ 4.2), 142.43 br.d.t (d) (C^{6b}, $^2J_{PNC^{6b}}$ 11.0, $^3J_{HC^{8b}CC^{6b}}$ 8.8–9.0), 142.13 br.d.t (d) (C^{6b}, $^2J_{PNC^{6b}}$ 10.9, $^3J_{HC^{8b}CC^{6b}}$ 8.8–9.0), 120.42 d.m (d) (C^{7b}, $^1J_{HC^{7b}}$ 162.0, $^3J_{PNCC^{7b}}$ 9.7), 120.14 d.m (d) (C^{7b}, $^1J_{HC^{7b}}$ 162.0, $^3J_{PNCC^{7b}}$ 9.7), 129.42 d.d (s) (C^{8b}, $^1J_{HC^{8b}}$ 161.9, $^3J_{HCCC^{8b}}$ 7.7), 129.35 d.d (s) (C^{8b}, $^1J_{HC^{8b}}$ 162.0, $^3J_{HCCC^{8b}}$ 7.7), 128.07 br.d.t (s) (C^{9b}, $^1J_{HC^{9b}}$ 163.3, $^3J_{HC^{7b}CC^{9b}}$ 7.6), 128.10 br.d.t (s) (C^{9b}, $^1J_{HC^{9b}}$ 163.3, $^3J_{HC^{7b}CC^{9b}}$ 7.6), 15.33 br.q.d (br.d) (C^{10b}, $^1J_{HC^{10b}}$ 129.7, $^3J_{P^3bCCC^{10b}}$ 3.5). $^{31}P–\{^1H\}$ NMR spectrum (162.0 MHz), δ_P, ppm (*J*, Hz): 252.1 br.d ($^2J_{PCP}$ 74.1), 250.1 br.d ($^2J_{PCP}$ 82.3), 16.1 d ($^2J_{PCP}$ 82.3), 12.4 d ($^2J_{PCP}$ 74.1). Mass spectrum (EI), *m*/*z*: 512 $[M]^{+\bullet}$ ($C_{21}H_{17}F_3N_2O_6P_2$, M_{calc} 512), 484 [*M* – C_2H_4], 466 [*M* – OEt – H], 439 [*M* – C(O)OEt – H], 421 [*M* – C(O)OEt – F + H], 403 [*M* – C(O)OEt – 2F + 2H], 382 [*M* – C(O)OEt – 3F + 2H], 238 [$C_9H_8N_2O_2P_2$], 222 [$C_9H_8N_2OP_2$], 178 [$C_8H_3O_3P$], 121 [$C_7H_4O_2$ + H], 77 [C_6H_5].

The NMR spectra (^{1}H, ^{13}C, $^{13}C–\{^1H\}$, DEPT, ^{31}P) were recorded on a Bruker Avance-400 instrument in $CDCl_3$ relative to internal HMDS (^{1}H) or solvent (^{13}C) and external H_3PO_4 (^{31}P). The IR spectra were recorded on a Bruker Vector-22 instrument from the sample film between KBr pellets. The mass spectrum was registered on a DFS Thermo Electron Corporation (USA) instrument. The energy of ionizing electrons is 70 eV, ion source temperature is 290°C, heating of the ampoule-evaporator of the direct input system was performed in the range from 100 to 350°C. Processing of mass spectral data was performed using a Xcalibur software.

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