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LETTERS TO THE EDITOR

Unusual Direction of the Reaction of 2-Trifluoroacetoxy-1,3-benzodioxaphosphorin-4-one with *N*-Methyl-*p*-Methoxybenzalimine

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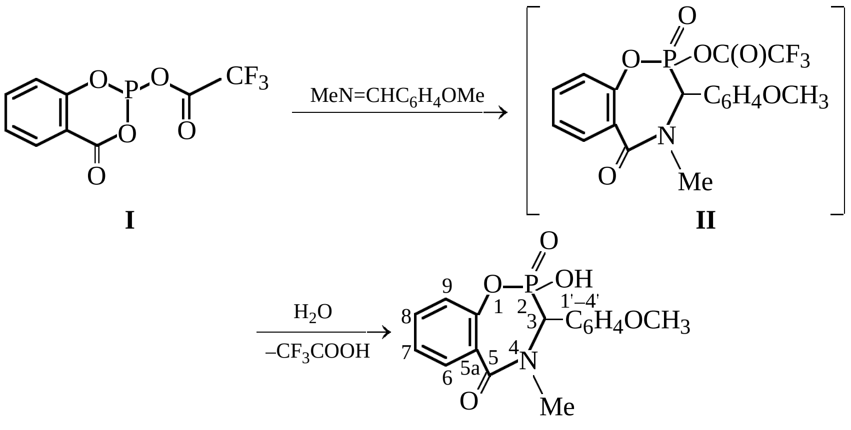
Mixed anhydrides of phosphorous and carboxylic acids (acyl phosphites) easily react with electrophilic and nucleophilic agents and present considerable interest as starting materials in organophosphorus synthesis [1]. Mixed anhydrides of trifluoroacetic and acyclic phosphorous acids are also highly prone to rearrangement to the corresponding α-(trifluoromethylcarbonyl) phosphonates [2]; under the action of imines they easily give 1-(*N*-trifluoroacylamino)alkyl phosphonates [3]. Mixed cyclic anhydride of salicylphosphorous and trifluoroacetic acids **I** [4] is a stable compound that contains two sufficiently active carbonyl groups bound with phosphorus and is readily react with nucleophilic imines. In the present work we showed for the first time that compound **I**, even though its exocyclic carbonyl group is strongly activated by the electron-acceptor trifluoromethyl substituent, unexpectedly reacts with *N*-methyl-*p*-methoxybenzalimine by the endocyclic carbonyl group. Phosphepine **II** that forms is susceptible to hydrolysis and easily converts into phosphonic acid **III** during isolation.



The ^{31}P NMR spectrum (in DMF) contains a signal at δ_P 22.7 ppm, and the IR spectrum contains strong C(O)N (1650 cm^{-1}), P=O (1290 cm^{-1}), and OH (3200 cm^{-1}, broad) absorption bands. The structure of phosphonic acid **III** was also confirmed by ^{1}H and ^{13}C NMR spectroscopy.

2-Hydroxy-4-methyl-3-(4-methoxyphenyl)-1,4,2λ^5-benzoxazaphosphepin-5-one 2-oxide (III). *N*-Metyl-*p*-methoxybenzalimine, 5.45 g, was slowly added at –25°C to a mixture of 10.25 g of 2-(trifluoromethylcarbonyloxy)-1,3-benzodioxaphosphorin-4-one (**I**) and 20 ml of ether. After 6–8 h, the white crystals

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were filtered off, several times washed with ether, and dried. Prolonged handling of the filtrate gave an additional crop of compound **III**. Yield 77%, mp 198°C. ^{1}H NMR spectrum (DMF-d_7) δ, ppm (J, Hz): 11.0 br.s (OH), 7.14 d.d (H^{6}, $^{3}J_{\mathrm{HCCH}}$ 7.7, $^{4}J_{\mathrm{HC^{8}CCH}}$ 1.8), 7.07 d.d.d.d (H^{8}, $^{3}J_{\mathrm{HC^{7}CH}}$ 7.5, $^{3}J_{\mathrm{HC^{9}CH}}$ 8.2, $^{4}\mathrm{HC^{6}CCH}$ *1.8,* $^{5}J_{\mathrm{POCCCH}}$ 1.2), 6.85 d.d.d.d (H^{7}, $^{3}J_{\mathrm{HC^{8}CH}}$ 7.5, $^{3}J_{\mathrm{HC^{6}CH}}$ 7.7, $^{4}J_{\mathrm{HC^{9}CCH}}$ 1.1, $^{6}J_{\mathrm{POCCCH}}$ 1.1), 6.72 d.d.d. (H^{9}, $^{3}J_{\mathrm{HC^{8}CH}}$ 8.2, $^{4}J_{\mathrm{HC^{7}CCH}}$ 1.1, $^{4}J_{\mathrm{POCCH}}$ 1.2), 4.67 d (H^{3}, $^{2}J_{\mathrm{PCH}}$ 14.1), 7.16 m and 6.46 m (H$^{2'}$ and H$^{3'}$, $AA'XX'$ spectrum, $^{3}J_{AX} = {}^{3}J_{A'X'} = 8.7$), 3.31 s (OCH$_3$), 2.37 d (NCH$_3$, $^{4}J_{\mathrm{PCNCH}}$ 0.5). ^{13}C NMR spectrum, δ$_{\mathrm{C}}$, ppm: 54.99 d (d.d) (C^{3}, $^{1}J_{\mathrm{PC}}$ 149.5, $^{1}J_{\mathrm{HC}}$ 131.6), 166.67 s (q.d.d) (C^{5}, $^{3}J_{\mathrm{HCNC}}$ 3.7–4.0, $^{3}J_{\mathrm{HC^{6}CC}}$ 3.7–4.0, $^{3}J_{\mathrm{HC^{3}CC}}$ 2.1), 127.21 d(m) (C^{5a}, $^{3}J_{\mathrm{POCC}}$ 1.6), 129.51 s (br.d.d) (C^{6}, $^{1}J_{\mathrm{HC}}$ 164.7, $^{3}J_{\mathrm{HC^{8}CC}}$ 7.8), 124.80 s (d.d) (C^{7}, $^{1}J_{\mathrm{HC}}$ 165.0, $^{3}J_{\mathrm{HC^{9}CC}}$ 7.8), 131.72 s (d.d) (C^{8}, $^{1}J_{\mathrm{HC}}$ 163.9, $^{3}J_{\mathrm{HC^{6}CC}}$ 9.3), 120.57 d (d.m) (C^{9}, $^{1}J_{\mathrm{HC}}$ 163.3, $^{3}J_{\mathrm{HC^{7}CC}}$ 6.3, $^{3}J_{\mathrm{POCC}}$ 3.1), 147.41 d (m) (C^{9a}, $^{3}J_{\mathrm{POC}}$ 8.3, $^{3}J_{\mathrm{HCCC}}$ 8.5–9.5, $^{3}J_{\mathrm{HHCCC}}$ 8.5–9.5, $^{3}J_{\mathrm{HCCC}}$ 9.5–9.9, $^{2}J_{\mathrm{HCC}}$ 2.8, $^{4}J_{\mathrm{HCCCC}}$ 1.2), 121.78 d (t.d.d) (C$^{1'}$, $^{3}J_{\mathrm{HC^{3'}CC}}$ 8.3, $^{2}J_{\mathrm{PCC}}$ 1.2), 131.18 d (d.d.d.d) (C$^{2'}$, $^{1}J_{\mathrm{HC}}$ 162.5, $^{3}J_{\mathrm{PCCC}}$ 8.2, $^{3}J_{\mathrm{HCCC}}$ 4.9), 113.30 s (d.d) (C$^{3'}$, $^{1}J_{\mathrm{HC}}$ 165.1, $^{3}J_{\mathrm{HCCC}}$ 4.8), 159.09 s (m) (C$^{4'}$), 54.34 s (q) (OCH$_3$, $^{1}J_{\mathrm{HC}}$ 144.0), 30.29 s (q.d) (NCH$_3$, $^{1}J_{\mathrm{HC}}$ 139.9, $^{3}J_{\mathrm{HCNC}}$ 3.2). Found, %: C 57.33; H 4.77; N 3.93; P 9.44. $C_{16}H_{16}NO_5P$. Calculated, %: C 57.65; H 4.80; N 4.20; P 9.31.

The NMR spectra were recorded on Varian Unity-300 (^{1}H, ^{31}P) and Bruker MSL-500 (^{13}C) spectrometers against internal HMDS or external H_3PO_4. The IR spectrum was obtained on a Specord M-80 instrument for suspension in mineral oil.

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