ISSN 1070-4280, Russian Journal of Organic Chemistry, 2009, Vol. 45, No. 12, pp. 1868–1870. © Pleiades Publishing, Ltd., 2009. Original Russian Text © L.M. Burnaeva, V.F. Mironov, Yu.Yu. Borisova, I.V. Konovalova, 2009, published in Zhurnal Organicheskoi Khimii, 2009, Vol. 45, No. 12, pp. 1869–1871.

> SHORT COMMUNICATIONS

Reaction of 2-Substituted 1-Phenyl-1,2-dihydro-4*H*-3,1,2benzoxazaphosphinin-4-ones with Bis(2,2,3,3-tetrafluoropropyl) 2-(4-Chlorobenzylidene)malonate

L. M. Burnaeva^a, V. F. Mironov^{a, b}, Yu. Yu. Borisova^a, and I. V. Konovalova^a

^a V.I. Ul'yanov-Lenin Kazan State University, ul. Kremlevskaya 18, Kazan, 420008 Tatarstan, Russia

^b Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia

Received April 23, 2009

DOI: 10.1134/S1070428009120239

Alkylidene derivatives of β -dicarbonyl compounds possess an activated C=C bond and are capable of reacting with cyclic and acyclic tervalent phosphorus compounds to give five- or four-coordinate phosphorus derivatives (phosphoranes, oxaphospholes, etc.) via formation of a new phosphorus–carbon bond [1–3]. Phosphorylated salicylic acid derivatives like 2-substituted 1,3,2-benzodioxaphosphinin-4-ones are known to react with arylmethylidenemalonates under mild conditions to produce 3-aryl-1,2 λ^5 -benzoxaphosphepin-5-one 2-oxides via formation of new C–C and P–C bonds [4–6].

The present communication reports on the reaction of bis(2,2,3,3-tetrafluoropropyl) 2-(4-chlorobenzylidene)malonate (I) with phosphorylated derivatives of *N*-phenylanthranilic acid, 2-substituted 1-phenyl-1,2dihydro-4*H*-3,1,2-benzoxazaphosphinin-4-ones IIa and IIb. These reactions led to the formation of benzofused seven-membered phosphorus-containing heterocycles, bis(2,2,3,3-tetrafluoropropyl) 2-substituted 3-(4-chlorophenyl)-5-oxo-1-phenyl-1,2,3,4-tetrahydro-1,2 λ^5 -benzazaphosphepine-4,4-dicarboxylate 2-oxides **IIIa** and **IIIb**. The reactions occurred under mild conditions (methylene chloride, 20°C) with a fairly high (compound **IIa**) or moderate (**IIb**) stereoselectivity: the ratio of diastereoisomers with respect to C³ was 10:1 for **IIIa** (δ_P 25.0 and 25.3 ppm) and 5:3 for **IIIb** (δ_P 20.2 and 20.1 ppm). The major stereoisomer of **IIIa** was isolated as individual substance by reprecipitation. The structure of the products was confirmed by the ¹H, ¹³C, and ¹⁹F NMR spectra. The fluoroalkoxycarbonyl substituents are nonequivalent, and the corresponding signals in the NMR spectra were doubled.

Presumably, the reaction follows a scheme involving nucleophilic attack by the phosphorus atom in III on the β -carbon atom at the double bond in ester I with



formation of dipolar intermediate **A** which is stabilized via intramolecular nucleophilic replacement at the carbonyl carbon atom with formation of a new C–C bond closing azaphosphepine ring.

Reaction of bis(2,2,3,3-tetrafluoropropyl) 2-(4-chlorobenzylidene)malonate (I) with 2-substituted 1-phenyl-1,2-dihydro-4*H***-3,1,2-benzoxaza-phosphinin-4-ones IIa and IIb** (general procedure). A mixture of 0.03 mol of diester I and 0.03 mol of benzoxazaphosphinine IIa or IIb in 15 ml of methylene chloride was kept for 2 months at room temperature. The solvent was distilled off to leave compound IIIa or IIIb as a light red thick oily liquid.

Bis(2,2,3,3-tetrafluoropropyl) 3-(4-chlorophenyl)-5oxo-1,2-diphenyl-1,2,3,4-tetrahydro-1,2λ⁵-benzazaphosphepine-4,4-dicarboxylate 2-oxide (IIIa) (diastereoisomer ratio 10:1) was precipitated with diethyl ether-pentane (1:1); the major isomer was isolated as a light pink powder. Yield 78%, mp 59°C. IR spectrum, v, cm⁻¹: 2920, 2854, 1758, 1686, 1594, 1460, 1377, 1283, 1250, 1197, 1163, 1111, 1015, 976, 837, 753, 721, 698, 554. ¹H NMR spectrum, δ , ppm (*J*, Hz): major diastereoisomer: 4.01 br.d.t (1H, OCH₂, ${}^{2}J_{HH} =$ 12.5, ${}^{3}J_{\text{HF}} = 12.5$), 4.29 br.d.t (1H, OCH₂, ${}^{2}J_{\text{HH}} = 12.5$, ${}^{3}J_{\text{HF}} = 13.2$), 4.41 br.d.t (1H, OCH₂, ${}^{2}J_{\text{HH}} = 13.2$, ${}^{3}J_{\text{HF}} =$ 12.5), 4.63 br.d.t (1H, OCH₂, ${}^{2}J_{HH} = 12.5$, ${}^{3}J_{HF} = 12.5$), 4.53 d (1H, 3-H, ${}^{2}J_{HP} = 12.5$), 5.70 t.t (1H, CHF₂, ${}^{2}J_{HF} = 52.8$, ${}^{3}J_{HF} = 3.7$), 5.99 t.t (1H, CHF₂, ${}^{2}J_{HF} =$ 52.8, ${}^{3}J_{\text{HF}} = 5.1$), 6.85 d (1H, 9-H, ${}^{3}J_{\text{HH}} = 7.3$), 7.02 d (2H, 11-H, 15-H, ${}^{3}J_{HH} = 8.1$), 7.10 m (3H, 12-H, 13-H, 14-H), 7.95 d.d (1H, 6-H, ${}^{3}J_{HH} = 7.3$, ${}^{4}J_{HH} = 1.5$). ¹³C NMR spectrum, $\delta_{\rm C}$ ppm (J, Hz) (hereinafter, multiplicity of the corresponding signal in the proton-decoupled spectrum is given in parentheses): major diastereoisomer: 48.13 br.d.d.t (d) (C^3 , ${}^1J_{PC} = 81.87$, ${}^{1}J_{\rm CH} = 127.2, {}^{3}J_{\rm CH} = 3.5-3.7), 71.74$ br.d.d (d) (C⁴, ${}^{2}J_{CH} = 127.2$, ${}^{2}J_{CH} = 5.5-5.7$, 71.74 bilded (d) (C⁵, ${}^{2}J_{CH} = 6.0$, ${}^{2}J_{CP} = 1.6-1.7$), 193.24 br.d.d (d) (C⁵, ${}^{3}J_{CH} = 4.7-5.0$), 128.22 m (d) (C^{5a}, ${}^{3}J_{CP} = 3.0$), 132.49 d.d (s) (C⁶, ${}^{1}J_{CH} = 165.0$, ${}^{3}J_{CH} = 8.3$), 127.62 d.d (s) (C⁷, ${}^{1}J_{CH} = 164.8$, ${}^{3}J_{CH} = 8.0$), 135.32 d.d (s) (C⁸, ${}^{1}J_{CH} = 163.4$, ${}^{3}J_{CH} = 8.6$), 130.50 br.d.m (d) (C^{9} , ${}^{1}J_{CH} = 163.1$, ${}^{3}J_{CH} = 6.2$, ${}^{3}J_{CP} = 3.0$), 143.21 d.d.m (d) (C^{9a}), 142.64 m (d) (C^{10} , ${}^{3}J_{CH} = 163.1$ 8.7–9.0, ${}^{2}J_{CP} = 4.6$), 125.84 d.m (d) (C¹¹, C¹⁵, ${}^{1}J_{CH} = 164.9$, ${}^{3}J_{CP} = 3.1$), 129.26 d.d (s) (C¹², C¹⁴, ${}^{1}J_{CH} =$ 161.1, ${}^{3}J_{CH} = 8.4$), 125.69 d.t (s) (C¹³, ${}^{1}J_{CH} = 162.9$, ${}^{3}J_{CH} = 7.4$, 132.71 m (br.s) (C¹⁶), 133.26 br.d (br.s) $C_{CH}^{17} = 7.4$, 132.71 m (b.s) (C⁻¹), 133.20 b.d (b.s) (C¹⁷, C²¹, ${}^{1}J_{CH} = 166.6$), 128.53 br.d (br.s) (C¹⁸, C²⁰, ${}^{1}J_{CH} = 167.6$), 134.89 t.t.d (d) (C¹⁹, ${}^{3}J_{CH} = 10.5$, ${}^{2}J_{CH} = 3.0$, ${}^{5}J_{CP} = 2.7$), 163.04 d.d.t (d) (C²² or C²⁶, ${}^{3}J_{CH} = 8.7-9.0$, ${}^{3}J_{CP} = 6.3$, ${}^{2}J_{CH} = 3.2$), 164.04 d.t (d) (C²⁶ or

 C^{22} , ${}^{3}J_{CP} = 14.1$, ${}^{3}J_{CH} = 3.0$), 61.03 t.t (t) (C^{23} or C^{27} , ${}^{1}J_{\text{CH}} = 152.4, {}^{2}J_{\text{CF}} = 29.7), 61.75 \text{ t.t (t) } (C^{27} \text{ or } C^{23}),$ ${}^{1}J_{CH} = 152.6, {}^{2}J_{CF} = 30.8), 113.54 \text{ t.t.m (t.t) (C}^{24} \text{ or C}^{28},$ ${}^{1}J_{CF} = 251.2, {}^{2}J_{CF} = 28.1, {}^{2}J_{CH} = 4.0, 3.4), 113.86 \text{ t.t.m}$ (t.t) (C²⁸ or C²⁴, ${}^{1}J_{CF} = 251.2, {}^{2}J_{CF} = 28.1, {}^{2}J_{CH} = 4.0, 3.4)$ 3.4–3.5), 108.81 t.d.t.m (t.t) (C^{25} or C^{29} , ${}^{1}J_{CF} = 250.5$, ${}^{1}J_{CH} = 192.7, {}^{2}J_{CF} = 33.6), 108.91 \text{ t.d.t.m}$ (t.t) (C²⁹ or C^{25} , ${}^{1}J_{FC} = 250.5$, ${}^{1}J_{CH} = 193.4$, ${}^{2}J_{CF} = 35.7$), 130.85 d.t (d) $(C^{30}, {}^{1}J_{PC} = 122.4, {}^{3}J_{CH} = 7.5), 131.04 \text{ d.d.d.d}$ (d) $(C^{31}, C^{35}, {}^{1}J_{CH} = 162.6, {}^{2}J_{CP} = 9.0, {}^{3}J_{CH} = 8.0-8.1), 128.68 \text{ d.d.d}$ (d) $(C^{32}, C^{34}, {}^{1}J_{CH} = 162.6, {}^{2}J_{CP} = 12.8, {}^{3}J_{CH} = 8.0, 132.73 \text{ d.t.d}$ (d) $(C^{33}, {}^{1}J_{CH} = 160.7, {}^{3}J_{CH} = 160.7, {}^{3}$ 8.1, ${}^{4}J_{CP} = 2.8$); the signals were assigned with account taken of the results of APT experiment. ¹⁹F NMR spectrum, $\delta_{\rm F}$, ppm: major diastereoisomer: -124.22 m and -124.44 m (2F, CF₂), -137.99 br.m and -138.66 br.m (2F, CHF₂, ${}^{2}J_{\text{FH}} = 53.4$ Hz); minor diastereoisomer: -125.19 m and -125.75 m (2F, CF₂); -140.05 br.d and -138.70 br.d (2F, CHF₂, ² $J_{FH} = 51.9$ Hz). Mass spectrum: m/z 773 $[M]^+$.

Bis(2,2,3,3-tetrafluoropropyl) 3-(4-chlorophenyl)-2-ethoxy-5-oxo-1-phenyl-1,2,3,4-tetrahydro- $1,2\lambda^5$ -benzazaphosphepine-4,4-dicarboxylate 2-oxide (IIIb) (diastereoisomer ratio 5:3). ¹H NMR spectrum, δ , ppm: major isomer: 4.53 d (1H, 3-H, ${}^{2}J_{HP}$ = 12.5 Hz), 5.58 t (1H, CHF₂, ${}^{2}J_{\text{HF}}$ = 57.0 Hz), 5.88 t $(1H, CHF_2, {}^{2}J_{HF} = 57.2 \text{ Hz}), 1.07 \text{ t} (3H, CH_3, {}^{3}J_{HH} =$ 7.3 Hz). ¹³C NMR spectrum, δ_C , ppm (*J*, Hz): major diastereoisomer: 48.12 d.d.t (d) (C^3 , ${}^{1}J_{CP} = 125.5$, ${}^{1}J_{CH} = 127.7$, ${}^{3}J_{CH} = 3.0$), 72.21 d (s) (C^4 , ${}^{2}J_{CH} = 5.4$), 190.83 br.d.d (s) (C^5 , ${}^{3}J_{CH} = 5.7$, 4.6), 135.03 d.d (s) $(C^8, {}^{1}J_{CH} = 160.1, {}^{3}J_{CH} = 7.0), 123.96 \text{ d.m (d) } (C^9, {}^{1}J_{CH} = 159.5, {}^{3}J_{CP} = 2.2), 142.03 \text{ m (d) } (C^{9a}, {}^{2}J_{CP} = 5.5), 140.90 \text{ m (d) } (C^{10}, {}^{2}J_{CP} = 6.1), 122.48 \text{ d.d.d (s)}$ $(C^{11}, C^{15}, {}^{1}J_{CH} = 159.5, {}^{3}J_{CH} = 5.7, 7.0), 123.57 \text{ d.t (s)}$ $(C^{13}, {}^{1}J_{CH} = 159.1, {}^{3}J_{CH} = 7.5), 134.56 \text{ m (d)} (C^{16},$ $^{2}J_{CP} = 2.8$), 136.80 m (s) (C¹⁹), 164.60 br.d (d) (C²² or C^{26} , ${}^{3}J_{CP} = 12.2$), 163.43 br.d (d) (C^{26} or C^{22} , ${}^{3}J_{CP} = 12.2$), 163.43 br.d (d) (C^{26} or C^{22} , ${}^{3}J_{CP} = 12.2$), 61.31 t.t.m (t) (C^{23} or C^{27} , ${}^{2}J_{CF} = 29.3$, ${}^{1}J_{CH} = 149.9$), 61.41 t.t.m (t) (C^{27} or C^{23} , ${}^{1}J_{CH} = 149.9$, ${}^{2}J_{CF} = 29.3$ 29.3), 113.5–113.7 four t.t (C^{24} , C^{28}), 109.12 d.t.t.m (t.t) (C^{25} or C^{29} , ${}^{1}J_{CF} = 242.2 - 245.0$, ${}^{1}J_{CH} = 197.0$, $^{2}J_{CF} = 34.8$), 108.99 d.t.t.m (t.t) (C²⁹ or C²⁵, $^{1}J_{CF} =$ 242.2–245.0, ${}^{1}J_{CH} = 197.0$, ${}^{2}J_{CF} = 34.8$), 64.56 t.d.q (d) $(C^{30}, {}^{1}J_{CH} = 148.4, {}^{2}J_{CP} = 6.6, {}^{3}J_{CH} = 4.5), 15.27 \text{ q.d.t}$ (d) $(C^{31}, {}^{1}J_{CH} = 127.6, {}^{3}J_{CP} = 6.6, {}^{3}J_{CH} = 3.0-3.5);$ minor diastereoisomer: 47.14 d.d.t (d) (C^3 , ${}^1J_{CP}$ = 132.1, ${}^{1}J_{CH} = 128.0 - 130.0$, ${}^{3}J_{CH} = 2.7 - 3.0$), 73.71 d (s) $(C^4, {}^2J_{CH} = 5.8), 191.29 \text{ br.d.d} (s) (C^5, {}^3J_{CH} = 5.1, 3.8-$ 4.0), 136.04 d.d (s) (C^8 , ${}^1J_{CH} = 164.0$, ${}^3J_{CH} = 6.5$), 128.10 d.m (d) (C^9 , ${}^1J_{CH} = 163.0$, ${}^3J_{CP} = 1.8$), 143.86 m

(br.s) (C^{9a}), 141.55 m (d) (C¹⁰, ${}^{2}J_{CP} = 3.9$), 122.36 d.d.d (s) (C¹¹, C¹⁵, ${}^{1}J_{CH} = 159.5$, ${}^{3}J_{CH} = 5.7$, 6.0), 123.46 d.t (s) (C¹³, ${}^{1}J_{CH} = 159.2$, ${}^{3}J_{CH} = 7.8$), 137.84 m (s) (C¹⁹), 134.90 m (d) (C¹⁶, ${}^{2}J_{CP} = 2.2$), 164.33 m (d) (C²² or C²⁶, ${}^{3}J_{CP} = 18.2$), 163.29 m (d) (C²⁶ or C²², ${}^{3}J_{CP} = 7.2$), 60.53 t.t.m (t) (C²³ or C²⁷, ${}^{1}J_{CH} = 149.9$, ${}^{2}J_{CF} = 29.3$), 60.57 t.t.m (t) (C²⁷ or C²³, ${}^{1}J_{CH} = 149.9$, ${}^{2}J_{CF} = 29.3$), 113.5–113.7 four t.t (C²⁴, C²⁸), 109.18 d.t.t.m (t.t) (C²⁵ or C²⁹, ${}^{1}J_{CF} = 242.2-245.0$, ${}^{1}J_{CH} = 197.0$, ${}^{2}J_{CF} = 34.8$), 109.34 d.t.t.m (t.t) (C²⁹ or C²⁵, ${}^{1}J_{CF} = 242.2-245.0$, ${}^{1}J_{CH} = 197.0$, ${}^{2}J_{CF} = 34.8$), 62.42 t.d.q (d) (C³⁰, ${}^{1}J_{CH} =$ 149.0, ${}^{2}J_{CP} = 7.1$, ${}^{3}J_{CH} = 4.5$), 15.88 q.d.t (d) (C³¹, ${}^{1}J_{CH} = 127.6$, ${}^{3}J_{CP} = 6.1$, ${}^{3}J_{CH} = 3.0-3.5$). Found, %: C 44.97; H 3.60. C₂₅H₂₄ClF₈NO₇P. Calculated, %: C 44.88; H 3.48.

The IR spectra were recorded on a Specord M-80 spectrometer from samples prepared as thin films (neat) or dispersed in mineral oil and placed between KBr plates. The NMR spectra were measured from solutions in CDCl₃ on Varian Unity-300 (300 MHz for ¹H, 121.42 MHz for ³¹P, and 287.2 MHz for ¹⁹F) and Bruker Avance-600 spectrometers (¹³C, ¹³C-{¹H}; APT, 150.9 MHz). The ¹H and ¹³C chemical shifts were determined relative to the residual proton and

carbon signals of the solvent; the ${}^{31}P$ chemical shifts were determined relative to H_3PO_4 as external reference; the ${}^{19}F$ chemical shifts were measured relative to hexafluorobenzene (internal reference) and were then recalculated to trichlorofluoromethane.

REFERENCES

- Arbuzov, B.A., Polezhaeva, N.A., Vinogradova, V.S., and Samitov, Yu.Yu., *Dokl. Akad. Nauk SSSR*, 1967, vol. 173, p. 93.
- Arbuzov, B.A., Dianova, E.N., and Vinogradova, V.S., Izv. Akad. Nauk SSSR, Ser. Khim., 1969, p. 1109.
- Arbuzov, B.A., Dianova, E.N., Vinogradova, V.S., and Petrova, M.V., *Dokl. Akad. Nauk SSSR*, 1970, vol. 195, p. 1094.
- Arbuzov, B.A., Dianova, E.N., and Vinogradova, V.S., Izv. Akad. Nauk SSSR, Ser. Khim., 1970, p. 2543.
- Burnaeva, L.M., Mironov, V.F., Romanov, S.V., Ivkova, G.A., Shulaeva, I.L., and Konovalova, I.V., *Russ. J. Gen. Chem.*, 2001, vol. 71, p. 488.
- Mironov, V.F., Zagidullina, E.R., Ivkova, G.A., Dobrynin, A.B., Gubaidullin, A.T., Latypov, Sh.K., Musin, R.Z., Litvinov, I.A., Balandina, A.A., and Konovalova, I.V., *Arkivoc*, 2004, part (xii), p. 95