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Synthesis of new spirophosphoranes bearing the phosphorus–carbon bond by cascade reactions of 2-(2-methyl-4-oxopent-2-yloxy)benzo-1,3,2-dioxaphosphole with activated carbonyl compounds

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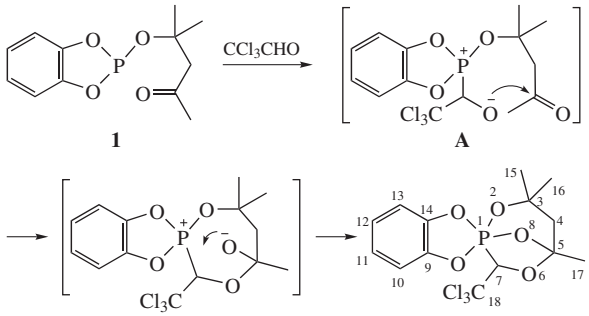
Cascade reactions of 2-(2-methyl-4-oxopent-2-yloxy)benzo-$\sigma^3\lambda^3$-1,3,2-dioxaphosphole with chloral, hexafluoroacetone, mezoxalic acid diethyl ester and trifluoropyruvic acid ethyl ester are a versatile approach to the synthesis of spirophosphoranes bearing a phosphorus–carbon bond with a high yield and stereoselectivity.

Cascade or tandem reactions (or domino reactions) and related processes in three-component systems are intensively developed in modern organic synthesis, which allows one to obtain complex heterocyclic structures.[1–5] Recently,[6–10] we applied this approach to the synthesis of complex 'cage' phosphoranes having a phosphorus–carbon bond by the example of the 2-(2-oxo-1,2-diphenylethoxy)benzo-1,3,2-dioxaphosphole and 2-(1-methyl-3-oxobut-2-en-1-yloxy)benzo-1,3,2-dioxaphosphole reactions with hexafluoroacetone and chloral. Phosphoranes are the key intermediates of the biologically important processes of phosphorylation and dephosphorylation.[11–13] They can also participate as intermediates in the synthesis of peptides.[14–18]

Here, we used a new P^{III}-derivative, 2-(2-methyl-4-oxopent-2-yloxy)benzo-1,3,2-dioxaphosphole **1**, obtained by the phosphorylation of diacetone alcohol,† for the synthesis of spirophosphoranes. Compound **1** was involved in reactions with highly reactive compounds such as chloral, hexafluoroacetone, mezoxalic acid diethyl ester and trifluoropyruvic acid ethyl ester.

The reaction of dioxaphosphole **1** with chloral (Scheme 1) leads to phosphorane **2**‡ having a signal at δ_P –24.3 ppm in the ^{31}P NMR spectrum that indicates the formation of the spirophosphorane with a phosphorus–carbon bond. The ^{13}C NMR data are in accordance with the supposed structure for **2**. The process is notable for a high diastereoselectivity: in spite of the formation of three chiral centres only one diastereoisomer was obtained and isolated. The reaction is likely to occur *via* the



Scheme 1

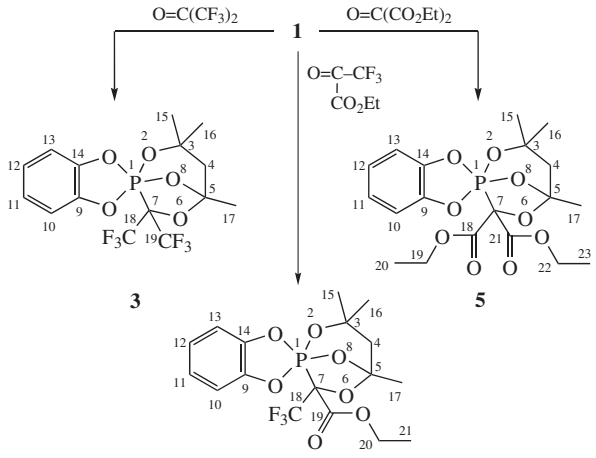
† Melting points are uncorrected; measurements were taken on a Boetius melting point apparatus. The NMR spectra were recorded on Bruker Avance-600 (^1H, 600 MHz; ^{13}C, 150.9 MHz) and Bruker CXP-100 (^{31}P, 36.48 MHz), spectrometers in $CDCl_3$ solution. The δ_H and δ_P values were determined relative to internal (HMDS) or external (H_3PO_4) standard. The δ_C values were determined relative to the deuterated solvent signal. IR spectra were recorded on a Bruker Vector-22 instrument in Nujol. The EI mass spectra were obtained on a TRACE MS Finnigan MAT instrument; the energy of ionizing electrons was 70 eV, the temperature of the ion source was 200 °C. The samples were introduced into the ion source using a direct inlet system. Heating of the ampoule was carried out in a programmed mode within the temperatures range of 35–150 °C at a rate of 35 K min^{-1}. The mass-spectrometric data were processed using the 'Xcalibur' system program.

2-(2-Methyl-4-oxopent-2-yloxy)benzo-1,3,2-dioxaphosphole **1**. 2-Chlorobenzo-1,3,2-dioxaphosphole (5.86 g, 0.034 mol) was added dropwise to the mixture of 2-hydroxy-2-methylpentan-4-one (3.9 g, 0.034 mol), 300 ml diethyl ether and triethylamine (3.39 g, 0.034 mol) in the argon atmosphere. The solution was stirred for 2 h at –15 °C and for 1 h to achieve 20 °C. Filtration of the NEt_3·HCl precipitate, and evacuation of a residue at 50 Torr until dry resulted in **1** as a transparent liquid, which was used further without additional purification. Yield of **1** is 95% (20.0 g). ^{31}P-{^1H} NMR ($CDCl_3$) δ_P: 137.8 (s).

‡ *7-Trichloromethyl-3,3,5-trimethyl-1,1-phenylenedioxy-1-phospha-2,6,8-dioxabicyclo[3.2.1^{1,5}]octane* **2**. The chloral (2.24 g, 0.015 mol) was added to the solution of dioxaphosphole **1** (3.87 g, 0.015 mol) in the mixture of CH_2Cl_2 at room temperature in the atmosphere of argon. The mixture was sealed off to the ampoule and was kept during a week at room temperature and then was dried in a vacuum (10 Torr) to afford light transparent liquid. The yield of **2** was 4.8 g (80%). IR (film, ν/cm^{-1}): 3059, 2985, 2953, 1728, 1622, 1573, 1449, 1436, 1384, 1306, 1266, 1204, 1174, 1113, 1083, 1031, 1004, 959, 898, 870, 844, 793, 777, 738, 701, 641. ^1H NMR, δ: 7.00 (br. d, 1H, H^{10}, $^3J_{HC^{11}C^{10}H}$ 7.5 Hz), 6.86 (m, 1H, H^{12}, $^3J_{HCC^{12}H}$ 7.5 Hz, $^3J_{HCC^{12}H}$ 7.5 Hz), 6.81 (m, 1H, H^{13}, $^3J_{HC^{12}C^{13}H}$ 7.5 Hz), 6.76 (m, 1H, H^{11}, $^3J_{HCC^{11}H}$ 7.5 Hz, $^3J_{HCC^{11}H}$ 7.5 Hz), 4.59 (d, 1H, H^7, $^2J_{PC^7H}$ 5.6 Hz), 2.20 and 2.09 (2m, 2H, H^4, A and B parts of AB-system, $^2J_{H^AH^B}$ 14.9 Hz), 1.65 (s, 3H, H^{17}), 1.46 and 1.26 (2s, 6H, H^{15}, H^{16}). ^{13}C NMR (hereinafter a multiplicity of the signal in ^{13}C-{^1H} spectrum is given in parentheses) δ: 80.91 [m (d), C^3, $^2J_{POC^3}$ 8.4 Hz, $^2J_{HCC^3}$ 4.1–4.0 Hz], 48.92 [br. t (br. s), C^4, $^1J_{HC^4}$ 127.5 Hz], 100.05 [m (d), C^5, $^2J_{POC^5}$ 8.3 Hz, $^2J_{HCC^5}$ 4.5–5.0 Hz, $^3J_{HC^7OC^5}$ 2.5–2.6 Hz], 81.34 [dd (d), C^7, $^1J_{PC^7}$ 167.0 Hz, $^1J_{HC^7}$ 160.5 Hz], 144.91 [m (br. s), C^9, $^3J_{HCCC^9}$ 8.4 Hz, $^3J_{HCCC^9}$ 8.5 Hz, $^2J_{HCC^9}$ 3.0–4.0 Hz], 110.74 [ddd (d), C^{10}, $^1J_{HC^{10}}$ 163.9 Hz, $^3J_{POCC^{10}}$ 17.0 Hz, $^3J_{HC^{12}CC^{10}}$ 8.8 Hz], 123.06 [dd (s), C^{11}, $^1J_{HC^{11}}$ 162.0 Hz, $^3J_{HC^{13}CC^{11}}$ 8.0 Hz], 120.03 [dd (s), C^{12}, $^1J_{HC^{12}}$ 163.1 Hz, $^3J_{HC^{10}CC^{12}}$ 8.0 Hz], 110.12 [ddd (d), C^{13}, $^1J_{HC^{13}}$ 164.2 Hz, $^3J_{POCC^{13}}$ 10.7 Hz, $^3J_{HC^{11}CC^{13}}$ 8.9 Hz], 140.75 [m (d), C^{14}, $^2J_{POC^{14}}$ 6.7 Hz], 31.29 [qm (d), C^{15}, $^1J_{HC^{15}}$ 128.5 Hz, $^3J_{POCC^{15}}$ 12.6 Hz, $^3J_{HCCC^{15}}$ 4.4 Hz], 28.03 [qm (d), C^{16}, $^1J_{HC^{16}}$ 128.0 Hz, $^3J_{POCC^{16}}$ 5.1 Hz, $^3J_{HCCC^{16}}$ 3.1–3.2 Hz], 30.24 [br. q (s), C^{17}, $^1J_{HC^{17}}$ 126.8 Hz]. ^{31}P-{^1H} NMR ($CDCl_3$) δ_P: –24.3 (s).

bipolar ion **A**, which anionic centre attacks the endocyclic carbonyl carbon to form species **B** with more separated charges. The latter is stabilized through the attack of oxygen at the phosphorus atom to give final product **2**.

The same result was obtained in reactions of dioxaphosphole **1** with hexafluoroacetone, trifluoropyruvic acid ethyl ester and mezoxalic acid diethyl ester. The above carbonyl compounds



Scheme 2

7,7-Bis(trifluoromethyl)-3,3,5-trimethyl-1,1-phenylenedioxy-1-phospha-2,6,8-dioxabicyclo[3.2.1^{1,5}]octane **3**. Hexafluoroacetone (1.99 g, 0.011 mol) was condensed to the solution of dioxaphosphole **1** (3.0 g, 0.012 mol) in 20 ml CCl_4 at –45–50 °C. The mixture was kept for 15 days at room temperature and then evacuated (10 Torr). Hexane (20 ml) was added to the reaction mixture and colourless crystals were obtained, which were filtered off and dried in a vacuum (10 Torr). The yield of **3** is 3.1 g (75%), mp 89–90 °C. IR (pellet, ν/cm^{-1}): 3063, 2988, 2941, 1797, 1673, 1611, 1549, 1491, 1450, 1385, 1345, 1215, 1145, 1107, 1068, 994, 850, 788, 661. ^{1}H NMR δ: 7.1–7.0 and 6.95–6.90 (m, 4H, H^{10}, H^{11}, H^{12}, H^{13}), 2.23 (q, H^4, 2H, A and B parts of AB-system, $^2J_{H^AH^B}$ 15.2 Hz), 1.60 (s, 3H, H^{17}), 1.49 (s, 3H, H^{15}), 1.27 (d, 3H, H^{16}, $^4J_{POCCH^{15}}$ 2.9 Hz). ^{13}C NMR, δ: 82.28 [dm (d), C^3, $^2J_{POC^3}$ 8.2 Hz, $^2J_{HC^4C^3}$ 4.1–4.3 Hz, $^2J_{HC^{15}C^3}$ 4.1–4.3 Hz, $^2J_{HC^{16}C^3}$ 4.1–4.3 Hz], 49.37 [br. t (d), C^4, $^1J_{HC^4}$ 129.9 Hz, $^3J_{POCC^4}$ 2.2 Hz], 101.24 [m (d), C^5, $^2J_{POC^5}$ 4.5 Hz, $^2J_{HCC^5}$ 4.7–5.3 Hz, $^2J_{HCC^5}$ 4.7–5.3 Hz], 75.99 [d sept (d sept), C^7, $^1J_{PC^7}$ 158.6 Hz, $^2J_{FCC^7}$ 31.0 Hz], 144.94 [ddd (s), C^9, $^2J_{POC^5}$ 8.0 Hz, $^3J_{HC^{11}CC^9}$ 6.9 Hz, $^3J_{HC^{13}CC^9}$ 6.9 Hz, $^3J_{HC^{10}C^9}$ 1.3–1.4 Hz], 111.06 [dm (d), C^{10}, $^1J_{HC^{10}}$ 165.2 Hz, $^3J_{POCC^{10}}$ 17.7 Hz, $^3J_{HC^{12}CC^{10}}$ 7.2 Hz], 123.51 [dd (s), C^{11}, $^1J_{HC^{11}}$ 162.5 Hz, $^3J_{HC^{13}CC^{11}}$ 8.0 Hz], 121.16 [dm (s), C^{12}, $^1J_{HC^{12}}$ 163.5 Hz, $^3J_{HC^{10}CC^{12}}$ 7.8 Hz, $^2J_{HCC^{12}}$ 2.2 Hz, $^2J_{HCC^{12}}$ 1.6 Hz], 110.61 [ddddd (d), C^{13}, $^1J_{HC^{13}}$ 165.1 Hz, $^3J_{POCC^{13}}$ 12.2 Hz, $^3J_{HC^{11}CC^{13}}$ 8.7 Hz, $^2J_{HCC^{13}}$ 1.1–1.2 Hz, $^4J_{HCCCC^{13}}$ 1.1–1.2 Hz], 140.95 [m (d), C^{14}, $^3J_{HCCC^{14}}$ 10.3 Hz, $^2J_{POC^{14}}$ 7.3 Hz, $^3J_{HCCC^{14}}$ 7.3 Hz, $^2J_{HCC^{14}}$ 3.8 Hz], 29.76 [qm (s), C^{16}, $^1J_{HC^{16}}$ 127.5 Hz, $^3J_{HCCC^{16}}$ 4.4–4.5 Hz, $^3J_{HCCC^{16}}$ 3.3–3.6 Hz, $^3J_{POCC^{16}}$ 0 Hz], 28.10 [qdd (d), C^{17}, $^1J_{HC^{17}}$ 128.7 Hz, $^3J_{POCC^{17}}$ 5.1 Hz, $^3J_{HC^4ACC^{17}}$ 3.7 Hz, $^3J_{HC^4BCC^{17}}$ 0 Hz], 30.50 [qdm (d), C^{15}, $^1J_{HC^{15}}$ 127.8 Hz, $^3J_{POCC^{15}}$ 13.5 Hz, $^3J_{HC^4CC^{15}}$ 4.4–4.5 Hz, $^3J_{HC^{16}CC^{15}}$ 4.4–4.5 Hz], 122.15 [qdq (qdq), C^{18}, $^1J_{FC^{18}}$ 287.2 Hz, $^2J_{PCC^{18}}$ 3.8 Hz, $^3J_{FCCC^{18}}$ 2.1 Hz], 122.02 [qdq (qdq), C^{19}, $^1J_{FC^{19}}$ 285.4 Hz, $^2J_{PCC^{19}}$ 2.0–2.2 Hz, $^3J_{FCCC^{19}}$ 2.0–2.2 Hz]. ^{31}P-{^{1}H} NMR δ_P: –28.0 (s). MS, *m/z*: found 420 $[M]^{+\cdot}$ (calc. for $C_{14}H_{12}F_6O_5P$, 420), 365 [M – 3F + 2H], 311 [M – 6F + 4H], 265 [$C_{12}H_{10}O_5P$].

7-Ethoxycarbonyl-7-trifluoromethyl-3,3,5-trimethyl-1,1-phenylenedioxy-1-phospha-2,6,8-dioxabicyclo[3.2.1^{1,5}]octane **4**. Trifluoropyruvic acid ethyl ester (1.59 g, 0.008 mol) dissolved in 5 ml of CH_2Cl_2 was added to the solution of dioxaphosphole **1** (2.09 g, 0.008 mol) in CH_2Cl_2 (5 ml) at room temperature in the atmosphere of argon. A little exo-effect was observed. The mixture was kept during a week (10 °C) and then was dried in a vacuum (10 Torr). Then, 15 ml of pentane was added to the reaction mixture and a cream-coloured precipitate was formed. Precipitate was filtered off and dried in a vacuum (10 Torr). The yield of **4** was 2.7 g (80%), mp 83–85 °C. IR (pellet, ν/cm^{-1}): 3420, 2984, 2941, 2873, 1751, 1625, 1602, 1492, 1465, 1447, 1430, 1391, 1355, 1254, 1214, 1185, 1175, 1141, 1110, 1074, 1034, 999, 980, 927, 882, 853, 822, 792, 772, 748, 701, 688, 657, 627, 550, 525, 490, 471, 429. ^{1}H NMR, δ: 7.13 (d, H^{10}, $^3J_{HC^{11}C^{11}H}$ 8.1 Hz), 7.00 (br. dd, H^{11}, $^3J_{HC^{12}C^{11}H}$ 7.7 Hz, $^4J_{HC^{13}C^{11}H}$ 1.1 Hz), 6.90 (m, H^{12}, H^{13}), 4.47 (m, H^{20}, B part of ABX_3 system, $^2J_{AB}$ 18.0 Hz, $^2J_{BX}$ 7.0–7.3 Hz), 4.42 (m, H^{20}, A part of ABX_3 system, $^2J_{AB}$ 18.0 Hz, $^2J_{AX}$ 7.0–7.3 Hz), 2.52 (q, H^4, AB system, $^3J_{H^AH^B}$ 22.5 Hz), 1.71 (d, H^{17}, $^4J_{POCC^{17}H}$ 1.5 Hz), 1.59 (s, H^{15}), 1.44 (s, H^{16}), 1.43 (t, H^{21}, $^3J_{H^{20}CCH^{21}}$ 7.0–7.3 Hz). ^{13}C NMR, δ: 82.04 [br. m (d), C^3, $^2J_{POC^3}$ 8.1 Hz], 49.47 [br. t (br. s), C^4, $^1J_{HC^4}$ 129.5 Hz], 101.46 [br. m (d), C^5, $^2J_{POC^5}$ 6.6 Hz], 76.46 [dq (dq), C^7, $^1J_{PC^7}$ 146.0 Hz, $^2J_{FCC^7}$ 29.7 Hz], 145.31 [br. m (s), C^9], 111.36 [dddd (d), C^{10}, $^1J_{HC^{10}}$ 164.3 Hz, $^3J_{POCC^{10}}$ 17.2 Hz, $^3J_{HC^{12}CC^{10}}$ 8.4 Hz, $^4J_{HC^{13}CCC^{10}}$ 2.9 Hz], 123.59 [dd (s), C^{11}, $^1J_{HC^{11}}$ 162.1 Hz, $^3J_{HC^{13}CC^{11}}$ 8.1 Hz], 121.00 [dd (s), C^{12}, $^1J_{HC^{12}}$ 161.8 Hz, $^3J_{HC^{10}CC^{12}}$ 8.1 Hz], 110.74 [ddd (d), C^{13}, $^1J_{HC^{13}}$ 164.7 Hz, $^3J_{POCC^{13}}$ 11.7 Hz, $^3J_{HC^{11}CC^{13}}$ 8.9 Hz], 141.11 [m (d), C^{14}, $^2J_{POC^{14}}$ 7.0 Hz], 30.84 [qdm (d), C^{15}, $^1J_{HC^{15}}$ 132.1 Hz, $^3J_{POCC^{15}}$ 16.5 Hz, $^3J_{HC^{16}CC^{15}}$ 4.4 Hz], 28.59 [qdm (d), C^{16}, $^1J_{HC^{16}}$ 128.8 Hz, $^3J_{POCC^{16}}$ 5.5 Hz, $^3J_{HCCC^{16}}$ 4.4 Hz], 30.26 [br. qm (br. s), C^{17}, $^1J_{HC^{17}}$ 127.3 Hz], 122.68 [qd (qd), C^{18}, $^1J_{FC^{18}}$ 285.0 Hz, $^2J_{POC^{18}}$ 2.2 Hz], 165.26 [br. s (s), C^{19}], 63.04 [tq (s), C^{20}, $^1J_{HC^{20}}$ 148.9 Hz, $^3J_{HC^{21}C^{20}}$ 4.4 Hz], 14.08 [q (s), C^{21}, $^1J_{HC^{21}}$ 127.3 Hz]. ^{31}P NMR ($CDCl_3$) δ_P: –25.9 (q, $^3J_{PCCF}$ 7.9–8.0 Hz). MS, *m/z*: found 424 $[M]^{+\cdot}$ (calc. for $C_{17}H_{20}F_3O_7P$, 420), 369 [M – Me_2CHCH], 368 [M – Me_2CHCH_2], 327 [M – CF_3 – C_2H_4], 326 [M – CF_3 – Et], 269 [M – – $C(CF_3)COOEt$ – H], 254 [M – $CF_3COCOOEt$], 253 [M – CF_3CO – CO_2 – – C_2H_4], 201 [$C_7H_6O_5P$], 173 [$C_6H_4O_2P(OH)_2$], 172 [$C_6H_4O_2P(O)OH$], 156 [$C_6H_4O_2POH$], 155 [$C_6H_4O_2PO$], 139 [$C_6H_4O_2P$], 108 [$C_6H_4O_2$], 99 [$Me_2C(O)CH_2CMe$], 98 [$Me_2C(O)CH_2CCH_2$], 97 [C_6H_9O], 83 [C_6H_{11}], 81 [C_6H_9], 82 [C_6H_{10}], 73 [COOEt], 69 [CF_3], 58 [Me_2CO], 45 [EtO], 42 [$MeCH{=}CH_2$], 29 [Et], 28 [C_2H_4], 15 [Me].

7,7-Bis(ethoxycarbonyl)-3,3,5-trimethyl-1,1-phenylenedioxy-1-phospha-2,6,8-dioxabicyclo[3.2.1^{1,5}]octane **5**. The diethylketomalonate (1.89 g, 0.01 mol) dissolved in 5 ml of CH_2Cl_2 was added to the solution of dioxaphosphole **1** (2.78 g, 0.01 mol) in 5 ml CH_2Cl_2 at room temperature in the atmosphere of argon. A little exo-effect was observed. The mixture was sealed off to the ampoule and was kept during a week at room temperature. The colourless crystals were filtered off, washed with dry Et_2O and dried in a vacuum (10 Torr). The yield of **5** was 2.9 g (70%), mp 97 °C. IR (pellet, ν/cm^{-1}): 3465, 3428, 2985, 2957, 2937, 2905, 1759, 1741, 1626, 1601, 1493, 1473, 1451, 1385, 1366, 1347, 1284, 1237, 1218, 1147, 1115, 1070, 1045, 998, 928, 908, 881, 853, 806, 746, 718, 647, 614, 575, 539, 499, 469, 431. ^{1}H NMR, δ: 7.09 (m, H^{10}, $^3J_{H^{11}CCH^{10}}$ 8.0 Hz, $^4J_{H^{12}CCCH^{10}}$ 1.5 Hz, $^4J_{POCCH^{10}}$ 1.2 Hz), 6.97 (m, H^{12}, $^3J_{H^{11}CCH^{12}}$ 7.6 Hz, $^3J_{H^{13}CCH^{12}}$ 7.9 Hz, $^4J_{H^{10}CCCH^{12}}$ 1.4 Hz), 6.89 (m, H^{13}, $^3J_{H^{12}CCH^{13}}$ 7.9–8.0 Hz, $^4J_{H^{11}CCCH^{13}}$ 1.1–1.2 Hz), 6.88 (m, H^{11}, $^3J_{H^{10}CCH^{11}}$ 8.0 Hz, $^3J_{H^{12}CCH^{11}}$ 7.6 Hz, $^4J_{H^{13}CCCH^{11}}$ 1.2 Hz, $^5J_{POCCCH^{11}}$ 1.3 Hz), 4.04 (m, H^{19}, B part of ABX_3 system, $^3J_{H^AH^B}$ 10.6 Hz, $^3J_{H^BH^X}$ 7.3 Hz), 4.09 (m, H^{19}, A part of ABX_3 system, $^3J_{H^AH^B}$ 10.6 Hz, $^3J_{H^AH^X}$ 7.3 Hz), 4.32 (m, H^{21}, A part of ABX_3 system, $^3J_{H^AH^B}$ 10.3 Hz, $^3J_{H^AH^X}$ 7.3 Hz), 4.41 (m, H^{21}, B part of ABX_3 system, $^3J_{H^AH^B}$ 10.3 Hz, $^3J_{H^BH^X}$ 7.3 Hz), 2.66 (d, H^4, B part of AB system, $^3J_{H^AH^B}$ 14.6 Hz), 2.20 (d, H^4, A part of AB system, $^3J_{H^AH^B}$ 14.6 Hz), 1.66 (d, $^4J_{POCCH}$ 1.7 Hz), 1.59 and 1.46 (s and d, H^{15}, H^{16}, H^{17}, $^4J_{POCCH}$ 3.1 Hz), 1.37 (t, H^{20}, $^3J_{HCCH}$ 7.1 Hz), 0.82 (t, H^{23}, $^3J_{HCCH}$ 7.1 Hz). ^{13}C NMR, δ: 81.73 [br. dm (d), C^3, $^2J_{POC^3}$ 8.1 Hz], 49.65 [br. tm (br. s), C^4, $^1J_{HC^4}$ 128.4 Hz], 101.05 [dm (d), C^5, $^2J_{POC^5}$ 7.7 Hz, $^2J_{HCC^5}$ 2.9 Hz], 79.99 [d (d), C^7, $^1J_{PC^7}$ 155.2 Hz], 144.37 [m (d), C^9, $^2J_{POC^9}$ 4.8 Hz], 111.12 [dddd (br. d), C^{10}, $^1J_{HC^{10}}$ 164.0 Hz, $^3J_{POCC^{10}}$ 18.0 Hz, $^3J_{HC^{12}CC^{10}}$ 7.7 Hz, $^2J_{HC^{11}C^{10}}$ 4.0 Hz], 123.16 [dd (s), C^{11}, $^1J_{HC^{11}}$ 161.8 Hz, $^3J_{HC^{13}CC^{11}}$ 8.1 Hz], 120.35 [dd (s), C^{12}, $^1J_{HC^{12}}$ 161.0 Hz, $^3J_{HC^{10}CC^{12}}$ 7.7 Hz], 110.42 [ddd (d), C^{13}, $^1J_{HC^{13}}$ 164.3 Hz, $^3J_{POCC^{13}}$ 10.9 Hz, $^3J_{HC^{11}CC^{13}}$ 8.9 Hz], 141.50 [m (d), C^{14}, $^2J_{POC^{14}}$ 7.0 Hz], 31.50 [qdm (d), C^{15}, $^1J_{HC^{15}}$ 128.0 Hz, $^3J_{POCC^{15}}$ 14.6 Hz, $^3J_{HCCC^{15}}$ 4.6–4.8 Hz], 28.32 [qdm (d), C^{16}, $^1J_{HC^{16}}$ 128.0 Hz, $^3J_{POCC^{16}}$ 4.0 Hz, $^3J_{HCCC^{16}}$ 4.0–4.5 Hz], 30.79 [br. qm (br. s), C^{17}, $^1J_{HC^{17}}$ 128.4 Hz], 167.11 [br. s (s), C^{18}], 62.68 [tq (s), C^{19}, $^1J_{HC^{19}}$ 148.6 Hz, $^2J_{HC^{20}C^{19}}$ 4.4 Hz], 14.05 [qt (s), C^{20}, $^1J_{HC^{20}}$ 127.3 Hz, $^2J_{HC^{19}C^{20}}$ 2.5–2.8 Hz], 166.59 [br. s (s), C^{21}], 62.27 [tq (s), C^{22}, $^1J_{HC^{22}}$ 148.6 Hz, $^2J_{HC^{23}C^{22}}$ 4.4 Hz], 13.18 [qt (s), C^{23}, $^1J_{HC^{23}}$ 127.7 Hz, $^3J_{HC^{22}CC^{23}}$ 2.8–3.0 Hz]. ^{31}P-{^{1}H} NMR ($CDCl_3$) δ_P: –25.7 (s). MS, *m/z*: found 428 $[M]^{+\cdot}$ (calc. for $C_{19}H_{25}O_9P$, 428), 373 [M – $Me_2CH{=}CH$], 372 [M – $2C_2H_4$], [M – $Me_2CH{=}CH_2$], 371 [M – Et – – C_2H_4], 331 [M – C_6H_9O], 330 [M – $C_6H_{10}O$], 257 [M – $C_6H_4O_2P(O)O$], 256 [M – $C_6H_4O_2P(O)OH$], 241 [M – $O{=}C(COOEt)_2$ – CH], 201 [C_6H_4-$O_2PO_2CH_2O$], 173 [$C_6H_4O_2P(OH)_2$], 172 [$C_6H_4O_2P(O)(OH)$], 156 [$C_6H_4O_2POH$], 155 [$C_6H_4O_2PO$], 139 [$C_6H_4O_2P$], 110 [$C_6H_4(OH)_2$], 109 [$C_6H_4O_2H$], 99 [$C_6H_{11}O$], 98 [$C_6H_{10}O$], 97 [C_6H_9O], 83 [C_6H_{11}], 82 [C_6H_{10}], 81 [C_6H_9], 73 [COOEt], 58 [Me_2CO], 56 [$Me_2C{=}CH_2$], 45 [OEt], 44 [CO_2], 42 [$MeC{=}CH_2$], 29 [Et], 28 [C_2H_4], 28 [CO].

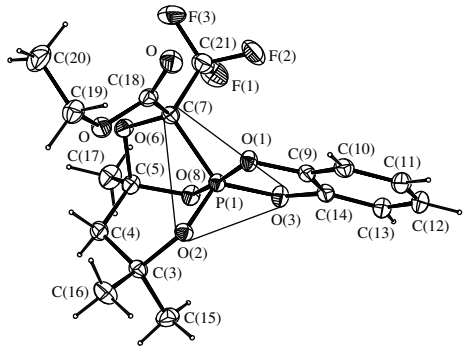


Figure 1 Molecular geometry of compound **4** in a crystal (the base of the trigonal bipyramid is shown by thin lines). Selected bond lengths (Å), bond and torsion angles (°): C(3)–C(4) 1.527(2), C(3)–O(2) 1.490(2), C(4)–C(5) 1.526(2), C(5)–O(8) 1.404(2), C(5)–O(6) 1.470(2), C(5)–C(17) 1.500(3), C(7)–O(6) 1.398(2), C(7)–C(21) 1.534(3), C(7)–C(18) 1.538(2), C(7)–P(1) 1.897(2), C(9)–C(14) 1.371(2), C(14)–O(3) 1.366(2), C(9)–O(1) 1.390(2), O(3)–P(1) 1.692(1), O(2)–P(1) 1.569(1), O(1)–P(1) 1.623(1), O(8)–P(1) 1.660(1), O(6)–C(5)–O(8) 105.2(1), O(8)–C(5)–C)17) 110.3(2), O(6)–C(5)–C(17) 106.7(2), O(8)–C(5)–C(4) 110.2(1), O(6)–C(5)–C(4) 109.4(1), O(6)–C(7)–P(1) 105.4(1), C(21)–C(7)–P(1) 111.6(1), C(18)–C(7)–P(1) 112.9(1), C(3)–O(2)–P(1) 123.9(1), C(7)–O(6)–C(5) 112.2(1), C(5)–O(8)–P(1) 109.59(9), O(2)–P(1)–O(3) 91.13(6), O(2)–P(1)–O(8) 97.75(6), O(1)–P(1)–O(8) 171.09(6), O(1)–P(1)–O(2) 119.32(6), O(1)–P(1)–O(3) 90.81(6), O(3)–P(1)–O(8) 85.40(6), O(2)–P(1)–C(7) 109.42(7), O(3)–P(1)–C(7) 90.77(6), O(8)–P(1)–C(7) 85.71(6), O(1)–P(1)–C(7) 85.71(6), C(7)–P(1)–O(3)–C(14) –141.1(1), O(8)–P(1)–O(2)–C(3) –7.3(1), O(3)–P(1)–O(1)–C(9) 9.0(1), C(7)–P(1)–O(1)–C(9) 100.8(1), O(2)–P(1)–C(7)–C(18) 51.9(1), O(1)–P(1)–C(7)–C(21) –7.8(2).

are usually used for the synthesis of σ^5,λ^5-1,3,2-dioxaphospholanes; however, all of them form 'cage' phosphoranes with a phosphorus–carbon bond in the reaction with dioxaphosphole **1** (Scheme 2).

The structure of phosphoranes **3**–**5** isolated in pure form was confirmed by ^{1}H and ^{13}C NMR data, which fit well the structures of bicyclic species. The signals of the C^9–C^{14} nuclei in compound **4** are broadened due to the pseudo-rotation process that is characteristic of the pentacoordinated phosphorus. The structure of compound **4** was also confirmed by single crystal X-ray diffraction (Figure 1).§ The configuration of the chiral atoms is $C^5_RC^7_SP^1_S$/$C^5_SC^7_RP^1_R$. Geometry of the phosphorus atom in the molecule of compound **4** is a trigonal bipyramid with the planar to within 0.0197(4) Å base, which is formed by the atoms P^1, O^2, O^1 and C^7. The atoms O^1 and O^8, occupying apical sets, deviate from this plane at distances of –1.621(1) and 1.712(1) Å, respectively [bond lengths P^1–O^1 and P^1–O^8 are 1.692(1) and 1.660(1) Å, the bond angle O^1–P^1–O^8 is 171.09(6)°]. The bond angles O^3–P^1–C^7, O^3–P^1–O^2, O^1–P^1–O^3, O^8–P^1–C^7, O^8–P^1–O^2 and O^8–P^1–O^3 are 85.71(6)–97.75(6)° indicating a trigonal-bipyramidal configuration of phosphorus. In this case, the equatorial bond lengths P^1–O^3 and P^1–O^2 are somewhat shorter than axial ones [1.630(1) and 1.569(1) Å]. The equatorial bond length P^1–C^7 is 1.897(2) Å. The dioxaphospholane ring $P^1O^1C^9C^{14}O^3$ is planar to within 0.1815(4) Å.

Thus, a cascade reaction of $\sigma^3\lambda^3$-1,3,2-dioxabenzophospholes, bearing a carbonyl groups at the δ-position to the phosphorus atom, with activated carbonyl compounds is a versatile synthetic approach to the spirophosphoranes with a phosphorus–carbon bond.

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§ The X-Ray diffraction data for compound **4** were collected on a Bruker Smart Apex II CCD diffractometer using graphite monochromated MoKα (0.71073 Å) radiation. Crystals of compound **4** ($C_{17}H_{20}F_3O_7P$) are monoclinic, a = 8.3941(5), b = 15.2652(8) and c = 15.2633(8) Å, β = = 100.926(1)°, V = 1920.4(2) Å^3, Z = 4, d_{calc} = 1.468 g cm^{-3}, space group $P2_1/n$. Cell parameters and intensities of 4174 independent reflections, from which 3239 with $I \geq 2\sigma$, were measured in the ω-scan mode, $\theta \leq 27°$. All raw data were corrected for absorption [μ(Mo) = 2.08 cm^{-1}] using SADABS program.[19] The structure was solved by the direct method using the SIR program[20] and refined by the full matrix least-squares using SHELXL97 program.[21] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and refined as riding atoms. All calculations were performed on PC using the WinGX program.[22] The final residuals were R_{ob} = 0.0341, R_{wob} = 0.0851. Data collections: images were indexed, integrated, and scaled using the APEX2 data reduction package.[23] All figures were made using the program PLATON.[24]

CCDC 747439 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2010.

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