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Synthesis of spirophosphoranes containing a phosphorus–carbon bond using the reactions of substituted benzo[*d*]-1,3,2-dioxaphospholes with diethyl acetylenedicarboxylate

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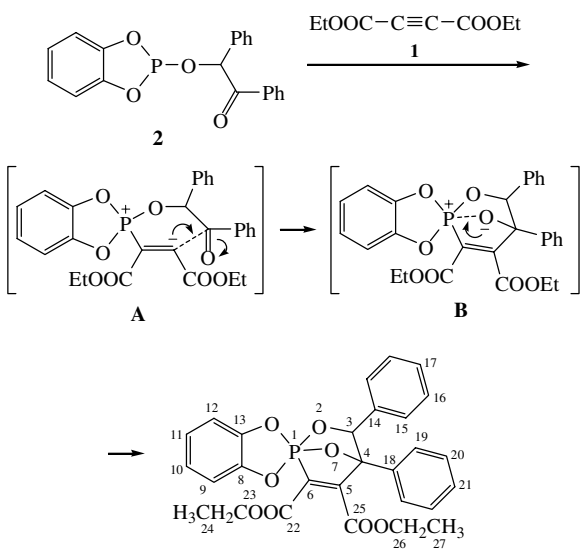
The reaction of 2-(2-oxo-1,2-diphenyl)ethoxy- and 2-(2-methylcarbonyl)phenyloxybenzo[*d*]-1,3,2-dioxaphospholes with diethyl acetylenedicarboxylate was used to synthesise 5,6-bis(ethoxycarbonyl)-3,4-diphenyl-1,1-phenylenedioxy-1-phospha-2,7-dioxabicyclo[2.2.1^{1,4}]hept-5-ene and 5-methyl-6,7-bis(ethoxycarbonyl)-1,1-phenylenedioxy-3,4-benzo-1-phospha-2,8-dioxabicyclo-[3.2.1^{1,5}]oct-6-ene in high yields.

The chemistry of hypervalent phosphorus compounds is of considerable interest because these compounds are involved in cellular metabolism and they have a decisive contribution to energy and information transfer processes.[1–6] Studies on phosphoranes containing the P($\sigma^5\lambda^5$) framework are complicated due to their high lability to hydrolysis. Therefore, the synthesis of stable phosphoranes containing a few chiral centres is of current interest. Recently, we suggested a new approach to the synthesis of stable bicyclic cage phosphoranes incorporating the phosphorus–carbon bond along with chiral phosphorus and carbon atoms.[7] It is based on the reactions of γ- and δ-carbonyl-substituted phosphorus(III) derivatives, *viz.*, 2-(2-oxo-1,2-diphenyl)-ethoxy- and 2-(1-methyl-3-oxobut-2-en-1-yloxy)benzo[*d*]-1,3,2-dioxaphospholes, with hexafluoroacetone; the reactions occur with high regio- and stereoselectivity to preferentially give one of the possible diastereomers.

Here, we expanded this approach to another reactive compound with a multiple bond, diethyl acetylenedicarboxylate **1**. Compound **1** readily reacted with 2-(2-oxo-1,2-diphenylethoxy)-benzo[*d*]-1,3,2-dioxaphosphole **2** to give pentacoordinate phosphorus derivative **3** (Scheme 1), which manifests itself as a singlet at δ_P –18.0 ppm in the ^{31}P-{^{1}H} spectrum, indicating the existence of one P–C bond. The ^{13}C and ^{13}C-{^{1}H} NMR spectra contain a set of signals from carbon atoms, whose constants and multiplicity are in good agreement with the assumed structure of **3**.† The spectrum contains doublets belonging to the C^3–C^6 nuclei of the bicyclic fragment, as well as doublets of the benzodioxaphospholane ring C^8 and C^{13} nuclei with constants due to spin–spin coupling with phosphorus. The proton at C^3 manifests itself as a doublet at δ 5.62 ($^3J_{POCH}$ 21.0 Hz).

The structure of phosphorane **3** is also confirmed by electron-impact (EI) mass spectrometric data. The EI mass spectrum contains a peak at *m*/*z* 520 corresponding to the [M$^+$] molecular ion. The fragmentation of **3** involves the elimination of an ethoxy group to give an ion with *m*/*z* 475 [M – OEt]$^+$. The ion with *m*/*z* 447 is probably due to the cleavage of a C–C bond with elimination of an ethoxycarbonyl substituent. This ion can subsequently eliminate a Me group to give an ion with *m*/*z* 432. The peak with *m*/*z* 414 in the mass spectrum is probably due to the ion resulting from the cleavage of P–O and C–C bonds in the five-membered ring containing two phenyl radicals.



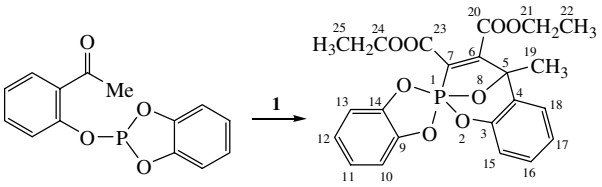
Scheme 1

Subsequently, the latter ion loses a C_2H_4 molecule due to the elimination of the ethoxy group. This process produces an ion with *m*/*z* 386. Fragmentation of another type with cleavage of two C–O bonds in the ring specified above gives an ion with *m*/*z* 341. This process can be accompanied by migration of a hydrogen atom to the neutral fragment to give an ion with *m*/*z* 340. The peak with a maximum intensity at *m*/*z* 105 corresponds to the ion [PhCO]$^+$. The presence of other fragment ions with small *m*/*z* values in the mass spectrum of compound **3** is probably due to the sequential fragmentation of the above ions.

The process probably starts with a nucleophilic attack of the phosphorus atom in phosphole **2** on a carbon atom in compound **1** resulting in bipolar ion **A**, which then undergoes stabilization due to the intramolecular attack of the carbanion centre on the exocyclic carbonyl group to give bipolar ion **B** with formation of a bond between the alkoxide anionic centre and the phosphorus atom (Scheme 1).

The reaction of 2-(2-methylcarbonyl)phenyloxybenzo[*d*]-1,3,2-dioxaphosphole **4**† with ester **1** also occurs under mild conditions (CH_2Cl_2), probably, *via* the same mechanism. It results in a stable derivative of the pentacoordinate phosphorus atom,

5-methyl-6,7-bis(ethoxycarbonyl)-1,1-phenylenedioxy-3,4-benzo-1-phospha-2,8-dioxabicyclo[3.2.1]oct-6-ene **5**, which crystallises from the reaction mixture. C–C, P–C and P–O bond formation, which is important for organic synthesis, occurs in both reactions.



4 **5**

Scheme 2

† Melting points (uncorrected) were measured with a Boetius melting point apparatus. NMR spectra were recorded on Bruker Avance-600 (^{1}H, 600 MHz; ^{13}C, 150.9 MHz) and Bruker CXP-100 (^{31}P, 36.48 MHz) spectrometers. The δ_H and δ_P values were determined relative to internal (HMDS) or external (H_3PO_4) standards. The IR spectrum was recorded on a Bruker Vector-22 instrument in Nujol. EI mass spectra were obtained on a TRACE MS Finnigan MAT instrument; the ionization energy was 70 eV and the ion source temperature was 200 °C. The samples were introduced into the ion source *via* a direct inlet system. The evaporating ampoule was heated from 35 to 150 °C at a rate of 35 K min^{-1}. The mass spectrometric data were processed using the Xcalibur system program. The synthesis of compound **2** was described previously.[7]

5,6-Bis(ethoxycarbonyl)-3,4-diphenyl-1,1-phenylenedioxy-1-phospha-2,7-dioxabicyclo[2.2.1^{1,4}]hept-6-ene **3**. Acetylenedicarboxylate **1** (1.8 g, 0.01 mol) was added under argon to a solution of dioxaphosphole **2** (3.8 g, 0.01 mol) in CH_2Cl_2 (10 ml) at room temperature. The mixture was sealed in an ampoule, kept for two weeks at room temperature and then dried *in vacuo* (10 Torr) to give a light-yellow oil. The yield of compound **3** was 3.64 g (70%). ^{1}H NMR ($CDCl_3$) δ: 7.41 (m), 7.37 (m), 7.27 (m), 7.24 (m), 7.18 (m), 7.13 (m), 6.92–7.02 (m, 14H, Ph, C_6H_4), 5.62 (d, 1H, H^3, $^3J_{POCH}$ 21.0 Hz), 4.16 (m, 1H, H^{23}, $^3J_{H^{24}CCH^{23}}$ 7.2–7.3 Hz), 4.07 (m, 1H, H^{26}, $^3J_{H^{27}CCH^{26}}$ 7.2–7.3 Hz), 1.08 (t, 1H, H^{24}, $^3J_{H^{23}CCH^{24}}$ 7.3 Hz), 1.02 (t, 1H, H^{27}, $^3J_{H^{26}CCH^{27}}$ 7.3 Hz). ^{13}C NMR ($CDCl_3$) (henceforth, the multiplicity of signals in the ^{13}C-{^{1}H} spectrum is given in parentheses) δ: 83.53 [ddt (d), C^3, $^1J_{HC^3}$ 155.6 Hz, $^2J_{POC^3}$ 6.1 Hz, $^3J_{HC^{15}CC^3}$ 4.8 Hz], 80.23 [br. dt (d), C^4, $^2J_{POC^4}$ 29.3 Hz, $^2J_{HC^{19}C^4}$ 3.8–4.0 Hz], 161.14 [br. d (d), C^5, $^2J_{PCC^5}$ 12.2 Hz], 133.23 [d (d), C^6, $^1J_{PC^6}$ 192.7 Hz], 145.91 [m (d), C^8, $^2J_{POC^8}$ 2.2 Hz, $^3J_{HC^{10}CC^8}$ 7.5 Hz, $^3J_{HC^{12}CC^8}$ 10.2 Hz], 111.21 [br. ddd (d), C^9, $^1J_{HC^9}$ 156.0 Hz, $^3J_{POCC^9}$ 17.1 Hz, $^3J_{HC^{11}CC^9}$ 9.0 Hz], 123.65 [dd (s), C^{10}, $^1J_{HC^{10}}$ 162.0 Hz, $^3J_{POCC^{10}}$ 12.7 Hz, $^3J_{HC^{12}CC^{10}}$ 8.1 Hz], 141.35 [m (d), C^{13}, $^3J_{POC^{13}}$ 6.6 Hz], 133.03 [br. td (d), C^{14}, $^3J_{POCC^{14}}$ 16.0 Hz, $^3J_{HC^{16}CC^{14}}$ 7.8 Hz], 126.30 [ddd (s), C^{15}, $^1J_{HC^{15}}$ 159.5 Hz, $^3J_{HC^{17}CC^{15}}$ 7.5 Hz, $^3J_{HC^3CC^{15}}$ 7.5 Hz], 127.84 [dd (s), C^{16}, $^1J_{HC^{16}}$ 160.7 Hz, $^3J_{HCCC^{16}}$ 7.5 Hz], 128.30 [dt (s), C^{17}, $^1J_{HC^{17}}$ 161.0 Hz, $^3J_{HC^{15}CC^{17}}$ 7.5 Hz], 134.21 [br. t (s), C^{18}, $^3J_{HC^{20}CC^{18}}$ 7.8 Hz], 128.80 [br. ddd (s), C^{19}, $^1J_{HC^{19}}$ 159.5 Hz, $^3J_{HC^{21}CC^{19}}$ 6.0 Hz, $^3J_{HC^3CC^{19}}$ 7.2 Hz], 128.03 [dd (s), C^{20}, $^1J_{HC^{20}}$ 160.1 Hz, $^3J_{HCCC^{20}}$ 7.2 Hz], 128.77 [dt (s), C^{21}, $^1J_{HC^{21}}$ 160.0 Hz, $^3J_{HC^{19}CC^{21}}$ 7.5 Hz], 163.82 [dt (d), C^{22}, $^2J_{PCC^{22}}$ 26.5 Hz, $^3J_{HC^{23}OC^{22}}$ 3.5 Hz], 61.96 [tq (s), C^{23}, $^1J_{HC^{23}}$ 148.7 Hz, $^2J_{HC^{24}C^{23}}$ 4.5 Hz], 13.62 [qt (s), C^{24}, $^1J_{HC^{24}}$ 127.3 Hz, $^2J_{HC^{23}C^{24}}$ 2.7 Hz], 160.51 [dt (d), C^{25}, $^3J_{PCCC^{25}}$ 15.5 Hz, $^3J_{HC^{26}OC^{25}}$ 3.0 Hz], 61.59 [tq (s), C^{26}, $^1J_{HC^{26}}$ 148.4 Hz, $^2J_{HC^{27}C^{26}}$ 4.5 Hz], 13.55 [qt (s), C^{27}, $^1J_{HC^{27}}$ 127.4 Hz, $^2J_{HC^{26}C^{27}}$ 2.7 Hz]. ^{31}P-{^{1}H} NMR ($CDCl_3$) δ_P: –18.0 (s). MS, *m/z*: 520 (6.0) [M]$^{+\cdot}$ (calc. for $C_{28}H_{25}O_8P$, 520), 475 (1.6) [M – OEt]$^+$, 432 (8.1) [M – 2OEt]$^+$, 414 (36.3) [M – O – 2OEt]$^+$, 386 (51.5) [M – 2O – 2OEt]$^+$, 340 (62.7) [M – C_2H_2 – 2Ph]$^+$, 261 (20.4) [M – Ph – 2COOEt]$^+$, 167 (74.0) [$C_7H_5O_3P$]$^+$, 156 (78.9) [$C_6H_5O_3P$]$^+$, 139 (63.9) [$C_6H_4O_2P$]$^+$, 77 (92.0) [Ph]$^+$, 29 (80.0) [Et]$^+$.

*2-(2-Methylcarbonylphenoxy)benzo[*d*]-1,3,2-dioxaphosphole* **4**. 2-Chlorobenzo[*d*]-1,3,2-dioxaphosphole (1.9 g, 0.01 mol) was added dropwise under argon to a mixture of 1-(2-hydroxyphenyl)ethanone (2.3 g, 0.01 mol), 300 ml of diethyl ether and triethylamine (1.1 g, 0.01 mol). 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 followed by evacuation of the residue at 50 Torr to dryness resulted in compound **4** as a light liquid, which was used without additional purification. The yield of compound **4** was 95% (3.8 g). ^{31}P-{^{1}H} NMR ($CDCl_3$) δ_P: 126.5 (s).

Phosphorane **5** manifests itself in the ^{31}P-{^{1}H} NMR spectrum as a singlet at δ_P –25.4. Data of the carbon spectrum confirm the assumed structure of **5**.‡ Note that the carbon signals of the benzodioxaphospholane ring are broadened considerably, probably, due to pseudo-rotation processes in the trigonal bipyramid of phosphorus or to a change in its configuration (the phosphorus and C^5 carbon atoms are chiral). The structure of phosphorane **5** is confirmed by mass-spectrometric data. The EI mass spectrum contains a peak at *m/z* 444 corresponding to the molecular ion [M$^{+\cdot}$]. The fragmentation of the molecule involves the elimination of an ethyl fragment to give the [M – Et]$^+$ ion with subsequent migration of a hydrogen atom to the neutral fragment to give an ion with *m/z* 416. The ion with *m/z* 326 is probably due to the cleavage of a C–C bond with elimination of ethoxycarbonyl and ethoxy substituents. Elimination of two ethoxycarbonyl fragments results in an ion with *m/z* 299. The peak with *m/z* 217 in the mass spectrum is probably due to the ion [$C_8H_{10}PO_5$]$^+$, which results from the cleavage of P–O, C–O and C–C bonds in the phosphabicyclooctane fragment. Subsequently, the latter ion loses a C_2H_4 molecule due to elimination of the ethoxy group. This process produces an ion with *m/z* 386 in the mass spectrum. Fragmentation of another type with cleavage of two C–O bonds in the ring specified above gives an ion with *m/z* 341. The peak with a maximum intensity at *m/z* 172 in the mass spectrum corresponds to the ion [$C_6H_4PO_4$]$^+$. The presence of other fragment ions with small *m/z* values in the mass spectrum of compound **5** is probably due to the sequential fragmentation of the above ions.

The configuration of the P^1 and C^5 atoms was established by X-ray diffraction analysis§ (P_SC_R/P_RC_S) (the configuration of the pentacoordinate phosphorus atom was determined using the rules published elsewhere[8]). Figure 1 shows the geometry of

‡ *5-Methyl-6,7-bis(ethoxycarbonyl)-1,1-phenylenedioxy-3,4-benzo-1-phospha-2,8-dioxabicyclo[3.2.1^{1,5}]oct-6-ene* **5**. Acetylenedicarboxylate **1** (4.67 g, 0.028 mol) was added under argon to a solution of dioxaphosphole **4** (7.53 g, 0.027 mol) in CH_2Cl_2 (10 ml) at room temperature. The mixture was sealed in an ampoule and kept for five months at room temperature. The light orange crystals were filtered off and dried *in vacuo* (10 Torr). The yield of compound **5** was 9.8 g (80%), mp 132–135 °C. ^{1}H NMR ($CDCl_3$) δ: 7.45 (dd, H^{15}, $^3J_{H^{16}CCH^{15}}$ 7.8 Hz, $^4J_{H^{17}CCCH^{15}}$ 1.4 Hz), 7.27 (dddd, H^{17}, $^3J_{H^{18}CCH^{17}}$ 8.2 Hz, $^3J_{H^{16}CCH^{17}}$ 7.5 Hz, $^4J_{H^{15}CCCH^{17}}$ 1.4 Hz, $^6J_{PCH^{17}}$ 1.6 Hz), 7.11 (ddd, H^{16}, $^3J_{H^{17}CCH^{16}}$ 7.5 Hz, $^3J_{H^{15}CCH^{16}}$ 7.8 Hz, $^4J_{H^{18}CCCH^{16}}$ 1.0 Hz), 6.96 (dd, H^{18}, $^3J_{H^{17}CCH^{18}}$ 8.2 Hz, $^4J_{H^{16}CCCH^{18}}$ 1.0 Hz), 7.07 and 6.98 (2br. m, 4H, H^{10}–H^{13}), 4.23 (m, A-part of the ABX$_3$-system, OCH_2, $^3J_{AB}$ 10.9 Hz, $^3J_{AX}$ 7.1 Hz), 4.30–4.29 (m, B-part of the ABX$_3$-system, OCH_2), 4.30–4.29 (m, A- and B-parts of the ABX$_3$-system, OCH_2), 1.29 and 1.30 (2t, X$_3$-part of the ABX$_3$-system, H^{22}, H^{25}, $^3J_{HH}$ 7.1 Hz), 2.00 (s, H^{19}). ^{13}C NMR ($CDCl_3$) δ: 151.72 [dddd (d), C^3, $^2J_{POC^3}$ 7.0 Hz, $^3J_{HCCC^3}$ 11.0 Hz, $^3J_{HCCC^3}$ 9.0 Hz, $^4J_{HCCCC^3}$ 1.2 Hz], 125.59 [m (d), C^4, $^3J_{POCC^4}$ 4.4 Hz], 20.60 [qd (d), C^5, $^1J_{HC^5}$ 129.5 Hz, $^3J_{PCCC^5}$ 10.4 Hz], 150.72 [dq (d), C^6, $^2J_{POC^6}$ 27.0 Hz, $^2J_{HC^{19}C^6}$ 4.2 Hz], 135.41 [d (d), C^7, $^1J_{PC^7}$ 193.4 Hz], 144.90 and 144.62 (2br. m, C^9 and C^{14}), 121.40 and 122.20 (2br. m, C^{10} and C^{11}), 110.02 and 111.85 (2br. m, C^{12} and C^{13}), 118.43 [ddd (d), C^{15}, $^1J_{HC^{15}}$ 162.8 Hz, $^3J_{POCC^{15}}$ 12.1 Hz, $^3J_{HC^{17}C^{15}}$ 8.0 Hz], 125.81 [br. dd (s), C^{18}, $^1J_{HC^{18}}$ 161.5 Hz, $^3J_{HC^{16}CC^{18}}$ 8.5 Hz], 123.74 [dd (s), C^{17}, $^1J_{HC^{17}}$ 163.3 Hz, $^3J_{HC^{15}CC^{17}}$ 8.3 Hz], 129.38 [ddd (s), C^{16}, $^1J_{HC^{16}}$ 163.0 Hz, $^3J_{HC^{18}CC^{16}}$ 8.7 Hz, $^2J_{HCC^{16}}$ 8.7 Hz], 160.83 [dt (d), C^{23}, $^2J_{PCC^{23}}$ 31.3 Hz, $^3J_{HC^{24}OC^{23}}$ 3.0 Hz], 163.66 [dt (d), C^{20}, $^3J_{PCCC^{20}}$ 16.6 Hz, $^3J_{HC^{21}OC^{20}}$ 3.6 Hz], 61.44 [tq (s), C^{24}, $^1J_{HC^{24}}$ 147.9 Hz, $^2J_{HC^{25}C^{24}}$ 4.2 Hz], 61.77 [tq (s), C^{21}, $^1J_{HC^{21}}$ 149.0 Hz, $^2J_{HC^{22}C^{21}}$ 4.2 Hz], 13.57 [qdd (s), C^{25}, $^1J_{HC^{25}}$ 127.4 Hz, $^2J_{HCC^{25}}$ 2.4 Hz, $^2J_{HCC^{25}}$ 3.0 Hz], 13.74 [qdd (s), C^{22}, $^1J_{HC^{22}}$ 124.8 Hz, $^2J_{HCC^{22}}$ 2.4 Hz, $^2J_{HCC^{22}}$ 3.0 Hz], 20.60 [qd (d), C^{19}, $^1J_{HC^{19}}$ 129.5 Hz, $^3J_{POCC^{19}}$ 10.4 Hz]. ^{31}P-{^{1}H} NMR ($CDCl_3$) δ_P: –25.4 (s). IR, ν/cm^{-1}: 3352, 2982, 2937, 1738, 1718, 1638, 1605, 1491, 1476, 1455, 1368, 1302, 1258, 1190, 1155, 1088, 1068, 1032, 930, 910, 875, 811, 764, 750, 730, 671, 642, 498. MS, *m/z*: 444 (11.2), [M]$^{+\cdot}$ (calc. for $C_8H_{10}O_5P$, 444), 416 (13.4) [M – Et + H]$^+$, 326 (40.5) [M – COOEt – OEt]$^+$, 299 (70.5) [M – 2COOEt]$^+$, 172 (100.0) [$C_6H_4PO_4$]$^+$, 110 (56.6) [$C_6H_6O_2$]$^+$.

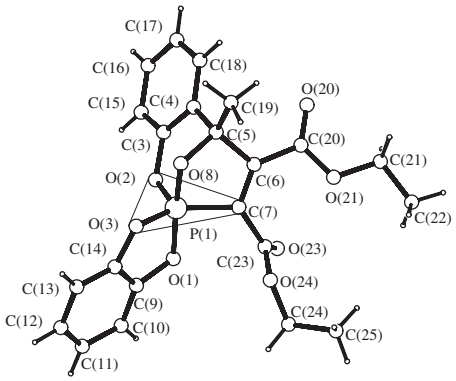


Figure 1 Molecular geometry of compound **5** in a crystal (the base of the trigonal bipyramid is shown by thin lines). Selected bond lengths (Å) and bond angles (°): P(1)–O(2) 1.612(2), P(1)–O(3) 1.630(2), P(1)–O(8) 1.6474(19), P(1)–O(1) 1.6940(19), P(1)–C(7) 1.822(3), O(3)–C(14) 1.389(3), O(2)–C(3) 1.403(3), O(1)–C(9) 1.367(3), O(8)–C(5) 1.442(3), C(3)–C(4) 1.397(4), C(7)–C(6) 1.331(4), C(7)–C(23) 1.490(4), C(5)–C(4) 1.511(4), C(5)–C(19) 1.511(4), C(5)–C(6) 1.527(4), C(6)–C(20) 1.494(4); O(2)–P(1)–O(3) 113.5(1), O(2)–P(1)–O(8) 97.1(1), O(3)–P(1)–O(8) 85.3(1), O(2)–P(1)–O(1) 91.5(1), O(3)–P(1)–O(1) 90.33(9), O(8)–P(1)–O(1) 171.3(1), O(2)–P(1)–C(7) 105.5(1), O(3)–P(1)–C(7) 141.0(1), O(8)–P(1)–C(7) 88.9(1), O(1)–P(1)–C(7) 89.8(1), C(14)–O(3)–P(1) 113.5(2), C(3)–O(2)–P(1) 122.4(2), C(9)–O(1)–P(1) 112.5(2), C(5)–O(8)–P(1) 109.6(2), C(6)–C(7)–P(1) 108.6(2), O(8)–C(5)–C(4) 104.9(2), O(8)–C(5)–C(6) 103.9(2), C(4)–C(5)–C(6) 109.6(2), C(7)–C(6)–C(5) 112.7(2).

the molecule. The phosphorus atom has an almost regular trigonal-bipyramidal configuration. The base of the trigonal bipyramid lies in the $O^2O^3C^7P^1$ plane [planar to within 0.0097(7) Å], from which the O^1 and O^8 atoms occupying apical positions deviate by 1.703(2) and –1.623(2) Å, respectively [the $O^1P^1O^8$ bond angle amounts to 171.3(1)°]. The sum of the $O^2P^1O^3$, $O^2P^1C^7$ and $O^3P^1C^7$ bond angles at the base of the bipyramid amounts to 360.0(1)°. The conformation of the phenylenedioxaphospholane ring is a flattened envelope [the P^1 atom deviates by –0.2108(7) Å from the $O^1C^9C^{14}O^3$ plane, which is planar to within 0.000(3) Å; the O^2, O^8 and C^7 atoms deviate from this plane by –1.753(2), –0.185(2) and 0.734(3) Å, respectively]. The other five-membered ring $O^8P^1C^7C^6C^5$ has the conformation of a more pronounced envelope [the O^8 atom deviates by –0.598(2) Å from the $P^1C^7C^6C^5$ plane, which is planar to within 0.041(3) Å]. The O^2 and C^4 atoms are arranged in the axial ring positions, whereas the O^3, O^8 and C^{19} atoms are in equatorial positions [they deviate by 1.523(2), 1.378(3), –0.942(2), –0.598(2) and –0.940(3) Å, respectively, from the $P^1C^7C^6C^5$ plane]. The $P^1O^2C^3C^4C^5O^8$ six-membered heterocycle in the molecule of **5** has an envelope conformation; the O^8 atom deviates by –0.828(2) Å from the $P^1O^2C^3C^4C^5$ fragment, which is planar to within 0.036(2) Å.

Note that phosphoranes **3** and **5** containing several chiral centres are formed as single diastereomers. Presumably, the reaction follows this pathway because new chiral centres are formed *via* conformationally rigid cyclic transition states (or intermediates) under strict spatial requirements for the mutual arrangement of substituents around such newly formed chiral centres.

Thus, the reaction of $\sigma^3\lambda^3$-benzophospholes, which contain carbonyl groups at γ- and σ-positions, with diethyl acetylenedicarboxylate can serve for the synthesis of $\sigma^5\lambda^5$-phosphoranes. It is important for organic synthesis that phosphorus–carbon, carbon–carbon and phosphorus–oxygen bonds are simultaneously formed.

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References

1 R. R. Holmes, *Acc. Chem. Res*., 2004, **37**, 746.
2 L. W. Tremblay, G. Zhang, J. Dai, D. Dunaway-Mariano and K. N. Allen, *J. Am. Chem. Soc*., 2005, **127**, 5298.
3 K. C. Kumara Swamy and N. Satish Kumar, *Acc. Chem. Res*., 2006, **39**, 324.
4 H. Xe and C. E. Stebbins, *Biophys. J*., 2006, **91**, 948.
5 J. Yang, T. Niu, A. Zhang, A. K. Mishra, Z. J. Zhao and G. W. Zhou, *J. Cell Biochem*., 2002, **84**, 47.
6 A. Munoz and L. Lamande, *Phosphorus Sulfur Silicon Relat. Elem*., 1990, **49/50**, 373.
7 L. M. Abdrakhmanova, V. F. Mironov, T. A. Baronova, M. N. Dimukhametov, D. B. Krivolapov, I. A. Litvinov, A. A. Balandina, Sh. K. Latypov and A. I. Konovalov, *Mendeleev Commun*., 2006, 320.
8 J. C. Martin and T. M. Balthazor, *J. Am. Chem. Soc*., 1977, **99**, 152.
9 A. Altomare, G. Cascarano, C. Giacovazzo and D. Viterbo, *Acta Crystallogr., Sect. A*, 1991, **47**, 744.
10 G. M. Sheldrick, *SHELXL97 – A Computer Program for Crystal Structure Determination*, University of Göttingen, 1997.
11 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
12 L. H. Straver and A. J. Schierbeek, *MOLEN. Structure Determination System*, Nonius B.V. Delft. Netherlands, 1994, vols. 1, 2.
13 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 34.

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§ *X-ray crystallographic data for* **5**. $C_{22}H_{21}O_8P$, $M = 444.36$, monoclinic, space group $P2_1/n$, $a = 7.564(2)$, $b = 17.360(4)$, $c = 16.041(2)$ Å, $\beta = 95.76(2)°$, $V = 2095.6(7)$ Å^3, $Z = 4$, $d_{calc} = 1.41$ g cm^{-3}. Cell parameters and intensities of 4390 independent reflections (2194 with $I \geq 2\sigma$) were measured on an Enraf-Nonius CAD-4 diffractometer in the $\omega/2\theta$-scan mode, $\theta \leq 26.30°$, using MoKα radiation with a graphite monochromator. No decrease in intensity was observed in three control measurements. Absorption correction was not applied. ($\mu_{Mo} = 1.79$ cm^{-1}). The structure was solved by the direct method using the SIR program[9] and refined by the full matrix least-squares method using the SHELX-97[10] software package. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealised. The final divergence factors are $R = 0.046$, $R_w = 0.102$ based on 2194 reflections with $F^2 \geq 2\sigma^2$. All calculations were performed on a PC using the WinGX[11] program. Cell parameters, data collection and data reduction were performed on an Alpha Station 200 computer using the MoLEN software.[12] The drawings of molecules were obtained using the PLATON program.[13]

CCDC 642850 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, 2007.