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A new approach to the synthesis of phosphoranes based on the reaction of benzo[*d*]-1,3,2-dioxaphospholes having a β- or γ-carbonyl group in exocyclic substituent with hexafluoroacetone

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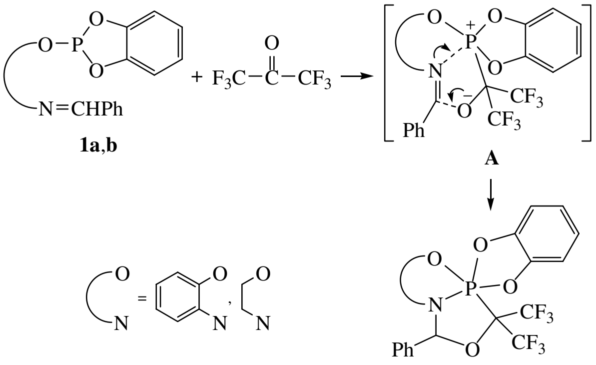
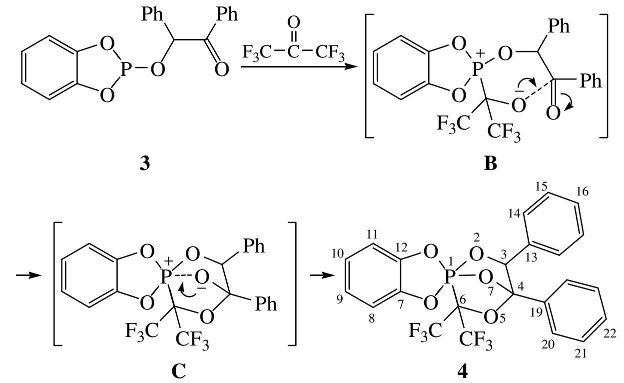
The reaction of 2-(2-oxo-1,2-diphenylethoxy)- and 2-(1-methyl-3-oxobut-2-en-1-yloxy)benzo[*d*]-1,3,2-dioxaphospholes with hexafluoroacetone is a versatile approach to the synthesis of 6,6-bis(trifluoromethyl)-3,4-diphenyl-1,1-phenylenedioxy-1-phospha-2,5,7-trioxabicyclo[2.2.1]heptane and 3,5-dimethyl-7,7-bis(trifluoromethyl)-1,1-phenylenedioxy-1-phospha-2,6,8-trioxabicyclo[2.2.1]oct-3-ene, respectively, in high yields.

Pentacoordinate phosphorus derivatives are key intermediates in phosphorylation reactions, which are of great importance in cell vital activity.[1–3] Recently, we found that the reaction of 2-benzylideneaminophenyl- and 2-benzylideneaminoethylbenzo[*d*]-1,3,2-dioxaphospholes **1a**,**b**, containing an N=C group at the γ-position to the phosphorus atom, with hexafluoroacetone can serve for the synthesis of phosphoranes containing a phosphorus–carbon bond, *viz.*, 3,3-bis(trifluoromethyl)-2,2-phenylenedioxy-5-phenyl-7,8-benzo-6-aza- and 3,3-bis(trifluoromethyl)-2,2-phenylenedioxy-5-phenyl-6-aza-1,4-dioxa-2-phosphabicyclo-[3.3.0^{2,6}]octanes **2a**,**b**.[4] Presumably, the reaction involves the intramolecular attack of the alkoxide ion of the intermediate P^+–C–O^--betaine (**A**) at the carbon of the N=C bond (Scheme 1).



Scheme 1



Scheme 2

In this study, we tried to synthesise phosphoranes in the reaction of hexafluoroacetone with trivalent phosphorus derivatives containing a carbonyl group at the β- or γ-position with respect to the phosphorus atom. In fact, 2-(2-oxo-1,2-diphenyl)ethoxybenzo-1,3,2-dioxaphosphole **3**, which was obtained by the phosphorylation of benzoin, readily reacts with hexafluoroacetone in dichloromethane to give a crystalline compound corresponding to the signal at δ_P –21.2 in the ^{31}P NMR spectrum. The chemical shift suggests the formation of a spirophosphorane, possibly, containing a phosphorus–carbon bond. The structure of this compound was established by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy.† The presence of a high-field doublet of septets, which corresponds to the carbon atom in the P–$C(CF_3)_2O$ fragment, in the ^{13}C NMR spectrum suggests unambiguously that the compound isolated is an individual diastereomer of spirophosphorane **4**. Complete assignment of ^{1}H and ^{13}C NMR spectra of **4** was accomplished by DEPT, 2D COSYGP, HSQC and HMBC experiments.[5] The ^{1}H NMR spectrum of compound **4** consists of a group of multiplets in the region δ 7.5–7.0 and a doublet at δ 5.67 ppm; the ^{13}C NMR spectrum of compound **4** contains 19 signals in the region δ 145–77. Note that a number of signals in ^{1}H and ^{13}C NMR spectra, which correspond to the resonance of the nuclei in the phenylenedioxaphospholane fragment (H^{8-11}, C^{7-12}), are much broader than other signals due to exchange process. Perhaps, this is the ligand exchange between equatorial and axial substituents at the phosphorus atom, *viz.*, O^1, O^3. Three groups of protons of the benzo moieties and phenyl groups are uniquely determined in the 2D COSY spectrum. The ^{13}C NMR chemical shifts of all hydrogenated carbons could be assigned unambiguously based on the 2D HSQC spectrum. The complete elucidation of the structure of compound **4** was based on the set of HMBC correlations shown schematically in Figure 1. The most important ones are between the protons at δ 5.67 (H^3), 7.17 ($H^{15,17}$) and the carbon resonance at 133.87 (C^{13}); the protons at δ 5.67 (H^3), 7.36 ($H^{20,24}$) and the carbon resonance at 101.24 (C^4); the protons at δ 7.24 ($H^{21,23}$) and the carbon resonance at 132.03 (C^{19}). Unfortunately, there are no HMBC correlations to some of carbon resonances (the signals of C^7/C^{12} are due to extensive broadening and those of C^6, C^{25} and C^{26} are due to these carbons 5–6 bonds away from the nearest proton) and could not be assigned directly. However, there are fine multiplet structures for C^6, C^{25} and C^{26} carbons due to spin–spin couplings with ^{19}F and ^{31}P, which make it possible to confirm the structure of the six-membered ring ($P^1O^2C^3C^4O^5C^6$). The rest of the broadened quaternary carbons with δ 144.5 and 140.5 can be assigned to C^{12} and C^7 (or *vice versa*).

Thus, experimental data cannot provide a way to differentiate the pairs C^7/C^{12}, C^8/C^{11} and C^9/C^{10}, respectively; therefore, a non-

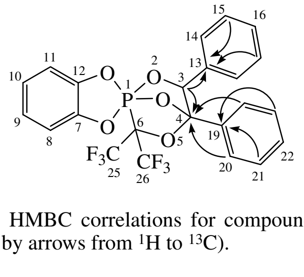


Figure 1 Principal HMBC correlations for compound **4** (the cross correlations are shown by arrows from ^{1}H to ^{13}C).

empirical calculation of ^{13}C chemical shifts (CS, GIAO B3LYP/6-31GD//RHF/6-31G[6]) was made to this end. A comparison of calculated CS *versus* experimental data gives good correlation and thus unequivocally proves our assignment for these carbons [δ: 144.51 (C^{12}), 140.46 (C^{7}), 124.53 (C^{10}), 122.08 (C^{9}), 111.69 (C^{8}), 111.21 (C^{11})]. The opposite assignment results in disagreement between experimental and theoretical data. Thus, the chemical structure of compound **4** was established by means of 2D NMR experiments and non-empirical calculation of CS.

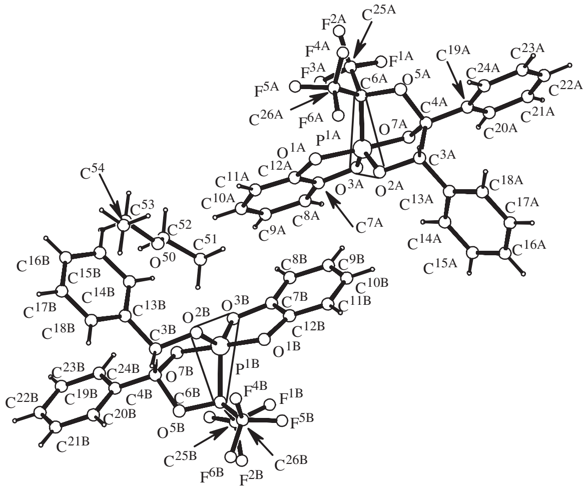


Figure 2 Geometry of the solvate of molecule **4** with diethyl ether in a crystal (two independent molecules; the base of the trigonal pyramid is shown by thin lines). Selected bond lengths (Å): P(1A)–O(3A) 1.618(2), P(1A)–O(1A) 1.665(2), P(1A)–O(7A) 1.686(2), P(1A)–C(6A) 1.891(3), P(1B)–O(2B) 1.604(2), P(1B)–O(3B) 1.613(2), P(1B)–O(1B) 1.664(2), P(1B)–O(7B) 1.692(2), P(1B)–C(6B) 1.888(3). Selected bond angles (°): O(2A)–P(1A)–O(3A) 125.6(1), O(2A)–P(1A)–O(1A) 92.4(1), O(3A)–P(1A)–O(1A) 91.9(1), O(2A)–P(1A)–O(7A) 91.9(1), O(3A)–P(1A)–O(7A) 85.1(1), O(1A)–P(1A)–O(7A) 175.6(1), O(2A)–P(1A)–C(6A) 101.8(1), O(3A)–P(1A)–C(6A) 131.6(1), O(1A)–P(1A)–C(6A) 95.0(1), O(7A)–P(1A)–C(6A) 84.6(1), O(1B)–P(1B)–O(7B) 176.4(1).

The reaction, probably, involves the initial formation of a bipolar ion with a P–C bond (**B**) (Scheme 2), in which an intramolecular attack of the alkoxide anion at the carbonyl group occurs to give betaine (**C**). The latter is stabilised by attacking the phosphorus atom to give spirophosphorane **4** as the end product formed with high stereoselectivity.

The structure of spirophosphorane **4** was also confirmed by X-ray diffraction analysis.‡ Figure 2 demonstrates the geometry of a solvate of two molecules of **4** with diethyl ether and presents selected parameters (bond lengths and bond angles). The phosphorus atom has a trigonal-bipyramidal configuration. The atoms C^{6}, O^{2} and O^{3} are arranged in equatorial positions

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† Melting points are uncorrected; measurements involved a Boetius melting point apparatus. NMR spectra were recorded on Bruker Avance-600 (^{1}H, 600 MHz; ^{13}C, 150.9 MHz), Bruker CXP-100 (^{31}P, 36.48 MHz) and Varian UNITY-300 (^{19}F, 287.17 MHz) spectrometers. The δ_{H} and δ_{P} values were determined relative to internal (HMDS) or external (H$_3$PO$_4$) standards. The δ_{F} values were determined relative to an internal (C$_6$F$_6$) standard. The δ_{C} values were determined relative to the signal of a deuterated solvent. IR spectra were recorded in Nujol using a Bruker Vector-22 instrument. EI mass spectra were obtained on a TRACE MS Finnigan MAT instrument; the energy of ionizing electrons was 70 eV, and the ion source temperature was 200 °C. The samples were introduced into the ion source through a direct inlet system. The ampoule vapourizer was heated in a programmed mode within a temperature range of 35–150 °C at a rate of 35 K min^{-1}. Mass-spectrometric data were processed using the Xcalibur software.

*2-(2-Oxo-1,2-diphenyl)ethoxybenzo[*d*]-1,3,2-dioxaphosphole* **3**. 2-Chlorobenzo[*d*]-1,3,2-dioxaphosphole (11.9 g, 0.06 mol) was added dropwise to a mixture of 2-oxo-1,2-diphenylethanol (9.8 g, 0.06 mol), diethyl ether (300 ml) and triethylamine (5.6 g, 0.06 mol) in an argon atmosphere. The solution was stirred for 2 h at –15 °C and then for 1 h to reach 20 °C. Filtration of the NEt$_3$·HCl precipitate and keeping the residue *in vacuo* at 50 Torr until dry resulted in compound **3** as a yellow liquid, which was then used without additional purification. The yield of compound **3** was 95% (20.0 g). ^{31}P-{^{1}H} NMR (CDCl$_3$) δ_{P}: 127.2 (s).

6,6-Bis(trifluoromethyl)-3,4-diphenyl-1,1-phenylenedioxy-1-phospha-2,5,7-trioxabicyclo[2.2.1]heptane **4**. Hexafluoroacetone (2.1 g, 0.013 mol) was condensed into a solution of dioxaphosphole **3** (4.05 g, 0.012 mol) in a mixture of CH$_2$Cl$_2$ and CCl$_4$ (30 ml, 1:1) at –45 to –50 °C. The mixture was kept for 5 days at room temperature and then kept *in vacuo* until the solvent volume decreased by a factor of two. The colourless precipitate was filtered off, washed with anhydrous diethyl ether and dried *in vacuo* (10 Torr). The yield of compound **4** was 3.1 g (50%), mp 116 °C. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ_{P}: –21.5 (s). ^{1}H NMR (CDCl$_3$) δ: 5.67 (d, 1H, H^{3}, $^{3}J_{\mathrm{POCH}}$ 19.2 Hz), 7.02 (br. m), 7.07 (br. m), 7.17 (m), 7.20 (m), 7.23 (m), 7.26 (br. m), 7.36 (br. m, H$^{9-12}$, H$^{14-16}$, H$^{20-22}$).^{13}C NMR (CDCl$_3$) δ (hereinafter, the multiplicity of signals in ^{13}C-{^{1}H} spectra is given in parentheses): 78.35 [d. sept (d. sept), C^{6}, $^{1}J_{\mathrm{PC^{6}}}$ 155.0 Hz, $^{2}J_{\mathrm{FCC^{6}}}$ 32.7 Hz], 88.75 [ddt (d), C^{3}, $^{1}J_{\mathrm{HC^{3}}}$ 157.7 Hz, $^{2}J_{\mathrm{POC^{3}}}$ 3.6 Hz, $^{3}J_{\mathrm{HCOCC^{3}}}$ 3.6 Hz], 101.24 [br. ddt (d), C^{4}, $^{2}J_{\mathrm{POC^{4}}}$ 26.1 Hz, $^{2}J_{\mathrm{HC^{3}C^{4}}}$ 3.7–4.2 Hz, $^{3}J_{\mathrm{HCO'CC^{4}}}$ 3.7–4.2 Hz], 111.22 [br. dm (br. d), C^{11}, $^{1}J_{\mathrm{HC^{11}}}$ 164.0 Hz, $^{3}J_{\mathrm{POCC^{11}}}$ 13.3 Hz], 111.72 [br. dm (br. d), C^{8}, $^{1}J_{\mathrm{HC^{8}}}$ 165.6 Hz, $^{3}J_{\mathrm{POCC^{8}}}$ 18.7 Hz], 121.08 [br. qd (br. qd), CF$_3$, $^{1}J_{\mathrm{FC}}$ 289.0 Hz, $^{2}J_{\mathrm{PCC}}$ 2.0–3.0 Hz], 121.88 [br. qd (br. qd), CF$_3$, $^{1}J_{\mathrm{FC}}$ 284.4 Hz, $^{2}J_{\mathrm{PCC}}$ 2.0–3.0 Hz], 122.04 [br. d (br. s), C^{9}, $^{1}J_{\mathrm{HC^{9}}}$ 162.5 Hz], 124.54 [br. d, (br. s), C^{10}, $^{1}J_{\mathrm{HC^{10}}}$ 163.0 Hz], 125.56 [ddd (s), C^{14}, $^{1}J_{\mathrm{HC^{14}}}$ 162.8 Hz, $^{3}J_{\mathrm{HC^{18}CC^{14}}}$ 6.5–7.0 Hz, $^{3}J_{\mathrm{HC^{16}CC^{14}}}$ 6.5–7.0 Hz], 127.14 [2ddd (s), C^{20}, C^{24}, $^{1}J_{\mathrm{HC^{20}}}$ 160.7 Hz, $^{3}J_{\mathrm{HC^{24}CC^{20}}}$ 6.8–7.0 Hz, $^{3}J_{\mathrm{HC^{22}CC^{20}}}$ 6.8–7.0 Hz, $^{1}J_{\mathrm{HC^{24}}}$ 163.2 Hz, $^{3}J_{\mathrm{HC^{20}CC^{24}}}$ 6.8–7.0 Hz, $^{3}J_{\mathrm{HC^{22}CC^{24}}}$ 6.8–7.0 Hz], 128.09 [dd (s), C^{15}, $^{1}J_{\mathrm{HC^{15}}}$ 162.5 Hz, $^{3}J_{\mathrm{HC^{17}CC^{15}}}$ 7.7 Hz], 128.15 [dd (s), C^{21}, $^{1}J_{\mathrm{HC^{21}}}$ 162.0 Hz, $^{3}J_{\mathrm{HC^{23}CC^{21}}}$ 7.7 Hz], 129.07 [dt (s), C^{16}, $^{1}J_{\mathrm{HC^{16}}}$ 161.0 Hz, $^{3}J_{\mathrm{HC^{14}CC^{16}}}$ 7.4 Hz], 129.63 [dt (s), C^{22}, $^{1}J_{\mathrm{HC^{22}}}$ 161.0 Hz, $^{3}J_{\mathrm{HC^{20}CC^{22}}}$ 7.5 Hz], 132.04 [dt (d), C^{13}, $^{3}J_{\mathrm{POCC^{13}}}$ 12.2 Hz, $^{3}J_{\mathrm{HC^{15}CC^{13}}}$ 7.4 Hz], 133.88 [td (br. d), C^{19}, $^{3}J_{\mathrm{HC^{21}CC^{19}}}$ 7.5 Hz, $^{3}J_{\mathrm{POCC^{19}}}$ 1.5 Hz], 140.45 [m (br. d), C^{7}, $^{2}J_{\mathrm{POC^{7}}}$ 6.0–7.0 Hz], 144.51 [m (br. d), C^{12}, $^{2}J_{\mathrm{POC^{12}}}$ 7.0–8.0 Hz]. ^{19}F NMR (CDCl$_3$) δ_{F}: –76.77 (m, CF$_3$), –76.55 (m, CF$_3$). IR (Nujol, ν/cm^{-1}): 3073, 1959, 1892, 1811, 1774, 1702, 1632, 1606, 1485, 1338, 1280, 1265, 1256, 1233, 1212, 1151, 1133, 1100, 1077, 1047, 1023, 989, 945, 920, 896, 864, 843, 830, 790, 767, 718, 710, 696, 679, 668, 638, 618, 595, 558, 541, 508, 496, 484, 420. MS, *m*/*z* (%): 516 (6.6) [M]$^{+\cdot}$ (calc. for C$_{23}$H$_{15}$F$_6$O$_5$P, 516), 497 (0.13) [M – F]$^{+}$, 411 (40.5) [M – – PhCO]$^{+}$, 410 (75.2) [M – PhCHO]$^{+}$, 350 (10.7) [M – (CF$_3$)$_2$CO]$^{+}$, 245 (40.2) [M – (CF$_3$)$_2$CO – PhCO]$^{+}$, 167 (79.9) [C$_8$H$_9$O$_2$P]$^{+}$, 139 (100.0) [C$_6$H$_4$O$_2$P]$^{+}$, 105 (89.6) [C$_7$H$_5$O]$^{+}$, 92 (67.2) [C$_7$H$_8$]$^{+}$, 77 (71.4) [Ph]$^{+}$, 69 (12.4) [CF$_3$]$^{+}$. A single crystal of compound **4** for the X-ray analysis was obtained by crystallisation from a diethyl ether–dichloromethane mixture as a solvate of two molecules of **4** with one molecule of diethyl ether, mp 113–117 °C (decomp.).

*2-(1-Methyl-3-oxobut-2-en-1-yloxy)benzo[*d*]-1,3,2-dioxaphosphole* **5**. 2-(*O*-trimethylsilyl)pent-2-en-3-one (14.1 g, 0.08 mol) was added dropwise to 2-chlorobenzo[*d*]-1,3,2-dioxaphosphole (14.3 g, 0.08 mol) in an argon atmosphere. The mixture was kept for 3 h at room temperature and then kept *in vacuo* (50 Torr) until dry. Compound **5** (light yellow liquid) was used without additional purification. The yield of compound **5** was 95% (18.0 g). ^{31}P-{^{1}H} NMR (CDCl$_3$) δ_{P}: 126.1 and 120.4 (2s).

‡ *X-ray analysis data for compound* **4**: 2C$_{23}$H$_{15}$F$_6$O$_5$P·O(C$_2$H$_5$)$_2$, M = 1106.76, triclinic, space group $P\bar{1}$, a = 11.194(2), b = 12.882(3) and c = 18.220(4) Å, α = 71.22(2)°, β = 78.34(2)°, γ = 76.530(2)°, V = 2395.9(9) Å^3, Z = 2, d_{calc} = 1.53 g cm^{-3}. Cell parameters and intensities of 10226 independent reflections (7016 reflections with $I \geq 2\sigma$) were measured on an Enraf-Nonius CAD-4 diffractometer in the $\omega/2\theta$ scan mode, $\theta \leq 80.87°$, using CuKα radiation with a graphite monochromator. An empirical correction for absorption based on ψ-scans was applied (μ_{Cu} 18.03 cm^{-1}). The structure was solved by the direct method using the SIR program[7] and refined by the full matrix least-squares method using the SHELX-97 software package.[8] All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealized. The final divergence factors are R = 0.066, R_w = 0.178 based on 7016 reflections with $F^2 \geq 2\sigma^2$. All calculations were performed on a PC using the WinGX software.[9] Cell parameters, data collection and data reduction were performed on an Alpha Station 200 computer using the MoLEN software.[10] The figures of molecules were prepared using the PLATON software.[11] The configuration of the chiral centres is $\mathrm{C}^{3}_{R}\mathrm{C}^{4}_{S}\mathrm{P}^{1}_{R}$ (**A**) and $\mathrm{C}^{3}_{S}\mathrm{C}^{4}_{R}\mathrm{P}^{1}_{S}$ (**B**) (for the nomenclature of chiral pentacoordinate compounds, see ref. 12).

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 625073. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.

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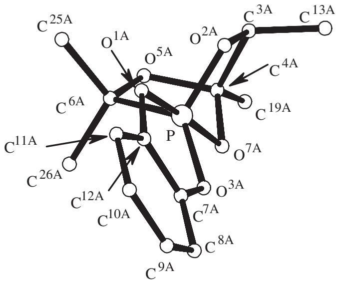
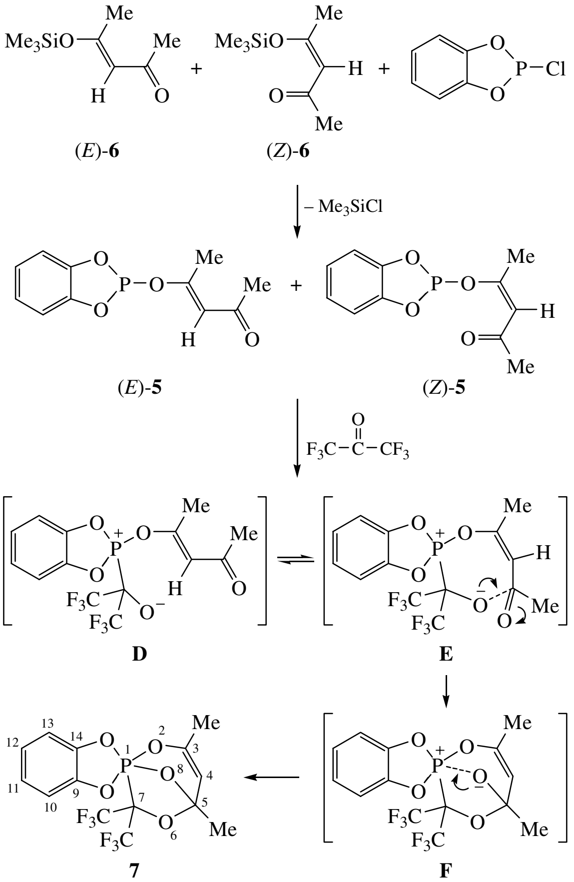


Figure 3 Conformations of bicyclic benzodioxaphosphole and bicycloheptane fragments in a molecule of **4A** (for simplicity, hydrogen, fluorine and C^{14-18}, C^{20-24} atoms are not shown).

and form, together with the phosphorus atom, a bipyramid base [planar to within 0.088(2) Å in a molecule of **A** or to within 0.098(2) Å in a molecule of **B**], whereas the atoms O^1 and O^7 occupy axial positions [their deviations from plane $O^2O^3P^1C^6$ are –1.731(2), 1.612(2) Å in a molecule of **A** and 1.731(2), –1.616(2) Å in a molecule of **B**]. The nearly planar phenylenedioxaphospholane ring occupies an axial-equatorial position. Note that the molecule of spirophosphorane **4** contains an extended planar fragment incorporating a phenylenedioxaphospholane ring and a phenyl substituent at C^4 ($O^1P^1O^3C^{7-12}O^7C^4C^{19-24}$) (Figure 3 demonstrates the conformations of heterocycles in molecule **4**). The remaining 1-phospha-2,5,7-trioxabicyclo[2.2.1]-heptane fragment of the molecule is arranged in the trigonal bipyramid in such a way that the P^1–O^7 bond (which is common for both five-membered rings) is axial, while the P^1–C^6 and P^1–O^2 bonds are located at the bypiramid base.

Compound **5** containing a carbonyl group at the γ-position to the phosphorus atom in the exocyclic substituent, like β-carbonyl-substituted phosphole **3**, can react with hexafluoroacetone by intramolecular cyclisation (Scheme 3). Starting heterocycle **5** was obtained by phosphorylation of the *E*- and *Z*-isomers of the trimethylsilyl derivative of acetylacetone **6**, 2-chlorobenzo-[*d*]-1,3,2-dioxaphosphole. Its ^{31}P-{^{1}H} NMR spectrum contains two signals at δ 126.1 and 126.4 in the ratio of 1:1, which also corresponds to the *Z*- and *E*-isomers. Although the geometric situation in the *E*-isomer does not favour the reaction with hexafluoroacetone occurring as intramolecular cyclisation, both isomers react to give a single compound corresponding to a high-field singlet with δ_P –25.0 in the ^{31}P-{^{1}H} NMR spectrum. The structure of this compound was established by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy.§ It was found that spirophosphorane **7** with a phosphorus–carbon bond was also formed in this case. We assume that the reaction starts with a nucleophilic attack of the phosphorus atom on the carbonyl group of hexafluoroacetone to give bipolar ions **D** and **E**. Presumably, bipolar ion **D** can be transformed to ion **E**. Because the phosphorus atom bears a positive charge, which enhances its electron-withdrawing properties, the energy of the double bond C=C decreases and rotation around it becomes possible. This probably results in an equilibrium transition of bipolar ion **D** into structure **E**, which is removed from the equilibrium mixture due to a fast intramolecular attack at the exocyclic carbonyl group to give bipolar ion **F**. The subsequent intramolecular attack of the alkoxide anion at the phosphorus atom results in phosphorane **7** as the final product.



Scheme 3

Thus, the use of phospholes **3** and **5** containing a carbonyl group at β- or γ-position to the phosphorus atom in a reaction with hexafluoroacetone enables highly stereoselective synthesis of spirophosphoranes with complex structures incorporating a phosphorus–carbon bond and containing several chiral centres. The method can be expanded to other functionally substituted derivatives of trivalent phosphorus containing activated multiple bonds as substituents.

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§ *3,5-Dimethyl-7,7-bis(trifluoromethyl)-1,1-phenylenedioxy-1-phospha-2,6,8-trioxabicyclo[2.2.1]oct-3-ene* **7**. Hexafluoroacetone (6.30 g, 0.038 mol) was condensed into a solution of dioxaphosphole **5** (8.93 g, 0.037 mol) in a mixture of CH_2Cl_2 and CCl_4 (30 ml, 1:1) at –45 to –50 °C. The mixture was kept for 5 days at room temperature and then kept *in vacuo* until the solvent volume decreased by a factor of two. The colourless crystals were filtered off, washed with anhydrous ether and dried *in vacuo* (10 Torr). The yield of compound **7** was 10.6 g (70%), mp 65 °C. ^{31}P-{^{1}H} NMR ($CDCl_3$) δ_P: –25.0 (s). ^{1}H NMR ($CDCl_3$) δ: 6.92–7.15 (m, H^{10-13}), 5.17 (m, H^4, ${}^4J_{\mathrm{HCC^5C^4H}}$ 2.1 Hz, ${}^4J_{\mathrm{HCC^3C^4H}}$ 2.1 Hz), 1.82 (dd, C^3Me, ${}^4J_{\mathrm{HC^4CCH}}$ 2.1 Hz, ${}^4J_{\mathrm{POCCH}}$ 1.2 Hz), 1.68 (d, C^5Me, ${}^4J_{\mathrm{HC^4CCH^4}}$ 2.1 Hz). ^{13}C NMR ($CDCl_3$) δ: 19.23 [qdd (d), *Me*C^3, ${}^1J_{\mathrm{HC}}$ 129.4 Hz, ${}^3J_{\mathrm{POCC}}$ 10.6 Hz, ${}^3J_{\mathrm{HC^4CC}}$ 2.9 Hz], 25.24 [qdd (d), *Me*C^5, ${}^1J_{\mathrm{HC}}$ 129.4 Hz, ${}^3J_{\mathrm{POCC}}$ 6.8 Hz, ${}^3J_{\mathrm{HC^4CC}}$ 1.9 Hz], 80.55 [d. sept (d. sept), C^7, ${}^1J_{\mathrm{HC^7}}$ 151.6 Hz, ${}^2J_{\mathrm{FCC^7}}$ 31.1 Hz], 99.70 [ddq (d), C^5, ${}^2J_{\mathrm{HC^5C^5}}$ 6.6 Hz, ${}^2J_{\mathrm{HCC^5}}$ 5.0 Hz, ${}^2J_{\mathrm{POC^5}}$ 5.0 Hz], 108.53 [ddqq (d), C^4, ${}^1J_{\mathrm{HC^4}}$ 169.7 Hz, ${}^3J_{\mathrm{POCC^4}}$ 5.2 Hz, ${}^3J_{\mathrm{HCCC^4}}$ 3.9–4.0 Hz, ${}^3J_{\mathrm{HCC^5C^4}}$ 3.9–4.0 Hz], 111.39 [ddddd (d), C^{13}, ${}^1J_{\mathrm{HC^{13}}}$ 165.7 Hz, ${}^3J_{\mathrm{POCC^{13}}}$ 12.8 Hz, ${}^3J_{\mathrm{HC^{11}CC^{13}}}$ 8.7 Hz, ${}^2J_{\mathrm{HC^{12}C^{13}}}$ 1.2 Hz, ${}^4J_{\mathrm{HC^{10}CCC^{13}}}$ 1.2 Hz], 111.86 [dddm (d), C^{10}, ${}^1J_{\mathrm{HC^{10}}}$ 165.3 Hz, ${}^3J_{\mathrm{POCC^{10}}}$ 18.7 Hz, ${}^3J_{\mathrm{HC^{12}CC^{10}}}$ 7.3 Hz, ${}^2J_{\mathrm{HC^{10}C^{11}}}$ 2.0 Hz, ${}^4J_{\mathrm{HC^{13}CCC^{10}}}$ 2.0 Hz], 122.18 [br. qm (br. qm), CF_3, ${}^1J_{\mathrm{FC}}$ 287.5 Hz, ${}^2J_{\mathrm{PCC}}$ 3.7–4.0 Hz, ${}^3J_{\mathrm{FCCC}}$ 1.7–2.0 Hz], 122.28 [br. qm (br. qm), CF_3, ${}^1J_{\mathrm{FC}}$ 285.0 Hz, ${}^2J_{\mathrm{PCC}}$ 2.0–2.5 Hz, ${}^3J_{\mathrm{FCCC}}$ 1.7–2.0 Hz], 122.36 [br. dd (s), C^{12}, ${}^1J_{\mathrm{HC^{12}}}$ 162.5 Hz, ${}^3J_{\mathrm{HC^{10}CC^{12}}}$ 7.7–7.8 Hz], 124.29 [dd (s), C^{11}, ${}^1J_{\mathrm{HC^{11}}}$ 162.7 Hz, ${}^3J_{\mathrm{HC^{13}CC^{11}}}$ 8.2 Hz], 141.33 [dddd (d), C^{14}, ${}^3J_{\mathrm{HC^{12}CC^{14}}}$ 8.5–8.6 Hz, ${}^3J_{\mathrm{HC^{10}CC^{14}}}$ 8.5–8.6 Hz, ${}^2J_{\mathrm{POC^{14}}}$ 8.0 Hz, ${}^2J_{\mathrm{HC^{13}C^{14}}}$ 3.7 Hz], 145.02 [dq (s), C^3, ${}^2J_{\mathrm{HC^4C^3}}$ 7.8–8.0 Hz, ${}^2J_{\mathrm{HCC^3}}$ 7.7–8.0 Hz], 154.17 [ddd (d), C^9, ${}^2J_{\mathrm{POC^9}}$ 9.1 Hz, ${}^3J_{\mathrm{HC^{11}CC^9}}$ 7.2 Hz, ${}^3J_{\mathrm{HC^{13}CC^9}}$ 7.2 Hz]. ^{19}F NMR ($CDCl_3$) δ_F: –74.62 (qd, CF_3, ${}^4J_{\mathrm{FCCCF}}$ 9.7 Hz, ${}^3J_{\mathrm{PCCF}}$ 5.1 Hz), –72.85 (qd, CF_3, ${}^4J_{\mathrm{FCCCF}}$ 9.7 Hz, ${}^3J_{\mathrm{PCCF}}$ 3.5 Hz). IR (ν/cm^{-1}): 1688, 1600, 1489, 1463, 1437, 1428, 1391, 1356, 1251, 1229, 1206, 1152, 1132, 1102, 1074, 1027, 984, 944, 880, 833, 809, 798, 771, 746, 711, 674, 666, 606, 577, 538, 508, 478, 460, 451, 420. MS, *m*/*z* (%): 404 (4.1) $[M]^{+\cdot}$ (calc. for $C_{14}H_{11}F_6O_5P$, 404), 238 (2.6) $[M-(CF_3)_2CO]^+$, 172 (100.0) $[C_7H_9O_3P]^+$, 156 (63.6) $[C_6H_9O_3P]^+$, 110 (41.6) $[C_6H_6O_2]^+$, 69 (25.6) $[CF_3]^+$.

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