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New synthesis of phosphine oxides bearing a 2-methyl-4-oxopent-2-yl substituent

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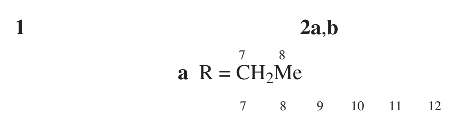
A new approach to the synthesis of substituted phosphine oxides bearing an oxo group at the γ-position to the phosphorus atom was developed.

A current trend in modern organic chemistry is the design of new phosphorus-containing ligands, which possess high stability and selectivity for complexations. Phosphine oxides are the most convenient precursors in the phosphine synthesis. Owing to a high chemical stability in acid and alkaline media and pronounced complexing properties with respect to the metal ions, phosphine oxides are used as ligands in metallocomplex catalysis[1–4] and bifunctional one,[5,6] for the creation of ion-selective electrodes[7,8] and extraction of metals.[9,10] Fluorescent complexes of phosphine oxides with rare-earth metals are the most suitable for the creation of OLEDs[11,12] due to a high light-emitting ability and stability.

Chiral phosphine oxides, as well as chiral phosphines, attract considerable attention due to their application as ligands for complex catalysts in asymmetric synthesis[13–15] and in other fields.[16]

Here, we propose a new approach to the synthesis of functionally substituted phosphine oxides, which contain an oxo group at the γ-position to the phosphorus atom. This approach involves the reaction of such easily available heterocycles as 1,2-oxaphospholene-2-oxides with organometallic compounds and results in a formation of the new P–C bond. Thus, the reaction of well-known 2-chloro-3,3,5-trimethyl-1,2-oxaphospholene-2-oxide **1**[17–19] with organomagnesium compounds in a ratio of 1:2 (Scheme 1) gives rise to the substitution of both exocyclic P–Cl and endocyclic P–O bonds. A cleavage of the cycle and a formation of dialkyl(2-methyl-4-oxopent-2-yl)-phosphine oxides **2** with high yields (> 90%) occur in this process.[†]

The structure and composition of isolated phosphine oxides **2** were established by NMR spectroscopy and high-resolution mass spectrometry. There is a peak of the protonated molecular ion with *m*/*z* 205 $[M + H]^{+\bullet}$ in the electron impact mass spectrum of phosphine oxide **2a**. The first step of decomposition leads to the elimination of the methyl or ethyl group bonded with phosphorus atom and causes the appearance of peaks with *m*/*z* 189 and 175 in the mass spectrum. The directions of the fragmentation involving the removal of an acetyl group and an acetone fragment are characteristic of the obtained phosphine



1 **2a**,**b**

a R = $\overset{7}{C}H_2\overset{8}{M}e$

b R = $\overset{7}{C}H_2\overset{8}{C}H_2\overset{9}{C}H_2\overset{10}{C}H_2\overset{11}{C}H_2\overset{12}{M}e$

Scheme 1

[†] 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), Bruker Avance-400 (^{1}H, 400 MHz; ^{13}C, 100.6 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.

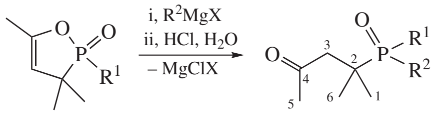
Diethyl(2-methyl-4-oxopent-2-yl)phosphine oxide **2a**. Compound **1** (5.7 g, 0.0316 mol) was added dropwise with stirring to the ethylmagnesium bromide prepared from magnesium (1.9 g, 0.079 mol) and ethyl bromide (5.9 ml, 8.6 g, 0.079 mol) in diethyl ether (30 ml) according to the standard procedure in the argon atmosphere. The reaction mixture was refluxed during 1 h, cooled to 20 °C and treated with water (30 ml) and then concentrated hydrochloric acid (7 ml). Water and organic layers were separated and the water layer was extracted three times with CH_2Cl_2. Combined methylene chloride extract and organic layer were evaporated and then dried in a vacuum (12 Torr, 100 °C) to give compound **2a**, a light-yellow oil, 5.6 g (86% yield), bp 100–102 °C (0.02 Torr), n_D^{20} 1.4831, d_4^{20} 1.038. Found (%): C, 58.60; H, 10.56; P, 15.36. Calc. for $C_{10}H_{21}O_2P$ (%): C, 58.80; H, 10.36; P, 15.16.

Dihexyl(2-methyl-4-oxopent-2-yl)phosphine oxide **2b** was prepared as described above from magnesium (9.16 g, 0.382 mol), 1-iodohexane (56.6 ml, 80.98 g, 0.382 mol) in diethyl ether (80 ml) and 1,2-oxaphospholene oxide **1** (30 g, 0.166 mol). Yield of **2b**, 47 g (90%), transparent oil, bp 160–162 °C (0.06 Torr), n_D^{20} 1.4695. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.88 (br. t, 6H, H^{12}, $^3J_{HCCH}$ 7.1 Hz), 1.25 (d, 6H, H^1, H^6, $^3J_{PCCH}$ 14.8 Hz), 1.27 (m, 8H, H^{10}, H^{11}), 1.36 (m, 4H, H^9, $^3J_{HCCH}$ 6.2–6.5 Hz), 1.56 (m, 4H, H^8, two AB-parts of two ABCD-spectra), 1.63 and 1.71 (2m, 4H, PCH^7, two CD-parts of two ABCD-spectra), 2.14 (s, 3H, H^5), 2.65 (d, 2H, H^3, $^3J_{PCCH}$ 8.0 Hz). ^{31}P-{^{1}H} NMR (36.46 MHz, $CDCl_3$) δ_P: 51.6 (s). MS, *m*/*z*: 317 $[M + H]^{+\bullet}$, 316 $[M]^{+\bullet}$, 287 [M – Et], 273 $[M - C_2H_3O]$, 279 $[M - C_3H_5O]$, 235 $[M - C_6H_9]$, 231 $[M - C_6H_{13}]$, 218 $[C_{12}H_{27}OP]$, 217 $[C_{12}H_{26}OP]$, 162 $[C_{12}H_{26}OP - C_4H_7]$, 161 $[C_6H_{14}OP - C_4H_8]$, 148 $[M - C_6H_{11} - C_5H_{10}]$, 133 $[C_6H_{14}OP]$, 99.0 $[C_6H_{11}O]$, 78, 55, 43, 29. Found (%): C, 68.22; H, 11.88; P, 9.89. Calc. for $C_{18}H_{37}O_2P$ (%): C, 68.32; H, 11.78; P, 9.79.

oxides and result in the appearance of peaks with *m/z* 161 and 147. An origination of other characteristic ions is caused by the subsequent decomposition of the above ions.

We have found that the utilization of such heterocycles as 2-alkyl-3,3,5-trimethyl-1,2-oxaphospholene-2-oxide **3**[17,18,20,21] bearing two exo- and endocyclic P–C bonds in the reaction with the organomagnesium compounds allows us to synthesize asymmetrically substituted phosphine oxides **4**, in which there are three different substituents at the phosphorus atom.[‡]

Thus, the reaction of oxaphospholenes **3** with Grignard reagents followed by hydrolysis resulted in the formation of 2-methyl-4-oxopent-2-ylphosphine oxides **4** with the yields of > 95%. Namely, the use of heterocycles such as **3** allows us to exclude the formation of by-products and supplies high reaction selectivity and the purity and high yield of phosphine oxides **4**.



3a,**b** **4a**,**b**

a $R^1 = \overset{7}{Me}$, $R^2 = \overset{8}{C}H_2\overset{9}{C}H_2\overset{10}{C}H_2\overset{11}{Me}$

b $R^1 = \overset{7}{C}H_2\overset{8}{Me}$, R^2 = 2-$MeOC_6H_4$

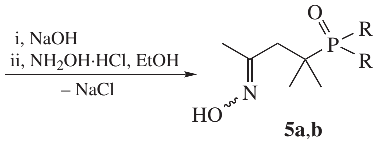
Scheme 2

The structures of the compounds obtained were confirmed by ^1H, ^{13}C, ^{31}P NMR, IR spectroscopy and mass spectrometry. The protons of methyl groups (C^1H_3, C^6H_3) are nonequivalent in the ^1H NMR spectrum of phosphine oxides **4** (δ 1.22 ppm, $^3J_{PCCH}$ 15.9 Hz; δ 1.54 ppm, $^3J_{PCCH}$ 11.4 Hz) that is caused by the presence of the asymmetric phosphorus atom. The protons of R^1 and R^2 substituents resonate as AB-part of the $ABMX_3$ system. The protons of the C^3H_2 group are also nonequivalent and are revealed in view of the AB-multiplet.

The resonance picture of the 2-methyl-4-oxopentyl substituent in ^{13}C NMR spectra has a similar character for all of the obtained compounds. A characteristic doublet ($^3J_{PCCC}$ 10–12 Hz) of carbonyl group is observed at the low-field region. The signals of the *sp*^{3} carbons are revealed in a high-field region. The doublets of C^2 and C^3 are the most easily interpreted due to the spin–spin coupling constants with phosphorus. Methyl groups C^1H_3 and C^6H_3 of phosphine oxides **4a**,**b** are nonequivalent in ^{13}C-{^1H} NMR as well as ^1H NMR spectra. There are no spectral evidences of the keto-enol tautomerism in compounds **2**, **4**. Moreover, the structure of phosphine oxide **4b** was confirmed by the single-crystal X-ray diffraction (Figure 1).[§] The phosphorus atom has a distorted tetrahedral configuration.

We have investigated chemical properties of compounds **2**. Oximes **5** were obtained by treatment of phosphine oxides **2** with hydroxylamine (Scheme 3).[¶]

2a,**b**



5a,**b**

a R = Et
b R = *n*-hexyl

Scheme 3

[‡] *Butyl(2-methyl-4-oxopent-2-yl)methylphosphine oxide* **4a** was prepared as described above from magnesium (1.1 g, 0.046 mol), 1-bromobutane (4.9 ml, 6.3 g, 0.046 mol) and 2,3,3,5-tetramethyl-1,2-oxaphosphol-4-ene-2-oxide **3a** (5.5 g, 0.0344 mol) in diethyl ether (60 ml). Yield of **4a**, 7.2 g (96%), a brown oil. ^1H NMR (600 MHz, $CDCl_3$) δ: 0.44 (t, 3H, H^{11}, $^3J_{HCCH}$ 7.3 Hz), 0.79 [d, 6H, H^1 (+ H^6), $^3J_{PCCH}$ 15.3 Hz], 0.80 [d, 6H, H^6 (+ H^1), $^3J_{PCCH}$ 15.3 Hz], 0.93 [d, 5H, H^7 (+ H^{10}), $^2J_{PCH}$ 11.7 Hz], 0.97 [m, 5H, H^{10} (+ H^7), $^3J_{HCCH}$ 7.3–7.4 Hz, $^3J_{HCCH}$ 7.3–7.4 Hz], 1.04, 1.13, 1.21, 1.29 (4m, 4H, $H^{8,9}$), 1.68 (s, 3H, H^5), 2.19–2.21 (m, 2H, H^3, AB-spectrum, $^3J_{PCCH}$ 8.8 Hz). ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 19.72 [qm (s), C^1, $^1J_{HC^1}$ 128.0 Hz], 33.49 [br. dm (d), C^2, $^1J_{PC^2}$ 66.8 Hz], 45.79 [br. t (s), C^3, $^1J_{HC^3}$ 125.4 Hz], 205.35 [m (d), C^4, $^3J_{PCCC^4}$ 12.3 Hz, $^2J_{HCC^4}$ 5.6–5.7 Hz, $^2J_{HCC^4}$ 5.6–5.7 Hz], 31.22 [q (s), C^5, $^1J_{HC^5}$ 127.4 Hz], 19.62 [qm (s), C^6, $^1J_{HC^6}$ 128.0 Hz], 8.20 [qd (d), C^7, $^1J_{HC^7}$ 128.9 Hz, $^1J_{PC^7}$ 63.0 Hz], 23.64 [br. tdm (d), C^8, $^1J_{PC^8}$ 63.9 Hz, $^1J_{HC^8}$ 125.2 Hz], 22.70 [tdm (d), C^9, $^1J_{HC^9}$ 125.0–127.0 Hz], 23.20 [tdm (d), C^{10}, $^1J_{HC^{10}}$ 125.0–127.0 Hz, $^3J_{PCCC^{10}}$ 13.6 Hz], 12.58 [qm (d), C^{11}, $^1J_{HC^{11}}$ 125.0 Hz, $^2J_{HCC^{11}}$ 3.7–3.9 Hz, $^3J_{HCCC^{11}}$ 3.7–3.9 Hz]. ^{31}P-{^1H} NMR (36.46 MHz, $CDCl_3$) δ_P: 54.7 (s). MS, *m/z*: 219 $[M + H]^{+\bullet}$, 203 [M – Me], 175 [M – – MeCO], 161 [M – C_3H_5O], 145 [$C_6H_{10}O_2P$], 119 [$C_5H_{12}PO$], 99 [$C_6H_{11}O$], 77.8, 66.9, 42.8, 18. Found (%): C, 60.43; H, 10.72; P, 14.39. Calc. for $C_{11}H_{23}O_2P$ (%): C, 60.53; H, 10.62; P, 14.19.

Ethyl(2-methyl-4-oxopent-2-yl)-2-methoxyphenylphosphine oxide **4b** was prepared as described above from magnesium (2.0 g, 0.0833 mol), 1-bromo-2-methoxybenzene (10.4 ml, 15.67 g, 0.0833 mol) and 2-ethyl-3,3,5-tetramethyl-1,2-oxaphosphol-4-ene-2-oxide **3b** (6.0 g, 0.0345 mol) in diethyl ether (70 ml). Water and organic layers were separated. Phosphine oxide **4b** was crystallized from organic layer as white precipitate. Yield of **4b**, 9.2 g (95%), mp 97–98 °C. ^1H NMR (600 MHz, $CDCl_3$) δ: 1.04 (dt, 3H, H^8, $^3J_{PCCH}$ 12.0 Hz, $^3J_{HCCH}$ 7.8 Hz), 1.17 (d, 3H, H^1, $^3J_{PCCH}$ 15.9 Hz), 1.34 (d, 3H, H^6, $^3J_{PCCH}$ 15.4 Hz), 2.03 (m, 1H, H^7, A-part of ABM_3X-spectrum, $^2J_{PCH}$ 14.5–15.0 Hz, $^2J_{HH}$ 14.5–15.0 Hz, $^3J_{HCCH}$ 7.6 Hz), 2.12 (s, 3H, H^5), 2.32 (m, H^7, 1H, B-part of ABM_3X-spectrum, $^3J_{HCCH}$ 7.6 Hz, $^2J_{PCH}$ 7.6 Hz, $^2J_{HH}$ 14.4–15.0 Hz), 2.48 (dd, 1H, H^3, A-part of ABX-spectrum, $^2J_{HH}$ 15.9 Hz, $^3J_{PCCC}$ 9.8 Hz), 2.79 (dd, 1H, H^3, B-part of ABX-spectrum, $^2J_{HH}$ 15.9 Hz, $^3J_{PCCC}$ 7.8 Hz), 3.84 (s, 3H, H^{15}), 6.92 (dd, 1H, H^{11}, $^4J_{PCCCH}$ 5.1 Hz, $^3J_{HCCH}$ 8.1 Hz), 7.12 (dd, 1H, H^{13}, $^3J_{HCCH}$ 7.8 Hz, $^3J_{HCCH}$ 7.3 Hz), 7.51 (br. dd, 1H, H^{12}, $^3J_{HCCH}$ 8.1 Hz, $^3J_{HCCH}$ 7.3 Hz), 7.98 (ddd, 1H, H^{14}, $^3J_{PCCH}$ 12.0 Hz, $^3J_{HCCH}$ 7.8 Hz, $^4J_{HCCCH}$ 1.4–1.7 Hz). ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 20.56 [br. qm (s), C^1, $^1J_{HC^1}$ 128.0 Hz, $^3J_{HCCC^1}$ 2.8 Hz], 35.76 [dm (d), C^2, $^1J_{PC^2}$ 67.9 Hz, $^2J_{HCC^2}$ 3.8 Hz], 47.26 [br. t (s), C^3, $^1J_{HC^3}$ 126.1 Hz], 206.22 [m (d), C^4, $^3J_{PCCC^4}$ 11.6–12.0 Hz, $^2J_{H^3CC^4}$ 5.7–6.0 Hz, $^2J_{H^2CC^4}$ 5.7–6.0 Hz], 31.57 [q (s), C^5, $^1J_{HC^5}$ 127.2 Hz], 21.15 [br. qm (s), C^6, $^1J_{HC^6}$ 128.0 Hz, $^3J_{HCCC^6}$ 2.8 Hz], 17.25 [tdq (d), C^7, $^1J_{HC^7}$ 126.8 Hz, $^1J_{PC^7}$ 66.1 Hz, $^2J_{HC^8C^7}$ 4.0–4.1 Hz], 5.13 [qdt (d), C^8, $^1J_{HC^8}$ 129.0 Hz, $^2J_{PCC^8}$ 5.7 Hz, $^2J_{HCC^8}$ 5.0–5.2 Hz], 116.86 [dm (d), C^9, $^1J_{PC^9}$ 82.6 Hz], 158.70 [m (d), C^{10}, $^2J_{PCC^{10}}$ 4.7 Hz], 109.95 [ddd (d), C^{11}, $^1J_{HC^{11}}$ 159.2 Hz, $^3J_{PCCC^{11}}$ 6.5 Hz, $^3J_{HC^{13}CC^{11}}$ 6.9–7.2 Hz], 133.09 [dd (s), C^{12}, $^1J_{HC^{12}}$ 160.0 Hz, $^3J_{HC^{14}CC^{12}}$ 8.9 Hz], 120.35 [ddd (d), C^{13}, $^1J_{HC^{13}}$ 163.0 Hz, $^3J_{PCCC^{13}}$ 9.7 Hz, $^3J_{HC^{11}CC^{13}}$ 7.3–7.5 Hz], 135.72 [dddd (d), C^{14}, $^1J_{HC^{14}}$ 163.4 Hz, $^3J_{HC^{12}CC^{14}}$ 8.4 Hz, $^2J_{PCC^{14}}$ 4.0 Hz, $^2J_{HC^{13}C^{14}}$ 4.0 Hz]. ^{31}P-{^1H} NMR (36.46 MHz, $CDCl_3$) δ_P: 55.3 (s). MS, *m/z*: 282 $[M]^{+\bullet}$, 267 $[M – Me]^+$, 253 $[M – Et]^+$, 254 $[M – C_2H_4]^+$, 266 [M – MeCOCH], 201 [M – $MeCCH_2Me_2$], 184 [EtP(O)-(H)C_6H_4OMe] [M – $C_6H_{10}O$] [M_1], 155 [M_1 – Et], 137 [M_1 – – MeOH – Me], 125 [M_1 – C_2H_4 – MeO], 107 [M_1 – EtPOH], 77 [Ph], 98 [$C_6H_{10}O$], 83 [$C_6H_{10}O$ – Me]. Found (%): C, 63.80; H, 8.23; P, 10.99. Calc. for $C_{15}H_{23}O_3P$ (%): C, 63.82; H, 8.21; P, 10.97.

[§] The X-ray diffraction data for compound **4b** were collected on an Enraf-Nonius CAD4 automatic diffractometer using graphite monochromated MoKα (0.71073 Å) radiation. Crystals of compound **4b** ($C_{15}H_{23}O_3P$) are monoclinic, $a = 12.159(6)$, $b = 8.185(4)$ and $c = 16.442(6)$ Å, $\beta = 108.55(3)°$, $V = 1551.3(12)$ Å^3, $Z = 4$, $d_{calc} = 1.209$ g cm^{-3}, space group $P2_1/c$. Cell parameters and intensities of 3138 independent reflections, from which 2544 with $I \geq 2\sigma$, were measured in the $\omega/2\theta$-scan, $\theta \leq 26.28°$ mode. Absorption correction was not applied [μ(Mo) = 1.79 cm^{-1}]. The structure was solved by a direct method using the SIR[22] program and refined by the full matrix least-squares using the SHELXL97 program.[23] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and refined as riding atoms. All calculations were performed on PC using WinGX program.[24] The final residuals were $R_{obs} = 0.0425$, $R_{w\,obs} = 0.1185$. Cell parameters, data collection and data reduction were performed on an Alpha Station 200 computer using the MolEN program.[25] All figures were made using the PLATON program.[26]

CCDC 746980 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.

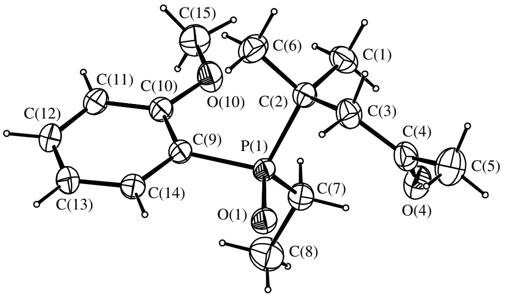


Figure 1 Molecular geometry of compound **4b** in a crystal. Selected bond lengths (Å), bond and torsion angles (°): P(1)–O(1) 1.493(2), P(1)–C(2) 1.862(2), P(1)–C(7) 1.825(2), P(1)–C(9) 1.813(2), O(4)–C(4) 1.208(3), O(10)–C(10) 1.368(2), O(10)–C(15) 1.416(3), C(4)–C(5) 1.511(4), C(3)–C(4) 1.492(3), C(2)–C(3) 1.548(3); O(1)–P(1)–C(2) 110.84(8), O(1)–P(1)–C(9) 108.30(8), O(1)–P(1)–C(7) 113.19(8), C(2)–P(1)–C(9) 109.43(8), C(2)–P(1)–C(7) 110.07(8), C(7)–P(1)–C(9) 104.77(9), C(3)–C(4)–C(5) 116.0(2), C(2)–C(3)–C(4) 119.5(2), P(1)–C(2)–C(3) 107.9(1), O(1)–P(1)–C(2)–C(3) 21.2(2), O(1)–P(1)–C(2)–C(1) 144.3(1), O(1)–P(1)–C(2)–C(6) –94.4(1), C(9)–P(1)–C(2)–C(3) 140.6(1), C(5)–P(1)–C(4)–C(14) –96.4(2), O(1)–P(1)–C(9)–C(10) –175.6(2), O(1)–P(1)–C(9)–C(14) –0.7(2), C(15)–O(6)–C(6)–C(10) 171.2(2), O(1)–P(1)–C(7)–C(8) 60.0(2).

The course of the hydroxyimination reaction was controlled by IR spectroscopy. Disappearing of an intense band of the carbonyl group at 1700–1720 cm^{-1} and appearing the less intense band of C=N group at 1640–1650 cm^{-1} indicate that the reaction has finished. A broad band due to the stretching vibrations of the hydroxyl group (3150–3300 cm^{-1}) also appeared when the reaction was complete. Any spectral confirmation of the imino-enamine tautomerism was not found. Two signals with the ratio of about 1:3 were observed in ^{31}P NMR spectra. The most signals were duplicated in ^{1}H NMR spectra and the integral signal strengths were also 1:3 due to the *E*,*Z*-isomerism relative to C=N bonds. As a whole, the spectral parameters of oximes **5a**,**b** are similar to those for the initial phosphine oxides **2a**,**b**.

In conclusion, a new effective synthetic approach to 2-methyl-4-oxopent-2-ylphosphine oxides, based on the reaction of 1,2-oxaphospholene derivatives with the Grignard reagents, has been developed.

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¶ *4-(Dihexylphosphoryl)-4-methylpentan-2-one oxime* **5b**. A solution of sodium hydroxide (0.3824 g, 0.01435 mol) in ethanol (10 ml) was added dropwise under stirring to the cold (ice-bath) mixture of compound **2b** (2 g, 0.00844 mol) and hydroxylamine hydrochloride (0.9972 g, 0.01435 mol) in ethanol (10 ml). The reaction mixture was refluxed during 1 h, then the solvent was evaporated to dryness in a vacuum (12 Torr, 60 °C). The residue was twice extracted with methylene chloride. The extract was separated from a water layer and dried in a vacuum (12 Torr, 60 °C) to give a light-yellow oil, which gradually formed crystals. Oxime **5b**, 1.9 g (89%), was obtained as the mixture of light-yellow crystals (the mixture of *E*- and *Z*-forms in a ratio of 1:3), mp 66–67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (t, H^{12}, $E + Z$, $^{3}J_{HCCH}$ 7.0 Hz), 1.17 (d, H^{1}, H^{6}, Z, $^{3}J_{PCCH}$ 14.7 Hz), 1.21 (d, H^{1}, H^{6}, E, $^{3}J_{PCCH}$ 14.6 Hz), 1.29 (m, H^{10}, H^{11}, $E + Z$), 1.38 (m, H^{9}, $E + Z$), 1.55–1.75 (m, H^{7}, H^{8}, $E + Z$), 2.11 (s, H^{5}, E + Z), 2.43 (d, H^{3}, Z, $^{3}J_{PCCH}$ 7.5 Hz), 2.59 (d, H^{3}, E, $^{3}J_{PCCH}$ 7.8 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 21.38 [br. qm (br. s), C^{1}, C^{6}, $Z + E$, $^{1}J_{HC}$ 127.7 Hz, $^{3}J_{HCCC}$ 4.9 Hz, $^{3}J_{HC^{3}CC}$ 4.9 Hz], 36.11 [dm (d), C^{2}, Z, $^{1}J_{PC^{2}}$ 64.0 Hz], 36.09 [dm (d), C^{2}, E, $^{1}J_{PC^{2}}$ 64.0 Hz], 40.75 [tm (d), C^{3}, Z, $^{1}J_{HC^{3}}$ 128.0 Hz, $^{2}J_{PCC^{3}}$ 1.0 Hz], 36.09 [tm (d), C^{3}, E, $^{1}J_{HC^{3}}$ 128.0 Hz, $^{2}J_{PCC^{3}}$ 2.2 Hz], 153.85 [m (d), C^{4}, Z, $^{3}J_{PCCC^{4}}$ 13.5 Hz, $^{2}J_{HC^{3}C^{4}}$ 6.6 Hz, $^{2}J_{HC^{5}C^{4}}$ 6.6 Hz], 153.49 [m (d), C^{4}, E, $^{3}J_{PCCC^{4}}$ 11.8 Hz, $^{2}J_{HC^{3}C^{4}}$ 6.6–6.7 Hz, $^{2}J_{HC^{5}C^{4}}$ 6.6–6.7 Hz], 30.84 [qt (br. s), C^{5}, Z, $^{1}J_{HC^{5}}$ 127.1 Hz, $^{3}J_{HC^{3}CC^{5}}$ 3.8 Hz], 23.26 [qm (d), C^{5}, E, $^{1}J_{HC^{5}}$ 127.2 Hz, $^{3}J_{HC^{3}CC^{5}}$ 3.8–4.0 Hz, $^{4}J_{PCCCC^{5}}$ 0.6 Hz], 24.55 [dm (d), C^{7}, Z, $^{1}J_{PC^{7}}$ 60.9 Hz], 24.47 [dm (d), C^{7}, E, $^{1}J_{PC^{7}}$ 60.9 Hz], 31.33 [tm (d), C^{8}, E + Z, $^{1}J_{HC^{8}}$ 126.0 Hz, $^{2}J_{PCC^{8}}$ 6.3 Hz], 31.27 [tm (d), C^{9}, E + Z, $^{1}J_{HC^{9}}$ 126.0 Hz, $^{3}J_{PCCC^{9}}$ 18.6 Hz], 22.47 [tm (s), C^{10}, $E + Z$, $^{1}J_{HC^{10}}$ 125.2 Hz, $^{3}J_{HCCC^{10}}$ 3.5–4.0 Hz, $^{2}J_{HCC^{10}}$ 3.5–4.0 Hz], 22.28 [tm (s), C^{11}, $E + Z$, $^{1}J_{HC^{11}}$ 127.7 Hz], 13.99 [qm (s), C^{12}, $E + Z$, $^{1}J_{HC^{12}}$ 124.5–125.0 Hz]. ^{31}P-{^{1}H} NMR (36.46 MHz, $CDCl_3$) δ_P: 56.8 (s), 56.6 (s). Found (%): C, 65.51; H, 11.34; N, 4.14; P, 9.41. Calc. for $C_{18}H_{38}NO_2P$ (%): C, 65.22; H, 11.55; N, 4.23; P, 9.34.