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LETTERS TO THE EDITOR

Reaction of 3,3,5-Trimethyl-2-chloro-1,2-oxaphospholene 2-Oxide with Grignard Reagents, a Convenient Approach to the Synthesis of Dialkyl(diaryl)-(1-methyl-4-oxopent-2-yl)phosphine Oxides

D. A. Tatarinov, V. F. Mironov, A. A. Kostin, T. A. Baronova, and B. I. Buzykin

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

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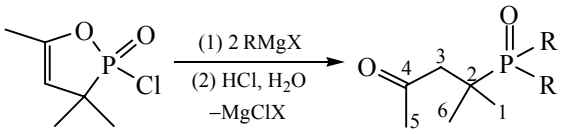
An important area in the chemistry of organophosphorus compounds is the design of new types of P-ligands containing, along with the phosphorus(III) atom or phosphoryl group, one or more other functional groups (amino, hydroxy, oxo, etc.). In this regard, of particular interest is a modification of the phosphine oxides, which are used widely and in diverse applications. Thus, the complexes of phosphine oxides with some metals show catalytic properties in a number of organic reactions [1] and are used for the preparation of ion-selective electrodes [2, 3], and in high-performance extraction of various metals [4, 5]. Fluorescent complexes of phosphine oxides with lanthanum group metals are used as light emitting components in organic light emitting diodes and devices based on them [6]. The functionalization of phosphine oxides by introduction of additional complexing groups extends their application, but is hampered by the lack of simple approaches to their synthesis allowing a wide variation of the nature of the substituents, particularly at the phosphorus atom.

We developed a new approach to the synthesis of a class of functionally substituted phosphine oxides containing carbonyl group in the γ-position to the phosphorus atom. It consists in the reaction of P-heterocycles such as 3,3,5-trimethyl-2-chloro-1,2-oxaphospholene 2-oxide (**I**) [7–9] with organomagnesium compounds in 1:2 ratio. After hydrolysis of the reaction mixture dialkyl(diaryl)(1-methyl-4-oxopent-2-yl)phosphine oxides (**II**) were isolated in high yields (above 90%).



I **IIa–IIc**

R = $CH_2CH_2CH_3$ (**a**), $CH_2CH_2CH_2CH_3$ (**b**), Ph (**c**).

The structure of phosphine oxides **II** was confirmed by ^1H, ^{31}P, and ^{13}C NMR spectroscopy, IR spectroscopy, and mass spectrometry.

(1-Methyl-4-oxopent-2-yl)dipropylphosphine oxide (IIa). To the Grignard reagent obtained by a usual procedure from 3.3 g (0.1375 mol) of magnesium and 12.5 ml (16.9 g, 0.1375 mol) of propyl bromide in 50 ml of diethyl ether was added dropwise 10 g (0.0554 mol) of chlorophospholene **I**. The reaction mixture was vigorously stirred for 30 min, then it was neutralized with 30 ml of water and 12 ml of concentrated hydrochloric acid at vigorous stirring and boiling. The organic layer was separated from the aqueous layer, the latter was extracted with three 200-ml portions of methylene chloride, the extracts were combined with the organic layer, the solvent was distilled off, and the residue was dried in a vacuum (12 mm Hg, 100°C). We isolated 12.0 g (93%) of compound **IIa** as a light yellow oil, bp 122–124°C (0.03 mm Hg), n_D^{20} 1.4760. IR spectrum, cm^{-1}: 732, 782, 830, 907, 944, 990, 1034, 1080, 1134, 1161, 1249, 1365, 1414, 1463, 1647, 1713, 2876, 2935, 2966. 0.93 br t (H^9, 6H, $^3J_{HCCH}$ 7.2–7.4), 1.19 d ($H^{1,6}$,

6H, $^3J_{PCCH}$ 15.5), 1.52 m (H^8, 4H, $^3J_{HCCH}$ 7.2–7.4, $^3J_{HCCH}$ 6.5–7.0), 1.73 and 1.82 two m (H^7, 4H, *AB*-part of $ABMX_2$ spectrum), 2.08 s (H^5, 3H), 2.69 d (H^3, 2H, $^3J_{PCCH}$ 9.8). ^{13}C NMR spectrum (D_2O), δ, ppm (*J*, Hz) (in parentheses is shown the shape of the signal in the ^{13}C–{^{1}H} NMR spectrum): 20.22 q.m (s) (C^{1,6}, $^1J_{HC^{1,6}}$ 128.6), 34.78 d.m (d) (C^2, $^1J_{PC^2}$ 63.1, $^2J_{HCC^2}$ 4.2, $^2J_{HCC^2}$ 3.6), 46.83 br.t.m (br.s) (C^3, $^1J_{HC^3}$ 128.0), 213.16 d.q.t (d) (C^4, $^3J_{PCCC^4}$ 11.4, $^2J_{HC^5C^4}$ 5.5–6.0, $^2J_{HC^3C^4}$ 5.5–6.0), 32.44 q.t.d (d) (C^5, $^1J_{HC^5}$ 128.0, $^3J_{HC^3CC^5}$ 3.6, $^4J_{PCCCC^5}$ 1.8), 25.35 br.t.d.m (d) (C^7, $^1J_{HC^7}$ 126.2, $^1J_{PC^7}$ 61.3, $^2J_{HC^8C}$7 3.0–4.0, $^3J_{HC^9CC}$7 6.0–7.0), 15.61 t. d.q.t. (d), (C^8, $^1J_{HC^8}$ 128.6, $^2J_{PCC^8}$ 5.0, $^2J_{HC^7C^8}$ 4.2–4.5, $^2J_{HC^9C^8}$ 4.2–4.5), 15.42 q.d.t.t (d), (C^9, $^1J_{HC^9}$ 126.3, $^3J_{PCCC^9}$ 15.0, $^2J_{HC^8C^9}$ 4.2, $^3J_{HC^7CC^9}$ 5.6–6.0). ^{31}P–{^{1}H} NMR spectrum: δ_P 56.4 ppm. Found, %: C 62.24; H 10.65; P 13.23. $C_{12}H_{25}O_2P$. Calculated, %: C 62.04; H 10.85; P 13.33.

Dibutyl-(1-methyl-4-oxopent-2-yl)phosphine oxide (IIb) was obtained by a similar method, yield 89%, bp 136°C (0.06 mm Hg), n_D^{20} 1.4745 (compare with the data [10]). IR spectrum, cm^{-1}: 460, 494, 723, 795, 900, 941, 966, 1049, 1092, 1145, 1168, 1308, 1361, 1381, 1413, 1465, 1714, 2872, 2959, 3416. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.92 br.t (H^{10}, 6H, $^3J_{HCCH}$ 7.2), 1.38 d (H^{1,6}, 6H, $^3J_{PCCH}$ 16.0), 1.45 m (H^9, 4H, $^3J_{HCCH}$ 7.2–7.4), 1.57 and 1.69, two m (H^8, 4H, $^3J_{HCCH}$ 7.2–7.4), 2.20 and 2.03, two m (H^7, 4H), 2.19 s (H^5, 3H), 2.90 br.d (H^3, 2H, $^3J_{PCCH}$ 11.7). ^{13}C NMR spectrum, δ, ppm (*J*, Hz) (in parentheses is shown the shape of the signal in the ^{13}C–{^{1}H} NMR spectrum): 20.99 q.m (s) (C^{1,6}, $^1J_{HC^{1,6}}$ 129.5, $^3J_{HC^3CC^{1,6}}$ 4.2–4.5, $^3J_{HC^{6,1}CC^{1,6}}$ 4.2–4.5), 34.63 br.d.m (d) (C^2, $^1J_{PC^2}$ 60.5), 47.87 br.t.m (br.s) (C^3, $^1J_{HC^3}$ 125.7), 205.56 d.q.t (d) (C^4, $^3J_{PCCC^4}$ 10.2, $^2J_{HC^5C^4}$ 5.4–5.6, $^2J_{HC^3C^4}$ 5.4–5.6), 31.44 q.d (d) (C^5, $^1J_{HC^5}$ 127.8, $^4J_{PCCCC^5}$ 1.3), 22.19 br.d.t (d) (C^7, $^1J_{PC^7}$ 58.0, $^1J_{HC^7}$ 127.9), 23.45 t.d.m (d), (C^8, $^1J_{HC^8}$ 125.1, $^2J_{PCC^8}$ 5.1, $^2J_{HC^9C^8}$ 5.1, $^2J_{HC}$7$_{C^8}$ 5.1, $^3J_{HC^{10}CC^8}$ 5.1–5.3), 23.52 t.d.m (d), (C^9, $^1J_{HC^9}$ 126.0, $^3J_{PCCC^9}$ 15.3, $^2J_{HC^8C^9}$ 3.4–4.1, $^2J_{HC^{10}C^9}$ 3.4–4.1, $^3J_{HC^7CC^9}$ 3.4–4.1), 12.95 q.t.t (s), (C^{10}, $^1J_{HC^{10}}$ 125.4, $^2J_{HC^9C^{10}}$ 3.4–4.1, $^3J_{HC^8CC^{10}}$ 3.4–4.1). ^{31}P–{^{1}H} NMR spectrum: δ_P 52.3 ppm. Found, %: C 64.47; H 11.35; P 11.86. $C_{14}H_{29}O_2P$. Calculated, %: C 64.59; H 11.23; P 11.90.

(1-Methyl-4-oxopent-2-yl)diphenylphosphine oxide (IIc) was obtained by a similar method from bromobenzene, yield 94%, mp 76–78°C (compare with the data [11–13]). IR spectrum, cm^{-1}: 429, 456, 513, 541, 583, 635, 709, 720, 756, 779, 836, 858, 943, 998, 1025, 1074, 1113, 1168, 1273, 1314, 1360, 1383 , 1437, 1467, 1482, 1591, 1712, 1904, 1973, 2878, 2938, 2976. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.43 d (H^{1,6}, 6H, $^3J_{PCCH}$ 15.9), 2.11 s (H^5, 3H), 2.73 d (H^3, 2H, $^3J_{PCCH}$ 7.3), 7.51–7.55 m (CH-*m*, CH-*p*, 6H, *AA'B*-part of the *AA'BMXX'* spectrum), 7.99 br.d.d (CHO, 4H, *XX'*-part of the *AA'BMXX'* spectrum $^3J_{HCCH}$ 8.0–8.3, $^3J_{PCCH}$ 8.3–8.5). ^{31}P–{^{1}H} NMR spectrum: δ_P 39.7 ppm. Mass spectrum, *m*/*z*: 301 [M + H]$^+$, 300 [M]$^+$, 285 [M – CH_3], 257 [M – C_2H_3O], 244 [M – C_3H_4O], 243 [M – C_3H_5O], 219 [M – C_6H_9], 202 [M – $C_6H_{10}O$], 201 [M – $C_6H_{11}O$], 155 [$C_{12}H_{11}$], 154 [$C_{12}H_{10}$], 125 [C_6H_7OP], 124 [C_6H_6OP], 99.0 [$C_6H_{11}O$], 81 [C_6H_9], 77, 57, 55, 43, 29. Found, %: C 71.93; H 7.09; P 10.27. $C_{18}H_{21}O_2P$. Calculated, %: C 71.98; H 7.05; P 10.31.

The ^{1}H, ^{13}C, ^{13}C–{^{1}H}, and ^{31}P–{^{1}H} NMR spectra were recorded on Bruker Avance-600 (600 MHz, ^{1}H, 150.9 MHz, ^{13}C) and Bruker CXP-100 instruments (36.48 MHz, ^{31}P) in $CDCl_3$ relative to internal HMDS or the signal of solvent, and to the external H_3PO_4. The IR spectra were taken on a Bruker Vector-22 instrument from suspensions of substances in mineral oil, or from thin films between the KBr plates. The mass spectra were recorded on a TRACE MS Finnigan MAT instrument at the energy of ionizing electrons 70 eV and ion source temperature 200°C. Heating of the evaporator ampule was carried out in a programmed mode from 35 to 150°C with a step 35 deg min^{-1}. The processing of mass-spectral data was performed using the program Xcalibur.

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