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

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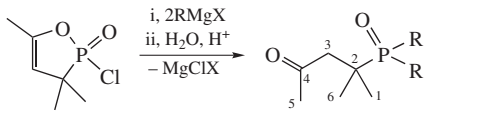
A new approach to the synthesis of substituted phosphine oxides bearing an oxo group at the γ-position to the phosphorus atom was developed.

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.