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LETTERS TO THE EDITOR

Reaction of Trivalent Phosphorus Acids Trimetylsilyl Esters with 3,5-Di-*tret*-butyl-4-hydroxybenzylidene Dichloride

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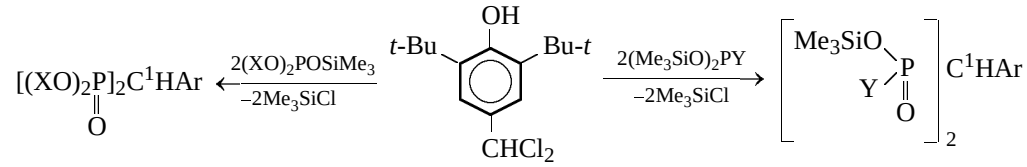
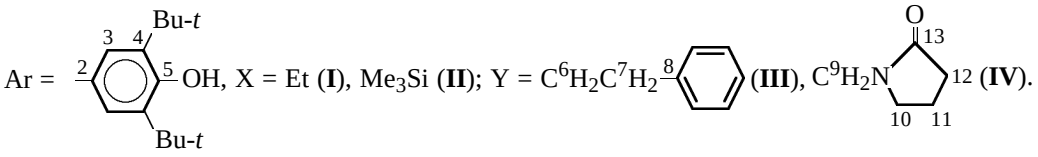
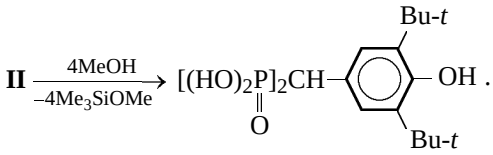
We have offered earlier convenient methods for the synthesis of some phosphorus-containing sterically hindered phenols which are of interest as perspective antioxidants and biologically active substances [1]. In the present work the reaction of trivalent phosphorus acids trimethylsilyl esters with readily available 3,5-di-*tert*-butyl-4-hydroxybenzylidene dichloride **A** [2] is shown to afford new methylenediphosphorus-containing compounds that include a fragment of sterically hindered phenol. Thus, trimethylsilyl phosphites as well as functional trimethylsilyl phosphonites in methylene chloride readily react with the chloride **A** according to the scheme of Arbuzov reaction forming diphosphonates (**I** or **II**) or diphosphinates (**III** or **IV**), respectively, in a high yield. Noteworthy that sterically hindered hydroxy group of chloride **A** does not enter in trimethylsilylation with the trimethylsilyl phosphite or trimethylsilyl phosphonite excess (cf. [1]).



I, II **A** **III, IV**



In reaction of diphosphonate (**II**), or diphosphinate (**III** and **IV**) with excess methanol we obtained white hygroscopic crystals of substituted acids with methylenediphosphorus group (**V**–**VII**).



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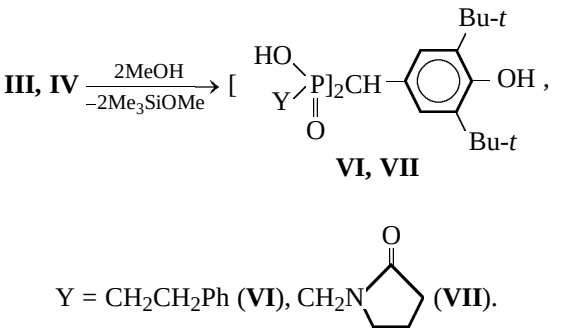
^{1}H NMR spectra of compounds (**I**–**VII**) contain characteristic signals of the methylenediphosphorus fragments PC^{1}HP and also signals of the substituted



aromatic fragments and fragments of pyrrolidone. According to the spectra, compound **IV** consists of two stereoisomers. We determined their ratio by means of ^{31}P NMR spectroscopy, the data for prevailing isomer are given first. The signal of methine proton in the PC^{1}HP fragment of the prevailing isomer are overlapped by the proton signals of pyrrolidone fragment. The methylene group proton signals of compounds **III**, **IV**, **VI**, and **VII** in the ^{1}H NMR spectra are partially overlapped and appear as multiplets.

Tetraethyl (3,5-di-*tert*-butyl-4-hydroxyphenyl)-methylenediphosphonate (I). To a solution of 6.8 g of diethyl trimethylsilyl phosphite in 20 ml of methylene chloride at cooling to 0°C and stirring was added a solution of 3.7 g of chloride **A** in 15 ml of methylene chloride. The mixture was stirred for 0.5 h, then heated to boiling and solvent was distilled off. To the rest 20 ml of hexane was added and the mixture was cooled to 0°C. The dropped white crystals were filtered off and kept in 0.5 mm Hg vacuum for 1 h. We obtained 5.7 g of diphosphonate **I**, yield 90%, mp 140°C (cf. [3]). ^{1}H NMR spectrum, δ, ppm: 1.11 t and 1.28 t (C*H*$_3$CH$_2$O, $^3J_{HH}$ 6 Hz), 1.42 s (Me$_3$C), 3.8–4.2 m (CH$_2$O), 3.62 t (C^{1}H, $^2J_{PH}$ 24 Hz), 5.45 br.s (OH), 7.24 s (C$_6$H$_2$). ^{13}C NMR spectrum, δ_C, ppm: 16.13 t and 16.34 t (*C*H$_3$CH$_2$O, $^3J_{PC}$ 3.5 Hz), 30.27 s (*Me*$_3$C), 34.32 s (Me$_3$*C*), 62.62 d and 63.33 d (CH$_2$O, $^2J_{PC}$ 3 Hz), 45.19 t (C^1, $^1J_{PC}$ 132 Hz), 120.12 t (C^2, $^2J_{PC}$ 6 Hz), 127.25 t (C^3, $^3J_{PC}$ 6 Hz), 135.87 s (C^4), 153.35 s (C^5). ^{31}P NMR spectrum, δ_P, ppm: 19.39 s.

Compounds **II**–**IV** were prepared similarly.

Tetra(trimethylsilyl) (3,5-di-*tert*-butyl-4-hydroxyphenyl)methylenediphosphonate (II). Yield of 89%, mp 156°C. ^{1}H NMR spectrum, δ, ppm: 0.13 s (Me$_3$Si), 1.41 s (Me$_3$C), 3.40 t (C^{1}H, $^2J_{PH}$ 26 Hz), 5.16 br.s (OH), 7.17 s (C$_6$H$_2$). ^{13}C NMR spectrum, δ_C, ppm: 0.78 s (Me$_3$Si), 30.18 s (*Me*$_3$C), 34.26 s (Me$_3$*C*), 48.79 t (C^1, $^1J_{PC}$ 140 Hz), 122.89 t (C^2, $^2J_{PC}$ 8.5 Hz), 127.31 t (C^3, $^3J_{PC}$ 6 Hz), 135.70 s (C^4), 153.16 s (C^5). ^{31}P, δ_P, ppm: 0.17 s.

Bis(trimethylsilyl) (3,5-di-*tert*-butyl-4-hydroxyphenyl)methylenebis(2-phenylethylphosphinate) (III). Yield 91%, mp 119°C. ^{1}H NMR spectrum, δ, ppm: 0.18 s (Me$_3$Si), 1.46 s (Me$_3$C), 3.29 t (C^{1}H, $^2J_{PH}$ 18 Hz), 7.0–7.3 m (C$_6$H$_2$, 2C$_6$H$_5$). ^{13}C NMR spectrum, δ_C, ppm: 1.23 s and 1.96 s (Me$_3$Si), 30.33 s (*Me*$_3$C), 34.39 s (Me$_3$*C*), 49.98 t (C^1, $^1J_{PC}$ 78.5 Hz); 120.98 t (C^2, $^2J_{PC}$ 7 Hz), 127.10 t (C^3, $^3J_{PC}$ 6 Hz), 136.34 s (C^4), 153.63 s (C^5), 33.17 d (C^6, $^1J_{PC}$ 96 Hz), 28.66 d (C^7, $^2J_{PC}$ 4 Hz), 141.29 d (C^8, $^3J_{PC}$ 16 Hz). ^{31}P NMR spectrum, δ_P, ppm: 37.96 s.

Bis(trimethylsilyl) (3,5-di-*tert*-butyl-4-hydroxyphenyl)methylenebis[*N*-(2-oxopyrrolidino)methylphosphinate] (IV). Yield 94%, mp 71°C. The first isomer, content 66%. ^{1}H NMR spectrum, δ, ppm: –0.08 s (Me$_3$Si), 1.24 s (Me$_3$C), 3.94 t (C^{1}H, $^2J_{PH}$ 17 Hz), 7.40 br.s (C$_6$H$_2$). ^{13}C NMR spectrum, δ_C, ppm: 0.90 s (Me$_3$Si), 30.07 s (*Me*$_3$C), 34.22 s (Me$_3$*C*), 50.17 t (C^1, $^1J_{PC}$ 78 Hz), 118.60 t (C^2, $^2J_{PC}$ 7 Hz), 126.25 s (C^3), 136.78 s (C^4), 153.70 s (C^5), 43.61 d (C^9, $^1J_{PC}$ 108 Hz), 48.47 s (C^{10}), 17.79 s (C^{11}), 30.00 s (C^{12}), 174.66 d (C^{13}, $^3J_{PC}$ 3 Hz). ^{31}P NMR spectrum, δ_P, ppm: 29.91 s. The second isomer. ^{1}H NMR spectrum, δ, ppm: –0.15 s (Me$_3$Si), 1.24 s (Me$_3$C), 7.40 br.s (C$_6$H$_2$). ^{13}C NMR spectrum, δ_C, ppm: 1.76 s (Me$_3$Si), 30.07 s (*Me*$_3$C), 34.22 s (Me$_3$*C*), 50.97 t (C^1, $^1J_{PC}$ 77 Hz), 119.52 t (C^2, $^2J_{PC}$ 5.5 Hz), 127.72 s (C^3), 135.99 s (C^4), 153.63 s (C^5), 43.50 d (C^9, $^1J_{PC}$ 106 Hz), 48.40 s (C^{10}), 17.72 s (C^{11}), 30.00 s (C^{12}), 174.46 s (C^{13}). ^{31}P NMR spectrum, δ_P, ppm: 29.18 s.

(3,5-Di-*tert*-butyl-4-hydroxyphenyl)methylenediphosphonic acid (V). To 30 ml of methanol at cooling to 10°C and stirring was added 7.6 g of diphosphonate **II**. The mixture was heated to boiling, solvent was distilled off, the residue was kept in vacuum of 1 mm Hg for 1 h. 4.2 g of acids **V** was isolated, yield 97%, mp 201°C. ^{1}H NMR spectrum, δ, ppm: 1.26 s (Me$_3$C), 3.60 t (C^{1}H, $^2J_{PH}$ 26 Hz), 7.22 s (C$_6$H$_2$). ^{13}C NMR spectrum, δ_C, ppm: 29.66 s (*Me*$_3$C), 34.17 s (Me$_3$*C*), 45.85 t (C^1, $^1J_{PC}$ 126 Hz), 123.42 t (C^2, $^2J_{PC}$ 7.5 Hz), 127.04 t (C^3, $^3J_{PC}$ 5.5 Hz), 139.87 s (C^4), 152.26 s (C^5). ^{31}P NMR spectrum, δ_P, ppm: 18.35 s. Found, %: C 47.19; H 6.97. C$_{15}$H$_{26}$O$_7$P$_2$. Calculated, %: C 47.37; H 6.89.

Acids **VI**–**VII** are similarly prepared.

(3,5-di-*tert*-butyl-4-hydroxyphenyl)methylenebis(2-phenylethylphosphinic) acid (VI). Yield 95%, mp 202°C. ^{1}H NMR spectrum, δ, ppm: 1.37 s (Me$_3$C), 3.82 t (C^{1}H, $^2J_{PH}$ 18 Hz), 7.36 s (C$_6$H$_2$). ^{13}C NMR spectrum, δ_C, ppm: 30.89 s (*Me*$_3$C), 35.03 s (Me$_3$*C*), 49.27 t (C^1, $^1J_{PC}$ 75 Hz), 123.14 t (C^2, $^2J_{PC}$ 5.5 Hz),

127.63 t (C^3, $^3J_{PC}$ 6 Hz), 139.47 s (C^4), 153.40 s (C^5), 31.59 d (C^6, $^1J_{PC}$ 94 Hz), 27.96 d (C^7, $^2J_{PC}$ 3 Hz), 142.26 d (C8, $^3J_{PC}$ 17 Hz). ^{31}P NMR spectrum, δ_P, ppm: 43.20 s. Found, %: C 66.68; H 7.69. $C_{31}H_{42}O_5P_2$. Calculated, %: C 66.89; H 7.60.

(3,5-di-*tert*-butyl-4-hydroxyphenyl)methylenebis[*N*-(2-oxopyrrolidino)methylphosphinic] acid (VII). Yield of 96%, mp 122°C. ^{1}H NMR spectrum, δ, ppm: 1.37 s (Me_3C), 3.64 t (C^1H, $^2J_{PH}$ 20 Hz), 7.27 s (C_6H_2). ^{13}C NMR spectrum, δ_C, ppm: 30.81 s (Me_3C), 34.94 s (Me_3C), 49.36 t (C^1, $^1J_{PC}$ 74 Hz), 121.57 t (C^2, $^2J_{PC}$ 5.5 Hz), 127.84 s (C^3), 138.76 s (C^4), 153.30 s (C^5), 42.75 d (C^9, $^1J_{PC}$ 106 Hz), 48.08 s (C^{10}), 17.94 s (C^{11}), 30.15 s (C^{12}), 174.31 s (C^{13}). ^{31}P NMR spectrum, δ_P, ppm: 35.01 s. Found, %: C 55.26; H 7.52. $C_{25}H_{40}N_2O_7P_2$. Calculated, %: C 55.35; H 7.43.

NMR spectra were registered on a Bruker Avance 400 spectrometer, solvents: $CDCl_3$ for compounds **I**–**IV**, D_2O for compound **V** or $(CD_3)_2SO$ for compounds **VI** and **VII**, reference compounds TMS (^{1}H, ^{13}C) and 85% H_3PO_4 in D_2O (^{31}P).

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