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**LETTERS
TO THE EDITOR**

Reaction of Substituted Benzalchlorides with Phosphorous Acid Esters

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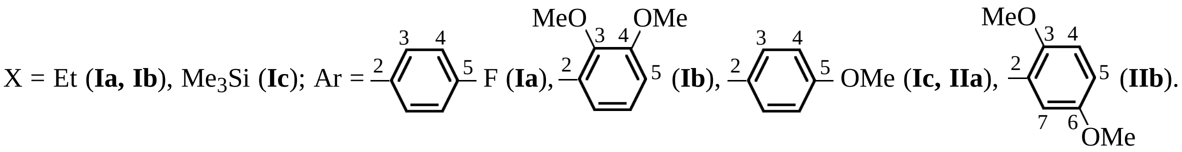
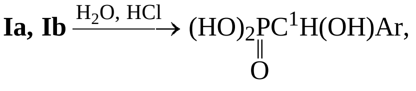
Functional methylenediphosphorus compounds are interesting as prospective ligands and biologically active compounds and also they are widely used in organic synthesis [1]. For the synthesis of arylmethylenediphosphonates of new type we studied reactions of triethyl- and tris(trimethylsilyl)phosphites taken in excess with a series of substituted benzalchlorides **A** prepared alongside the methods described esrlier [2]. We found that this reaction proceeds by the scheme of Arbuzov rearrangement only at heating the mixture to 150–160°C in the presence of zinc chloride as a catalyst and results, depending on the structure of the parent compounds, in formation of substituted phosphonates **I** or diphosphonates **II**. However, we failed to involve unsubstituted benzalchloride to this reaction under similar conditions.

$$\underset{\textbf{Ia–Ic}}{(XO)_2P(O)C^1H(Cl)Ar} \xleftarrow[-XCl]{(XO)_3P} \underset{\textbf{A}}{ArCHCl_2} \xrightarrow[-2EtCl]{2(EtO)_3P} \underset{\textbf{IIa, IIb}}{[(EtO)_2P(O)]_2C^1HAr},$$

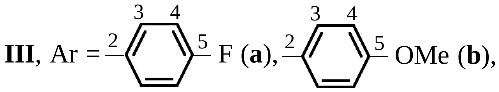


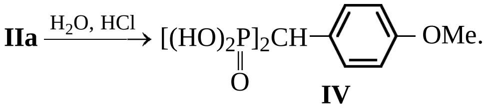
The phosphonates **Ia** and **Ic** and diphosphonate **IIa** can be easily hydrolyzed to form phosphonic **III** and diphosphonic **IV** acids, respectively. Under these conditions occurs also cleavage of chlorine–carbon bond.



$$\textbf{Ia, Ib} \xrightarrow{H_2O,\ HCl} (HO)_2\underset{\underset{O}{\|}}{P}C^1H(OH)Ar,$$

IIIa, IIIb





$$\textbf{IIa} \xrightarrow{H_2O,\ HCl} [(HO)_2\underset{\underset{O}{\|}}{P}]_2CH\text{–}C_6H_4\text{–}OMe.$$

IV

NMR spectra of compounds **I**–**IV** contain typical signals of PC^1H and PC^1HP fragments and of substituted aromatic fragments.

Diethyl (4-fluorophenyl)chloromethylphosphonate (Ia). A mixture of 3 g 4-fluorobenzalchloride, 7 g of triethylphosphite and 0.1 g of zinc chloride was heated at 150–160°C for 2 h and then was distilled. 3 g of phosphonate **Ia** was obtained, yield 64%, mp 152°C (2 mm Hg), n_D^{20} 1.4885. ^1H NMR spectrum, δ, ppm: 4.75 d (C^1H, $^2J_{PH}$ 12 Hz), 6.82 d (C^3H, $^3J_{HH}$ 8 Hz), 7.32 d (C^4H, $^3J_{HH}$ 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 52.52 d (C^1, $^1J_{PC}$ 160 Hz), 130.16 t (C^2, $^2J_{PC}$ = $^4J_{FC}$ 3.5 Hz), 130.69 d.d (C^3, $^3J_{PC}$ 6 Hz, $^3J_{FC}$ 8 Hz), 115.26 d (C^4, $^2J_{FC}$ 22 Hz), 162.68 d (C^5, $^1J_{FC}$ 248 Hz). ^{31}P NMR spectrum, δ_P, ppm: 16.89 s. Found, %:

C 46.89; H 5.26. $C_{11}H_{15}ClFO_3P$. Calculated, %: C 47.07; H 5.39.

Compounds **Ib**, **Ic**, and **II** were obtained by similar procedure.

Diethyl (2,3-dimethoxyphenyl)chloromethylphosphonate (Ib). Yield 68%, mp 184 °C (2 mm Hg), n_D^{20} 1.5139. ^{1}H NMR spectrum, δ, ppm: 5.35 d (C^{1}H, $^2J_{PH}$ 16 Hz), 3.60 s and 3.65 s (OMe), 6.64–7.17 m (C^{5}H, C^{6}H, C^{7}H). ^{13}C NMR spectrum, δ_C, ppm: 45.63 d (C^1, $^1J_{PC}$ 163 Hz), 55.52 s and 55.73 s (OMe), 121.56 d (C^2, $^2J_{PC}$ 4 Hz), 146.59 d (C^3, $^3J_{PC}$ 9 Hz), 152.04 s (C^4), 124.04 s (C^5), 117.97 s (C^6), 112.81 d (C^7, $^3J_{PC}$ 3 Hz). ^{31}P NMR spectrum, δ_P, ppm: 17.96 s.

Bis(trimethylsilyl) (4-methoxyphenyl)chloromethylphosphonate (Ic). Yield 81%, mp 166 °C (1 mm Hg), mp 65°C. ^{1}H NMR spectrum, δ, ppm: 0.09 s and 0.19 s (Me_3Si), 4.71 d (C^{1}H, $^2J_{PH}$ 12 Hz), 3.72 s (MeO), 6.80 d (C^{3}H, $^3J_{HH}$ 8 Hz), 7.36 d (C^{4}H, $^3J_{HH}$ 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 0.63 s and 0.79 s (Me_3Si), 54.63 d (C^1, $^1J_{PC}$ 168 Hz), 55.21 s (MeO), 126.90 t (C^2, $^2J_{PC}$ 3 Hz), 130.21 d (C^3, $^3J_{PC}$ 6 Hz), 113.75 s (C^4), 159.94 s (C^5). ^{31}P NMR spectrum, δ_P, ppm: –0.79 s.

Tetraethyl (4-methoxyphenyl)methylenediphosphonate (IIa). Yield 78%, mp 202°C (2 mm Hg), n_D^{20} 1.4982. ^{1}H NMR spectrum, δ, ppm: 3.47 t (C^{1}H, $^2J_{PH}$ 24 Hz), 3.54 s (MeO), 6.63 d (C^{3}H, $^3J_{HH}$ 8 Hz), 7.17 d (C4H, $^3J_{HH}$ 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 44.37 t (C^1, $^1J_{PC}$ 132.5 Hz), 54.89 s (MeO), 121.66 t (C^2, $^2J_{PC}$ 8 Hz), 131.29 t (C^3, $^3J_{PC}$ 6.5 Hz), 113.69 s (C^4), 158.90 s (C^5). ^{31}P NMR spectrum, δ_P, ppm: 18.74 s. Found, %: C 48.59; H 7.05. $C_{16}H_{28}\cdot O_7P_2$. Calculated, %: C 48.73; H 7.16.

Tetraethyl (2,5-dimethoxyphenyl)methylenediphosphonate (IIb). Yield 76%, mp 212°C (2 mm Hg), n_D^{20} 1.5008. ^{1}H NMR spectrum, δ, ppm: 3.52 s and 3.55 s (MeO), 4.35 t (C^{1}H, $^2J_{PH}$ 26 Hz), 6.45–6.60 m (C^{4}H, C^{5}H), 7.18 s (C^{7}H). ^{13}C NMR spectrum, δ_C, ppm: 35.48 t (C^1, $^1J_{PC}$ 133 Hz), 55.29 s and 56.30 (OMe), 119.28 t (C^2, $^2J_{PC}$ 8 Hz), 150.78 t (C^3, $^3J_{PC}$ 7 Hz), 111.78 s and 113.94 s (C^4, C^5), 153.08 s (C^6), 116.21 t (C^7, $^3J_{PC}$ 4.5 Hz). ^{31}P NMR spectrum, δ_P, ppm: 19.05 s. Found, %: C 48.02; H 7.06. $C_{17}H_{30}O_8P_2$. Calculated, %: C 48.11; H 7.13.

4-Fluorophenyl(hydroxymethyl)phosphonic acid (IIIa). A mixture of 3 g of phosphonate **Ia** and 20 ml of conc. hydrochloric acid was heated on a boiling water bath for 4 h and then evaporated to dtryness at 7 mm Hg. 30 ml of water was added which was thed distilled off in a vacuum. 2 g of acid **IIIa** was obtained, yield 92%, mp 69°C. ^{1}H NMR spectrum, δ, ppm: 4.72 d (C^{1}H, $^2J_{PH}$ 12 Hz), 7.10–7.15 m (C^{3}H), 7.41–7.44 m (C^{4}H). ^{13}C NMR spectrum, δ_C, ppm: 70.10 d (C^1, $^1J_{PC}$ 160 Hz), 136.71 s (C^2), 129.66 s (C^3), 114.69 d (C^4, $^2J_{FC}$ 21 Hz), 161.76 d (C^5, $^1J_{FC}$ 244 Hz). ^{31}P NMR spectrum, δ_P, ppm: 18.52 s (see [3]).

Compounds **IIIb** and **IV** were prepared by similar procedure.

4-Methoxyphenyl(hydroxymethyl)phosphonic acid (IIIb). Yield 96%, mp 78°C. ^{1}H NMR spectrum, δ, ppm: 4.71 d (C^{1}H, $^2J_{PH}$ 12 Hz), 3.44 s (OMe), 6.67 d (C^{3}H, $^3J_{PH}$ 8 Hz), 7.12 d (C^{4}H, $^3J_{PH}$ 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 69.77 d (C^1, $^1J_{PC}$ 160 Hz), 129.02 s (C^2), 55.16 s (OMe), 128.52 d (C^3, $^3J_{PC}$ 6 Hz), 113.87 s (C^4), 158.29 s (C^5). ^{31}P NMR spectrum, δ_P, ppm: 20.76 s, (see [3]).

(4-Methoxyphenyl)methylenediphosphonic acid (IV). Yield 96%, mp 86°C. ^{1}H NMR spectrum, δ, ppm: 3.49 t (C^{1}H, $^2J_{PH}$ 26 Hz), 3.57 s (OMe), 6.65 d (C^{3}H, $^3J_{PH}$ 8 Hz), 7.20 d (C^{4}H, $^3J_{PH}$ 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 45.06 t (C^1, $^1J_{PC}$ 126.5 Hz), 124.96 t (C^2, $^2J_{PC}$ 7.5 Hz), 131.08 t (C^3, $^3J_{PC}$ 6 Hz), 117.72 s (C^4), 157.76 s (C^5), 54.74 s (OMe). ^{31}P NMR spectrum, δ_P, ppm: 17.72 s. Found, %: C 33.94; H 4.38. $C_8H_{12}O_7P_2$. Calculated, %: C 34.06; H 4.29.

NMR spectra were registered on a Bruker Avance 400 instrument, solvents: $CDCl_3$ for compounds **I** and **II**, D_2O for compounds **III** and **IV**; references TMS (^{1}H and ^{13}C) and 85% H_3PO_4 in D_2O (^{31}P).

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