ISSN 1070-4280 Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 5, pp. 770–771. © Pleiades Publishing, Inc. 2006.
Original Russian Text © S.A. Aristov, A.V. Vasil'ev, A.P. Rudenko, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, No.5, pp. 785–786.

SHORT COMMUNICATIONS

Oxidation of Dialkyl Arylethynylphosphonates in a System $CF_3CO_2H–CH_2Cl_2–PbO_2$

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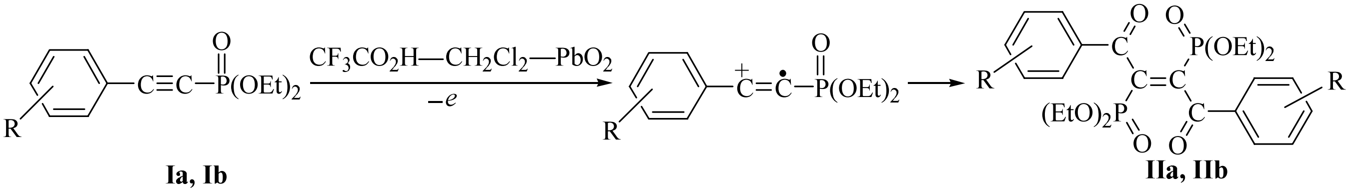
Received November11, 2005

DOI: 10.1134/S1070428006050228

α,β-Unsaturated phosphonates and versatile compounds synthesized therefrom find wide practical applications as incombustible polymers, antibiotics, various biologically active substances, and convenient intermediates in the synthesis of 1-arylethylphosphonates possessing immunosuppressor properties with the central type action [1].

We formerly demonstrated that the one-electron oxidation of acetylene compounds resulted in products of the oxidative dimerization, 1,1,2,2-tetraaroylethenes [2] and other difficultly available carbonyl derivatives of the unsaturated series [3, 4]. This communication reports on the preparative opportunities provided by oxidation of dialkyl arylethynylphosphonates **Ia** and **Ib** in a system $CF_3CO_2H–CH_2Cl_2–PbO_2$ via intermediate formation of cation-radicals of compounds **Ia** and **Ib** to afford dicarbonyl diphosphonates **IIa** and **IIb**. Polyfunctional compounds **IIa** and **IIb** belong to a new class of substances which can be valuable synthons for preparation of carbo- and heterocyclic derivatives.



R = 4-MeO (**a**), 2,4,6-Me$_3$ (**b**).

Substrates **Ia** and **Ib** containing electron-donor groups R were oxidized into final products **IIa** and **IIb** within 3.5 and 21 h in 62 and 15% yields respectively. Under similar conditions at 20°C within 30 h the attempt failed to oxidize diethyl phenylethynylphosphonate possessing higher oxidation potential than compounds **Ia** and **Ib**: The unreacted initial compound was quantitatively recovered from the reaction mixture.

The structure of compounds **IIa** and **IIb** was established from IR, ^{1}H, ^{13}C, ^{31}P NMR, and mass spectra. We assigned to compounds **IIa** and **IIb** the *trans*-(*E*-) configuration based on the formation of related compounds of *trans*-(*E*-) configuration in the similar cation-radical reactions of arylpropynone derivatives ArC≡CCOR [2–4].

Initial diethyl arylethynylphosphonates **Ia** and **Ib** were prepared by the Michaelis–Becker reaction [5] treating sodium diethyl phosphate with 1-bromo-2-arylethynes prepared by procedure [6]. Diethyl phenylethynylphosphonate was obtained by method [7].

Diethyl 4-methoxyphenylethynylphosphonate (Ia). Yield 32%, oily substance. IR spectrum, ν, Cm^{-1}: 2185 (C≡C), 1250 (P=O). ^{1}H NMR spectrum, δ, ppm: 1.38 t (6H, 2Me, *J* 7.3 Hz), 3.82 s (3H, MeO), 4.20 quintet

(4H, $2CH_2$, J 7.3 Hz), 6.86 d ($2H_{arom}$, J 8.8 Hz), 7.49 d ($2H_{arom}$, J 8.8 Hz). Found, %: C 57.97; H 6.02. $C_{13}H_{17}O_4P$. Calculated, %: C 58.21; H 6.39 .

Diethyl 2,4,6-trimethylphenylethynylphosphonate (**Ib**). Yield 34%, oily substance. IR spectrum, ν, cm^{-1}: 2185 (C≡C), 1250 (P=O). ^1H NMR spectrum, δ, ppm: 1.38 t (6H, 2Me, J 7.3 Hz), 2.27 s (3H, Me), 2.40 s (6H, 2Me), 4.21 quintet (4H, $2CH_2$, J 7.3 Hz), 6.86 s ($2H_{arom}$). Found, %: C 64.38; H 7.80. $C_{15}H_{21}O_3P$. Calculated, %: C 64.27; H 7.55.

Tetraethyl [1,2-bis(4-methoxyphenylcarbonyl)]-ethene-1,2-diyl-1,2-diphosphonate (IIa). To a solution of 0.14 ml of CF_3CO_2H in 3 ml of CH_2Cl_2 at 0°C while vigorous stirring was added 100 mg (0.37 mmol) of compound **Ia**, then 88 mg (0.37 mmol) of PbO_2, and the stirring of the reaction mixture was continued for 3.5 h. On completion of the reaction the mixture was poured into 50 ml of chloroform. The chloroform solution was washed with water, with a saturated solution of $NaHCO_3$, again with water, dried over Na_2SO_4, and the solvent was distilled off. The residue was subjected to column chromatography on silica gel. Eluent petroleum ether (bp 40–70°C)–ethyl acetate. Yield 65 mg (62%), mp 162–163°C. IR spectrum, ν, cm^{-1}:1670 (C=O), 1250 (P=O). ^1H NMR spectrum, δ, ppm: 1.10 br.s (12H, 4Me), 3.88 s (6H, 2MeO), 3.94 br.s (8H, $4CH_2$), 6.98 d ($4H_{arom}$, J 8.5 Hz), 8.04 d ($4H_{arom}$, J 8.5 Hz). ^{13}C NMR spectrum, δ, ppm: 15.9 (Mε), 55.5 (OMe), 63.4 (OCH_2), 113.7, 129.3, 132.3, 146.8 d (C=C, J_{CP} 162.9 Hz), 164.1, 190.8 t (C=O, J_{CP} 9.7 Hz). ^{31}P NMR spectrum, δ, ppm: 7.31 s. Mass spectrum, m/z (I_{rel}, %): 568 (3) $[M]^+$, 433 (10), 135 (100), 107 (5), 92 (5), 77 (9). Found, %: C 55.11; H 5.99. $C_{26}H_{34}O_{10}P_2$. Calculated, %: C 54.93; H 6.03. M 568.16.

Tetraethyl [1,2-bis(2,4,6-trimethylphenylcarbonyl)]ethene-1,2-diyl-1,2-diphosphonate (IIb) was prepared by the same procedure as compound **IIa** from 100 mg (0.36 mmol) of substrate **Ib** by oxidation with 85 mg (0.36 mmol) of PbO_2 in a mixture of 0.14 ml of CF_3CO_2H and 3 ml of CH_2Cl_2 at 20°C within 21 h. Yield 16 mg (15%), mp 184–185°C. IR spectrum, ν, cm^{-1}: 1670 (C=O), 1250 (P=O). ^1H NMR spectrum, δ, ppm: 1.11 br.s (12H, 4Me, J 7.1 Hz), 2.27 s (6H, 2Me), 2.53 s (12H, 4Me), 3.96 m (8H, $4CH_2$), 6.85 s ($4H_{arom}$). Mass spectrum, m/z (I_{rel}, %): 592 (6) $[M]^+$, 455 (20), 438 (11), 409 (32), 335 (16), 297 (24), 147 (100), 119 (42), 91 (18). Found, %: C 60.86; H 7.08. $C_{30}H_{42}O_8P_2$. Calculated, %: C 60.80; H 7.14. M 592.24.

^1H, ^{13}C, and ^{31}P NMR spectra were registered on a spectrometer Bruker AM-500 (operating frequencies 500, 125.76, and 202.5 MHz respectively) in $CDCl_3$. As internal references served the residual signal of $CHCl_3$ (δ 7.25 ppm) for ^1H, the signal of $CDCl_3$ (δ 77.0 ppm) for ^{13}C, and the signal of H_3PO_4 (85% water solution) was used as external reference (δ 0.0 ppm) for ^{31}P. IR spectra of solutions of compounds in chloroform were recorded on a spectrophotometer Specord 75 IR. Mass spectra were measured on an MKh-1321 instrument, ionizing voltage 70 eV, direct admission of the sample into the ion source at the temperature 100–120°C.

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