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Sonochemical Activation of Condensing Phosphorylation of Bifunctional Hydroxyl-Containing Compounds

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Abstract — Condensing phosphorylation of 1,6-hexanediol, 1,4-dihydroxybenzene, 4,4'-dihydroxybiphenyl, and 2,2-bis(4'-hydroxyphenyl)propane by phenylphosphonous acid tetraethylamide was effected by treatment of the disperse reaction system with high-frequency sound. This treatment ensures efficient shift of the phase equilibrium in the course of condensation and increases the yield of phenylphosphonous acid oligoesters.
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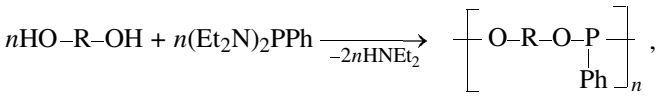
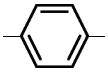
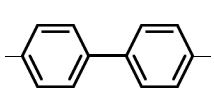
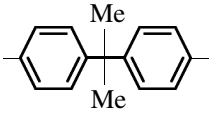
Oligo(phenylphosphonites) are of some practical interest as intermediates in the synthesis of novel coordination catalysts. For example, rhodium complexes of oligo(arylene phenylphosphonites) show high catalytic activity in hydrogenation of carbon dioxide and surpass in this respect the corresponding complexes with the simplest phosphorus-containing ligands [1, 2]. Usually oligo(phenylphosphonites) are formed by thermal treatment of a disperse system consisting of a bifunctional phosphorylating agent, phenylphosphonous acid tetraalkylamide, and bifunctional hydroxyl-containing compounds with removal of the released dialkylamine as a gas [3].

We performed the condensing phosphorylation of bifunctional hydroxyl-containing compounds under the action of high-frequency sound on the disperse reaction system, which allowed us to efficiently shift the phase equilibrium to the desired direction and to increase the yield of phenylphosphonous acid oligoesters.



I–VIII

R = –$(CH_2)_6$– (**I, V**);  (**II, VI**);

 (**III, VII**);  (**IV, VIII**).

The sonochemical synthesis of oligo(phenylphosphonites) **I**–**IV** was carried out without a solvent in a temperature-controlled reactor at 90°C under argon using a source of high-frequency sound (15 kHz, 50 W cm^{-2}; Fig. 1).

Simultaneously we performed common thermal condensing phosphorylation at 90°C, with the sonic transmitter switched off (compounds **V**–**VIII**).

A comparative analysis of the ^{31}P NMR spectra of compounds **I**–**IV** showed that the contribution of the terminal groups [–ORO–P(Ph)NEt_2] to the composition of the molecules prepared by the sonochemical method is significantly reduced (Table 1). We should note increased reactivity of 1,6-hexanediol

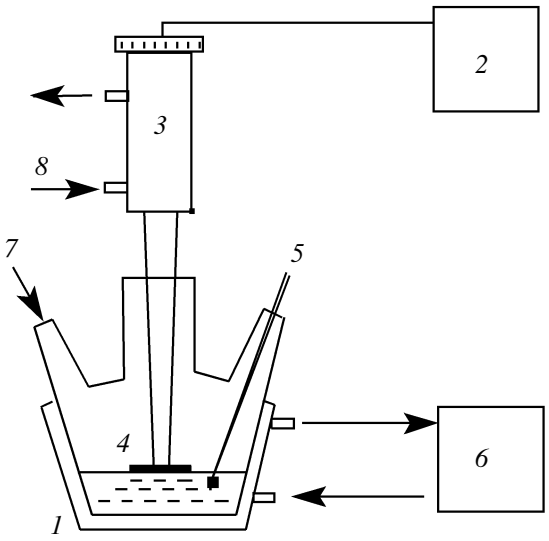


Fig. 1. Schematic diagram of the apparatus for performing sonochemical condensing phosphorylation: (*1*) reactor, (*2*) UZDN-1 disperser, (*3*) sonic transmitter, (*4*) working part of the transmitter, (*5*) thermocouple, (*6*) thermostat, (*7*) argon inlet, and (*8*) water for cooling.

which shows lower, compared to phenols, reactivity in phosphorylation under the conditions of common thermal condensation (Fig. 2).

The mass-spectral characteristics of both products prepared by sonochemical and thermal condensation were measured using the MALDI method (matrix laser desorption ionization). Examples of using this method for the analysis of phosphorus polymers are given in [3–5]. The MALDI data confirmed that intensification of the condensation process by sonic treatment led to a decrease in the content of the terminal groups [–ORO–P(Ph)NEt_2] and increase in the content of phenylphosphonous acid oligoesters. Figure 3 shows a fragment of the mass spectrum of compound **III** prepared by sonic treatment of the reaction mixture consisting of 4,4'-dihydroxybiphenyl and phenylphosphonous acid tetraethyldiamide. The product is a mixture of oligophosphonites differing from each other in the mass of the elementary unit [–OROP(Ph)–]. The difference between the peaks characterizing the group of compounds corresponded to a mass of 292 Da. The main group of compounds giving the strongest peak consists of acyclic phenylphosphonous acid oligoesters containing no terminal amide group at the phosphorus atom (Table 2). The group of cyclic oligoesters makes a smaller contribution. The contribution of oligomeric compounds with the [–ORO–P(Ph)NEt_2] terminal groups to the composition of product **III** is insignificant. It should be noted that in the mass spectrum there is a group of peaks belonging to an unknown type of oligo(phenylphosphonites) (Fig. 3). The difference between the major peaks corresponds to the mass of 292 Da.

The mass spectral study of oligo(phenylphosphonite) **VII** prepared under common thermal conditions revealed its instability. This is seen from irreproducibility of its mass-spectral patterns. To stabilize the oligo(phenylphosphonite) samples, we oxidized them to the corresponding oligo(phenylphosphonate). Figure 4 shows a fragment of the mass spectrum of the oxidized form of **VII**. The product is a mixture of oligophosphonates differing in the mass of the elementary unit [–OROP(O)(Ph)–]. The difference between the major peaks characterizing a group of the compounds corresponds to the mass of 308 Da. Unlike the spectrum of oligomer **III**, the spectrum of the sample prepared by sonic treatment contains only peaks of acyclic oligomers with terminal amide group at the phosphorus atom. In the mass spectrum, the

Table 1. ^{31}P NMR data (dioxane) for oligo(phenylphosphonites) **I–VIII**

Comp. no.	δ_P, ppm	Integral intensity ratio	Signal assignment
I	154.9	–	[–ORO–P(Ph)O–], ORO: 1,6-dioxyhexane
II	131.8, 159.3	1 : 11	[–ORO–P(Ph)NEt_2], [–ORO–P(Ph)O–], ORO: 1,4-oxyphenyl
III	131.3, 159.4	1 : 10	[–ORO–P(Ph)NEt_2], [–ORO–P(Ph)O–], ORO: 4,4'-dioxybiphenyl
IV	131.7, 159.2	1 : 8	[–ORO–P(Ph)NEt_2], [–ORO–P(Ph)O–], ORO: 2,2-bis(4'-oxyphenyl)propane
V	95.6, 130.5, 154.2	0.3 : 1 : 3	$(NEt_2)_2PPh$, [–ORO–P(Ph)NEt_2], [–ORO–P(Ph)O–], ORO: 1,6-dioxyhexane
VI	131.9, 159.2	1 : 1.5	[–ORO–P(Ph)NEt_2], [–ORO–P(Ph)O–], ORO: 1,4-oxyphenyl
VII	131.4, 159.4	1 : 1.5	[–ORO–P(Ph)NEt_2], [–ORO–P(Ph)O–], ORO: 4,4'-dioxybiphenyl
VIII	131.7, 159.2	1 : 0.5	[–ORO–P(Ph)NEt_2], [–ORO–P(Ph)O–], ORO: 2,2-bis(4'-oxyphenyl)propane

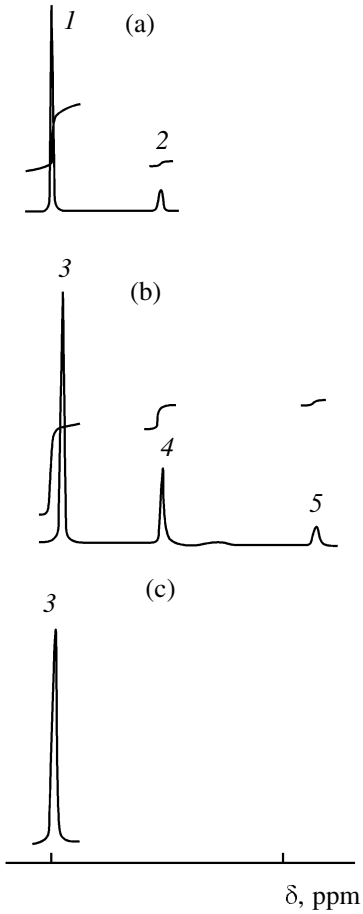


Fig. 2. ^{31}P NMR spectra of oligophosphonites (a) **III** {peak *1* at 159.4 ppm, [–OROP(Ph)O–]; peak *2* at 131.3 ppm, [OROP(Ph)NEt_2]}, (b) **V** {peak *3* at 154.2 ppm, [–OArOP(Ph)O–]; peak *4* at 130.5 ppm, [–ORO–P(Ph)NEt_2]; and peak *5* at 95.6 ppm, $(NEt_2)_2PPh$}, and (c) **I** {peak *3* at 154.9 ppm, [–ORO–P(Ph)O–]} in dioxane solution. ORO: (a) 4,4'-dioxybiphenyl and (b, c) 1,6-dioxyhexane.

most intense is the peak corresponding to the acyclic ion $Et_2NP(O)(Ph)[–OROP(O)(Ph)–]NEt_2 + H^+$ (Table 3).

The heaviest detected peaks in the mass spectra of oligomers **I**–**IV** prepared by the sonochemical technique are within the range 2500–3500 Da. This range significantly exceeded the upper boundary of the range of masses for compounds **V**–**VIII** (1500–2000 Da).

Thus, the sonic treatment favors uniform distribution of the reactants and efficient evacuation of dialkylamine from the reaction mixture and allows acceleration of the condensing phosphorylation of bifunctional hydroxyl-containing compounds. The condensation process is shifted toward the formation of phenylphosphonous acid oligoesters of higher molecular weight compared to the oligomers prepared by the traditional thermochemical method.

EXPERIMENTAL

The ^{31}P NMR spectra were recorded on a Bruker WP-80 spectrometer operating at 32.4 MHz. The chemical shifts were measured against external 85% H_3PO_4. MALDI mass spectra were recorded on an Autoflex II instrument (Bruker Daltonics, Germany) equipped with a nitrogen laser (λ = 337 nm) in the mode of recording positive ions. The spectra were obtained with a time-of-flight mass analyzer. The

Table 2. Characteristic ions corresponding to the linear and cyclic compounds in the mass spectrum of oligo(biphenyl-4,4'-diyl phenylphosphonite) **III** within the range 600–2500 Da

Ion, ORO: 4,4'-dioxybiphenyl	*m/z*	*I*, %
$H[–OROP(Ph)–]_2NEt_2 + H^+$	658.0	53.8
$H[–OROP(Ph)–]_2OROH + H^+$	771.1	41.3
$[–OROP(Ph)–]_3 + H^+$	877.2	42.3
$H[–OROP(Ph)–]_3NEt_2 + H^+$	950.3	17.7
$H[–OROP(Ph)–]_3OROH + H^+$	1063.5	56.2
$[–OROP(Ph)–]_4 + H^+$	1169.5	15.5
$H[–OROP(Ph)–]_4OROH + H^+$	1355.7	30.5
$[–OROP(Ph)–]_5 + H^+$	1462.5	6.4
$H[–OROP(Ph)–]_5OROH + H^+$	1648.8	12.3
$H[–OROP(Ph)–]_6OROH + H^+$	1940.8	14.1
$H[–OROP(Ph)–]_7OROH + H^+$	2232.7	8.6
$H[–OROP(Ph)–]_8OROH + H^+$	2524.5	5.0

Table 3. Characteristic ions corresponding to the compounds detected in the mass spectrum of the oxidized form of oligo(biphenyl-4,4'-diyl phenylphosphonite) **VII** within the range 550–1600 Da

Ion, ORO: 4,4'-dioxybiphenyl	*m/z*	*I*, %
$Et_2NP(O)(Ph)[–OROP(O)(Ph)–]NEt_2 + H^+$	577.6	100
$H[–OROP(O)(Ph)–]_2NEt_2 + H^+$	690.7	21.1
$Et_2NP(O)(Ph)[–OROP(O)(Ph)–]_2NEt_2 + H^+$	885.6	88.0
$H[–OROP(O)(Ph)–]_3NEt_2 + H^+$	998.6	11.2
$Et_2NP(O)(Ph)[–OROP(O)(Ph)–]_3NEt_2 + H^+$	1193.5	30.4
$H[–OROP(O)(Ph)–]_4NEt_2 + H^+$	1306.5	10.6
$Et_2NP(O)(Ph)[–OROP(O)(Ph)–]_4NEt_2 + H^+$	1502.6	11.8
$H[–OROP(O)(Ph)–]_5NEt_2 + H^+$	1615.9	2.6

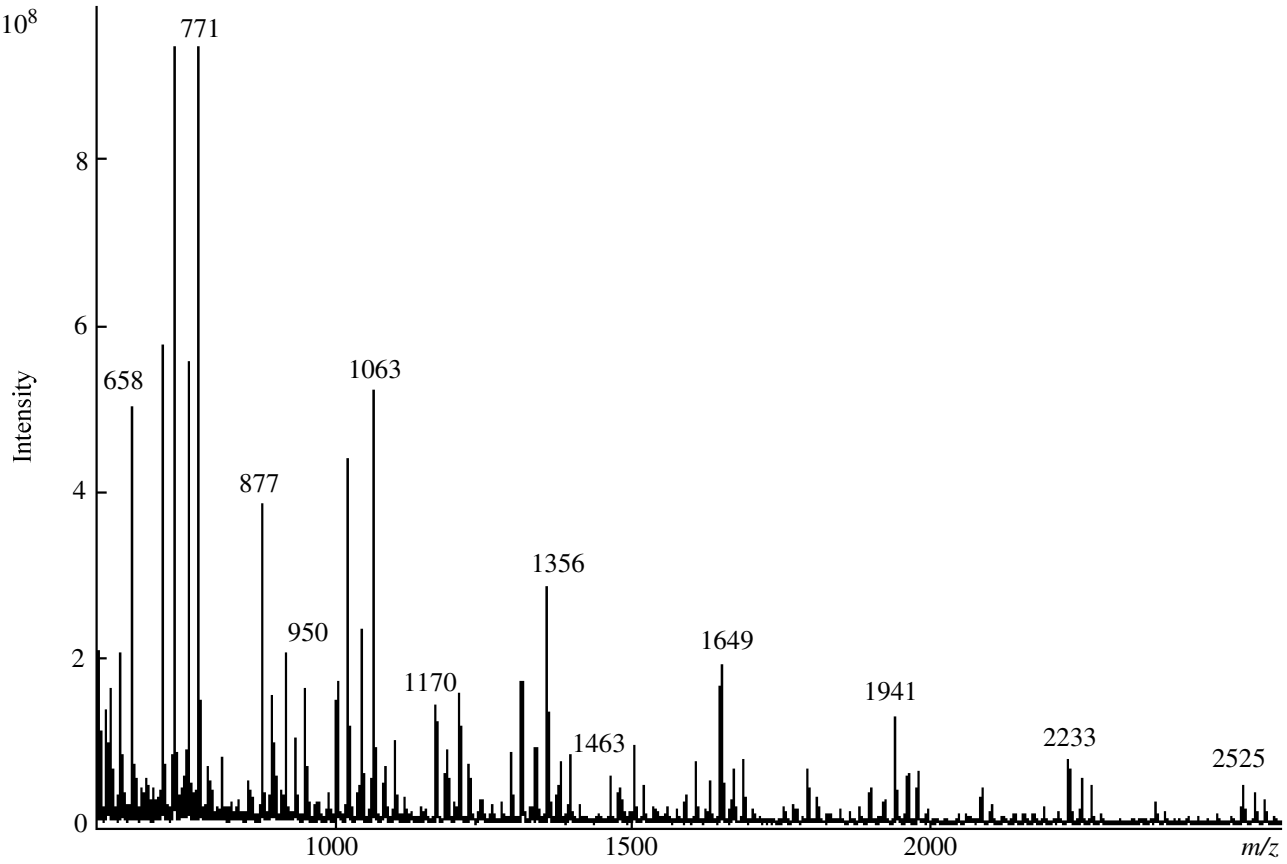


Fig. 3. A fragment of the mass spectrum of oligo(phenylphosphonite) **III** prepared by sonic treatment of a mixture of 4,4'-dihydroxybiphenyl with phenylphosphonous acid tetraethyldiamide.

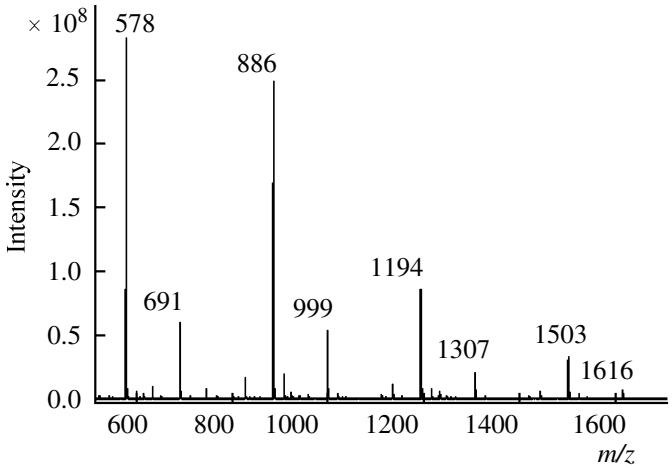


Fig. 4. A fragment of the mass spectrum of the oxidized form of oligo(phenylphosphinite) **III** prepared by thermochemical reaction of 4,4'-dihydroxybiphenyl with phenylphosphonous tetraethyldiamide.

samples were prepared by the method of "dried drop." To dissolve the matrix (2,4,6-trihydroxyacetophenone) and the oligomer samples, we used tetrahydrofuran (THF). The matrix : oligomer molar ratio was approximately 500 : 1.

The syntheses of oligo(arylene phenylphosphonites) was performed neat in argon flow. We used disperser UZDN-1 with a frequency of 15 kHz and power 50 W cm^{-2} as a source of high-frequency sound.

Oligo(hexane-1,6-diyl phenylphosphonite) (I). To 2.02 g (8 mmol) of phenylphosphonous acid tetraethyldiamide placed into the reactor thermostated at 90°C using a water jacket, 0.94 g (8 mmol) of 1,6-hexanediol was added in an argon flow. The working part of the high-frequency sonic transmitter was arranged on the surface of the reaction mixture. The mixture was kept for 30 min, after which the UZDN-1 device was switched on, and the sonic treatment was performed for 60 min. The product was a transparent viscous substance, soluble in dioxane, THF, and DMSO. ^{31}P NMR spectrum, δ_P, ppm, dioxane: 154.9. Mass spectrum (MALDI): up to 2500 Da.

Oligo(1,4-phenylene phenylphosphonite) (II) was prepared by the same procedure from 2.02 g (8 mmol) of phenylphosphonous acid tetraethyldiamide and 0.88 g (8 mmol) of 1,4-dihydroxybenzene. The product was a solid transparent substance soluble in dioxane, THF, and DMSO. Softening point 95–100°C.

^{31}P NMR spectrum, δ_P, ppm (integral intensity of the signal), dioxane: 131.8 (1), 159.3 (11). Mass spectrum (MALDI): up to 3500 Da.

Oligo(biphenyl-4,4'-diyl phenylphosphonite) (III) was prepared by the same procedure from 2.02 g (8 mmol) of phenylphosphonous acid tetraethyldiamide and 1.49 g (8 mmol) of 4,4'-dihydroxybiphenyl. The product was a transparent solid substance soluble in dioxane, THF, and DMSO. Softening point 125–130°C. ^{31}P NMR spectrum, δ_P, ppm (integral intensity of the signal), dioxane: 131.3 (1), 159.4 (10). Mass spectrum (MALDI): up to 3000 Da.

Oligo(2,2-diphenylpropane-4',4''-diyl phenylphosphonite) (IV) was prepared by the same procedure from 2.02 g (8 mmol) of phenylphosphonous acid tetraethyldiamide and 1.82 g (8 mmol) of 2,2-bis(4'-hydroxyphenyl)propane. The product was a solid transparent substance soluble in dioxane, THF, and DMSO. Softening point 105–110°C. ^{31}P NMR spectrum, δ_P, ppm (integral intensity of the signal), dioxane: 131.7 (1), 159.2 (8). Mass spectrum (MALDI): up to 2600 Da.

Oligo(hexane-1,6-diyl phenylphosphonite) (V). To 2.02 g (8 mmol) of phenylphosphonous acid tetraethyldiamide placed into the reactor thermostated at 90°C using a water jacket, 0.94 g (8 mmol) of 1,6-hexanediol was added in argon flow. The mixture was heated for 90 min. The product was a transparent viscous substance soluble in dioxane, THF, and DMSO. ^{31}P NMR spectrum, δ_P, ppm (integral intensity of the signal), dioxane: 95.6 (0.3), 130.5 (1), 154.2 (3). Mass spectrum (MALDI): up to 1500 Da.

Oligo(1,4-phenylene phenylphosphonite) (VI) was prepared by the same procedure from 2.02 g (8 mmol) of phenylphosphonous acid tetraethyldiamide and 0.88 g (8 mmol) of 1,4-dihydroxybenzene. The product was a transparent viscous substance soluble in dioxane, THF, and DMSO. ^{31}P NMR spectrum, δ_P, ppm (integral intensity of the signal), dioxane: 131.9 (1), 159.2 (1.5). Mass spectrum (MALDI): up to 2000 Da.

Oligo(biphenyl-4,4'-diyl phenylphosphonite) (VII) was prepared by the same procedure from 2.02 g (8 mmol) of phenylphosphonous acid tetraethyldiamide and 1.49 g (8 mmol) of 4,4'-dihydroxybiphenyl. The product was a white viscous substance soluble in dioxane, THF, and DMSO. ^{31}P NMR spectrum, δ_P, ppm (integral intensity of the signal), dioxane: 131.4 (1), 159.4 (1.5). Mass spectrum (MALDI): up to 1800 Da.

Oligo[2,2-diphenylpropane-4',4''-diyl phenylphosphonite) (VIII) was prepared by the same procedure from 2.02 g (8 mmol) of phenylphosphonous acid tetraethyldiamide and 1.82 g (8 mmol) of 2,2-bis-(4-hydroxyphenyl)propane. The product was a transparent viscous substance soluble in dioxane, THF, and DMSO. ^{31}P NMR spectrum, δ_P, ppm (integral intensity of the signal), dioxane: 131.7 (1), 159.2 (0.5). Mass spectrum (MALDI): up to 1500 Da.

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