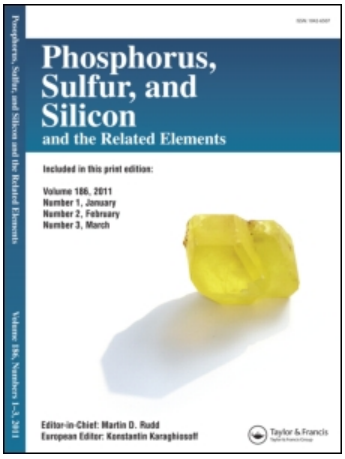


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# Hydroxyoligophosphites and -Phosphonites on the Basis of 1,4:3,6-Dianhydro-D-sorbitol

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# Hydroxyoligophosphites and -Phosphonites on the Basis of 1,4:3,6-Dianhydro-D-sorbitol

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*The interaction of 1,4:3,6-dianhydro*-D-*sorbitol with phosphorous and phenylphosphonous acid amidochlorides leads to oligophosphites and -phosphonites with free hydroxyl groups on the periphery of their molecules. The obtained compounds were introduced into reactions via the transformation of trivalent phosphorus and hydroxyl groups.*

**Keywords** Hydroxyl groups; oligophosphites; sorbitol; phosphorylation;

We found earlier that 1,4:3,6-dianhydro-*D*-sorbitol (HO—Z—OH) **1**, a rigid skeleton diol with two hydroxyls that are *endo*- and *exo*-orientated with respect to the internal chiral cavity, has some peculiar chemical features (Scheme 1).

This compound differs from the related 1,4:3,6-dianhydro-*D*-mannitol **2** by the peculiar phosphorylation: the reaction of diol **1** with phosphorous and phenylphosphonous acid amidochlorides at a molar ratio of 1:2 results in the formation of previously unknown oligophosphites and -phosphonites whose molecules are edged with phosphamide groups,[1] rather than of expected bisamidophosphonites and -diamidophosphites.

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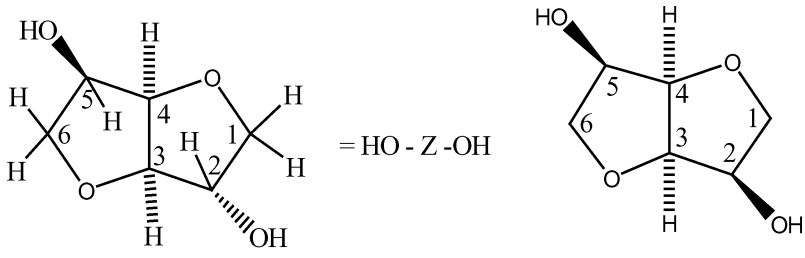
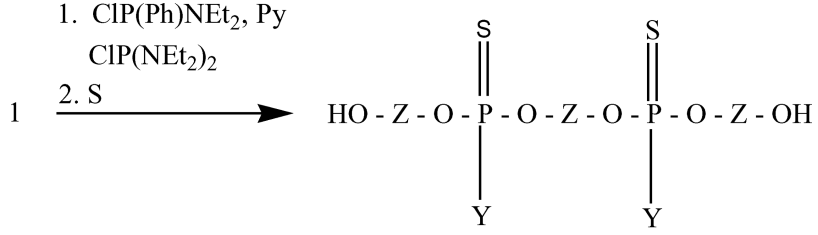



**1** **2**

**SCHEME 1**

## RESULTS AND DISCUSSION

The aim of this work is to study the phosphorylation of diol **1** with diethylamidophenylphosphonous acid chloride and tetraethyldiamidophosphorous acid chloride at the reagent ratio ensuring the retention of some hydroxyl groups in the resulting products. We first studied the reaction of diol **1** with acid amidochlorides at room temperature in pyridine at a molar ratio of 1:1; both reaction products and unreacted acid amidochlorides were detected in the reaction mixture by $^{31}P$ NMR spectroscopy. After the mixture was stabilized by sulfur addition, structures with terminal hydroxyl groups (**4** and **5**) were assigned to the reaction products from the data of $^{1}H$ and $^{31}P$ NMR spectroscopy and MALDI-TOF spectrometry (Scheme 2).

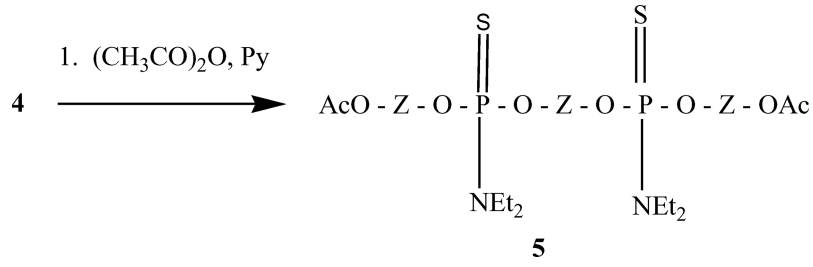



Y = Ph (**3**), $NEt_2$ (**4**) **3, 4**

**SCHEME 2**

To study the reactivity of compound **5**, we acylated it with an excess of acetic anhydride in pyridine at 20°C. The reaction product was isolated and characterized by $^{1}H$ NMR (Scheme 3).

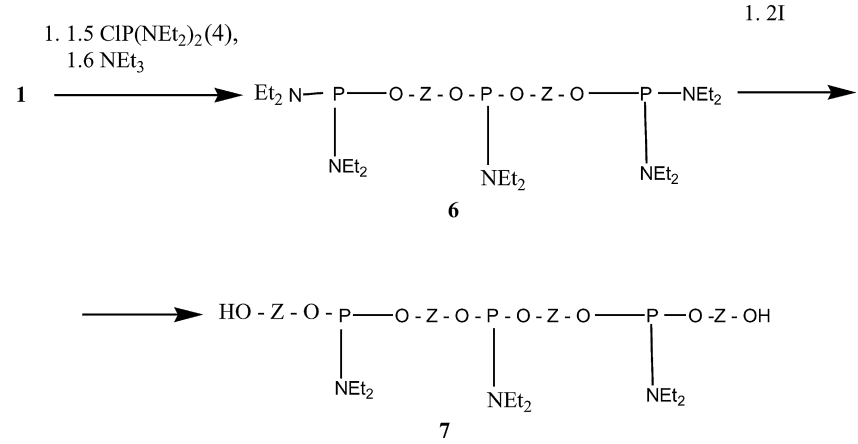
The second part of the work was devoted to the study of more complicated oligophosphite systems with terminal hydroxyl groups. The stepwise elongation of the main chain was used. The first step of the synthesis included the phosphorylation of diol **1** with




**SCHEME 3**

tetraethyldiamidophosphorous acid chloride at a molar ratio of 1:1.5 in benzene in the presence of a 10% molar excess of triethylamine (an activator of hydroxyl groups and an acceptor of the released hydrogen chloride), which allowed us to obtain triamidophosphite **6** as the major reaction product (Scheme 4).





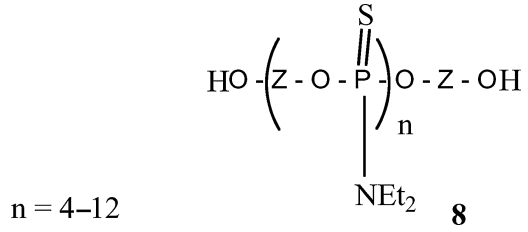

**SCHEME 4**

Note that the $^{31}P$ NMR spectrum of compound **6** contains signals at 134, 137 (phosphorus nuclei of tetraethyldiamidophosphite residues) and 147 ppm (phosphorus nuclei of diethylamidophosphite residues) at an integral ratio of 2:1. Intermediate **6** was further introduced into the reaction with the double molar amount of diol **1**.

In the $^{31}P$ NMR spectrum of the reaction mixture, which contains signals at 134 and 137 ppm, disappeared and a single signal appeared at 147 ppm, which corresponds to the structure of **7**. This result indicated that the reaction proceeded only at the terminal P(III)-amide groups. The reaction mixture was treated with sulfur. From the

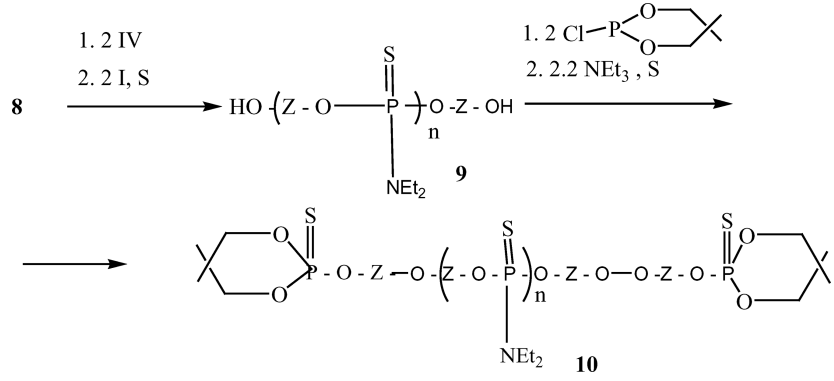
MALDI-TOF spectrometry data, the final product **8** contains, along with tris-thionoamidophosphate whose structure corresponds to intermediate **7**, a mixture of oligothionoamidophosphates with 4–12 base links (n) in their molecules. (Note that the mass spectrum of compound **10** contains signals corresponding to complexes with sodium ions.)

Presumably, the sulfurization process included the disproportionation of the initial compound, resulting in the formation of low molecular byproducts, which next were separated from higher oligomers (Scheme 5).




**SCHEME 5**

The study of the transformation of oligothioamidophosphates **8** also was launched. For this purpose, their chain was elongated by the phosphorylation with diamidophosphorous acid chloride at free terminal groups and two more equivalents of diol **1** then were added. Thus, more complicated oligothioamidophosphates **9** were obtained. We found that during the performed reactions, complex systems with hydroxyl groups in terminal positions were obtained. This conclusion was derived from the phosphorylation of oligomers **9** with 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane (Scheme 6).




**SCHEME 6**

The analysis of the reaction mixture by $^{31}P$ NMR spectroscopy showed that the phosphorylation occurred at free terminal hydroxyl groups, as was evidenced by the appearance of a signal at 121 ppm. After a sulfur addition, product **9** was isolated and studied by $^{1}H$ and $^{31}P$ NMR spectroscopy and MALDI-TOF mass spectrometry. It was shown that the product **10** was also a mixture of oligomers. A characteristic feature of the these transformations is that they proceeded under unexpectedly mild conditions and with high yields, with the regular oligophosphorylation at the early stage.

In the summary, it may be noted that we proposed a method for the synthesis of previously unknown linear oligophosphoric compounds on the basis of the chiral dianhydrosorbitol system. These compounds are of interest for expanding work in the field of supramolecular chemistry



## EXPERIMENTAL

$^{1}H$ NMR spectra were recorded on a Bruker WM-200 instrument at a frequency of 200 MHz; $^{31}P$-{$^{1}H$} NMR spectra were recorded on a Bruker WP-80 spectrometer at a frequency of 32.4 MHz. TMS was used as an internal standard for $^{1}H$ NMR spectra, and 85% $H_3PO_4$ was used as an external standard for $^{31}P$ NMR spectra. Mass spectra were recorded on a Varian Mat-731 spectrometer and a Bruker Reflex III MALDI-TOF instrument. All syntheses were conducted in dry solvents under a dry nitrogen atmosphere. Thin-layer chromatography was performed on Silufol UV-366 plates using (A) chloroform–ethanol 3:1 and (B) benzene–dioxane 3:1 eluents.

### Product 3

Diethylamidophenylphosphorous acid chloride (1.76 g, 5.47 mmol) was added to 0.80 g (5.47 mmol) of diol **1** in 5 mL of pyridine at 20°C while being stirred. The reaction mixture was stirred for 2 h; 0.35 g of fine ground sulfur was added, and the mixture was stirred for 3 more h. The precipitated pyridine hydrogen chloride was filtered off; the solvent was evaporated under vacuum and the residue was ground with 20 mL of water until a powdery material was formed, filtered, and dried under vacuum (1 mm Hg) at 70°C for 3 h. Yield 2.93 g (75%), m.p. 90–92°C, $R_f$ 0.87 (A), 0.65 (B). $^{31}P$ NMR ($C_5H_5N$): $\delta$ 87.06, 86.37. $^{1}H$ NMR ($CDCl_3$, $\delta$): 2.37 m (2H, OH), 3.60–5.06 m (24H, $C_{18}H_{24}$), 7.45 m (6H, $CH_{m-,p-,arom}$), 7.86 m (4H, $CH_{o-,arom}$). Mass spectrum of compound **3** m/e: 714.11 (100.0%), 715.12 (34.4%), 716.11 (8.9%), 716.12 (8.7%), 717.11

(3.1%), 715.11 (1.6%), 717.12 (1.5%). Anal. calcd. for $C_{30}H_{36}O_{12}P_2S_2$: C, 50.42; H, 5.08; P, 8.67. Found: C, 49.89; H, 5.06; P, 8.60.

## Product 4

Tetraethyldiamidophosphorous acid chloride (0.28 g, 1.36 mmol) was added to 0.20 g (1.36 mmol) of diol **1** in 5 mL of pyridine at 20°C while being stirred. The reaction mixture $^{31}$P NMR: $\delta$ 146.9 and 147.6. The reaction mixture was stirred for 2 h; 0.04 g of fine ground sulfur was added, and the mixture was stirred for 4 more h at 20°C. The precipitated pyridine hydrochloride and sulfur excess were filtered off; the solvent was removed under vacuum, and the resulting oil was ground with 20 mL of water in a porcelain mortar until the formation of a solid product and was dried under vacuum. Yield 0.76 g (80%). $R_f$ 0.82 (A), 0.65 (B). $^{31}$P NMR ($C_5H_5N$): $\delta$ 74.6, 75.7. $^1$H NMR ($CDCl_3$, $\delta$): 1.09–1.12 m (12H, $NCH_2\underline{CH_3}$), 3.21 m (8H, $N\underline{CH_2}CH_3$, $^3J_{HP}$ 11.0), 3.63–4.81 m (24H, $C_{18}H_{24}$). Mass spectrum of compound **4** m/e: 704.20 (100.0%), 705.20 (31.7%), 706.19 (8.9%). Anal. calcd. for $C_{26}H_{46}N_2O_{12}P_2S_2$: C, 44.31; H, 6.58; P, 8.79. Found: C, 44.26; H, 6.50; P, 8.65.

## Product 5

Tetraethyldiamidophosphorous acid chloride (0.72 g, 2.05 mmol) was added to 0.30 g (2.05 mmol) of diol **1** in 5 mL of pyridine while being stirred at 20°C. The reaction mixture $^{31}$P NMR: $\delta$ 146.9 and 147.6. The reaction mixture was stirred for 2 h; 0.04 g of finely ground sulfur was added, and the mixture was stirred for 4 more h at 20°C; 0.8 g of acetic anhydride was added, and the reaction mixture was stirred for 3 more h. The precipitated pyridine hydrochloride and sulfur excess were filtered off, and the solvent was removed under vacuum. The resulting oil was dissolved in a benzene–dioxane mixture (3:1) and was isolated by column chromatography using benzene–dioxane (3:1) as an eluent. Yield 1.1 g (70%), $R_f$ 0.7 (B). $^{31}$P NMR ($C_5H_5N$): $\delta$ 74.6, 75.7, 75.9. $^1$H NMR ($CDCl_3$, $\delta$): 1.11 m (12H, $NCH_2$ $\underline{CH_3}$), 2.05–2.10 d (6H, $CH_3$, $COCH_3$), 3.21 m (8H, $N\underline{CH_2}CH_3$, $^3J_{HP}$ 13.0), 3.63–4.80 m (24H, $C_{18}H_{24}$).

## Product 8

Tetraethyldiamidophosphorous acid chloride (0.43 g, 2.05 mmol) was added to 0.2 g (1.36 mmol) of diol **1** and 0.3 mL of triethylamine in 6 mL of benzene while being stirred at 20°C. The reaction mixture $^{31}$P NMR: $\delta$ 134.5, 137.2, 147.8. Diol **1** (0.4 g, 2.72 mmol) then was added. The reaction mixture $^{31}$P NMR: $\delta$ 147.7. The reaction mixture was stirred

for 2 h; 0.17 g of fine ground sulfur was added, and the mixture was stirred for 3 more h at 20°C. The reaction mixture $^{31}$P NMR: $\delta$ 74.4, 74.9, 75.6, 76.4. The precipitated triethylamine hydrochloride and sulfur excess were filtered off, and the solvent was removed under vacuum. The resulting oil was dissolved in a benzene–dioxane mixture (3:1) and was isolated by column chromatography using benzene–dioxane (3:1) as an eluent. Yield 0.43 g, $R_f$ 0.6 (B). Mass spectrum of compound **8** m/z: 1006.30 (3500 a. i.), 1285.40 (4700 a. i.), 1564.40 (2500 a. i.), 1843.40 (2100 a. i.), 2122.50 (1100 a. i.), 2401.50 (900 a. i.), 2680.60 (800 a. i.), 2959.60 (700 a. i.), 3238.50 (600 a. i.).

## Product 10

Tetraethyldiamidophosphorous acid chloride (0.11 g) and 0.08 g of diol **1** were added to 0.26 g of compound **8** and 0.08 mL of triethylamine in 5 mL of benzene while being stirred. The reaction mixture $^{31}$P NMR: $\delta$ 134.4 and 137.2. Finely ground sulfur (0.02 g) was added, and the mixture was stirred for 2 h at 20°C. The reaction mixture $^{31}$P NMR: $\delta$ 74.4, 74.9, 76.5, 78.6. 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane 0.02 g and 0.023 mL of triethylamine were added to compound **9** and 0.02 mL of triethylamine in 5 mL of benzene at 20°C. The reaction mixture (compound **9**) $^{31}$P NMR: $\delta$ 121.8, 74.5, 75.5. The reaction mixture was stirred for 2 h; 0.17 g of fine ground sulfur was added, and the mixture was stirred for 3 more h at 20°C. The reaction mixture (compound **10**) $^{31}$P NMR: $\delta$ 60.1, 74.5, 75.8. The precipitated triethylamine hydrochloride and sulfur excess were filtered off, and the solvent was removed under vacuum. The resulting oil was dissolved in a benzene–dioxane mixture (3:1) and the product was isolated by column chromatography using benzene–dioxane (3:1) as an eluent. The yield of the fraction composed of oligomers with n = 6–8 was 0.56 g, $R_f$ 0.5 (B). Mass spectrum of compound **10** m/z: 1892.40 (1200 a. i.), 2117.40 (1100 a. i.), 2451.40 (1000 a. i.).

## REFERENCE

[1] G. I. Kurochkina, G. S. Bratash, M. K. Grachev, L. K. Vasyanina, and E. E. Nifantiev, *Dokl. Akad. Nauk*, **397,** 210 (2004).