Phosphorylation of the 2,2′-Dihydroxy-1,1′-dinaphthylmethane and Synthesis of Phosphamacrocycles on its Basis

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Phosphorylation of 2,2'-dihydroxy-1,1'-dinaphthylmethane with diamidophosphites with different substituents at phosphorus atom was investigated. It was demonstrated that leaving of either two amide groups or phenyl group occurs upon formation of 1,3,2-dioxaphosphacine. Phosphamacrocyclic systems containing fragments of 2,2'-dihydroxy-1,1'-dinaphthylmethane and aromatic diols – resorcinol and 1,3-dihydroxynaphthalene – were synthesized, their low stability in solution is specified. Oxidation reactions of the synthesized compounds were studied.

Keywords: Phosphorylation, 2,2'-dihydroxy-1,1'-dinaphthylmethane, diamidophosphites, aromatic diols, molecular assembly, NMR spectroscopy, X-ray.

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Фосфорилирование 2,2′-дигидрокси-1,1′-динафтилметана и синтез фосфомакроциклов на его основе

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Проведено фосфорилирование 2,2'-дигидрокси-1,1'-динафтилметана диамидофосфитами фосфористой кислоты с различными заместителями у атома фосфора; показана принципиальная возможность ухода как двух амидных групп, так и фенильного заместителя при образовании 1,3,2-диоксафосфацина. Синтезированы фосфомакромоциклические системы, содержащие в своей структуре остатки 2,2'-дигидрокси-1,1'-динафтилметана и ароматических диолов – резорцина и 1,3-диоксинафталина, отмечена их низкая устойчивость в растворах. Рассмотрены окислительные реакции синтезированных систем.

Ключевые слова: Фосфорилирование, 2,2'-дигидрокси-1,1'-динафтилметан, диамидофосфиты, ароматические диолы, молекулярная сборка, спектроскопия ЯМР, рентгеноструктурный анализ.
**Introduction**

Active studies of phosphorylation of naphthalene derivatives with two distal hydroxy-groups with di- and triamides of phosphorous acid were performed over last decade.\(^{[1-4]}\) As a result, there were synthesized macrocyclic compounds containing several fragments of macrocyclic diols and derivatives of phosphorus and phosphoric acids, which can be referred either as phosphacyclophanes or as benzocrown ethers.\(^{[7]}\) Such compounds can be used in synthesis of polynuclear complexes with transition metals for catalytic purposes, as well as supramolecular receptors which can capture ions and small molecules, and for structural tasks of modern organoelemental chemistry.

2,2'-Dihydroxy-1,1'-dinaphthylmethane 1 was investigated in reactions with derivatives of trivalent phosphorus together with other diatomic phenols. It was shown that application of alkyleneamidophosphites and other cyclic derivatives of P\(^{III}\) has afforded open-chain molecules, which have been used as ligands for asymmetric catalysis.\(^{[8,9]}\) Phosphorylation of 1 with triamidophosphites and other acyclic derivatives have resulted in formation of cyclic products – 1,3,2-dioxaphosphacines.\(^{[10-12]}\) At the same time, compound 1 has never been applied as a building block in synthesis of macrocyclic systems.

Therefore, the aim of the present investigation was to study applicability of 1 in synthesis of phosphamacrocycles.

**Results and Discussion**

At the first step, hexabutyltriamidophosphate (HBTA) 2a and trimorpholinophosphite (TMF) 2b were used as phosphorylating agents due to their low rate of phosphorylation in 1,4-dioxane in comparison with other triamides of phosphorous acid.\(^{[13]}\) However, even at reagent ratio 1:2a,2b = 1:3 the formation of bisamidophosphites was not observed in \(^{31}P\) NMR spectra of reaction mixtures. Instead of them, in both cases 1,3,2-dioxaphosphacines 3a and 3b were obtained (\(\delta_p = 140.1\) and 134.3 ppm respectively) (Scheme 1). Therefore, even application of phosphorylating agents 2a,2b with bulky substituents did not result in formation of bisphosphorylated derivatives.

At the next step, other phosphorylating agents were applied, namely, butyl and phenyl esters of phosphorous acid tetraethylidiamide 4a,b as well as phenyl ester of phosphorous acid tetrabutyldiamide 4c. Phosphorylation of 1 with these reagents was performed in acetonitrile and 1,4-dioxane (Scheme 2).

In the case of 4a irrespectively on reagent ratio (1:1, 1:2 or 1:3) in \(^{31}P\) NMR spectra there was observed a singlet with \(\delta_p = 147.6\) ppm corresponding to 1,3,2-dioxaphosphacine 5a with ester substituent at P\(^{III}\) atom. Notably, neither phosphacine 3 or bisphosphorylated system 5 were not formed. Therefore, it can be concluded that upon phosphorylation of 1 by diamidophosphite containing aliphatic ester fragment, the leaving of amide groups is favourable. The rate of phosphorylation increases when passing from 1,4-dioxane to acetonitrile, which is common for this type of reactions.

Again, irrespectively on reagent ratio the reaction of bisnaphthol 1 with tetaethylidiamidophosphite 4b has yielded 1,3,2-dioxaphosphacines 3c and 5b together with bisphosphorylated derivatives 6b (Scheme 2). The latter compounds were found to be unstable and they gradually have converted into mixture of 3c and 5b. Apparently, this process occurs via intramolecular dismutation\(^{[14,15]}\) which leads to thermodynamically favourable 8-membered ring system (Scheme 3).

The rate of this cyclization is faster in acetonitrile, while in 1,4-dioxane bisphosphorylated derivatives 6b,c are more stable (up to 3 weeks).

Noteworthy, in contrast to diamidoester 4a, in the case of 4b leaving of amide or ester fragments upon phosphorylation is equiprobable independently on reagent ratio as evidenced by \(^{31}P\) NMR spectroscopy. Upon phosphorylation of bisnaphthol 1 with tetaethylidiamidophosphite 4b in 1,4-dioxane or reaction mixture in one day after beginning in NMR spectrum there were observed resonance signals \(\delta_p = 133.8\) (6b) and 132.9 ppm (4b), while in one week there were observed resonance signals \(\delta_p = 142.0\) (3c), 140.6 (5b) and 132.9 ppm (4b) with integral ratios 1:1:2.

An application of acetonitrile instead of 1,4-dioxane has resulted in increase of reaction rate\(^{[16]}\) in two hours after beginning in \(^{31}P\) NMR spectrum of reaction mixture there was observed only 6b, however its signal has vanished in NMR spectrum afterwards.

In the case of tetrabutyldiamidophosphite 4c phosphorylation of 1 was very slow. Even after 1 day in \(^{31}P\) NMR spectrum the most intensive signal was \(\delta_p = 132.5\) ppm corresponding to starting diamide 4c, minor signal with \(\delta_p = 142.6\) ppm corresponded to bisphosphorylated product 6c (Scheme 2). The latter have remained in reaction mix-
Scheme 2.

Scheme 3.
ture even after 2 weeks after the beginning of reaction, together with \(5b\) (\(\delta_R = 141.8\) ppm), \(3a\) (\(\delta_R = 140.5\) ppm) and \(4c\) (\(\delta_R = 132.5\) ppm). The integral ratios were 1.5:1:1:6. The slow reaction rate can be explained by lower reactivity of \(4c\).

With the aim to separate and identify phosphorylated products, the reaction mixtures were sulfurized and column chromatography was used to isolate 1,3,2-dioxaphosphacines \(7a,c\) and \(8a,b\) and bisphosphorylated thione derivatives \(9b,c\). Because of similarity of solubility and chromatographic mobility, isolation of compounds in pure forms was tedious, so the yields of individual thiones were modest. Physical-chemical properties of \(7c\) have coincided with the previously reported data.[17]

X-Ray diffraction analysis of crystalline \(8a\) was performed (Figure 1, Table 1). It has evidenced that the macrocyclic part of the molecule adopts \textit{bath-bath} conformation. [17] Stability of this conformation can be tentatively explained by the presence of bulky butoxy-substituent.

![Figure 1. Molecular structure of 2-thione-2-O-butyl-4,5,7,8-dinaphtho-1,3,2-dioxaphosphacine 8a (a) and fragment of molecules packing in crystal (b).](image)

**Table 1.** Bond lengths (Å) and angles for 2-thione-2-O-butyl-4,5,7,8-dinaphtho-1,3,2-dioxaphosphacine 8a.

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<th>Angle (°)</th>
<th>(\omega, \text{ grad})</th>
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The observed formation of phosphacines upon phosphorylation of 1 with acyclic amidophosphites has precluded formation of macrocycles containing two fragments of bis-naphthol. Therefore, we have proposed two-step approach to 14-membered macrocyclic systems, containing a fragment of bis-naphthol 1 and a fragment of resorcinol 10 or 1,3-dihydroxynaphthalene 11. This approach implies synthesis of primary bisphosphorylation of diols 10 and 11 with hexaethyltriamidophosphite (HETA) 2c with subsequent cyclization of resulting bisphosphorylated derivatives 12 and 13 with bisnaphthol 1 (Scheme 4).

Reactions were performed in 1,4-dioxane. The completion of bisphosphorylation of diols 10 and 11 was confirmed by 31P NMR spectroscopy – there was observed a singlet at δP = 132.8 ppm, which is characteristic for diamidoesters of phosphorous esters with aromatic radicals – 12 and 13. Then, bisphenol 1 was added to reaction mixture and the mixture was kept for 3 days. During this time the signal at 132.8 ppm gradually vanished and a new signal at 140.5 ppm became intensive. This signal corresponded to the target amidodies ters.

Resulting macrocycles 14 and 15 were found to be unstable. In solution they have rearranged with the formation of 1,3,2-dioxaphosphacine 3c and uniform cyclophanes.

However, we have tried to isolate target macrocycles. With this aim the reaction mixtures containing products with δP = 140 ppm were evaporated to minimal volume and cooled resulting in formation of oily product. The solvent was decanted, the oil was washed with cold acetonitrile and dried in vacuo. Their NMR spectra corresponded to the target macrocycles 14 and 15, however, they also contained resonance signals of 1,3,2-dioxaphosphacine 3c impurity. Isolation of pure macrocycles was possible only after their conversion into thiones and phosphates.

Sulfurization of cyclophosphites 14 and 15 was performed with elemental sulfur in CH2Cl2 during 1 day. Resulting cyclo(bisthioneamidophosphates) 16 and 17 were isolated by column chromatography in 30 and 25 % yields respectively as viscous oils. Their 31P NMR spectra contained singlets in 68 ppm region, what corresponded to amidooesters of thionephosphoric acid.

Oxidation of cyclophosphites 14 and 15 was performed with urea peroxide in CH2Cl2 for 1 day. Phosphates 18 and 19 were isolated by precipitation with hexane. They were isolated as low-melting powders in 79 and 65 % yields respectively. Their 31P NMR spectra contained singlets at 1 ppm which corresponded to monoamidophosphates. 1H NMR spectrum of compound 19 revealed some broadening of resonance signals.

Conclusions

1. We have investigated phosphorylation of 2,2′-dihydroxy-1,1′-dinaphthylmetane with derivatives of P(NEt2)3 – hexabutyltriamide, trimorpholinephosphite, tetraethyl- and tetrabutyldiamidophenylphosphites, as well as tetraethyldiamidobutylphosphite.

2. The equiprobable leaving of amide or aromatic ester substituent was found upon formation of 1,3,2-dioxaphosphacine.

3. We have synthesized phosphamacrocyclic systems, containing 2,2′-dihydroxy-1,1′-dinaphthylmethane as a building block, the oxidation reactions of these macrocycles were investigated.

Experimental

All syntheses were conducted in dry solvents under an argon atmosphere. 1H, 13C and 31P NMR spectra were recorded on a JEOL ECX-400 spectrometer operating at 400, 100.5 and 161.8 MHz...
respectively; $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$; chemical shifts (δ, ppm) were referenced to TMS (H and $^{13}$C) or to 85 % H$_3$PO$_4$ (14P). Spin-spin coupling constants (J) are given in Hz. Mass spectra were measured on a Bruker Ultraflext MALDI-TOF spectrometer using a nitrogen laser (λ = 337 nm) and trihydrory-anthracene as a matrix. Crystals of compound 3aa have been obtained by crystallization from hexane. X-ray analysis was performed on an automatic CAD-4 Ehral-Nonius diffractometer ($\beta$-filter, λ = Mo-Ka 0.71073 A) 20 data collection, δ$_\theta$ = 24.88°). Colorless triclinic crystal (C$_{H}$O$_{5}$P, M = 434.46, size 0.56 × 0.40 × 0.15 mm, a = 9.881(2), b = 10.846(2) A, c = 11.482(2) A, α = 87.10(3)°, β = 74.82(3)°, γ = 71.12(3)°. V = 112.95(5) A$^3$, Z = 2, p = 1.258 mg/cm$^3$, Number of reflections: 4433, independent reflections: 4172 (R(int) = 0.0200). F(000) = 456, R$_{P}$ = 0.0431, wR$_F$ = 0.1307. Refinement method: full-matrix least squares on $F^2$ for non-hydrogen atoms. All hydrogen atoms have included in the refinement with fixed parameters (placed in calculated positions) in the isotropic approximation. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre (CCDC 1052567). Column adsorption chromatography was performed on silica gel 100-250; TLC was performed on Silufol plates (UV-254) using C$_{6}$H$_6$-hexane, 5:1 (A), C$_{6}$H$_6$-dioxane, 3:1 (B). Detection was achieved using iodine vapor treatment and calculation.

2,2'-Dihydroxy-1,1'-dinaphthylmethane 1 was synthesized by the method from HBTM 2aa in tetrahydro- and tetrabutylammonium 2,3-bis(4-pyridyl)ethanol (3b).

2-Butylidiamino-4,5,7,8-dinaphtho-1,3-diphasphocine (3a).

A solution of 1.25 g (3 mmol) HBTM 2aa in 5 ml of 1,4-dioxane was added to a solution of 0.3 g (1 mmol) of bisnaphthol 1 in 4 ml of 1,4-dioxane. The reaction mixture was kept at room temperature for 2 h. The solvent was evaporated in vacuo (12 mm Hg), and the residue was chromatographed on a column, the resulting product was eluted by hexane-dioxane (10:1) system. The resulting material was dried in vacuo for 1.5 h (1 mm Hg, 60 °C). Yield 0.41 g (89%). R. 2.09 (A). H NMR δ ppm: 0.97 (6H, t, J$_{HH} = 7.3$, CH$_3$), 1.40 (4H, m, CH$_2$), 1.70 (4H, m, CH$_2$), 3.75 (4H, m, J$_{HH} = 4.6$, N-C$_6$H$_5$), 7.35 (4H, dd, J$_{HH} = 7.8$, J$_{HH} = 4.6$, O-C$_6$H$_5$), 4.56 (1H, dd, J$_{HH} = 16.1$, J$_{HH} = 6.6$, Ar-C$_6$H$_5$), 5.09 (1H, dd, J$_{HH} = 16.1$, J$_{HH} = 8.7$, Ar-C$_6$H$_5$), 7.18 (2H, d, J$_{HH} = 8.7$, CH$_3$), 7.39 (2H, dd, J$_{HH} = 7.0$, 7.6, CH$_3$), 7.50 (2H, dd, J$_{HH} = 7.0$, 8.3, CH$_3$), 7.63 (2H, dd, J$_{HH} = 8.7$, CH$_3$), 7.81 (2H, dd, J$_{HH} = 6.2$, 8.2, CH$_3$), 8.21 (2H, dd, J$_{HH} = 8.7$, CH$_3$). C NMR δ ppm: 114.1 (CH$_3$), 128.9 (C$_{H}$O$_{5}$P), 126.8 (C$_{H}$O$_{5}$P), 128.9 (C$_{H}$O$_{5}$P), 130.9 (C$_{H}$O$_{5}$P), 131.0 (C$_{H}$O$_{5}$P), 149.7 (C$_{H}$O$_{5}$P). H NMR (1,4-dioxane) δ ppm: 140.1. 2-Morpholino-4,5,7,8-dinaphtho-1,3,2-diphasphocine (3b).

A solution of 1.86 g (3 mmol) TMF 2b in 5 ml of 1,4-dioxane was added to a solution of 0.3 g (1 mmol) of bisnaphthol 1 in 4 ml of 1,4-dioxane. The reaction mixture was kept at room temperature for 2 h. The solvent was evaporated in vacuo (12 mm Hg); the residue was added to the 5 ml of acetonitrile. After 12 h the crystals precipitated were filtered off, washed with hexane and acetonitrile. The resulting material was dried in vacuo for 1.5 h (1 mm Hg, 60 °C). Yield 0.37 g (90%). Mp 189–190 °C. R. 0.32 (A). H NMR δ ppm: 3.33 (4H, m, J$_{HH} = 7.8$, J$_{HH} = 4.6$, N-C$_6$H$_5$), 3.75 (4H, dd, J$_{HH} = 4.6$, O-C$_6$H$_5$), 4.56 (1H, dd, J$_{HH} = 16.1$, Ar-C$_6$H$_5$), 5.09 (1H, dd, J$_{HH} = 16.1$, Ar-C$_6$H$_5$), 7.18 (2H, d, J$_{HH} = 8.7$, CH$_3$), 7.39 (2H, dd, J$_{HH} = 7.0$, 7.6, CH$_3$), 7.50 (2H, dd, J$_{HH} = 7.0$, 8.3, CH$_3$), 7.63 (2H, dd, J$_{HH} = 8.7$, CH$_3$), 7.81 (2H, dd, J$_{HH} = 6.2$, 8.2, CH$_3$), 8.21 (2H, dd, J$_{HH} = 8.7$, CH$_3$). C NMR δ ppm: 114.1 (CH$_3$), 128.9 (C$_{H}$O$_{5}$P), 126.8 (C$_{H}$O$_{5}$P), 128.9 (C$_{H}$O$_{5}$P), 130.9 (C$_{H}$O$_{5}$P), 131.0 (C$_{H}$O$_{5}$P), 149.7 (C$_{H}$O$_{5}$P). H NMR (1,4-dioxane) δ ppm: 140.1. Phosphorylation of 2,2'-dihydroxy-1,1'-dinaphthylmethane 1 with diiodoesters of phosphoric acid 4a-c (general procedure). Solution of diiodo-phosphate 4a-c in 4 ml of acetonitrile or 1,4-dioxane was mixed with solution of 1 mmol of bisnaphthol 1 in acetonitrile or dioxane respectively, at room temperature. After 2 h the mixture was filtered off, washed with ethyl acetate and dried in vacuo (12 mm Hg). The remaining oleic precipitate was washed twice with cold acetonitrile and dried in vacuo for 2 h (1 mm Hg, 60 °C).

1,3,1',2'-Dinaphthylamine-7,1'-benzene-4,6,8,10-tetracazo-5,9-di(ethylidiamide)phosphocyloactane (14). Yield 0.14 g (25 %). Oiliness substance. R. 0.80 (B). H NMR δ ppm: 1.19 (6H, t, J$_{HH} = 7.0$, CH$_3$), 1.25 (6H, t, J$_{HH} = 7.0$, CH$_3$), 3.31 (8H, m, J$_{HH} = 11.0$, N-C$_6$H$_5$), 4.55 (4H, d, J$_{HH} = 16.2$, Ar-C$_6$H$_5$), 5.26 (1H, d, J$_{HH} = 16.2$, Ar-C$_6$H$_5$).
found, %: C, 64.34; N, 3.89. Calculated, %: C, 64.45; N, 3.55. 0 °C and filtered, the solvent was removed left for 24 h at room temperature. Then the solution was cooled to

Thionophosphoramidates (16, 17) (general procedure). Sulphur 0.064 g (2 mmol) was added to cyclophosphite (14, 15) in 5 ml of dichloromethane. The mixture was stirred for 3 h at room temperature and left for 24 h. The solution was filtered, the solvent was evaporated down to a small volume, and 10 ml hexane was added; after 10 min the solution was decanted from precipitate. The procedure was repeated twice. The resulting material was dried in vacuo for 2 h (1 mm Hg, 70 °C).

I, 3(1,2)-Dinaphtholina-7(1,3)-benzene-4,6,8,10-tetraoxa-5,9-di(diethylamidate)thionophosphacyclodecaphane (17). Yield 0.20 g (30 %). Oil substance. Rf 0.61 (A). 1H NMR δ ppm: 1.00 (9H, t, CH3), 1.02 (3H, t, J = 7.2, CH3), 3.22 (8H, m, = 13.9, N-CH2), 4.70 (1H, d, J = 16.1, Ar-CH), 5.14 (1H, d, J = 16.8, Ar-CH), 6.66 (2H, d, J = 8.0, o-CH), 6.79 (1H, d, J = 4.0, o'-CH), 6.85 (1H, m, J = 8.0, m-CH), 7.12 (2H, dd, J = 8.8, J = 1.5, CH), 7.38 (2H, dd, J = 7.3, 7.8, CH), 7.48 (2H, dd, J = 7.7, J = 1.5, CH), 7.66 (2H, dd, J = 8.8, CH), 7.76 (2H, dd, J = 8.0, J = 1.2, CH), 8.19 (2H, dd, J = 8.0, CH). 13P NMR (1,4-dioxane) δ ppm: 66.8. Found, %: C, 62.07; H, 5.69; N, 3.85. Calcd: C, 62.12; H, 5.66; N, 3.85.

References


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