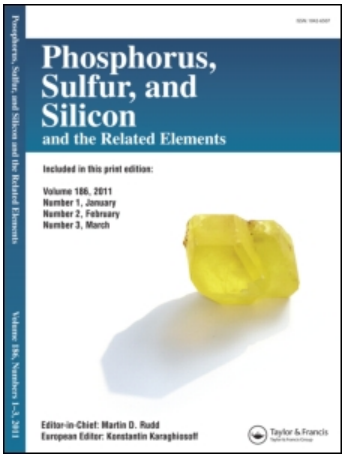

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New Effects in Cyclophosphorylation of Polyatomic Phenols by Phosphorous Acid Amides

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NEW EFFECTS IN CYCLOPHOSPHORYLATION OF POLYATOMIC PHENOLS BY PHOSPHOROUS ACID AMIDES

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Electronic effects in the design of new types of phosphocontaining cavity systems were considered. The matter of this phenomenon consists in supramolecular interaction of the organic radicals of substrates with the cyclophosphorylating reagents.

Keywords: Cavity systems; cyclophosphorylation; supramolecular interaction

INTRODUCTION

Amides of phosphorous acids are actively used in the cyclophosphorylation of polyatomic phenols. According to the literature data[1] these reactions are strictly followed to the classic scheme of phenolysis of P—N bonds. We introduced aromatic diamidoesters in the investigations of the design of new types of aromatic phosphocontaining cavity systems. It led to the observation of new effects to which consideration the present work is dedicated.

RESULTS AND DISCUSSION

The first part of the work includes the comparison between the cyclophosphorylation of calix[4]rezorcinarenes by aliphatic and aromatic

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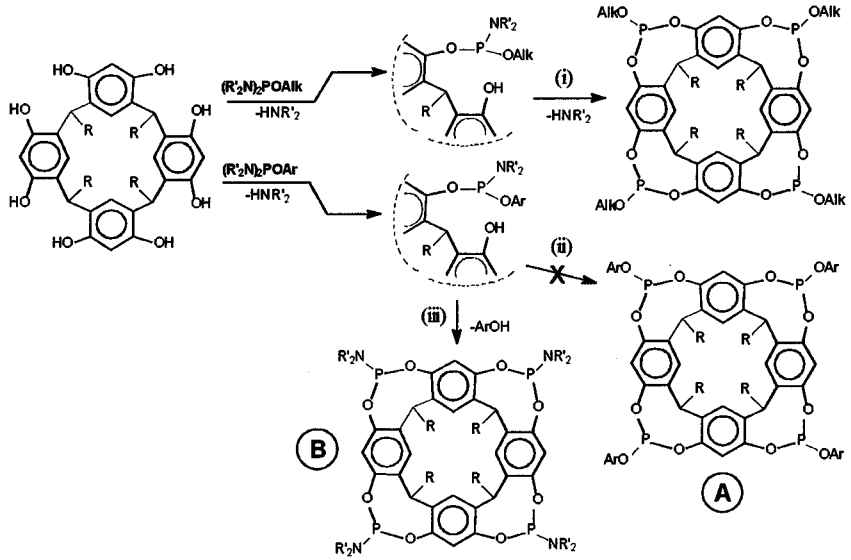
diamidoesters of phosphorous acid. We revealed that they behave differently in this reaction (Scheme 1).



SCHEME 1

The transformation of aliphatic reagents follows the classical scheme, which includes two consecutive stages of the phenolysis of phosphoamide bonds (i).[2] Aromatic derivatives react differently.[3] The first stage involves the standard phenolysis of the phosphamide bond, which yields phosphorous acid amidoesters, as is evidenced by the NMR spectra of reaction mixtures. The second stage does not follow the conventional scheme, and the expected aryloxyphosphocavitands **A** (ii) are not formed. Amidophosphocavitands **B** (iii) are released in this case.

The obtained results indicate that we broke the phosphoester bond in mild conditions, which is generally passive in phosphorylation. At the same time, the phosphoamid bond, which is generally active in this process, remains intact.

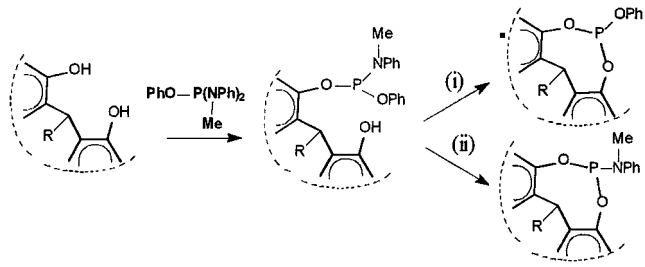
The phosphoamide nature of phosphocine cycles, individuality of isolated stereoisomers, and symmetry of the polycyclic molecular skeleton were rigorously proven by NMR spectroscopy and X-ray diffraction analysis.

The unusual cyclization is probably due to the stacking interaction between two benzene rings of intermediate products. In fact, this is the quasi-molecular recognition of the pairs of benzene rings close in space. In this interaction, the phosphorus-bearing unit is arranged in such a way that the phenoxy group is at the surface of the calixarene matrix,

and the amido group moves to the periphery. Such arrangement of the intermediate allows the cyclophosphorylation to proceed through the rupture of the P—O bond.

In closing the consideration of a new effect in the cyclophosphorylation of calixarenes, we performed an additional experiment. It involved the interaction between a calixarene and an amidophosphite, which molecules contained oxygen and nitrogen atoms bound to phenyl radicals.

If our reasoning is true, the stacking interaction between the benzene nuclei of calixarene and the benzene nuclei of the phoshoester and phosphamide fragments can be expected at the second stage of the synthesis. Such orientation of nuclei should result in two directions of cyclization: phosphite (i) and amidophosphite (ii) (Scheme 2). We established this result experimentally.



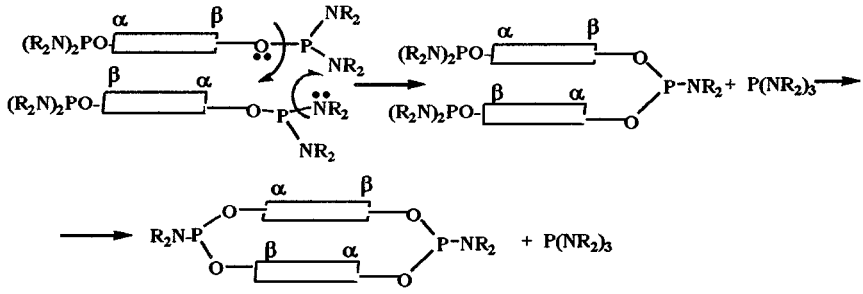
SCHEME 2

Thus, we first established the supramolecular determinancy of changes in the reactivity of the O—P—N fragment in the reaction with phenol.

Note that the geometrical factor plays an essential role in the realization of the effect considered. If the geometrical requirements are not satisfied, as in the substitution of the phenyl group by the benzyl group in the reagent, the cyclophosphorylation proceeds through the rupture of the P—N bond, that is, by the classical scheme.

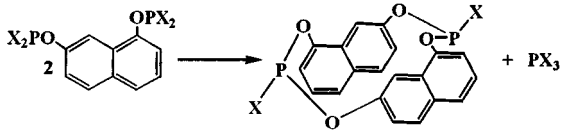
In this work, we began to extend the new cyclophosphorylation procedure to the modification of other phenolic systems, including dioxophenols, dioxonaphtols, pyrocatehols.

The second part of the work is devoted to specific effects observed in the synthesis of cyclophosphophosphorylated dihydroxynaphthalenes. This study was performed with the object of creating new cavitand systems containing naphthalene fragments bound by phosphorus bridges. The work was started by the cyclophosphorylation of symmetrical dihydroxynaphthalenes with phosphorous acid triamides at the equimolecular ratio of reagents. In the conducted experiments either



SCHEME 3

complex conformationally mobile sixteen-membered or rigid bidecks architectures were obtained. Meanwhile it turned out to be possible to synthesize with high yields the individual cyclodinaphtyldiphosphites from unsymmetric dioxonaphtols. Towards this end the disproportion of bisdiamidophosphites of these diols was suggested.



SCHEME 4

We suppose that the route of the reaction revealed by us includes the formation of supramolecular construction. The latter contains two parallel naphtol nuclei which fixed due to electronic effects, mainly due to stacking interactions. To support this hypothesis we estimated the stability of some aromatic amidophosphites, including diamidophenylphosphites. It was established that all these compounds were disproportionate under storage at room temperature (Figure 1).

To summarize this work, we may note that the strategy in the synthesis of phosphorus-bearing cavitands cannot be based only on the classical methods of phosphorylation. It requires the thorough analysis of intermediates and the active implication of concepts of supramolecular chemistry.

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