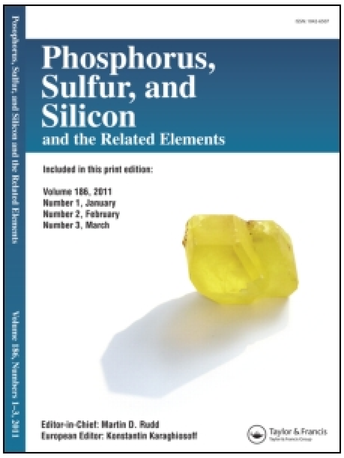

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PHOSPHOCONTAINING CYCLODEXTRINS AS A NEW CLASS OF SUPRAMOLECULAR STRUCTURES

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Principal peculiarities of the use of phosphocontaining cyclodextrins as a new class of supramolecular structures are discussed. For the first time cyclodextrin perphosphite has been obtained and isolated in an individual state by the treatment of β-cyclodextrin with triazolide neopentylenephosphorous acid. Cyclodextrin perphosphite exhibited an unusual transphosphorylation under reaction with some chlorophosphites. The inclusion of adamantane into the cyclodextrin cavity results in slowing this reaction down. Some water-soluble cyclodextrin derivatives displayed high activity as phase transfer catalysts in biphase catalysis.

Keywords: Cyclodextrin; inclusion complexes; transphosphorylation

INTRODUCTION

Easy access of natural cyclodextrins (α-,β-,γ-c.ds.: $n = 1,2,3$) and their numerous derivatives found a wide use for the solution of many urgent practical tasks, for example, for the formation of various inclusion compounds and for the incapsulation and solubilization of drugs, perfumes, and so on. A chemical modification of c.ds. essentially expands their possibilities for the creation of such supramolecular ensembles as catenanes, rotaxanes, polyrotaxanes, molecular tubes, etc. Unfortunately, regioselective chemical modification of c.ds. is still a very difficult experimental task, especially for the making of c.ds. derivatives with definite

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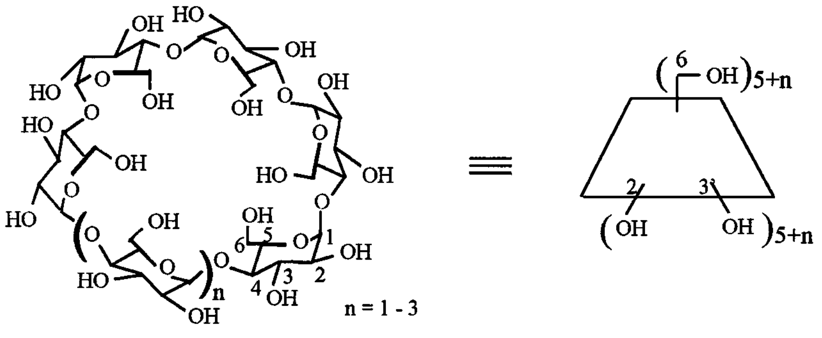
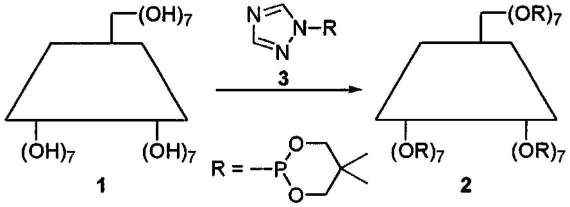


FIGURE 1

(enlarged) volume of the internal chiral cavity. In this presented work some possibilities of new c.ds. derivatives for obtaining supramolecular structures, possessing the enlarged cavity of a c.d. frame and the enhanced ability to form inclusion compounds, are considered.

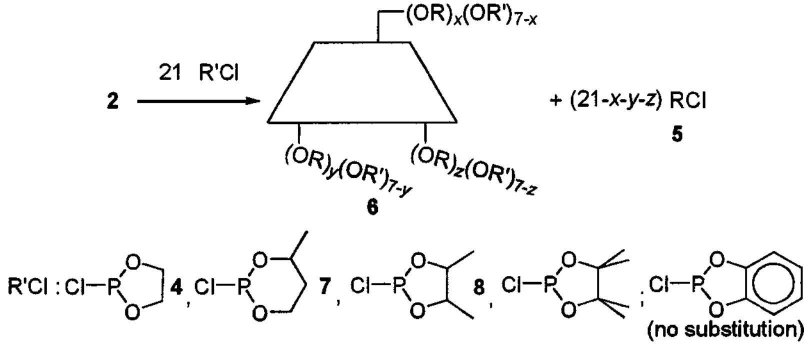
RESULTS AND DISCUSSION

Recently we succeeded in synthesizing the first representative of c.ds. perphosphite **2** obtained by us in an individual state by the treatment of β-cd. **1** with triazolide of neopentylenephosphorous acid **3**.



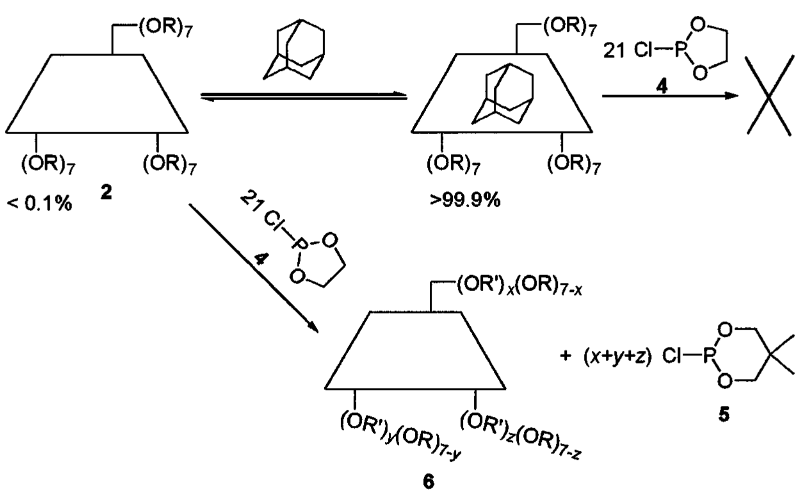
The reaction was performed in benzene (60°C, 2 h) under excess of a phosphorylating reagent **3**. The phosphorylation degree was monitored by ^{31}P NMR spectroscopy. Cd. perphosphite derivative **2** was isolated by flash chromatography on freshly calcinated Al_2O_3 and characterized by ^1H, ^{31}P NMR spectroscopy, MALDI mass-spectrometry, and element analysis.

It turns out that the obtained P(III)-cd. derivative **2** sharply differs from other analogous esters of neopentylenephosphorous acid. Thus, according to ^{31}P NMR data during the treatment of derivative **2** by 21 equivalent of chloroethylenephosphite **4**, a fast partial displacement of 5,5-dimethyl-1,3,2-dioxaphosphorinane residues by 1,3,2-dioxaphospholane ones occurs that leads to the evolvement of corresponding quantities of chloroneopentylenephosphite **5** and to the formation of cd. derivative **6** with mixed phosphocontaining residues. Some other chlorophosphites (R′-Cl) turned out to be capable of transphosphorylation with **2** as well, but with different substitution degrees.



We made an assumption that transphosphorylating reagent could be first included in the cd. cavity and then transformed at a *supramolecular* level. The main point of such transformation consists of closing in covalently bound phosphites groups of a "host" and a "guest," owing that the redistribution of bounds easily occurs, i.e., new perphosphites of β-cd. are formed. The obtained product has more compact substituents, and due to that it is a more stable compound.

To verify this hypothesis we carried out the experiment on the transphosphorylation in the presence of adamantane. It is known that



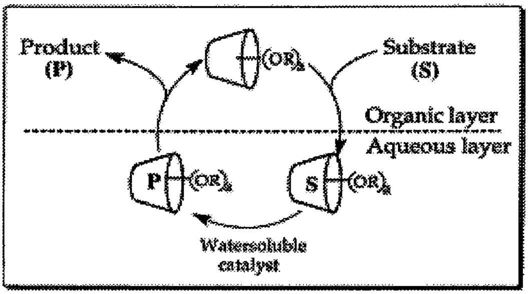


FIGURE 2

the structure and size of the adamantane molecule conform to the structure and size of the β-cd. cavity (and of many its derivatives), and therefore they easily form strong inclusion compounds. Obviously, that corresponding inclusion compound, on the basis of perphosphites of β-cd., cannot include transphosphorylating agent. The experiment clearly showed that adamantane "turns off" the transphosphorylation. Thus, the hypothesis about *supramolecular* level of this original reaction was confirmed experimentally. The following experiments on transphosphorylation by the mixtures of two chlorophosphites different in nature revealed that this process is a result of complex competitive *supramolecular* interactions at two steps (*a* and *b*): for the inclusion into cd. cavity (*a*) and for the interaction with neopentylenephosphite residues (*b*).

Some watersoluble cds. derivatives, including phosphocontaining ones, found a use in the biphase catalysis. In this case they are of importance as a molecular carrier to transfer hydrophobic substrate from an organic layer into a water layer where the homogeneous catalyst is present. Phosphate-containing cds. turned out to be the promising inverse phase transfer catalysts carriers for the palladium catalyzed cleavage of water-insoluble alkyl allyl carbonates. Thus the process of molecular recognition between the cds. derivative and a substrate allowed to perform substrate-selective catalytic reactions which cannot be achieved in homogeneous or biphase media with conventional transition metal catalysts.