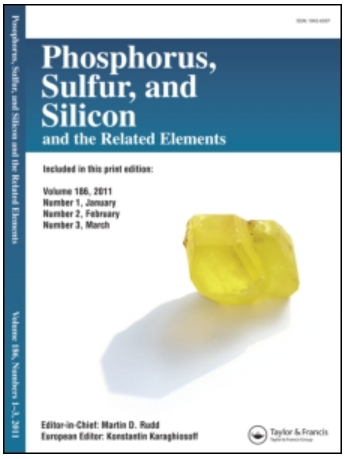

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Synthesis of New Macrocyclic Aryl Phosphonates. X-Ray Structure and Clathration Properties

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Williamson condensation of bis-*o*-hydroxy aryl phosphonates with dihaloalkylaryl derivatives yields the title compounds. They show interesting stereochemical aspects and some of them can be used in chiral recognitions and separations.

Keywords: Chiral macrocycles – Supramolecular separations – Stereochemical aspects

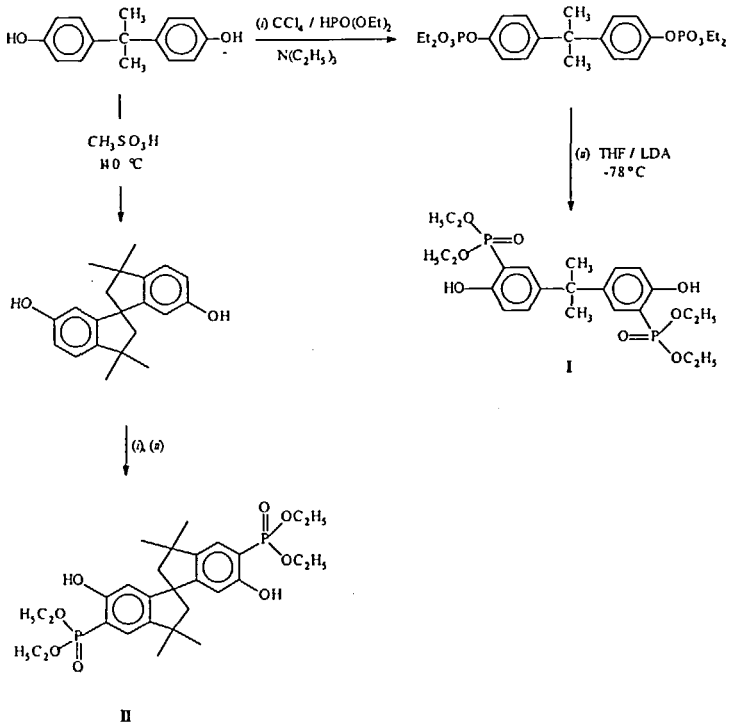
INTRODUCTION

By adapting the synthetic strategy described by Redmore *et al.*[1], we were able to produce, in very good yields, bis-*ortho*-hydroxy aryl phosphonates **I** and **II** by [1,3]-sigmatropic rearrangement of bis-*ortho* metallated aryl diethyl phosphates[2] (Scheme I).

Besides the interest in obtaining flame retardant and thermally stable polymers, compounds **I** and **II** can be also used for preparing novel macrocyclic polyethers possessing ancillary groups (the phosphonic ones) which can improve their water solubility or their complexing properties.

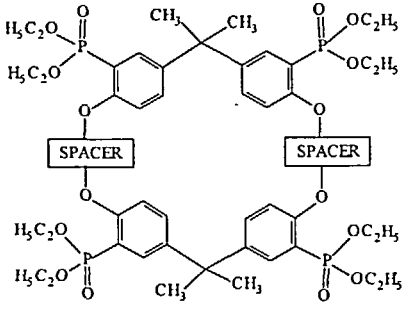
Therefore, by using monomer **I**, three novel macrocycles **III-V** were prepared by condensing it with 2,6-bis(bromomethyl) pyridine, 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene and α,α'-dibromo-*p*-xylene, respectively, under reflux conditions in acetonitrile in the presence of solid K_2CO_3, as acid acceptor.

Scheme I: Synthesis of new ortho-hydroxy aryl phosphonates.



The three novel macrocycles were fully characterized by ^{1}H-, ^{13}C-, ^{31}P-NMR, FAB-MS techniques and for macrocycle **III** the solid state structure was determined by X-ray analyses[3].

All macrocycles are conformationally mobile at room temperatures, even on the NMR time scale. Macrocycle **III** was found to include one mol of cyclohexane in its cavity and, by taking advantages of such property, the [2 + 2] macrocycle could be separated selectively from the reaction mixture by formation of the inclusion complex with cyclohexane: in other words, a "supramolecular" purification method was successfully used.



On the contrary, by condensing under similar conditions the spirobi-indane monomer **II** with 1,3- or 1,4-dialkylaryl halides we got in very good yields only the [1 + 1] macrocycles **VI-XII** (Scheme II).

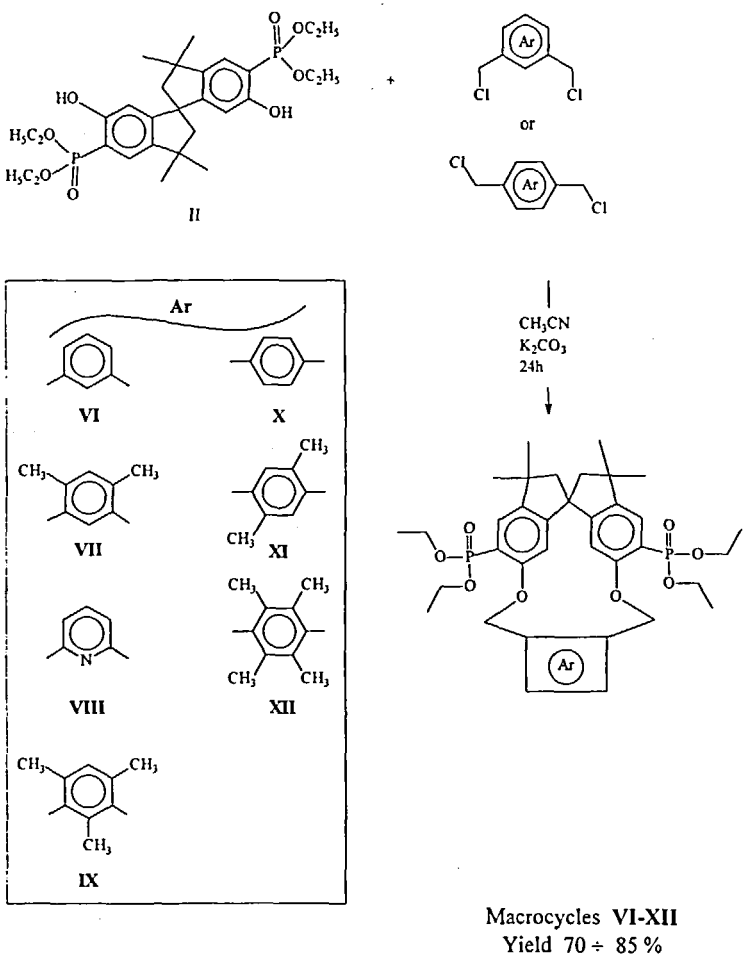
The solid state structures of compound **IX** was successfully solved by X-ray analyses, which indicate that the solvent molecules are enclathrated in the crystal lattice and show a great deal of disorder.

By NMR analyses, it was shown that the cycles **VI-VIII** show mobility of the aryl rings, which by π radians rotation, average the benzylic bridging protons as well as the spirobiindane phosphonic groups. Macrocycle **IX**, as well as that ones obtained by condensing monomer **II** with 1,4-bis-chloromethyl aryl derivatives, *i.e.*, compounds **X-XII**, are all stereochemically rigid on the NMR time scale.

Considering that the spirobi-indane phosphonate monomer **II** is a preorganized dissymetric molecule which exists as a pair of enantiomers, this compound can be used as a chiral template for building chiral polycondensates or inducing chirality in replicating strands and thus the obtained macrocycles could be of interest for chiral recognitions and separations.

Macrocycles **VII** and **IX** form inclusion complexes with cyclohexane and compound **IX** shows restricted rotation of the mesityl ring on the NMR time-scale, at room temperatures.

Scheme II: Macrocycles formed from the spirobi-indane phosphonate monomer **II**.



Macrocycles **VI-XII**
Yield 70 ÷ 85 %

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[3] G.A. Consiglio, S. Failla, P. Finocchiaro, M. Visi and K.I. Hardcastle, *Supramolecular Chemistry*, submitted.