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 K₂CO₃, as acid acceptor.



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

The three novel macrocycles were fully characterized by ¹H-, ¹³C-, ³¹P-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.

References

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