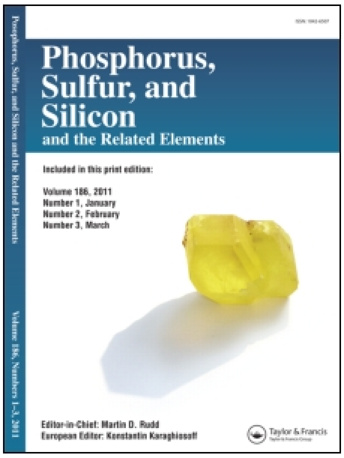

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Phosphorus-Containing Macrocyclic "Host"-Molecules. Synthesis, Structure and Properties

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PHOSPHORUS-CONTAINING MACROCYCLIC "HOST"-MOLECULES. SYNTHESIS, STRUCTURE AND PROPERTIES

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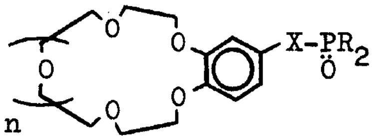
Abstract Macrocyclic "host"-molecules (crown-ethers, calixarenes, calixresorcynolarenes and cyclotricatechylenes) functionalized with exocyclic phosphorus groups are discussed.

INTRODUCTION

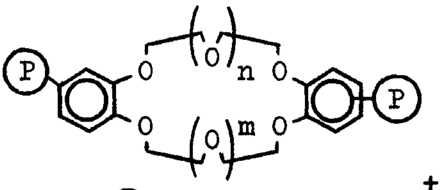
Complexation of organophosphorus compounds is an obgect of numerous studies. The discovery of macrocyclic "host"-molecules (crown-ethers, cyclophanes etc.) gave new ideas for the investigation of complexants containing the phosphorus groups as additional complexing centres for metals and neutral organic molecules. We have synthesized and investigated the phosphorylated crown-ethers, calixarenes, calixresorcynolarenes and cyclotricatechylenes.

CROWN-ETHERS

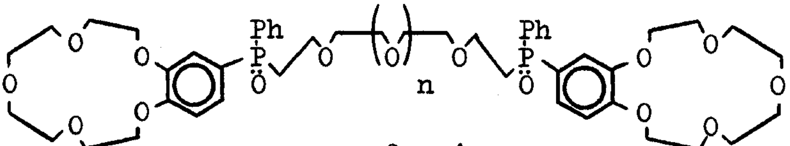
Crown-ethers functionalized with exocyclic phosphorus groups were obtained by the interaction of bromo- or iododerivatives of monobenzo- and dibenzocrown-ethers with trivalent phosphorus compounds, alkenylphosphonates under the conditions of metal catalyzed Arbuzov, Michaelis-Bekker and Hek reactions. Based on these compounds, crown-ethers (including bis-crown-ethers and polymeric crown-ethers) with various substituents at the phosphorus atom were synthesized. The influence of phosphorus groups on the complexation of the crown-ethers with alkali-, alkali-earth metals as well as some neutral small organic molecules was investigated.[1,2]



$n=0-2$, X="-",$CH=CH(CH_2)_m$



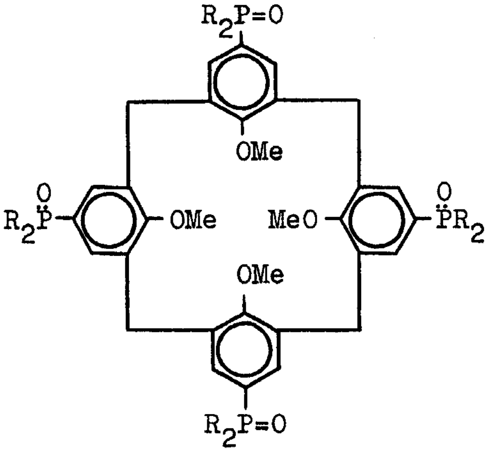
$n.m=1,2$; Ⓟ $=R_2P(X),Ph_2P,R_4\overset{+}{P}$



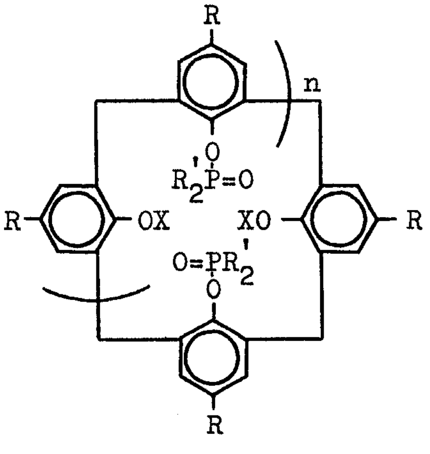
$n = 0 \div 4$

CALIXARENES

The upper rim and lower rim phosphorylated calixarenes were synthesized both by the nikel catalyzed Arbuzov reaction of tetramethyl ether of tetrabromocalixI4Iarene and the reaction of calixarentetroles and octoles with chlorophosphates.[3] Partially phosphorylated compounds were obtained in the presence of triethylamine. The use of sodium hydride leads to completely phosphorylated calixarenes.



R = Alk, Ph



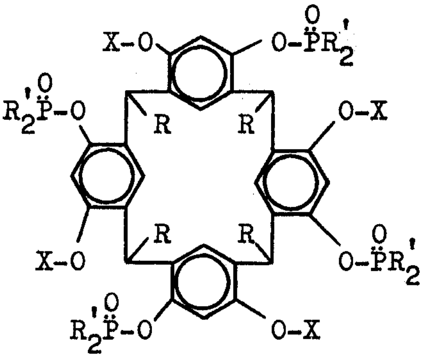
R = H, t-Bu; R' = Alk; n = 1,2

X = H, $R'_2P(O)$

The molecular structure of some lower rim phosphorylated calixarenes was examined by the X-ray method. The molecule diphosphorylated calixI4Iarene (R=H, R'=EtO) retains the "cone" conformation, which is suitable for the inclusion of a "guest". Dihedral angles between the benzene rings and the plane of the CH_2-groups are 100 and 140°. The data of the NMR spectra analysis show the molecules of the lower rim diphosphorylated and tetraphosphorylated calixI4Iarenes to be stereochemically rigid. The molecule of hexaphosphorylated calixI6Iarene ($R=H$, $R'=EtO$) is centrosymmetrical; The opposite benzene rings are parallel. The angles between the benzene rings and the main plane of a macrocycle are 39, 61,and 108°. In solution under room temperature the molecule is flexible.

CALIXRESORCYNOLARENES

The methods of both complete and partial functionalyzation of calixresorcynolarenes with phosphorus substituents have been developed.[4]



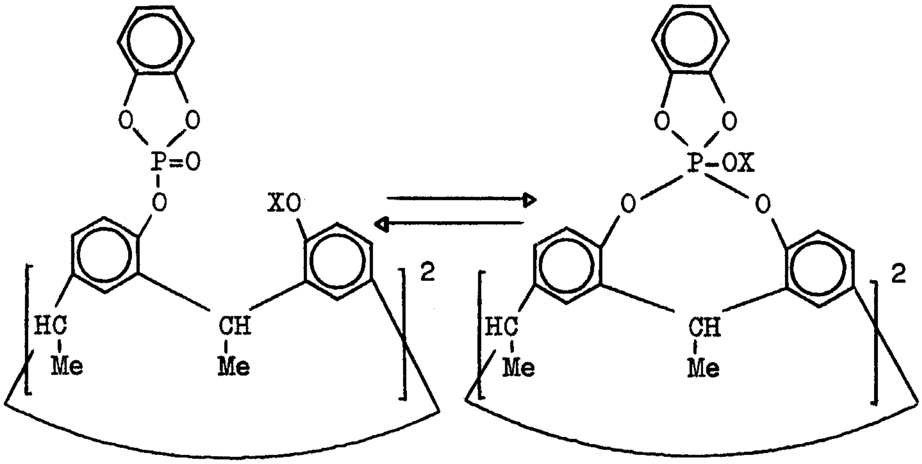
$X = H, R'_2P(O)$

$R' = AlkO, ArO, OH$

$R'_2 = o\text{-}C_6H_4O_2$

$R = Me, n\text{-}C_5H_{11}, n\text{-}C_7H_{15}, n\text{-}C_{15}H_{31}, Ph$

The NMR spectra have confirmed octaphosphorylated calixresorcynolarenes to exist in a "boat" conformation where two opposite benzene rings are coplanar to the main plane of a molecule and two others are perpendicular to it (C_{2v} symmetry). This conformation is flexible at temperatures above -30° C, and rapid positional exchange of perpendicular and coplanar rings is observed. The "boat" conformation of tetraphosphorylated compounds is rigid, no exchange of benzene rings orientation being observed. An increase in the "boat" conformation rigidity is due to the formation of strong intramolecular hydrogen bonds between the hydroxyl groups and basic oxygen atoms of neighbouring phosphoryl groups. A characteristic feature of the tetraphosphorylated compounds is the absence of any elements of symmetry in their molecules. Spatial proximity of the phosphoryl groups and the nucleophilic oxygen atoms of neighbouring benzene rings in the tetrakis-benzdioxaphospholanyl derivatives lead to the reversible intramolecular addition of either hydroxyl or trimethylsiloxy groups by the P=O bond.[5]



X = H, Me_3Si

The position of an equilibrium between the opened and closed forms depends on temperature and the nature of the solvents used. The basic solvents, such as pyridine and triethylamine exert the most strong effect.

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