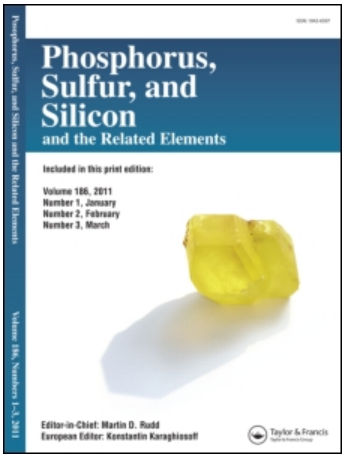

Phosphorus, Sulfur, and Silicon and the Related Elements

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PHOSPHORYLATED CALIXARENES IN DESIGN OF RECEPTORS FOR METAL CATIONS AND ORGANIC MOLECULES

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A series of calix[4,6]arenes functionalized with phosphinoxyde, diphosphindioxyde, and carbamoylphosphinoxide groups, which possess high binding ability to metal cations or protodonative organic molecules and are linked to the wide rim of macrocyclic skeleton by different spacers, has been synthesized.

Keywords: Calixarenes; complexation; organophosphorus compounds

Organophosphorus compounds (tributylphosphate, bis-2-ethylhexylphosphoric acid, carbamoylphosphine oxides, etc.) are widely used as ionophores in industrial processes of extraction actinides, lanthanides, uranium, and plutonium from high- and low-active radioactive wastes (TRUEX and PUREX processes).[1] However, despite the achievements in this field, the problem of higher efficiency and selectivity of organophosphorus extractants remains a focus of modern research. A promising approach in the design of the highly selective extractants is the functionalization of a macrocyclic frame of calixarenes by phosphoryl-containing fragments, forming pseudo-cavities including metal cations with complementary sizes and topology.[2–6] In this paper, we present a synthesis of new calix[4,6]arenes bearing phosphoryl, diphosphindioxyde, and carbamoylphosphinoxide groups at the macrocyclic wide rim that are promising as binders for metal cations or protonodonative organic molecules.

To vary the binding properties, calixarenes **2** with same [$Ph_2P{=}O$, $Bu_2P{=}O$, $(i\text{-}PrO)_2P{=}O$, $(HO)_2P{=}O$)] or different substituents [Ph(i-PrO)

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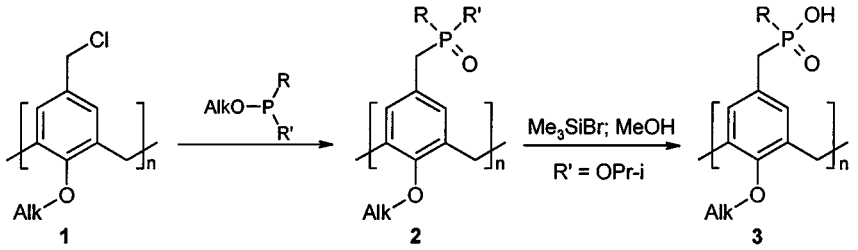

FIGURE 1

P=O, Ph(Me)P=O, Et_2N(Bu)P=O, Ph(HO)P=O, Bu(HO)P=O] at phosphorus atom differenced with electron parameters [σ^{ϕ} −1.54 (Et_2N), −1.22 (Bu), −0.48 or −0.59 (Ph), −0.39 (OH), −0.29 (i-PrO)] or steric nature have been synthesised by the Arbuzov or Michaelis-Becker reaction of chloromethylcalix[4,6]arene **1** and the next consecutive treatment of the P—OPr—i derivatives with trimethylbromosilane and methanol.

Calix[4]arenes 5(X=O) bearing four diphenylphosphinylmethoxymethyl groups have been synthesised by two different methods. The first method consists of the reaction of chloromethylcalix[4]arene **1** with diphenylmethylolphosphine oxide. The second method is based on the reaction of tetrakis-(hydroxymethyl)-tetrapropoxy-calix[4]arene **4** with diphenyliodomethylphosphine oxide (or diphenyltosyloxymethylphosphine oxide).

Tetrakis-(diphenylphosphinylmethyltiomethyl)-tetrapropoxycalix-[4]arene **5** (X = 5) bearing sulfur atoms as the additional complexing centers was synthesised by the reaction of mercaptomethylcalix[4]arene **4** (X = 5) with diphenyltosyloxymethylphosphine oxide in the presence of a base.

Tetrakis-(diphenylphosphinylethylsulphenylmethyl)-calix[4]arene tetrapropyl ether **6** was synthesised by the alkylation of

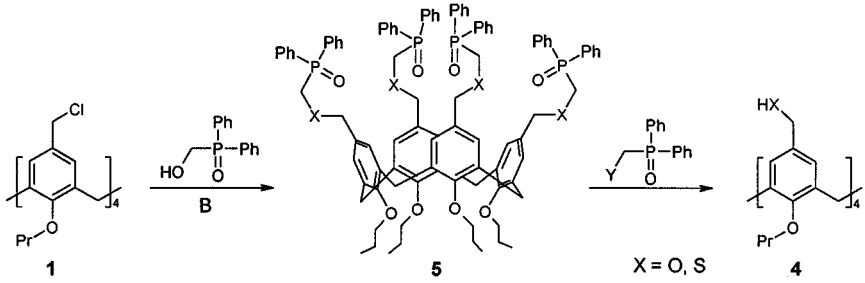

FIGURE 2

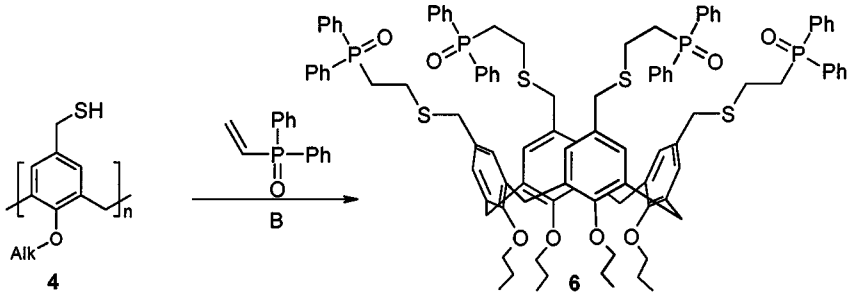

FIGURE 3

tetramercaptomethylcalix[4]arene **4** with diphenylvinylphosphinoxyde in the presence of bases.

New calix[4]arene synthon **7** possessing four chemically active P(O)(Ph)—H fragments linked to the wide rim by CH_2 spacers, which can be used for synthesis of more complex organophosphorus derivatives, has been synthesised by the reaction of **2** (R=Ph, R′=OPr-i) with lithium aluminium hydride. The synthetic potential of **7** is demonstrated by the transformation of its phenylhydrophosphinyl groups into phenyldibutylaminocarbonylmethylphosphinyl (**8**) or phenyl-2-diphenylphosphinylethylphosphinyl (**9**) groups.

It has been found that calixarenes synthesize bind metal cations much more effeciently than corresponding acyclyc organophosphorus complexants in the result of the co-operative macrocyclic effect. Complexation of the calixarenes with a number of benzene derivatives (alkyl benzenes, halogenated benzenes, substituted benzaldehydes, phenols, and benzoic acids) has been studied by RP HPLC method. Association constants K_A are in the range of 13-329 M^{-1} (acetonitrile-water 86:14 solution).

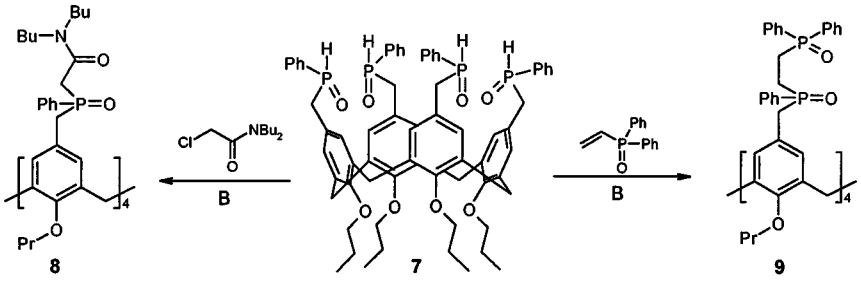

FIGURE 4

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