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LETTERS TO THE EDITOR

A Cyclic Hydrophosphoryl Derivative of Calix[4]resorcinolarene

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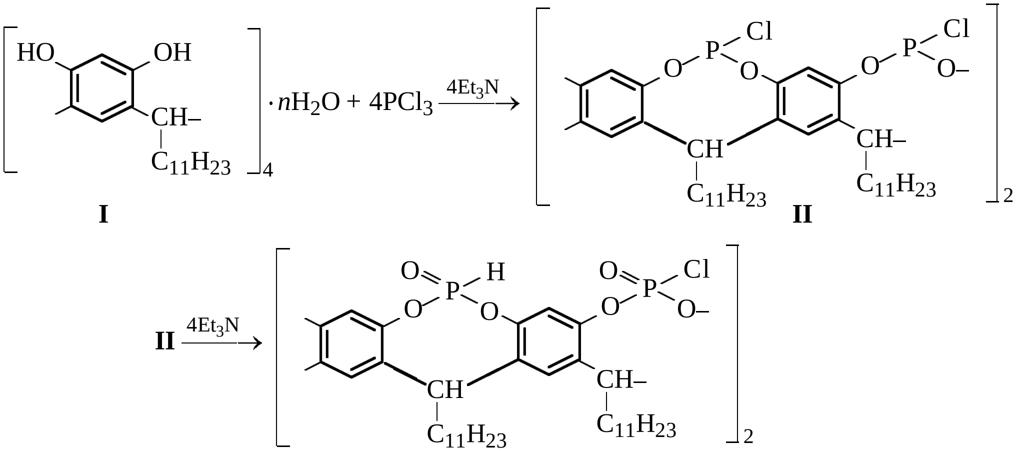
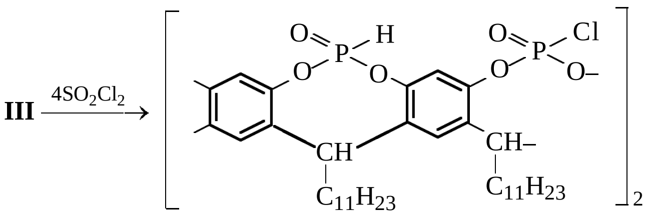
There are no published data on hydrophosphoryl derivatives of calix[4]resorcinolarenes. We performed the reaction of calix[4]resorcinolarene **I** with phosphorus(III) chloride in the presence of triethylamine. The reactant ratio was 1 : 4 : 4. According to the ^{31}P NMR data, heating of the reaction mixture in toluene led to formation of two products, phosphorochloridite **II** (δ_P 125.2 ppm) and cyclic phosphonate **III** (δ_P –4.3 ppm) at a ratio of 1 : 1. After addition of further 4 equiv of triethylamine to the reaction mixture, the signal of chloride **II** disappeared from the spectrum, and the only product was cyclic phosphonate **III** ($^1J_{PH}$ = 769 Hz). Its structure was deduced from the ^{1}H and ^{31}P NMR and IR spectra, elemental analysis, and molecular weight determination. The ^{1}H NMR spectrum of **III** contains a broadened singlet at δ 3.03 ppm belonging to protons of six water molecules (in keeping with the signal intensity), which occupy the molecular cavity. Presumably, water molecules were present in the initial calixresorcin[4]arene, and they took part in the process. According to published data [1], the number of such water molecules may be as large as several tens; they are involved in a complex system of hydrogen bonds with the phenolic hydroxy groups. It is surprising that addition of excess amine leads to activation of the inner water molecules.



III

Treatment of phosphonate **III** with sulfuryl chloride yields cyclic chlorophosphate **IV**. The latter was also synthesized by oxidation of **II**. Products **IV** obtained by the two methods were identical in the melting point and spectral parameters.

2,8,14,20-Tetraundecylpentacyclo[19.3.1.$1^{3,7}$.$1^{9,13}$.$1^{15,19}$]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen-6,10 : 12,16 : 18,22 : 24,4-octayl tetraphosphonate (III). A solution of 2 g of calixarene **I** in 100 ml of toluene was



IV

mixed with 0.99 g of phosphorus(III) chloride, and 1.46 g of triethylamine was added under stirring. The mixture was heated under reflux for 12 h and cooled, 1.46 g of triethylamine was added, and the mixture was kept for 2 days. The solvent was removed, and the residue was washed with chloroform and dried under reduced pressure. Yield 1.9 g (81%), mp 132–134°C. IR spectrum, ν, cm^{-1}: 1253 (P=O), 2444 (P–H). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 t (12H, CH_3CH_2, $^3J_{HH}$ = 6.9 Hz), 1.12–1.36 m [72H, $(CH_2)_9$], 2.10–2.28 m (8H, CH_2CH), 3.03 s (12H, H_2O), 4.50 t (4H, C*H*CH_2, $^3J_{HH}$ = 6.9 Hz), 6.62 s (4H, *o*-H), 7.12 s (4H, *m*-H). ^{31}P NMR spectrum: δ_P –4.3 ppm, $^1J_{PH}$ = 769 Hz). *M* 1290. Found, %: P 8.92. $C_{72}H_{120}O_{18}P_4$. Calculated, %: P 8.88.

2,8,14,20-Tetraundecylpentacyclo[19.3.1.-$1^{3,7}$.$1^{9,13}$.$1^{15,19}$]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen-6,10 : 12,16 :-18,22 : 24,4-octayl tetra(chlorophosphate) (III). Sulfuryl chloride, 1.25 g, was added to a solution of 3 g of compound **III** in 30 ml of carbon tetrachloride. The mixture was kept for 5 days at 20°C, the solvent was removed, and the residue was washed with chloroform. Yield 1.85 g (56%), mp 253°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.85–0.88 m (12H, CH_3CH_2), 1.25 m [72N, $(CH_2)_9$], 2.21–2.35 m (8H, CH_2CH), 4.62 t (4H, C*H*CH_2, $^3J_{HH}$ = 6.9 Hz), 6.61 s (4H, *o*-H), 7.14 s (4H, *m*-H). ^{31}P NMR spectrum: δ_P –15.82 ppm. Found, %: Cl 9.88; P 9.12. $C_{72}H_{104}Cl_4O_{12}P_4$. Calculated, %: Cl 9.95; P 8.69.

The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The ^1H and ^{31}P NMR spectra were obtained on Bruker WM-250 and Bruker MSL-400 instruments at 250.13 and 166.93 MHz, respectively. The chemical shifts were measured relative to the residual proton signals of $CDCl_3$ (^1H) and 85% H_3PO_4 as external reference (^{31}P).

ACKNOWLEDGMENTS

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