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LETTERS TO THE EDITOR

Hydrophosphoryl Derivatives of Calix[4]resorcinolarenes

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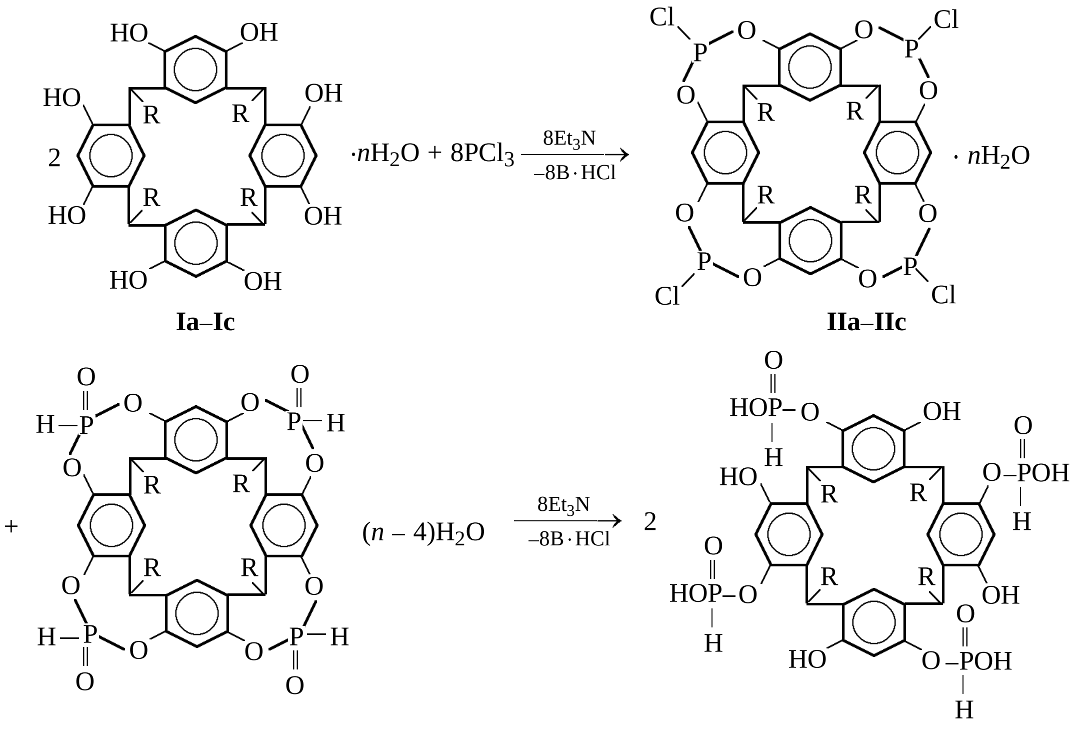
Recently we showed that the reaction of calyx[4]resorcinolarenes **Ia-c** with phosphorus trichloride in 1 : 4 molar ratio in the absence of bases leads to formation only of corresponding cyclic phosphorochloridites **IIa**–**IIc** [1]. It occured that carrying out this reaction in the presence of 4 moles of triethylamine gives another unexpected synthetic result. Heating of benzene solution of calyxarene **Ia** or **Ib** with phosphorus trichloride and triethylamine in 1 : 4 : 4 molar ratio (80°C, 3 h) according to ^{31}P NMR spectra leads to formation of a mixture of cyclic acid chlorides and cyclic hydrophosphoryl derivatives of calyx[4]resorcinolarene (**IIa** δ_P 125.68 ppm; **IIIa** δ_P –2.35 ppm, $^1J_{PH}$ 758 Hz), (**IIb** δ_P 125.83 ppm; **IIIb** δ_P –2.89 ppm, $^1J_{PH}$ 760 Hz) in approximately 1 : 1 molar ratio. Addition of extra four equivalents of the base to the reaction mixture is accompanied by disappearance of the signals of phosphacyclanes **IIa, IIb** and **IIIa, IIIb** and formation of linear hydrophosphoryl compounds **IVa** (δ_P 5.91, $^1J_{PH}$ 714 Hz) or **IVb** (δ_P 6.53, $^1J_{PH}$ 721 Hz), respectively isolated in a high yield.



Ia–Ic **IIa–IIc** **IIIa–IIIc** **IVa, IVb**

R = C_5H_{11} (**a**), C_6H_{13} (**b**), $C_{11}H_{23}$ (**c**).

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Evidently, on the first stage of the process calyxarene **IIa**–**IIc** react with phosphorus trichloride to form cyclic phosphorochloridite which under the action of intercavital water molecules [2] is converted to cyclic acid **IIIa**–**IIIc**. Subsequent hydrolysis is accompanied by the cleavage of dioxaphosphocyne fragments with formation of final hydrophosphoryl compounds **IVa** or **IVb**. Note, that hydrolysis of compounds **IIa, IIb** and **IIIa, IIIb** to the final products **IVa, IVb** takes place only in the presence of the latter bases, and the increase in the length of the alkyl radical (compound **III**) improves stability of cyclic hydrophosphoryl compound, and it may be isolated pure. Heating of the mixture of starting reagents in benzene in 1 : 4 : 8 molar ratio also leads to formation of incomplete phosphite **IVa** or **IVb**, but in this case it is a problem to isolate them pure because of the presence of small amounts of compounds **II, III**. Note, that no data about the preparation of hydrophosphoryl derivatives of calyx[4]resorcinolarenes was published.

4,6,16,18-Tetrahydroxy-10,12,22,24-tetrakis-(hydroxyhydrophosphoryloxy)-2,8,14,20-tetrapentylcalyx[4]resorcinolarene (IVa). A mixture of 0.5 g of calyxarene **Ia**, 0.45 g of phosphorus trichloride, 0.26 g of triethylamine, and 30 ml of benzene were refluxed under argon. Then 0.26 g of triethylamine was added, and the reaction mixture was heated for extra 4 h. Solvent was evaporated, obtained precipitate was filtered off and purified by precipitation from benzene with hexane. Compound **IVa**, 0.6 g (90%) was obtained, mp 82°C. IR spectrum, ν, cm^{-1}: 1620 (C_6H_4), 2430 (P–H), 3250 (OH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.88 br.m [12 H, C*H*$_3$–CH$_2$, $^3J_{HH}$ 6.9 Hz], 1.22 m [24H, $(CH_2)_3$], 4.40 br.m (4H, C*H*–CH$_2$), 6.20 br.s. (4H, *o*-CH$_{arom}$), 9.63 br.s (4H, OH). ^{31}P NMR spectrum, δ_P, ppm: 5.91 ($^1J_{PH}$ 714 Hz). Found, %: P 12.10.

4,6,16,18-Tetrahydroxy-10,12,22,24-tetrakis-(hydroxyhydrophosphoryloxy)-2,8,14,20-tetrahexylcalyx[4]resorcinolarene (IVb). It was obtained analogously from 0.5 g of calyxarene **Ib**, 0.42 g of phosphorus trichloride and 0,5 g of triethylamine. Yield 0.54 g (82%), mp 153°C. IR spectrum, ν, cm^{-1}: 1620 (C_6H_4), 2440 (P–H), 3230 (OH). ^{1}H NMR spectrum, δ, ppm: 0.89 br.m (12H, C*H*$_3$–CH$_2$, $^3J_{HH}$ 6.9 Hz), 1.29 br.m [32H, $(CH_2)_4$], 2.36 m (8H, C*H*$_2$–CH), 4.24 br.m (4H, C*H*–CH$_2$), 6.34 br.s (4H, *o*-CH$_{arom}$), 7.39 s (4H, *m*-CH$_{arom}$), 9.69 br.s (4H, OH). ^{31}P NMR spectrum, δ_P, ppm: 6.53, $^1J_{PH}$ 721 Hz. Found, %: C 56.95; H 7.53; P 10.99. $C_{52}H_{76}O_{16}P_4$. Calculated, %: C 57.78; H 7.04; P 11.48.

IR spectra were recorded on an UR-20 spectrometer in vaseline oil. ^{1}H and ^{31}P NMR spectra were measured on a Bruker WM-250 (250.13 MHz) and Bruker MSL-400 (166.93 MHz) spectrometers against the signals of residual protons of deuterated solvents ($CDCl_3$) and the external 85% phosphoric acid.

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