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Cyclic Phosphorochloridites, Phosphorochloridates, and Phosphorochloridothioates Based on Calix[4]resorcinolarenes

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Abstract — Phosphorylation of calix[4]resorcinolarenes with PCl_3 yields cyclic phosphorochloridites. Cavitands containing cyclic phosphorochloridite fragments in the upper rim are readily oxidized with SO_2Cl_2 to the corresponding phosphorochloridates and take up four equivalents of sulfur on heating to form cyclic phosphorochloridothioates.

Recently there has been a great deal of interest in calixarenes and their organophosphorus derivatives [1–4]. Thanks to their cup shape, they are capable of inclusion and retention of a wide range of organic molecules and ions. An urgent problem is development of procedures for functional substitution of calixarenes with the aim to obtain efficient complexing agents, extractants, etc. Of particular interest are cavitands containing reactive groups, e.g., P(IV)Cl fragments, on the upper rim of the calixarene matrix. These derivatives can be synthetic precursors of novel organophosphorus container compounds, carceplexes and chemicarceplexes.

Published data show that calix[4]resorcinolarenes are readily phosphorylated with organyl phosphorochloridates or phosphonic chlorides to form cavitands containing four dioxaphosphocin rings [5–8]. However, previous attempts to prepare by similar procedures compounds containing a P(O)Cl fragment failed. Koide *et al*. [9] studied phosphorylation of C-undecylcalix[4]resorcinolarene with $POCl_3$ in the presence of pyridine at various reactant ratios (from 1 : 1 to 1 : 39) and obtained complex mixtures of cyclic and acyclic phosphates with various content of phosphate fragments (from 1 to 6.3). Phosphorylation was incomplete even at a large excess of $POCl_3$.

We attempted to prepare cavitands with cyclic phosphorochloridate fragments on the upper rim by phosphorylation of calix[4]resorcinolarenes **Ia**–**Ic** with $POCl_3$ and $PSCl_3$ at various molar ratios (from 1 : 1 to 1 : 8) in the absence of a base. However, these reactions also failed to give cyclic phosphorochloridates or -chloridothioates.

At a molar ratio of calixarene to $POCl_3$ of 1 : 4, according to mass spectrometry, the reaction products are acyclic cavitands containing three (*M* 1175) and four (*M* 1292) phosphorodichloridate groups in a 3 : 4 ratio.

Phosphorylation of calix[4]resorcinolarenes with $PSCl_3$, according to the ^{31}P NMR spectra, yields a mixture of products containing both cyclic and acyclic phosphorus fragments (δ_P 46 and 59 ppm) whose ratio depends on the nature of the solvent and on reaction conditions. We failed to isolate individual products from the reaction mixture.

It should be noted that this result is unexpected, as linear and aromatic diols and triols are smoothly phosphorylated with both $PSCl_3$ and $POCl_3$ to give the corresponding dioxaphosphacyclanes. Apparently, specific structural features of calix[4]resorcinolarenes, in particular, strong intermolecular association, prevent approach of the reagent molecules to the hydroxy groups.

Since we failed to prepare the desired cavitands with cyclic phosphorochloridate or -chloridothioate fragments on the upper rim by direct phosphorylation of calix[4]resorcinolarenes with $POCl_3$ or $PSCl_3$, we attempted their synthesis through the corresponding cyclic phosphorochloridites. The only example of phosphorylation of calix[4]resorcinolarene (with methyl substituents on the lower rim) with PCl_3,

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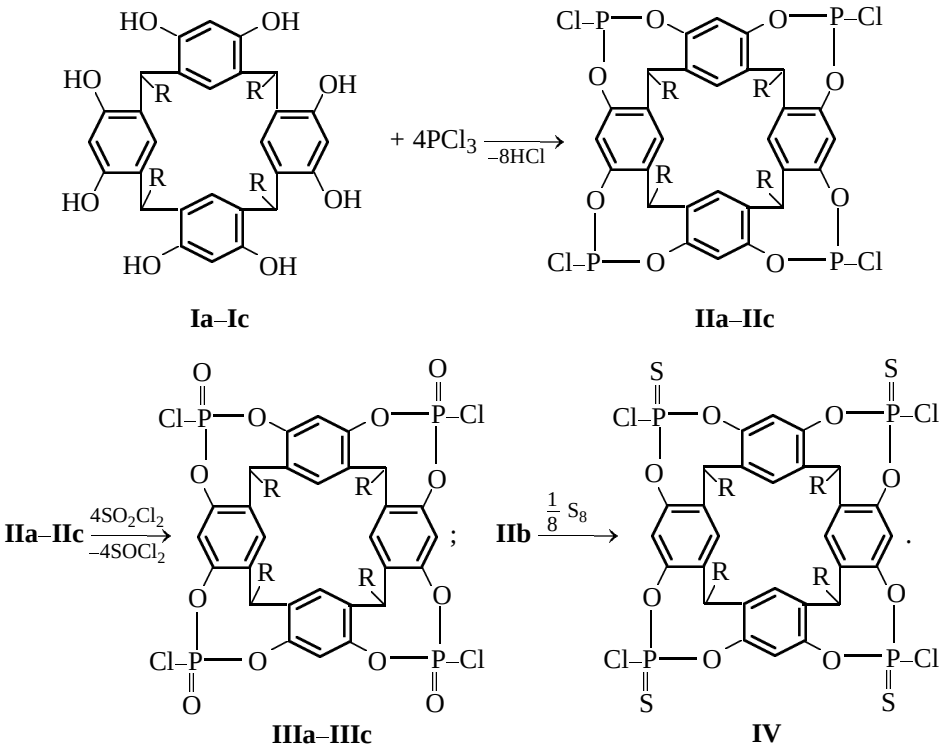
yielding the cyclic phosphorochloridite, was reported by Vollbrecht *et al*. [10]. Reactions of PCl_3 with calixarenes **Ia**–**Ic** were performed in refluxing benzene or toluene for 3–4 h and gave cavitands **IIa**–**IIc** in high yield. Phosphorochloridites **IIa**–**IIc** were oxidized with dimethyl sulfoxide, molecular oxygen, hydrogen peroxide, and sulfuryl chloride. In the first three cases, according to the ^{31}P NMR spectra, the reaction pathway was not unequivocal, and mixtures of products were obtained. Oxidation with SO_2Cl_2 occurred smoothly, and cavitands **IIIa**–**IIIc** were obtained in high yields.



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

It is known that addition of sulfur to cyclic chlorides of trivalent phosphorus acids is performed by their heating with $PSCl_3$ and distillation of the formed PCl_3 [11–13]. It was specially noted in [11] that heating under rigorous conditions of 1-chloro-4,5-benzo-2,6,1-dioxaphosphorin-3-one with sulfur did not yield the corresponding phosphorochloridothioate. With **IIb** as example, we showed that cavitands containing cyclic phosphorochloridite fragments on the upper rim take up four equivalents of sulfur on heating to give cavitands **IV**. The compositions and structures of the products were proved by elemental analysis and also by ^1H and ^{31}P NMR and IR spectroscopy.

EXPERIMENTAL

The IR spectra were measured in mineral oil on a UR-20 spectrophotometer. The ^1H and ^{31}P NMR spectra were recorded on Bruker WM-250 and Bruker MSL-400 spectrometers at working frequencies of 250.13 and 166.93 MHz, respectively, relative to the residual proton signals of the deuterated solvents [$CDCl_3$, $(CD_3)_2CO$] and external 85% H_3PO_4.

1,21,23,25-Tetrapentyl-5,9,13,17-tetrachloro-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2]-dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]-bis[1,3,2]benzodioxaphosphocin IIa. A mixture of 1.8 g of calixarene **Ia** and 1.2 g of PCl_3 in 100 ml of dry benzene (or toluene) was refluxed for 3.5 h in an argon atmosphere. After removal of the solvent, the residue was washed with benzene and dried in a vacuum. Compound **IIa** was obtained; yield 2.23 g (93%). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (12H, C*H*$_3$CH$_2$, $^3J_{HH}$ 7.0 Hz), 1.30 m [24H, CH$_3$(C*H*$_2$)$_3$], 2.24 m (8H, C*H*$_2$CH), 4.59 t (4H, C*H*CH$_2$, $^3J_{HH}$ 7.8 Hz), 7.05–7.27 m (8H, CH_{arom}). ^{31}P NMR spectrum, δ_P, ppm: 125.48, 125.04. Found, %: C 55.98; H 5.67; Cl 12.90; P 12.06. $C_{48}H_{56}Cl_4O_{12}P_4$. Calculated, %: C 56.14; H 5.46; Cl 13.84; P 12.08.

1,21,23,25-Tetrahexyl-5,9,13,17-tetrachloro-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2]-dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]-bis[1,3,2]benzodioxaphosphocin IIb was prepared similarly to IIa from 2 g of calixarene **Ib** and 1.32 g of PCl_3. Yield 2.33 g (89%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.90 t (12H, C*H*$_3$CH$_2$, $^3J_{HH}$ 7.1 Hz), 1.30 m [24H, CH$_3$(C*H*$_2$)$_3$], 2.20 m (8H, C*H*$_2$CH), 4.43 t (4H, C*H*CH$_2$, $^3J_{HH}$ 7.8 Hz), 7.15–7.37 m (8H, CH$_{arom}$). ^{31}P NMR spectrum, δ_P, ppm: 127.79, 125.67. Found, %: C 57.12; H 6.09; Cl 12.92; P 10.86. $C_{52}H_{64}Cl_4O_8P_4$. Calculated, %: C 57.67; H 5.91; Cl 13.12; P 11.46.

1,21,23,25-Tetraundecyl-5,9,13,17-tetrachloro-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2]-dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]-bis[1,3,2]benzodioxaphosphocin IIc was prepared similarly to **IIa** from 1 g of calixarene **Ic** and 0.74 g of PCl_3. Yield 1.07 g (87%). ^{31}P NMR spectrum, δ_P, ppm: 127.91. Found, %: C 63.36; H 7.40; Cl 10.40; P 9.01. $C_{72}H_{104}Cl_4O_8P_4$. Calculated, %: C 63.43; H 7.63; Cl 10.42; P 9.10.

1,21,23,25-Tetrapentyl-5,9,13,17-tetrachloro-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^5]-dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]-bis[1,3,2λ^5]benzodioxaphosphocin IIIa. To a solution of 2.05 g of **IIa** in 30 ml of dry benzene, 1.08 g of SO_2Cl_2 was added dropwise with stirring. The solution strongly warmed up, and a yellow precipitate formed, which was filtered off, washed with three portions of benzene, and dried to constant weight. Compound IIIa was obtained; yield 1.9 g (87%); mp 234°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 m [12H, C*H*$_3$(CH$_2$)$_4$], 1.37 m [24H, (C*H*$_2$)$_3$], 2.30 m (8H, C*H*$_2$CH), 4.65 t (4H, C*H*CH$_2$, $^3J_{HH}$ 6.3 Hz), 7.05–7.27 m (8H, CH$_{arom}$). ^{31}P NMR spectrum, δ_P, ppm: –14.68. Found, %: C 52.64; H 5.60; Cl 12.95; P 10.85. $C_{48}H_{56}Cl_4O_{12}P_4$. Calculated, %: C 52.84; H 5.13; Cl 13.02; P 11.37.

1,21,23,25-Tetrahexyl-5,9,13,17-tetrachloro-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^5]-dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]-bis[1,3,2λ^5]benzodioxaphosphocin IIIb was prepared similarly to **IIIa** from 2.16 g of **IIb** and 1.08 g of SO_2Cl_2. Yield 2.17 g (95%), mp 257°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.88 m [12H, C*H*$_3$(CH$_2$)$_5$], 1.30 m [32H, (C*H*$_2$)$_4$], 2.30 m (8H, C*H*$_2$CH), 4.62 t (4H, C*H*CH$_2$, $^3J_{HH}$ 6.3 Hz), 7.15–7.37 m (8H, CH$_{arom}$). ^{31}P NMR spectrum, δ_P, ppm: –14.56 ppm. Found, %: C 54.87; H 5.66; Cl 11.95; P 10.36. $C_{52}H_{64}Cl_4O_{12}P_4$. Calculated, %: C 54.45; H 5.58; Cl 12.39; P 10.82.

1,21,23,25-Tetraundecyl-5,9,13,17-tetrachloro-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^5]-dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]-bis[1,3,2λ^5]benzodioxaphosphocin IIIc was prepared similarly to **IIIa** from 2.72 g of **IIc** and 1.08 g of SO_2Cl_2. Yield 2.56 g (90%), mp 253°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85–0.88 m [12H, C*H*$_3$(CH$_2$)$_{10}$], 1.25 m [72H, (C*H*$_2$)$_9$], 2.21–2.35 m (8H, C*H*$_2$CH), 4.67 t (4H, C*H*CH$_2$, $^3J_{HH}$ 6.3 Hz), 7.14–7.33 m (8H, CH$_{arom}$). ^{31}P NMR spectrum, δ_P, ppm: –14.90. Found, %: C 65.94; H 7.60; Cl 10.60; P 9.12. $C_{72}H_{104}Cl_4O_{12}P_4$. Calculated, %: C 66.35; H 7.06; Cl 10.90; P 9.52.

1,21,23,25-Tetrahexyl-5,9,13,17-tetrachloro-5,9,-13,17-tetrathio-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,-25*H*-bis[1,3,2λ^5]dioxaphosphocino[5,4-*i*:5′,4′-*i*′]-benzo[1,2-*d*:5,4-*d*′]bis[1,3,2λ^5]benzodioxaphosphocin IV. A mixture of 1.8 g of **IIb** and 0.28 g of sulfur was refluxed in 20 ml of dry toluene for 2 h. A part of the solvent was removed, and the light yellow crystalline precipitate was separated, washed with toluene, and dried in a vacuum. Compound **IVb** was obtained; yield 1.65 g (82%); mp 183°C. IR spectrum, ν, cm^{-1}: 470 (P–Cl), 680 (P=S), 930 br (P–O–C), 1605 (CH$_{arom}$). ^{31}P NMR spectrum, δ_P, ppm: 47.95. Found, %: C 50.76; H 5.22; Cl 11.52; P 9.92; S 10.40. $C_{52}H_{64}Cl_4O_8P_4S_4$. Calculated, %: C 51.57; H 5.28; Cl 11.73; P 10.24; S 10.57.

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REFERENCES

1. Izatt, R.M. and Christensen, J.J., *Synthesis of Macrocycles: Design of Selective Complexing Agents*, New York: Wiley, 1987, p. 95.
2. Gutsche, C.D., *Calixarenes*, Cambridge: Royal Soc. Chem., 1989, p. 132.
3. Vicens, J. and Bohmer, V., *Calixarenes, a Versatile Class of Macrocyclic Compounds*, Dodrecht: Kluwer Academic, 1991, p. 15.
4. Kal'chenko, V.I., Shivanyuk, A.N., Pirozhenko, V.V., and Markovskii, L.N., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 9, pp. 1562–1563.
5. Kazakova, E.Kh., Davletshina, G.R., and Konovalov, A.I., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 3, pp. 407–410.
6. Lippmann, T., Dalcanale, E., and Mann, G., *Tetrahedron Lett.*, 1994, no. 35, pp. 1685–1687.
7. Lippmann, T., Wilde, H., Dalcanale, E., Mavilla, L., Mann, G., Heyer, U., and Spera, S., *J. Org. Chem.*,

1995, vol. 60, no. 1, pp. 235–240.

8. Delangl, P. and Dutasta, J.P., *Tetrahedron Lett.*, 1995, no. 36, pp. 9325–9327.
9. Koide, Y., Tetrasaki, H., Sato, H., Shosenji, H., and Yamada, K., *Bull. Chem. Soc. Jpn.*, 1996, vol. 69, no. 3, pp. 785–790.
10. Vollbrecht, A., Neda, I., Thonnessen, H., Jones, P.G., Harris, R.K., Crowe, L.A., and Schmutzler, R., *Chem. Ber.*, 1997, vol. 130, pp. 1715–1719.
11. Chvertkina, L.V., Smirnova, S.B., Chvertkin, B.Ya., and Khokhlov, P.S., *Zh. Obshch. Khim.*, 1992, vol. 62, no. 11, pp. 2516–2518.
12. Shi-Xian, Y., Yu-Gui, L., Xiao-Gao, L., and Ting-Yang, L., *Acta Chim. Sin.*, 1984, vol. 42, no. 2, pp. 168–175.
13. Ivanova, Zh.M., Stukalo, E.A., Tishchishina, N.S., and Derkach, G.I., *Zh. Obshch. Khim.*, 1970, vol. 40, no. 9, pp. 1942–1948.