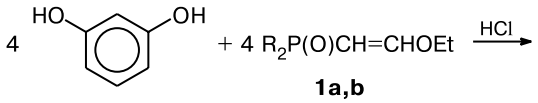
A new approach to the synthesis of calix[4]resorcinarenes with phosphorylmethyl substituents at the lower rim of the molecule

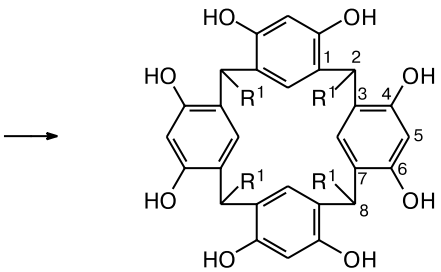
A. R. Burilov,[a] Yu. M. Volodina,[a] I. R. Knyazeva,[a] M. A. Pudovik,[a]★
W. D. Habicher,[b] and A. I. Konovalov[a]

[a]A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan Research Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843 2) 75 2253. E-mail: pudovik@iopc.knc.ru
[b]Institute of Organic Chemistry, Dresden University of Technology,
13 Mommsenstrasse, D-01062 Dresden, Germany.
Fax: (351) 463 4093

Syntheses of calix[4]resorcinarenes usually involve tetramerization of aliphatic or aromatic aldehydes with resorcinol and its derivatives.[1—3] Previously,[4] we have investigated reactions of phosphorus-containing acetals with resorcinol for the first time and found them to be a route to novel calix[4]resorcinarenes bearing phosphorus-containing alkyl fragments at the lower rim of the molecule. However, this method suffers from a number of limitations associated with difficulties in the synthesis of phosphorylated acetals. With the aim of developing a simpler and versatile method for the preparation of functionalized calix[4]resorcinarenes, we used for the first time ethoxyvinylphosphonates **1a,b** as phosphorus-containing partners in the reaction with resorcinol. These compounds are easily accessible and substituents at the P atom can be varied. The reactions of ethoxyvinylphosphonates **1a,b** with resorcinol gave calix[4]resorcinarenes **2a,b** in high yields. Compound **2a** was formed upon hydrolysis of one RO group at all the four phosphorus atoms during its isolation and purification. Calixarene **2b** is significantly more resistant to hydrolysis.



1a,b



2a,b

1: R = OBu (**a**), OC_7H_{15} (**b**)
2: R^1 = $CH_2P(O)(OH)OBu$ (**a**), $CH_2P(O)(OC_7H_{15})_2$ (**b**)

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker MSL-400 instrument (400.13, 100.62, and 166.93 MHz, respectively) in CD_3OD. The δ values are referenced to signals for the residual protons of the deuterated solvent (^1H, ^{13}C) and to 85% H_3PO_4 as the external standard (^{31}P). Mass spectra were recorded on a MALDI 2 V5.2.0 instrument with a 1,8,9-trihydroxyanthracene matrix. Ethoxyvinylphosphonates **1a,b** were prepared according to an earlier described procedure.[5]

4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetrakis[(butoxyhydroxyphosphoryl)methyl]pentacyclo[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-dodecaene (2a). A solution of vinylphosphonate **1a** (1.82 g, 6.9 mmol) in 4 mL of ethanol was added dropwise to a stirred mixture of resorcinol (0.75 g, 6.9 mmol), water (8 mL), ethanol (8 mL), and conc. HCl (1.4 mL). The reaction mixture was stirred at 50 to 60 °C for 0.5 h and left at 20 °C for seven days. Then the solvent was removed *in vacuo* and the residue was reprecipitated from ethanol with water. The product was filtered off and kept *in vacuo* (40 °C, 0.06 Torr) to a constant weight to give compound **2a** (1.26 g, 68%), m.p. 164—166 °C. Found (%): C, 52.61; H, 6.57; P, 11.72. $C_{48}H_{68}O_{20}P_4$. Calculated (%): C, 52.94; H. 6.25; P, 11.40. IR, ν/cm^{-1}: 1195 (P=O); 3340 (OH). ^1H NMR, δ: 1.10 (t, 12 H, $CH_2C\underline{H}_3$, ^3J = 7.0 Hz); 1.55 (br.m, 16 H, $\underline{CH}_2C\underline{H}_2CH_3$); 1.89 (m, 8 H, $C\underline{H}_2P$); 4.20 (m, 8 H, $OC\underline{H}_2$); 5.17 (br.m, 4 H, $C\underline{H}$); 6.48 (s, 4 H, *o*-H_{arom}); 7.32 (s, 4 H, *m*-H_{arom}). ^{13}C NMR, δ: 13.99 (q, CH_3, $^1J_{C,H}$ = 124.4 Hz); 19.64 (t, $(CH_2)_2$, $^1J_{C,H}$ = 122.1 Hz); 33.48 (t, CH_2P, $^1J_{C,H}$ = 125.6 Hz); 66.71 (t, CH_2O, $^1J_{C,H}$ = 142.6 Hz); 69.65 (dd, $\underline{C}HCH_2P$, $^1J_{C,H}$ = 150.9 Hz, $^2J_{C,P}$ = 7.0 Hz); 104.05 (d, *m*-C_{arom}, $^1J_{C,H}$ = 155.9 Hz); 122.53 (s, $\underline{C}_{arom}CH$); 130.0 (d, *o*-C_{arom}, $^1J_{C,H}$ = 154.6 Hz); 154.26 (s, $\underline{C}_{arom}OH$). ^{31}P NMR, δ: 31.76. MS, *m/z*: 1114 [M + Na].

4,6,10,12,16,18,22,24-Octahydroxy-2,8,14,20-tetrakis[(diheptyloxyphosphoryl)methyl]pentacyclo[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-dodecaene (2b) was obtained analogously from resorcinol (1.20 g, 11 mmol) and vinylphosphonate **1b** (3.80 g, 11 mmol). The yield of compound **2b** was

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2544—2545, November, 2004.

3.82 g (85.1%), m.p. 138—140 °C. Found (%): C, 63.67; H, 9.75; P, 8.02. $C_{88}H_{148}O_{20}P_4$. Calculated (%): C, 64.08; H, 8.98; P, 7.52. IR, ν/cm^{-1}: 1255 (P=O); 3340 (OH). ^{1}H NMR, δ: 0.90 (t, 12 H, $CH_2C\underline{H}_3$, ^3J = 7.0 Hz); 1.27—1.37 (br.m, 96 H, $(C\underline{H}_2)_6CH_3$); 1.99 (m, 8 H, $C\underline{H}_2P$); 3.67 (m, 8 H, $OC\underline{H}_2$); 4.07 (br.m, 4 H, $C\underline{H}CH_2$); 6.27 (s, 4 H, *o*-H_{arom}); 7.11 (s, 4 H, *m*-H_{arom}). ^{31}P NMR, δ: 32.77. MS, *m*/*z*: 1650.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 02-03-33037) and the International Bureau of the Federal Ministry of Education and Scientific Research (Germany, BMBF, RUS 02/034).

References

1. C. D. Gutsche, *Calixarenes*, The Royal Society of Chemistry, Cambridge, 1989, 132.
2. J. Vicens and V. Böhmer, *Calixarenes, a Versatile Class of Macrocyclic Compounds*, Kluwer Academic Publishers, Dordrecht, 1991, 15.
3. Z. Asfari, V. Böhmer, J. Harrowfield, and J. Vicens, *Calixarenes-2001*, Kluwer Academic Publishers, Dordrecht—Boston—London, 2001.
4. E. V. Popova, Yu. M. Volodina, A. R. Burilov, M. A. Pudovik, W. D. Habicher, and A. I. Konovalov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 1815 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1968].
5. V. V. Kormachev and M. S. Fedoseev, *Preparativnaya khimiya fosfora* [*Preparative Chemistry of Phosphorus*], Perm, 1992, 158 (in Russian); USSR Inventor´s Certificate 883 047; *Byull. Izobret.*, 1981, 43.

Received July 22, 2004