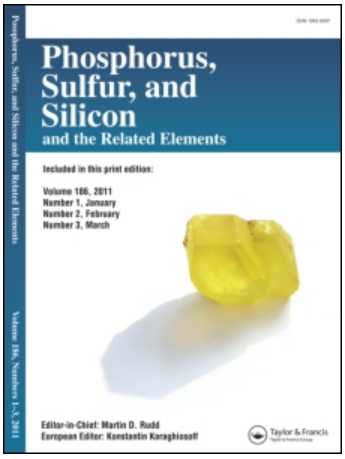

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FUNCTIONALISATION OF C-UNDECYLCALIX[4]RESORCINARENE WITH PHOSPHORUS- AND FLUORINE-CONTAINING SUBSTITUENTS

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Dedicated to Professor Gerhard Fritz on the Occasion of his 75th Birthday

(Received July 4, 1995)

The reaction of C-undecylcalix[4]resorcinarene **2** with hexamethyldisilazane furnished the octakis-trimethylsilylated derivative **3**. Treatment of **3** with PF_2Cl gave the tetrakis-trimethylsiloxy-tetrakis-difluorophosphite derivative **4**. For the synthesis of the octakis-difluorophosphite derivative **5** it was necessary to lithiate **2** with n-BuLi, followed by reaction with PF_2Cl. Both **4** and **5** are unstable and undergo transformation with elimination of Me_3SiF and PF_3, with formation of mixtures of unidentified products. Treatment of **2** with PCl_5 led to the octakis-PCl_4 derivative **6** which underwent solvolysis with ethanol. The solvolysis product was identified as the symmetric octakis-phosphate derivative **7**.

Key words: Undecylcalix[4]resorcinarene, phosphorus-fluorine compounds, supramolecular chemistry.

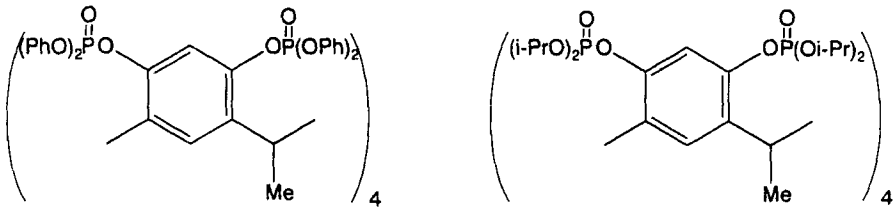
INTRODUCTION

The chemistry of the calixarenes is attracting constantly increasing interest, as reflected in the growing number of relevant publications. Within this group of compounds the C-undecylcalix[4]arene **2** constitutes an interesting reagent and synthon which is characterized by its special properties.[1–8] A series of phosphorus-containing derivatives of p-tert-butylcalix[4]arene is known.[9–20] The functionalisation of C-methylcalix[4]resorcinarene **1** with phosphorus-containing groups has already been described.[21] In the reaction of **1** with diphenylchlorophosphate and diisopropylchlorophosphate the octakis-phosphate ester derivatives **A** and **B** are formed.

The functionalisation of C-undecyl-calix[4]resorcinarene **2** with phosphorus- and fluorine-containing groups gave rise to spectroscopically interesting derivatives which were expected to display interesting ligand properties in coordination compounds.

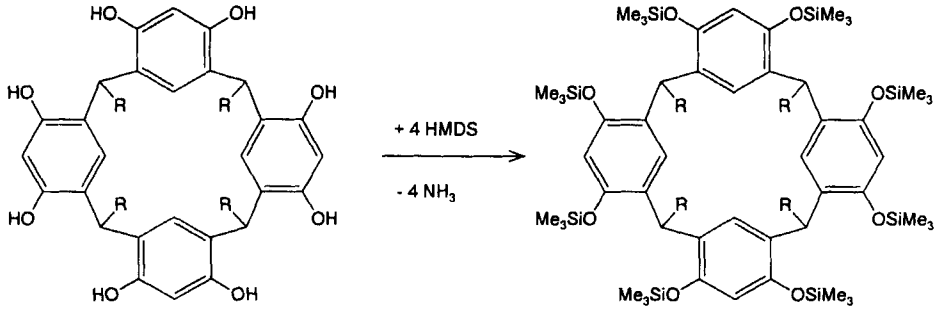
RESULTS AND DISCUSSION

We describe in this note the functionalisation of **2** to the new calixarene-difluorophosphites **4** and **5**. **2** was allowed to react with hexamethyldisilazane (HMDS) to give the octakis-trimethylsilylether **3**. The reaction of **3** with chlorodifluorophosphine, and phosphorus pentachloride are described, subsequently.



A B

FIGURE 1



1: R = Me
2: R = $(CH_2)_{10}CH_3$

3: R = $(CH_2)_{10}CH_3$

FIGURE 2

SYNTHESIS OF 3–5

In the reaction of **2** with HMDS the octakis(trimethylsiloxy)calixarene derivative **3** was formed in good yield. In contrast to earlier studies on p-tert-butylcalix[4]arene which led to the incompletely silylated product **C**,[12] the above reaction of **2** furnished the per-trimethylsilylated product **3**. Compound **3** is closely related to a tetrakis Me_2SiO_2-bridged calix[4]arene **D** which was reported by Cram and his co-workers in 1988.[25] The ^1H- and ^{13}C-NMR data, the mass spectra, and the analytical data prove the complete substitution of all hydroxy protons. The multiplicity of the ^1H- and ^{13}C-resonances of the Me_3Si-groups in the NMR spectra is due to different conformations.[22] It is suggested that the observation of two types of PF_2 groups in a 1:1 ratio by both ^{19}F and ^{31}P n.m.r. spectroscopy is due to the presence of two different conformational isomers of **5**.

The reaction of the trimethylsilylated p-tert-butylcalix[4]arene **C** with PF_2Cl, depending on the stoichiometry of the reactants, led to the mono- and di-substituted difluorophosphite derivatives **E** and **F**.[12] By contrast, **3** was found to react with PF_2Cl with exclusive formation of the tetrakis-(difluorophosphite)tetrakis-(trimethysiloxy)calix[4]arene derivative **4**, whose identity was established on the basis of ^1H-, ^{13}C-, ^{19}F-, ^{31}P-NMR, mass spectrometric, and analytical data.

The moderately stable octakis-difluorophosphite **5** was obtained only after lithiation of **2** with n-butyllithium, followed by reaction with PF_2Cl. **5**, like **E** and **F**, was found to undergo a transformation after 1 d at −35°C with formation of PF_3[12] and

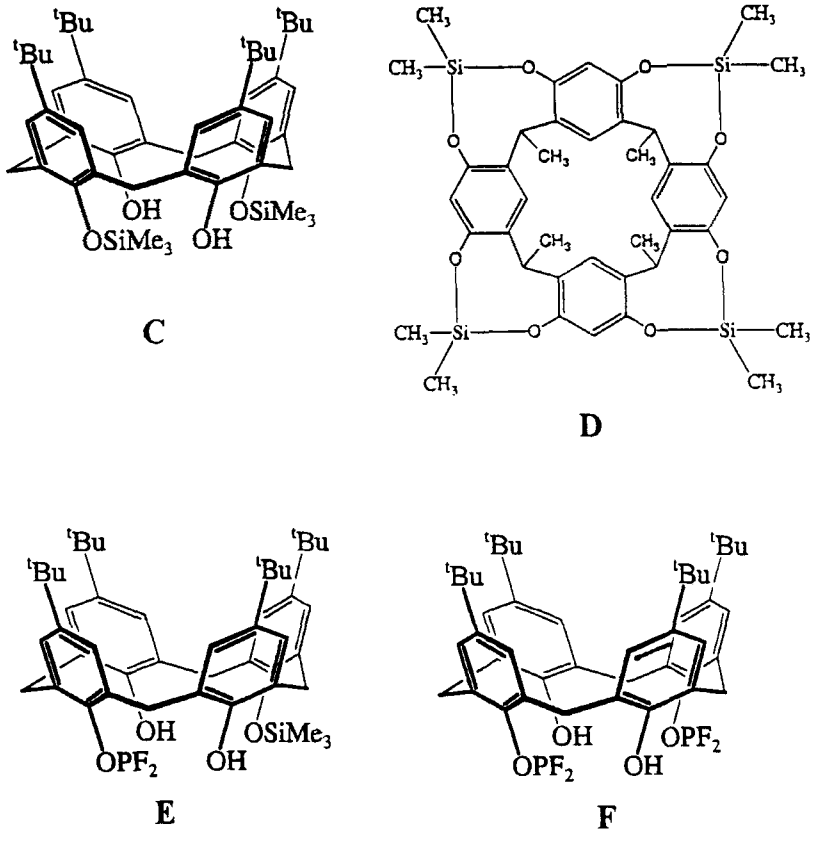


FIGURE 3

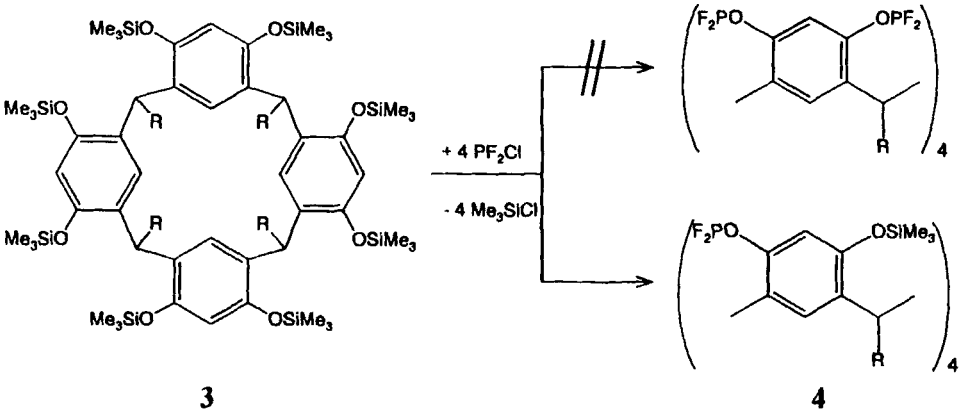
a mixture of different products with P(:O)(F)(O) and $-P(:O)F_2$ structural elements. This was established by ^{31}P-NMR-spectroscopy ($\delta(^{31}P)$ = 120.05 ppm, d, J(PF) = 1357.5 Hz, and $\delta(^{31}P)$ = −0.28 ppm (t, J(PF) = 1328.4 Hz).

PREPARATION OF 7

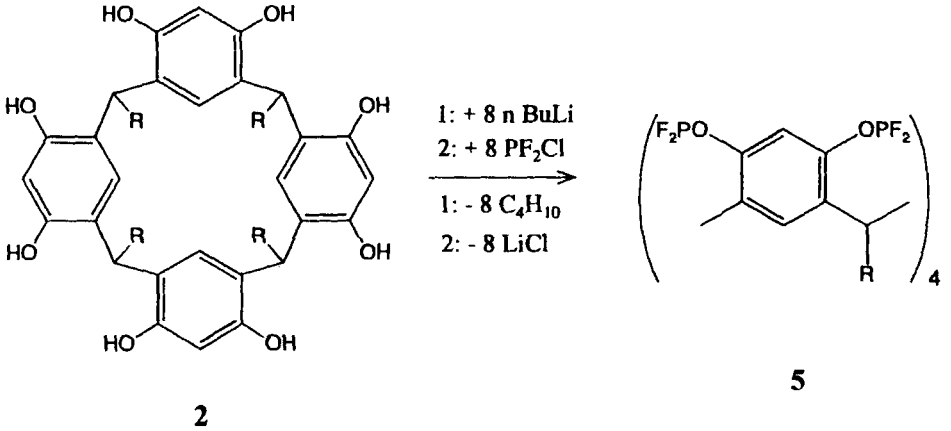
The reaction of p-tert-butylcalix[4]arene with PCl_5 was found to lead to the formation of a derivative **G** which upon the action of ethanol gave an unsymmetrical p-tert-butylcalix[4]arene bisphosphate **H**.[20]

The reaction of **2** with PCl_5 was found to take an entirely different course. While the intermediate product **6** was not fully identified its subsequent reaction with ethanol which furnished the oktakis(diethylphosphate) derivative, proved that no bridging of oxygen atoms via phosphorus has taken place.

The identity of **7** was confirmed by ^{1}H-, ^{13}C-, ^{19}F-, ^{31}P-NMR and IR data, and by elemental analysis.



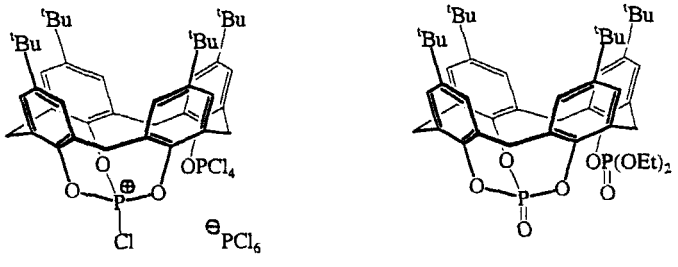
3 4



2 5

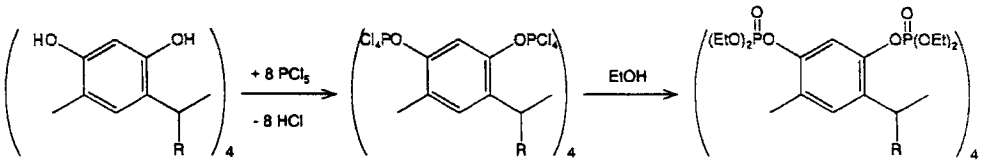
$R = (CH_2)_{10}CH_3$

FIGURE 4



G H

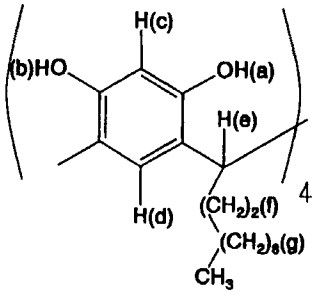
FIGURE 5



2 6 7

$R = (CH_2)_{10}CH_3$

FIGURE 6



1

FIGURE 7

EXPERIMENTAL

The experimental conditions and spectroscopic methods (NMR, IR, mass spectrometry) corresponded to those described in Reference 23. The abbreviation "i.v." refers to a pressure of 0.1 mm Hg.

All chemicals used in this research were commercial products, except for chlorodifluorophosphine which was synthesized, following Reference 24.

Synthesis of 3

Hexamethyldisilazane (0.72 g; 4.45 mmol) and 0.5 ml of trimethylchlorosilane were added to a solution of 1.00 g (0.89 mmol) of **2** in 30 ml of toluene. The faintly yellow solution was subsequently refluxed (with magnetic stirring) for 2 d. During this period ammonium chloride was found to be deposited gradually. After the 2 d reflux period the solvent and other volatile products were removed i.v., and 30 ml of diethyl ether were added to the residue. The ammonium chloride precipitated was removed by filtration, and was washed with three 5 ml portions of diethyl ether. After removal of the diethyl ether i.v. **3** was isolated as a colourless solid. Yield: 1.28 g (85.5%); m.p.: 70°C.

^{1}H-NMR ($CDCl_3$; c.f. Figure 7): δ = 0.00, 0.10, 0.38 (3s, CH_3Si), δ = 0.86 (t, ^3J(HH) = 6.7 Hz, CH_3), δ = 1.22 (s, H^g), δ = 1.85 (s, H^f), δ = 4.36 (t, ^3J(HH) = 7.1 Hz, H^e), δ = 6.14 (s, H^c), δ = 7.17 (s, H^d). —^{13}C-NMR ($CDCl_3$): δ = 0.37, 0.82, 1.06 (3s, CH_3Si) δ = 14.14 (s, CH_3), δ = 22.73–35.75 (10s, CH_2), δ = 36.30 (s, CH-R), δ = 106.65–151.74 (6s, C-aromat.). EI-MS, m/z (%): 1681.2 (82) $[M]^+$, 1525.9 (100) $[M\text{-}C_{11}H_{23}]^+$, 840.6 (16) $[M/2]^+$, 685.4 (84) $[M/2\text{-}C_{11}H_{23}]^+$. —$C_{96}H_{176}O_8Si_8$ (1683.16): calc. C 68.52, H 10.52; found C 68.37, H 10.78

Preparation of 4

A solution of 0.60 g (0.36 mmol) of **3** in 25 ml of dichloromethane was placed into a heavy-wall glass tube, fitted with a TEFLON® stopcock, and was cooled to −196°C. PF_2Cl (1.50 g; 14.4 mmol) was condensed onto this solution which was allowed to warm up to room temperature within 1 h. Subsequently, the solvent and other volatile products were removed i.v. After drying i.v. (3 h) the product **4** was left as a brownish viscous oil. Yield: 0.56 g (94%).

^{1}H-NMR ($CDCl_3$; c.f. Figure 7): δ = 0.08 (s, CH_3Si), δ = 0.87 (t, ^3J(HH) = 6.5 Hz, CH_3), δ = 1.25 (s, H^g), δ = 1.88 (s, H^f), δ = 4.31 (s, H^e), δ = 5.28 (s, H^c), δ = 6.51 (s, H^d). —^{13}C-NMR ($CDCl_3$): δ =

0.28 (s, CH_3Si), δ = 14.15 (s, CH_3), δ = 22.77–36.26 (10s, CH_2), δ = 36.42 (s, CHR), δ = 110.77–151.88 (6s, C-aromat.). —^{19}F-NMR ($CDCl_3$): δ = −43.49 (d, ^1J(PF) = 1328.0 Hz). —^{31}P-NMR ($CDCl_3$): δ = 113.50 (t, ^1J(PF) = 1327.6 Hz). —EI-MS, m/z (%): 1664.8 (54) $[M]^+$, 1509.7 (79) $[M\text{-}C_{11}H_{23}]^+$, 832.4 (14) $[M/2]^+$, 677.2 (72) $[M/2\text{-}C_{11}H_{23}]^+$. $C_{84}H_{140}F_8O_8P_4Si_4$ (1666.26): calc. C 60.55, H 8.47; found C 59.68, H 8.43.

Preparation of **5**

A solution of 1.00 g (0.89 mmol) of **2** in 60 ml THF was placed in a heavy-wall glass tube, fitted with a TEFLON®stopcock. In the course of 2 h 3.42 g of a 15% solution of n-butyl-lithium in n-hexane (0.51 g; 18 mmol of n-BuLi) were added dropwise at room temperature to the above solution of **2**. The colour of the solution changed from faintly yellow to red, and a red brown solid was precipitated. The solvent and other volatile products were removed i.v. The residue thus left was dissolved in 50 ml of dichloromethane. At −196°C, PF_2Cl (1.8 g; 17.3 mmol) was condensed onto this solution. Within 1 h the reaction mixture was allowed to warm up to room temperature. Subsequently stirring was continued for 3 d while the solution assumed a yellow colour. After removal of the solvent i.v. (3 h) 20 ml of diethyl ether were added to the residue. A colourless precipitate of LiCl thus formed was removed by filtration, and was washed twice with 5 ml portions of diethyl ether. The product **5** was obtained as a yellow oil after the ether was removed i.v. Yield: 1.01 g (75.3%).

^{1}H-NMR ($CDCl_3$; c.f. Figure 7): δ = 0.90 (t, ^3J(HH) = 6.50 Hz, CH_3), δ = 1.29 (s, H^g), δ = 1.81 (s, H^f), δ = 4.46 (s, H^c), δ = 5.26 (s, H^c), δ = 6.70 (s, H^d). —^{13}C-NMR ($CDCl_3$): δ = 14.28 (s, CH_3), δ = 22.84–36.76 (10s, CH_2), δ = 36.99 (s, CHR), δ = 111.02–151.85 (6s, C aromat.). —^{19}F-NMR ($CDCl_3$): δ = −44.47 (d, ^1J(PF) = 1328.4 Hz), δ = −43.05 (d, ^1J(PF) = 1326.8 Hz). —^{31}P-NMR (CH_2Cl_2): δ = 112.95 (t, ^1J(PF) = 1328.6 Hz), δ = 111.76 (t, ^1J(PF) = 1329.0 Hz). $C_{72}H_{104}F_{16}O_8P_8$ (1649.44): calc. C 52.41, H 6.36; found C 52.34, H 6.52.

Formation of the Intermediate **6**

Phosphorus pentachloride (0.93 g; 4.5 mmol) was added to a solution of 0.56 g (0.5 mmol) of **2** in 20 ml of THF. The reaction mixture was refluxed with stirring for 20 min. Within a few minutes the faintly yellow solution turned colourless. The solvent was then stripped off i.v. The residue thus left was employed in the subsequent experiment without further purification and exhaustive characterization.

^{1}H-NMR ($CDCl_3$; c.f. Figure 7): δ = 0.87 (g, CH_3), δ = 1.25 (s, H^g), δ = 1.84 (s, H^f), δ = 4.58 (s, H^c), δ = 6.23 (s, H^c), δ = 7.20 (s, H^d). —^{31}P-NMR ($CDCl_3$): δ = −13.41 (s).

Synthesis of **7**

Product **6**, as described above, was solvolyzed by addition of 20 ml of ethanol at room temperature. The solution was kept at −30°C overnight and **7** was obtained as a solid residue. The product was collected by filtration, and was obtained as a brownish, glassy solid after being dried i.v. for 4 h. Yield: 0.96 g (87.5%).

^{1}H-NMR ($CDCl_3$): δ = 0.86 (s, CH_3), δ = 1.26 (s, H^g), δ = 1.60 (m, $POCH_2\underline{CH_3}$), δ = 1.86 (s, H^f), δ = 3.55 (m, $POCH_2CH_3$), δ = 4.39 (s, H^c), δ = 6.70 (s, H^c), δ = 7.18 (s, H^d). —^{13}C-NMR ($CDCl_3$): δ = 14.13 (s, CH_3), δ = 15.92 (s, $POCH_2\underline{CH_3}$), δ = 22.71–31.95 (10s, CH_2(R)), δ = 36.31 (s, CH-R), δ = 70.28 (d, ^2J(PC) = 36.8 Hz), $PO\underline{CH_2}CH_3$), δ = 116.93–147.34 (6s, C-aromat.). —^{31}P-NMR in ($CDCl_3$): δ = −11.52 (s). —IR (n-Hexan): ν(P(:O)) = 1266 (st), 1020 (st), 605 (m). —$C_{104}H_{184}O_{32}P_8$ (2194.38): calc. C 56.92, H 8.45; found C 56.98, H 8.33.

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