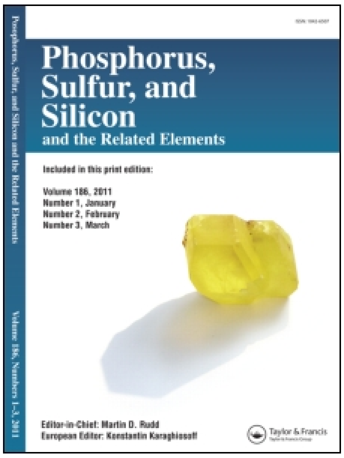

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AMIDOPHOSPHITES IN THE CHEMISTRY OF CALYX[4]RESORCINOLARENE

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The possibility of using phosphorous amides for the phosphorylation of calyx[4]resorcinolarenes is found. This reaction can be directed to the synthesis of their octaphosphorylated derivatives or phosphocavitands. It is shown that the obtained compounds demonstrate substantially different properties depending on the character of their molecular matrix.

Key words: Calyx[4]resorcinolarenes, phosphorous amides, phosphorylation, sulfurization, cavitands.

INTRODUCTION

Calyx[4]resorcinolarenes offer promise for the design of macroheterocycles.[1,2] With this connection, the formation, of phosphocavitands[3–5] and other phosphorus systems[5–7] has been reported in the past few years. So far only phosphorous[3,5] and phosphoric[4,6,7] chlorides were used as phosphorylating agents in the presence of amines. However such an approach is not very suitable because of the holding of amine hydrochlorides released in the interior cavity of generated systems,[5] as well as because of the formation of a diastereomeric mixture in the case of cyclophosphorylation with dichlorophosphates.[4] On this basis, we investigated the possibility of phosphorylation of calyx[4]resorcinolarenes with phosphorous amides which showed their advantages in generation of various composite organophosphorus compounds.[8]

RESULTS AND DISCUSSION

We performed the reaction of tetramethylcalyx[4]resorcinolarene **1a** with phosphorous di- and triamides taken in the molar ratios of 1:4 as an example of directed cyclophosphorylation (yields of the cavitands **2a**–**c** 70–80%).

The structure of the obtained compounds is proved by means of NMR spectroscopy (Table I).

Amidophosphites **2a,b** change into amidothiophosphates **3a,b** under heating with sulfur. The reaction is stereoselective and results in only tetrasulfides with axial orientation of the thiophosphoryl groups as determined by means of NMR spectroscopy (Table I) and X-ray analysis.[9] However, the analogous reaction with the phosphitocavitands **2c,d** leads to a diastereomeric tetrasulfide mixture. The stereochemical distinction found between these two related processes appears to be dependent on the spatial orientation of phosphite (**2c,d**) and amidophosphite (**2a,b**) functional groups in the phosphocavitands **2a**–**d**.

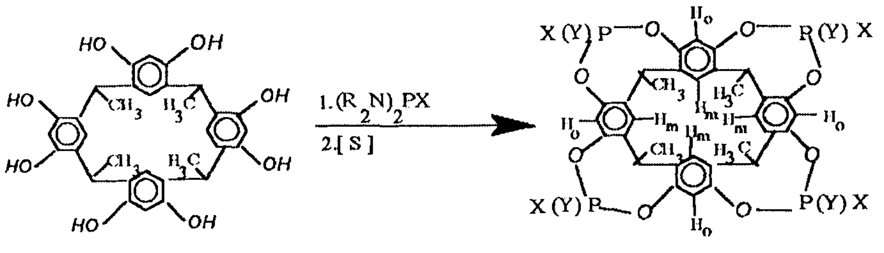
TABLE I

^1H and ^{31}P NMR spectra parameters of phosphorylated calixresorcinarenes ($CDCl_3$)

№	δ^{31}_P ,ppm	δ^1_H, ppm						
comp.		H_{vm}	H_{hm}	H_0		CH	R	X
2a	141.3, s	7.26, s, 4H		6.49, s, 4H		4.80, k, 4H	1.73, d,12H,CH_3	2.80, d, 24H, NCH_3
2b	142.6, s	7.24, s, 4H		6,49, s, 4H		4.80, k, 4H	1.73,d,12 H,CH_3	3.28, m, 16 H, NCH_2; 1.17, t, 24 H , CH_3
2c*	130.1, s	7.39, s, 4H		6.61, s, 4H		4.83, k, 4H	1.79,d,12 H,CH_3	3.90, d, 12 H, OCH_3
3a	68.5, s	7.21, s, 4H		6.55, t, 4H		4.75, k, 4H	1.77,d,12 H,CH_3	2.95, d, 24 H, NCH_3
3b	66.7, s	7.38, s, 4H		6.56, t, 4 H		4.74, k, 4H	1.84,d,12H, CH_3	3.43, m, 16 H, NCH_2; 1.20, t, 24H, CH_3
3c*	58.3, s	7.33, s, 4H		6.65, t, 4H		4.82, k, 4H	1.81,d,12H, CH_3	4.43, m, 8H, OCH_2; 1.46, t, 12H, CH_3
4a	115.0, s 115.3, s	7.36, s, 2H	6.11, s, 2H	6.90, s, 2H	6.50, s, 2H	4.69, k, 4H	1.49,d,12H, CH_3	3.23-4.38, m, 32H, OCH_2; 0.67, s, 12H, CH_3 0.78, s, 12H, CH_3,; 1.14, s, 12H, CH_3; 1.31, s, 12H, CH_3
4d	71.9, s 73.8,s	7.47, s, 2H	6.29, s, 2H	7.45, s, 2H	7.39, s, 2H	4.65, k,4H	1.49,d,12H, CH_3	3.00-3.57, m, 64H, NCH_2; 0.93, t, 24H, CH_3 0.99, t, 24H, CH_3; 1.10,t,24H, CH_3; 1.20, t, 24H, CH_3
4e*	72.0,s 73.6, s	6.41, s, 2H	6.33, s, 2H	7.34, s, 2H	7.47, s, 2H	5.80, s, 4H	6.79-6.89,m, 20H, Ph	2.53-3.28, m, 64H, NCH_2; 0.77, t, 24H, CH_3; 0.97, t, 24H, CH_3; 1.03, t, 24H, CH_3; 1.05, t, 24H, CH_3

* CD_2Cl_2

Scheme 1



1a

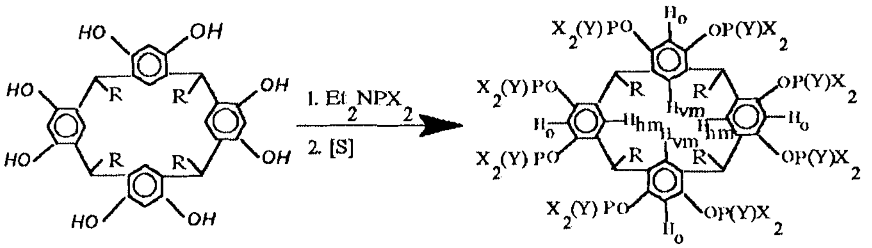
2 a-d, 3a-c

2. a. X= NMe$_2$, Y= l.e.p.; b. X= NEt$_2$, Y= l.e.p.;
c. X= OMe, Y= l.e.p.; d. X=OEt, Y= l.e.p..

3. a. X= NMe$_2$, Y= S; b. X= NEt$_2$, Y= S; c. X= OEt, Y= S.

l.e.p. - lone electron pair

Scheme 2



1a, b

4 a-e

4.a R= Me, X$_2$ = (-OCH$_2$)$_2$C(CH$_3$)$_2$, Y =l.e.p.; b. R = Me, X =NEt$_2$, Y =l.e.p.;
c. R=Ph, X = NEt$_2$, Y =l.e.p.; d. R = Me, X =NEt$_2$, Y =S; e. R= Ph, X=NEt$_2$, Y=S.

l.e.p. - lone electron pair

Amidophosphites **2a,b** do not react with alcohols under usual conditions, as distinct from other amidophosphites,[8] this is also a peculiarity of phosphocavitands.

Octol **1a** and its phenyl analog **1b** turn into octophosphite **4a** and octoamidophosphites **4b,c** when excess of phosphorous mono- and triamides are used.

The obtained products **4a–c** add sulfur under usual conditions. In addition, they easily undergo alcoholysis with the cleavage of a phosphamide bond.

EXPERIMENTAL

All the synthesis were performed in dry deoxygenated solvents under argon. ^{1}H NMR spectra were recorded on a Bruker AM-400 spectrometer with TMS as an internal standard. ^{31}P NMR spectra (at 32.4 MHz, 85% H_3PO_4 as an external standard) were recorded on a Bruker WP 80 spectrometer.

Phosphitocavitands **2a–c**. A solution of the corresponding amide (11.7 mmol) in dioxane (15 ml) was slowly added to a suspension of octol **1a** (2.9 mmol) in dioxane (60 ml) under stirring at 70–90°C. Cavitands **2a–c** were reprecipitated from dioxane by adding hexane and dried in vacuum.

Amidophosphitocavitand **2a** (stereoisomer). Yield 72%. M.p 270–272°C (decomp.). $C_{40}H_{48}N_4O_8P_4$, 836.74, Calc. C 57.42, H 5.78, N 6.70, P 14.81. Found C 57.02 H 5.84, N 6.92, P 14.76.

Amidophosphitocavitand **2b** (stereoisomer). Yield 74%. M.p 272–274°C (decomp.). $C_{48}H_{64}N_4O_8P_4$, 948.96, Calc. C 60.75, H 6.80, N 5.90, P 13.06. Found C 60.27, H 6.85, N 6.19, P 13.05.

Phosphitocavitand **2c** (stereoisomer). Yield 77%. M.p. 270–272°C (decomp.). $C_{36}H_{36}O_{12}P_4$, 784.57. Calc. C 55.11, H 4.63, P 15.79, Found C 54.71, H 4.69, P 15.63.

Thiophosphatocavitands **3a–c**. A. A suspension of cavitand **2** (0.1 mmol) and sulfur (0.45 mmol) in dioxane (10 ml) was stirred for 1 hr at 55–60°C.

B. A solution of corresponding amide (11.7 mmol) in dioxane (15 ml) was added to a suspension of octol **1a** (2.9 mmol) in dioxane (60 ml) at 70–90°C. The reaction mixture was allowed to cool to 50°C and sulfur (12 mmol) was added.

Thiophosphatocavitands **3a–c** (A, B) were isolated by reprecipitation with hexane from dioxane and dried under vacuum.

Amidothiophosphatocavitand **3a** (stereoisomer) (method A). Yield 95%. M.p. > 350°C. $C_{40}H_{48}N_4O_8P_4S_4$, 965.00. Calc. C 49.79, H 5.01, N 5.81, P 12.84, S 13.29. Found C 49.39, H 5.24, N 5.80, P 12.38, S 13.21.

Amidothiophosphatocavitand **3b** (stereoisomer) (method B). Yield 72%. M.p. > 350°C. $C_{48}H_{64}N_4O_8P_4S_4$, 1077.22. Calc. C 53.52, H 5.99, N 5.20, P 11.50, S 11.91. Found C 53.03, H 6.39, N 5.20, P 11.02, S 11.73.

Thiophosphatocavitand **3c** (stereoisomer) (method B). Yield 19%. M.p. > 350°C. $C_{40}H_{44}O_{12}P_4S_4$, 968.94. Calc. C 49.58, H 4.58, P 12.79, S 13.24. Found C 49.32, H 4.85, P 12.32, S. 13.20

Calyxresorcinolarene **4a**. Octol **1a** (0.2 mmol) and diethylamidoneopentylene phosphite (1.6 mmol) in dioxane (2 ml) were stirred for 30 hrs at gradually elevated temperature from 20 up to 100°C. The formed precipitate was filtered, washed with hexane and dried in vacuum. Yield 52%. M.p. 283–284°C. $C_{72}H_{104}O_{24}P_8$, 1665.39. Calc. C 51.93, H 6.29, P 14.88. Found C 51.76, H 6.71, P 15.11.

Calyxresorcinolarene **4d**. Octol **1a** (0.8 mmol) was slowly added to phosphorous hexaethyltriamide (11 mmol) under stirring, then sulfur (11.3 mmol) in benzene (5 ml) was added and the mixture was stirred for 1 hr. Benzene was evaporated, hexane was added to the residue, the formed precipitate was filtered and dried in vacuum. Yield 54%. M.p. 250–251°C. $C_{96}H_{184}N_{16}O_8P_8S_8$, 2194.95. Calc. C 52.53, H 8.45, N 10.21, P 11.29, S 11.69. Found C 52.47, H 8.75, N 9.86, P 10.99, S. 11.64.

Calyxresorcinolarene **4e**. Octol **1b** (0.9 mmol) and phosphorous hexaethyltriamide (11 mmol) in benzene (10 ml) were stirring for 4 hrs, then sulfur (12 mmol) was added and the mixture was stirred for 0.5 hr. The product was reprecipitated by adding hexane, filtered and dried in vacuum. Yield 69%. M.p. 264–265°C. $C_{112}H_{192}N_{16}O_8P_8S_8$, 2395.19. Calc. C 56.16, H 8.08, N 9.36, P 10.35, S 10.71. Found C 56.02, H 8.39, N 9.04, P 9.98, S 10.70.

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REFERENCES

1. D. J. Cram, *Angew. Chemie*, **100**, 1041 (1988).
2. D. J. Cram, *Nature*, **356**, 29 (1992).
3. M. Foa and S. Strologo, Eur. Pat. 487036 (1992). *C. A.* Vol. 117: P 213761v.
4. T. Lippmann, E. Dalkanale and G. Mann, *Tetrahed. Lett.*, **35**, 1688 (1994).
5. W. Xu, J. P. Rourke, J. J. Vittal and R. J. Puddephatt, *Inorg. Chem.*, **34**, 323 (1995).

6. L. N. Markovski, V. I. Kalchenko, D. M. Rudkevich and A. N. Shivanyuk, *Mendeleev Commun.*, **106,** (1992).
7. V. I. Kalchenko, D. M. Rudkevich, A. N. Shivanyuk, I. F. Tsybal, V. V. Pirogenko and L. N. Markovski, *Zhur. Obshch. Khim.*, **64,** 731 (1994).
8. E. E. Nifantyev and M. K. Gratchev, *Russian Chem. Rev.*, **63,** 575 (1994).
9. E. E. Nifantyev, V. I. Maslennikova, E. V. Panina, A. R. Bekker, L. K. Vasyanina, K. A. Lisenko, M. Yu. Antipin, and Yu. T. Struchkov, *Mendeleev Commun.* **4,** 131 (1995).