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Mendeleev Commun., 1995, **5(4)**, 131–133

Mendeleev Communications

Synthesis and Structure of Phosphito- and Thiophosphatocavitands

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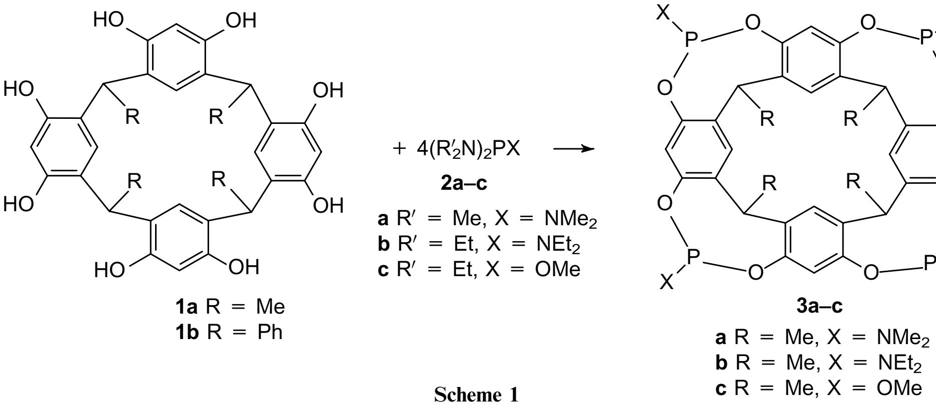
Phosphitocavitands, which on sulfurization result in all-*cis*-thiophosphatocavitands, have been obtained by phosphocyclization of octahydroxytetramethyl[1_4] metacyclophane with amides of phosphorous acid, as confirmed by ^{1}H and ^{31}P NMR spectroscopy and X-ray analysis.

Cavitands are skeleton heterocycles that have a molecular cup structure. In recent years considerable study has been made of these compounds in terms of supramolecular chemistry.[1,2] However, the synthesis of their organophosphorus derivatives is little understood: only a short communication[3] and a patent[4] describing in general terms the possibility of metacyclophane phosphocyclization by dichlorides of trivalent phosphorus acids have been published.

The present paper is concerned with the synthesis of evidence for a possible reaction of metacyclophanes with phosphocavitands by cyclophosphorylation of octahydroxy-[1_4]metacyclophanes with phosphorous amides, commonly used in fine organic synthesis to create complex skeleton systems in particular.[5] Furthermore, some structural and other fundamental problems of cavitand chemistry are solved. Octahydroxytetramethyl(tetraphenyl)[1_4]metacyclo-phanes **1** and both phosphorous triamides **2a,b** and phosphorous diamidoester **2c** are used as starting substances (Scheme 1).[†]

Phosphorylation of tetramethyl derivatives **1a** proceeds selectively and results in the 1,3,2-dioxaphosphocine systems **3a**–**c**. According to ^{31}P NMR spectroscopy, the crude products comprise individual compounds with minor amounts of stereoisomers. On reprecipitation, the minor isomers are separated or transformed into the major ones. Tetraphenylmetacyclophane **1b**, because of its conformational features,[6] is phosphorylated with more difficulty. Therefore, we failed to separate stereoisomers resulting from cyclophosphorylation[7] and to isolate pure cavitands. This fact demonstrates the severity of the synthetic problem under investigation.

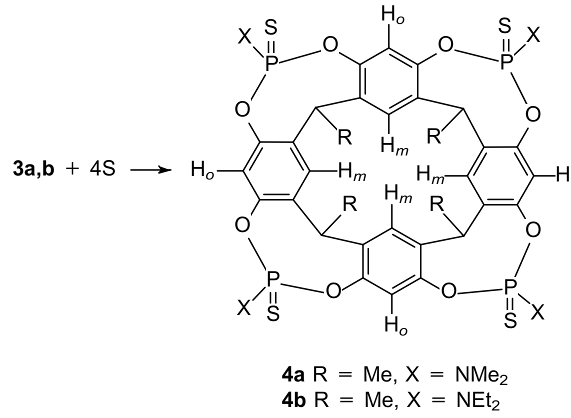
[†] Cyclophosphorylation was performed in dioxane at 65–100 °C under vigorous stirring. Cavitands **3a**–**c** were isolated by reprecipitation from dioxane on adding hexane. Yields of the products **3a**–**c** were 70–80%, m.p. 270–275 °C (decomp.). Their identity and structure were proved by means of ^{1}H and ^{31}P NMR spectroscopy (Table 1). The elemental analysis data are consistent with the theoretical values.



Scheme 1

This work begins to study the chemical features of the phosphocavitands obtained. It is found that they are alkylated with difficulty and that the phosphoamides **3a,b** are not subject to alcoholysis under the usual conditions. Thus, the compounds obtained manifest notable chemical peculiarities; for example, they add sulfur to form thiophosphoryl derivatives **4**‡ (Scheme 2).§

It is significant that the cavitand molecule adds sulfur stereoselectively only through the axial orbitals of trivalent phosphorus. Such a stereoconsistent sulfurization phenomenon for a polyphosphite system appears to be the first to be revealed. The axially-oriented sulfur atoms seem to make the cavitand bowl deeper and create possibilities for the building of new rims within it.



Scheme 2

Table 1 ^{1}H and ^{31}P NMR spectral parameters of phosphocavitands.

Cavi-tands	δ_P ^{a} (ppm)	δ_H /ppm^b (^3J/Hz)					
		H_m	H_o	$CHCH_3$	$CHCH_3$	NCH_2CH_3	NCH_2CH_3
3a^c	141.3	7.26	6.49	4.80	1.73 (7.3 HH)		
3b	142.6	7.27	6.49	4.80	1.73 (7.4 HH)	3.28 (9.8 HP)	1.17
3c^d	130.1	7.39	6.61	4.83	1.79 (8.3 HH)		
4a	69.2	7.21	6.55	4.75	1.77 (7.3 HH)		
4b^e	66.7	7.38	6.56	4.74	1.84 (7.4 HH)	3.43 (13.2 HP)	1.20

^{a}32.4 MHz, $CHCl_3$, against H_3PO_4. ^{b}400 MHz, $CDCl_3$, against TMS. ^{c}NMe: 2.8 ($^3J_{HP}$ 10.3). ^{d}CD_2Cl_2, OMe: 3.90 ($^3J_{HP}$ 8.8). ^{e}NMe: 2.95 ($^3J_{HP}$ 12.4).

The structural peculiarities of the cavitands **4a,b** were studied by NMR spectroscopy (see Table 1) and those of the compound **4b** by X-ray analysis.¶

The crystals of **4b** contain a molecule of cavitand, a solvate molecule of methanol and chloroform. Within a crystal of tetragonal symmetry, the molecule of **4b** occupies a special position and possesses fourth-order crystallographic symmetry. The fourth-order axis passes through the macrocyclic nucleus normally to the central plane of the molecule. The geometric characteristics for the structure of **4b** have the expected values for an all-*cis*-cavitand (see Fig. 1). The solvate molecule of methanol resides in the cavity (on the axis 4 of the cavitand) and forms a hydrogen bond O–H···S with thiophosphoryl groups (the distance S...O 3.19 Å fits the hydrogen bonds of moderate strength).

The work was performed within the program 'Russian Foundation for Basic Research'.

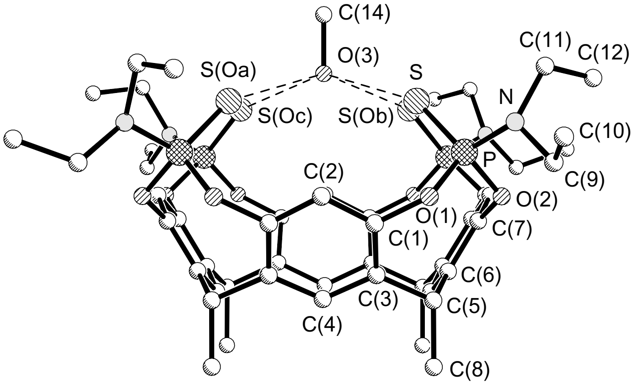


Fig. 1 Principal bond lengths (Å) and bond angles (°) in the structure **4b**: P=S 1.904 (2), P–O(1) 1.610(4), P–O(2) 1.607(4), P–N 1.644(4); S–P–N 117.3(2), S–P–O(1) 115.6(2), S–P–O(2) 114.8(1), O(1)–P–O(2) 102.8(2), N–P–O(1) 100.1(2), N–P–O(2) 104.1(2).

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‡ It should be noted that a paper on phosphocyclization of octahydroxy[1_4]metacyclophane **1** by dichlorophosphate has recently been published.[8] In that case the reaction occured with no selectivity and resulted in a mixture of diastereoisomers.

§ Sulfur addition occurs in dioxane on heating at 50–60 °C for 0.5 h. Yields of cavitands **4a,b** are 90–95%, m.p. > 300 °C.

¶ *Crystallographic data for* **4b**: Tetragonal crystals, space group $P4/n$, at −90 °C, $a = b = 18.883(5)$ Å, $c = 10.233(3)$ Å, $V = 3649(2)$ Å^3, $Z = 4$, d_{calc} = 1.441 g cm^{-3}, μ(MoKα) = 7.09 cm^{-1}, $F(000) = 1628$. Intensities of 5225 reflections were measured on a Syntex-P2_1 diffractometer at −90 °C (MoKα radiation, Θ/2Θ scan, 2Θ < 50°), and 2255 independent observed ones with $I > 2\sigma(I)$ were used in calculations and refinement. The structure was solved by a direct method and refined by least-squares in an anisotropic-isotropic (H atoms and atoms of the methyl alcohol molecule) approximation to $R = 6.74\%$, w_R = 7.40% and GOF = 1.54. All calculations were performed using the program SHELXTL PLUS on an IBM PC/AT computer. Atomic coordinates, thermal parameters, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre (CCOC), see 'Notice to Authors', *Mendeleev Commun.*, 1995, issue no. 1.

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Received: Moscow, 14th February 1995
Cambridge, 6th April 1995; Com. 5/01016K