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Interaction of resorcinol–octanal cyclotetramer with bis(*N*,*N*-diethylamido)menthylphosphite

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The interaction of octahydroxytetraheptyl[1$_4$]methacyclophane 1 with bis(*N*,*N*-diethylamido)menthylphosphite under mild conditions with a different ratio of initial reagents (1 : 8, 1 : 4, 1 : 2) yields either the completely phosphorylated optically active product (for ratio 1 : 8), or the product of partial phosphorylation (for ratio 1 : 4); the corresponding phosphates and thiophosphates also were obtained. An optically inactive product with two tetraresorcinol fragments united by phosphite bridges is formed under more severe reaction conditions and with a ratio of reagents 1 : 2.

Calixresorcinol[4]arenes are cyclic oligomers which have a molecular cavity and which can be used for chiral recognition of molecules after asymmetrical modification. Asymmetry can be caused by the structure of calixresorcinol[4]arenes or can be produced by the introduction of chiral fragments. Optically active organophosphorus compounds can be used as chiral substituents.

Synthesis of chiral organophosphorus derivatives of calixresorcinol[4]arene **1**, obtained by the condensation of resorcinol[1] with octanal, is described in this paper. Phosphorylation of resorcinol cyclotetramer by achiral organophosphorus reagents was described earlier.[2–6] (−)-Bis(*N*,*N*-diethylamido)menthylphosphite (BAMP), synthesized by the reaction of (−)-menthol with hexaethyltriamidophosphite, was used as a chiral agent.[†]

Phosphorylation[‡] of compound **1** by chiral BAMP was conducted under various reaction conditions. Optically active compound **2** was obtained under mild conditions with a reagent ratio 1 : 8 and is a painpink brittle film. This completely phosphorylated product contains six acyclic amidomenthylphosphite fragments with δ_P 147.6 ppm and also cyclic menthylphosphite fragment with δ_P 133.1 ppm according to ^{31}P NMR spectroscopy. Compound **2** adds elemental sulfur[§] turning into optically active product **3**, which contains two non-equivalent four-coordinated phosphorus atoms with δ_P 67.5 and 55.4 ppm. It must be noted that both signals in the NMR spectrum of products **2** and **3** are some

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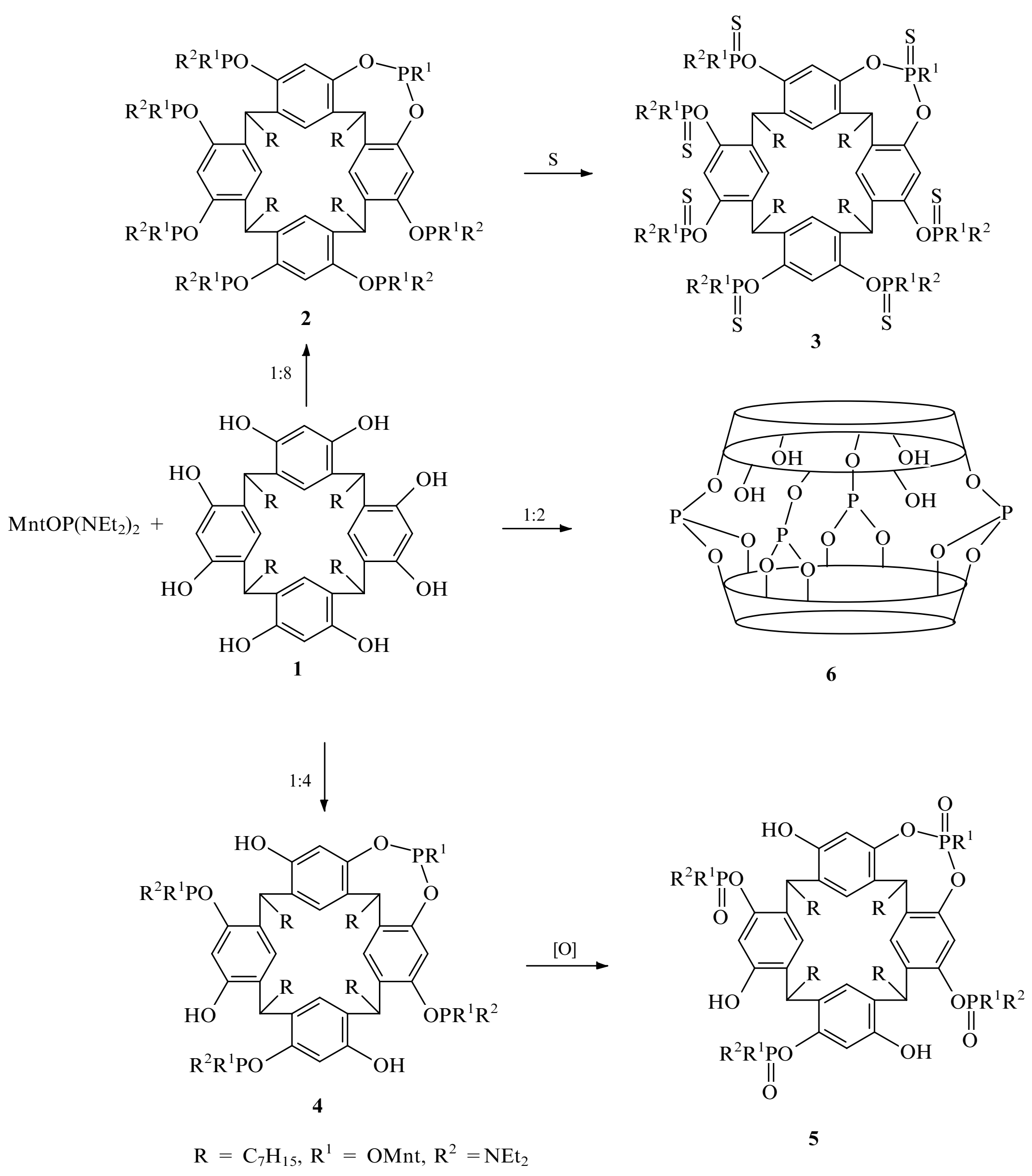
[†] *Synthesis of* (−)-*bis*(N,N-*diethylamido*)*menthylphosphite* (*BAMP*) *and* (−)-*bis*(N,N-*diethylamido*)*thiophosphate*. A mixture of 3.12 g (0.02 M) (−)-menthol and 4.94 g (0.02 M) hexamethyltriamidophosphite in 15 ml of dry dioxane was heated at 95 °C for 10 h. 1.35 g of diethylamine was isolated. After removal of the solvent and distillation of the residue, 4.6 g of bis(*N*,*N*-diethylamido)menthylphosphite was obtained, bp 113 °C (0.09 Torr), n_D^{20} = 1.4751, δ_P 133.2 ppm, $[\alpha]_{578}^{20}$ = −50.5 (benzene). $C_{18}H_{39}N_2OP$, M = 330.49. Calc. C 65.40, H 11.90, N 8.48, P 9.38%. Found C 65.71, H 11.60, N 8.52, P 9.25%.

0.05 g (0.0016 M) of sulfur was added to the solution of 0.5 g (0.0016 M) BAMP in 5 ml of benzene. After 24 h benzene was removed, the residue was dissolved in hexane and the solution filtered. The solvent was removed *in vacuo* and the residue was dried at 50 °C (0.07 Torr). 0.53 g of (−)-bis(*N*,*N*-diethylamido)thiophosphate was obtained, δ_P 76,66 ppm, R_f 0.77 (chloroform–acetone, 1 : 1), $[\alpha]_{578}^{20}$ = −39.3 (benzene). $C_{18}H_{39}N_2OPS$, M = 362.55. Calc. C 59.63, H 10.84, N 7.73, P 8.54, S 8.84%. Found C 59.31, H 10.95, N 7.45, P 8.34, S 8.95%.



Scheme 1 Scheme of interaction by the variety ratio of **1** and $MntOP(NEt_2)_2$.

wide. The product was purified by chromatography and is a light-brown powder with the same values of δ_P as the raw product. Since δ_P 133.1 ppm in the spectrum of compound **2** could be determined from an admixture of initial BAMP, we have added to the latter sulfur in a special experiment and obtained bis(*N*,*N*-diethylamido)menthylthiophosphate† with δ_P 76.67 ppm, which differs from the value of product **3**. So, in spite of the ratio of reagents 1 : 8 used, we did not register the formation of a cavitand with eight amidomenthylphosphite groups.

When a ratio of initial reagents 1 : 4 was used, a compound with three hydroxyl groups, one cyclic menthylphosphite fragment (δ_P 133.1 ppm) and three acyclic amidomenthylphosphite groups (δ_P 147 ppm) was obtained. This optically active compound is a brittle glass and turns to phosphate **5** (δ_P -14.8, 3.68 ppm), with mp 85–86 °C , $[\alpha]_{578}^{20} = -31$ (benzene) after oxidation by peracetic acid.

Reaction with a ratio of reagents 1 : 2 yields a product containing cyclic and acyclic fragments with chemical shifts δ_P 146 and 133.1 ppm. When the reaction mixture was heated in dioxane a signal characteristic of cyclic phosphites appeared instead of the latter. The product of the reaction is a powder, which does not have opticaly activity and does not contain a

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[‡] *General phosphorylation procedure:* 0.0078 M (or 0.0038 M) BAMP was added to 0.0095 M solution of octol **1** in 30 ml of benzene at room temperature under argon. The mixture was stirred for 30 min, concentrated under reduced pressure and dried for 20 h at 20–35 °C (0.005 Torr). The following products were obtained:

2 mp 61–63 °C, $[\alpha]_{578}^{20} = -36$ (benzene). $C_{150}H_{265}N_6O_{15}P_7$. M = 2606. Calc. C 69.00, H 10.17, N 3.22, P 8.32%. Found C 69.49, H 10.78, N 2.72, P 7.58%.

4 mp 63–65 °C, $[\alpha]_{578}^{20} = -12$ (benzene). $C_{104}H_{110}N_2O_{12}P_4 \cdot 2Et_2NH$. M = 1835. Calc. C 70.44, H 10.06, N 2.93, P 6.49%. Found C 69.72, H 11.06, N 3.25, P 7.27%.

30 ml of dioxane was added to the reaction mixture with a reagent ratio 1 : 2 after removal of benzene and heated during 2 h at 90–95 °C. The solvent was removed and the product was dried for 8 h (0.002 Torr) at 90 °C.

6 $C_{112}H_{148}O_{16}P_4 \cdot 8Et_2NH$. M = 2456. Calc. C 70.36, H 9.61, N 4.56, P 5.05%. Found C 70.37, H 10.48, N 5.54, P 5.77%.

[§] *The procedure of sulfur addition*: A mixture of 1.2 g of product (**2** or **6**) and 0.2 g of sulfur in 15 ml of xylene was boiled for 8 h. Excess sulfur was filtered off, the solvent was removed, and the residue was purified by chromatography on a silica gel column. Eluent $CHCl_3$–C_6H_6 (1 : 1), then $CHCl_3$.

3 mp 71–73 °C, $[\alpha]_{578}^{20} = +14$ (benzene). $C_{150}H_{265}N_6O_{15}P_7$. M = 2830. Calc. C 63.60, H 9.36, N 2.96, P 7.66, S 7.91%. Found C 64.07, H 10.43, N 2.34, P 6.66, S 8.54%; M = 3000.

menthyl fragment. These spectral and elemental analysis data, and the absence of optical activity, allow us to propose a dimeric structure for **6**. The initially formed phosphorylation product cyclises on heating to a dioxaphosphorane ring. Subsequent intermolecular interaction yields a so-called 'ball' structure **6**. Elemental data prove that each molecule of compound **6** includes eight molecules of diethylamine located apparently in the hydrophobic cavity. The addition of elemental sulfur to compound **6** gives a product **7** with a signal δ_P 56.2 ppm, stretching vibration O–H bond 3400 cm^{-1} in the IR spectrum and mp 99–100 °C.

Thus, the interaction of octol **1** with BAMP allows us to obtain optically active phosphorus-containing derivatives of octahydroxytetraheptyl[1_4]methacyclophane. Under more severe conditions intermolecular interaction with substitution of the menthyl group and formation of a cage structure in which tetraresorcinol fragments are connected by phosphite bridges can take place.

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