

SHORT
COMMUNICATIONSDesign of Phosphorus-Containing Macrocycles
on the Basis of Dipentaerythritol

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Recent studies have shown that phosphorus-containing macrocycles can be synthesized from various diols [1–3]. The present communication reports on extension of source of raw materials for the synthesis of phosphorus-containing macroheterocycles via the use of trivalent phosphorus reagents in cyclizations with dipentaerythritol (**I**). Such reactions lead to the formation of macrocyclic ensembles containing two bulky fragments with quaternary carbon atoms. These and other structural features could endow macroheterocycles with new capabilities related to molecular recognition of inorganic and organic compounds.

We have found that dipentaerythritol (**I**) reacts with chlorobis(diethylamino)phosphine (**II**) to give macrocyclic system **III**; product **III** was stabilized by treatment with sulfur in pyridine to obtain 10-membered amidophosphorothioate **IV** (Scheme 1). Insofar as alcohol **I** is poorly soluble, it was preliminarily heated in pyridine at 70°C for 1 h under vigorous stirring. The reaction with phosphine **II** was carried out at 2°C (2 min), followed by keeping for 2 h at 20°C. Crude phosphoramidite **III** was then treated with molecular sulfur in pyridine, and amidophosphorothioate **IV** thus formed was isolated by column chromatography on

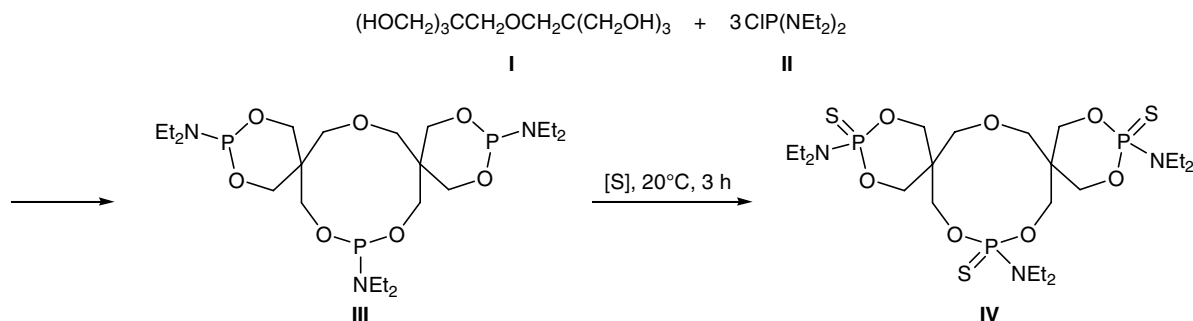
silica gel [hexane–ethyl acetate, 7:1 (A)]. By reaction of dipentaerythritol (**I**) with hexaethylphosphorous triamide (**V**) we obtained symmetric structure **VI** containing four phosphorus(III) moieties, and the subsequent sulfurization of **VI** gave compound **VII** (Scheme 2) which was isolated by column chromatography on silica gel (eluent system A).

3,13,18-Tris(diethylamino)-2,4,8,12,14,17,19-hepta-oxa-3,13,18-triphosphadispairo[5.3.5.5]icosane (III). ^{31}P NMR spectrum, δ_{P} , ppm: 146.23 (2P, P^3 , P^{13}), 148.40 (1P, P^{18}).

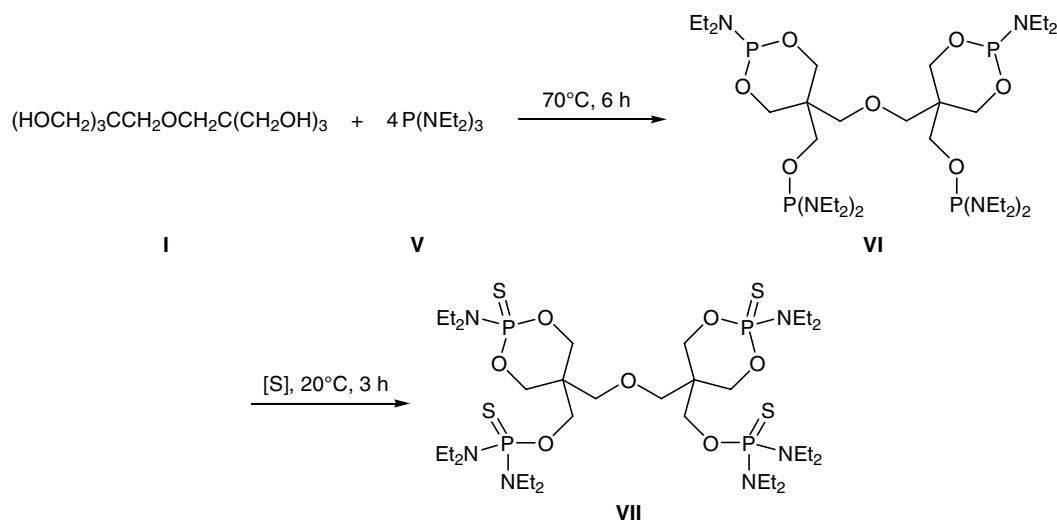
3,13,18-Tris(diethylamino)-2,4,8,12,14,17,19-hepta-oxa-3 λ^5 ,13 λ^5 ,18 λ^5 -triphosphadispairo[5.3.5.5]icosane 3,13,18-trisulfide (IV). Yield 38%, $n_{\text{D}}^{20} = 1.5431$, $R_{\text{f}} 0.60$ [hexane–ethyl acetate, 2:1 (B)], 0.41 [hexane–dioxane, 3:1 (C)]. ^{31}P NMR spectrum, δ_{P} , ppm: 75.16 (2P, P^3 , P^{13}), 76.63 (1P, P^{18}). Found, %: C 40.84; H 7.20; N 6.41; P 13.91. $M 653.43$ (^{12}C). $\text{C}_{22}\text{H}_{46}\text{N}_3\text{O}_7\text{P}_3\text{S}_3$. Calculated, %: C 40.43; H 7.08; N 6.42; P 14.19. $M 653.76$; $M 653.52$ (^{12}C).

5,5'-Oxydimethylenebis(1-diethylamino-1,3,2-dioxaphosphinan-5-ylmethyl) bis(*N,N,N',N'*-tetraethylphosphorodiamidite) (VI). ^{31}P NMR spectrum, δ_{P} , ppm: 146.37 ($\text{P}(\text{NEt}_2)$), 135.43 [$\text{P}(\text{NEt}_2)_2$].

Scheme 1.



Scheme 2.



***O,O'*-5,5'-Oxydimethylenebis(1-diethylamino-1-thioxo-1,3,2λ⁵-dioxaphosphinan-5-ylmethyl) bis-(*N,N,N',N'*-tetraethylamidophosphorothioate) (VII).** Yield 71%, $n_D^{20} = 1.5221$, R_f 0.61 (B), 0.42 (C). ³¹P NMR spectrum, δ_p , ppm: 74.87 [P(S)NEt₂], 79.73 [P(S)(NEt₂)₂]; intensity ratio 1:1. Found, %: C 44.18; H 8.39; N 8.81; P 12.89. *M* 932.65 (¹²C). C₃₄H₇₆N₆O₇P₄S₄. Calculated, %: C 43.76; H 8.21; N 9.01; P 13.28. *M* 933.19; *M* 932.82 (¹²C).

The single-isotope (¹²C) molecular weights were determined on a Bruker UltraFlex instrument (Bruker Daltonics, FRG). Thin-layer chromatography was performed using Silufol UV-254 plates.

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