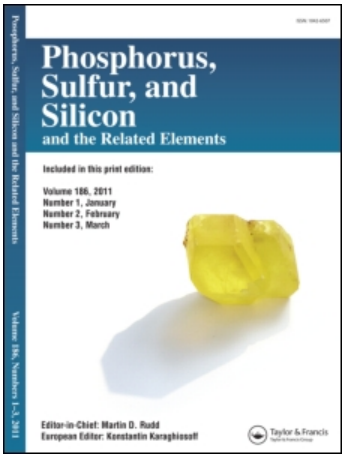

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Selective Oxidative Imination of Phosphocavitands

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SELECTIVE OXIDATIVE IMINATION OF PHOSPHOCAVITANDS

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The study of the oxidative imination of amidophosphitocavitands showed that only three out of four phosphorus atoms in the macrocycle underwent oxidation, which resulted in phosphocavitands with phosphorus atoms of different coordination numbers.

Keywords: Oxidative imination; phosphocavitands

INTRODUCTION

Amidophosphitocavitands **1**, being phosphorous acid diesteramides, readily enter into oxidation reactions.[1–4] The study of reactions of these macrocycles with sulphur-, selenium-, and oxygen-containing agents showed that all of the phosphorus atoms present in the molecule were subjected to oxidation. The oxidation proceeded stereoselectively to form symmetric systems with inward axial oxygen atoms and equatorial amide groups. It should be noted that in all processes mentioned above, the substituent newly attached to phosphorus atom was monoatomic and of a small size. Therefore there were no steric hindrances for the placing of four oxidizer's atoms inside the cavitand cup.

RESULTS AND DISCUSSION

This work deals with the study of the oxidative imination of the amidophosphitocavitands **1**. We used phenyl azide as the reagent. Hence,

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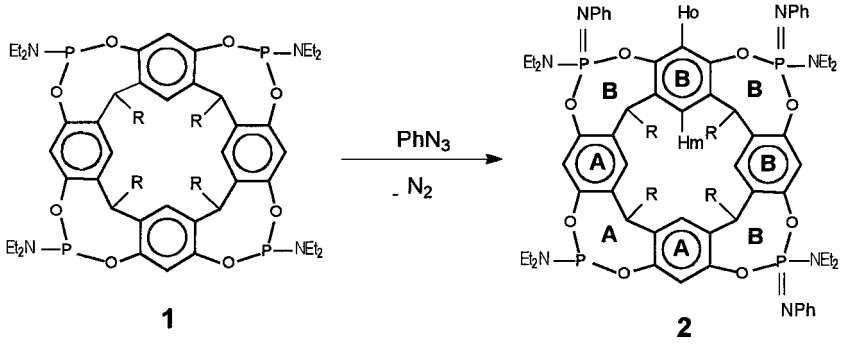
the oxidation of phosphorus atoms was accompanied by the introduction of polyatomic and bulky phenylimino groups in this case.

The reaction proceeded in chloroform, dioxane, and without solvent at different reagent ratios in the temperature range from 20°C to 100°C.

The experimental results showed that no complete oxidation of the amidophosphitocavitands **1** took place under the conditions studied. The macrocyclic systems **2** thus obtained contained imino groups at three phosphorus atoms only; the fourth remained trivalent (Scheme 1).



1a, 2a R=CH_3, **1b,2b** R=C_3H_7, **1c,2c** R=C_6H_{13}

SCHEME 1

Even the use of a large excess of phenyl azide and prolonged-heating of the reaction mixture at a high temperature had no effect. All attempts at intensifying the process and attaching a imino group to the fourth phosphorus atom of the cavitand resulted in destruction of the macromolecular system.

The triiminophosphates **2** were obtained with yields of 48–86%. The composition of cavitands **2** was confirmed by the elemental analysis. The structure of **2** was supported by NMR spectroscopy. The ^{31}P NMR spectra of the iminophosphates **2** exhibited three singlets: a downfield signal in the region typical of cyclic amidophosphites and two upfield signals, with the integral intensity ratio of 1:1:2. Doubling of signals from all protons was observed in the ^1H NMR spectra and was due to the chemical nonequivalence of the protons in the aromatic and phosphocine rings **A** and **B**, as well as to the magnetic equivalence of the protons of the methylene bridges and the diethylamide groups in the phosphocine rings **B**. The integral intensities of the signals corresponded to the theoretical values. It should be noted that, from the data of elemental analysis and ^1H NMR spectra, each molecule of cavitand **2a** retains two dioxane molecules, and the molecule of **2c** retains one molecule of dioxane.

EXPERIMENTAL

All syntheses were performed in dry deoxygenated solvents under argon. ^{1}H NMR spectra were recorded on a Bruker WM-200 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.

Iminophosphocavitands 2a–c

A solution of the corresponding cavitand **1** (0.054 gram (**2a**), 0.061 gram (**2b**), 0.070 gram (**2c**)/0.057 mmol) and phenyl azide (0.027 gram/ 0.227 mmol) in dioxane (0.8 ml) was kept at 20°C for 14 days. The iminophosphates **2a–c** were precipitated from dioxane by addition of hexane and dried in vacuo.

Iminophosphocavitand 2a

Yield 86%; m.p. 253–255°C. NMR ^{31}P, δ, ppm ($CHCl_3$): 145.21, −11.03, −12.64; NMR ^{1}H, δ, ppm ($CDCl_3$): 1.06, t, 6H; 1.22, t, 18H (NCH_2—CH_3); 1.64, d, 3H; 1.84, d, 9H (CH—CH_3); 3.07, m, 4H; 3.33, m, 12H (NCH_2); 3.73, s, 16H ($C_4H_8O_2$); 4.61, q, 1H; 4.88, q, 3H (CH—CH_3); 6.11, d, 4H; 6.25, d, 2H; 6.41–6.59, m, 9H (H_{NPh}); 6.24, s, 2H; 6.85, s, 2H (Ho); 7.21, s, 2H; 7.32, s, 2H (Hm). $C_{66}H_{79}N_7O_8P_4 \cdot 2$, $C_4H_8O_2$, M 1398.51, Calcd. C 63.55, H 6.84, N 7.01, P 8.86. Found: C 63.30, H 6.49, N 7.24, P 8.87.

Iminophosphocavitand 2b

Yield 82%; m.p. 230–232°C. NMR ^{31}P, δ, ppm ($CHCl_3$): 145.01, −10.42, −11.04; NMR ^{1}H, δ, ppm ($CDCl_3$); 0.94, t, 3H (CH_2—CH_2—CH_3); 1.05, t, 15H (9H CH_2—CH_2—CH_3, 6H NCH_2—CH_2); 1.22, t, 18H (NCH_2—CH_3); 1.44, m, 8H (CH_2—CH_2—CH_3); 2.09, m, 2H; 2.28, m, 6H (CH_2—CH_2—CH_3); 3.09, m, 4H; 3.31, m, 12H (NCH_2); 4.43, t, 1H; 4.69, t, 3H (CH—Pr); 6.11, d, 1H; 6.20, d, 1H; 6.41–6.59, m, 9H; 6.96–7.12, m, 4H (H_{NPh}); 6.24, s, 2H; 6.88, s, 2H (Ho); 7.20, s, 2H; 7.28, s, 2H (Hm). $C_{74}H_{95}N_7O_8P_4$, M 1334.51, Calcd. C 66.60, H 7.18, N. 7.35, P 9.28. Found: C 66.32, H 7.06, N 7.77, P 9.38.

Iminophosphocavitand 2c

Yield 49%; m.p. 130–135°C. NMR ^{31}P, δ, ppm ($CHCl_3$): 144.9, −12.1. −13.7. NMR ^{1}H, δ, ppm ($CDCl_3$): 0.92, t, 9H; 1.07, t, 3H (($CH_2)_5$CH_3); 1.11, t, 6H; 1.21, t, 18H (NCH_2CH_3); 1.34, bs, 24H; 1.43, bs, 8H

(CH_2—(CH_2)$_2$—CH_3); 2.09, m, 2H; 2.31, m, 6H (CH_2—(CH_2)$_2$—CH_3); 3.15, m, 4H; 3.26, m, 12H (NCH_2); 3.71, s, 8H ($C_4H_8O_2$); 4.41, t, 1H; 4.67, t, 3H (CH); 6.11, d, 1H; 6.20, d, 1H; 6.49–6.68, m, 9H; 6.96–7.17, m, 4H (H_{NPh}); 6.25, s, 2H; 6.85, s, 2H (Ho); 7.21, s, 2H; 7.31, s, 2H (HM). $C_{86}H_{119}N_7O_8P_4 \cdot C_4H_8O_2$ *M* 1590.94, Calcd. C 67.94, H 8.05, N 6.16, P 7.79. Found: C 67.51, H 7.89 N 6.19, P 7.26.

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