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SHORT COMMUNICATIONS

A Convenient Synthesis of 2,7-Dioxa-5,10-diaza-3λ^5,8λ^5-diphospha-1,6(1,4)-dibenzenacyclodecaphanes

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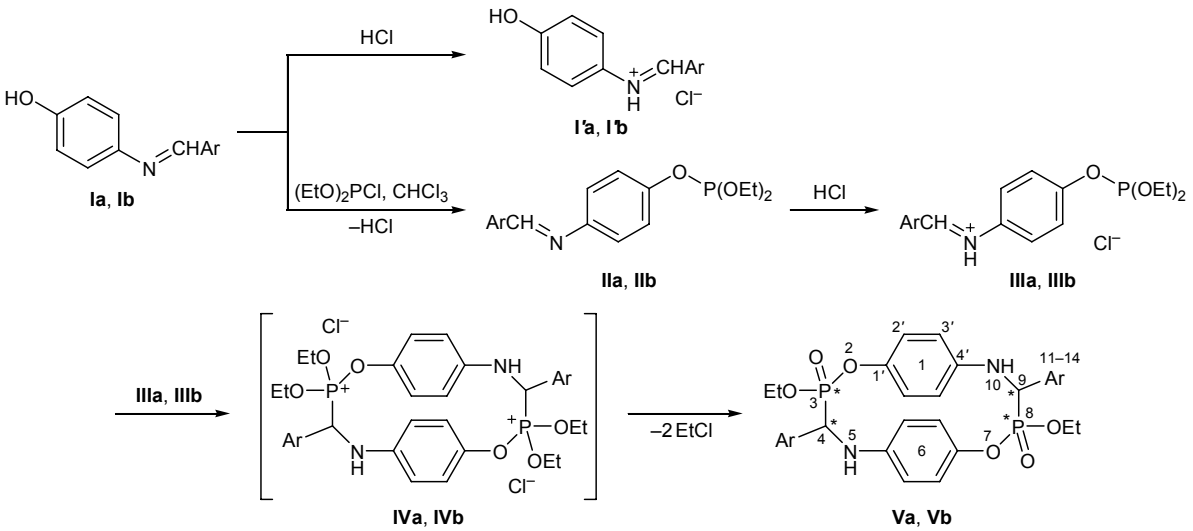
Phosphorus-containing macrocyclic compounds attract interest from the viewpoint of supramolecular chemistry as model structures for studying molecular recognition and complexation processes. Therefore, much attention is given to the development of methods of synthesis of such compounds [1–7].

We previously showed for the first time [8] that *p*-(benzylideneamino)phenol in the absence of other bases reacts with dialkyl phosphorochloridites in chloroform to give phosphorus-containing [4.4]paracyclophane analogs. The present communication reports on the results of analogous reactions with substituted iminophenols both in the absence (Scheme 1) and in the presence of other base (Scheme 2).

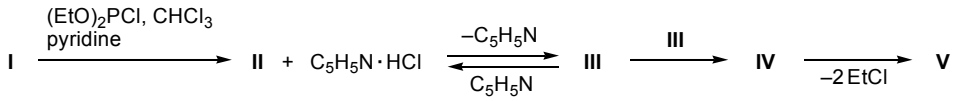
The reaction of diethyl phosphorochloridite with 4-(arylmethylideneamino)phenols **Ia** and **Ib** at a ratio of 1:1 (20°C, $CHCl_3$) was carried out in an argon atmosphere (Scheme 1). If no other base was added, the reaction was accompanied by separation of some solid from the reaction mixture. Analogous pattern was observed previously in the reaction of 4-(benzylideneamino)phenol with dialkoxy(chloro)phosphines [8]. On the basis of the ^{1}H NMR data and elemental analysis, the precipitate was identified as iminophenol hydrochloride **I′a** or **I′b**. Thus in the absence of other base, both phosphites **IIa** and **IIb** and initial iminophenols **Ia** and **Ib** act as acceptors of hydrogen chloride liberated during the process. The most probable way of formation of [4.4]paracyclophanes **Va** and **Vb** involves initial generation from diethyl phosphorochloridite and iminophenol **I** of iminium salts **III** which undergo cyclization to macrocyclic quasiphos-

Scheme 1.



Ar = 4-$MeOC_6H_4$ (**a**), 4-BrC_6H_4 (**b**).

Scheme 2.



phonium intermediates **IV** via intermolecular "head-to-tail" nucleophilic attack by the phosphorus atom on electrophilic carbon atoms of the iminium group. Intermediates **IV** are then converted into final macrocycles **V** as a result of dealkylation as in Arbuzov reaction.

The structure of macrocyclic compounds **Va** and **Vb** was confirmed by the ^{1}H, ^{13}C, and ^{31}P NMR, IR, and mass spectra and elemental analyses. In the ^{1}H NMR spectra of **Va** and **Vb** doublet signals from two protons in the PCH fragments ($^2J_{HP}$ = 23–24 Hz) were observed in the expected region, at δ 4–5 ppm. Taking into account the presence in molecules **V** of four pairwise equivalent chiral centers, these doublets are likely to correspond to five possible diastereoisomers (three *d*,*l* and two nonequivalent *meso* forms). It should also be taken into account that two nonequivalent phosphorus atoms in some diastereoisomers may be characterized by different coupling constants $^2J_{PH}$; therefore, different signals may be observed in the ^{31}P–{^{1}H} NMR spectra.

The reactions of diethyl phosphorochloridite with iminophenols **Ia** and **Ib** in the presence of pyridine as external base were not accompanied by formation of hydrochlorides **I′a** and **I′b** (Scheme 2). In this case, reactive imino phosphite hydrochlorides **IIIa** and **IIIb** are formed via transfer of HCl from pyridine hydrochloride to initially generated imino phosphites **IIa** and **IIb**. The occurrence of such equilibrium process is indicated by the presence in the ^{31}P–{^{1}H} NMR spectra of a weak downfield signal corresponding to structure **IIIa** or **IIIb**, δ_P 134.9 (**IIa**, **IIb**), 135.1 and 135.2 ppm (**IIIa**, **IIIb**). The reaction in the presence of pyridine is characterized by appreciably higher yield of **Va** and **Vb**, 78 and 70%, respectively, against 65 and 56% in the reaction with no base.

3,8-Diethoxy-4,9-bis(4-methoxyphenyl)-2,7-dioxa-5,10-diaza-3λ^5,8λ^5-diphospha-1,6(1,4)-dibenzenacyclodecaphane-3,8-dione (Va). A solution of 1 g (6.39 mmol) of diethyl phosphorochloridite in 15 ml of anhydrous chloroform was added over a period of 1 h under stirring at room temperature in an argon atmosphere to a suspension of 1.45 g (6.39 mmol) of 4-(4-methoxybenzylidene)aminophenol (**Ia**) in 70 ml of anhydrous chloroform. The mixture was stirred for 1 h more and was kept for 11 days under argon. The yellow precipitate was filtered off and washed with chloroform and diethyl ether to isolate 0.35 g of solid iminophenol hydrochloride **I′a**. The filtrate was evaporated under reduced pressure, the residue was treated with anhydrous diethyl ether, and the resulting powder was filtered off, washed with diethyl ether (2×10 ml), and dried under reduced pressure. The product (1.6 g) was recrystallized from butanol. A thick oily substance separated from the butanol solution and was treated with diethyl ether to obtain solid compound **Va** which was stable on exposure to air. Yield 1.32 g (65%), mp 125–129°C. IR spectrum, ν, cm^{-1}: 3297 (NH); 1247, 1202 (P=O), 1032, 980 (P–O–C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.02 br.t, 1.12 m, 1.18 br.t, 1.27 t, 1.32 m (15H, CH_3, $^3J_{HH}$ = 7.0 Hz); 3.74 br.s (5H, OCH_3, OCH_2); 3.92 br.m, 4.09 br.m, 4.18 br.m (6H, OCH_2); 4.70 br.d (1H, PCH, $^2J_{PH}$ = 24.0 Hz), 4.73 br.d (1H, PCH, $^2J_{PH}$ = 23.4 Hz), 4.76 br.d (1H, PCH, $^2J_{PH}$ = 23.7 Hz); 6.44 br.m, 6.50 br.m, 6.84 br.m, 7.34 br.m (16H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (multiplicity in the proton-decoupled spectrum is given in parentheses): 16.25 q.m (d), 16.27 q.m (d), 16.37 q.m (d), 16.46 q.m (d) ($CH_2\mathbf{C}H_3$, $^1J_{HC}$ = 127.4–127.5, $^3J_{PC}$ = 5.6–6.0, $^2J_{HC}$ = 3.0 Hz); 55.24 br.q (d) (OCH_3, $^1J_{CH}$ = 144.0 Hz); 55.33 br.d.d.m (br.d), 55.41 br.d.d.m (br.d), 55.57 br.d.d.m (br.d), 55.61 br.d.d.m (br.d), 55.80 br.d.d.m (br.d) (PC, $^1J_{PC}$ = 152.7–153.5, $^1J_{HC}$ = 150–152 Hz); 62.59 br.t.m (br.d), 63.23 br.t.m (br.d), 63.29 br.t.m (br.d), 64.08 br.t.m (br.d) (OCH_2, $^1J_{CH}$ = 148.1–148.9, $^2J_{PC}$ = 5.7–6.9, $^2J_{CH}$ = 4.5 Hz); 114.12 br.d.m (br.s) (C^{13}, $^1J_{HC}$ = 160.5 Hz); 114.58 br.d.m (br.s) ($C^{3'}$, $^1J_{HC}$ = 158.0 Hz); 121.24 br.d.m (br.s), 121.05 br.d.m (br.s) ($C^{2'}$, $^1J_{HC}$ = 160.9–161.2 Hz); 127.09 br.m (br.d) (C^{11}, $^2J_{PC}$ = 8.5–8.6 Hz); 129.13 br.d.m (d), 129.21 br.d.m (d) (C^{12}, $^1J_{HC}$ = 160.0–161.0, $^3J_{PC}$ = 5.3 Hz); 142.29 m (d), 142.30 m (d), 142.45 m (d), 142.55 m (d) ($C^{4'}$, $^3J_{PC}$ = 10.5–11.0 Hz); 143.56 br.m (br.d), 143.71 br.m (br.d), 143.75 br.m (br.d) ($C^{1'}$, $^2J_{PC}$ = 10.5–11.0 Hz); 159.42 m (s), 159.46 m (s), 159.48 m (s) (C^{14}). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 19.9, 20.3, 23.2. Mass spectrum: *m/z* 639 $[M + H]^+$. Found, %: C 59.97; H 5.91; N 4.68; P 10.19. $C_{32}H_{36}N_2O_8P_2$. Calculated, %: C 60.19; H 5.64; N 4.39; P 9.72. *M* 638.59.

4,9-Bis(4-bromophenyl)-3,8-diethoxy-2,7-dioxa-5,10-diaza-3λ^5,8λ^5-diphospha-1,6(1,4)-dibenzenacyclodecaphane-3,8-dione (Vb). A solution of 0.60 g (3.83 mmol) of diethyl phosphorochloridite in 10 ml of

chloroform was added over a period of 1 h under stirring at 20°C in a dry argon atmosphere to a suspension of 1.01 g (3.66 mmol) of 4-(4-bromobenzylideneamino)phenol (**Ib**) in 40 ml of anhydrous chloroform containing 0.3 g (3.80 mmol) of freshly distilled pyridine. The mixture was stirred for 1 h more and was kept for 5 days. It was then filtered, the solvent was distilled off from the filtrate under reduced pressure, the residue was treated with anhydrous diethyl ether, and the precipitate was filtered off, washed with diethyl ether (2×10 ml), and recrystallized from butanol. A thick oily substance separated from the butanol solution and was treated with diethyl ether to obtain off-white solid compound **Vb** which was stable on exposure to air. Yield 0.94 g (70%), mp 154–158°C. IR spectrum, ν, cm^{-1}: 3303 (NH); 1243, 1200 (P=O); 1034 (P–O–C). ^{1}H NMR spectrum ($CDCl_3$–acetone-d_6, 1:1), δ, ppm: 1.01 br.m, 1.12 br.m, 1.22 br.m (6H, $CH_2C\mathbf{H}_3$); 3.77 br.m, 3.92 br.m, 4.78 br.m (4H, OCH_2); 4.72 br.d, 4.74 br.d, 4.78 br.d (2H, 4-H, 9-H, $^2J_{PH}$ = 24.7–25.0 Hz); 6.41 br.m (4H, 3′-H); 6.65 br.m, 6.79 br.m (4H, 2′-H); 7.31 br.m, 7.35 br.m (8H, 12-H, 13-H). ^{31}P NMR spectrum ($CDCl_3$–acetone-d_6, 1:1), δ_P, ppm: 18.4, 18.8, 19.1, 19.4, 19.6, 22.1, 22.6. Mass spectrum: *m*/*z* 737 $[M + H]^+$. Found, %: C 49.22; H 3.91; N 4.23; P 8.63. $C_{30}H_{30}Br_2N_2O_6P_2$. Calculated, %: C 48.91; H 4.08; N 3.80; P 8.42. *M* 736.34.

The NMR spectra were measured on a Bruker Avance-400 spectrometer at 400 (^{1}H), 100.6 (^{13}C), and 162 MHz (^{31}P). The IR spectra were recorded on a Bruker Vector-22 instrument from thin films placed between KBr plates. The Mass spectra were obtained on a Dynamo MALDI TOF mass spectrometer (Thermo Bioanalysis Finnigan, USA) equipped with a pulse UV laser (λ 337 nm); nitroaniline was used as matrix.

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