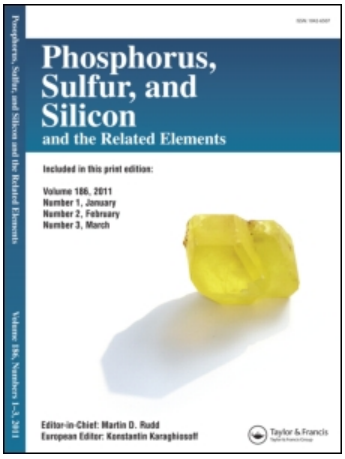

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GENERAL APPROACH TO THE SYNTHESIS OF SYMMETRICAL 1,3,2-DIAZAPHOSPHOCANES

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GENERAL APPROACH TO THE SYNTHESIS OF SYMMETRICAL 1,3,2-DIAZAPHOSPHOCANES

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Synthesis of eight-membered phosphorus-nitrogen heterocycles has been performed by phosphocyclization of the corresponding diamines using different derivatives of phosphorous acid. The structures of diazaphosphocanes were supported by elemental analysis; ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy; and x-ray diffraction analysis.

Keywords: Diazaphosphocan

1,3,2-Diazaphosphocyclanes containing 4–7-membered phosphorus-nitrogen heterocycles have been studied in detail[1–3]. These compounds are shown to have peculiar chemical features and to be promising for development of fine organic synthesis.

The reaction of *N,N*-dimethyl-*p*-toluidine with phosphorus oxychloride and phosphorus thiochloride resulting in formation of eight-membered phosphorus-nitrogen heterocycles was studied previously by Shaw *et al.*[4–6]. No further publications concerned with 1,3,2-diazaphosphocanes are available.

This is to give notice that 1,3,2-diazaphosphocanes belonging to different chemical types can be obtained by the direct cyclophosphorylation of 2,2′-methylene-bis-*p*-toluidine (**1**) and its derivatives with phosphorus

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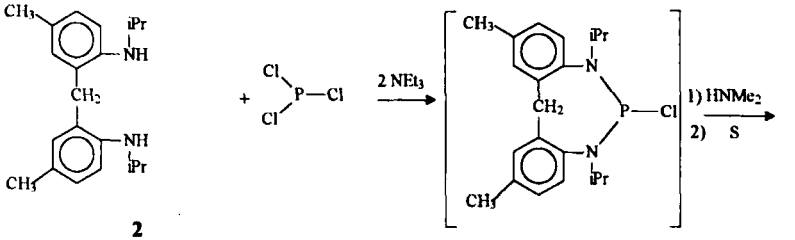
acid chlorides. The high lability of 1,3,2-diazaphospho(III)canes should be noted, in distinction from the 5–7 membered analogues known to date, wich significantly complicated the operations. So, the reaction of *N,N'*-diisopropyl-2,2'-methylene-bis-*p*-toluidine (**2**) with phosphorus trichloride in the presence of triethylamine gives 2-chloro-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocan. This is very unstable compound. It was stabilized using dimethylaminolysis in combination with sulfurization. Resulting 2-dimethylamido-2-thio-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocan (**3**) was isolated with a yield of 45%

The structure of this compound was supported by ^{1}H and ^{31}P NMR spectroscopy, and its spatial organization was confirmed by x-ray diffraction analysis (see figure).



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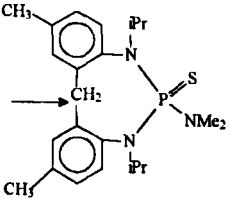
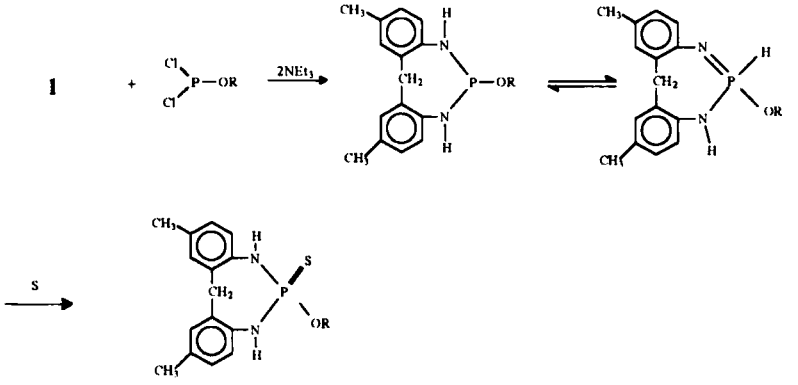


3

Diamine **2** was also subjected to cyclophosphorylation with dichlorides of ethyl-, phenyl-, and diethylamidophosphorous acids. The corresponding 2-substituted 1,3,2-diazaphosphocanes were obtained and isolated as thiophosphates (**4–6**).

The phosphocyclization of diamine **1** with alkyldichlorophosphites follows an unusual pathway. Mixtures of two tautomeric forms are the products:



7,8 **R = Et (7), Bu (8)**

This equilibrium is evidenced by the appearance of two signals at 113 and 6.23 (J_{PH} 614 Hz) in the ^{31}P NMR spectrum. It is important that the only product (**7, 8**) forms at the treatment of the system obtained by sulfur in both cases.

The obtained eight-membered cyclic systems containing a trivalent phosphorus atom are very labile. For example, the interaction between the primary diamine **1** and phenyldichlorophosphite resulted in formation of the corresponding 2-phenoxy derivative, for which the above prototropy was not observed. However, the compound obtained was readily hydrolyzed with formation of an incomplete diazaphosphocan amide (**9**), when chromatographied on silica gel.

Some of the compounds studied are susceptible to dimerization, as was shown during their study using mass spectrometry.

P-N(1) = 1.648(4), P-N(3) = 1.663(3), P-N(2) = 1.667(3), N(2)-C(1) = 1.442(5), N(2)-C(16) = 1.501(5), N(3)-C(9) = 1.439(2), N(3)-C(19) = 1.500(5), C(6)-C(7) = 1.507, C(7)-C(8) = 1.512(5), C(1)-C(6) = 1.394, C(8)-C(9) = 1.400(5).

N(1)-P-N(3) = 110.37(17), N(1)-P-N(2) = 102.95(17), N(3)-P-N(2) = 103.92(16), N(1)-P-S = 111.15(15), N(3)-P-S = 110.97(12), N(2)-P-S = 116.98(12), C(22)-N(1)-P = 125.6(4), C(23)-N(1)-P = 120.8(4), C(1)-N(2)-C(16)= 118.0(3), C(1)-N(2)-P = 122.1(2), C(16)-N(2)-P = 117.8(3), C(9)-N(3)-C(19) = 118.1(3), C(9)-N(3)-P = 121,9(2), C(19)-N(3)-P

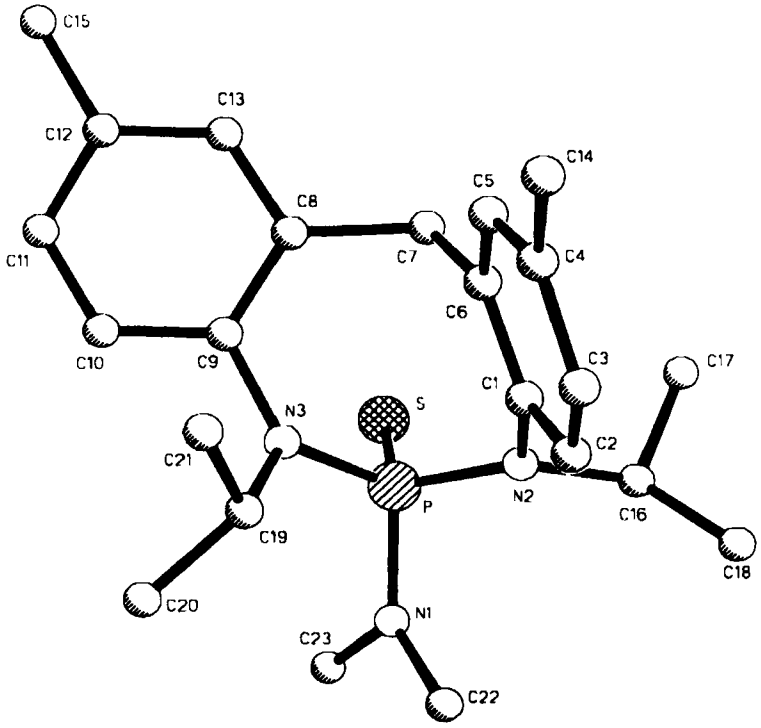


FIGURE The structure of **3** from the x-ray diffraction analysis data

= 119.6(3), C(2)-C(1)-N(2) = 119.3(3), C(6)-C(1)-N(2) = 121.8(3), C(1)-C(6)-C(7) = 122.6(4), C(6)-C(7)-C(8) = 114.2(3), C(8)-C(9)-N(3) = 122.0(3)

EXPERIMENTAL

^{31}P NMR spectra were recorded on a Bruker WP-80 instrument; ^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer. Mass-spectrometric studies were performed by the electron impact method on a Kratos MS-890 instrument. X-ray diffraction analysis was carried out on a Syntex P-1. An X-ray analysis of **3** was performed on a Syntex P-1 diffractometer using Cu-K_α radiation (λ= 1.54178 A). Crystals are orthorhombic, space

group *Pbca*, $C_{23}H_{34}N_3PS$, Z 8, d_{calc} 1.179 g/cm^3, a 14.908(3), b 16.547(3), c 18.988(3) A. The structure was solved by a direct method and was refined anisotropically basing on 2148 independent reflections with I $2\sigma(I)$ to a final R=0.029. All calculations have been done using SHELX97 package.

General procedure

Phosphorus trichloride or dichloride of alkyl- (aryl- or dialkylamido-) phosphorous acid was added slowly to a solution of 0.01 mol of diamine **(1, 2)** and 0.02 mol of triethylamine in dry benzene under stirring at 5–10°C. The reaction mixture was stirred at the room temperature; triethylamine hydrochloride was filtered off, and the raw cyclic reaction product was used. In order to obtain the corresponding thioderivatives **(3–8)**, sulfur was added. The reaction mixture was stirred for 2–3 h; the solvent was removed, and the target product was isolated either by recrystallization from benzene **(4)** or using the column chromatography on silica gel 45/75 **(3, 5–8)**.

2-Thio-2-dimethylamido-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocan (3)

Yield = 45%, m.p. 141–142°C. $\delta_P(CHCl_3)$ 69.80. MS, m/e: 415. ^{1}H NMR ($CDCl_3$, δ): 1.24 d (6H, CH_3^a, $^3J_{HH}$ 6.4 Hz), 1.3 d (6H, CH_3^B, $^3J_{HH}$ 7.83 Hz), 2.33 d (6H, $N(CH_3)_2$, $^3J_{HP}$10.9Hz), 2.23 s (3H, CH_3^{11}), 2.27 s (3H, $CH_3^{11'}$), 3.09 m (1H, CH^{iPr}, $^3J_{HP}$15.3Hz, $^3J_{HH}$7.83Hz, $^3J_{HH}$6.4Hz), 3.74 d (1H, CH_2, $^2J_{HH}$ 14.74 Hz), 4.06 m (1H, CH^{i-Pr} $^3J_{HP}$15.3Hz, $^3J_{HH}$7.83Hz, $^3J_{HH}$6.4Hz), 4.7 d (1H, CH_2, $^2J_{HH}$ 14.74 Hz), 6.56–7.09 m (6H, Ar). Found, %: C 66.3; H 8.39; P 7.07 $C_{23}H_{34}N_3PS$. Calcd., %: C 66.5; H 8.19; P 7.14.

2-Thio-2-ethoxy-1,3-diisopropyl-4,5;7,8-dibenzo-11,11'-dimethyl-1,3,2-diazaphosphocan (4)

Yield = 45%, m.p. 164–166°C. $\delta_P(CHCl_3)$ 71.51. MS, m/e: 416. ^{1}H NMR ($CDCl_3$, δ): 0.25 (0.28) dd (6H, $CH_3^{a,B}$, $^3J_{HH}$ 2.56 Hz,), 1.1 t (3H, $C\underline{H}_3CH_2O$, $^3J_{HH}$ 6.83 Hz), 1.35 d (3H, CH_3^a, $^3J_{HH}$ 6.83 Hz), 1.44 d (3H, CH_3^B, $^3J_{HH}$ 6.83 Hz), 2.28 s (6H, $CH_3^{11,11'}$), 3.77 m (1H, CH^{i-Pr}, $^3J_{HP}$ 15.37 Hz, $^3J_{HH}$2.56Hz, $^3J_{HH}$6.83Hz), 3.90 m (1H, CH^{i-Pr}, $^3J_{HP}$ 15.37 Hz,

$^3J_{HH}$ 2.56Hz, $^3J_{HH}$6.83Hz), 3.95 m (2H $CH_3C\underline{H}_2O$, $^3J_{HP}$ 8.53 Hz, $^3J_{HH}$ 6.83Hz), 4.04 d (1H, CH_2, $^2J_{HH}$ 14.51 Hz), 4.17 d (1H, CH_2, $^2J_{HH}$ 14.51 Hz), 6.94–7.11 m (6H, Ar). Found, %: C 65.90; H 8.26; P 6.26. $C_{23}H_{33}N_2OPS$. Calcd., %: C 66.3; H 7.9; P 7.4.

2-Thio-2-phenoxy-1,3-diisopropyl-4,5;7,8-dibenzo-11,11′-dimethyl-1,3,2-diazaphosphocan (5)

Yield = 30%, m.p. 165–166°C. $\delta_P(C_6H_6)$ 67.57. ^{1}H NMR (C_6H_6, δ): 0.36 (0.40) dd (6H, $CH_3^{a,B}$, $^3J_{HH}$ 6.8 Hz), 1.39 d. (3H, CH_3^a, $^3J_{HH}$ 6.4 Hz), 1.47 d. (3H, CH_3^B, $^3J_{HH}$ 6.4 Hz), 2.06 s (3H, CH_3^{11}), 2.1 s (3H, $CH_3^{11'}$), 4.1 m (1H, CH^{iPr} $^3J_{HP}$15Hz, $^3J_{HH}$6.8Hz, $^3J_{HH}$6.4Hz), 4.20 d (1H, CH_2, $^2J_{HH}$ 14.52 Hz), 4.28 d (1H, CH_2, $^2J_{HH}$ 14.52 Hz), 4.64 m (1H, CH^{iPr} $^3J_{HP}$15Hz, $^3J_{HH}$6.8Hz, $^3J_{HH}$6.4Hz), 6.78–7.34 m (11H, Ar).

2-Thio-2-diethylamido-1,3-diisopropyl-4,5;7,8-dibenzo-11,11′-dimethyl-1,3,2-diazaphosphocan (6)

Yield = 42%, m.p. 170–171°C. $\delta_P(CHCl_3)$ 70.97. MS, m/e: 443. ^{1}H NMR ($CDCl_3$, δ): 1.23 d (12H, CH_3^{iPr}, $^3J_{HH}$7.46 Hz), 1.27 m (6H, $C\underline{H}_3CH_2$-, $^3J_{HH}$6.83Hz), 2.28 s (3H, CH_3^{11}), 2.32 s (3H, $CH_3^{11'}$), 3.16 q (1H, CH^{iPr}, $^3J_{HH}$7.46Hz), 3.25 m (2H, -$\underline{CH}_2$-CH_3, $^3J_{HH}$6.83Hz, $^3J_{HP}$ 12.81 Hz), 3.48 m (2H, -$\underline{CH}_2$-CH_3, $^3J_{HH}$6.83Hz, $^3J_{PH}$ 13.23 Hz), 3.79 d (1H, CH_2, $^2J_{HH}$ 14.72 Hz), 4.03 q (1H, CH^{iPr}, $^3J_{HH}$6.83Hz), 4.64 d (1H, CH_2, $^2J_{HH}$ 14.72 Hz), 6.97–7.12 m (6H, Ar).

2-H-2-Oxo-4,5;7,8-dibenzo-11,11′-dimethyl1,3,2-diazaphosphocan (9)

Yield = 35%. m.p. 172–173°C. δ_P ($CHCl_3$) 10.31. MS, m/e: 272. ^{1}H NMR ($CDCl_3$, δ): 2.29 s (6H, $CH_3^{11,11}$), 3.93 d (1H, CH_2, $^2J_{HH}$ 14.29 Hz), 4.03 d (1H, CH_2, $^2J_{HH}$ 14.29 Hz), 4.97 s (2H, $NH^{1,3}$, $^3J_{HH}$ 2.2 Hz), 7.68 d (1H, J_{PH} 614 Hz), 6.86–7.11m (6H, Ar).

Note: Letters *a* and *e* denote two magnetically unequivalent methyl groups in isopropyl radicals.

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