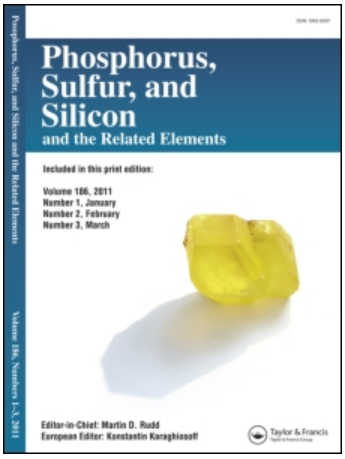

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Synthesis of N-Phosphorylated 1,2-Azaphosphetidines

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SHORT COMMUNICATION
Synthesis of N-Phosphorylated 1,2-Azaphosphetidines

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The present paper gives a description of *N*-phosphorylated 1,2-azaphosphetidines (**4, 5**) for the first time.

Interaction between 2-bromoethylamine hydrobromide **1,** dialkylchlorophosphite **2** and triethylamine under mild conditions results, probably, in 2-bromoethylamino-*N,N*-bis(dialkoxyphosphite) **3,** which undergoes thermolysis and yields **4**.[1,2]

The compounds **4a–4c** are colorless, clear liquids, distillable in vacuo and easily soluble almost in all inert organic solvents. Their structure is confirmed by micro-analysis, molecular weight determination, IR and ^{31}P-NMR spectroscopic data.

Analytical data and some physical properties of the compound **4** are presented in Table 1. Table 2 lists some spectroscopic parameters of the compounds **4a–4c**. The IR spectra of the compounds **4a–4c** show strong absorption at 1260–1250 cm^{-1}, 1040–1030 cm^{-1}, which is characteristic for the P=O bond and the P—O-Alk

TABLE 1

Physical properties and analytical data

Reaction Product No.	Alk	Yield[a] %	B.p. °C (torr)	Formula	Found (%) C	H	N	Calc. (%) C	H	N
4a	Et	32	93–94(0.06)	$C_8H_{19}NO_4P_2$	37.84	7.63	5.40	37.65	7.50	5.49
4b	i-Pr	34	84–85(0.03)	$C_{11}H_{25}NO_4P_2$	44.73	8.34	4.57	44.43	8.48	4.71
4c	n-Bu	31	137–138(0.05)	$C_{14}H_{31}NO_4P_2$	49.68	9.13	4.58	49.56	9.21	4.13

[a] Yield of product, isolated by double distillation.

TABLE 2

Spectroscopic data

Compd.	^{31}P NMR[a] (ppm)[b]	(PNP)/Hz	Mol. Wt. (MS) Found	Calc.	IR (film) P=O	max cm^{-1}[c] P—O-Alk
4a	20.36; 126.98	30	255	255.18	1260–1250	1040–1030
4b	21.97; 126.8	38	297	297.28	1260–1250	1040–1030
4c	22.87; 127.6	26	339	339.36	1260–1250	1040–1030

[a] Phosphorus chemical shifts were measured on TESLA BS 487 B Spectrometer at 30 MHz relative to 85% H_3PO_4 as external standard.

[b] All values refer to pure liquids.

[c] Infrared spectra were obtained on SPECORD 75 IR spectrophotometer (C. Zeiss).

group, respectively.[3] Each compound **4a–4c** shows two signals in the ^{31}P-NMR spectrum one between 22.87 to 20.36 ppm, this being characteristic of four-coordinated phosphorus centers, and the other between 127.6 to 126.98 ppm characteristic of three-coordinated phosphorus centers.[4] Intensive molecular ion peaks corresponding to the molecular mass of monomer are observed in the mass spectra of the compounds **4a–4c**.

$$\underset{\mathbf{1}}{HBr\cdot H_2NCH_2CH_2Br} + \underset{\mathbf{2}}{(AlkO)_2PCl} \xrightarrow{Et_3N} \underset{\mathbf{3}}{[(AlkO)_2P]_2NCH_2CH_2Br} \xrightarrow[-AlkBr]{\Delta}$$

$$\longrightarrow \underset{\mathbf{4}}{(AlkO)_2P{-}N(H_2C{-}CH_2){-}P(=O)(OAlk)} \xrightarrow{TsN_3} \underset{\mathbf{5}}{(AlkO)_2P(=NTs){-}N(H_2C{-}CH_2){-}P(=O)(OAlk)}$$

The exocyclic dialkoxyphosphite group reacts easily with tosyl azide; resulting in oxidative imination and P=N bond formation.

EXPERIMENTAL

0.1 Mol **1** was treated with 0.2 mol **2** and 0.3 mol Et_3N in a mixture of anhydrous benzene and chloroform (2:1) at 2–4°C. The mixture was stirred for 2 hours at 20°C, triethylamine hydrochloride and hydrobromide were filtered. Then the solvents were evaporated (in vacuo), and the residue was distilled under reduced pressure.

The solution of TsN_3 (0.1 mol) in anhydrous ether was added dropwise to the solution of **4a** (0.1 mol) in anhydrous ether at 20°C. The mixture produced compound **5** on standing for five hours at 20°C. Yellow mass (80%) from benzene-petroleum ether mixture (boiling p. 40–70°C), m.p. 57–59°C. Anal. Calcd. for $C_{15}H_{26}N_2O_6P_2S$: C, 42.46; H, 6.18; S, 7.55. Found: C, 42.44; H, 6.12; S, 7.52. IR spectrum: bonds at 1280–1270 cm^{-1} (P=N), 1240 cm^{-1} (P=O), 2900, 2950 cm^{-1} (C—H), 1040–1030 cm^{-1} (P—O-Alk). ^{31}P-NMR spectrum (ref. H_3PO_4): 25.5 ppm; −5.57 ppm.

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