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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of N-Phosphorylated 1,2-Azaphosphetidines

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To cite this Article Gubnitskaya, E. S. , Parkhomenko, V. S. , Semashko, Z. T. and Samaray, L. I.(1983) 'Synthesis of N-Phosphorylated 1,2-Azaphosphetidines', Phosphorus, Sulfur, and Silicon and the Related Elements, 15: 2, 257 - 258 $^{\circ}$

To link to this Article: DOI: 10.1080/03086648308073302

URL: http://dx.doi.org/10.1080/03086648308073302

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

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(Received August 30, 1982)

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 microanalysis, molecular weight determination, IR and ³¹P-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		Yield ^a	B.p.		Found (%)			Calc. (%)		
No.	Alk	%	°C (torr)	Formula	C	Н	N	C	H	N
4a	Et	32	93-94(0.06)	C ₈ H ₁₉ NO ₄ P 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- B u	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.	31P NI	Mol. Wt. (MS)		IR (film)	max cm ^{-1c}	
	$(ppm)^b$	(PNP)/Hz	Found	Calc.	P=O	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% H₃PO₄ as external standard.

^b All values refer to pure liquids.

^{&#}x27;Infrared spectra were obtained on SPECORD 75 IR spectrophotometer (C. Zeiss).

group, respectively.³ Each compound 4a-4c shows two signals in the ³¹P-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.

$$HBr \cdot H_2NCH_2CH_2Br + (AlkO)_2PCl \xrightarrow{Et_3N} [(AlkO)_2P]_2NCH_2CH_2Br \xrightarrow{\Delta} AlkBr$$

$$1 \qquad 2 \qquad 3$$

$$OAlk \qquad NTs OAlk$$

$$OAlk \qquad OAlk \qquad OAlk$$

$$OAlk \qquad OAlk$$

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

5

EXPERIMENTAL

0.1 Mol 1 was treated with 0.2 mol 2 and 0.3 mol Et₃N 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 TsN₃ (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). ³¹P-NMR spectrum (ref. H_3PO_4): 25.5 ppm; -5.57 ppm.

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