Russian Journal of General Chemistry, Vol. 71, No. 3, 2001, pp. 327–329. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 3, 2001, pp. 360–362.

Reactions of *N,N'*-Dimethyl-*N,N'*-bis(trimethylsilyl)-methylphosphonic Diamide with Chloral and Chloromethyldimethylchlorosilane

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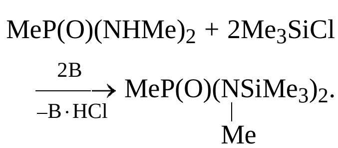
Received December 21, 1999

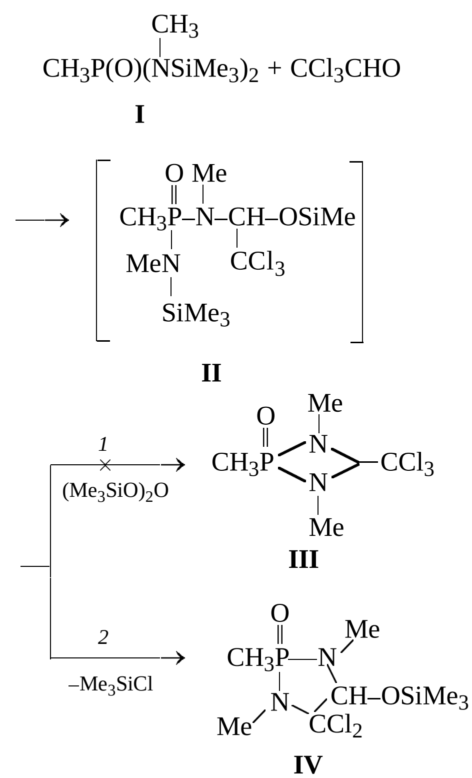
Abstract—*N,N'*-Dimethyl-*N,N'*-bis(trimethylsilyl)methylphosphonic diamide reacts with chloral to form 1,2,3-trimethyl-4,4-dichloro-5-trimethylsiloxy-1,3,2-diazaphospholidine 2-oxide and with chloromethyldimethylchlorosilane to form 1,2,3,4,4-pentamethyl-1,3-diaza-2-phospha-4-silacyclopentane 2-oxide.

A promising route to polyheterophosphacyclanes involves the use of polyfunctional derivatives of four-coordinate phosphorus in which two or more structural fragments can interact intramolecularly to form ring systems. This approach was successful in synthesis of chloromethylphosphonates (-phosphinates) containing urea, thiourea, and other groups at the phosphorus atom; it allowed synthesis of various saturated and unsaturated phosphacyclanes [1–3]. By phosphorylation of heptamethyldisilazane with chloromethylphosphonic chloride derivatives we prepared (*N*-trimethylsilyl)chloromethylphosphonic amides which were converted to 1,4,2-diazaphospholidin-5-ones [4]. Proceeding with these studies, we attempted to prepare *N,N'*-dimethyl-*N,N'*-bis(trimethylsilyl)methylphosphonic diamide **I** with the aim of its further transformation into new cyclic compounds. However, the reaction of methylphosphonic dichloride with heptamethyldisilazane (1 : 2 ratio) occurs by several pathways and gives a mixture of products. We were able to prepare **I** by silylation of *N,N'*-dimethylmethylphosphonic diamide with trimethylchlorosilane in the presence of a base (1 : 2 : 2 ratio):



I

The only example of the reaction of chloral with a four-coordinate phosphorus compound containing a P–NR–$SiMe_3$ fragment is reported in [5]. It was concluded that chloral is not inserted into the N–Si bond; instead, the Wittig reaction occurs with the tautomeric imide form [5]. Nevertheless, there were good grounds to expect that the reaction of **I** with chloral would yield the insertion product **II** in which there are two possibilities of ring closure: elimination of siloxane to form diazaphosphetidine **III** and elimination of trimethylchlorosilane to form phosphacyclane **IV**. The reaction readily occurs at room temperature and yields 1,2,3-trimethyl-4,4-dichloro-5-trimethylsiloxy-1,3,2-diazaphospholidine 2-oxide **IV**.

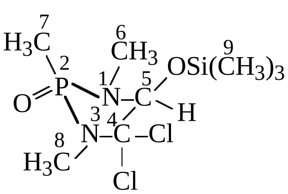


According to the NMR spectra, diazaphospholidine **IV** exists in solution in the form of cis and trans iso-

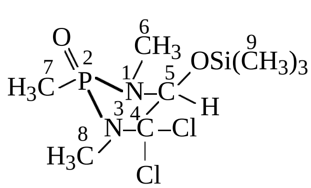
^{1}H, ^{13}C, and ^{31}P NMR spectra of 1,2,3-trimethyl-4,4-dichloro-5-trimethylsiloxy-1,3,2-diazaphospholidine 2-oxide **IV**: chemical shifts (δ, ppm) and coupling constants (*J*, Hz)

Nucleus	*cis*-**IV**		*trans*-**IV**	
	δ	*J*	δ	*J*
P	30.46		31.31	
C^6	27.95	2.4 (PNC^6)	27.30	3.3 (PNC^6)
		138.6 (C^6H)		138.6 (C^6H)
C^7	12.42	116.6 (PC^7)	27.30	3.3 (PC^7)
		127.0 (C^7H)		127.0 (C^7H)
C^8	26.63	0 (PNC^8)	26.0	0 (PNC^8)
		138.0 (C^8H)		138.0 (C^8H)
C^4	104.28	6.4 (PC^4)	104.28	6.4 (PC^4)
	87.24	9.9 (PC^5)	87.90	9.6 (PC^5)
		162.0 (C^5H)		162.0 (C^5H)
C^9	0.84	119.0 (C^9H)	1.01	119.0 (C^9H)
C^6H_3	2.73	12.0 ($P\text{–}NC^6H$)	2.70	12.0 ($P\text{–}NC^6H$)
C^7H_3	1.57	15.0 ($P\text{–}C^7H$)	1.60	15.0 ($P\text{–}C^7H$)
C^8H_3	2.85	9.0 ($P\text{–}NC^8H_3$)	2.85	9.0 ($P\text{–}NC^8H_3$)
C^5H	5.79	8.0 ($P\text{–}NC^5H$)	5.85	8.0 ($P\text{–}NC^5H$)
C^9H_3	0.41	–	0.41	–

mers (see the table) differing in the relative orientation of the $OSiMe_3$ group and methyl substituent at phosphorus. Both methyl substituents at nitrogen atoms probably occupy the equatorial position, as the parameters of their ^{1}H and ^{13}C NMR signals are close in both isomers. On the other hand, it is known that the configuration of the nitrogen atom bound to four-coordinate phosphorus becomes approximately planar [6]. Assignment of the doubled signals in the NMR spectra was made on the basis of the "contraction effect."



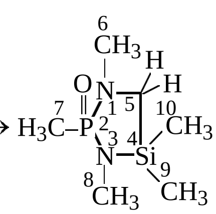
cis-**IV**



trans-**IV**

In the sterically strained cis isomer of **IV** the NMR signals of the exocyclic (δ_{C7} 12.42, δ_{C9} 0.84 ppm) and endocyclic (δ_{C5} 87.24, δ_P 30.46 ppm) atoms are observed in the higher field as compared to the less strained trans isomer (δ_{C7} 13.42, δ_{C9} 1.01, δ_{C5} 87.90, δ_P 31.31 ppm). According to the ^{31}P NMR spectrum, the ratio of *cis*-**IV** to *trans*-**IV** in chloroform is 74 : 26.

In silylation of **I** with chloromethyldimethylchlorosilane, formation of a cyclic structure could be expected. Indeed, we isolated from the reaction mixture 1,2,3,4,4-pentamethyl-1,3-diaza-2-phospha-4-silacyclopentane 2-oxide **V**, with release of two trimethylchlorosilane molecules:

$\mathbf{I} + ClCH_2SiMe_2Cl \longrightarrow$  $+ 2Me_3SiCl.$

V

The ^{31}P NMR chemical shift in **V** is δ_P 39.0 ppm. In the ^{13}C NMR spectrum the signal from the $P\text{–}CH_3$ carbon atom is observed at δ_{C7} 12.42 ppm ($^{1}J_{PC7}$ 113.4, $^{1}J_{C7H}$ 126.3 Hz). The methyl groups at the nitrogen atoms are nonequivalent: δ_{C6} 25.82, δ_{C8} 35.64 ppm ($^{2}J_{PNC6}$ 2.4, $^{2}J_{PNC8}$ 7.7, $^{1}J_{C6H}$ 137.3, $^{1}J_{C8H}$ 135.9 Hz). The highest-field signals are those from the methyl groups at the silicon atom, which are also nonequivalent: δ_{C9} –2.36 and δ_{C10} –1.88 ppm ($^{1}J_{C9H}$ 119.7, $^{1}J_{C10H}$ 119.5 Hz). In the low field are observed signals from the endocyclic methylene carbon atom, δ_{C5} 37.97 ppm ($^{2}J_{PNC5}$ 9.7, $^{1}J_{C5H}$ 127.5 Hz). In the ^{1}H NMR spectrum, the proton signal of the methyl group at phosphorus is a doublet at 1.30 ppm ($^{2}J_{CH}$ 15 Hz). The protons of the methyl groups at nitrogen atoms are nonequivalent: δ_{C6H} 2.62, δ_{C8H} 2.58 ppm

($^3J_{PNC6H}$ 8, $^3J_{PNC8H}$ 12 Hz). The protons of two methyl groups at the silicon atom are also nonequivalent: δ 0.17 and 0.26 ppm; methylene protons give a multiplet in the range δ 2.18–2.58 ppm.

EXPERIMENTAL

The NMR spectra were taken on Bruker MSL-400 (^{13}C, ^{13}C–{1H} 100.6 MHz, ^{31}P–{^{1}H} 161.8 MHz) and Varian T-60 (^{1}H, 60 MHz) spectrometers, references TMS and H_3PO_4.

***N,N'*-Dimethyl-*N,N'*-bis(trimethylsilyl)methylphosphonic diamide II.** To a mixture of 12.2 g of phosphonate **I** and 20.2 g of triethylamine in 100 ml of anhydrous chloroform, we added dropwise 21.8 g of trimethylchlorosilane. The mixture was allowed to stand for 12 h. Triethylamine hydrochloride was separated, the solvent was removed, and the residue was vacuum-fractionated to give 6.5 g (25%) of phosphonate **II**, bp 72°C (0.009 mm Hg), d_4^{20} 0.9609, n_D^{20} 1.4559. δ_P 36 ppm. Found, %: P 11.65; Si 19.73. $C_9H_{27}N_2OPSi_2$. Calculated, %: P 11.78; Si 21.03.

1,2,3-Trimethyl-4,4-dichloro-5-trimethylsiloxy-1,3,2-diazaphospholidine 2-oxide IV. A mixture of 1.33 g of phosphonate **I** and 0.74 g of chloral in 20 ml of ether was heated for 1 h, and the crystals that precipitated on cooling were filtered off. Yield of **IV** 0.9 g (60%), mp 142–143°C. Found, %: P 9.87; Si 9.03. $C_8H_{19}Cl_2N_2O_2PSi$. Calculated, %: P 10.16; Si 9.18.

1,2,3,4,4-Pentamethyl-1,3-diaza-2-phospha-4-silacyclopentane 2-oxide V. A mixture of 2.3 g of phosphonate **II** and 1.2 g of chloromethyldimethylchlorosilane was heated for 2 h at 120°C. Vacuum fractionation gave 1.2 g (72%) of **III**, bp 80–82°C (0.09 mm), mp 34°C. δ_P 39 ppm. Found, %: P 15.85; Si 14.04. $C_6H_{17}N_2OPSi$. Calculated, %: P 16.12; Si 14.58.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 00-03-32837).

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