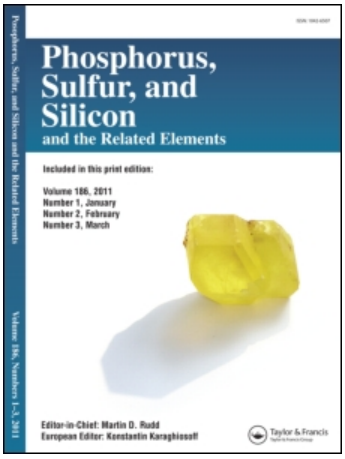

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E. E. Nifantyev[a]; V. I. Maslennikova[a]; L. K. Vasyanina[a]; A. R. Bekker[a]; N. B. Nesterenko[a]
[a] Moscow Pedagogical State University, Moscow, Russia

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2-TRICHLOROSILYL-1,3,2-DIHETEROPHOSPHORINANES

E. E. NIFANTYEV, V. I. MASLENNIKOVA, L. K. VASYANINA, A. R. BEKKER and N. B. NESTERENKO

Moscow Pedagogical State University, Nesvizhsky per 3, Moscow 119021, Russia

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Synthesis, study of steric structure and chemical features of new 2-trichlorosilyl-1,3,2-diaza- and dioxaphosphorinanes are reported. The main step for the synthesis of these compounds is the reaction of the corresponding cyclic hydrides with silicon tetrachloride.

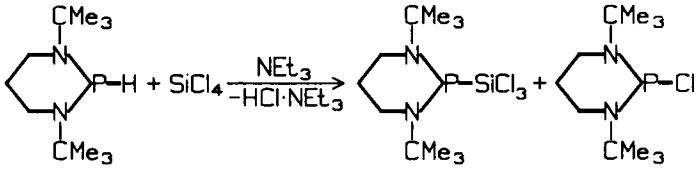
Key words: 2-H-1,3,2-diheterophosphorinane; silylation; 2-trichlorosilyl-1,3,2-diaza- and -dioxaphosphorinanes; ^{31}P and ^{29}Si NMR data.

INTRODUCTION

Formerly 2-triorganylsilyl- and -germyl-1,3,2-diazaphosphorinanes, first stable derivatives of trivalent phosphorus containing geminal donor-acceptor groups have been obtained in our laboratory.[1,2] Investigation of such systems is of interest for a number of fundamental problems in organophosphorus chemistry. But the method used for their synthesis turned out to be complex and not of general character. On this account we continued the search of more suitable synthetic routes. A possibility of dialkylaminophosphine silylation with silicon tetrachloride was recently reported by E. Niecke with co-authors.[3] We applied this reaction to the synthesis of phosphorinanes containing geminal donor-acceptor fragments at the phosphorus atom and showed that some 2-H-1,3,2-diheterophosphorinanes are also easily silylated by silicon tetrachloride in the presence of triethylamine.

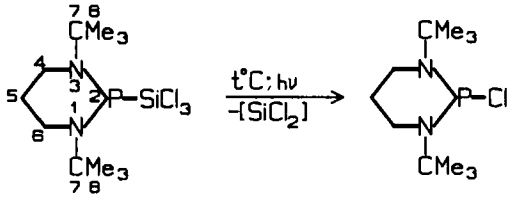
RESULTS AND DISCUSSION

At first, the interaction between 2-H-1,3-di-*tert*-butyl-1,3,2-diazaphosphorinane **1** and silicon tetrachloride was investigated:



By means of ^{31}P NMR spectroscopy it was shown that the reaction occurs ambiguously and results in two products: 2-trichlorosilyl-1,3-di-*tert*-butyl-1,3,2-di-

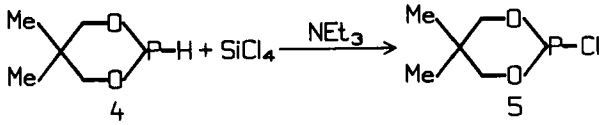
azaphosphorinane **2** (δ ^{31}P 68 ppm) and 2-chloro-1,3-di-*tert*-butyl-1,3,2-diazaphosphorinane **3** (δ ^{31}P 150 ppm). As deduced from ^{31}P NMR spectra, the ratio of the diazaphosphorinanes **2** and **3** depends on synthetic conditions. Thus, the fraction of diazaphosphorinane **2** in the reaction mixture accounted for up to 90% in diluted solution at low temperature (0–5°C) in the dark. Increase of reagent concentrations, heating, and irradiation of the reaction mixture result in changing of products ratio in favor of phosphorinane **3**. On this account one can suppose that diazaphosphorinane **2** initially formed by silylation of the hypophosphite derivative **1** transforms to diazaphosphorinane **3** through silylene fragment [$SiCl_2$] elimination under heating or irradiation[4]:



2 3

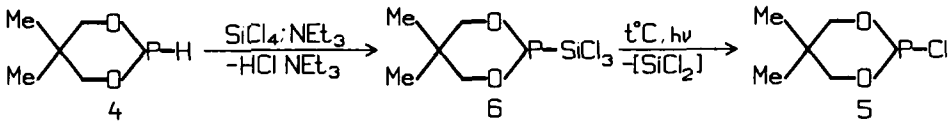
Diazaphosphorinane **2** was isolated by distillation under high vacuum. Its structure was confirmed by means of ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectroscopy. A singlet (δ 68 ppm) was observed in the ^{31}P NMR spectrum of compound **2**. A downfield shift of the phosphorinane **2** signal in comparison to those of P-silylated 1,3,2-diazaphosphorinanes previously obtained ($\Delta\delta \sim 20$ ppm)[1,2] is due to the deshielding of the phosphorus nucleus by three chlorine atoms. A doublet (δ-57 ppm, $^{1}J_{PSi}$ 41.7 Hz) was observed in the ^{29}Si NMR spectrum of phosphorinane **2**. In the ^{1}H and ^{13}C NMR spectra the signals of the proton and carbon nucleus of the phosphorinane ring and those of the *tert*-butyl groups corresponded to the supposed structure **2**. Some characteristic ^{1}H NMR data made it possible to predict the chair-conformation of phosphorinane ring: δ $H_a^{4,6}$ 3.30 ppm; $^{3}J_{HP}$ 0.9 Hz; δ $H_e^{4,6}$ 3.06 ppm; $^{3}J_{HP}$ 3.2 Hz.

We attempted to apply the results obtained for 2-H-1,3,2- diazaphosphorinane **1** to the silylation of 2-H-5,5-dimethyl-1,3,2-dioxaphosphorinane **4** with silicon tetrachloride. But only dioxaphosphorinane **5** was found in the products of interaction between dioxaphosphorinane **4** and silicon tetrachloride in the presence of triethylamine under the above mentioned conditions. The ^{31}P NMR spectrum showed only a singlet (δ 146.8 ppm) corresponding to chlorophosphite **5**.



4 5

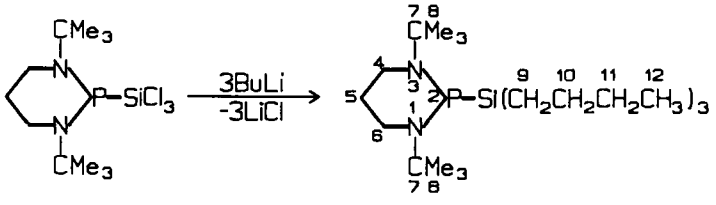
Investigation of the silylation of dioxaphosphorinane **4** by means of ^{31}P and ^{29}Si NMR spectroscopy within 203 and 293 K showed that 2-trichlorosilyl-5,5-dimethyl-1,3,2-dioxaphosphorinane **6** was formed at 213 K (δ ^{31}P 175 ppm and δ ^{29}Si-90.8 ppm).



4 6 5

When the temperature rises in the spectrometer probe up to 263 K the dioxaphosphorinane **6** is transformed to dioxaphosphorinane **5** which splits off a silylene fragment [$SiCl_2$], whose formation was proved by the appearance of the ^{29}Si NMR signals in the region of 5–6 ppm, typical for a compound of type $(SiCl_2)_n$.[5] A further increase of the temperature results in a fast and total transformation of phosphorinane **6** to phosphorinane **5** (Table I). Thus the conclusion that a hetero-atom has an important effect on the stability of silylated 1,3,2-diheterophosphorinanes can be drawn.

Systems containing trichlorosilyl groups are known to exchange easily chlorine atoms while interacting with nucleophiles. To investigate such a possibility we considered an example of interaction between diazaphosphorinane **2** and butyl lithium:



2 7

TABLE I

Composition of phosphorinane **4** and $SiCl_4$ interaction products with temperature variation (D_8-toluene)

temp, K	$\delta^{31}P$, ppm	$^1J_{PH}$, Hz	$\delta^{29}Si$, ppm	$^1J_{PSi}$, Hz	Compounds
203	147.3	168.7	-19.4		**4** $SiCl_4$
213–253	147.3	168.7	-19.4		**4** $SiCl_4$
	175		-90.8	77.4	**6**
263	147.3	168.7	-19.4		**4** $SiCl_4$
	175		-90.8	77.4	**6**
	146.8		5 – 6		**5** $(SiCl_2)_n$
273	175		-90.8	77.4	**6**
	146.8		5 – 6		**5** $(SiCl_2)_n$
293	146.8		5 – 6		**5** $(SiCl_2)_n$

The reaction was carried out at low temperature without isolation of diazaphosphorinane **2** from the reaction mixture. The structure of the diazaphosphorinane **7**, isolated by high vacuum distillation in a yield of 60%, was established by means of ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectroscopy. The ^{31}P NMR spectrum of compound **7** shows a singlet (δ 44.9 ppm), and its ^{29}Si NMR spectrum exhibits a doublet (δ-4.34 ppm, $^{1}J_{PSi}$ 15.7 Hz). ^{1}H and ^{13}C NMR spectra of the ring moiety of phosphorinane **7** are similar to those of 2-triethylsilyl-1,3-*tert*-butyl-1,3,2-diazaphosphorinane obtained by interaction between diazaphosphorinane **3** and triethylsilyl lithium.[2]

The proposed method of the synthesis of 2-trialkylsilyl-1,3,2-diazaphosphorinanes is more convenient and simpler compared with known ones.

EXPERIMENTAL

All the syntheses were performed in dry deoxygenated solvents under dry deoxygenated argon. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer (at 100.6 MHz for ^{13}C, with TMS as an internal standard). ^{31}P NMR spectra (at 32.4 MHz, 85% H_3PO_4 as an external standard) and ^{29}Si NMR spectra (at 15.9 MHz, TMS as an internal standard) were recorded on a Bruker WP 80 spectrometer.

2-Trichlorosilyl-1,3-di-tert-butyl-1,3,2-diazaphosphorinane (**2**). Silicon tetrachloride (8.8 mmol) in benzene (5 mL) was slowly added to the solution of diazaphosphorinane **1** (7.8 mmol) and triethylamine (8.8 mmol) in benzene (10 mL) with stirring at 0–5°C. The reaction mixture was stirred for 2 h at room temperature; triethylamine hydrochloride was filtered off, and from the filtrate benzene evaporated and the residue distilled under 5×10^{-4} mm Hg and bath temperature of 50–60°C. The yield of diazaphosphorinane **2** is 65%. ^{1}H NMR (C_6D_6): 1.15 (s, 18H, H^8); 1.25 (m, 2H, H^5); 3.06 (m, 2H, $H_e^{4,6}$); 3.30 (m, 2H, $H_a^{4,6}$). ^{13}C NMR (C_6D_6): 29.6 (d, $^{3}J_{CP}$ 1.8 Hz, C^5); 30.1 (d, $^{3}J_{CP}$ 13.6 Hz, C^8); 45.1 (d, $^{2}J_{CP}$ 4.8 Hz, $C^{4,6}$); 57.1 (d, $^{2}J_{CP}$ 20.2 Hz, C^7). ^{31}P NMR (C_6H_6): 68 (s). ^{29}Si NMR (C_6D_6): −57 (d, $^{1}J_{PSi}$ 41.7 Hz).

$C_{11}H_{24}Cl_3N_2PSi$. Calc. C 37.77, H 6.92, P 8.86. Found C 37.28, H 6.42, P 8.51.

Interaction between 2-H-1,3,2-dioxaphosphorinane (**4**) *and silicon tetrachloride.*

A. The silicon tetrachloride (8.8 mmol) in benzene (5 mL) was added to the solution of dioxaphosphorinane **4** (8.3 mmol) and triethylamine (8.8 mmol) in benzene (10 mL). After stirring for 2 h at room temperature a singlet was only observed in the ^{31}P NMR spectrum of the reaction mixture for diazaphosphorinane **3** (δ 146.8 ppm).

B. The reaction was carried out directly in the probe of the NMR spectrometer. Silicon tetrachloride (5.3 mmol) was added to the solution of dioxaphosphorinane **4** (5.2 mmol) and triethylamine (6.3 mmol) in deuterotoluene (3 mL) at −70°C. The reaction progressed under gradual temperature increase from −70 up to 20°C (Table I).

2-Tributylsilyl-1,3-di-tert-butyl-1,3,2-diazaphosphorinane (**7**). Silicon tetrachloride (7.8 mmol) in benzene (5 mL) was added to the solution of diazaphosphorinane **1** (7.8 mmol) and triethylamine (8.8 mmol) in benzene (10 mL) at 0–5°C. After stirring for 2 h at room temperature the reaction mixture was cooled (0°C) and treated with a 2N solution of butyl lithium in hexane (15 mL) at 0–5°C, followed by stirring for 2 h at room temperature. The precipitates of lithium chloride and triethylamine hydrochloride were filtered off, solvents evaporated and the residue was distilled at 5×10^{-4} mm Hg and a bath temperature of 100–120°C. The yield of diazaphosphorinane (**7**) is 60%. ^{1}H NMR (C_6D_6): 0.91 (m, $^{3}J_{PH}$ 5.2 Hz, 6H, H^9); 1.0 (t, 9H, H^{12}); 1.27 (s, 18H, H^8) 1.46 (m, 6H, H^{11}); 1.56 (m, 6H, H^{10}); 1.70 (m, 1H, H_a^5); 3.14 (m, $^{3}J_{PH}$ 0.7 Hz, 2H, $H_a^{4,6}$); 3.34 (m, $^{3}J_{PH}$ 3.5 Hz, 2H, $H_e^{4,6}$); ^{13}C NMR (C_6D_6): 14.0 (s, C^{12}); 15.4 (d, $^{2}J_{CP}$ 16.5, C^9); 27.6 (d, $^{3}J_{CP}$ 3.6, C^{10}); 28.0 (s, C^{11}); 31.2 (d, $^{3}J_{CP}$ 12.1, C^8); 31.3 (d, $^{3}J_{CP}$ 2.5, C^5); 42.7 (d, $^{2}J_{CP}$ 4.8, $C^{4,6}$); 56.9 (d, $^{2}J_{CP}$ 19.1, C^7). ^{31}P NMR (C_6D_6): 45 (s). ^{29}Si NMR (C_6D_6): − 4.34 (d, $^{1}J_{PSi}$ 15.7 Hz).

$C_{23}H_{51}N_2PSi$. Calc. C 66.61, H 12.39 P 7.47. Found C 66.36, H 12.14, P 7.16.

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