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Synthesis of 1,3,4-thiaza- and 1,3,4-oxazaphosphol-2-ines based on *N*-phosphorylated (thio)ureas

M. A. Pudovik, L. K. Kibardina, R. Kh. Al'myanova, R. M. Kamalov, and A. N. Pudovik*

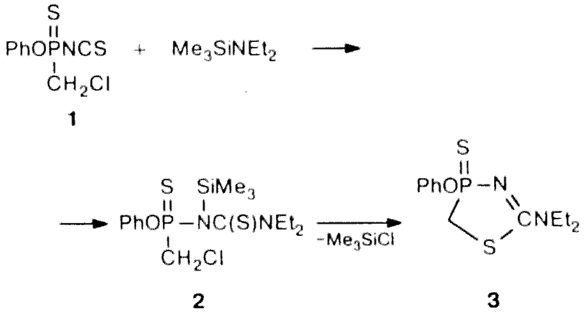
A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan' Scientific Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420083 Kazan', Russian Federation.
Fax: 007 (8 432) 75 2253

The reactions of *O*-phenyl chloromethylisothiocyanatothioxophosphonate and *O*-phenyl chloromethylisocyanatophosphonate with trimethylsilyldiethylamine lead to the formation of 1,3,4-thiazaphosphol-2-ine and 1,3,4-oxazaphosphol-2-ine, respectively. Phosphorylation of *N*-methyl-*N'*-phenyl-*N,N'*-bis(trimethylsilyl)urea with *O*-phenyl chloromethylchlorophosphonate gives 1,3,4-diazaphospholidin-2-one.

Key words: chloromethylphosphonates, silylated amines and ureas, heterocyclization, 1,3,4-oxazaphosphol-2-ine, 1,3,4-diazaphospholidin-2-one.

The synthesis of various 2-substituted 1,3,4-thiazaphospholines based on chloromethylisothiocyanato(thio)phosphonates has been previously developed.[1–3] It includes the addition of protonic nucleophiles (amines, mercaptans, and phosphines) to form *N*-phosphorylated thioureas, dithiocarbamates, and thioamides as intermediates followed by their intramolecular alkylation at the sulfur atom of the thio group by a chloromethyl group.

It has been established that silylated derivatives can be used instead of protonic nucleophiles themselves. The addition of trimethylsilyldiethylamine to *O*-phenylchloromethylisocyanatothioxophosphonate (**1**) is accompanied by the intermediate addition of silicon-containing *N*-phosphorylated thiourea (**2**). The latter is very unstable and immediately cyclizes to 2-diethylamino-4-thioxo-4-phenoxy-1,3,4-thiazaphospholine (**3**) accompanied by the elimination of trimethylchlorosilane.



The similar reaction of *O*-phenylchloromethylisocyanatophosphonate (**4**) with trimethylsilyldiethylamine occurs readily at room temperature. After 1 day the spectrum contains two signals at δ_P 24 and 51 ppm in a ratio of 5 : 1 assigned to phosphorylated urea (**5**) and oxazaphospholine (**6**), respectively.

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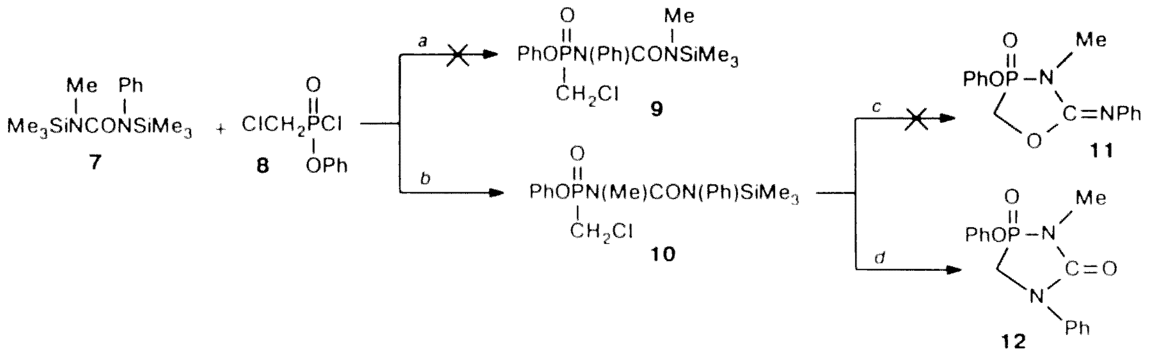
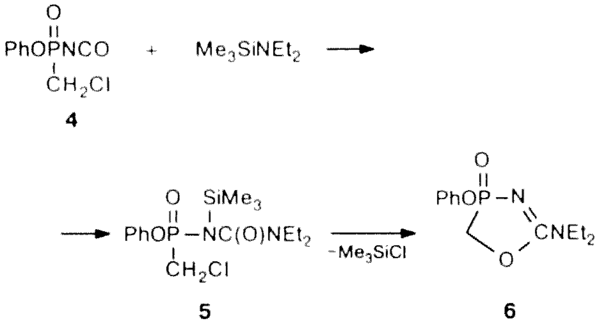
Scheme 1





According to the ^{31}P NMR data, after 1 week the reaction mass consists of the same products, but in a ratio of 1 : 5, which is evidence of cyclization. The IR spectrum of individual product **6** contains an absorption band of the C=N bond (1640 cm^{-1}).

The reaction of *N*-methyl-*N'*-phenyl-*N,N'*-bis(trimethylsilyl)urea (**7**) with *O*-phenyl chloromethylchlorophosphonate (**8**) was studied with the purpose of elucidating the possible extension of method found to the series of *N*-phosphorylated ureas (Scheme 1).

We assumed that the formation of isomeric *N*-phosphorylated ureas (**9**) (direction *a*) or product **10** (direction *b*) is possible at the first stage of the reaction. For these compounds, as shown in Scheme 1 for phosphonate **10**, intramolecular cyclization can occur by alkylation of either the carbamide oxygen atom (direction *c*) or the nitrogen atom (direction *d*). In the first case, the formation of oxazaphospholidine (**11**) would be expected, and in the second case diazaphospholidinone (**12**) would be formed. Transformations of this type have not yet been described. All spectral data show that the reaction product has the structure of 1,3,4-diazaphospholidin-2-one (**12**). Its IR spectrum contains an intense signal at 1725 cm^{-1}, which confirms reliably the existence of a carbamide group in the molecule. In the ^{1}H NMR spectrum, and the protons of the methyl group are seen as a doublet at 3.04 ppm ($^3J_{\mathrm{HP}}$ = 7.60 Hz), and the protons of the methylene group are characterized by two doublets of doublets (the AB part of the ABX-system) with δ_A 4.03 and δ_B 3.96 ppm, $^2J_{\mathrm{AB}}$ = 13.60, $^2J_{\mathrm{PA}}$ = 13.76, and $^2J_{\mathrm{PB}}$ = 16.76 Hz. The data obtained testify unambiguously that in the first stage the phosphorylation occurs at the nitrogen atom attached to the methyl group (direction *b*).

Experimental

^{31}P NMR spectra were recorded on a YaMR KGU-4 instrument (10.2 MHz), with an 85 % solution of H_3PO_4 as the standard. ^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer at 250.13 MHz, TMS as the internal standard. IR spectra were recorded on a UR-20 spectrometer in the frequency range from 400 to 3600 cm^{-1}.

2-Diethylamino-4-phenoxy-4-thioxo-1,3,4-thiazaphosphol-2-ine (3). A solution of trimethylsilyldiethylamine (1.45 g, 10 mmol) in ether (15 mL) was added dropwise to a solution of isothiocyanate **1** (2.63 g, 10 mmol) in anhydrous ether (10 mL). The reaction mixture was kept for 24 h. A crystalline product was filtered off and washed with ether. Phospholine **3** (1.72 g, 57 %) with m.p. 72 °C was obtained.[1]

2-Diethylamino-4-oxo-4-phenoxy-1,3,4-oxazaphosphol-2-ine (6). A mixture of isocyanate **4** (4.63 g, 20 mmol) and trimethylsilyldiethylamine (2.9 g, 20 mmol) was heated for 5 h at 60 °C. Compound **6** (2.46 g, 46 %) with b.p. 225–226 °C (0.05 Torr) and n_D^{20} 1.5379 was isolated by fractionation *in vacuo*. ^{31}P NMR, δ: 51 s. Found (%): C, 53.48; H, 6.62; N, 10.11; P, 11.48. $C_{12}H_{17}N_2O_3P$. Calculated (%): C, 53.73; H, 6.35; N, 10.40; P, 11.55.

3-Methyl-4-oxo-4-phenoxy-1-phenyl-1,3,4-diazaphospholidin-2-one (12). A solution of silylurea **7** (2.94 g, 10 mmol) and phosphonate **8** (2.25 g, 10 mmol) in benzene (20 mL) was heated for 3 h. After 24 h the crystals were filtered off and washed with ether. Phospholidine **12** (1.81 g, 60 %) with m.p. 136 °C was obtained. ^{31}P NMR, δ: 21. Found (%): N, 9.04; P, 10.27. $C_{15}H_{15}N_2O_3P$. Calculated (%): N, 9.27; P, 10.26.

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