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Reactions of Bis(chloromethyl)phosphinic(-Phosphinothioic) Chlorides with Silylated Carbamates and Trimethylsilyl *N*-Trimethylsilylacetimidoate

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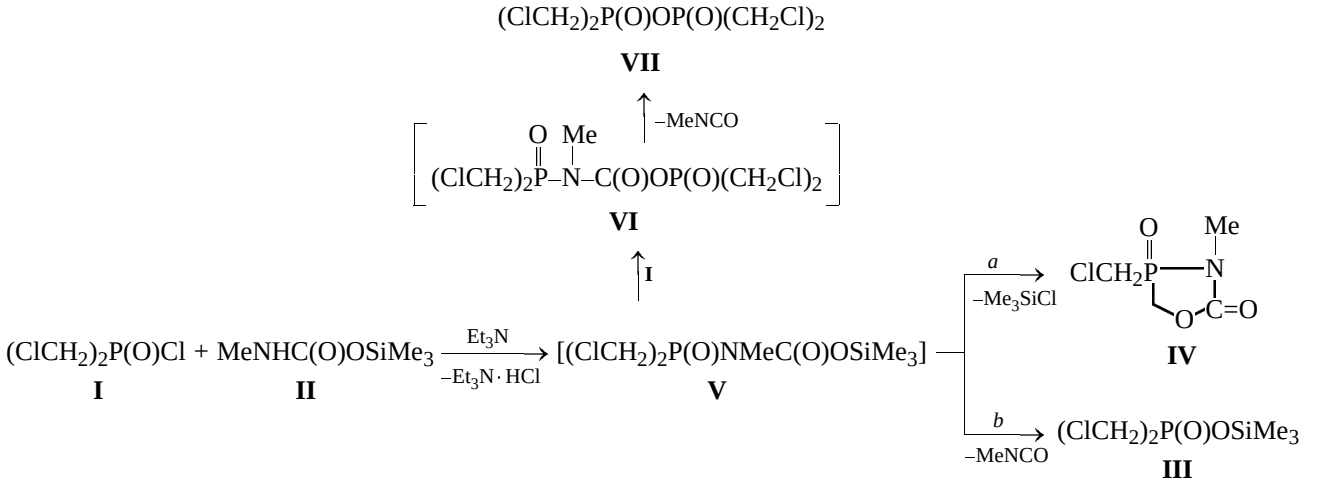
Abstract — Bis(chloromethyl)phosphinic chloride reacts with trimethylsilyl methylcarbamate in benzene in the presence of a base to give trimethylsilyl bis(chloromethyl)phosphinate. The same reaction performed without a solvent and in the absence of a base yields trimethylsilyl bis(chloromethyl)phosphinate and bis(chloromethyl)phosphinic anhydride. Reaction of bis(chloromethyl)phosphinic chloride with trimethylsilyl diethylcarbamate yields *N*,*N*-diethylbis(chloromethyl)phosphinic amide. The reaction of bis(chloromethyl)phosphinic (-phosphinothioic) chlorides with trimethylsilyl *N*-trimethylsilylacetimidoate was studied.

Chloromethylphosphonic (-phosphinic) chlorides exhibit a high phosphorylating power [1], and polyfunctional chloromethyl derivatives of four-coordinate phosphorus show promise in synthesis of polyhetero-phosphacyclanes [2–4]. Proceeding with these studies, we performed reactions of bis(chloromethyl)phosphinic chloride **I** and its thio analog with some silylated carbamates and with mono- and disilylated acetamides.

We found that trimethylsilyl methylcarbamate **II** reacts with bis(chloromethyl)phosphinic chloride **I** in benzene in the presence of a base with heat evolution and formation of triethylamine hydrochloride and trimethylsilyl bis(chloromethyl)phosphinate **III**.



However, cyclization of **V** into phospholidinone **IV** with release of trimethylchlorosilane (pathway *a*) does not occur. Owing to low stability, phosphinate **V** even at 20°C undergoes fast β-cleavage to give phosphinate **III** (pathway *b*). Such transformations were observed previously in the series of functionally substituted chloromethylphosphonates (-phosphinates) [5]. Reaction of **I** and **II** without a solvent and in the absence of a base at 20°C, according to the ^{31}P NMR spectra, yields simultaneously silyl phosphinate **III**

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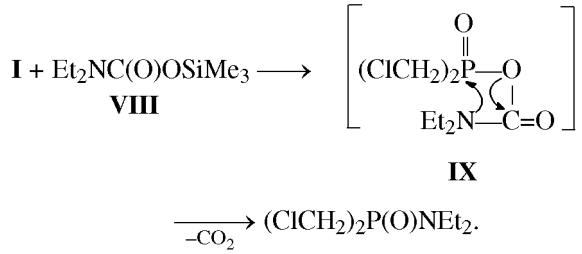
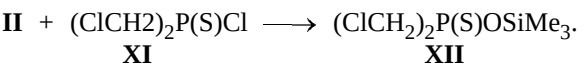
and bis(chloromethyl)phosphinic anhydride **VII**, which were isolated pure. Apparently, under these conditions intermediate **V**, along with β-cleavage to silyl phosphinate **III**, undergoes phosphorylation with reactive phosphinic chloride **I**. The resulting diphosphorylated carbamate **VI** decomposes to phosphinic anhydride **VII** with release of methyl isocyanate, which also was isolated and identified.

This assumption is confirmed by the result of the reaction of **I** with trimethylsilyl diethylcarbamate **VIII**:



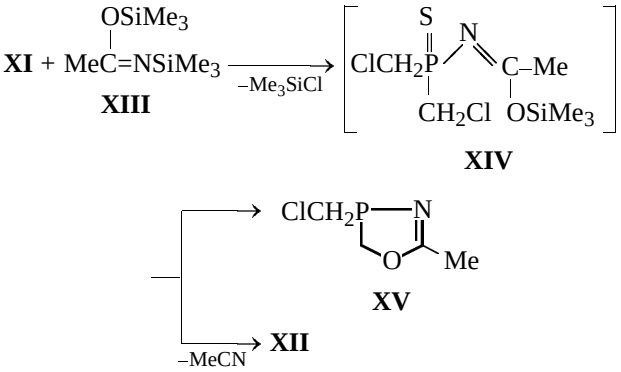
In this case the reactants contain no secondary amino group, and their reaction at 20°C involves cleavage of the O–Si bond and intermediate formation of unstable *O*-phosphorylated carbamate **IX**, which eliminates CO_2 to give *N*,*N*-diethylbis(chloromethyl)phosphinic amide **X**. It should be noted that the methyl analog of **IX**, acetyl bis(chloromethyl)phosphinate, decomposes differently, yielding phosphinic anhydride **VII** and acetic anhydride [6]. Phosphinic amide **X** was also prepared by independent synthesis from phosphinic chloride **I** and diethylamine.

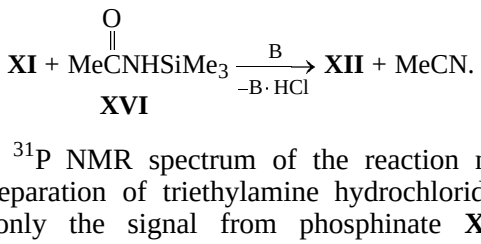
Reaction of silyl carbamate **II** with bis(chloromethyl)phosphinothioic chloride **XI** at 120°C for 2 h also yielded the cleavage product, *O*-trimethylsilyl bis(chloromethyl)phosphinothioate **XII**:



We also studied reactions of **I** and **XI** with silylated acetamide derivatives. We expected that compound **XI** would react with trimethylsilyl *N*-trimethylsilylacetimidoate **XIII** by two pathways: with release of two trimethylchlorosilane molecules and formation of phospholine **XV** and with cleavage of intermediate thiophosphinic amide **XIV** to trimethylsilyl phosphinothioate **XII**. Actually on heating of equimolar amounts of **XI** and **XIII** we obtained **XII** as a sole product.

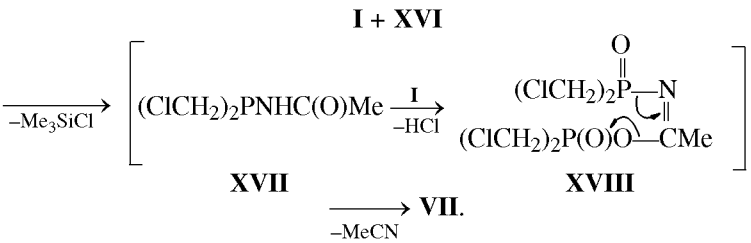
We also failed to detect the expected intermediates in reaction of chloride **XI** with *N*-trimethylsilylacetamide **XVI** performed under mild conditions (benzene, 20°C):





The ^{31}P NMR spectrum of the reaction mixture after separation of triethylamine hydrochloride contains only the signal from phosphinate **XII** (δ_P 74 ppm), indicating fast decomposition of the phosphorylation product. Apparently, the initially formed phosphinic amide undergoes 1,3-N–O migration of the trimethylsilyl group and reversibly transforms into imide **XIV**, which undergoes β-elimination with release of the acetonitrile molecule and formation of the final product.

Reaction of phosphinic chloride **I** with silylacetamide **XVI** in diethyl ether in the presence of a base at cooling yields siloxy phosphinic amide **V**. The same reaction performed without a solvent and in the absence of a base occurs with heat release and yields phosphinic anhydride **VII**.



Apparently, the initially formed *N*-phosphorylated acetamide **XVII** is phosphorylated with the initial phosphinic chloride **I** to form compound **XVIII**, which decomposes to anhydride **VII** and acetonitrile.

EXPERIMENTAL

The ^{31}P NMR spectra were taken on a KGU-4 NMR spectrometer (10.2 MHz), external reference 85% H_3PO_4. The ^1H NMR spectra were obtained on a Varian T-60 spectrometer (60 MHz, internal reference TMS).

Reaction of bis(chloromethyl)phosphinic chloride I with trimethylsilyl methylcarbamate II. *a*. To a solution of 2.3 g of **II** and 1.5 g of triethylamine in 20 ml of benzene at 20°C we slowly added 2.7 g of phosphinic chloride **I**. After 8 h, 1.8 g (86%) of triethylamine hydrochloride was separated, and the solvent was removed. Vacuum fractionation gave 1.6 g (44%) of silyl phosphinate **III**, bp 68–69°C (0.06 mm), n_D^{20} 1.4625. ^{31}P NMR spectrum: δ_P 28 ppm [7]. ^1H NMR spectrum (CCl_4), δ, ppm: 0.65 s (9H, CH_3Si), 3.85 d (4H, CH_2P, $^3J_{HP}$ 7 Hz). Found P, %: 13.11. $C_5H_{13}Cl_2O_2PSi$. Calculated P, %: 13.18.

b. Phosphinic chloride **I** (3.6 g) was mixed with carbamate **II** (2.9 g), and after 0.5 h the ^{31}P NMR spectrum of the reaction mixture was recorded; signals from silyl phosphinate **III** (δ_P 28 ppm), phosphinic anhydride **VII** (δ_P 38 ppm), and phosphinic chloride **I** (δ_P 52 ppm) were observed. After 8 h the mixture was fractionated, and 0.42 g (20%) of methyl isocyanate, bp 43°C, n_D^{20} 1.3825 [8], and 1.08 g (23%) of silyl phosphinate **III**, bp 69–70°C (0.08 mm), n_D^{20} 1.4612, were obtained. ^{31}P NMR spectrum: δ_P 28 ppm. Also we isolated 0.86 g (28%) of phosphinic anhydride **VII**, bp 145–150°C (0.08 mm), mp 65°C. ^{31}P NMR spectrum: δ_P 38 ppm [9]. ^1H NMR spectrum (CCl_4), δ, ppm: 3.86 d (8H, CH_2P, $^3J_{HCP}$ 9 Hz).

Trimethylsilyl bis(chloromethyl)phosphinate III. To a solution of 2.6 g of **XVI** and 2.0 g of triethylamine in 30 ml of ether we added dropwise 3.6 g of **I** with cooling to 15°C. After 2 h triethylamine hydrochloride was separated, the solvent was removed, and the residue was vacuum-fractionated. Yield of **III** 2.6 g (55%), bp 86°C (0.2 mm), n_D^{20} 1.4645. ^{31}P NMR spectrum: δ_P 28 ppm. Found P, %: 12.97. $C_5H_{13}Cl_2O_2PSi$. Calculated P, %: 13.18.

Bis(chloromethyl)phosphinic anhydride VII. A 3.6-g portion of **I** was mixed with 2.6 g of **XVI**; the mixture spontaneously warmed up to 80°C. After 3 h the mixture was vacuum-fractionated to give 1 g (30%) of **VII**, bp 145–149°C (0.08 mm), mp 65–67°C. ^{31}P NMR spectrum: δ_P 38 ppm [9].

***N,N*-Diethylbis(chloromethyl)phosphinic amide X.** *a*. A mixture of 3.6 g of **I** and 3.8 g of **VIII** was kept for 14 days at 20°C. Vacuum fractionation gave 2.9 g (67%) of **X**, bp 110–111°C (0.08 mm), mp 56–58°C. ^{31}P NMR spectrum: δ_P 36 ppm. Found, %: N 6.31; P 13.99. $C_6H_{14}Cl_2NOP$. Calculated, %: N 6.42; P 14.22.

b. To a solution of 7.3 g of diethylamine in 20 ml of ether, we added dropwise 9.1 g of **I**. The reaction mixture was left for 5 h at 20°C. Diethylamine hydrochloride was separated, the solvent was removed, and the residue was vacuum-fractionated to give 7.5 g (68%) of X, bp 84°C (0.08 mm), mp 57°C. ^{31}P NMR spectrum: δ_P 36 ppm.

Trimethylsilyl bis(chloromethyl)phosphinothioate XII. *a*. A mixture of 3.95 g of **XI** and 4.1 g of **II** was heated for 2 h at 120°C. Fractionation gane 2.9 g (59%) of **XII**, bp 75°C (0.06 mm), n_D^{20} 1.5070. ^{31}P NMR spectrum: δ_P 72 ppm. Found, %: P 11.86; Si 10.63. $C_5H_{13}Cl_2OPSSi$. Calculated, %: P 12.35; Si 11.15.

b. To a solution of 3.9 g of silylamide **XVI** and 3 g of triethylamine in 30 ml of benzene, we added 5.9 g of **XI**. The mixture was left for 5 h, 3.4 g (81%) of triethylamine hydrochlolride was separated, and the solvent was removed. Vacuum fractionation gave 2.2 g (29%) of **XII**, bp 78°C (0.08 mm), n_D^{20} 1.5063. ^{31}P NMR spectrum: δ_P 72 ppm. Found P, %: 12.01. $C_5H_{13}Cl_2OPSSi$. Calculated P, %: 12.35.

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REFERENCES

1. Terent'eva, S.A., Pudovik, M.A., and Pudovik, A.N., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 2, p. 339.
2. Pudovik, M.A., Krepysheva, N.E., Al'myanova, R.Kh., Kamalov, R.M., and Pudovik, A.N., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 3, pp. 360–363.
3. Kamalov, R.M., Khailova, N.A., Gazikasheva, A.A., Chertanova, L.F., Pudovik, M.A., and Pudovik, A.N., *Dokl. Akad. Nauk SSSR*, 1991, vol. 316, no. 6, pp. 1406–1410.
4. Kamalov, R.M., Stepanov, G.S., Chertanova, L.F., Gazikasheva, A.A., Pudovik, A.N., and Pudovik, M.A.,

Heteroatom Chem., 1992, vol. 3, no. 2, pp. 115–125.

5. Terent'eva, S.A., Pudovik, M.A., and Pudovik, A.N., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 1, pp. 23–27.
6. Khailova, N.A., Shaimardanova, A.A., and Pudovik, M.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, no. 11, pp. 2383–2385.
7. Pudovik, M.A., Al'myanova, R.Kh., Kamalov, R.M., and Pudovik, A.N., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 3, pp. 364–365.
8. Naumov, Yu.A., Bazhanova, L.G., and Knyazeva, A.P., *Metody Poluch. Khim. Reakt. Prep.*, 1966, no. 18, pp. 123–125.
9. Moedritzer, K., *J. Am. Chem. Soc.*, 1961, vol. 83, no. 21, pp. 4381–4384.