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LETTERS TO THE EDITOR

Reaction of Bis(chloromethyl)phosphinoyl Chloride and Phenyl (Chloromethyl)phosphonochloridate with Diethyl Bis(trimethylsilyl)phosphoramidite

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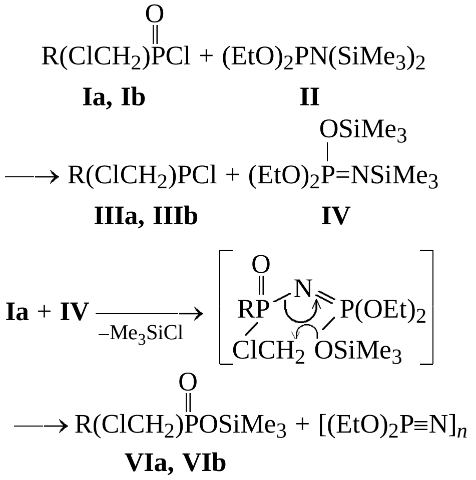
It was found that the reactions of bis(chloromethyl)phosphinoyl chloride (**Ia**) or phenyl (chloromethyl)phosphonochloridate (**Ib**) with diethyl bis(trimethylsilyl)phoshoramidite (**II**) are accompanied by liberation of chlorotrimethylsilane and formation of trimethylsilyl bis(chloromethyl)phosphinate (**VIa**) or trimethylsilyl phenyl (chloromethyl)phosphonate (**VIb**), respectively.



$$\underset{\textbf{Ia, Ib}}{\mathrm{R(ClCH_2)}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{Cl}} + \underset{\textbf{II}}{\mathrm{(EtO)_2PN(SiMe_3)_2}}$$

$$\longrightarrow \underset{\textbf{IIIa, IIIb}}{\mathrm{R(ClCH_2)PCl}} + \underset{\textbf{IV}}{\mathrm{(EtO)_2}\overset{\mathrm{OSiMe_3}}{\overset{|}{\mathrm{P}}}\mathrm{{=}NSiMe_3}}$$

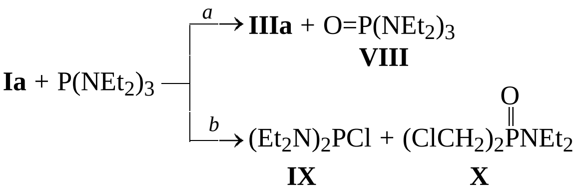
$$\textbf{Ia} + \textbf{IV} \xrightarrow[-\mathrm{Me_3SiCl}]{} \left[\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}(\mathrm{ClCH_2})\cdots\mathrm{N}\cdots\mathrm{P(OEt)_2}(\mathrm{OSiMe_3})\right]$$

$$\longrightarrow \underset{\textbf{VIa, VIb}}{\mathrm{R(ClCH_2)}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{OSiMe_3}} + \mathrm{[(EtO)_2P{\equiv}N]}_n$$

$\mathrm{R{=}ClCH_2}$ (**a**), PhO (**b**).

The ^{31}P NMR spectrum of the reaction mixture of phosphinoyl chloride **Ia** and phosphoroamidite **II** contains signals of trimethylsilyl phosphinate **VIa** (δ_P 26 ppm), bis(chloromethyl)phosphinous chloride (**IIIa**) (δ_P 98 ppm), and residual phosphoramidite **II**. The experimental evidence obtained suggests that the first stage of the reaction involves oxidation of phosphoroamidite **II** to diethyl trimethylsilyl (trimethylsilyl)phosphorimidate (**IV**) and, corresponingly, reduction of compound **Ia** and **Ib** to compounds **IIIa** and **IIIb**, respectively.

Phosphorimidate **IV** reacts with the starting compounds **Ia** and **Ib** to form intermediates **Va** and **Vb**, which, as previously shown [1], undergo β-cleavage to give final products **VIa** and **VIa**, as well as oligomeric product **VII**.



$$\textbf{Ia} + \mathrm{P(NEt_2)_3} \xrightarrow{a} \textbf{IIIa} + \underset{\textbf{VIII}}{\mathrm{O{=}P(NEt_2)_3}}$$

$$\textbf{Ia} + \mathrm{P(NEt_2)_3} \xrightarrow{b} \underset{\textbf{IX}}{\mathrm{(Et_2N)_2PCl}} + \underset{\textbf{X}}{\mathrm{(ClCH_2)_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{NEt_2}}$$

The oxidative ability of phosphinoyl chloride **Ia** toward P(III) derivatives was also illustrated by studying its reaction with hexaethylphosphorous triamide by ^{31}P NMR spectroscopy. In this case, both redox [**IIIa** (δ_P 98 ppm) and **VIII** (δ_P 24 ppm)] and exchange reaction products [**IX** (δ_P 160 ppm) and **X** (δ_P 36 ppm)] were detected.

Trimethylsilyl bis(chloromethyl)phosphinate (VIa). A mixture of 3.63 g of compound **Ia** and 5.62 g of compound **II** was heated for 3 h at 140°C. Fractionation in a vacuum gave 1.3 g (55%) of compound **VIa**, bp 68°C (0.06 mm), n_D^{20} 1.4530 [1]. ^{31}P NMR spectrum: δ_P 26 ppm. ^{1}H NMR spectrum (CCl_4), δ, ppm: 0.49 s (9H, CH_3Si), 3.83 d (4H, CH_2P, $^3J_{HCP}$ 6 Hz). Found, %: P 13.26. $C_5H_{13}Cl_2O_2PSi$. Calculated, %: P 13.18.

Phenyl trimethylsilyl (chloromethyl)phosphonate (VIb) was obtained analogously from 4.5 g of compound **Ib** and 5.62 g of compound **II**. Yield 2.25 g (81%), bp 75°C (0.02 mm), n_D^{20} 1.5217 [1]. ^{31}P NMR spectrum: δ_P 5 ppm. ^{1}H NMR spectrum (CCl_4), δ, ppm: 0.47 s (9H, CH_3Si); 3.83 d (2H, CH_2P, $^3J_{HCP}$ 6 Hz), 7.23 m (5H, CH_{arom}). Found,%: P 11.22. $C_{10}H_{16}ClO_3PSi$. Calculated,%: P 11.13.

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The ^1H NMR spectra were recorded on a Varian T-60 spectrometer (60 MHz) against internal TMS. The ^{31}P NMR spectra were measured on a KGU-4 spectrometer (10.2 MHz) against external 85% phosphoric acid.

ACKNOWLEDGMENTS

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