Russian Journal of General Chemistry, Vol. 73, No. 9, 2003, pp. 1495–1496. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 9, 2003, pp. 1581–1582.
Original Russian Text Copyright © 2003 by Sal'keeva, Nurmagambetova, Kurmanaliev.

LETTERS TO THE EDITOR

Mechanism of Reactions of P(III) Amidoesters with Carboxylic Acid Chlorides

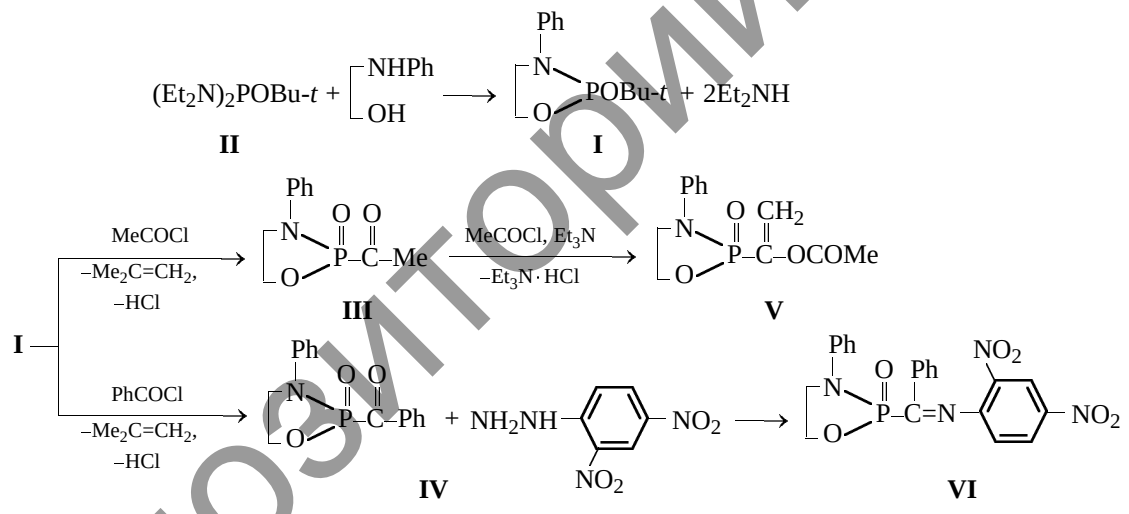
L. K. Sal'keeva, M. T. Nurmagambetova, and O. Sh. Kurmanaliev

Buketov Karaganda State University, Karaganda, Kazakhstan

Received June 24, 2002

One of us previously showed [1, 2] that *tert*-butyl phosphoramidites react with acetyl chloride by an Arbuzov reaction scheme to form phosphorochloridites and acetylphosphonates via a quasiphosphonium intermediate. 2-*tert*-Butoxy-3-phenyl-1,3,2-oxazaphospholane (**I**) obtained by transamidation of *tert*-butyl tetraethylphosphorodiamidite (**II**) with 2-(phenylamino)ethanol has not been studied in these reactions.

We found that oxazaphospholane **I**, too, reacts with carboxylic acid chlorides also by an Arbuzov reaction scheme to give acetylphosphonamidate **III** and benzoylphosphonamidate **IV**.



2-*tert*-Butoxy-3-phenyl-1,3,2-oxazaphospholane (I), oil, isolated by column chromatography on silica gel, eluent 1 : 1 ethyl acetate–benzene, n_D^{20} 1.5076. IR spectrum, ν, cm^{-1}: 1020 (P–O–C), 1080 (C–O), 1320 (P–N), 1450, 1470, 1580 (Ph). ^{31}P NMR spectrum: δ_P 136.7 ppm.

2-Acetyl-3-phenyl-1,3,2λ^5-oxazaphospholane 2-oxide (III), bp 98–100°C (3 mm), n_D^{20} 1.5270, d_4^{20} 1.3752. IR spectrum, ν, cm^{-1}: 1220 (P=O), 1720 (C=O). ^{31}P NMR spectrum: δ_P 21.1 ppm. Found, %: C 53.33, N 6.22; P 13.78.

2-(α-Acetoxyvinyl)-3-phenyl-1,3,2λ^5-oxazaphospholane 2-oxide (V), bp 110–112 (2 mm), n_D^{20} 1.4853, d_4^{20} 1.1552. IR spectrum, ν, cm^{-1}: 1230 (P=O), 1620 (C=C), 1700 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.6 s (CH_3C=O), 6.3 d (H_2C=, $^3J_{PH}$ 4 Hz). Found, %: C 53.57; H 5.28; N 5.43; P 11.46. $C_{12}H_{14}NO_4P$. Calculated, %: C 53.24; H 5.24; N 5.24; P 11.61.

2-Benzoyl-3-phenyl-1,3,2λ^5-oxazaphospholane 2-oxide (IV), oil, isolated by column chromatography on silica gel, eluent 1 : 1 ethyl acetate–benzene, n_D^{20}

Репозиторий КарГУ

1.5288. IR spectrum, ν, cm^{-1}: 1225 (P=O), 1710 (C=O). ^{31}P NMR spectrum: δ_P 27.7 ppm.

2-[(2,4-Dinitrophenylhydrazono)(phenyl)methyl]-3-phenyl-1,3,2λ^5-oxazaphospholane 2-oxide, mp 135°C.

The IR spectra were recorded on a Specord IR-75 spectrometer in thin layer. The ^1H NMR spectra were obtained on a Varian T-60 spectrometer (60 MHz) against internal TMS. The ^{31}P NMR spectra were measured on a Bruker WP-80 spectrometer (32.44 MHz) against external 85% phosphoric acid.

REFERENCES

1. Gazizov, T.Kh., Sal'keeva, L.K., Gafurov, E.K., and Kazantsev, A.V., *Zh. Obshch. Khim.*, 1988, vol. 58, no. 5, p. 1155.
2. Sal'keeva, L.K., Usmanova, L.N., and Gazizov, T.Kh., *Zh. Obshch. Khim.*, 1992, vol. 62, no. 2, p. 353.

Репозиторий КарГУ