ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 2, pp. 328–329. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © M.A. Pudovik, R.Kh. Bagautdinova, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 2, pp. 338–339.

LETTERS TO THE EDITOR

Reaction of *O*-Phenylchloromethylisothiocyanatothiophosphonate with Aliphatic Diamines

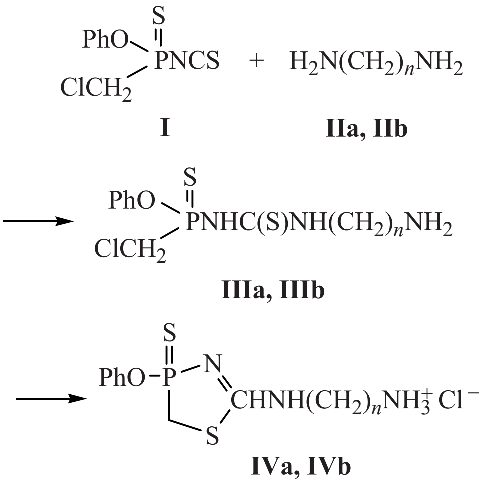
M. A. Pudovik and R. Kh. Bagautdinova

Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences,
ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia
fax: (8432) 752253
e-mail: pudovik@iopc.knc.ru

Received July 8, 2008

DOI: 10.1134/S1070363209020285

It has been shown earlier that chloromethylisothiocyanatothiophosphonates add aliphatic and aromatic amines to form phosphorylated thioureas which can closure cycle yielding 1,3,4-thiazaphosphols [1, 2]. We carried out some reactions of *O*-phenyl chloromethylisothiocyanatothiophosphonate **I** with aliphatic diamines for the purpose of continuing this line of studying. We assumed that on using of equimolar reagents quantities the secondary amino group will play a role of internal base to provide heterocyclization of urea or thiourea.



I **IIa, IIb**

IIIa, IIIb

IVa, IVb

II–IV: *n* = 2 (**a**), *n* = 3 (**b**).

Reaction of isothiocyanate **I** with diamines **IIa** and **IIb** proceeds smoothly at room temperature producing with high yield 1,3,4-thiazaphosphols **IVa** and **IVb** containing ammonium fragment. We failed to isolate or register spectrally the intermediately formed phosphorylated thioureas **IIIa** and **IIIb**. It suggests that they transform rapidly into the end cyclic products.

2-(2-Ammonium chloride)ethylamino-4-thioxo-4-phenoxy-1,3,4-thiazaphosphol (IVa). To a solution of 2.07 g of isothiocyanate **I** in 20 ml of benzene was added 0.47 g of ethylenediamine **IIa** at stirring and cooling to 5ºC. This mixture was kept for 3 days at 20°C. Then precipitate was separated and washed with benzene. Yield 1.36 g (54%), mp 161.5–163°C. IR spectrum (KBr), ν, cm^{-1}: 1242 (POPh), 1463 (Ph), 1565 (C=N), 2521, 2576, 2677, 2712 (NH_3^+), 3423 (NH). ^1H NMR spectrum (($(CD_3)_2CO$), δ, ppm: 3.27 br.m (4H, CH_2N), 3.54 d.d (1H, PCH_2, $^2J_{PH}$ 3.3 Hz, $^2J_{HH}$ 13.57 Hz), 3.99 d.d (1H, PCH_2, $^2J_{PH} = {}^2J_{HH}$ 12.84 Hz), 7.16–7.39 m (5H, Ph), 9.08 s (3H, NH_3^+). ^{31}P NMR spectrum (C_6H_6), δ_P, ppm: 117.31. Found, %: C 37.05; H 4.51; N 12.69; P 9.52. $C_{10}H_{15}ClN_3OPS_2$. Calculated, %: C 37.10; H 4.68; N 12.98; P 9.56.

2-(3-Ammonium chloride)propylamino-4-thioxo-4-phenoxy-1,3,4-thiazaphosphol (IVb) was prepared similarly from 1.02 g of isothiocyanate **I** and 0.28 g of diamine **IIb**. Yield 0.62 g (48%), mp 218–220°C. IR spectrum (KBr), ν, cm^{-1}: 1220 (POPh), 1470 (Ph), 1595 (C=N), 2425, 2552, 2650, 2705 (NH_3^+), 3436 (NH). ^{31}P NMR spectrum (C_6H_6), δ_P, ppm: 117.42. Found, %: C 38.97; H 4.95; N 12.38; P 8.99. $C_{11}H_{17}ClN_3OPS_2$. Calculated, %: C 39.11; H 5.08; N 12.44; P 9.16.

The IR spectra were registered on a UR-20 spectrometer in the range of 400–3600 cm^{-1} (vaseline oil).

The ^1H NMR spectra were measured on a Bruker WM-250 spectrometer (250.132 MHz) relative to internal TMS. The ^{31}P NMR spectra were taken on a Bruker MSL-400 NMR-Fourier spectrometer (100.62 MHz).

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (grant no. 06-03-32085).

REFERENCES

1. Khailova, N.A., Bagautdinova, R.Kh., Kataeva, O.N., Pudovik, M.A., Alfonsov, V.A., and Pudovik, A.N., *Synlett.*, 2006, no. 10, p. 1613.
2. Khaylova, N.A., Krepysheva, N.E., Saakyan, G.M., Bagautdinova, R.Kh., Shaymardanova, A.A., Zyablikova, T.A., Azancheev, N.M., Litvinov, I.A., Gubaydullin, A.T., Zverev, V.V., Pudovik, M.A., and Pudovik, A.N., *Zh. Obshch. Khim*., 2002, vol.72, no. 7, p. 1145.