ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 10, pp. 2274–2275. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © M.A. Pudovik, R.Kh. Bagautdinova, D.A. Pudovik, A.R. Burilov, A.S. Gazizov, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 10, pp. 1751–1752.

LETTERS TO THE EDITOR

1,3,4-Thiazaphosphol-2-ines Containing Acetal Groups in the Molecule

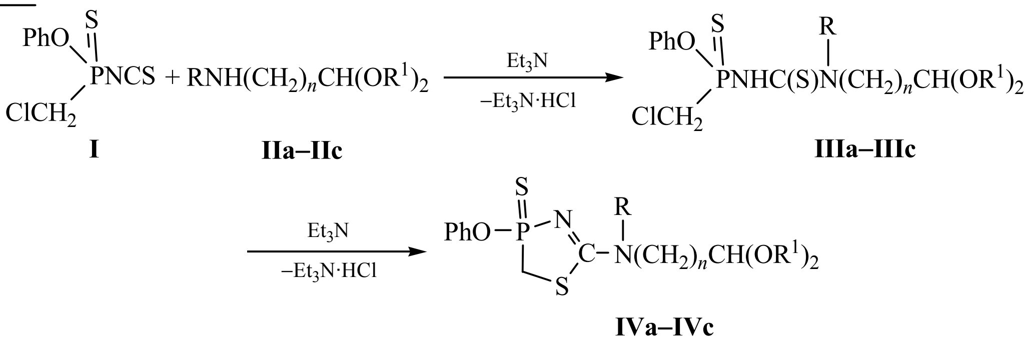
M. A. Pudovik, R. Kh. Bagautdinova, D. A. Pudovik, A. R. Burilov, and A. S. Gazizov

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 March 2, 2009

DOI: 10.1134/S1070363209100296

Primary and secondary amines were shown to react readily with chloromethyliso(thio)cyanato(thio)phosphonates to form the corresponding ureas or thioureas. The latter undergo ring closure to 1,3,4-oxaza(thiaza) phosphols in the presence of base [1–3]. We assumed that the use of C-substituted amines in this reaction can produce ring structures with P–C endocyclic bond containing additional functional groups. These compounds are of interest as the base compounds in organic and organoelemental synthesis. To realize this assumption we involved aminoacetals **IIa–IIc** into the reaction with phosphorylated isothiocyanate **I**. These reactions proceed readily in the presence of base under mild conditions to give 1,3,4-thiazaphosphols containing acetal fragments in the molecule. The course of the reaction includes intermediate formation of phosphorylated thioureas **IIIa–IIIc**. They were not isolated nor registered spectrally due to the fast transformation into the end-products. Cyclization occurs as a result of a nucleophilic attck by thione sulfur atom on the chloromethyl carbon atom to release hydrogen chloride as triethylamine hydrochloride.



II, III, IV, R = R^1 = Me, *n* = 1 (**a**); R = H, R^1 = Me, *n* = 1 (**b**); R = H, R^1 = Et, *n* = 3 (**c**).

2-[*N*-Methyl-*N*-(*O,O*-dimethyl)ethyl]amino-4-phenoxy-4-thioxo-1,3,4-thiazaphosphol-2-ine (IVa). To a mixture of 0.66 g of aminoacetal **IIa**, 0.60 g of triethylamine in 20 ml of anhydrous benzene was dropwise added 1.48 g of isocyanate **I**. The reaction mixture was kept for 24 h. Triethylamine hydrochloride was separated. Benzene solution was treated with distilled water (3×10 ml), dried with anhydrous sodium sulfate and concentrated in a water-jet pump vacuum. Yield 0.55 g (28%), colorless viscous liquid. Mass spectrum, *m*/*z*: 346 [M^+]. ^{1}H NMR spectrum [$(CD_3)_2CO$: C_6H_6=1:1], δ, ppm: 3.10 s (3H, NCH_3), 3.36 s (3H, OCH_3), 3.38 s (3H, OCH_3), 3.40 d (2H, NCH_2, $^3J_{HH}$ 3.15 Hz), 3.58 d. d (1H, PCH_2, $^2J_{PH}$ 3.6, $^2J_{HH}$ 13.50 Hz), 3.89 d. d (1H, PCH_2, $^2J_{PH}$ = $^2J_{HH}$ = 13.50 Hz), 4.63 t (1H, OCH, $^3J_{HH}$ 5.40 Hz), 7.21–7.41 m

(5H, Ph). ^{31}P NMR spectrum (acetone-d_6 : C_6H_6 = 1:1], δ_P, ppm: 115.70. Found, %: C 44.45; H 5.56; N 7.43; P 8.41; S 17.97. $C_{13}H_{19}N_2O_3PS_2$. Calculated, %: C 45.06; H 5.54; N 8.09; P 8.94; S 18.51.

2-[*N*-(*O,O*-Dimethyl)ethyl]amino-4-phenoxy-4-thioxo-1,3,4-thiazaphosphol-2-yne (IVb) was prepared similarly from 0.59 g of aminoacetal **IIb**, 0.6 g of triethylamine and 1.48 g of isothiocyanate **I**. Yield 0.90 g (49%), colorless viscous liquid. ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 3.34 s (3H, OCH_3), 3.35 s (3H, OCH_3), 3.40 d (2H, NCH_2, $^3J_{HH}$ 3.15 Hz), 3.53 d. d (1H, PCH_2, $^2J_{PH}$ 3.60, $^2J_{HH}$ 13.05 Hz), 3.60 m (2H, NCH_2), 3.90 d. d (1H, PCH_2, $^2J_{PH}$ = $^2J_{HH}$ 13.05 Hz), 4.53 t (1H, OCH, $^3J_{HH}$ 4.95 Hz), 7.18-7.23 m (5H, Ph), 7.82 s (1H, NH). ^{31}P NMR spectrum (acetone-d_6), δ_P, ppm: 117.96. Found, %: C 43.45; H 5.18; N 7.93; P 9.21. $C_{12}H_{17}N_2O_3PS_2$. Calculated, %: C 43.35; H 5.16; N 8.43; P 9.32.

2-[*N*-(*O,O*-Diethyl)butyl]amino-4-phenoxy-4-thioxo-1,3,4-thiazaphosphol-2-yne (IVc) was prepared similarly from 0.94 g of aminoacetal **IIc**, 0.6 g of triethylamine, and 1.54 g of isothiocyanate **I**. Yield 1.47 g (65%), colorless viscous liquid. ^{1}H NMR spectrum, [$(CD_3)_2CO$], δ, ppm: 1.07–1.20 m (6H, CH_3), 1.86–1.95 m (2H, CH_2), 2.03–2.08 m (2H, CH_2), 3.45–3.62 m (2H, NCH_2), 3.60 d. d (1H, PCH_2, $^2J_{PH}$ 3.76, $^2J_{HH}$ 13.51 Hz), 3.73–3.92 m (4H, OCH_2), 3.94 d. d (1H, PCH_2, $^2J_{PH}$ 5.41, $^2J_{HH}$ 13.51 Hz), 5.10 t (1H, OCH, $^2J_{HH}$ 4.95 Hz), 7.19–7.28 m (5H, Ph), 7.43 s (1H, NH). ^{31}P NMR spectrum (acetone-d_6), δ_P, ppm: 116.67. Found, %: C 49.00; H 6.18; N 7.07; P 8.33; S 16.49. $C_{16}H_{25}N_2O_3PS_2$. Calculated, %: C 49.46; H 6.50; N 7.21; P 7.97; S 16.51.

The IR spectra were registered on a UR-20 spectrometer in the range of 400–3600 cm^{-1} (mineral oil). The ^{1}H NMR spectra were measured on a Bruker AVANCE-600 spectrometer (600 MHz). The ^{31}P NMR spectra were recorded on a Bruker MSL-400 spectrometer (162 MHz). The mass spectra were taken on a TRACE-MS Finnigan-MAT device.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (grant no. 09-03-00029).

REFERENCES

1. 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, p. 1406.
2. Khailova, N.A., Krepysheva, N.E., Saakyan, G.M., Bagautdinova, R.Kh., Shaimardanova, A.A., Zyablikova, T.A., Azancheev, N.M., Litvinov, I.A., Gubaidullin, A.T., Zverev, V.V., Pudovik, M.A., and Pudovik, A.N., *Zh. Obshch. Khim*., 2002, vol. 72, no. 7, p. 1145.
3. Chmutova, G.A., Zverev, V.V., Pudovik, M.A., Khailova, N.A., and Pudovik, A.N*., Zh. Obshch. Khim*., 2003, vol. 73, no. 11, p. 1793.