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LETTERS TO THE EDITOR

Reaction of Dimethyl Chloroacetylenephosphonate with 1-Methyl-5-thio-1,2,3,4-tetrazole

E. B. Erkhitueva, D. M. Egorov, A. V. Dogadina, A. V. Khramchikhin, and B. I. Ionin

St. Petersburg State Institute of Technology, Moskovskii pr. 26, St. Petersburg, 190013 Russia
e-mail: serlxa@yandex.ru

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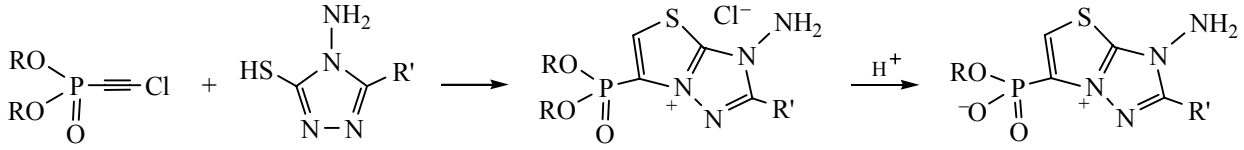
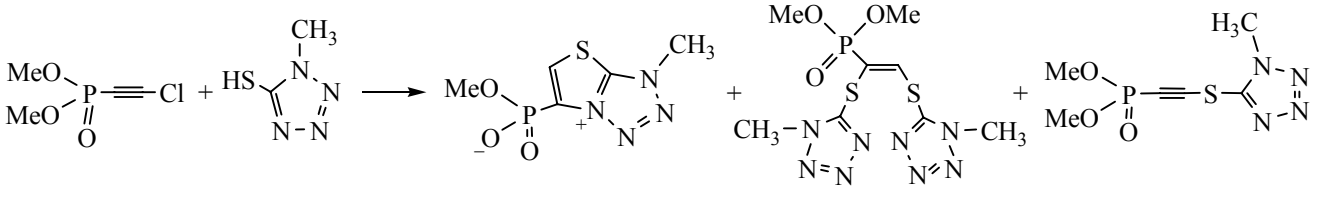
We have recently shown that the reaction of dimethyl chloroacetylenephosphonate with 4-amino-5-methyl-3-thio-1,2,4-triazole proceeds with a high chemo- and regioselectivity to afford the corresponding phosphorylated thiazolotriazolium chloride [1].

In a subsequent report we have shown that the same reaction occurs with a number of other 5-substituted 4-amino-3-thio-1,2,4-triazoles. Thus, starting from thiazolotriazolium chlorides we obtain the corresponding phosphonates of zwitterionic structure, which are the main product when using dimethyl chloroacetylenephosphonate [2].



R = Me, Et, *i*-Pr, R' = Me, Et, Pr, (*o*-MeO)Ph.

In this work we found that the reaction of dimethyl chloroacetylenephosphonate with 1-methyl-5-thio-1,2,3,4-tetrazole proceeds less unequivocally. The reaction was carried out under the conditions similar to [1, 2], at room temperature in anhydrous acetonitrile with vigorous stirring of the equivalent amounts of the reagents.



I **II** **III**

The cyclization product, namely, thiazolotetrazoliium **I** zwitterion, is the main reaction product. In addition, aliphatic phosphonate **II** and thioacetylenephosphonate **III** were detected in the reaction mixture. In the ^{31}P NMR spectrum of the reaction mixture the bicyclic ion **I** is manifested as an intense signal at δ_P –7.09 ppm. The signals with lower intensity at δ_P 13.46 and 3.10 ppm correspond to phosphonate **II** and thioacetylenephosphonate **III**, respectively.

During the reaction, the formation of thiazolotetrazolium chloride was detected (δ_P –2.42 ppm). Under the action of acidic tetrazole, the latter obviously is readily converted to the corresponding zwitterion **I**, which was isolated in 45% yield as

crystals. Its structure was confirmed by the ^{1}H, ^{13}C, ^{31}P NMR spectra.

In the ^{1}H NMR spectrum of zwitterion **I** the olefinic protons resonate in a weak field as a doublet signal at δ 8.25 with the spin-spin coupling constant with the phosphorus nucleus $^{3}J_{HP}$ 4.0 Hz. The intensities of the signals of methoxy groups, methyl moieties at the tetrazole ring nitrogen atom, and the olefinic proton correspond to thiazolotetrazolium zwitterion. In the ^{13}C NMR spectrum the olefinic carbon atoms are manifested as characteristic doublet signals at δ_C 131.15 ($^{1}J_{CP}$ 177.0 Hz) and 132.25 ($^{2}J_{CP}$ 13.0 Hz).

After the solvent removal, phosphonate **II** was isolated as the crystals from acetonitrile layer followed by the recrystallization from ethanol. The ^{1}H NMR spectrum of **II** contains the doublet signal of olefinic protons at δ 8.57 ($^{3}J_{HP}$ 16.0 Hz). In the ^{13}C NMR spectrum there are the doublet signals of olefinic carbon atoms at δ_C 116.33 ($^{1}J_{CP}$ 199.2 Hz) and 152.47 ($^{2}J_{CP}$ 22.1 Hz). The signals assignment was confirmed by the two-dimensional ^{1}H–^{13}C NMR spectroscopy. Due to the constant value $^{3}J_{HP}$ 16.0 Hz, we assumed that phosphonate **II** is the *Z*-isomer. For a more definite proof of the structure of phosphonate **II**, it was obtained by the authentic synthesis starting from dimethyl chloroacetylenephosphonate and 1-methyl-5-thiol-1,2,3,4-tetrazole sodium salt.

The formation of thioethynylphosphonate **III** is due to the substitution of chlorine atom in the initial chloroacetylenephosphonate. The formation of ethenylphosphonate **II** may be regaded as the thiotetrazole addition to the triple bond of phosphonate **III**. According to the ^{13}C NMR spectrum, the polarization of the latter is opposite to that in the initial chloroacetylenephosphonate (δ_C, ppm): dimethyl 2-chloroethynylphosphonate, 58.79 (C^{1}, $^{1}J_{CP}$ 301.6 Hz), 78.43 (C^{1}, $^{1}J_{CP}$ 301.6 Hz); thioacetylenephosphonate **III**, 88.05 (C^{1}, $^{1}J_{CP}$ 287.7), 82.92 (C^{2}, $^{2}J_{CP}$ 49.2 Hz). In accordance with the literature data [3], the classical nucleophiles and binucleophiles add only to the chloroacetylene carbon atom of the initial dimethyl 2-chloroethynylphosphonate.

Dimethyl 3-methyl-3*H*-thiazolo[3,2-*d*]tetrazol-7-ylium-6-methylphosphonate (I). Yield 45%, mp >220°C (decomp.). ^{1}H NMR spectrum, δ, ppm (CD_3OD): 3.69 d (3H, CH_3O, $^{3}J_{HP}$ 12.0 Hz), 4.53 s (3H, CH_3N), 8.25 d (1H, =CH, $^{3}J_{HP}$ 4.0 Hz). ^{13}C NMR spectrum, δ_C, ppm (CD_3OD): 36.91 (CH_3N), 52.14 d (CH_3O, $^{2}J_{CP}$ 5.0 Hz), 131.15 d (C^{6}, $^{1}J_{CP}$ 177.0 Hz), 132.25 d (C^{5}, $^{2}J_{CP}$ 13.0 Hz), 155.48 d (C^{8}, $^{3}J_{CP}$ 8.0 Hz). ^{31}P NMR spectrum, δ_P, ppm: –7.09 (CD_3OD), –8.13 (DMSO-d_6), –5.28 (D_2O).

Dimethyl 1,2-bis[(1-methyl-1*H*-1,2,3,4-tetrazol-5-yl)thio]ethenylphosphonate (II). Yield 20%, mp 211–213°C. ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 3.65 d (6H, CH_3O, $^{3}J_{HP}$ 12.1 Hz), 4.05 s (3H, CH_3N), 4.12 s (3H, CH_3N), 8.57 d (1H, =CH, $^{3}J_{HP}$ 16.0 Hz). ^{13}C NMR spectrum, δ_C, ppm ($CDCl_3$): 34.14 (CH_3N), 34.43 (CH_3N), 58.10 d (CH_3O, $^{2}J_{CP}$ 8.0 Hz), 116.33 d (PC=, $^{1}J_{CP}$ 199.2 Hz), 149.15 (SC=N), 149.64 (SC=N), 152.47 d (=CHS, $^{2}J_{CP}$ 22.1 Hz). ^{31}P NMR spectrum, δ_P, ppm: 11.58 ($CDCl_3$), 13.46 (D_2O).

Dimethyl 2-[(1-methyl-1*H*-1,2,3,4-tetrazol-5-yl)-thio]ethynylphosphonate (III). Yield 16%. ^{1}H NMR spectrum, δ_H, ppm (CD_3OD): 3.60 d (6H, CH_3O, $^{3}J_{HP}$ 12.0 Hz), 4.18 s (3H, CH_3N). ^{13}C NMR spectrum, δ_C, ppm (CD_3OD): 33.97 (CH_3N), 53.02 d (CH_3O, $^{2}J_{CP}$ 5.0 Hz), 82.92 d (≡CS, $^{2}J_{CP}$ 49.2 Hz), 88.05 d (PC≡, $^{1}J_{CP}$ 287.7 Hz), 150.16 (C=N). ^{31}P NMR spectrum, δ_P, ppm: 2.06 ($CDCl_3$), 3.10 (D_2O).

The ^{1}H, ^{13}C, ^{31}P NMR spectra were taken on a Bruker Avance instrument operating at 400 (^{1}H), 100.61 (^{13}C) and 161.98 MHz (^{31}P).

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