ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 11, pp. 2377–2378. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © E.B. Erkhitueva, A.V. Dogadina, A.V. Khramchikhin, B.I. Ionin, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 11, pp. 1925–1926.

LETTERS
TO THE EDITOR

Reaction of 4-Amino-3-mercapto-5-methyl-1,2,4-triazole with Chloroacetylenephosphonate

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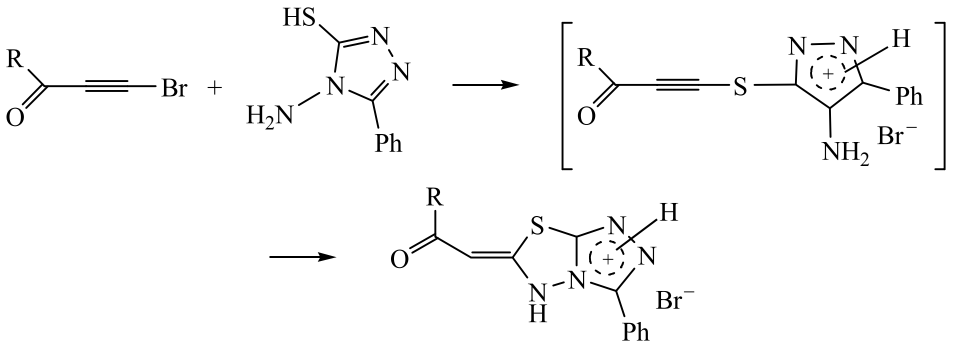
Received September 21, 2011

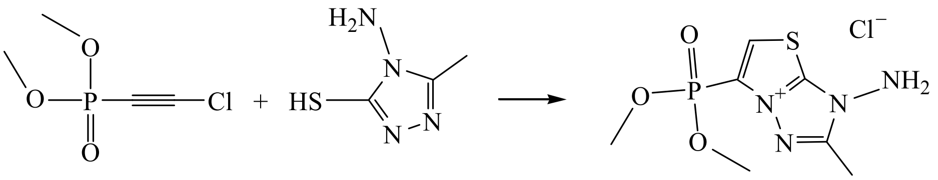
DOI: 10.1134/S1070363211110296

The reaction of 4-amino-3-mercapto-5-phenyl-1,2,4-triazole with 1-bromo-2-acetylenes is known to proceed at 20°C in acetonitrile medium to form the corresponding 2-acylmethylene-5-phenyl-3*H*-1,3,4-thiadiazolo-[2,3-*d*]-1*H*(2*H*)-1,2,4-triazolium bromides. The reaction occurs as a nucleophilic substitution of bromine atom to afford the intermediate ethynyl sulfide followed by the intramolecular cyclization involving the amino group to form the corresponding 1,3,4-thiadiazolo-1,2,4-triazolium bromide [1]:



R = Ph, 2-thienyl.

We found that the reaction of dimethyl chloroethynephosponate with 4-amino-3-mercapto-5-methyl-1,2,4-triazole proceeds readily under the same conditions and run chemoselective through the similar substitution of the chlorine atom, but the subsequent cyclization takes place involving the nitrogen atom in 2 position of the triazole ring to give the triazolium heterocyclic salt. The NH_2 fragment is not involved into the cyclization:



The reaction was performed in acetonitrile at room temperature by stirring the equivalent amounts of the starting reagents for 3–5 h. The reaction progress was monitored by NMR spectroscopy.

The structure of the obtained compound was confirmed by the ^{1}H, ^{13}C, ^{31}P NMR spectroscopy. Thus, in the ^{1}H NMR spectrum the signals of methoxy groups at phosphorus are the doublets at δ 3.94 ppm

($^3J_{HP}$ 11.6 Hz), the methyl group in the ring induces a singlet at δ 2.72 ppm. The olefinic proton resonance is shifted downfield at δ 8.53 ppm ($^2J_{HP}$ 4.4 Hz). The signals integral intensions in the NMR spectrum confirm the structure of the obtained compounds. In the ^{13}C NMR spectrum the ring methyl group appears as a singlet at δ 10.10 ppm, methoxy groups resonate as a doublet at δ 53.24 ppm with a small coupling constant with the phosphorus nucleus. A doublet signal at δ 119.68 ppm with a large spin–spin coupling constant belongs to the C^1 carbon atom. The C^2 carbon atom is represented by a doublet at δ 126.00 ppm with a small constant of spin-spin interaction.

According to the X-ray diffraction, the obtained compound is a thiazolo[3,2-*b*]-1,2,4-triazolium chloride. The cation is thiazolo[3,2-*b*]-1,2,4-triazole heterocycle. The formal positive charge on the nitrogen atom N^1 causes strong shortening of the N^1–N^2 bond [1.3766(19) Å]. The chloride anion in the crystal is located near to the sulfur atom.

Similar aromatic structures without phosphorus atom are known to form at the intramolecular cyclization of aryl(alkyl)substituted 2*H*-1,2,4-triazolo-β-ketosulfides [2] and cyclodehydration of pyridine- [3] or alkylsubstituted [4] 4*H*-1,2,4-triazolic acids.

3-Amino-6-(dimethoxyphosphoryl)-2-methyl-3*H*-tiazolo[3,2-*b*]-1,2,4-triazol-7-ylium chloride. mp 221–224°C. ^{1}H NMR spectrum, (400.13 MHz, D_2O), δ, ppm: 2.71 s (3H, CH_3), 3.94 d (6H, OCH_3, $^3J_{HP}$ 11.6 Hz), 8.53 d (1H, CH, $^3J_{HP}$ 5.6 Hz). ^{13}C NMR spectrum, (100.61 MHz, D_2O), δ_C, ppm: 10.10 (C^5), 53.24 d (OCH_3, $^2J_{CP}$ 6.0 Hz), 119.68 d (C^1, $^1J_{CP}$ 189.8 Hz), 126.00 d (C^2, $^2J_{CP}$ 12.3 Hz), 154.83 d (C^3, $^3J_{CP}$ 8.7 Hz), 160.56 (C^4, $^3J_{CP}$ 8.7 Hz). ^{31}P NMR spectrum (161.98 MHz, D_2O): δ_P 2.68 ppm.

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