ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 11, pp. 2119–2121. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © A.A. Fazullina, L.V. Ryapisova, L.B. Kashevarova, S.V. Fridland, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 11, pp. 1929–1931.

LETTERS
TO THE EDITOR

Reactions of Benzaldehyde Dimethylhydrazone with Phosphorous Acids

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Received November 26, 2012

DOI: 10.1134/S1070363213110303

As shown previously, reactions of dimethylhydrazones of chloro- and nitrobenzaldehydes with phosphorous acids in the presence of alkali metal alcoholates and triethylamine as catalysts (as well as without the catalysts) led to the corresponding salts rather than to phosphonates [1].

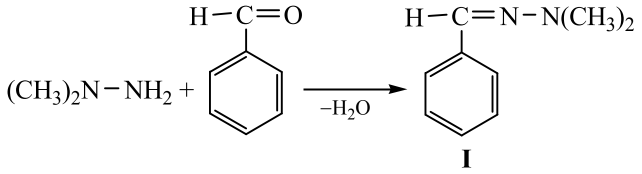
Phosphorylated hydrazones could only be obtained via the intermediate formation of α-oxyphosphonates [2].

The attempt to reduce the dealkylating ability of dimethylamino group of hydrazones by prior synthesis of dimethylammonium salt of hydrazone also led to phosphoramidate instead of the desired phosphonate [3].

The peculiarities of the above-mentioned processes were due to the effects of the aromatic ring substituents [3]. Therefore, it was of interest to investigate the reactions of unsubstituted benzaldehyde dimethylhydrazone with diethyl and diphenyl phosphites.

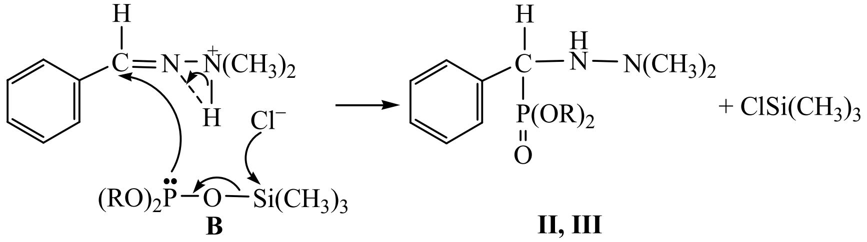
Benzaldehyde *N*,*N*-dimethylhydrazone **I** was prepared via the reaction of benzaldehyde with unsymmetrical dimethylhydrazine.

The reactions of the so obtained hydrazone with diethyl and diphenyl phosphites were performed under different conditions.



In the classic Pudovik reaction, the bases (various amines) are used as catalysts. However, the reaction in the presence of triethylamine as a catalyst did not lead to the phosphonates.

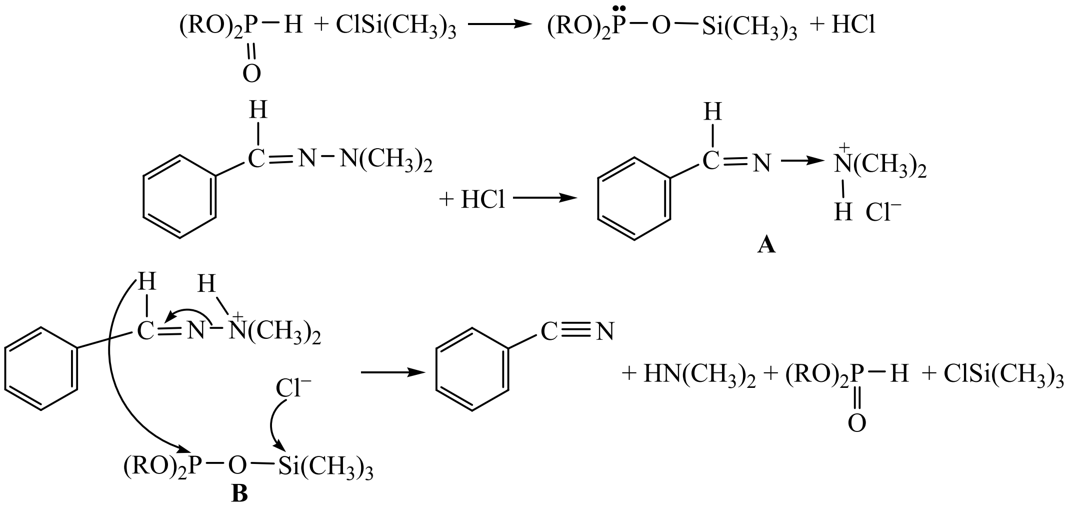
Trimethylchlorosilane is known to affect the reactions of phosphorous acids with olefins resulting in phosphonates. In particular, it reacts with diethyl phosphite to form trimethylsilyldiethyl phosphite and hydrogen chloride, changing pH of the medium. It is known that the presence of acidic impurities in phosphoric acids promoted the phosphonates formation [4]. Basing on that knowledge, we introduced the catalytic amount of trimethylchlorosilane to the reaction of benzaldehyde dimethylhydrazone **I** with diethyl phosphite. As a result, diethyl(1-phenyl-1-dimethylhydrazino)phosphonate **II** was isolated in the form of white crystalline substance. Its structure was confirmed by elemental analysis, IR, and ^{31}P NMR spectroscopy data.



R = C_2H_5 (**II**), C_6H_5 (**III**).

In the case of diphenyl phosphite, which was not capable of dealkylation, the reaction with hydrazone **I** proceeded in the absence of trimethylchlorosilane to give the target phosphonate **III**. However, the reaction was very slow. Introduction of trimethylchlorosilane significantly accelerated it.

When phosphorylation of **I** was performed at 90–110°C, the reactions with both diethyl and diphenyl phosphites resulted in benzonitrile **IV**. This could be explained by the fact that at high temperatures the quaternary hydrazone **A** did not form the intermediate adduct **B**, and the reaction started with the N–N bond rupture. The reaction scheme could be represented as follows.



Benzaldehyde *N*,*N*-dimethylhydrazone (I). A mixture of 12.4 g (0.11 mol) of benzaldehyde and 17.7 g (0.29 mol) of *N*,*N*-dimethylhydrazine was stirred at room temperature during 2 h and then at 45°C during 1 h. The target hydrazone was isolated by vacuum distillation. Yield 66.78% (11.56 g), bp 119–120°C (15 mm Hg), n_D^{20} 1.5986, d_4^{20} 0.9983 g cm^{-3}. IR spectrum, ν, cm^{-1}: 1570 (C=N), 740, 1520, 1600 (C_6H_5). Found, %: C 72.23; H 8.02; N 18.45. $C_7H_{12}N_2$. Calculated, %: C 72.97; H 8.11; N 18.92.

Diethyl 1-phenyl-1-dimethylhydrazinophosphonate (II). 4.7 g (0.03 mol) of diethyl phosphite and 1–2 drops of trimethylchlorosilane were added to 5.1 g (0.04 mol) of **I**. The mixture was stirred during 3 h at 60°C. The precipitate was washed with acetone and vacuum-filtered off. Yield 55% (2.6 g), mp 127°C. IR spectrum, ν, cm^{-1}: 1280 (P=O), 3300–3400 (NH). ^{31}P NMR spectrum: δ_P 18.26 ppm. Found, %: C 53.55; H 8.15; N 9.54; P 10.23. $C_{13}H_{23}N_2O_3P$. Calculated, %: C 54.56; H 8.36; N 9.76; P 10.8.

Diphenyl 1-phenyl-1-dimethylhydrazinophosphonate (III). 8 g (0.03 mol) of diphenyl phosphite and 1–2 drops of trimethylchlorosilane were added to 5.1 g (0.04 mol) of **I**. The mixture was stirred during 1 h at 60°C and distilled under reduced pressure. Yield 38% (4.93 g), bp 107–109°C (22 mm Hg). IR spectrum, ν, cm^{-1}: 1270 (P=O), 3300–3400 (NH). ^{31}P NMR spectrum: δ_P 20.74 ppm. Found, %: C 64.98; H 6.35; N 7.54; P 8.23. $C_{21}H_{23}N_2O_3P$. Calculated, %: C 65.8; H 6.27; N 7.31; P 8.09.

Benzonitrile (IV). *a*. A mixture of 6 g (0.04 mol) of **I**, 7.3 g (0.05 mol) of diethyl phosphite, and 0.5 g of trimethylchlorosilane was stirred for 3 h at 89–90°C, and then distilled under reduced pressure. Yield 19.38% (0.81 g), bp 105–107°C (20 mm Hg), n_D^{20} 1.5246, d_4^{20} 0.9991 g cm^{-3}. IR spectrum, ν, cm^{-1}: 2225 (C≡N), 740, 1520, 1600 (C_6H_5). Found, %: C 85.51; H 1.0; N 14.02. C_7H_5N. Calculated, %: C 84.85; H 1.01; N 14.14.

b. A mixture of 4.2 g (0.028 mol) of **I**, 8.63 g (0.037 mol) of diphenyl phosphite, and 0.5 g of trimethylchlorosilane was stirred during 3 h at 109–110°C, and then distilled under reduced pressure. Yield 52.40% (4.45 g), bp 82–84°C (13 mm Hg). IR spectrum, ν, cm^{-1}: 2229 (C≡N), 740, 1520, 1600 (C_6H_5). Found, %: C 85.01; H 1.0; N 14.35. C_7H_5N. Calculated, %: C 84.85; H 1.01; N 14.14.

IR spectra (suspension in mineral oil) were recorded with UR-20 spectrometer. ^{31}P NMR spectra were registered with Bruker WM-250 spectrometer operating at 101.27 MHz.

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