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6-PHOSPHORYL-1,3,4-THIADIAZINES

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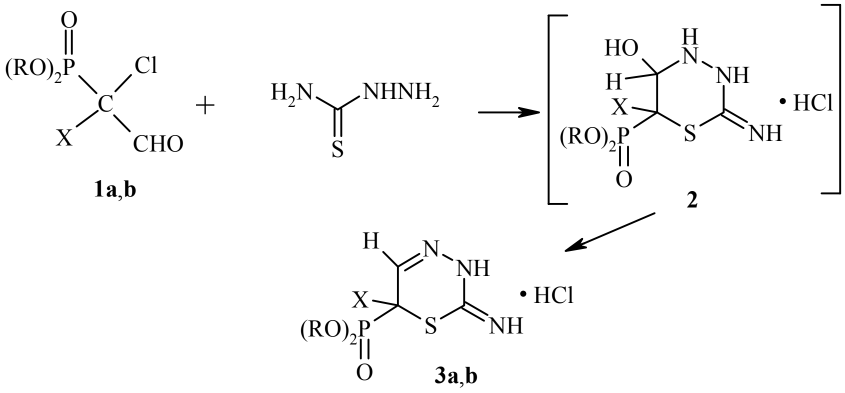
The heterocyclization of α-halocarbonyl compounds with thiosemicarbazides proceeds to give thiazoles [1], pyrazoles [2], thiazolines [3], thiadiazines [4], and other compounds [5] depending on the nature of the starting electrophilic substrate and the reaction conditions.

We thus undertook a study of the reactions of phosphoryl-α-chloroacetaldehydes **1a** and **1b** with thiosemicarbazide to establish the nature of the condensation products formed and develop a synthesis for C-phosphorylated heterocycles.

The cyclocondensation of chloro aldehydes **1** with thiosemicarbazide proceeds in ether solution at -5°C. The ${}^{1}H$, ${}^{13}C$, and ${}^{31}P$ NMR spectral data indicated the formation of thiadiazine **3**.



1, **3** **a** R = *i*-Pr, X = H; **b** R = Et, X = Ph

The finding of two doublets of doublets in the vicinity of 4.6 and 7.6 ppm with coupling constants ${}^{2}J_{HH} = 7.5$, ${}^{2}J_{PH} = 13.75$, and ${}^{3}J_{PH} = 3.75$ Hz, respectively, and the lack of a signal at about 5 ppm characteristic for the methine proton in hemiaminals suggest the formation of thiadiazine **3** and not intermediate hemihydrazinal **2**. The azomethine proton in the ${}^{1}H$ NMR spectrum of **3b** appears at 7.8 ppm as a doublet with coupling constant ${}^{3}J_{PH} = 7.5$ Hz.

The chemical shifts of the phosphorus nuclei in **3a** and **3b** are at 13.1-13.5 ppm.

6-(Diisopropoxyphosphoryl)-2-imino-3H,6H-1,3,4-thiadiazine Hydrochloride (3a). Aldehyde **1a** (0.98 g, 4 mmol) in ether (15 ml) was added with stirring and cooling to -5°C to a suspension of thiosemicarbazide (0.37 g, 4 mmol) in ether (15 ml). The reaction mixture was stirred at room temperature for 6 h and the solvent was then removed. A mixture of 1:1 ether–acetonitrile was added to the residue. The

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crystalline precipitate was filtered off, washed with ether, and recrystallized from acetonitrile to give 1.1 g (86%) of compound **3a**; mp 120-122°C. IR spectrum, ν, cm^{-1}: 1287 (P=O), 1630 (C=N), 3200 (NH). ^{31}P NMR spectrum (32 MHz, $CHCl_3$, 85% H_3PO_4 as the standard), δ, ppm: 13.1. ^{1}H NMR spectrum (100 MHz, $CDCl_3$, HMDS as the internal standard), δ, ppm, (*J*, Hz): 1.30 (12H, dt, $4CH_3$); 4.60 (1H, dd, $^2J_{HH}$ = 7.5, $^2J_{PH}$ = 13.75, CHS); 5.00 (2H, m, 2OCH); 6.90 (1H, br. s, NH); 7.20 (1H, br. s, $^+$NH); 7.60 (1H, dd, $^3J_{HH}$ = 7.5, $^3J_{PH}$ = 3.75, =CHN); 11.40 (1H, br. s, =NH). ^{13}C NMR spectrum (100 MHz, $CDCl_3$, TMS as the internal standard), δ, ppm, (*J*, Hz): 182.5 (s, S–C=NH), 140.82 (s, C=N), 55.8 (d, $^1J_{C,P}$ = 50, P–CH–S), 49.75 (d, $^1J_{C,H}$ = 162, P–CH–S). Found, %: Cl 11.42; N 13.36; P 9.91; S 10.20. $C_9H_{19}ClN_3O_3PS$. Calculated, %: Cl 11.25; N 13.31; P 9.83; S 10.14.

6-(Diethoxyphosphorylphenyl)-2-imino-3H-1,3,4-thiadiazine (3b) was obtained analogously from aldehyde **1b** (1.18 g, 4 mmol) and thiosemicarbazide (0.37 g, 4 mmol). Yield of compound **3b** 1.3 g (88%); mp 128-130°C. ^{31}P NMR spectrum (32 MHz, $CHCl_3$, 85% H_3PO_4 as the standard), δ, ppm: 13.5. ^{1}H NMR spectrum (100 MHz, $CDCl_3$, HMDS as the internal standard), δ, ppm, (*J*, Hz): 1.00 (6H, dt, $2CH_3$); 4.00 (4H, m, $2OCH_2$); 7.30 (1H, br. s, $^+$NH); 7.50 (5H, m, Ph); 7.80 (1H, d, $^3J_{PH}$ = 7.5, =CHN); 11.00 (1H, br. s, =NH). Found, %: Cl 9.81; N 11.64; P 8.62; S 8.86. $C_{13}H_{19}ClN_3O_3PS$. Calculated, %: Cl 9.77; N 11.55; P 8.53; S 8.80.

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