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2-DIALKOXYPHOSPHORYL-1,4-DIHYDROBENZODIAZINES

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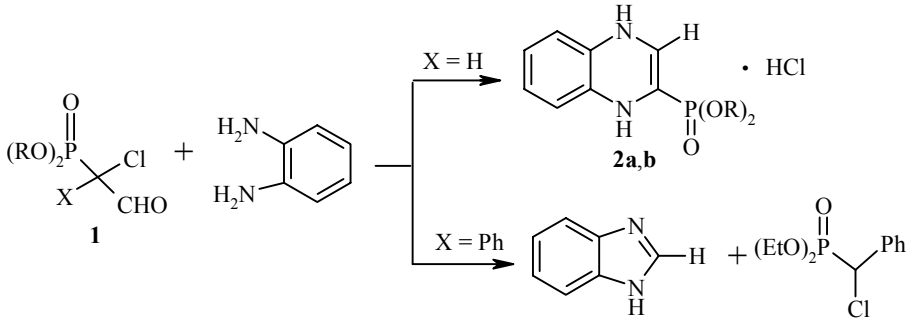
The condensation of α-halocarbonyl compounds with *o*-phenylenediamine proceeds to give linear enamines [1], benzodiazines [2], and benzimidazole (cleavage of a carbon–carbon bond) [3]. Hence, it was of interest to study the reactions of chlorophosphorylacetaldehydes **1** with *o*-phenylenediamine.

The reaction of chloro aldehydes **1a-1c** with *o*-phenylenediamine proceeds through two pathways. 1) Chloro aldehydes **1a** and **1b** undergo heterocyclization to give phosphorylated benzodiazines **2**. 2) In the case of chloro aldehyde **1c**, a C–C bond is broken to give benzimidazole and chlorobenzylphosphonate.



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

2-Diethoxyphosphoryl-1,4-dihydrobenzodiazine Hydrochloride (2a). A solution of aldehyde **1a** (0.86 g, 4 mmol) in ether (5 ml) was added with stirring to a solution of *o*-phenylenediamine (0.43 g, 4 mmol) in ether (20 ml) at 0°C. The reaction mixture was stirred with cooling for 1 h and at room temperature for 2 h. The precipitate of **2a** was filtered off and recrystallized from ethanol–acetonitrile to give 1.03 g (84%) **2a**, mp 112-113°C. IR spectrum, ν, cm^{-1}: 1280, 1635, 3200. ^{31}P NMR spectrum, δ, ppm: 13.0. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J* (Hz): 1.10 (6H, t, $2CH_3$); 4.00 (4H, m, $2OCH_2$); 6.80 (2H, q, Ph); 7.15 (2H, q, Ph); 7.80 (1H, d, $^{2}J_{PH}$ = 7.5, CH); 13.25 (1H, s, NH); 14.10 (1H, s, NH). Found, %: Cl 11.85; N 9.17; P 10.31. $C_{12}H_{18}ClN_2O_3P$. Calculated, %: Cl 11.66; N 9.19; P 10.18.

2-Diisopropoxyphosphoryl-1,4-dihydrobenzodiazine Hydrochloride (2b) was obtained analogously in 87% yield; mp 121-122°C. IR spectrum, ν, cm^{-1}: 1285, 1640, 3250. ^{31}P NMR spectrum: 13.16. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J* (Hz): 1.15 (12H, t, $4CH_3$); 4.50 (2H, m, 2OCH); 6.90 (2H, q, Ph); 7.10 (2H, q, Ph); 7.80 (1H, d, $^{3}J_{PH}$ = 7.5, CH); 13.30 (1H, s, NH); 14.20 (1H, s, NH). Found, %: Cl 10.76; N 8.54; P 9.45. $C_{14}H_{22}ClN_2O_3P$. Calculated, %: Cl 10.68; N 8.42; P 9.32.

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Reaction of Aldehyde 1c with *o*-Phenylenediamine. A solution of *o*-phenylenediamine (0.43 g, 4 mmol) in ether (20 ml) was added with stirring dropwise to a solution of aldehyde **1c** (1.16 g, 4 mmol) in ether at from 0 to -5°C. The precipitate of benzimidazole was filtered off and the filtrate was evaporated. Distillation of the residue in vacuum using an oil pump gave the diethyl ester of α-chlorobenzylphosphonic acid.

Benzimidazole was obtained in 85.1% yield (0.4 g); mp 169-170°C (identical with the reported value [4]). A mixed probe did not give a depressed melting point.

Diethyl Ester of α-Chlorobenzylphosphonic Acid was obtained in 95.2% yield (1.0 g); bp 115-116°C (0.05 mm Hg). ^{31}P NMR spectrum: 17.1. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.15 (6H, dt, $2CH_3$); 4.00 (4H, m, $2OCH_2$); 4.90 (1H, d, CHCl); 7.35 (5H, m, Ph). Found, %: Cl 13.57; P 11.85. $C_{11}H_{16}ClO_3P$. Calculated, %: Cl 13.52; P 11.81.

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