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LETTERS TO THE EDITOR

Synthesis and Acid-Base Properties of Some New γ-Aminophosphoryl Compounds

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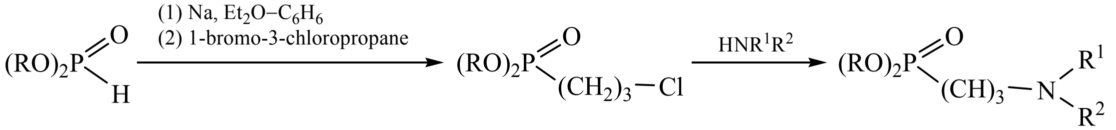
We have previously determined the dissociation constants of acids conjugated with α- [1] and β-aminophosphoryl compounds [2] in an aqueous propan-2-ol medium. The basicity was shown to be reduced by 4–5 or 2–3 pK_a units in the case of introducing one or two methylene groups respectively between the phosphorus and nitrogen atoms. In this work we present data on the acid-base properties of their γ-analogs, γ-aminopropylphosphonates **I**–**IV**. They were synthesized by the amination of the corresponding dialkyl 3-chloropropylphosphonates obtained by the Michaelis–Becker reaction of dialkyl phosphites with 1-bromo-3-chloropropane [3].



R = i-C_3H_7, R^1 = H, R^2 = C_4H_9 (**I**); R, R^2 = C_4H_9, R^1 = H (**II**); R = cyclo-C_6H_{11}, R^1 = H, R^2 = C_4H_9 (**III**); R = C_4H_9, R^1, R^2 = C_8H_{17} (**IV**).

Using the potentiometric titration in an aqueous (50 vol %) propan-2-ol medium by the procedure [1], we determined the ionization constants (pK_a ±0.05) of γ-phosphorylamines **I**, **III**, and **IV** at 298±0.2 K, which equaled 9.99, 7.46 and 6.84, respectively. Comparing these values with the pK_a values of such amines-precursors as butyl amine, dibutyl amine, and dioctyl amine measured under the same conditions (9.74, 9.60, and 8.98, respectively), it is possible to say that the phosphorylation of amines with the 3-phosphorylpropyl group reduces the basicity of the amine center in the γ-phosphoryl amines **III** and **IV** by an average of 2 units, and in the primary butylamine it practically does not change. The reason for the higher basicity of the secondary phosphoryl amines has been discussed in [1, 2]. Thus, the obtained results are in good agreement with the previously determined regularity: The effect of the electron-withdrawing phosphoryl group on the basicity is reduced as the distance from the amine center increases [2].

The synthesis method and characterization of diisopropyl 3-*N*-butylaminopropylphosphonate **I** was described in [3]. The spectral characteristics of compounds **II** and **III** will be reported later.

Dibutyl 3-*N*-butylaminopropylphosphonate (II). Yield 68%, bp 131°C (0.3 mm Hg), n_D^{20} 1.4425. ^{31}P NMR spectrum, δ_P, ppm: 33 ppm.

Dicyclohexyl 3-*N,N*-dibutylaminopropylphosphonate (III). Yield 59% (after purifying by the oxalate method [4]), yellow oil, n_D^{20} 1.4775. ^{31}P NMR spectrum, δ_P, ppm: 31.0 ppm.

Dibutyl 3-*N,N*-dioctylaminopropylphosphonate (VI). Yield 80%, bp 195°C (40 Pa), n_D^{20} 1.4532. IR spectrum, ν, cm^{-1}: 1249 (P=O), 1024 (P–O–C), 1363 (C–N) (film). ^{1}H NMR spectrum ($CDCl_3$), δ_P, ppm: (*J*, Hz): 0.83 t and 0.87 t (6H, CH_3, C_8H_{17}), 0.88 t and 0.93 t (6H, CH_3, C_4H_9), 1.15–1.80 m {40H, $P[CH_2\underline{(CH_2)}_2CH_3]_2$, $N(CH_2\underline{(CH_2)}_6CH_3)_2$, $P\underline{CH_2}\underline{CH_2}CH_2N$}, 2.33 t {4H, N[$\underline{CH_2}$($CH_2$)$_6$$CH_3$]$_2$}, 2.40 t (2H, $PCH_2CH_2\underline{CH_2}N$), 3.91–4.01 m {4H, P[$\underline{CH_2}$($CH_2$)$_2$$CH_3$]$_2$}. ^{31}P NMR spectrum, δ_P, ppm: 33.0 ppm.

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