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LETTERS TO THE EDITOR

Phosphorylation of *N*-Acetyl-*N,N'*-ethyleneurea with Phosphorus Pentachloride

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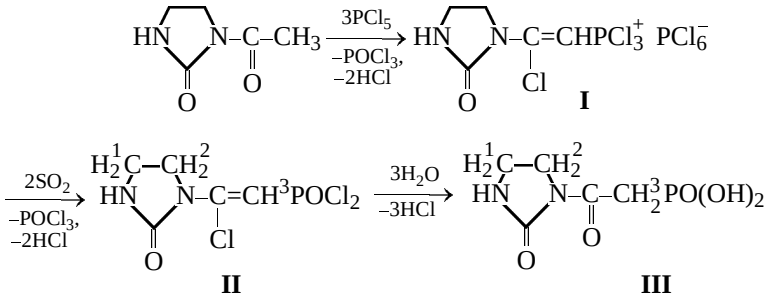
We found that *N*-acetyl-*N,N'*-ethyleneurea (1-acetylimidazolidin-2-one) reacts with PCl_5 to form 2-(2-oxo-1-imidazolidinyl)-2-chloroethenyltrichlorophosphonium hexachlorophosphorate **I**.



Phosphorus pentachloride attacks the oxygen atom of the acetyl group of acetylethyleneurea, but the steric and conformational hindrance in the cyclic ureide moiety does not allow the intramolecular attack of the N–H nitrogen atom by the organyltrichlorophosphonium cation of **I** with the formation of a heterocycle, as we observed previously in phosphorylation of acyclic trisubstituted ureides [1]. Compound **I**, when treated with SO_2, transforms into 2-(2-oxo-1-imidazolidinyl)-2-chloroethenylphosphonic dichloride **II**; its hydrolysis yields 2-oxo-2-(2-oxo-1-imidazolidinyl)ethylphosphonic acid **III**.

Salt I. A solution of 2.0 g of *N*-acetyl-*N,N'*-ethyleneurea in 50 ml of $CHCl_3$ was added dropwise with stirring at room temperature to a solution of 13.0 g of PCl_5 in 100 ml of chloroform. A white finely crystalline precipitate of **I** formed; after standing for a day, it was separated, washed with chloroform, and dried in a vacuum. Yield 6.5 g (79%). ^{31}P NMR spectrum, δ_P, ppm: 80.2 d (PCl_3, $^2J_{PH}$ 38.9 Hz), –295.5 s (PCl_6^-).

Compound II. Dry sulfur dioxide was passed through a suspension of 6.5 g of **I** in 50 ml of chloroform until the crystals fully dissolved. The volatiles were removed in a vacuum, and the residue was recrystallized three times from chloroform. Yield 0.5 g (15%), mp 98–103°C (dec.). ^{1}H NMR spectrum, δ, ppm: 3.52 t (CH_2^1, $^3J_{HH}$ 8.4 Hz), 4.10 t (CH_2^2), 5.38 s (NH), 7.14 d (H^3, $^2J_{HP}$ 21.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 155.98 s (C=O), 143.89 d (CCl, $^2J_{CP}$ 6.5 Hz), 103.28 d (CH^3, $^1J_{CP}$ 176.4 Hz), 45.75 s (CH_2^2), 36.38 s (CH_2^1). ^{31}P NMR spectrum, δ_P, ppm: 27.9 d ($^2J_{PH}$ 21.1 Hz). Found, %: C 23.20; H 2.28; Cl 39.48; N 10.54. $C_5H_6Cl_3N_2O_2P$. Calculated, %: C 22.77; H 2.28; Cl 40.38; N 10.63.

Compound III. A fivefold excess of water was added dropwise with stirring to a suspension of 0.6 g of **II** in dioxane. The resulting solution was kept at room temperature for 30 min, after which the solvent was removed in a vacuum. The residue was recrystallized from ethanol. Yield 0.3 g (65%). Colorless finely crystalline powder, mp 153–154°C (dec.). ^{1}H NMR spectrum, δ, ppm: 3.57 d (CH_2^3, $^2J_{HP}$ 21.8 Hz), 3.28 t

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(CH_2^1, $^2J_{HH}$ 8.2 Hz), 3.75 t (CH_2^2), 7.64 s (NH). ^{13}C NMR spectrum, δ_C, ppm: 35.28 d (CH_2^3, $^1J_{CP}$ 126.3 Hz), 35.33 s (CH_2^1), 42.21 d (CH_2^2), 155.8 s [NC(O)N], 165.7 d [*C*(O)CH_2^3, $^2J_{CP}$ 6.9 Hz]. ^{31}P NMR spectrum, δ_P, ppm: 16.0 t ($^2J_{PH}$ 21.8 Hz). Found, %: C 27.51; H 4.38; N 12.62; P 14.30. $C_5H_9N_2O_5P$. Calculated, %: C 28.86; H 4.36; N 13.46; P 14.88.

The ^1H, ^{13}C, and ^{31}P NMR spectra (solutions in $C_6D_5NO_2$ for **I**, $CDCl_3$ for **II**, and DMSO-d_6 for **III**) were recorded on a Bruker DPX-400 spectrometer, working frequencies 400.13, 100.62, and 161.98 MHz, respectively, internal reference TMS.

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