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LETTERS TO THE EDITOR

Synthesis and Properties of Propargyl Ester of 2-Chloro-2-phenylethenephosponocytisinidic Acid

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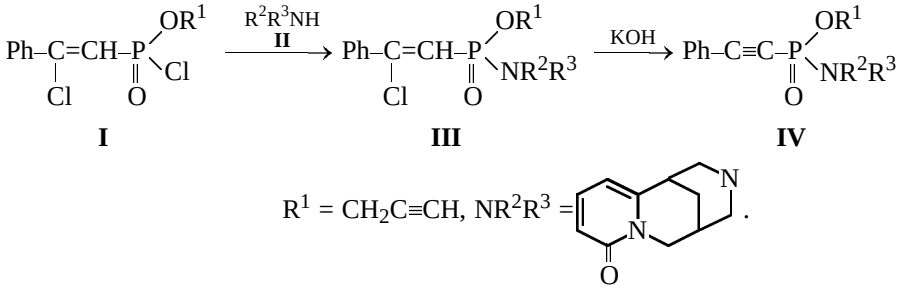
Proceeding with search for new hepatoprotectors in the series of natural alkaloids [1], we studied the reaction of 2-propynyl 2-chloro-2-phenylethenephosphonochloridate **I** [2] with cytisine **II** in absolute benzene in an inert atmosphere.

The product **III** is a colorless crystalline substance readily soluble in organic solvents. It is interesting from the viewpoint of both chemical structure and synthetic potential.

Propargyl 2-chloro-2-phenylethenephosphonocytisinidate **III** readily eliminates HCl on treatment with KOH in ethanol to form propargyl phenylethynephosphonocytisinidate **IV**:



The IR spectra of **III** and **IV** contain characteristic bands of the $C{=}O_{amide}$ (1670–1660 cm^{-1}), P=O (1230–1210 cm^{-1}), and POC (1050–1020 cm^{-1}) fragments. The terminal C≡C bond gives a strong band at about 2160 cm^{-1}.

Propargyl 2-chloro-2-phenylethenephosphonocytisinidate III. A solution of 1 g of cytisine **II** and 0.53 g of triethylamine in benzene was added dropwise with stirring in an inert gas atmosphere at 10–15°C to a solution of 1.43 g of chloride **I** in 20 ml of benzene. The precipitate of triethylammonium chloride was separated, the solvent was removed, and the residue was passed through a column packed with silica gel (eluent benzene). Yield of **III** 1.96 g (88%), mp 208–209°C. ^{1}H NMR spectrum, δ, ppm: 6.48 d (1H, CH^1), 7.10 d (1H, CH^2), 5.85 d (1H, CH^3), 3.20 m (1H, CH^4), 2.0 m (2H, CH^5), 2.58 m (1H, CH^6), 3.82 m (2H, CH^7), 2.44 m (4H, $CH^{8,9}$), 1.10 m (3H, CCH_3), 4.00 s (1H, C≡CH). Found, %: C 61.88; H 5.28; N 6.47. $C_{22}H_{22}ClN_2O_3P$. Calculated, %: S 61.61; H 5.13; N 6.53.

Propargyl phenylethynephosphonocytisinidate IV. A solution of 1 g of **III** in 10 ml of ethanol was slowly added with stirring to a solution of 0.12 g of KOH in 15 ml of anhydrous ethanol. The mixture was stirred for 3 h at room temperature and then for 1 h at 50–60°C. The KCl precipitate was filtered off, and the solvent was removed in a vacuum. The residue was purified by column chromatography on silica gel (eluent benzene), and the target product was isolated as a mobile light yellow oil. Yield 0.69 g (75%).

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Found, %: C 67.21; H 5.50; N 7.03. $C_{22}H_{21}N_2O_3P$. Calculated, %: C 67.34; H 5.35; N 7.14.

The IR spectra were recorded on a UR-20 spectrophotometer (KBr), and the ^1H NMR spectrum, on a Varian Mercury-300 spectrometer (300 MHz, $CDCl_3$, internal reference HMDS).

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