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LETTERS TO THE EDITOR

Phosphorylation of C-Alkenylsubstituted Pyrazoles with Phosphorus Pentachloride

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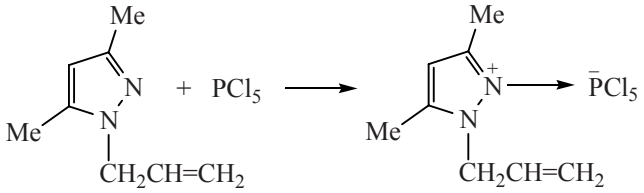
The reaction of phosphorus pentachloride with styrenes affords unsaturated organophosphorus compounds in which the phosphorus chloride substituent is attached to the carbon atom of the double bond [1]. *N*-Vinylsubstituted azoles are also phosphorylated at the double bond [2–3]. Phosphorylation of *C*-alkenylazoles with phosphorus pentachloride was not studied until now.

The presence in the azole cycles the "pyridine" nitrogen atoms with enhanced nucleophilicity could direct the attack of phosphorus pentachloride to the heterocycle rather than to the double bond of *C*-vinylazoles to give donor–acceptor complexes. Indeed, the reaction of phosphorus pentachloride with 1-allyl-3,5-dimethylpyrazole led to formation of the donor–acceptor complex **I**.



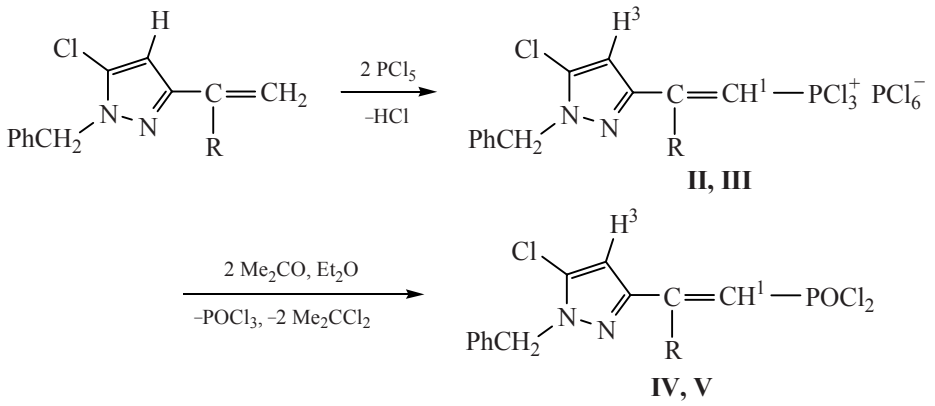
I

In the ^{31}P NMR spectrum of compound **I** a singlet signal at –264.3 ppm characteristic of hexacoordinate phosphorus atom [3] is observed.

It was established that 1-benzyl-5-chloro-3-vinyl-1*H*-pyrazole and 1-benzyl-5-chloro-3-isopropenyl-1*H*-pyrazole are phosphorylated with phosphorus pentachloride at the vinyl and isopropenyl groups to afford organyltrichlorophosphonium hexachlorophosphates **II** and **III**. Hexachlorophosphates **II, III** readily undergo conversion into phosphonic acids dichlorides **IV, V** upon the action of acetone in di-ethyl ether.

2-(1-Benzyl-5-chloro-1*H*-pyrazol-3-yl)-1-propenyltrichlorophosphonium hexachlorophosphate (III). The solution of 0.5 g of 1-benzyl-5-chloro-3-isopropenyl-1*H*-pyrazole in 2 ml of benzene was added dropwise upon stirring to the solution of 1.5 g of phosphorus pentachloride in 5 ml of benzene. Compound **III** is isolated as a heavy oil crystallized overnight to give yellow crystals hydrolyzed in the air. Yield of **III** 1.2 g (91%). ^{31}P NMR spectrum ($MeNO_2$), δ_P, ppm: 77.0 d (PCl_3^+, $^2J_{PH}{}^1$ 60.3 Hz); –294.4 s (PCl_6^-).

2-(1-Benzyl-5-chloro-1*H*-pyrazol-3-yl)-1-propenylphosphonic acid dichlorides (V). 1.2 g of compound **III** was treated with the solution of 1 ml of acetone in 3 ml of diethyl ether and after the solution was formed the volatile products were removed in vacuum. Compound **V** is formed as an orange oil. Yield 0.63 g (92%). ^{1}H NMR spectrum, δ, ppm: 2.34 d (3H, CH_3, $^4J_{PH}$ 1.2 Hz); 5.36 s (2H, CH_2); 6.18 d (1H, H^1, $^2J_{PH}{}^1$



R = H^2 (**II, IV**), Me (**III, V**).

34.3 Hz); 6.79 s (1H, H^3); 7.28–7.35 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 24.81 d (CH_3, $^3J_{CP}$ 26.8 Hz), 53.56 s (CH_2), 106.68 s (C^4), 121.42 d (CH^1, $^1J_{CP}$ 150.4 Hz), 127.51, 127.88, 128.24, 128.82 (Ph), 135.12 s (C^3), 146.99 d (*C*Me, $^2J_{CP}$ 9.9 Hz), 152.01 s (C^5). ^{31}P NMR spectrum, δ_P, ppm: 28.9 d ($POCl_2$, $^2J_{PH^1}$ 34.3 Hz). Found, %: C 44.25; H 3.51; Cl 29.17; N 9.02; P 8.43. $C_{13}H_{12}Cl_3N_2OP$. Calculated, %: C 44.67; H 3.46; CI 30.42; N 8.01; P 8.86.

^1H, ^{13}C and ^{31}P NMR spectra were registered on a Bruker DPX 400 spectrometer in $CDCl_3$ at working frequencies of 400.13, 100.62 and 161.98 MHz, respectively. ^1H and ^{13}C chemical shifts were measured relative to TMS, ^{31}P chemical shifts relative to H_3PO_4.

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