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LETTERS TO THE EDITOR

Reaction of Diethyl 2-phenylethylphosphonite with Methyl Phenylpropiolate

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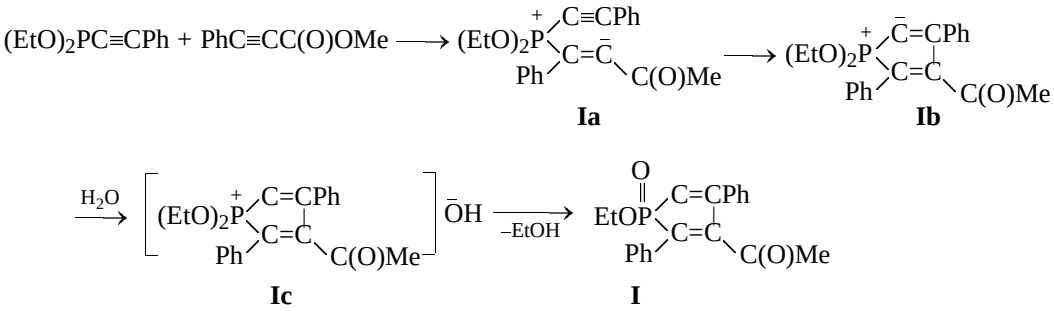
Addition of α,β-unsaturated P(III) derivatives to electron-deficient unsaturated systems such as alkenes and alkynes may be accompanied by intramolecular cyclization. The possibility of formation of cyclic intermediates in such reactions was first noted in the course of studying the reaction of diphenyl(1-phenylethenyl)phosphine with acrylonitrile. When performed in the presence of aromatic aldehydes, the reaction yielded phosphine oxides whose structure suggested the occurrence of the Wittig reaction between the unstable cyclic ylide and the aldehyde [1]. The reaction of diphenyl(vinyl)phosphine with dimethyl acetylenedicarboxylate in the presence of water (1 : 1 : 1 reactant ratio) yielded the acyclic phosphine oxide, presumably originating from the hydrolysis of the intermediate cyclic ylide [2]. Phosphorus-containing heterocycles were not obtained in the above studies as final products, apparently because the conditions did not favor preservation of the cyclic structure of the formed ylides, primarily owing to the presence of two phenyl substituents with the strong $P–C_{arom}$ bonds at the phosphorus atom.

Contrastingly, we found that, under similar conditions (110°C and the equimolar amount of water), diethyl (2-phenylethynyl)phosphonite reacts with methyl phenylpropiolate to give a heterocyclic compound, 3-methoxycarbonyl-2,4-diphenyl-1-oxo-1-ethoxy-λ^5-phosphole **I**, as the major final product.



The ^{31}P NMR spectrum of the reaction mixture contains two signals with the chemical shifts δ_P 47.2 ppm and 14.2 ppm (intensity ratio 2 : 1). The major signal belongs to phosphole **I**, and the minor signal can be tentatively assigned to the acyclic phosphinate $(EtO)_2P(O)(CPh{=}CHCOOMe)(C{\equiv}CPh)$ arising from protonation of bipolar ion **Ia**. Phosphole **I** is a colorless crystaline substance. Its ^{31}P NMR spectrum contains a signal at δ_P 47.2 ppm characteristic of the five-membered phosphorus-containing heterocycles with the C–P(O)–C bond system [3]. The cyclic structure of **I** was confirmed by the presence of the signal of the olefinic proton in the ^1H NMR spectrum (doublet, δ 6.03 ppm, $^2J_{PH}$ 25.8 Hz), and also by the absence of the C≡C absorption band in the IR spectrum.

Note that this result was obtained at slow addition of a mixture of methyl phenylpropiolate and water to the phosphonite. When water was added after brief

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refluxing of phosphonite with methyl propiolate, the reaction mixture became tarry. According to ^{31}P NMR spectrum, it contained five organophosphorus compounds.

Contrary to the above-mentioned [2] reaction of diphenyl(vinyl)phosphine with dimethyl acetylenedicarboxylate, formation of heterocycle **I** is probably favored by two factors. One of them is the presence of the ethoxy group at the phosphorus atom of diethyl (2-phenylethynyl)phosphonite, which is capable of dealkylation in the intermediate cyclic phosphorane **Ib** with the thermodynamically favorable formation of the P=O bond. The other factor is the formation of phosphole which is more stable than phospholene, the product that could be formed in the reaction involving ethylenic phosphonites.

3-Methoxycarbonyl-2,4-diphenyl-1-oxo-1-ethoxy-λ^5-phosphole I. A mixture of 0.01 mol of methyl phenylpropiolate, 0.01 mol of water, 5 ml of toluene, and 5 ml of dioxane was added dropwise over a period of 30 min to a refluxing solution of 0.001 mol of phosphonite in 10 ml of toluene. The mixture was refluxed for 1 h, after which the solvent was removed at reduced pressure. The residue was treated with 10 ml of ether and kept at 0°C for a day. The crystals of phosphole **I** were filtered off and recrystallized from benzene. Yield 31%, mp 133–134°C. IR spectrum, ν, cm^{-1}: 1020 (P–O–C), 1230 (P=O), 1720 (C=O). ^1H NMR spectrum, δ, ppm: 1.24 t (3H, CH_3), 3.58 s (3H, OCH_3), 4.08 m (2H, OCH_2), 6.03 d (1H, CH=, $^2J_{PH}$ 25.8 Hz), 7.30–7.68 m (10H, $2C_6H_5$). ^{31}P NMR spectrum: δ_P 47.2 ppm. Found, %: C 67.52; H 5.50; P 8.91. $C_{20}H_{19}O_4P$. Calculated, %: C 67.79; H 5.40; P 8.74.

The IR spectrum of phosphole **I** was recorded on an IKS-29 spectrometer in KBr pellet. The ^1H NMR spectrum of phosphole was measured on a Bruker AM-500 spectrometer (500.1 MHz) with the internal stabilization by the resonance line of ^2H in $CDCl_3$. The ^{31}P NMR spectra were recorded on a Bruker AC-200 spectrometer (81.4 MHz) in $CDCl_3$ against 85% H_3PO_4.

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