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LETTERS TO THE EDITOR

First Example of Direct Phosphorylation of Vinyl Silanes with Elemental Phosphorus in Superbasic Media

A. V. Artem'ev, N. K. Gusarova, A. O. Korocheva, E. A. Matveeva, and B. A. Trofimov

A.E. Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: boris_trofimov@irioch.irk.ru

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The reaction of elemental phosphorus in the presence of strong bases with acetylenes, electrophilic alkenes, and organyl halides discovered and successfully developed during the last decades became a new general approach to the formation of the carbon–phosphorus bond and led to new convenient chlorine-free methods of synthesis of earlier unknown or inaccessible organic phosphines, phosphine oxides, and phosphinic acids [1–3]. So far, electrophilic alkenes utilized in this reaction were aryl- and hetaryl-substituted ethenes (styrenes, 2-vinylnaphthalene, vinylpyridines [1–3]), as well as allylbenzenes [4] and 1*H*-indene [5].

Here we present the first example of direct phosphorylation with elemental (red) phosphorus of vinyltrimethylsilane in the superbasic medium KOH/DMSO. The reaction proceeds in the presence of small amounts of water on heating (100°C, 3 h) and, after acidification of the reaction mixture, leads to 2-(trimethylsilyl)ethylphosphinic acid **1** in 5% yield. The yield of acid **1** is not increased when carrying out the reaction under milder conditions (Scheme 1, 60°C, 3 h).

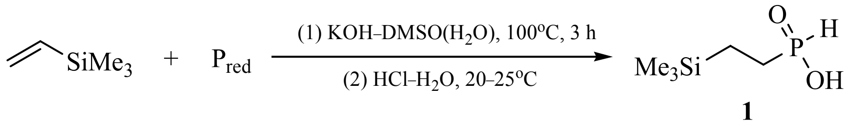
Under the given conditions the major phosphorus-containing product of the reaction was found to be potassium hypophosphite (δ_P = 3.2 ppm, triplet, $^1J_{PH}$ 461 Hz) formed by alkaline hydrolysis of elemental phosphorus. The low yield of acid **1** is apparently due to the ease of splitting of the C_{sp2}–Si bond of vinyltrimethylsilane in highly basic medium with elimination of ethylene.

Note that acid **1** was prepared earlier in 50% preparative yield (85% yield from NMR) by radical addition of sodium hypophosphite to vinyltrimethylsilane in air in the presence of Et_3B (100 mol %) [6].

Thus, by the example of vinyltrimethylsilane we have demonstrated for the first time the principal possibility of direct phosphorylation of vinylsilanes with elemental phosphorus in superbasic conditions.

2-(Trimethylsilyl)ethylphosphinic acid (1). To the heated at 100°C and vigorously stirred suspension of red phosphorus (3.10 g, 100 mmol), ground alkali $KOH·0.5H_2O$ (8.00 g, 123 mmol), DMSO (40 mL) and H_2O (1 mL) in the course of 1 h the solution of vinyltrimethylsilane (8.00 g, 80 mmol) in DMSO (10 mL) was added dropwise. The reaction mixture was stirred for 3 h at the same temperature, cooled to 20–25°C, and diluted with distilled water (50 mL). The insoluble residue was filtered off, the filtrate was acidified with 35% aqueous HCl solution to pH = 1 and extracted with chloroform (3 × 20 mL). Chloro-

Scheme 1.



form extracts were washed with water (2 × 20 mL), dried over Na_2SO_4, the solvent was removed, the residue was dried in a vacuum (30°C, 1 mmHg) to obtain 0.70 g (5%) of acid **1**. Colorless crystals, mp 53–55°C (hexane). ^{1}H NMR spectrum, δ_H, ppm (*J*, Hz): 0.00 s (9H, Me), 0.65–0.72 m (2H, CH_2P), 1.62–1.70 m (2H, CH_2Si), 7.01 d (1H, PH, $^1J_{PH}$ 540), 12.27 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): –2.3 (Me), 5.9 d (CH_2Si, $^2J_{PC}$ 1.7), 23.2 d (CH_2P, $^1J_{PC}$ 91.7). ^{31}P NMR spectrum, δ_P, ppm (*J*, Hz): 39.4 d ($^1J_{PH}$ 540 Hz). ^{29}Si NMR spectrum, δ_{Si}, ppm (*J*, HHz): 3.5 d ($^3J_{PSi}$ 28.5). IR spectrum (film), cm^{-1}: 2384 ($\nu_{P–H}$), 1660 br ($\nu_{O–H}$), 1250 ($\nu_{Si–C}$), 1181 ($\nu_{P=O}$), 981 ($\nu_{P–O}$), 694 ($\nu_{P–C}$). Found, %: C 36.26; H 9.25; P 18.45. $C_5H_{15}O_2PSi$. Calculated, %: C 36.13; H 9.10; P 18.63.

^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were registered in $CDCl_3$ solution on a DPX-400 spectrometer (400.1, 100.6, 161.9, and 79.5 MHz, respectively). IR spectrum was recorded on a Bruker AV-400 spectrometer. Commercial vinyltrimethylsilane, red phosphorus, $KOH·0.5H_2O$ and DMSO (0.5% H_2O) were used.

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