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LETTERS
TO THE EDITOR

Nucleophilic Addition of Phosphine to 1-Vinylimidazole

N. K. Gusarova, S. I. Verkhoturova, S. N. Arbuzova, T. I. Kazantseva, and B. A. Trofimov

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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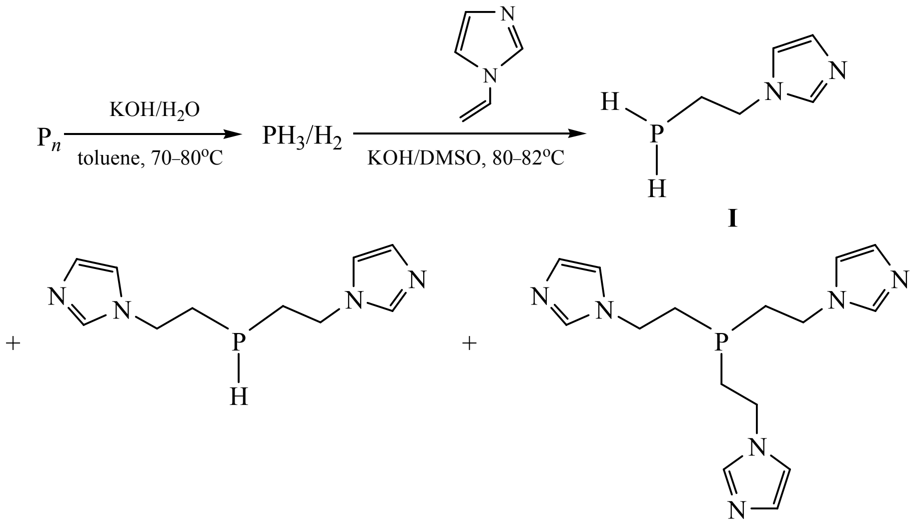
Phosphine is one of the most available and efficient phosphinating reagents because of the elaborated method of its generation *in situ* from red phosphorus and potassium hydroxide in water-organic medium [1–3]. Based on the reactions of radical and nucleophilic addition of phosphine to various alkenes {styrenes [1, 4], vinylnaphthalene [3, 5], vinylpyridines [2, 3, 6], vinylchalcogenides [7, 8], and aryl (hetaryl)acetylenes [2, 3, 9]} the earlier unknown or difficulty accessible secondary and tertiary phosphines and their derivatives have been obtained, which are potential ligands for the design of metal complex catalysts and building blocks for organophosphorous synthesis. Therefore, the elaborated chlorine-free method for the preparation of organic phosphines is an obvious alternative to the synthesis of organophosphorus compounds with the use of phosphorus halides.

In the present work, this procedure is further developed by the example of the reaction studied for the first time of phosphine with 1-vinylimidazole, whose typical reactions are the processes of radical addition [10] and radical polymerization [11].

Recently it was shown that at the UV irradiation or in the presence of azobisisobutyronitrile (AIBN) 1-vinylimidazole readily reacts with secondary phosphines [12] and phosphinechalcogenides [13] to give the corresponding tertiary phosphines and phosphinechalcogenides. The addition of diphenylphosphine to 4-*tert*-butyl-1-vinylimidazole in the presence of large amounts of *t*-BuOK and *n*-BuLi (>40 mol %) was also reported [14].

Our experiments have shown that the reaction of phosphine with 1-vinylimidazole under the conditions of free-radical initiation (AIBN, 78–80°C, 7 h, dioxane, atmospheric pressure) is of low effectivity (conversion of 1-vinylimidazole is 23%) and practically gives no organic phosphines (according to the data of



I

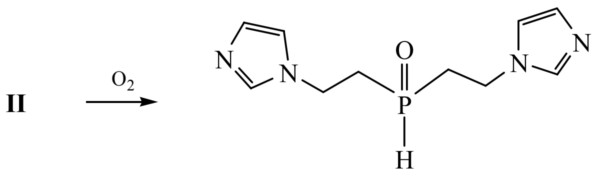
II

III

^{31}P NMR spectroscopy and elemental analysis). The oligomer of 1-vinylimidazole containing small amounts of phosphorus (up to 3 mass%, corresponding to 1 molecule of phosphine per 9 molecules of 1-vinylimidazole) was isolated.

In contrast, it turned out that in the superbasic suspension KOH–DMSO (with a small content of water) phosphine reacts with 1-vinylimidazole at heating (80–82°C) with the formation of the *anti*-Markovnikov adducts: primary (**I**), secondary (**II**), and tertiary (**III**) phosphines. Phoshine was generated mixed with hydrogen from red phosphorus and KOH in water-toluene medium and used in the reaction of phosphination without isolation and purification.

When slowly adding 1-vinylimidazole to the suspension KOH–DMSO (H_2O) saturated with phosphine simultaneously passing phosphine we were able to obtain the secondary phosphine **II** isolated in 15% yield as the corresponding phosphine oxide **IV**.



IV

Therefore, by the example of the reaction of 1-vinylimidazole with phosphine it was shown that vinylimidazoles can be involved not only in the radical processes traditional for them but also react with phosphorus-centered nucleophiles in superbasic media. This is a fundamental contribution both to the chemistry of phosphorus and the chemistry of vinylimidazole.

Bis[2-(1*H*-imidazolyl)ethyl]phosphine oxide (IV). To the mixture of 10 g of powdered KOH, 50 ml of DMSO, and 4.3 ml of H_2O heated to 80°C, flushed with argon and saturated with phosphine, 2 g of 1-vinyl-imidazole in 10 ml of DMSO was added dropwise in the course of 2.5 h with simultaneous bubbling of phosphine. Phosphine was bubbled for 1 h at 80–82°C, then the reaction mixture was flushed with argon, diluted with the same volume of water, and extracted successively with ether and chloroform. The ether extract was washed with water, dried over potassium carbonate, ether was removed, the residue was dried in a vacuum to give 0.18 g of the mixture of 1-vinylimidazole and primary phosphine **I** in the ratio of 10:1 (^{1}H, ^{31}P NMR). The chloroform extract was dried over potassium carbonate, chloroform removed under a reduced pressure, DMSO was removed in a vacuum. The residue was washed with ether, dried in a vacuum to obtain 0.38 g (15%) of bis[2-(1*H*-imidazolyl)ethyl]phosphine oxide **IV** as a light-yellow oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.29 m (4H, CH_2P), 4.23 m (4H, CH_2N), 6.89 s, 7.09 s and 7.48 s (6H, CH). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 23.3 d ($^1J_{PH}$ 467 Hz). Found, %: C 50.08; H 6.59; N 23.32; P 12.62. $C_{10}H_{15}N_4OP$. Calculated, %: C 50.42; H 6.35; N 23.52; P 13.00.

^{1}H and ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13 and 161.98 MHz, respectively), external reference 85% H_3PO_4.

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