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LETTERS TO THE EDITOR

Synthesis of 1-Methyl-2-phenyl- and Bis(1-methyl-2-phenylethyl)phosphinic Acids from Red Phosphorus and Allylbenzene

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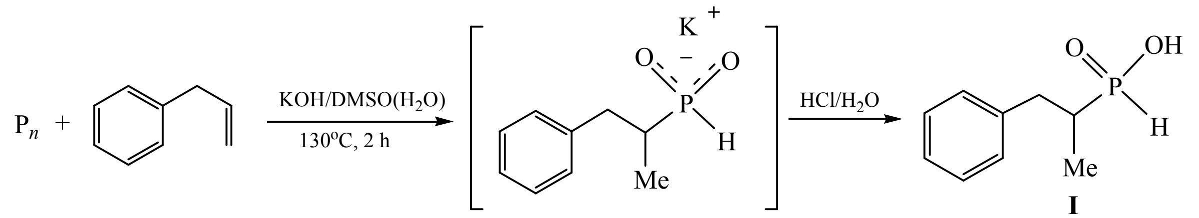
Phosphinic acids are widely used as extragents of heavy metals, antipyrens, ligands for the design of metal complexes, building blocks in organic synthesis, and as biologically active compounds [1, 2]. At the same time, these acids still remain difficultly accessible compounds, since the methods of their synthesis are laborious, production-unfriendly, and based on toxic phosphorus halides [1]. Direct reactions of elemental phosphorus with electrophiles (organyl halides, acetylenes, or alkenes) in the presence of strong bases is an evident alternative to these methods for the formation of the C–P bond opening a practical route to the synthesis of the key organophosphorus compounds, including organophosphorus acids [3, 4]. For example, phosphorylation of vinylarenes (styrenes [5, 6], 2-vinylnaphthalene [7], vinylpyridines [8, 9]) with red phosphorus in the system KOH–DMSO presents an efficient method for the preparation of tertiary phosphine oxides and phosphinic acids (the latter, as a rule, are formed in a low yield).

Here we report on the synthesis of 1-methyl-2-phenylethyl- (**I**) and bis(1-methyl-2-phenylethyl)phosphinic acids (**II**) by the reaction of allylbenzene with red phosphorus in a superbasic medium.

The phosphorylation of allylbenzene with red phosphorus in the superbasic medium KOH–DMSO(H_2O) at 130°C (argon, 2 h) results in the selective formation of the potassium salt of 1-methyl-2-phenylethyl-phosphinic acid. Free phosphinic acid **I** was isolated in 58% yield (calculated with respect to allylbenzene) from the acidified reaction mixture after dilution with water.

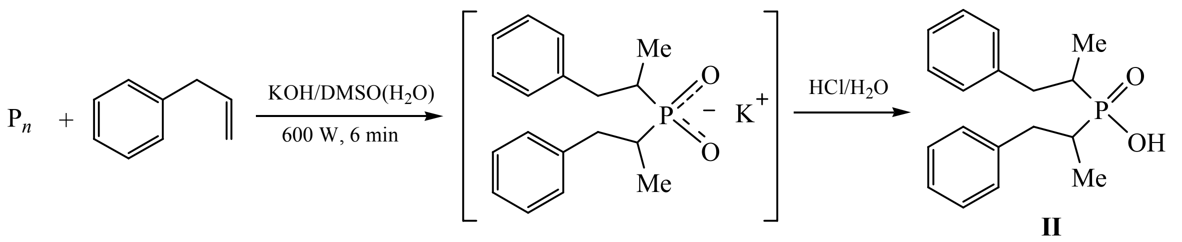


I

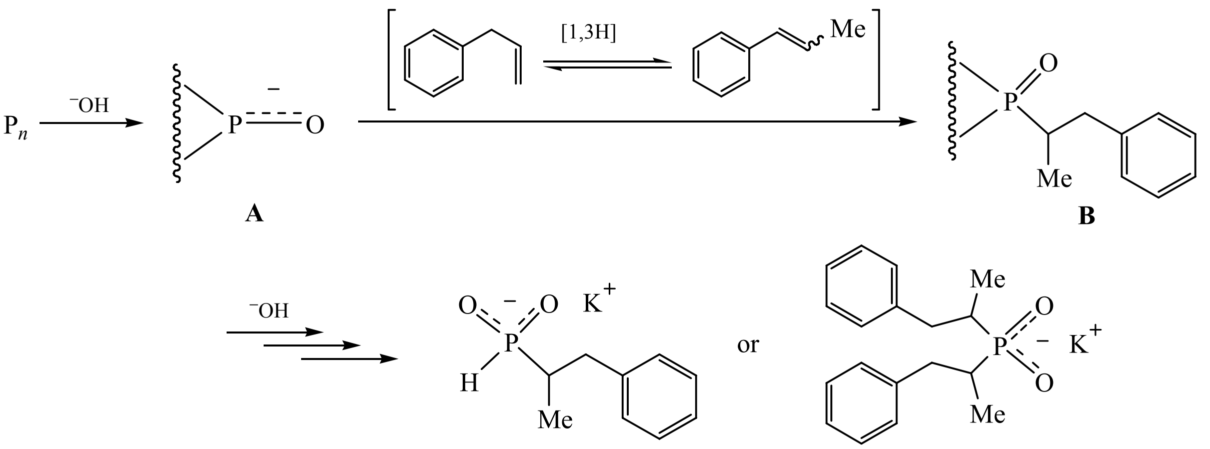
Besides, *E*-prop-1-enylbenzene was isolated as a by-product in 10% yield.

Carrying out the reaction under microwave activation (600 W) allows not only the reduction of the reaction time to 6 min, but also changes its chemoselectivity. Under these conditions, the potassium salt of bis(1-methyl-2-phenylethyl)phosphinic acid is formed as the major product. The free phosphinic acid **II** was isolated by extraction from the acidified reaction mixture in 9% yield.

Apparently, the potassium salts of acids **I** and **II** are formed as a result of nucleophilic addition of phosphinite anions **A,** generated from red phosphorus under



the action of hydroxide ions, to prop-1-enylbenzene, the product of [1,3]-isomerization of allylbenzene in the superbasic medium. The subsequent splitting of the P–P bond in the formed intermediate **B** by hydroxide ions results, depending on the conditions, in the potassium salt of acid **I** or **II**.



Therefore, based on the reaction of red phosphorus with allylbenzene in the system KOH–DMSO, the synthesis of the hitherto unknown phosphinic acids is elaborated. The discovered reaction expands the existing notions on the reactivity of elemental phosphorus in the reactions with unsaturated compounds in superbasic media and opens (with the prospect of its extension to other allylarenes) a simple and efficient route to the earlier unknown or hardly accessible organophosphorus acids, potential extragents, antipyrens, reactive building blocks, and biologically active compounds [1, 2].

1-Methyl-2-phenylethylphosphinic acid (I). A mixture of red phosphorus (3.10 g, 0.10 mol), ground KOH·0.5H$_2$O (7.16 g, 0.11 mol), allylbenzene (4.73 g, 0.04 mol), 30 ml of DMSO, 0.63 ml of H$_2$O, and hydroquinone (0.07 g) was vigorously stirred at 130°C under argon for 2 h. The reaction mixture was cooled, diluted with water (30 ml), acidified with concentrated aqueous HCl, and extracted with chloroform (3×20 ml). The chloroform extracts were washed with water (2×20 ml), dried over calcium chloride, chloroform was removed, the residue was evacuated to remove *E*-prop-1-enylbenzene (35–40°C, 1 mm Hg). The obtained oil was reprecipitated from chloroform into hexane to obtain 4.25 g (58%) of acid **I**, colorless oil. IR spectrum (film), ν, cm^{-1}: 3620, 3086, 3062, 3028, 2968, 2933, 2876, 2632, 2374, 2356, 2343, 1667, 1603, 1496, 1455, 1380, 1243, 1202, 1175, 1080, 1058, 1028, 968, 903, 862, 820, 756, 729, 710, 700, 668, 657, 641, 621, 595, 584, 571, 521, 472. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.94 d.d (3H, Me, $^3J_{HH}$ 7.1, $^3J_{PH}$ 19.2), 1.87–1.95 m (1H, CHP), 2.34–2.43 m (1H, CH$_2$Ph), 3.06–3.14 m (1H, CH$_2$Ph), 6.90 d (1H, PH, $^1J_{PH}$ 535.0), 6.92–7.08 m (5H, Ph), 13.56 br.s (1H, OH). ^{13}C NMR spectrum, δ$_C$, ppm (*J*, Hz): 10.88 (Me), 34.91 (CH$_2$Ph), 35.03 d (CHP, $^1J_{PC}$ 95.6), 126.59 (C-*p*), 128.69 (C-*o*), 129.36 (C-*m*), 139.03 d (C-*i*, $^3J_{PC}$ 14.1). ^{31}P NMR spectrum, δ$_P$, ppm (*J*, Hz): 40.00 d ($^1J_{PH}$ 535.0). Found, %: C 58.49; H 7.18; P 16.71. $C_9H_{13}O_2P$. Calculated, %: C 58.69; H 7.11; P 16.82.

***E*-Prop-1-enylbenzene**, 0.47 g (10%). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.03 d (3H, Me, $^3J_{HH}$ 6.1), 6.37 d.d (1H, C*H*Me, $^3J_{HH}$ 15.4, $^3J_{HH}$ 6.1), 6.58 d

(C*H*Ph, 1H, $^3J_{HH}$ 15.4), 7.28–7.43 m (5H, Ph). Found, %: C 91.40; H 8.41. $C_9H_{13}O_2P$. Calculated, %: C 91.47; H 8.53.

Bis(1-methyl-2-phenylethyl)phosphinic acid (II). A mixture of red phosphorus (0.34 g, 11 mmol), ground $KOH{\cdot}0.5H_2O$ (0.84 g, 13 mmol), allylbenzene (1.56 g, 13 mmol), 15 ml of DMSO, 0.07 ml of H_2O, and hydroquinone (0.03 g) was irradiated in a microwave oven at 600 W for 6 min. The reaction mixture was cooled, diluted with water (20 ml), and extracted with chloroform. The aqueous layer was acidified with concentrated aqueous HCl and extracted with chloroform (2×20 ml). The chloroform extracts were washed with water (2×20 ml), dried over calcium chloride, chloroform was removed, the residue was evacuated to obtain 0.18 g (9%) of acid **II**, colorless oil. IR spectrum (film), ν, cm^{-1}: 3441, 3083, 3060, 3024, 2955, 3000, 2850, 1603, 1495, 1453, 1387, 1377, 1253, 1144, 766, 756, 734, 707, 599, 483. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.13-1.24 m (6H, Me), 2.40–2.42 m (2H, CHP), 2.57–2.65 m (2H, CH_2Ph), 3.43–3.48 m (2H, CH_2Ph), 7.11–7.34 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 12.96, 13.01 and 13.07 d (Me, $^2J_{PC}$ 2.2), 32.64, 32.68, 32.73, 321.82 d (PCH, $^1J_{PC}$ 57.5, 58.1, 57.6, 57.4), 36.25, 36.22 d (CH_2Ph, $^2J_{PC}$ 1.5), 126.70 (C-*p*), 128.88 (C-*o*), 129.19 (C-*m*), 139.66 d and 139.70 d (C-*i*, $^3J_{PC}$ 11.8 and 12.6). ^{31}P NMR spectrum, δ_P, ppm: 56.43. Found, %: C 71.65; H 7.44; P 10.05. $C_{18}H_{23}O_2P$. Calculated, %: C 71.50; H 7.67; P 10.24.

IR spectra were recorded on a Bruker IFS-25 spectrometer. ^1H, ^{13}C, ^{31}P NMR spectra were registered on a Bruker DPX-400 spectrometer (400.13, 101.61, 161.98 MHz, respectively) in C_6D_6, external standard 85% H_3PO_4 (^{31}P NMR). Microwave radiation was performed in a microwave oven Samsung 181 DNR. Commercial red phosphorus (KSAN “SIA,” China) was used.

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