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SHORT COMMUNICATIONS

Direct Phosphorylation of β-Alkylstyrenes with Elemental Phosphorus under Trofimov–Gusarova Reaction Conditions

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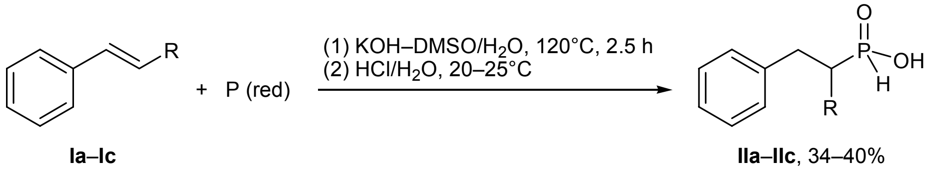
In the past decades, the Trofimov–Gusarova reaction of red phosphorus with electrophilic reagents in heterogeneous strongly basic media, e.g., in a system alkali metal hydroxide–polar aprotic solvent (DMSO, HMPA) or under conditions of phase-transfer catalysis, has been successfully developed and opened new prospects in chlorine-free and environmentally acceptable syntheses of previously unknown or difficultly accessible organic phosphines, phosphine oxides, and phosphonic and phosphinic acids [1–3]. Alkenes (styrenes [4], 1*H*-indene [5], allylbenzenes [6], vinylpyridines [7]), alkynes [8, 9], and alkyl [10], allyl [11], benzyl [12], aryl [13], and hetaryl halides [14] were used as electrophiles in these reactions. We recently showed that 1-methoxy-2-[(*E*)-prop-1-en-1-yl]benzene reacts with red phosphorus in KOH–DMSO to give 2-(2-methoxyphenyl)-1-methylethylphosphinic acid in 63% yield [15].

In this work we made an attempt to accomplish direct phosphorylation of styrenes having a C_3–C_5 alkyl group in the β-position with elemental phosphorus in superbasic medium. The presence of such groups may hamper nucleophilic addition of phosphorus-centered anions generated by cleavage of P–P bonds of elemental phosphorus under the action of hydroxide ions. In fact, β-alkylstyrenes **Ia**–**Ic** reacted with red phosphorus in a KOH/DMSO suspension (in the presence of a small amount of water) at 120°C (2.5 h) to afford previously unknown phosphinic acids **IIa**–**IIc** in 34–40% yield (unoptimized). The reaction mixtures also contained unreacted styrenes **Ia**–**Ic** (^{1}H NMR) and primary phosphines (^{31}P NMR).

In summary, the direct phosphorylation of various β-alkylstyrenes with elemental phosphorus is readily realized under Trofimov–Gusarova reaction conditions to afford previously unknown phosphinic acids with high selectivity. The products attract interest as promising intermediate products for organic synthesis [16] and ligands for the preparation of metal complexes [17].

1-Phenylpentan-2-ylphosphinic acid (IIa). A mixture of 3.10 g (100 mmol) of red phosphorus, 8.00 g (123 mmol) of powdered $KOH\cdot0.5H_2O$, 5.85 g (40 mmol) of 1-phenylpent-1-ene (**Ia**), 30 mL of DMSO, and 1 mL of water was heated for 2.5 h at 120°C under vigorous stirring in an argon atmosphere. The mixture was cooled, diluted with water (50 mL), and extracted with chloroform (3×20 mL). The combined extracts were washed with water (2×30 mL), dried over K_2CO_3, and evaporated. The residue was a yellowish oily material which contained (according to the ^{1}H and ^{31}P NMR data) unreacted alkene **Ia** and 1-phenylpentan-2-ylphosphine (δ_P –123 ppm, t, $^1J_{PH}$ = 190.6 Hz).



Ia–**Ic** **IIa**–**IIc**, 34–40%

R = Pr (**a**), Bu (**b**), C_5H_{11} (**c**).

The aqueous phase was acidified with 35% aqueous HCl to pH 1 and extracted with chloroform (3× 20 mL). The combined extracts were washed with water (3×15 mL) and dried over Na_2SO_4, the solvent was distilled off, and the residue was dried under reduced pressure (35–40°C, 1 mm). Yield 3.38 g (40%), yellowish oily substance. IR spectrum, ν, cm^{-1}: 2366 s (P–H), 1172 s (P=O). ^1H NMR spectrum, δ, ppm: 0.91 t (3H, Me, ^3J = 6.7 Hz), 1.41–1.59 m and 1.66–1.80 m [4H, $(C\mathbf{H}_2)_2Me$], 2.01–2.11 m (1H, CHP), 2.72–2.82 m and 3.08–3.16 m (1H each, $C\mathbf{H}_2Ph$), 7.04 d (1H, PH, ^1J = 542 Hz), 7.26–7.37 m (5H, Ph), 12.08 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 13.9 (Me), 20.5 d ($\mathbf{C}H_2Me$, ^3J = 8.6 Hz), 28.3 d ($\mathbf{C}H_2Et$, ^2J = 1.7 Hz), 33.0 (CH_2Ph), 39.5 d (CHP, ^1J = 95.7 Hz), 126.4 (C^p), 128.4 and 129.0 (C^o, C^m), 138.6 d (C^i, ^3J = 12.4 Hz). ^{31}P NMR spectrum: δ_P 41.86 ppm (^1J = 542 Hz). Found, %: C 62.25; H 8.07; P 14.59. $C_{11}H_{17}O_2P$. Calculated, %: C 62.11; H 8.17; P 14.44.

Phosphinic acids **IIb** and **IIc** were synthesized in a similar way from alkenes **Ib** and **Ic**.

1-Phenylhexan-2-ylphosphinic acid (IIb). Yield 38%, yellowish oily substance. IR spectrum, ν, cm^{-1}: 2384 s (P–H), 1174 s (P=O). ^1H NMR spectrum, δ, ppm: 0.82 t (3H, Me, ^3J = 7.1 Hz); 1.19–1.28 m, 1.30–1.53 m, 1.60–1.75 m [6H, $(C\mathbf{H}_2)_3Me$]; 1.92–2.02 m (1H, CHP), 2.65–2.75 m and 3.00–3.09 m (1H each, $C\mathbf{H}_2Ph$), 6.97 d (1H, PH, ^1J = 539 Hz), 7.19–7.64 m (5H, Ph), 11.60 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 13.7 (Me), 22.6 ($\mathbf{C}H_2Me$), 25.9 d ($\mathbf{C}H_2Pr$, ^2J = 1.7 Hz), 29.4 d ($\mathbf{C}H_2Et$, ^3J = 7.8 Hz), 33.0 ($\mathbf{C}H_2Ph$), 39.7 d (CHP, ^1J = 94.8 Hz), 126.4 (C^p), 128.5 and 129.0 (C^o, C^m), 138.6 d (C^i, ^3J = 12.4 Hz). ^{31}P NMR spectrum: δ_P 41.11 ppm (^1J = 539 Hz). Found, %: C 63.70; H 8.46; P 13.69. $C_{12}H_{19}O_2P$. Calculated, %: C 63.64; H 8.61; P 13.49.

1-Phenylheptan-2-ylphosphinic acid (IIc). Yield 34%, yellowish oily substance. IR spectrum, ν, cm^{-1}: 2383 s (P–H), 1155 s (P=O). ^1H NMR spectrum, δ, ppm: 0.81 t (3H, Me, ^3J = 7.0 Hz); 1.14–1.25 m, 1.29–1.51 m, 1.59–1.74 m [8H, $(C\mathbf{H}_2)_4Me$]; 1.91–2.01 m (1H, CHP), 2.65–2.74 m and 3.00–3.08 m (1H each, $C\mathbf{H}_2Ph$), 6.96 d (1H, PH, ^1J = 541 Hz), 7.18–7.29 m (5H, Ph), 12.71 br.s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 14.0 (Me), 22.4 ($\mathbf{C}H_2Me$), 26.3 ($\mathbf{C}H_2Bu$), 27.1 d ($\mathbf{C}H_2Pr$, ^3J = 7.8 Hz), 31.8 ($\mathbf{C}H_2Et$), 33.1 ($\mathbf{C}H_2Ph$), 39.9 d (CHP, ^1J = 94.8 Hz), 126.5 (C^p), 128.6 and 129.2 (C^o, C^m), 138.9 d (C^i, ^3J = 12.5 Hz). ^{31}P NMR spectrum: δ_P 41.15 ppm (^1J = 541 Hz). Found, %: C 64.98; H 8.81; P 12.89. $C_{13}H_{21}O_2P$. Calculated, %: C 64.84; H 8.77; P 12.61.

The IR spectra were recorded on a Bruker IFS-25 spectrometer from thin films. The ^1H, ^{13}C, and ^{31}P NMR spectra were measured on a Bruker DPX-400 instrument at 400.13, 101.61, and 161.98 MHz, respectively, using $CDCl_3$ as solvent and 85% H_3PO_4 as external reference for ^{31}P. Alkenes **Ia**–**Ic** were synthesized by dehydration of the corresponding 1-phenylalkan-1-ols in the presence of *p*-toluenesulfonic acid. Red phosphorus was commercial product (KSAN SIA, China).

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