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LETTERS TO THE EDITOR

Nanocomposites of Red Phosphorus in the Reaction with 4-Methoxystyrene

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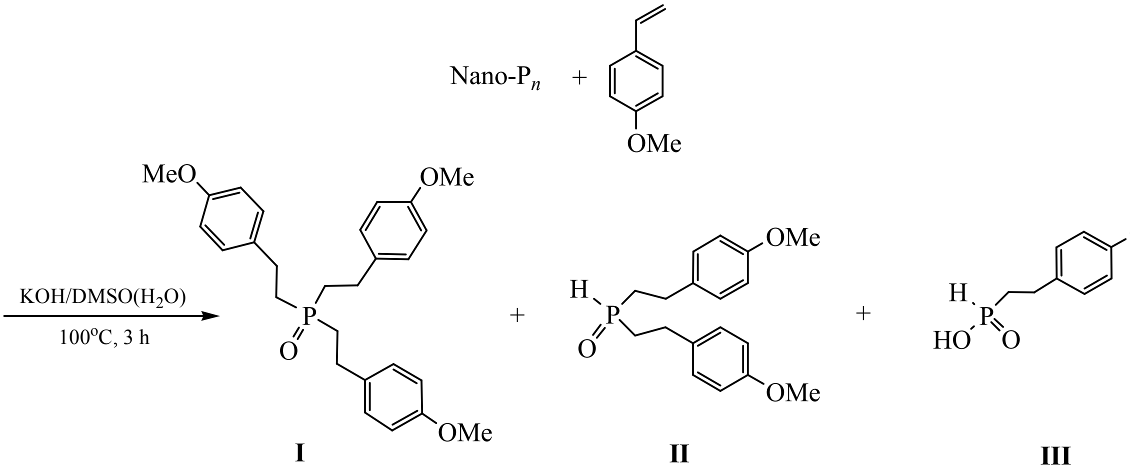
The development of the new method of activation of red phosphorus based on the use of heterogeneous superbasic catalytic media and reagents has led to the creation of nontraditional methods for the formation of the carbon-phosphorus bond and allowed a direct introduction of the phosphorus atom into the available organic compounds (organyl halides, acetylenes, vinylpyridines, styrene, etc.) [1–3]. As a result, new one-pot syntheses of diverse organic phosphines, phosphine oxides, and phosphinic acids have been developed [1–3], which earlier were prepared by multistep reactions from toxic and aggressive phosphorus halides.

Recently, new phosphorylating reagents were introduced into the organophosphorus synthesis: nanocomposites of red phosphorus possessing a higher reactivity with respect to conventional amorphous modifications of red phosphorus [4, 5]. These nanocomposites are prepared by the radiation-induced polymerization of white phosphorus in the presence of terminating additives (benzene, graphite, sulfur, etc.) [6].

Here, we first report on the reaction of red phosphorus and its nanocomposite with 4-methoxystyrene in the superbasic system KOH–DMSO. The possibility of realization of such a reaction was not evident since 4-methoxystyrene was known to be a weak electrophilic alkene [7–10].

The experiments showed that heating (100°C, 3 h) of the suspension of the nanocomposite of red phosphorus, 4-methoxystyrene, KOH and DMSO in the presence of small amounts of water results in the formation of a mixture of tris[2-(4-methoxyphenyl)-ethyl]phosphine oxide (**I**), bis[2-(4-methoxyphenyl)-ethyl]phosphine oxide (**II**), and 2-(4-methoxyphenyl)-



ethyl]phosphinic acid (**III**) in the total yield of 34% and the ratio of 1 : 1.3 : 1.2 (from the ^{31}P NMR spectroscopy data).

Under similar conditions, (KOH–DMSO, 100°C, 3 h) amorphous red phosphorus reacts with 4-methoxystyrene to give the tertiary phosphine oxide **I** in a low yield (~3%).

Therefore, nanocomposites of elemental phosphorus synthesized from white phosphorus using high energies possess enhanced reactivity relative to the conventional technical red phosphorus. In the presence of strong bases these nanocomposites rather effectively phosphorylate even such weakly electrophilic alkene as 4-methoxystyrene.

Nanocomposite of red phosphorus (nano-P_n) was prepared by radiation-induced (γ-radiation of ^{60}Co) polymerization of white phosphorus in benzene at room temperature (time of irradiation 93 h, absorbed dose 117 kGy at the dose rate of 0.35 Gy s^{-1}). From the data of the scanning and transmission electron microscopy, the nanocomposite consists mainly of particles of spherical or elliptic form of 30–50 nm size [5]. Elemental analysis: P (80.48%), C (8.13%), H (0.68%), O (10.71%).

Reaction of the nanocomposite of red phosphorus with 4-methoxystyrene in the system KOH–DMSO. The mixture of 0.34 g of the nanocomposite of red phosphorus, 0.84 g of ground $KOH{\cdot}5H_2O$, 15 ml of DMSO, 0.07 ml of water, 1.78 g of 4-methoxystyrene and 0.01 g of hydroquinone was stirred for 3 h at 100°C. The reaction mixture was cooled, diluted with equivalent amount of water, extracted with chloroform (100% conversion of phosphorus). The chloroform extracts were washed with water, dried over potassium carbonate, solvent was removed under reduced pressure, the residue was kept in a vacuum to remove unreacted 4-methoxystyrene, 0.85 g (48% conversion). The residue was dried in a vacuum to obtain 0.21 g of the mixture containing, according to the ^{31}P NMR spectroscopy data, phosphine oxide **I** (47.01 ppm) and phosphine oxide **II** (33.11 ppm, d, $^1J_{PH}$ 456 Hz) in the ratio of 1: 1.4. Yield 9% and 12%, respectively. The water layer was treated with 30% aqueous HCl to pH 4–5, extracted with chloroform, the extracts were dried with calcium chloride, chloroform was removed, the residue was dried in a vacuum to obtain 0.15 g of acid **III**. Yield 11%; colorless powder, mp 229–232°C (ethanol). ^{1}H NMR spectrum (D_2O), δ, ppm: 1.80–1.88 m (2H, CH_2P), 2.7–-2.82 m (2H, CH_2Ar), 3.83 s (3H, OMe), 6.94 d (1H, PH, $^1J_{PH}$ 505.7 Hz), 6.94 and 7.48 m (4H, Ar), 8.02 br. s (1H, OH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 25.94 (CH_2Ar), 32.72 d (CH_2P, $^1J_{PC}$ 94.2 Hz), 54.95 (OMe), 113.80 (C_o), 129.01 (C_m), 134.27 (C_i), 147.61 (C_p). ^{31}P NMR spectrum (D_2O), δ, ppm: 30.18 d, $^1J_{PH}$ 505.8 Hz. IR (KBr, ν, cm^{-1}): 3436, 2956, 2935, 2837, 2295, 2100, 2600, 1629, 1613, 1585, 1514, 1465, 1443, 1421, 1302, 1250, 1210, 1176, 1129, 1057, 1036, 938, 919, 903, 847, 817, 783, 736, 637, 620, 581, 549, 520, 490, 474, 442. Found, %: C, 54.27; H, 6.73; P, 15.76. $C_9H_{13}O_3P$. Calculated, %: C, 54.00; H, 6.55; P, 15.47.

Tris[2-(4-methoxyphenyl)ethyl]phosphine oxide (I) was prepared under the above conditions from 0.34 g of technical amorphous red phosphorus in the yield of 3%. Colorless powder, mp 129–131°C (hot hexane). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.93–2.0 m (6H, CH_2P), 2.79–2.86 m (6H, $CH_2C_6H_4$), 3.74 m (9H, Me), 6.80–6.83 and 7.06–7.08 m (12H, C_6H_4). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 26.91 (CH_2Ar), 30.40 d (CH_2P, $^1J_{PC}$ 61.5 Hz), 55.28 (Me), 114.11 (C_o), 129.04 (C_m), 132.87 d (C_i, $^3J_{PC}$ 12.5 Hz), 158.3 (C_p). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 47.01. IR spectrum (KBr), cm^{-1}: 3058, 3016, 2955, 2932, 2908, 2870, 2836, 1610, 1583, 1512, 1461, 1440, 1419, 1337, 1320, 1301, 1275, 1243, 1180, 1161, 1129, 1099, 1033, 1010, 955, 948, 851, 832, 816, 788, 751, 722, 675, 553, 541, 525, 469. Found, %: C 71.57; H 7.33; P 6.70. $C_{27}H_{33}O_4P$. Calculated, %: C 71.66; H 7.35; P 6.84.

IR spectra were taken on a Bruker IFS-25 in thin layer and in KBr pellets. ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded on a Bruker DPX 400 spectrometer (400, 100, 162 MHz, respectively), internal standard HMDS, external standard 85% H_3PO_4 (^{31}P).

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