ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 12, pp. 2401–2404. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © B.A. Trofimov, S.F. Malysheva, A.V. Artem'ev, N.A. Belogorlova, L.V. Klyba, N.K. Gusarova, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 12, pp. 1983–1986.

Acetylene Phosphorylation with Elemental Phosphorus in the KOH–DMSO System

**B. A. Trofimov, S. F. Malysheva, A. V. Artem'ev,
N. A. Belogorlova, L. V. Klyba, and N. K. Gusarova**

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

Received August 4, 2014

Abstract—Reaction of red phosphorus with acetylene in multiphase superbasic KOH–DMSO system has been studied. The phosphorylation of acetylene results in poly(divinylphosphinic acid).

Keywords: acetylene, red phosphorus, hydrophosphorylation, polymer of divinylphosphinic acid

DOI: 10.1134/S1070363214120081

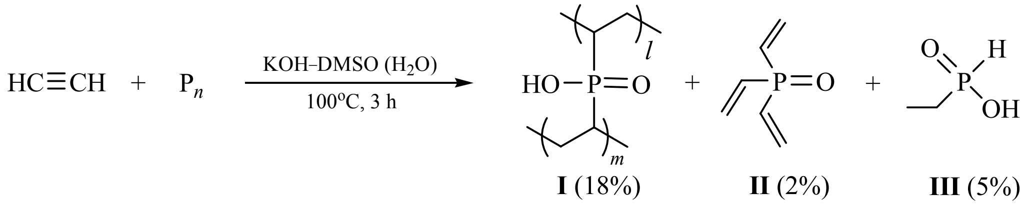
Direct reactions of elemental phosphorus with organic electrophiles in superbasic systems like alkali hydroxide: polar aprotic solvent (dimethylsulfoxide DMSO, hexamethylphosphoramide HPMA) or under conditions of interphase catalysis are convenient preparation methods for organophosphorus compounds, alternative to conventional procedures [1–3]. Basing on this approach, such electrophiles as phenylacetylene, aryl- and hetarylalkenes, and organyl halides have been phosphorylated, opening a way to simple preparation of previously unknown or difficultly accessible phosphines, phosphine oxides, and organophosphorus acids [1–3]. The reaction of acetylene and elementary (red) phosphorus has been poorly studied; it is known to yield traces of trivinylphosphine [4]. The reaction has been carried out in a KOH–H_2O–N_2H_4–HPMA system at 105–115°C in a pressure reactor (acetylene pressure of 15 at).

Here we present preliminary results of investigation of red phosphorus reaction with acetylene in a multiphase superbasic KOH–DMSO (H_2O) medium. Minor admixture of water (~4 vol % with respect to DMSO) was applied to accelerate proton transfer process.

Polymer of divinylphosphinic acid (**I**) was formed within 3 h at 100°C in the described system (pressure reactor, initial acetylene pressure of 14 at, room temperature), the product yield was 18% with respect to phosphorus. The side organophosphorus products, ethylphosphinic acid **II** and trivinylphosphine oxide **III** were isolated in 5% and 2% yields respectively (Scheme 1).

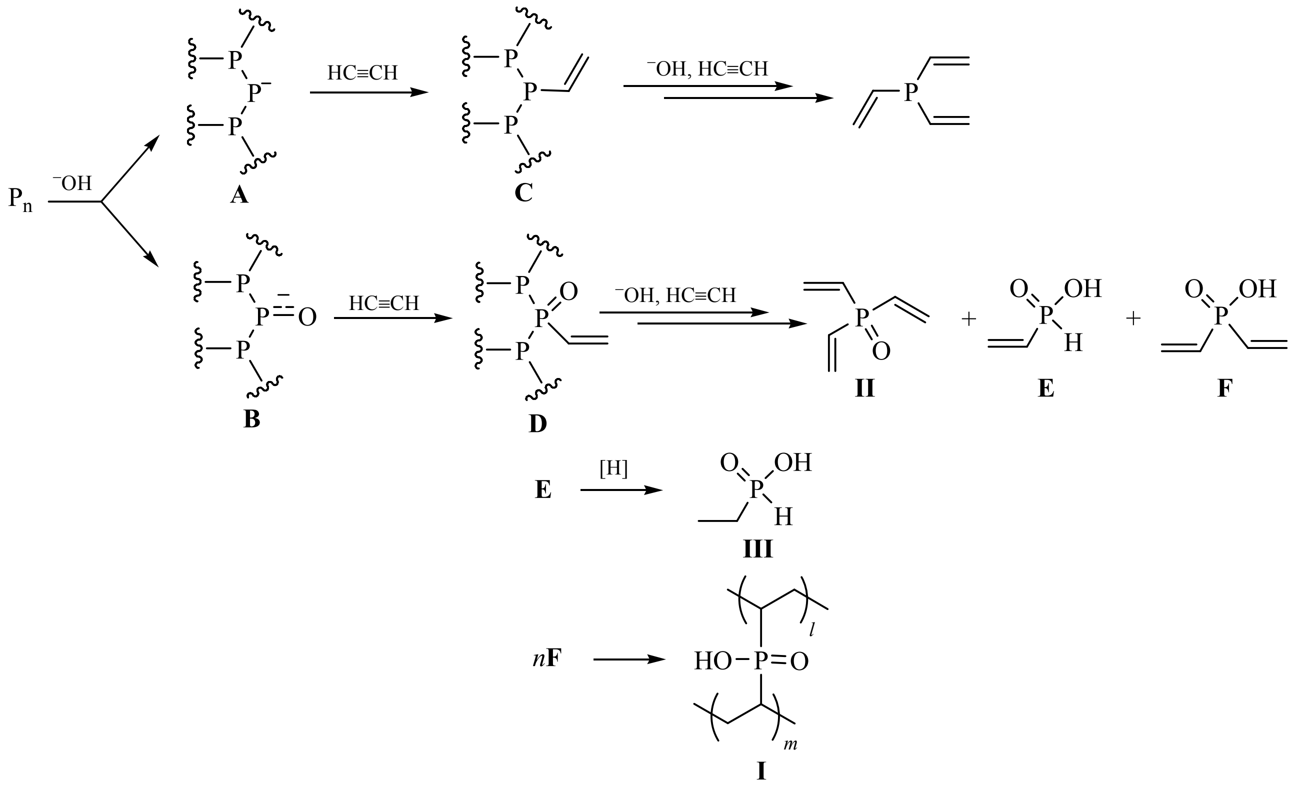
Polymer **I** was a light-brown powder, insoluble in water and organic solvents but almost completely (80%) soluble in aqueous alkali. The presence of the fraction insoluble in aqueous alkali pointed to the formation of crosslinked (three-dimensional) structures. Elemental analysis data for compound **I** coincided with the theoretical composition of poly(divinylphosphinic acid). Acid-base titration data were in line with the polymeric acid structure as well. IR

Scheme 1.

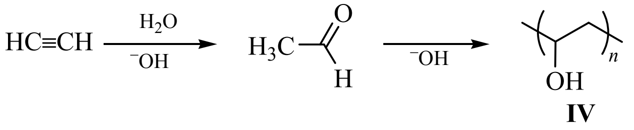


I (18%) **II** (2%) **III** (5%)

Scheme 2.



Scheme 3.



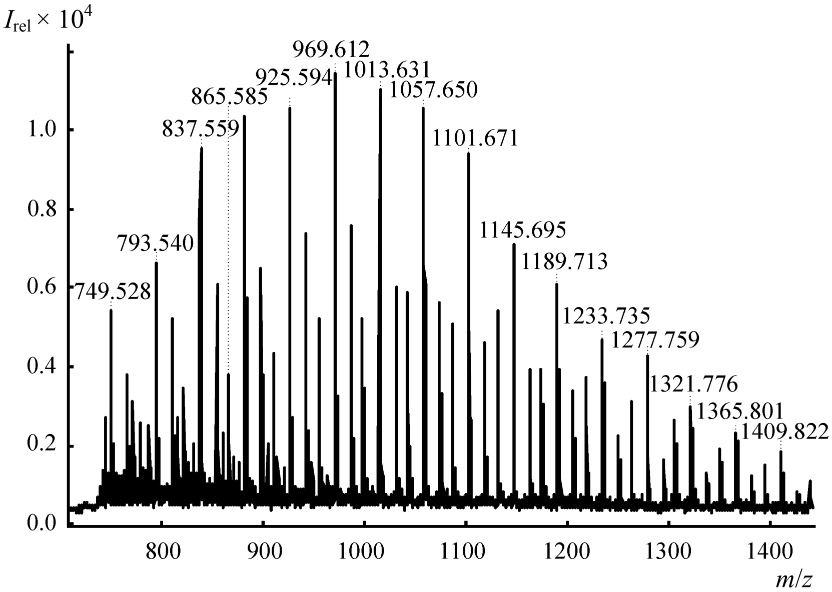
spectrum of polymer **I** contained the absorption band at 961 cm^{-1}, typical of P–OH group; the band at 1157 cm^{-1} was assigned to the P=O vibrations, and the band at 753 cm^{-1} was assigned to the P–C vibration. Broad bands at 3450–3300 and 1650–1630 cm^{-1} corresponded to vibrations of the OH end groups. Stretching and bending vibrations of the C–H bonds gave rise to the bands at 2920–2890 and 1412 cm^{-1}, respectively.

According to the commonly accepted views [1–3], the cleavage of the P–P bonds of elemental phosphorus in the KOH–DMSO system led to generation of polyphosphide (**A**) and polyphosphinite (**B**) anions. In the studied case, the expected pathway was the anions addition to acetylene, and the subsequent splitting of the rest P–P bonds in the formed intermediate **C** and **D** should yield trivinylphosphine (from phosphide ions) along with phosphine oxide **II**, mono- (**E**) and divinylphosphinic (**F**) acids (from phosphonite anions). The acid **E** hydrogenation with hydrogen evolving in the course of reaction of red phosphorus with alkali gave ethylphosphinic acid **III**, whereas anionic polymerization of divinylphosphinic acid **F** yielded polymer **I** (Scheme 2).

Traces of polyacetaldehyde **IV** were identified among the reaction products as well. Under the reaction conditions, acetaldehyde might be formed via base-catalyzed hydration of acetylene (water vinylation) (Scheme 3).

Mass spectrum of polymer **IV** (MALDI) contained mainly the peaks assigned to polyacetaldehyde of various polymerization degree (see figure).

The optimized phosphorylation reaction of acetylene can be used for preparation of polydivinylphosphinic acid, a new promising fire-retarding agent



MALDI mass spectrum of polymer **IV** cations. *m/z* 749 H[–C_2H_4O–]$_{17}$, $n = 23$, $M_n = 1041.030$; *m/z* 765 HO[–C_2H_4O–]$_{17}$, $n = 22$, $M_n = 998.230$; and *m/z* 777 C_2H_5[–C_2H_4O–]$_{17}$, $n = 24$, $M_n = 1072.050$.

to be applied for fabrics and polymeric materials. The polyacid can be used as efficient cationite and ion sorbent as well (after crosslinking).

EXPERIMENTAL

IR spectra were recorded using a Bruker Vertex 70 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were registered with a Bruker DPX-400 spectrometer (400.13, 101.61, and 161.98 MHz, respectively) in $CDCl_3$ solution with 85% H_3PO_4 as an external reference (^{31}P). Mass spectrum (MALDI) was recorded using a UltrafleXtreme III TOF/TOF (Bruker Daltonics) mass spectrometer equipped with a nitrogen laser (337 nm) operating in the reflectron mode. The results were processed using FlexAnalysis 3.3 (Bruker Daltonics) software. The sampling was performed following the dried drop method.

Reaction of red phosphorus with acetylene in KOH–DMSO. A mixture of red phosphorus (3.1 g, 0.100 mol), $KOH \cdot 0.5H_2O$ powder (8.00 g, 0.123 mol), 50 mL of DMSO, and 2 mL of water was placed in a 1 L rotating steel reactor and saturated with acetylene to the pressure of 14 at. Acetylene was then released to eliminate air from the reaction mixture, and then the reactor was again saturated with acetylene to 14 at (at room temperature). The reaction mixture was heated at 100°C during 3 h. After cooling, the reaction mixture was diluted with water (50 mL) and acidified with HCl to pH ~ 1. The formed precipitate was filtered off, washed with DMSO (2 × 10 mL), water (4 × 20 mL), and ethanol (2 × 10 mL), and dried in a vacuum (1.5 mmHg, 40–45°C). The DMSO-soluble fraction (polymer **IV**) was identified by means of MALDI mass spectroscopy. Yield of polymer **I** 2.1 g (18%).

Water and DMSO were distilled off from the filtrate in a vacuum (~1.5 mmHg), the residue was diluted with ethanol, acidified with conc. HCl (3 mL), and evaporated to dryness. The residue was diluted with water (≈15 mL) and extracted with chloroform (3 × 10 mL). The extract was dried over $MgSO_4$, the solvent was eliminated, and the residue was dried in a vacuum. Yield of ethylphosphinic acid **III** 0.45 g (5%).

Gaseous reaction products were condensed from the reactor into a cooled trap (–78°C). The condensate (0.6 g) was a colorless liquid containing trivinylphosphine (δ_P –26.7 ppm) and trivinylphosphine oxide (δ_P 17.8 ppm). Trivinylphosphine oxide (0.23 g, 2%) was isolated from the mixture after 1 d keeping in air at 23°C and subsequent chromatographic separation (silica gel, chloroform as eluent).

Polymer of divinylphosphinic acid (I). Yield 2.1 g (18%), light-brown powder, carbonized upon heating in a vacuum at > 210°C. IR spectrum, ν, cm^{-1}: 3450–3300 s (O–H), 2920–2890 s (C–H), 1650–1630 s [δ(O–H)], 1412 m [δ(C–H)], 1157 s (P=O), 961 m [δ(P–OH)], 753 m (C–P). Found, %: C 41.01; H 6.21; P 27.50. $(C_4H_7O_2P)_n$. Calculated, %: C 40.69; H 5.98; P 26.23. Acid–base titration: 14.9% of OH groups (calculated 14.4%).

Trivinylphosphine oxide (II). Yield 0.23 g (2%), colorless crystals, mp 95–97°C. ^{1}H NMR spectrum, δ, ppm: 6.27 m (1H), 6.18 m (1H), 6.23 m (1H, $^2J_{HH}$ 2.0, $^3J_{HH}$ 12.5, $^3J_{HH}$ 18.9, $^2J_{PH}$ 23.6, $^3J_{PH}$ 41.9, $^3J_{PH}$ 22.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 134.1 (CH_2), 130.54 (CH, $^1J_{PC}$ 99.6 Hz). ^{31}P NMR spectrum: δ_P 17.7 ppm. Found, %: C 56.11; H 7.17; P 24.01. C_6H_9OP. Calculated, %: C 56.25; H 7.08; P 24.18.

Ethylphosphinic acid (III). Yield 0.45 g (5%), colorless powder, mp 142°C. IR spectrum, ν, cm^{-1}: 2360 s (P–H), 1171 s (P=O). ^{1}H NMR spectrum, δ, ppm: 1.11 d.t (3H, Me, $^3J_{HH}$ 7.7 Hz, $^3J_{PH}$ 21.2 Hz), 1.72 d.q (2H, $^3J_{HH}$ 7.7 Hz, $^2J_{PH}$ 16.2 Hz, $^3J_{\underline{H}PC\underline{H}}$ 1.7 Hz, CH_2P, 6.99 d.t (1H, PH, $^1J_{PH}$ 541 Hz, $^3J_{\underline{H}PC\underline{H}}$ 1.7 Hz), 10.95 s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 4.4 (Me, ^2J 3.3 Hz), 22.0 d (CH_2P, ^2J 93.2 Hz). ^{31}P NMR spectrum: δ_P 41.27 ppm (d, ^1J 541 Hz). Found, %: C 25.41; H 7.37; P 32.71. $C_2H_7O_2P$. Calculated, %: C 25.54; H 7.50; P 32.93.

ACKNOWLEDGMENTS

This work was financially supported by President of the Russian Federation (program of support of leading scientific schools, grant NSh-156.2014.3).

REFERENCES

1. Trofimov, B.A., Rakhmatulina, T.N., Gusarova, N.K., and Malysheva, S.F., *Russ. Chem. Rev.*, 1991, vol. 60, no. 12, p. 1360.
2. Trofimov, B.A. and Gusarova, N.K., *Mendeleev Commun.*, 2009, vol. 19, p. 295. DOI: 10.1016/j.mencom.2009.11.01.
3. Gusarova, N.K., Arbuzova, S.N., and Trofimov, B.A., *Pure Appl. Chem.*, 2012, vol. 84, p. 439. DOI: 10.1351/PAC-CON-11-07-11.
4. Potapov, V.A., Amosova, S.V., and Khangurov, A.V., *Russ. Chem. Bull.*, 1989, p. 195.