ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 7, pp. 1307–1308. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © S.F. Malysheva, A.V. Artem'ev, N.A. Belogorlova, A.O. Korocheva, N.K. Gusarova, B.A. Trofimov, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 7, pp. 1210–1211.

LETTERS TO THE EDITOR

First Example of the C_{sp^2}–P Bond Formation in the Reaction of Red Phosphorus with Hetaryl Halides

S. F. Malysheva, A. V. Artem'ev, N. A. Belogorlova, A. O. Korocheva, N. K. Gusarova, 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

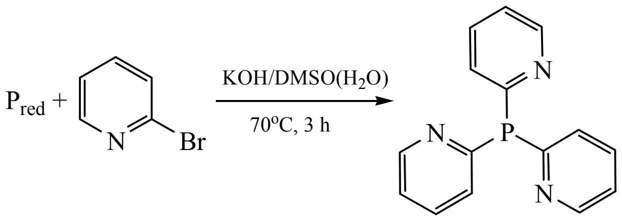
Received February 20, 2012

DOI: 10.1134/S1070363212070213

Direct reactions of red and white phosphorus with electrophiles (aryl- and hetarylalkenes, arylacetylenes, alkyl, allyl, and benzyl halides) in superbasic systems alkali metal hydroxide – dipolar aprotic solvent (DMSO, HMPTA) or under the conditions of phase transfer catalysis are now considered as a novel chlorine-free method of formation of the C–P bond [1, 2]. Within this approach, the one-pot methods have been elaborated for the synthesis of various phosphines, phosphine oxides, and phospinic acids [1, 2] which had earlier been obtained by multistep processes from phosphorus halides. However, in the case of the substitution reaction only the C_{sp^3}–P bond was formed. Recently, tris(1-naphthyl)phosphine was synthesized from red phosphorus and 1-naphthyl bromide in the system KOH–DMSO [3]. To the best of our knowledge, there are no data in the literature on the formation of the C_{sp^2}–P in the reactions of elemental phosphorus with hetaryl halides in superbasic systems.

In the present work we report for the first time on the direct phosphination of hetaryl halides in the system red phosphorus–strong base by the example of 2-bromopyridine.

Red phosphorus reacts with 2-bromopyridine in the superbasic suspension KOH–DMSO with small additives of water at heating (70°C, 3 h, argon) to form tris(2-pyridyl)phosphine **I** in 55% yield.



I

This reaction is the first example of the formation of the C_{sp^2}–P bond in the reaction of elemental phosphorus with hetaryl halides and it opens a convenient route to the synthesis of the hitherto hardly accessible tris(2-pyridyl)phosphine, a polydentate ligand for the design of multipurpose metal complexes [4–7].

The obtained results contribute to the chemistry of phosphorus, organophosphorus compounds, pyridine and P,N-ligands, as well as to the theory of nucleophilic aromatic substitution.

Tris(2-pyridyl)phosphine (I). To a mixture of red phosphorus (3.1 g, 0.10 mol), KOH·0.5H_2O (13.0 g, 0.20 mol), water (2 ml) and DMSO (40 ml) heated to 70°C, a solution of 2-bromopyridine (7.9 g, 0.05 mol) in DMSO (10 ml) was added dropwise at stirring in the course of 30 min. The reaction mixture was stirred for 4.5 h at 70°C, cooled, diluted with water (50 ml), and extracted with chloroform (3×30 ml). The chloroform extracts were washed with water (5×15 ml), dried over potassium carbonate, the solvent was removed, the residue was evacuated (44–50°C, 1 mm Hg), 1.5 g of unreacted 2-bromopyridine was recovered (conversion 81%). The residue was crystallized from isopropanol to give 1.96 g of phosphine **I**, yield 55% (to the reacted 2-bromopyridine). Colorless crystalline powder, mp 115–116°C (113°C [8]). IR spectrum, ν, (KBr), cm^{-1}: 3038, 2963, 2904, 1575, 1560, 1451, 1425, 1415, 1282, 1278, 1145, 1086, 1043, 988, 962, 909, 897, 775, 767, 741, 723, 714, 620, 551, 515, 504, 498, 427, 408, 395. ^1H NMR spectrum, δ, ppm (*J*, Hz): 7.19–

7.24 m (3H, H^5), 7.42 d (3H, H^3, $^3J_{HH}$ 7.0), 7.59–7.65 m (3H, H^4), 8.74 d (3H, H^6, $^3J_{HH}$ 3.7). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 122.6 (C^5), 129.0 d (C^2, $^1J_{CP}$ 19.3), 136.3 d (C^4, $^3J_{CP}$ 2.6), 150.0 d (C^3, $^2J_{CP}$ 19.3), 161.3 (C^6). ^{31}P NMR spectrum, δ_P –1.98 ppm. Found, %: C 67.95; H 4.68; N 15.73; P 11.74. $C_{15}H_{12}N_3P$. Calcd, %: C 67.92; H 4.56; N 15.84; P 11.68.

IR spectrum was recorded on a Bruker Vertex 70 spectrometer. ^1H, ^{13}C, and ^{31}P NMR spectra were registered on a Bruker DPX-400 spectrometer (400.13, 101.61 and 161.98 MHz, respectively) in $CDCl_3$, external standard 85% H_3PO_4 (^{31}P). Commercial red phosphorus, 2-bromopyridine, and DMSO (1% of water) were used.

ACKNOWLEDGMENTS

This work was performed with the financial support from the Russian Foundation for Basic Research (grant no. 11-03-00286a) and the President of the Russian Federation (The Program of Supporting of Leading Scientific Schools, grant no. NSh-1550.2012.3).

REFERENCES

1. Trofimov, B.A. and Gusarova, N.K., *Mendeleev Comm.*, 2009, vol. 19, no. 6, p. 295.
2. Gusarova, N.K., Arbuzova, S.N., and Trofimov, B.A., *Pure Appl. Chem.*, 2012, vol. 84, no. 3, p. 439.
3. Kuimov, V.A., Malysheva, S.F., Gusarova, N.K., Vakul'skaya, T.I., Khutsishvili, S.S., and Trofimov, B.A., *Heteroatom Chem.*, 2011, vol. 22, no. 2, p. 198.
4. Newkome, G.R., *Chem. Rev.*, 1993, vol. 93, no. 6, p. 2067.
5. Zhang, Z.Z. and Cheng, H., *Coord. Chem. Rev.*, 1996, vol. 147, p. 1.
6. Espinet, P. and Soulantica, K., *Coord. Chem. Rev.*, 1999, vols. 193–195, p. 499.
7. Sadimenko, A.P., *Adv. Heterocycl. Chem.*, 2011, vol. 104, p. 391.
8. Bowen, R.J., Garner, A.C., Berners-Price, S.J., Jenkins, I.D., and Sue, R.E., *J. Organomet. Chem.*, 1998, vol. 554, p. 181.