Russian Journal of General Chemistry, Vol. 74, No. 4, 2004, pp. 635–636. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 4, 2004, pp. 695–696.

LETTERS
TO THE EDITOR

Facile Synthesis of Tris(1-naphthylmethyl)phosphine Oxide: A Route to Design of Complexing Luminophores

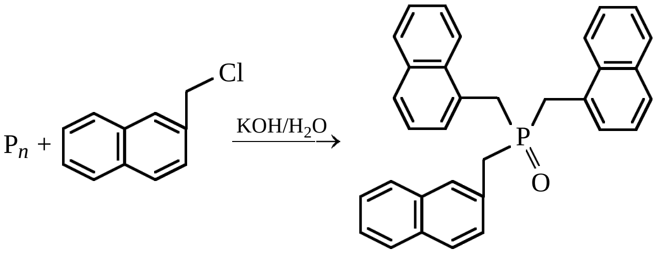
N. K. Gusarova, B. A. Trofimov, S. F. Malysheva, B. G. Sukhov, V. A. Kuimov, N. A. Belogorlova, V. I. Smirnov, and N. B. Kurmankulov

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, Russia

Received August 19, 2003

In the course of the development of a procedure for direct phosphorylation of electrophiles with elemental phosphorus in superbasic media [1–5], we have performed for the first time a direct reaction of red phosphorus with 1-(chloromethyl)naphthalene, which appeared to be a convenient route to the previously unknown tris(1-naphthylmethyl)phosphine oxide **I**, a promising luminescent molecule, synthetic intermediate (e.g., for the Wittig–Horner reaction, similar to tribenzylphosphine oxide [5–9]), and ligand. The presence of bulky naphthyl radicals suggests that the catalysts based on this molecule (or on its reduced species) will exhibit specific activity in the catalytic processes of chlorine substitution in chloroarenes and formation of C–C, C–N, and C–O bonds [10], including the polymerization of olefins.

Phosphorylation of 1-(chloromethyl)naphthalene with red phosphorus proceeds on heating the reactants at 78–95°C in the KOH–dioxane (or benzene)–H_2O system in the presence of benzyltriethylammonium chloride as the phase-transfer catalyst. Phosphine oxide **I** is formed in 70% yield based on the 1-(chloromethyl)naphthalene taken into the reaction.



I

Phosphine oxide **I** is a luminophore. Its luminiscence spectrum does not noticeably differ from that of naphthalene. The combination in one molecule of luminescent substituents and phosphine oxide group taking part in specific complex formation with rare-earth elements is a principally new approach to development of liquid and solid scintillators with the required characteristics, e.g., for solving such a basic problem as neutrino detection [11].

Thus, an efficient and facile route to phosphine oxide **I** opens real prospects for the further comprehensive study and application of this compound. Apparently, the design of phosphine oxide luminophores based on halomethyl derivatives of other highly condensed aromatic and heteroaromatic compounds such as anthracene, tetracene, carbazole, etc. is also possible.

Tris(1-naphthylmethyl)phosphine oxide I. To a suspension of 1.04 g of red phosphorus, 1.14 g of 1-(chloromethyl)naphthalene, 11.95 g of KOH, and 0.17 g of triethylbenzylammonium chloride in 20 ml of dioxane (purged with argon), 5 ml of water was added dropwise over a period of 1 min. The reaction mixture was stirred for 3 h at 90–95°C under argon, diluted by a factor of 2 with water, and extracted with chloroform. The extract was dried over potassium carbonate, and chloroform was distilled off under reduced pressure. The residue was precipitated from chloroform into hexane and crystallized from benzene to give 0.71 g (70%) of phosphine oxide **I**, mp 260°C. IR spectrum: ν(P=O) 1160 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 3.5 d (6H, CH_2, $^2J_{PH}$ 13.5), 7.36–7.46 m and 7.73–7.83 m (21H, $C_{10}H_7$). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 42.44. Luminescence spectrum, ν, cm^{-1}: 30 000–24 800 (with the vibronic peaks at 29 420, 27 780, 26 460, and 26 250) at excitation in the absorption band at 33 000–32 500 cm^{-1}. Found, %: C 84.18; H 5.83; P 6.91. $C_{33}H_{27}OP$. Calculated, %: C 84.23; H 5.78; P 6.58.

The IR spectrum was recorded on a Specord IR-75 spectrometer in KBr pellets. The ^1H and ^{31}P NMR spectra were taken on a Bruker DPX-400 spectrometer (400 and 161.98 MHz, respectively). The luminescence spectrum was obtained on an experimental installation consisting of a DKSsh-1000 excitation source, an MDR-2 monochromator, and an FEU-79 photoelectron multiplier.

ACKNOWLEDGMENTS

The study was financially supported by the RF President's Program for support of leading scientific schools (project no. NSh-2241.2003.3).

REFERENCES

1. Trofimov, B.A., Rakhmatulina, T.N., Gusarova, N.K., and Malysheva, S.F., *Usp. Khim.*, 1991, vol. 60, no. 12, p. 2621.
2. Gusarova, N.K., Malysheva, S.F., Arbuzova, S.N., and Trofimov, B.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, no. 9, p. 1695.
3. Trofimov, B.A., Arbuzova, S.N., and Gusarova, N.K., *Usp. Khim.*, 1999, vol. 68, no. 3, p. 240.
4. Sukhov, B.G., Gusarova, N.K., Malysheva, S.F., and Trofimov, B.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2003, no. 6, p. 1172.
5. Malysheva, S.F. and Arbuzova, S.N., *Sovremennyi organicheskii sintez* (Modern Organic Synthesis), Rakhmankulov, D.L., Ed., Moscow: Khimiya, 2003, p. 160.
6. Gusarova, N.K., Ivanova, N.I., Reutskaya, A.M., Arbuzova, S.N., and Trofimov, B.A., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 11, p. 1922.
7. Ivanova, N.I., Reutskaya, A.M., Arbuzova, S.N., Baikalova, L.V., Afonin, A.V., Gusarova, N.K., and Trofimov, B.A., *Khim. Geterotsikl. Soedin.*, 2000, no. 2, p. 262.
8. Gusarova, N.K., Ivanova, N.I., Reutskaya, A.M., Arbuzova, S.N., Baikalova, L.V., Deryagina, E.N., Russavskaya, N.V., and Trofimov, B.A., *Zh. Org. Khim.*, 2001, vol. 37, no. 12, p. 1807.
9. Ivanova, N.I., Gusarova, N.K., Reutskaya, A.M., Shaikhutdinova, S.I., Arbuzova, S.N., and Trofimov, B.A., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 6, p. 927.
10. Sturmer, R., *Angew. Chem.*, 1999, vol. 111, no. 22, p. 3509.
11. Nesterova, N.P., Barabanov, I.R., Bezrukov, L.B., Yanovich, E.A., and Nifant'ev, E.E., Abstracts of Papers, *13-ya Mezhdunarodnaya konferentsiya po khimii soedinenii fosfora, 4-i Mezhdunarodnyi simpozium po khimii i primeneniyu fosfor-, sera- i kremnii-organicheskikh soedinenii "Peterburgskie vstrechi"* (13th Int. Conf. on Chemistry of Phosphorus Compounds, 4th Int. Symp. on Chemistry and Applications of Organophosphorus, Organosulfur, and Organosilicon Compounds "Petersburg Meetings"), St. Petersburg, 2002, p. 125.