Letters to the Editor

Biographical radiation-induced defect formation as a method for the activation of red phosphorus in reactions with arylalkenes

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In recent years, it has been reported that the modification of the chemical properties of red phosphorus (both in inorganic[1—2] and organic[3—6] processes) can be regulated by controlled defect formation in its structure.

New data on the effect of biographical defects on the reactivity of elementary phosphorus were obtained in direct phosphorylation of arylalkenes in a KOH—DMSO system. Red phosphorus $*P_n$ synthesized by radiation-induced polymerization of white phosphorus in benzene (with ^{60}Co as the radiation source) and containing P—P—R-type defects (R is a benzene fragment)[5] reacts with styrene at room temperature to give diphenethylphosphine oxide (**1**) and phenethylphosphinic acid (**2**) in a total yield of 15%. With commercial red phosphorus P_n produced by thermal polymerization of white phosphorus, the total yield of organophosphorus compounds **1** and **2** did not exceed 2%. Under similar conditions, white phosphorus P_4 is more reactive: the total yield of compounds **1** and **2** is 30%.

In phosphorylation of 2-vinylnaphthalene (90—96 °C), defective $*P_n$ is superior to both P_n and P_4 to give tris[2-(2-naphthyl)ethyl]phosphine oxide (**3**), 2-(2-naphthyl)ethylphosphinic acid (**4**), and bis[2-(2-naphthyl)ethyl]phosphine oxide (**5**) as the major reaction products in a total yield of 73% (product ratio 1.6 : 1.2 : 1). Under comparable conditions, phosphorylation of 2-vinylnaphthalene with P_4 or P_n is less efficient but more selective (phosphine oxide **3** is formed in 58 and 44% yield, respectively). In addition, the above reaction with P_n affords acid **4** in 11% yield.

The formation of oxygen-containing compounds **1**—**5** seems to be in accord with the proposed mechanism.[7]

Compounds **1**—**5** were isolated and identified by comparing their ^1H and ^{31}P NMR spectra (Bruker DPX-400; 400 and 161.98 MHz, respectively; $CDCl_3$) with spectroscopic data for authentic samples.[8,9]

References

1. G. V. Astakhova, S. N. Kamorskii, V. V. Korolev, V. V. Makarenko, and L. B. Soroka, *Khim. Prom-st´*, 1990, 30.

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2. G. T. Shechkov, A. V. Domin, and N. M. Neskorodova, *Zh. Prikl. Khim.*, 1993, **66**, 1948 [*Russ. J. Appl. Chem.*, 1993, **66** (Engl. Transl.)].
3. N. K. Gusarova, Yu. V. Smetannikov, B. G. Sukhov, S. F. Malysheva, N. P. Tarasova, and B. A. Trofimov, *Zh. Obshch. Khim.*, 2001, **71**, 688 [*Russ. J. Gen. Chem.*, 2001, **71** (Engl. Transl.)].
4. N. K. Gusarova, B. G. Sukhov, S. F. Malysheva, T. I. Kazantseva, Yu. V. Smetannikov, N. P. Tarasova, and B. A. Trofimov, *Zh. Obshch. Khim.*, 2001, **71**, 768 [*Russ. J. Gen. Chem.*, 2001, **71** (Engl. Transl.)].
5. N. K. Gusarova, S. I. Shaikhudinova, T. I. Kazantseva, B. G. Sukhov, V. I. Dmitriev, L. M. Sinegovskaya, Yu. V. Smetannikov, N. P. Tarasova, and B. A. Trofimov, *Khim. Geterotsikl. Soedin.*, 2001, 628 [*Chem. Heterocycl. Compd.*, 2001 (Engl. Transl.)].
6. B. A. Trofimov, B. G. Sukhov, N. K. Gusarova, S. F. Malysheva, V. V. Tirskii, L. I. Ruzhnikov, and E. F. Martynovich, *Dokl. Akad. Nauk*, 2002, **382**, 214 [*Dokl. Chem.*, 2002 (Engl. Transl.)].
7. N. K. Gusarova, S. F. Malysheva, S. N. Arbuzova, and B. A. Trofimov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1695 [*Russ. Chem. Bull.*, 1998, **47**, 1645 (Engl. Transl.)].
8. S. N. Arbuzova, N. K. Gusarova, S. F. Malysheva, L. Brandsma, A. I. Albanov, and B. A. Trofimov, *Zh. Obshch. Khim.*, 1996, **66**, 57 [*Russ. J. Gen. Chem.*, 1996, **66** (Engl. Transl.)].
9. N. K. Gusarova, S. I. Shaikhudinova, T. I. Kazantseva, S. F. Malysheva, B. G. Sukhov, N. A. Belogorlova, V. I. Dmitriev, and B. A. Trofimov, *Zh. Obshch. Khim.*, 2002, **72**, 768 [*Russ. J. Gen. Chem.*, 2002, **72** (Engl. Transl.)].

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