Russian Journal of General Chemistry, Vol. 74, No. 7, 2004, pp. 1128–1129. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 7, 2004, pp. 1219–1220.

LETTERS TO THE EDITOR

Reaction of Activated Red Phosphorus with Allyl Bromide under Phase-Transfer Catalysis

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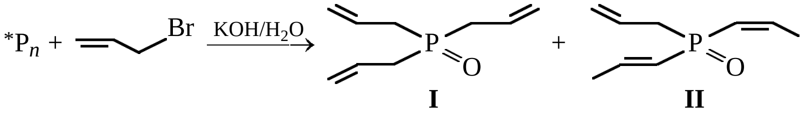
Received July 18, 2003

Common red phosphorus (P_n) reacts with allyl halides (bromide and chloride) on heating (45–75°C) under phase-transfer catalysis to form mixtures of tertiary unsaturated phosphine oxides (total yield up to 23%), among which products of prototrophic isomerizations of tri(propen-2-yl)phosphine oxide (**I**) prevail. These are di(propen-2-yl)[(*E*)-propen-1-yl]-, di(propen-2-yl)- [(*Z*)-propen-1-yl]-, (propen-2-yl)[(*E*)-propen-1-yl][(*Z*)-propen-1-yl]-, di[(*E*)-propen-1-yl]-(propen-2-yl)-, di[(*Z*)-propen-1-yl](propen-2-yl)-, tri-[(*E*)-propen-1-yl]-, and di[(*E*)-propen-1-yl][(*Z*)-propen-1-yl]phosphine oxides [1]. At room temperature this reaction gives mainly the kinetically controlled product, phosphine oxide **I**, in a yield less than 2% (in this case, the phosphorus conversion is 18%) [1].

We found that, under similar conditions (20–22°C, 3 h, 60% aqueous KOH–dioxane) activated red phosphorus ($^*P_n$) obtained by the radiation-induced polymerization of white phosphorus in benzene and containing organophosphorus structural elements such as P_n–P–Ph [2, 3] reacts with allyl bromide to form phosphine oxide **I** and (propen-2-yl)[(*E*)-propen-1-yl]-[(*Z*)-propen-1-yl]phosphine oxide **II** with the total yield of 39% at their molar ratio of 3 : 1.



I **II**

Two more phosphorus compounds were isolated from the reaction mixture after appropriate work-up (acidification of the aqueous layer). The ^1H and ^{31}P NMR spectra allow these compounds to be identified as di(propen-2-yl)phosphinic (**III**) and propen-2-ylphosphinic (**IV**) acids (total yield 24%). The conversion of activated phosphorus in this case is quantitative.

Thus, activated red phosphorus is a more effective phosphorylating agent than common red phosphorus, which makes it possible to carry out the reaction with allyl bromide under mild temperature conditions and to obtain kinetically controlled products.

Activated red phosphorus containing 85 wt% phosphorus was synthesized at room temperature upon γ-irradiation (^{60}Co) of saturated solutions of white phosphorus in benzene at absorbed dose rate of 0.78 Gy/s. Unchanged white phosphorus was washed off with benzene. The P_n–P–Ph and P–O–C bonds in the resulting sample were detected by IR and X-ray photoelectron spectroscopy [2].

Reaction of activated red phosphorus with allyl bromide. To a mixture of 0.25 g of activated red phosphorus, 0.79 g of allyl bromide, and 5.0 g of KOH in 9 ml of dioxane, 5.0 g of water was added dropwise over a period of 15 min. The temperature during the addition was kept at 22–25°C using a water bath. At this temperature the reaction mixture was stirred for an additional 3 h. The dioxane layer was separated and dried over potassium carbonate; the dioxane was distilled off at a reduced pressure, and the residue was evacuated. We obtained 0.1 g of the reaction product, which contained, according to the ^1H and ^{31}P NMR spectra, phosphine oxides **I** and **II** in the 3 : 1 ratio (identified using authentic samples [1]). Phosphine oxide **I**. ^1H NMR spectrum, δ, ppm (J, Hz): 2.55 d.d (6H, H^3, $^3J_{HH}$ 7.6, $^2J_{PH}$ 14.8), 5.15 d.d (3H, H^1, $^2J_{HH}$ 1.0, $^3J_{HH}$ 15.2), 5.19 d.d (3H, H^1, $^3J_{HH}$ 10.5), 5.76 sextet (3H, H^2). ^{13}C NMR spectrum, δ_C, ppm (J_{PC}, Hz): 33.10 d (C^3, $^1J_{PC}$ 62.7), 120.62 d (C^1, $^3J_{PC}$ 11.2), 127.35 d (C^2, $^2J_{PC}$ 7.2). ^{31}P NMR spectrum: δ_P 41.04 ppm. Phosphine oxide **II**. ^1H NMR spectrum, δ, ppm (J, Hz): 1.92 m (3H, H^4, J_{HH} 6.4), 2.15 m (3H, H^7), 2.65 d.d (2H, H^3, $^2J_{HH}$ 5.0, $^2J_{PH}$ 10.0), 5.17–5.24 m (2H, H^1), 5.55 d.d (1H, H^9, $^3J_{HH}$ 12.9, $^2J_{PH}$ 24.4), 5.62 d.d (1H, H^6, $^3J_{HH}$ 12.9, $^2J_{PH}$ 24.4), 5.78–5.87 m (1H, H^2), 6.62 m (2H, $H^{5,8}$). ^{31}P NMR spectrum: δ_P 30.89 ppm.

A 30% aqueous solution of HCl was added to the aqueous-alkaline layer to pH 4. The resulting solution was treated with chloroform, chloroform extracts were dried over $CaCl_2$, the solvent was distilled off at a reduced pressure, and the residue was dried in a vacuum. We obtained 0.2 g of the reaction product, which contained, according to the ^{31}P NMR spectrum, phosphine oxides **I** (0.028 g, 14%) and **II** (0.028 g, 14%) (i.e., the total yield of these phosphine oxides was 39%), and two more phosphorus compounds having signals in the ^{31}P NMR spectrum at δ_P, ppm: 48.29 s and 36.02 d (J_{PH} 549.0 Hz), with integral intensity of 57 and 15%, respectively. These two compounds were separated from phosphine oxides **I** and **II** by column chromatography (sorbent Al_2O_3, eluent diethyl ether–benzene–hexane, 8 : 1 : 1). The ^1H NMR spectrum of the mixture of these compounds contains proton signals of the allyl fragment, δ, ppm: 2.60–2.80 m (H^1), 5.20–5.30 m (H^3), and 5.79–5.85 m (H^2).

The ^1H, ^{13}C, and ^{31}P NMR spectra in $CDCl_3$ were obtained on a Bruker DPX-400 spectrometer (400, 100, and 161.98 MHz, respectively).

ACKNOWLEDGMENTS

The work was financially supported by the President of the Russian Federation within the framework of the program “Leading Scientific Schools” (project no. NSh-2241.2003.3) and by the Russian Foundation for Basic Research (project no. 03-03-32821).

REFERENCES

1. Malysheva, S.F., Sukhov, B.G., Gusarova, N.K., Afonin, A.V., Shaikhudinova, S.I., Kazantseva, T.I., Belogorlova, N.A., Kuimov, V.A., Plotnikova, G.V., and Trofimov, B.A., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 7, p. 1182.
2. Tarasova, N.P., Nad’’yarnykh, G.V., Kostikov, V.V., Chistyakov, V.N., and Smetannikov, Yu.V., *Vysokomol. Soedin., Ser. A*, 1996, vol. 38, no. 9, p. 1467.
3. Sukhov, B.G., Gusarova, N.K., Malysheva, S.F., and Trofimov, B.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2003, no. 6, p. 1172.