

# Letters to the Editor

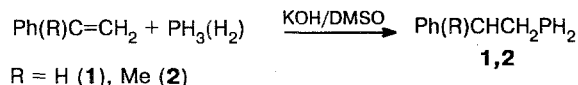
## Synthesis of primary phosphines from phosphine and arylenes

N. K. Gusarova, S. N. Arbusova, S. F. Malysheva, M. Ya. Khil'ko, A. A. Tatarinova,  
V. G. Gorokhov, and B. A. Trofimov\*

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,  
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.  
Fax: +7 (395 2) 466 434

Phosphine is known to add to styrene in hexane in the presence of radical initiators under elevated (28–30 atm) pressure at 70 °C giving (2-phenylethyl)phosphine, bis(2-phenylethyl)phosphine, and tris(2-phenylethyl)phosphine in 36, 29, and 6 % yields respectively.<sup>1</sup>

We have found that (2-phenylethyl)phosphine (1) and (2-methyl-2-phenylethyl)phosphine (2) can be obtained under normal pressure from styrene or  $\alpha$ -methylstyrene and phosphine generated, along with hydrogen, from red phosphorus and saturated aqueous solution of alkali metal hydroxide. Phosphorylation takes place by the action of a superstrong base when phosphine–hydrogen mixture is vigorously passed through a suspension of KOH/DMSO heated up to 50–55 °C and simultaneously 1-phenylalkene is slowly added to the reaction vessel. The yield of primary phosphines (1, 2) is 20–30 % (not optimized).



In the absence of KOH no reaction occurs, which is evidence of its nucleophilic character.

**(2-Phenylethyl)phosphine (1).** To a suspension of 10 g of KOH, 40 mL of DMSO, and 6.45 mL of water saturated with phosphine-hydrogen mixture (obtained in accordance with a known procedure<sup>2</sup>), a solution of 2.96 g of styrene in 10 mL of DMSO was added dropwise over 4 h at 55–57 °C with continuous bubbling of phosphine-hydrogen mixture at a rate of 20–25 mL min<sup>-1</sup>. The reaction mixture was stirred for 2 h

at 50–55 °C with a flow of phosphine, then cooled, flushed with nitrogen, diluted with water, and extracted with ether. Ethereal extracts were washed with water and dried over K<sub>2</sub>CO<sub>3</sub>. Ether was evaporated, and the residue was fractionated *in vacuo* to give 1.05 g (20 %) of phosphine 1, b.p. 46–48 °C (1 Torr),  $n_D^{20}$  1.5532 (see Ref. 1: b.p. 75 °C (8 Torr),  $n_D^{20}$  1.5494; see Ref. 3: b.p. 73 °C (3 Torr),  $n_D^{20}$  1.5565). <sup>31</sup>P NMR (CDCl<sub>3</sub>,  $\delta$ ): –139.7 ( $J_{\text{H-P-H}}$  = 198 Hz). IR,  $\nu/\text{cm}^{-1}$ : 2280 (P–H). Found (%): C, 69.05; H, 7.88; P, 21.98. C<sub>8</sub>H<sub>11</sub>P. Calculated (%): C, 69.55; H, 8.03; P, 22.42.

**(2-Methyl-2-phenylethyl)phosphine (2)** was prepared as described above from  $\alpha$ -methylstyrene and phosphine in 30 % yield, b.p. 65–67 °C (2 Torr),  $n_D^{20}$  1.5482. <sup>31</sup>P NMR (CDCl<sub>3</sub>,  $\delta$ ): –148.6 ( $J_{\text{H-P-H}}$  = 198 Hz). IR,  $\nu/\text{cm}^{-1}$ : 2280 (P–H). Found (%): C, 71.45; H, 8.28; P, 19.95. C<sub>9</sub>H<sub>13</sub>P. Calculated (%): C, 71.04; H, 8.61; P, 20.35.

The work was performed under financial support of the Russian Foundation for Basic Research (Grant No. 93-03-18389).

### References

1. M. M. Rauhut, H. A. Currier, A. M. Semsel, and V. P. Wystrach, *J. Org. Chem.*, 1961, **26**, 5138.
2. B. A. Trofimov, L. Brandsma, S. N. Arbusova, S. F. Malysheva, and N. K. Gusarova, *Tetrahedron Lett.*, 1994, **35**, 7647.
3. G. M. Bogolyubov and A. A. Petrov, *Zh. Org. Khim.*, 1963, **33**, 3774 [*J. Org. Chem. USSR*, 1963, **33** (Engl. Transl.)].

Received February 3, 1995;  
in revised form April 11, 1995