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LETTERS TO THE EDITOR

Photochemical Phosphination of Bromotoluenes

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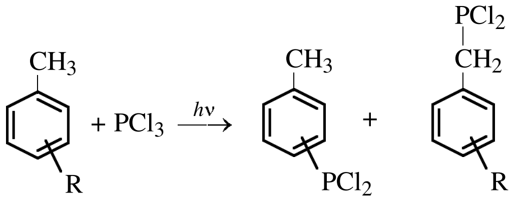
Side-chain radical halogenation of alkylarenes is a known reaction. The mechanism of this reaction has been firmly established, and the reaction has been widely used in organic synthesis [1]. Photochemical phosphination with phosphorus trihalides has been found to involve initial photoinitiated dissociation of the $PHlg_3$ molecule [2]. As a result, a halogen radical is formed, which makes possible a reaction similar to halogenation. According to [3], photoinitiated reaction of phosphorus tribromide with various alkylarenes leads mainly to benzyldibromophosphines.

We found that an analogous reaction of phosphorus trichloride with bromtoluenes takes another pathway involving preferential bromine substitution in the aromatic ring to form corresponding dichloro(tolyl)phosphines.

The reaction was conducted using an immersion mercury lamp. The total yield of phosphorus-containing products was up to 16%. They comprised a major product formed by bromine substitution in the ring along with, probably, isomeric dichloro(tolyl)phosphines (compounds **I**), as well as minor products formed by substitution of methyl hydrogen by a dichlorophosphino group (compounds **II**).



I **II**

R = 4-Br (**a**), 2-Br (**b**), 3-Br (**c**). **I** : **II** = 19 : 1.

The same reaction with bromobenzene failed.

In the absence of UV irradiation the reaction did not occur. The structure of the resulting compounds was confirmed by ^1H, ^{13}C, and ^{31}P NMR spectroscopy.

Dichloro(*p*-tolyl)phosphine (Ia). 4-Bromotoluene, 24 g, was added dropwise with stirring at 45°C over the course of 1 h under UV irradiation with a low-pressure immersion mercury lamp to 329.7 g of PCl_3. The mixture was irradiated for 4 h, after which unreacted PCl_3 and 4-bromotoluene were distilled off, and the residue was distilled in vacuo to obtain 4.91 g of a fraction boiling at 80–110°C (1 mm). It contained, according to ^{31}P NMR data, dichloro(*p*-tolyl)phosphine (**Ia**) and ca. 1% of (4-bromobenzyl)dichlorophosphine (**IIa**). The yield of compound **Ia** was 4.5 g (15% per bromotoluene), bp 87°C (1 mm). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.83 t (2I, $^3J_{HP}$ 8 Hz), 7.34 d (2H), 2.46 s (3H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 142.01 s (C_p), 136.81 d (C_i, $^1J_{CP}$ 52.84 Hz), 131.09 d (C_o, $^2J_{CP}$ 28.69 Hz), 129.21 d (N_i, $^3J_{CP}$ 9.56 Hz), 21.27 s (CH_3). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 161.87 s.

(4-Bromobenzyl)dichlorophosphine (IIa). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 177.15 t ($^2J_{HP}$ 13.62 Hz).

Dichloro(*o*-tolyl)phosphine (Ib). Yield 5.2 g (16% per bromotoluene), bp 80°C (1 mm). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.1–8.2 m (4H), 2.64 d (3H, $^4J_{HP}$ 4.01 Hz). ^{13}N NMR spectrum ($CDCl_3$), δ_C, ppm: 137.25 d (C_i, $^1J_{CP}$ 52.71 Hz), 21.06 d (CH_3, $^3J_{CP}$ 5.4 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 163.86 s.

(2-Bromobenzyl)dichlorophosphine (IIb). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 181.19 t ($^2J_{HP}$ 14.21 Hz).

2Dichloro(*m*-tolyl)phosphine (Ic). Yield 2.1 g (9.7% per bromotoluene), bp 84°C (1 mm). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.2–7.8 m (4H), 2.45 s (3H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 139.70 d (C_i, $^1J_{CP}$ 51.55 Hz), 138.38 d (C_3, $^3J_{CP}$ 8.14 Hz), 133.23 d (C_4), 130.06 d (C_2, $^2J_{CP}$ 31.20 Hz), 128.43 d (C_5, $^3J_{CP}$ 8.14 Hz), 126.83 d (C_6, $^2J_{CP}$ 31.20 Hz), 21.00 s (CH_3). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 161.88 s.

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(3-Bromobenzyl)dichlorophosphine (IIa). ^{31}P NMR spectrum (CDCl$_3$), δ_P, ppm: 178.91 t ($^2J_{HP}$ 10.57 Hz).

The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker C-200 instrument, the operating frequencies were, respectively, 200.132, 50.327 and 81.026 MHz. The chemical shifts are given relative to internal TMS (^{1}H, ^{13}C) and external 85% H$_3$PO$_4$ (^{31}P).

REFERENCES

1. *Comprehensive Organic Chemistry,* Barton, D.H. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 1. Translated under the title *Obshchaya organicheskaya khimiya,* Moscow: Khimiya, 1982, vol. 1, p.388.
2. Krivchun, M.N., Baklanov, M.A., Sendurev M.V., and Ionin, B.I., *Zh. Obshch. Khim.,* 1988, vol. 58, no. 4, p. 758.
3. Müller, G., Waldkircher, M., and Winkler, M., *Z. Naturforsch. B,* 1994, vol. 49, no. 12, p. 1606.