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LETTERS
TO THE EDITOR

Reactions of Polybromoethanes with Four-Coordinate Phosphorus Acid Esters

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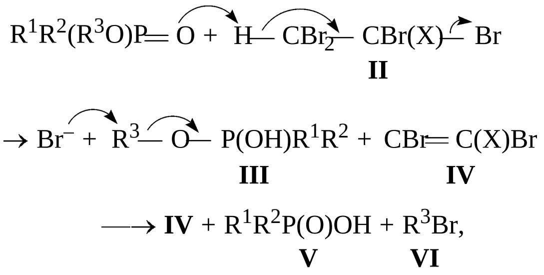
Previously we reported on reactions of organic polychlorides with such aprotic nonionic reagents as four-coordinate phosphorus acid esters **I** [1] and orthoformates [2]. However, data on reactions of polybrominated hydrocarbons **II** with compounds **I** are lacking.

We found that 1,1,2,2-tetrabromo- and pentabromoethanes **II** under the action of four-coordinate phosphorus acid esters at 160–180°C undergo exclusively dehydrobromination to form tri- and tetrabromoethylenes **IV** and acidic esters of four-coordinate phosphorus acids **V**.



$$R^1R^2(R^3O)P{=}O + H{-}CBr_2{-}CBr(X){-}Br$$

II

$$\rightarrow Br^- + R^3{-}O{-}P(OH)R^1R^2 + CBr{=}C(X)Br$$

III **IV**

$$\longrightarrow \mathbf{IV} + R^1R^2P(O)OH + R^3Br,$$

V **VI**

I, R^1 = Me, R^2 = EtO, R^3 = Et (**a**); R^1 = R^2 = Et, R^3 = Me (**b**); R^1 = R^2 = MeO, R^3 = Me (**c**); **II, IV**, X = H (**a**), Br (**b**); **V**, R^1 = Me, R^2 = EtO (**a**); R^1 = R^2 = Et (**b**), R^1 = R^2 = MeO (**c**); **VI**, R^3 = Me (**a**), Et (**b**).

The reaction progress was monitored by ^{1}H NMR, namely, by variation of the intensities of the signals at δ 6.0, 6.45, 7.15, and 11–12 ppm [$CHBr_2$ in **IIa** and **IIb**, BrHC= in **IVa**, and P(O)OH in **V**, respectively]. The spectra were taken every 3 h.

We believe that esters **I** exhibit electron-donor properties, and their phosphoryl oxygen atom attacks positively polarized hydrogen. Intermediates **III** eliminate alkyl bromide **VI**.

Reactions of diethyl methylphosphonate Ia and trimethyl phosphate Ib with 1,1,2,2-tetrabromoethane IIa. A 1 : 1 mixture of **I** and **II** was heated in a sealed ampule until the singlet of the methine proton in **IIa** (δ 6.0 ppm) disappeared from the ^{1}H NMR spectrum.

a. A mixture of 5.54 g of diethyl methylphosphonate **Ia** and 12.59 g of **IIa** was heated at 180°C for 10 h. Distillation of the reaction mixture gave 0.61 g (15%) of ethyl bromide, bp 38–39°C, n_D^{20} 1.4245 (reference data [3]: bp 38.4°C, n_D^{20} 1.4239), 7.58 g (79%) of tribromoethylene, bp 75°C (20 mm Hg), n_D^{20} 1.5970 {reference data [3]: bp 53°C (9 mm Hg), n_D^{20} 1.5992}, and 1.64 g (37%) of ethyl hydrogen methylphosphonate, bp 107–109°C (0.2 mm Hg), n_D^{20} 1.4223. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 12.4 s (1H, POH), 3.91 quintet (2H, OCH_2, $^3J_{HH}$ = $^3J_{PH}$ 7.5 Hz), 1.28 d (3H, PMe, J_{PH} 18.8 Hz), 1.19 t (3H, CH_2CH_3, J_{HH} 7.5 Hz). δ_P 33 ppm.

b. A mixture f 2.43 g of trimethyl phosphate **Ib** and 6 g of **IIa** was heated at 180°C for 20 h. Distillation of the reaction mixture gave 3.81 g (45%) of tribromoethylene, bp 59–60°C (10 mm Hg), n_D^{20} 1.5965, and 1.42 g (31%) of dimethyl hydrogen phosphate, bp 128–129°C (0.4 mm Hg), n_D^{20} 1.4065 {reference data [4]: bp 79–80°C (0.001 mm Hg)}. ^{1}H NMR spectrum

($CDCl_3$), δ, ppm: 12.1 s (1H, POH), 3.51 d (6H, POMe, J_{PH} 12.5 Hz).

Reaction of methyl diethylphosphinate Ic with pentabromoethane IIb. *a*. A mixture of 3.95 g of **Ic** and 12.32 g of **IIb** (1 : 1) was heated in a sealed ampule at 100°C for 13 h. The colorless crystals formed in the process were washed with cold water; 3.83 g (38%) of tetrabromoethylene was obtained, mp 55°C (reference data [3]: mp 56.5°C). Distillation of the liquid fraction gave 1.61 g (45%) of diethylphosphinic acid, bp 122–125°C (0.2 mm Hg), n_D^{20} 1.4542. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.13 d.t (6H, CH_2CH_3, $^3J_{PH}$ 20, $^3J_{HH}$ 7.2 Hz), 1.66 d.q (4H, CH_2CH_3, $^2J_{PH}$ 14, $^3J_{HH}$ 7.2 Hz), 12.1 s (1H, POH). δ_P 55 ppm.

The ^1H NMR spectra were recorded on Bruker WP-80 and Tesla BS-567A spectrometers (80 and 100 MHz, respectively). The proton chemical shifts are given relative to TMS. The ^{31}P NMR spectra were recorded on an RYa-2303 spectrometer (21 MHz), external reference 85% H_3PO_4.

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