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LETTERS
TO THE EDITOR

Reaction of 1,1,2,2-Tetrabromoethane with Triethyl Orthoformate

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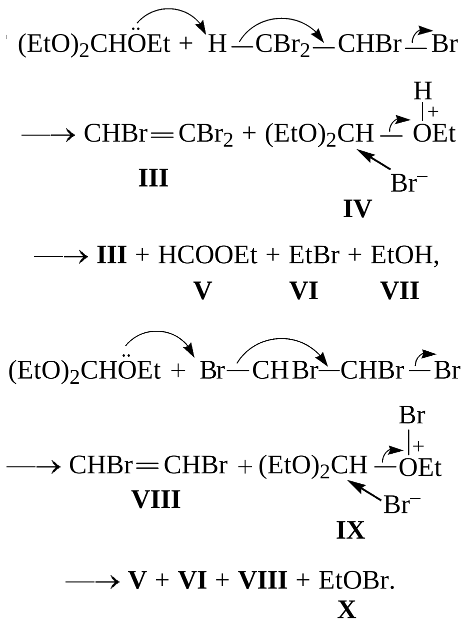
Polychlorinated hydrocarbons undergo dechloroalkoxylation under the action of orthocarboxylic acid esters **I**. The reaction yields aldehydes [1], their acetals [1, 2], and carboxylic acid derivatives [3].

No data are available on reactions of ortho esters **I** with organic polybromides **II**. We found that 1,1,2,2-tetrabromoethane reacts with triethyl orthoformate to form a complex mixture of products. Distillation of the reaction mixture with a deflegmator yields only fractions enriched in one or another component. Therefore, the reaction products were identified by ^{1}H NMR spectroscopy and gas chromatography. Below are the compound formula, its number, ^{1}H NMR data (δ, ppm, $CDCl_3$), and retention time (s). $CHBr{=}CBr_2$, **III**, 7.15 s, 405; CHBr=CHBr, **VIII**, 7.05 s, 230; HCOOEt, V, 7.93 s, 4.09 q ($^3J_{HH}$ 7.5 Hz), 1.15 t ($^3J_{HH}$ 7.5 Hz), 92; EtBr, **VI**, 3.27 q ($^3J_{HH}$ 7.5 Hz), 1.55 t ($^3J_{HH}$ 7.5 Hz), 45; EtOH, **VII**, 3.75 s, 3.50 q ($^3J_{HH}$ 7.5 Hz), 1.0 t ($^3J_{HH}$ 7.5 Hz), 95; MeCOOEt, **XIV**, 3.95 q ($^3J_{HH}$ 7.5 Hz), 1.01 t ($^3J_{HH}$ 7.5 Hz), 1.85 s, 65; $MeCH(OEt)_2$, **XIII**, 4.5 q ($^3J_{HH}$ 5.5 Hz), 1.2 d ($^3J_{HH}$ 5.5 Hz) (the OEt signals are obscured by signals of other ethoxyl hydrogen atoms), 70.

Compounds **I** and **II** were taken in ratios of 1 : 2, 1 : 1, 2 : 1, and 4 : 1. The ^{1}H NMR spectra of the reaction mixtures show that the ortho ester is consumed considerably faster than tetrabromoethane, and tetrabromoethane is completely converted only at 4 : 1 ratio of the reactants. It is interesting that the ratio of polybromoethenes **III** and **VIII**, primary reaction products, also depends on the reactant ratio, being 5.6 : 1, 1.4 : 1, 0.75 : 1, and 0 : 1 at **I** : **II** = 1 : 2, 1 : 1, 2 : 1, and 4 : 1, respectively. These data show that, firstly, ortho ester **I** is involved in secondary processes; second, dilution of the reaction mixture with the ortho ester affects the ratio of the dehydrobromination and debromination pathways in the overall elimination process. At 1 : 2 ratio of the reactants, tribromoethylene **III** can be isolated pure by distillation of the reaction mixture, whereas at the 4 : 1 ratio dibromoethylene **VIII**, despite the absence of **III**, cannot be isolated pure, because its fraction also contains acetal **XIII** and ethyl acetate **XIV**.

Thus, in contrast to the reactions studied in [1–3], the ortho ester does not exhibit dehaloalkoxylating reactivity toward **II**. We believe that compounds **I** and **II** react along two major pathways: dehydrobromination and debromination.

Apparently, in both the cases ester **I** shows electron-donor properties, and its oxygen atom attacks the positively polarized hydrogen (dehydrobromination) or chlorine (debromination) atom. Intermediates **IV** and **IX** transform into ethanol **VII** and ethyl hypobromite **X**. The latter, being unstable and highly reactive, apparently gives rise to acetal **XIII** and ethyl acetate **XIV**. Ethyl hypobromite decomposes very readily to form hydrogen bromide **XII** and acetaldehyde **XI** [4]. In turn, acetaldehyde under the action of **I** and ethanol [5] undergoes acetalization; it also reacts with ethyl hypobromite **X** to form ethyl acetate **XIV** and hydrogen bromide **XII**. We confirmed experimentally that, when stored at temperatures below



0°C, compound **X** gradually transforms into **XII** and **XIV**. Goldschmidt et al. [6] reported on the formation of ethyl acetate **XIV** by spontaneous decomposition of ethyl hypobromite. An interesting feature is a high content of ethanol in the reaction mixture at any reactant ratio, suggesting its formation not only by the dehydrobromination, but also by decomposition of the ortho ester under the action of HBr [7].

Reaction of triethyl orthoformate I with 1,1,2,2-tetrabromoethane II. *a. 1 : 2 ratio.* A mixture of 37.52 g of tetrabromide **II** and 8.05 g of ortho ester **I** was heated in a sealed ampule at 180°C for 10 h. The ^{1}H NMR spectrum of the reaction mixture revealed the presence of ethyl formate **V**, ethyl bromide **VI**, ethanol **VII**, and tribromoethylene **III** as major products, with minor amounts of ethyl acetate **XIV** and dibromoethylene **VIII**; no acetal **XIII** was detected. A strong singlet at δ 6.05 ppm can be assigned to the proton of unchanged tetrabromoethane **II**. The conversion of **II** and the ratio of **III** and **VIII**, calculated from the relative intensities of the signals at δ 7.15, 7.05, 6.50, and 6.05 ppm, are 54.2% and 5.6 : 1. Readily volatile compounds were transferred in a vacuum into a trap cooled with liquid nitrogen. Distillation of the residue gave 9.5 g (55%) of tribromoethylene, bp 58–59°C (10 mm Hg), n_D^{20} 1.5975. Distillation of the condensate from the trap gave a fraction boiling in the range 38–56°C (8.2 g) and consisting of **V** and **VI**. The bottoms contained **II, V, VII, VIII**, and **XIV**, with compounds **II** and **VII** being the major components.

b. 2 : 1 ratio. The ^{1}H NMR spectrum of the reaction mixture obtained by heating a mixture of 10.03 g of **II** and 9.03 g of **I** at 180°C for 10 h largely resembles the spectrum of the mixture obtained at a 1 : 2 ratio. However, new signals belonging to protons of acetal **XIII** appeared, the ratio of **III** and **VIII** became 0.7 : 1, and the conversion of the tetrabromide increased to ~90%. Distillation gave 9.74 g of a fraction boiling in the range 44–55°C. The bottoms, according to ^{1}H NMR spectra, contained compounds **II**, **III**, **VIII**, **XIII**, and **XIV**; we failed to separate these components by distillation and obtained only fractions containing these compounds in various ratios. By repeated distillation of the low-boiling fraction we obtained 4.23 g of ethyl bromide, bp 38–39°C and 2.21 g of ethyl formate, bp 53–54°C.

Transformation of ethyl hypobromite X into ethyl acetate XIV. A solution of 2.11 g of ethanol in 3.73 g of water was mixed with a solution of 1.84 g of NaOH in 3.73 g of water; the mixture was cooled to 0°C. Then 6.96 g of bromine was added dropwise while cooling to 5–10°C. A small oily layer of **X** formed over the reaction mixture; it was separated, dried over $CaCl_2$, and allowed to stand in a refrigerator for a day, after which a ^{1}H NMR spectrum was recorded. The following signals ($CDCl_3$, δ, ppm) were observed: 3.95 q (2H, OCH_2, $^3J_{HH}$ 7.5 Hz), 1.01 t (3H, OCH_2CH_3, $^3J_{HH}$ 7.5 Hz), 1.85 s (3H, CH_3); these signals correspond to ethyl acetate **XIV**.

The ^{1}H NMR spectra were recorded on Bruker WP-80 and Tesla BS-567A spectrometers operating at 80 and 100 MHz. The proton chemical shifts are given relative to TMS. Chromatographic analysis of reaction mixtures was performed on a Tsvet-500 chromatograph under the following conditions: vaporizer temperature 180°C, column temperature 120°C, detector temperature 200°C, carrier gas flow rate 30 ml min^{-1}, flame ionization detector, carrier gas N_2, liquid phase PEG-20M (Carbowax). The peaks were identified by retention times (s).

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