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LETTERS TO THE EDITOR

Reaction of 1-Alkoxy-1-haloalkanes with Orthoformic Esters

M. B. Gazizov, M. A. Pudovik, K. M. Gazizov, R. F. Karimova, R. A. Khairullin, A. S. Romakhin, and V. V. Nikitin

Kazan State Technological University, Kazan, Tatarstan, Russia

Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, Kazan, Tatarstan, Russia

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We found a previously unknown reaction between 1-alkoxy-1-haloalkanes **Ia**–**Ie** and orthoformic esters **IIa** and **IIb**, yielding 1,1-dialkoxyalkanes **IIIa**–**IIId**, alkyl formates **IVa** and **IVb**, and alkyl halides **Va** and **Vb**. On mixing of compounds **I** and **II** in a 1:1 ratio, heat release was observed, weak at Hlg = Cl and considerable at Hlg = Br. The reaction progress was followed by ^{1}H NMR spectroscopy.

When the reaction products had close boiling points, they were not isolated individual, and their structures were assessed on the basis of the ^{1}H NMR spectra. Thus, on mixing of compound **Ia** with trimethyl orthoformate, a temperature rise of 4–5°C was observed. After 6 h, the ^{1}H NMR spectrum of the reaction mixture no longer showed signals of the starting compounds (δ, ppm: 3.6 s (3H, OMe), 5.33 s (2H, CH_2) (compound **Ia**) and 3.13 s (9H, OMe), 4.75 s (1H, CH) (compound **IIa**)] and showed the following signals: 3.2 s (6H, OMe), 4.31 s (2H, CH_2) (compound **IIIa**), 3.6 s (3H, OMe), 7.95 s (1H, CH) (compound **IVa**), and 2.94 s (3H, Me) (compound **Va**). In the other cases, products **III** were isolated individual by distillation.

$$\underset{\textbf{Ia–Ie}}{R^1CH(OR^2)Hlg} + \underset{\textbf{IIa, IIb}}{CH(OR^2)_3} \longrightarrow \underset{\textbf{IIIa–IIId}}{R^1CH(OR^2)_2} + \underset{\textbf{A}}{HC(OR^2)_2Hlg},$$

$$\textbf{A} \longrightarrow \underset{\textbf{IVa, IVb}}{HCOOR^2} + \underset{\textbf{Va, Vb}}{R^2Hlg},$$

I, R^1 = H (**a**), Ph (**b, c**), Me (**d, e**); R^2 = Me (**a, b**), Et (**c**–**e**); Hlg = Cl (**a**–**d**), Br (**e**). **II**, R^2 = Me (**a**), Et (**b**). **III**, R^1 = H, R^2 = Me (**a**); R^1 = Ph, R^2 = Me (**b**), Et (**c**); R^1 = Me, R^2 = Et (**d**). **IV, V**, R^2 = Me (**a**), Et (**b**).

We suggest that the exchange process begins with attack by the oxygen lone pair of ortho ethers **II** on the electropositive methine carbon atom of compounds **I**; the subsequent four-membered cyclic electron transfer leads to compounds **III** and **A**. The latter are unstable and readily decompose into alkyl formates **IV** and alkyl halides **V** [1].

Dimethoxy(phenyl)metane (IIIb) was obtained from 7.67 g of compound **Ib** and 5.72 g of ortho ether **IIa**, yield 72%, bp 82–83°C (12 mm) (bp 208°C [2]), n_D^{20} 1.5010. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.2 s (6H, OMe), 5.3 s (1H, CH), 7.3 m (5H, Ph).

Diethoxy(phenyl)methane (IIIc) was obtained from 2.05 g of compound **Ic** and 1.79 g of ortho ether **IIb**, bp 87–88°C (10 mm), n_D^{20} 1.4842 (bp 217–218°C, n_D^{15} 1.4843 [3]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.13 t (6H, Me, $^3J_{HH}$ 7.0 Hz), 3.4 q (4H, OCH_2, $^3J_{HH}$ 7.0 Hz), 5.42 s (1H, CH), 7.3 m (5H, Ph).

1,1-Diethoxyethane (IIId). *a*. Ortho ether **IIb**, 3.1 g, was added dropwise with stirring to 3.2 g of compound **Ie**. The reaction mixture warmed up from 22 to 29°C. It was stirred at 25°C and distilled to obtain 0.98 g (63%) of ethyl formate, bp 53–54°C, n_D^{20} 1.3598 (bp 54.3°C, n_D^{20} 1.3597 [4]) and 1.5 g (61%) of compound **IIId**, bp 100–101°C, n_D^{20} 1.3810 (bp 102–104°C, n_D^{20} 1.3819 [4]).

b. Ortho ether **IIb**, 3.1 g, was added dropwise to 2.27 g of compound **Id**. The reaction mixture warmed up by 2°C. After 12 h, it was distilled to obtain 0.96 g (62%) of ethyl formate, bp 53–54°C, n_D^{20} 1.3596, and 1.45 g (59%) of compound **IIId**, bp 100–101°C, n_D^{20} 1.3805.

The ^{1}H NMR spectra were measured on Bruker WP-80 (80 MHz) and Tesla BS-567A (100 MHz) spectrometers, internal reference TMS.

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