

LETTERS
TO THE EDITOR

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

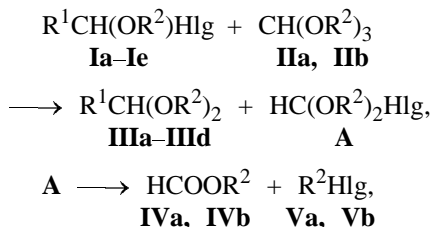
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We found a previously unknown reaction between 1-alkoxy-1-haloalkanes **Ia–Ie** and orthoformic esters **IIa** and **IIb**, yielding 1,1-dialkoxyalkanes **IIIa–IIIc**, alkyl formates **IVa** and **IVb**, and alkyl halides **Va** and **Vb**. On mixing 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 ^1H 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 ^1H NMR spectra. Thus, on mixing of compound **Ia** with trimethyl orthoformate, a temperature rise of 4–5°C was observed. After 6 h, the ^1H 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, CH₂) (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, CH₂) (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.



I, R¹ = H (**a**), Ph (**b**, **c**), Me (**d**, **e**); R² = Me (**a**, **b**), Et (**c–e**); Hlg = Cl (**a–d**), Br (**e**). **II**, R² = Me (**a**), Et (**b**). **III**, R¹ = H, R² = Me (**a**); R¹ = Ph, R² = Me (**b**), Et (**c**); R¹ = Me, R² = Et (**d**). **IV**, **V**, R² = 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. ^1H NMR spectrum (CDCl₃), 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]). ^1H NMR spectrum (CDCl₃), δ , ppm: 1.13 t (6H, Me, $^3J_{\text{HH}}$ 7.0 Hz), 3.4 q (4H, OCH₂, $^3J_{\text{HH}}$ 7.0 Hz), 5.42 s (1H, CH), 7.3 m (5H, Ph).

1,1-Diethoxyethane (IIIc). *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 **IIIc**, 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 **Ie**. 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 **IIIc**, bp 100–101°C, n_{D}^{20} 1.3805.

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

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