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## LETTERS TO THE EDITOR

## **New Reaction of Organic Monohalides with Orthoformates**

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No information on reaction of organic halides with orthoformic acid esters is available in the literature. At the same, this reaction might give important unsymmetrical ethers.

We are the first to find that organic monohalides possessing a high electrophilic reactivity, such as chlorotriphenyl-, chlorodiphenyl-, and bromodiphenylmethanes (Ia–Ic),in appropriate temperature conditions react with orthoformates IIa–IIc. Mixtures of compounds I and II (molar ratio 1:1.1) were heated in sealed ampules at 100–150°C to give unsymmetrical ethers IIIa, IIIb–IVa–IVc containing several benzene rings. Haloacetals Va–Vc formed by the same reaction decompose into alkyl formats VIa–VIc and alkyl halides [1].

 $Ph_nH_{3-n}CHlg + HC(OR)_3 \rightarrow Ph_nH_{3-n}COR + HC(OR)_2Hlg,$ Ia-Ic IIIa, IIIb, IVa-IVc Va-Vc

> $Va-Vc \longrightarrow HCOOR,$ -RHlg VIa-VIc

**I**, n = 3, Hlg = Cl (**a**); n = 2, Hlg = Cl (**b**), Br (**c**). **II**, R = Me (**a**), Et (**b**), Bu (**c**). **III**, n = 3, R = Me (**a**), Et (**b**). **IV**, n = 2, R = Me (**a**), Et (**b**), Bu (**c**). **V**, Hlg = Cl, R = Me (**a**), Et (**b**), Hlg = Br, R = Et (**c**). **VI**, R = Me (**a**), Et (**b**), Bu (**c**). Bu (**c**).

Reaction progress was followed by means of dynamic <sup>1</sup>H NMR spectroscopy. As the reaction mixture was heated, the intensity of the singlet signals at  $\delta$ 6.17, 6.31, 4.85, and 5.0 ppm of compounds **Ib**, **Ic**, **IIa**, and **IIb** decreased and that of the signals at  $\delta$  5.2 (s), 5.39 (s), 3.4 (s), 3.53 (q) ppm from the methine, methoxyl, and methylene oxide protons of compounds **IVa** and **IVb**, as well as at  $\delta$  3.0 (s), 3.4 (q), and 8.0 (s) ppm from the methoxyl, methylene oxide, and methane protons of products **IIIa**, **IIIb**, and **VIa–VIc** increased. By the end of heating the signals at  $\delta$  4.85, 5.0 and 6.17, 6.31 ppm disappeared completely, whereas the signal at  $\delta$  8.0 ppm compared in intensity with those at  $\delta$  5.2 and 5.39 ppm.

**Reaction of compounds Ia and IIa.** A mixture of 3 g monochloride **Ia** and 1.26 g of ortho ester **IIa** was heated at 150°C for 6 h and then distilled to obtain 2.45 g (83%) of methoxytriphenylmethane (**IIIa**), mp 81–83°C (from hexane). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.5–7.02 m (15H, Ph), 3.0 s (3H, OMe).

Ethoxytriphenylmethane (IIIb), 2.85 (92%), was obtained from 3 g of monochloride Ia and 1.76 g of ortho ester IIb (150°C, 7 h), mp 84°C (from hexane). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.4–7.0 m (15H, Ph), 3.4 q (2H, OCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> 7.5 Hz), 1.18 t (3H, Me, <sup>3</sup>J<sub>HH</sub> 7.5 Hz).

**Methoxydiphenylmethane** (IVa), 2.76 g (71%), was obtained from 4 g of monochloride Ib and 2.3 g of ortho ester IIa (150°C, 6 h), bp 81–83°C (0.05–0.08 mm Hg), nD 0 1.5628. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.58–7.22 m (10H, Ph), 5.2 s (1H, CH), 3.5 s (3H, OMe).

**Ethoxytriphenylmethane** (**IVb**). *a*. From 2.48 g of monochloride **Ib** and 1.99 g of ortho ester **IIb** (150°C, 7 h) we obtained 1.65 g (64%) of compound **IVb**, bp 149–150°C (9 mm Hg),  $n_D^{20}$  1.5505. <sup>1</sup>H NMR spectrum, δ, ppm: 7.55–7.18 m (10H, Ph), 5.39 s (1H, CH), 3.53 q (2H, OCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> 7.5 Hz), 1.2 t (3H, Me, <sup>3</sup>J<sub>HH</sub> 7.5 Hz).

*b*. From 3 g of monobromide **Ic** and 1.98 g of ortho ester **IIb** (150°C, 2 h) we isolated 1.43 g (56%) of compound **IVb**, bp 150–151°C (9 mm Hg),  $n_{\rm D}^{20}$  1.5498.

**Butoxydiphenylmethane** (IVc), 4.13 g (89%), was obtained from 3.9 g of monochloride Ib and 4.92 g of

ortho ester **IIc** (150°C, 13 h), bp 100–101°C (0.037 mm Hg),  $n_D^{20}$  1.5324. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.55–7.13 m (10H, Ph), 5.35 s (1H, CH), 3.5 t (2H, OCH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> 6.25 Hz), 1.25–1.81 m [4H, (CH<sub>2</sub>)<sub>2</sub>], 0.97 t (3H, Me, <sup>3</sup>J<sub>HH</sub> 6.25 Hz).

The <sup>1</sup>H NMR spectra were measured on a Tesla BC-567A spectrometer at 100 MHz in acetone- $d_6$ -CCl<sub>4</sub> relative to TMS.

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## REFERENCES

1. Mezheretskii, V.V., Olekhnovich, E.P., Luk'yanov, S.M., and Dorofeenko, G.N., *Ortoefiry v organicheskom sinteze* (Ortho Esters in Organic Synthesis), Rostov-on-Don: Rostov. State. Univ., 1976.