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New Reaction of Benzylidene Chloride with Trialkyl Orthoformates

M. B. Gazizov, K. M. Gazizov, M. A. Pudovik, A. A. Mukhamadiev, R. F. Karimova,
A. I. Sadykova, and Corresponding Member of the RAS O. G. Sinyashin

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Alkali-metal alcoholates [1] and methyl esters of phosphorus(IV) acids [2, 3] are known to be used for dehaloalkoxylation of organic gem-polyhalides. The final products of these reactions are carbonyl-containing compounds and their derivatives, which play an important role in organic synthesis. Highly reactive inorganic gem-polyhalides, for example, P(III) and Si(IV) halides, readily undergo dehaloalkoxylation with orthoesters [4]. However, there is no data in the literature on the use of the latter in reactions with much less reactive organic gem-polyhalides.

In this paper, we describe a new reaction between benzylidene chloride (**I**) and trialkyl orthoformates (**II**) to form, depending on reagent ratio (1 : 2.2 or 1 : 1) and temperature conditions (225 or 237°C), benzaldehyde or its acetals, which have been isolated in their individual states in good yields. The reactions of acetal **V** with compound **I**, as well as α-chloroether **III** with trialkyl orthoformates, have been carried out experimentally for the first time. A general scheme for the reaction of benzylidene chloride with trialkyl orthoformates has been suggested.

A mixture of compounds **I** and **II** in 1 : 1 or 1 : 2.2 ratios was heated in a sealed ampule. The structure of reaction products was established by ^{1}H NMR spectroscopy, while the reaction mixture composition was determined by gas chromatography. The major products of the reaction were found to be dialkyl acetal (**V**), alkyl formate (**VI**), alkyl halide (**VII**), and benzaldehyde (**VIII**):

$$\underset{(\mathbf{I})}{\mathrm{PhCHCl_2}} + \underset{(\mathbf{IIa},\ \mathbf{IIb})}{\mathrm{HC(OR)_3}} \longrightarrow \underset{(\mathbf{III})}{\mathrm{PhCH(OR)Cl}} + \underset{(\mathbf{IV})}{\mathrm{HC(OR)_2Cl}},$$

$$\mathbf{III} + \mathbf{II} \longrightarrow \underset{(\mathbf{V})}{\mathrm{PhCH(OR)_2}} + \mathbf{IV},$$

$$\mathbf{IV} \longrightarrow \underset{(\mathbf{VI})}{\mathrm{HCOOR}} + \underset{(\mathbf{VII})}{\mathrm{RCl}},$$

$$\mathbf{V} + \mathbf{I} \longrightarrow 2\mathbf{III},$$

$$\mathbf{III} \longrightarrow \underset{(\mathbf{VIII})}{\mathrm{PhCHO}} + \mathbf{VII},$$

$$\mathbf{II.}\ \mathrm{R = Me\ (a),\ Et\ (b)}.$$

The formation of a marked amount of alkyl benzoate (**IX**) also attracted our attention.

To reveal optimal reaction conditions, we used dynamic ^{1}H NMR spectroscopy. The spectra were recorded every 6 h, with volatile compounds **VI** and **VII** being removed from the reaction mixture after sampling and before the ampule was sealed. Alteration in the integrated intensities of the following resonance signals of initial reactants and reaction products was monitored (δ, ppm): $\mathrm{PhCHCl_2}$, 6.7 (s, $\mathrm{CHCl_2}$); $\mathrm{HC(OMe)_3}$, 4.8 (s, CH), 3.13 (s, Me); $\mathrm{PhCH(OMe)_2}$, 5.3 (s, $\mathrm{CHO_2}$), 3.2 (s, Me); PhCHO, 9.95 (s, CHO); HCOOMe, 7.95 (s, CH), 3.6 (s, Me); MeCl, 2.88 s; PhCOOMe, 3.8 (s, Me). The reaction between compounds **Ia** and **IIa** was found to proceed slowly at 180°C, but its rate increased noticeably above 220°C. The table presents reaction conditions and the yields of products **I**, **II**, **V**, **VIII**, and **IX**. The heating of a mixture of reagents **I** and **IIa** for 28 h at 225°C (in the ratio of 1 : 2.2) leads mainly to acetal **Va**. When heating time was increased to 39 h, compounds **I** and **IIa** were completely consumed and only a negligible amount of benzaldehyde **VIII** was detected in the reaction mixture. Its content in the mixture increases considerably if the reaction is carried out at 237°C.

Upon heating a mixture composed of compounds **I** and **IIa** in a 1 : 1 ratio at 225°C for 28 h, the orthoformate reacts completely, and the ratio of resultant acetal **Va** and initial benzylidene chloride is 0.95 : 1.0. When the resulting reaction mixture was heated at 237°C for 14 h, ^{1}H NMR spectrum shows no signals at δ 5.3 and 3.2 ppm from acetal **Va**. Benzaldehyde becomes the main component of the reaction mixture, although the products **I**, **VIa**–**VIIa**, and **IXa** are also present in different amounts. Benzaldehyde is the main reaction product if a 1 : 1 mixture of compounds **I** and **IIa** is directly heated at 237°C for 24 h, but negligible quantities of benzylidene chloride and acetal **Va** also remain unspent.

Kazan State Technological University, ul. Lenina 18, Kazan, 420008 Tatarstan, Russia

Arbuzov Institute of Organic and Physical Chemistry, ul. Lenina 18, Kazan 8, 420008 Tatarstan, Russia

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Table

Initial reagents	Initial reagent ratio	Reaction temperature, °C	Heating duration, h	Content of products				
				I	**II**	**V**	**VIII**	**IX**
I + **IIa**	1 : 2.2	225	28	5.7	7.9	71.0	0.0	11.4
	1 : 2.2	225	39	0.0	0.0	80.5	0.3	14.44
	1 : 1	237	24	3.4	0.0	5.2	75.1	13.1
I + **Va**	1 : 1	237	10	2.1	–	1.4	88.0	8.5
	1 : 1	237	14	1.0	–	0.0	90.1	8.8

The above experimental data indicate that the reaction leads only to acetal **V** at 225°C and the reagent ratio of 1 : 2.2, whereas at 237°C and a 1 : 1 reagent ratio, the reaction of resultant compound **V** with benzylidene chloride results in benzaldehyde. The separately studied reaction between compounds **I** and **V** also leads to the formation of product **VIII**.

We believe that a substitution of an alkoxy group for the chlorine atom in benzylidene chloride takes place at the first stage of the reaction. The resulting α-chloroether **III** further undergoes an exchange reaction with trialkyl orthoformate to give acetal **V**. Chloroacetal **IV** decomposes into alkyl formate **VI** and alkyl chloride **VII** [4]. Under more severe temperature conditions, acetal **V** behaves as a dechloroalkoxylating agent toward benzylidene chloride. Under conditions where there is a shortage or absence of trialkyl orthoformate, α-chloroether **III** undergoes thermal decomposition to yield benzaldehyde and alkyl chloride [5]. Compound **IX** seems to form upon thermal decomposition of acetal **V** [6].

No data were reported in the literature on the reaction of α-haloethers with trialkyl orthoformates. We have established that the reaction of compounds **II** and **III** occurs at room temperature to produce acetal **V** and products **VI** and **VII**. It becomes understandable why only acetal **V** is formed at a 1 : 2.2 ratio of reagents **I** and **II** and why only a trace amount of benzaldehyde is detected in the reaction mixture.

EXPERIMENTAL

^{1}H NMR spectra were recorded on Bruker WP-80 and Tesla BS-567A spectrometers at 80 and 100 MHz, respectively. Proton chemical shifts are given relative to TMS. Chromatographic analysis of reaction mixtures was carried out on a Tsvet-500 chromatograph. Chromatography conditions: injector temperature 180°C, column temperature 120°C, detector temperature 200°C, 30 mL/min carrier gas flow rate, flame ionization detection, nitrogen as carrier gas, PEG 20M (Carbowax) as liquid phase. Peak identification was performed by retention time in seconds: $PhCHCl_2$ 282, PhCOOMe 223, PhCHO 172, $PhCH(OMe)_2$ 150, $HC(OMe)_3$ 38, HCOOMe + MeCl 33. Experiments were carried out under dry nitrogen atmosphere.

Benzaldehyde dimethyl acetal (Va). A. A mixture of 15 mmol of benzylidene chloride and 33 mmol of orthoformate **IIa** was heated in a sealed ampule for 39 h at 225°C. The reaction mixture was fractionated with a distilling column to give 1.75 g (76%) of acetal **Va**, bp 83–84°C (12 mmHg) and 208–209°C, n_D^{20} 1.5010 (lit.: bp 208°C [7]). **B.** A mixture of 54 mmol of orthoformate **IIa** and 49 mmol of compound **IIIa** was kept for 24 h at 20°C. Distillation of the reaction mixture afforded 5.39 g (72%) of acetal **Va**, bp 82–84°C (12 mmHg), n_D^{20} 1.5005.

Benzaldehyde diethyl acetal (Vb). A. A mixture of 15 mmol of compound **I** and 33 mmol of orthoformate **IIb** was heated for 40 h at 225°C. Distillation gave 2.17 g (80%) of acetal **Vb**, bp 87–88°C (10 mmHg), n_D^{20} 1.4842 (lit.: bp 217–221°C, n_D^{20} 1.4843 [7]. **B.** A mixture of 12.1 mmol of orthoformate **IIb** and 12 mmol of compound **IIIb** was kept for 24 h at 20°C to yield 1.52 g (70%) of acetal **Vb**, bp 87–88°C (10 mmHg), n_D^{20} 1.4839.

Benzaldehyde (VIII). A. A mixture of 20.75 mmol of compound **I** and 20.75 mmol of orthoformate **IIa** was heated for 24 h at 237°C. Distillation gave 1.63 g (74%) of benzaldehyde **VIII**, bp 70–71°C (14 mmHg), n_D^{20} 1.5430 (lit.: bp 62°C (10 mmHg), n_D^{20} 1.5463 [8]. **B.** The above mixture was heated for 28 h at 225°C and 14 h at 237°C to give 1.58 g (72%) of benzaldehyde, bp 70–71.5°C (14 mmHg). **C.** A mixture of 10.16 mmol of compound **I** and 11.17 mmol of acetal **Va** was heated for 14 h at 237°C to produce 0.92 g (85%) of benzaldehyde, bp 70–71°C (14 mmHg).

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