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LETTERS TO THE EDITOR

New Reaction of Di- and Trichloromethylbenzenes with Orthoformic Esters

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We have discovered a new reaction of di- and trichloromethylbenzenes I with orthoformic esters II and found that the product structure depends on the nature of X, temperature, and reagent ratio. Thus, at X = Hand reagent ratio 1:2.2, the major reaction product after 39-h heating at 225°C is acetal V. Increasing the heating temperature to 237°C and changing the reagent ratio to 1:1 favors formation of aldehyde VI. At X = Cl, reagent ratios 1:1 and 1:3, temperature 180°C, and reaction time 10–17 h, the major products are benzoic acid chloride VIII or ester IX. Irrespective of the nature of X, alkyl formate X and alkyl halide VII are also formed.

 $PhCXCl_2 + HC(OR)_3 \longrightarrow PhCX(OR)Cl + HC(OR)_2Cl,$ III Ι Π IV $\mathbf{IIIa} + \mathbf{II} \longrightarrow \mathbf{PhCH(OR)}_2 + \mathbf{IV},$ $\mathbf{V} + \mathbf{I} \longrightarrow 2\mathbf{IIIa}$ IIIa \longrightarrow PhCHO + RCl, VI VII IIIb \longrightarrow PhCOCl + VII, VIII VIII + II \longrightarrow PhCOOR + IV, IX $IV \longrightarrow HCOOR + VII,$ Х

I, III, X = H (a), Cl (b); I, III–V, VII, X, R = Me (a), Et (b); IX, R = Et.

Compounds I exhibit a clearly pronounced electrophilic reactivity toward oxygen-containing organic compounds [1, 2]. As follows of the above data, benzotrichloride Ib is a stronger electron acceptor than benzylidene chloride Ia. We suggest that the reaction involves initial substitution of one chlorine atom in compounds I by an alkoxy group. The resulting α -chloroether IIIa further exchanges with ortho ester II to form acetal V. Similar conversion of α chloroethers was previously described [3]. Under more rigid temperature conditions (237°C), acetal V acts as a dechloroalkoxylating agent toward benzylidene chloride Ia. When insufficient or no ortho ester II is present, compound IIIa undergoes thermal decomposition into benzaldehyde (VI) and alkyl chloride **VII**. α, α -Dichloroether **IIIb** is much more labile than α -chloroether IIIa and decomposes into alkyl halide VII and benzoyl chloride (VIII). The latter is alkoxylated with the ortho ester to give ethyl benzoate IX. Chloroacetal IV, too, is unstable and decomposes into alkyl formate X and compound VII [4].

Reaction between compounds Ib and IIb. *a. Ratio 1:1.* Trichloride **Ib**, 2.59 g, and 1.96 g of ortho ester **IIb** was heated at 180°C for 10 h in a sealed ampule. Distillation gave 1.73 g of a mixture of compounds **VIII** and **IX** in a 2:1 ratio (¹H NMR data), bp 104–106°C (8 mm).

b. Ratio 1:3. A mixture of 1.95 g of trichloride **Ib** and 4.44 g of ortho ester **IIb** was heated at 180°C for 17 h. Distillation gave 1.36 g of ethyl benzoate, bp 101–102°C (10 mm Hg), n_D^{20} 1.5071 (published data [5]: bp 212.6°C, n_D^{20} 1.5068). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.25 t (3H, Me, ³J_{HH} 7.5 Hz), 4.25 t (2H, OCH₂, ³J_{HH} 7.5 Hz), 7.8 m (5H, Ph).

Benzaldehyde dimethyl acetal (Va). *a*. A mixture of 2.41 g of benzylidene chloride and 3.5 g of ortho ester **Ha** was heated for 39 h at 225°C in a sealed ampule. Distillation gave 1.75 g (76%) of acetal **Va**, bp 83–85°C (12 mm) and 208–209°C, n_D^{20} 1.5010 (published data [6]: bp 208°C). ¹H NMR spectrum

(CDCl₃), δ, ppm: 3.5 s (6H, OMe), 5.3 s (1H, CH), 7.3 m (5H, Ph).

b. A mixture of 5.73 g of ortho ester **Ha** and 7.67 g of compound **HHa** was left to stand for 24 h at 20°C. Distillation gave 5.39 g (72%) of acetal **Va**, bp 82–84°C (12 mm Hg), $n_{\rm D}^{20}$ 1.5005.

Benzaldehyde diethyl acetal (Va). *a*. A mixture of 2.42 g of compound I and 4.89 g of ortho ester IIb was heated for 40 h at 225°C. Distillation gave 2.17 g (80%) of acetal **Vb**, bp 87– 88°C (10 mm Hg), n_D^{20} 1.4842 (published data [6]: bp 217–221°C, n_D^{20} 1.4843). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.12 t (6H, Me, ³J_{HH} 7.5 Hz), 3.48 q (4H, OCH₂, ³J_{HH} 7.5 Hz), 7.3 m (5H, Ph).

b. A mixture of 1.79 g of ortho ester **IIb** and 2.06 g of compound **IIIb** was allowed to stand for 24 h at 20°C to obtain 1.52 g (70%) of acetal **Vb**, bp 87–88°C (10 mm Hg), $n_{\rm D}^{20}$ 1.4839.

Benzaldehyde (VI). *a*. A mixture of 3.34 g of compound **Ia** and 2.2 g of ortho ester **IIa** was heated for 24 h at 237°C. Distillation gave 1.63 g (74%) of benzaldehyde (**VI**), bp 70–71°C (14 mm Hg), n_D^{20} 1.5430 {published data [5]: 62°C (10 mm Hg), n_D^{20} 1.5430}. ¹H NMR spectrum (CDCl₃), δ , ppm: 7.3–7.9 m (5H, Ph), 9.95 s (1H, CHO).

b. A mixture of 1.64 g of compound **Ia** and 1.7 g of acetal **Va** was heated for 14 h at 237°C to obtain 0.92 g (85%) of compound **VI**, bp 70–71°C (14 mm Hg).

The ¹H NMR spectra were measured on a Tesla BC-567A spectrometer (100 MHz) against TMS.

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