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LETTERS TO THE EDITOR

Transformation of Trichloromethyl Arenes to Methyl Arenecarboxylates and Arene–Carbonyl Chlorides Under the Action of Methyl Esters of Tetracoordinate Phosphorus Acids

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It is established that the reaction of trichloromethylarenes **Ia**–**Ic** with two equivalents of dimethyl methylphosphonate **II** (30 h, 200°C) leads to formation of methyl arenecarboxylates **IIIa**–**IIIc** and also the cyclic anhydride of methylphosphonic acid **IV**.

$$\underset{\mathbf{Ia}\text{–}\mathbf{Ic}}{3\mathrm{ArCCl_3}} + \underset{\mathbf{II}}{6\mathrm{MeP(O)(OMe)_2}}$$

$$\longrightarrow \underset{\mathbf{IIIa}\text{–}\mathbf{IIIc}}{3\mathrm{ArCOOMe}} + \underset{\mathbf{IV}}{2[\mathrm{MeP(O)O}]_3} + \underset{\mathbf{V}}{9\mathrm{MeCl}},$$

I, III, Ar = Ph (**a**), 3-$\mathrm{ClC_6H_4}$ (**b**), 4-$\mathrm{ClC_6H_4}$ (**c**).

At a 1 : 1 molar ratio of starting compounds **Ia** and **II** and 180°C reaction yields benzoyl chloride **VIa** and not methyl benzoate as the main product.

$$3\mathbf{Ia} + 3\mathbf{II} \longrightarrow \underset{\mathbf{VIa}}{3\mathrm{PhCOCl}} + \mathbf{IV} + 6\mathbf{V}.$$

Under the same conditions 3-(trichloromethyl)-chlorobenzene **Ib** or 4-(trichloromethyl)chlorobenzene **Ic** gives a mixture of acid chloride and ester, **IIIb**, **VIb** and **IIIc**, **VIc** respectively, and some part of the starting trichloromethyl arene remains unreacted. From the obtained experimental results it follows that trichloromethylarenes under the action of methyl P(IV) acid ester firstly form arenecarbonyl chloride **VIa**–**VIc**. Their subsequent reaction with an excess of **II** gives ester **IIIa**–**IIIc**. Model reaction between the compounds **II** and **VIa** really leads to corresponding products **IIIa** and **IV**. According to the published data [1–3] reaction of carboxylic acid chloride with dialkyl alkylphosphonate yields carboxylic acid anhydride of and esteroanhydrides of alkylphosphonic acid. Considering these data, we have proposed that the transformation of acid chloride **VIa** to the ester **IIIa** includes the intermediate formation of benzoic acid anhydride **VII**. In the separate experiment it was shown that the reaction of anhydride **VII** with the phosphonate **II** finishes by the formation of the ester **IIIa** and anhydride **IV**.

$$\underset{\mathbf{VII}}{3\mathrm{(PhCO)_2O}} + 3\mathbf{II} \longrightarrow 6\mathbf{IIIa} + \mathbf{IV}.$$

Methyl diethylphosphinate **VIII** and trimethylphosphate **IX** were also involved in the discovered reaction. On the whole synthetic result of the reaction of trichloromethylarenes with methyl esters of P(IV) acids is determined by the nature of starting reagents, their ratio and the temperature conditions of the process.

Methyl benzoate (IIIa). *a*. A mixture of 5.45 g of trichloromethylbenzene **Ia** and 6.92 g of compound **II** were heated for 30 h at 200°C. 2.98 g (76%) of compound **IIIa**, bp 80–81°C (10 mm), n_D^{20} 1.5148 [5], and 2.73 g (63%) of the anhydride **IV**, mp 111–112°C. ^{1}H NMR spectrum ($\mathrm{CDCl_3}$), δ, ppm: 1.2–1.5 m (9H, $\mathrm{CH_3}$–P), δ_P 16 ppm. Found, %: P 39.81. $\mathrm{CH_3O_2P}$. Calculated, %: P 39.74. Mass spectrum: *m/z* 234 $[\mathrm{MePO_2}]_3^+$.

b. A mixture of 4.36 g of trichloromethylbenzene **Ia** and 4.37 g of compound **IX** was heated for 32 h at

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200°C. Compound **IIIa**, 1.78 g (58.7%) was obtained, bp 79–80°C (10 mm), n_D^{20} 1.5147.

c. A mixture of 5.05 g of compound **Ia** and 14 g of compound **VIII** was heated for 27 h at 200°C to give 3.0 g (86%) of compound **IIIa**, bp 80–81°C (10 mm), n_D^{20} 1.5150, and 8.31 g (71.2%) of diethylphosphinic acid anhydride, bp 113°C (0.05 mm), δ_P 60 ppm. Found, %: P 27.50. $C_8H_{20}O_3P_2$. Calculated, %: P 27.39.

d. A mixture of 5.71 g of acid chloride **VI** and 5.04 g of phosphonate **III** was heated for 16 h at 210°C to give 8.1 g (67.5%) of compound **IIIa**, bp 103–105°C (40 mm), n_D^{20} 1.5135, and 2.15 g (66%) of anhydride **IV**, mp 111–113°C, δ_P 16 ppm.

Methyl 3-chlorobenzoate (IIIb). A mixture of 2.28 g of 3-(trichloromethyl)chlorobenzene **Ib** and 2.46 g of phosphonate **II** was heated for 53 h at 180°C to give 1.37 g (81%) of compound **IIIb**, bp 140–142°C (12 mm), n_D^{20} 1.5490 [6]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.8 s (3H, $COOCH_3$), 7.2–8.2 m (4H, C_6H_4). IR spectrum, ν, cm^{-1} 1733 (C=O). From the chloroform solution 0.98 g (42%) of anhydride **IV** were isolated, mp 112–113°C, δ_P 16 ppm.

Methyl 4-chlorobenzoate (IIIc). This compound was obtained analogously from 2.35 g of compound **Ic** and 2.54 g of phosphonate **II**. Yield 1.38 g (79%), bp 136–137°C (10 mm), mp 43°C [6]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.8 s (3H, $COOCH_3$), 7.2–8.2 m (4H, C_6H_4). IR spectrum, ν, cm^{-1}: 1735 (C=O). From the chloroform solution 1.05 g (44%) of the anhydride **IV** was isolated, mp 111–113°C, δ_P 16 ppm.

Reaction of 3-(trichloromethyl)chlorobenzene (Ib) with compound (II). A mixture of 2.32 g of compound **Ib** and 1.25 g of phosphonate **II** was heated for 40 h at 180°C. Fractionation of the liquid part of reaction mixture gave two fractions with bp 107–110°C (14 mm) and 110–130°C (14 mm). According to IR and ^{1}H NMR spectra the first fraction consisted of a mixture of compounds **IIIb** and **VIb** in 2 : 1 ratio. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.8 s (3H, $COOCH_3$), 7.2–8.2 m (4H, C_6H_4). IR spectrum, ν, cm^{-1}: 1733, 1766 (C=O). The second fraction is a mixture of compounds **Ib, IIIb**, and **IVb**. From the chloroform solution of the solid part of reaction mixture 0.48 g (41%) of the anhydride **IV** was obtained, mp 111–112°C, δ_P 16 ppm.

Benzoyl chloride (VIa). A mixture of 5.45 g of trichloromethylbenzene **Ia** and 3.46 g of compound **II** was heated in a sealed ampule for 30 h at 180°C. Distillation of reaction mixture gave 3.04 g (78%) of compound **VIa**, bp 75–76°C (10 mm), n_D^{20} 1.5521 [4]. Crystallization of the solid part from chloroform gave 1.82 g (57%) of methylphosphonuc acid anhydride **IV** mp 111 3112°C.

IR spectra of compounds were recorded on an UR-20 spectrometer in thin layer in the range of 400–4600 cm^{-1}. ^{1}H NMR spectra were measured on a Tesla BS-567A spectrometer (100 MHz) against internal TMS. ^{31}P NMR spectra were registered on a RYa-2303 spectrometer (21.0 MHz) against external 85% phosphoric acid. Mass spectra were obtained on a MX-1310 spectrometer at the ionizing voltage 70 V, ion collector current 30 μA, and the average temperature of the ion source 120°C. Accurate measurement of mass was carried out automatically by the reference peaks of perfluorocerosene at the resolving power *R* 15000.

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