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LETTERS TO THE EDITOR

Reaction of Acyl Halides and P(III) Chlorides with Alkyl Diphenyl(or Triphenyl)methyl Ethers

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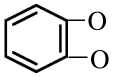
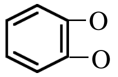
It is known that ortho esters of carboxylic acids and acetals are used for dehaloalkoxylation of acyl halides **I** and P(III) chlorides [1–4]. However, the use of ethers for this purpose has never been reported.

In our work we discovered a new reaction of compounds **I** and **II** with alkyl diphenyl(or triphenyl)methyl ethers **III**, which proceeds regioselectively: The halogen atom is substituted exclusively by an alkoxy group. The alternative reaction pathway involving the diphenyl(or triphenyl)methoxy group is not realized, and we failed to detect alkyl halides R^2Hal even in trace amounts.

$$\underset{\mathbf{I}}{R^1COHlg} + \underset{\mathbf{III}}{Ph_nH_{3-n}COR^2} \longrightarrow \underset{\mathbf{IV}}{R^1COOR^2} + \underset{\mathbf{V}}{Ph_nH_{3-n}CHlg},$$

I, R^1 = Me, Hlg = Cl (**a**), Br (**b**); R^1 = Ph, Hlg = Cl (**c**); **III**, n = 2, R^2 = Me (**a**), Et (**b**); n = 3, R^2 = Me (**c**), Et (**d**); **IV**, R^1 = Me, R^2 = Me (**a**), Et (**b**); R^1 = Ph, R^2 = Me (**c**), Et (**d**); **V**, n = 2, Hlg = Cl (**a**), Br (**b**); n = 3, Hlg = Cl (**c**), Br (**d**).

$$\underset{\mathbf{II}}{X_2PCl} + \mathbf{III} \longrightarrow \underset{\mathbf{VI}}{X_2POR^2} + \mathbf{V},$$

II, X = Cl (**a**), X_2 =  (**b**); **VI**, R^2 = Et, X = Cl (**a**), X_2 =  (**b**).

To assess the relative activity of the reagents and their transformation degree, we studied this reaction by means of dynamic ^{1}H NMR spectroscopy, taking ^{1}H NMR spectra every 5 min and tracing the intensity of the signals at δ, ppm (assignment, comp. no.): 6.31 s (CH, **Vb**), 6.17 s (CH, **Va**), 3.2 s (OMe, **IIIa**), 3.0 s (OMe, **IIIc**), 3.5 q (OCH_2, **IIIb**), 3.05 q (OCH_2, **IIId**), 3.8 s (OMe, **IVc**), 4.05 q (OCH_2, **IVb**), 4.2 q (OCH_2, **IVd**). It was found that the reactivity of compounds **I**, **II**, and **III** depends on their nature. Bromo derivative **Ib** is more active than its chloro analogs **Ia** and **Ic**; acetyl chloride and phosphorus trichloride are found more reactive than benzoyl chloride and *o*-phenylene phosphorochloridite, respectively, and triphenyl derivatives **IIIc** and **IIId** are less active than diphenyl derivatives **IIIa** and **IIIb**, probably, by steric reasons.

Reaction of acyl halides I with alkyl diphenyl(or triphenyl)methyl ethers. A mixture of equal quantities of compound **I** and **III** was kept at room temperature for 18 h or heated in a sealed ampule at 70°C for 13 h; with less active acyl halides, the mixture was additionally heated at 100°C for 10 h. Ether **IV** was collected under high vacuum in a liquid nitrogen trap and then distilled. Halides **V** were isolated by recrystallization from hexane or by high-vacuum distillation.

a. A mixture of 1.65 g of **Ib** and 3 g of **IIIc** was kept at 25°C for 18 h to form 0.98 g (83%) of compound **IVb**, bp 77°C, n_D^{20} 1.3725 (published data: bp 77°C, n_D^{20} 1.3723 [5]). ^{1}H NMR spectrum, δ, ppm: 1.15 t (3H, Me, $^3J_{HH}$ 7.5 Hz), 1.9 s (3H, COMe), 4.05 q (2H, OCH_2, $^3J_{HH}$ 7.5 Hz). Yield of **Vb** 2.6 g (80%), bp 96–98°C (0.06 mm Hg), n_D^{20} 1.6200; mp 45°C {pulished data: bp 172°C (11 mm Hg), mp 45°C [5]}. ^{1}H NMR spectrum, δ, ppm: 6.31 s (1H, CHBr), 7.1–7.6 m (10H, Ph).

b. A mixture of 1.34 g of **Ib** and 3 g of **IIIc** was heated at 70°C for 13 h to obtain 0.65 g (81%) of compound **IVa**, bp 57°C, n_D^{20} 1.3642 {published data: bp 57°C, n_D^{20} 1.3619 [2]}, ^{1}H NMR spectrum, δ, ppm: 1.9 s (3H, COMe), 3.8 s (3H, OMe), and 3.39 g (97%) of halide **Vd**, mp 152–153°C (published mp 152°C [5]), ^{1}H NMR spectrum, δ, ppm: 7.02–7.5 m (15H, Ph).

c. A mixture of 1.36 g of **Ia** and 5 g of **IIId** was heated at 70°C for 13 h to obtain 1.25 g (82%) of **IVb**, bp 77°C, n_D^{20} 1.3722 and 4.68 g (97%) of **Vc**, mp 112–113°C {published data: bp 230–235°C (20 mm Hg), mp 112°C [5]}. ^{1}H NMR spectrum, δ, ppm: 7.1–7.5 m (15H, Ph).

d. A mixture of 0.85 g of **Ib** and 2.08 g of **IIId** was heated at 70°C for 13 h to prepare 0.45 g (74%) of **IVb**, bp 77°C, n_D^{20} 1.3755 and 1.81 g (81%) of **Vd**, mp 151–152°C.

e. A mixture of 0.97 g of **Ic** and 2 g of **IIId** was heated at 70°C for 25 h and then at 100°C for 10 h to obtain 0.81 g (78%) of **IVd**, bp 91–92°C (15 mm Hg), n_D^{20} 1.5055 {published data: bp 106°C (25 mm Hg), n_D^{20} 1.5052 [5]}. ^{1}H NMR spectrum, δ, ppm: 1.2 t (3H, Me, $^3J_{HH}$ 7.5 Hz), 4.2 q (2H, OCH_2, $^3J_{HH}$ 7.5 Hz), 7 m (5H, Ph) and 1.64 g (86%) of **IVc**, bp 161°C (0.14 mm Hg), mp 112°C.

f. A mixture of 1.31 g of **Ic** and 1.85 g of **IIIa** was heated at 70°C for 25 h and at 100°C for 10 h to give 0.91 g (72%) of **IVc**, bp 199–200°C, n_D^{20} 1.5172 {published data: bp 199.5°C, n_D^{20} 1.5170 [5]}. ^{1}H NMR spectrum, δ, ppm: 3.8 s (3H, OMe), 7 m (5H, Ph) and 1.5 g (80%) of **Va**, bp 155°C (10 mm Hg), n_D^{20} 1.5945 {published data: bp 159°C (12 mm Hg), n_D^{20} 1.5959 [5]}. ^{1}H NMR spectrum, δ, ppm: 6.17 s (1H, CHCl), 7.2–7.6 m (10H, Ph).

Reaction of P(III) chlorides II with alkyl diphenyl(or triphenyl)methyl ethers. *a*. A mixture of 1.2 g of **IIb** and 2 g of **IIId** was heated at 70°C for 5 h and distilled with a Vigreux column to obtain 1.05 g (83%) of ethyl *o*-phenylene phosphite (**VIb**), bp 87–88°C (15 mm Hg), n_D^{20} 1.5091 {published data: bp 86°C (11 mm Hg), n_D^{20} 1.5085 [6]}. ^{1}H NMR spectrum, δ, ppm: 1.11 t (3H, Me, $^3J_{HH}$ 7.5 Hz), 3.6 quintet (2H, OCH_2, $^3J_{HH} = {}^3J_{PH} = 7.5$ Hz), 7.25 s (4H, $C_6H_4O_2$). The residue was crystallized from hexane to isolate 1.54 g (80%) of **Vc**, mp 111– 112°C.

b. A mixture of 6.43 g of **IIa** and 3.36 g of **IIId** was kept at 25°C for 30 days and then distilled with a Vigreux column to obtain 1.3 g (78%) of ethyl phosphorodichloridite (**VIa**), bp 55–58°C (150 mm Hg), n_D^{20} 1.4662 {published data: bp 55–60°C (150 mm Hg), n_D^{20} 1.4660 [7]}. ^{1}H NMR spectrum, δ, ppm: 1.26 t (3H, Me, $^3J_{HH}$ 7.5 Hz), 4.25 quintet (2H, OCH_2, $^3J_{HH} = {}^3J_{PH} = 7.5$ Hz). The residue was crystallized from hexane to isolate 2.6 g (80%) of **Vc**, mp 112–113°C.

c. A mixture of 7.75 g of **IIa** and 3 g of **IIIb** was kept at 25°C for 30 days and then distilled with a Vigreux column to obtain 1.68 g (81%) of **VIa**, bp 55–59°C (150 mm Hg), n_D^{20} 1.4661, and 2.39 g (84%) of **Va**, bp 155°C (10 mm Hg), n_D^{20} 1.6000.

The ^{1}H NMR spectra were recorded on a Bruker WP-80 and Tesla BS-567A spectrometers operating at 80 and 100 MHz, respectively. The chemical shifts were measured for $CDCl_3$ solutions against TMS.

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