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LETTERS TO THE EDITOR

Transformation of 4-Nitrobenzyl Halides at the Action of Phosphinates and Carboxylic Acids Orthoesters

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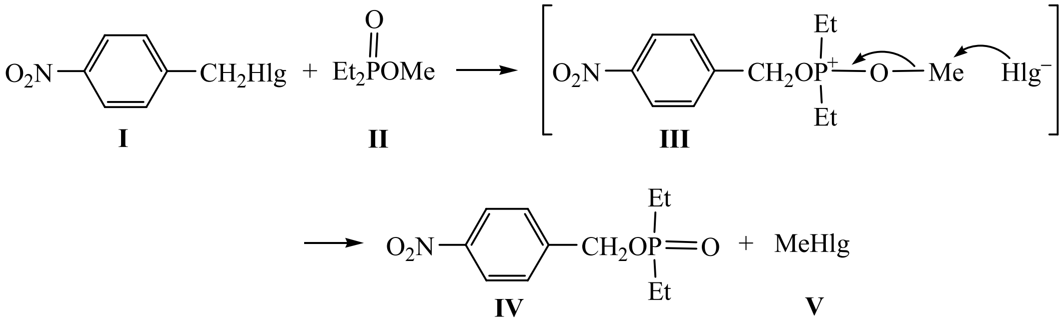
Previously we studied the reaction of organic *gem*-di- and trihalides with methyl esters of P(IV) acids [1] and trialkyl orthoformates [2]. However, the literature contains no information on the reaction of the above reagents with organic monohalides.

We first discovered that methyl diethylphosphinate **II** reacts with halides **Ia** and **Ib** at 150 and 180°C, respectively, to form 4-nitrobenzyl diethylphosphinate **IV**. Apparently, the phosphinate **II** attacks the methylene carbon of halide **I** by its more nucleophilic phosphoryl oxygen. The resulting quasiphosphonium salt **III** can be stabilized via the second stage of the Arbuzov reaction to release methyl halide **V** and to form a stable phosphinate **IV**.

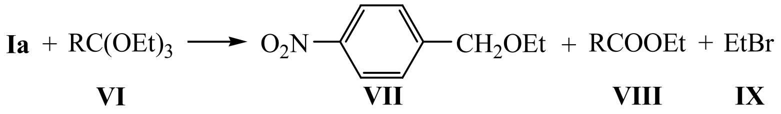


I, III, V: Hlg = Br (**a**), Hlg = Cl (**b**).

4-Nitrobenzyl bromide **Ia** was found to be subjected to dehaloalkoxylation with triethyl orthoformate **VIa** at 220ºC to form 4-(nitrobenzyl) ethyl ether **VII**. At the same time its chlorine analog **Ib** under these conditions remains inert toward compound **VIa**. More nucleophilic triethyl ortoacetate **VIb** reacts with bromide **Ia** under milder conditions (180ºC).

The reaction proceeds through the substitution of the bromine atom by ethoxy group to form 4-(nitrobenzyl) ethyl ether **VII** and a labile α-bromacetal, which decomposes into compound **VIII** and ethyl bromide **IX**. It is assumed that the exchange process begins with an attack on the electropositive methylene carbon of compound **Ia** with the lone electron pair of the oxygen atom of orthoester **VI**. The subsequent four-member cyclic electron transfer leads to the reaction products.

A new method for the synthesis of 4-(nitrobenzyl) ethyl ether **VII** via the reaction of 4-nitrobenzyl



VI, VIII: R = H (**a**), R = CH$_3$ (**b**).

bromide **Ia** with carboxylic acids orthoethers **VI** has several advantages over existing methods [3–5]: the starting materials are commercially accessible, the reaction proceeds in the absence of any solvent and catalyst, the treatment is simple, and the reaction product can be easily isolated.

The reactivity of the compounds **I** and **VI** in these reactions were found to depend on the halogen nature in compounds **Ia** and **Ib** and the structure of the orthoesters **VIa** and **VIb**. Thus, it was observed that 4-nitrobenzyl bromide **Ia** is more active than its chlorine analogue **Ib**, and triethyl orthoacetate **VIb** is more reactive than triethyl orthoformate **VIa** towards 4-nitrobenzyl bromide **Ia**. The reactions were carried out in the sealed ampules in a dry nitrogen atmosphere with heating. The optimal heating temperature was found by increased internal pressure (due to the alkyl halide liberation) revealed at the intermittent opening the ampule to remove the volatile products. The reaction progress was monitored by the ^{1}H and ^{31}P NMR spectroscopy.

4-Nitrobenzyl diethylphosphinate (IV). *a.* A mixture of 3.24 g (0.015 mol) of 4-nitrobenzyl bromide **Ia** and 4.08 g (0.030 mol) of methyl diethylphosphinate **II** was kept in a sealed ampule at 150ºC for 4 h and then distilled. Yield 1.74 g (45%), bp 133–135ºC (0.2 mm Hg). ^{1}H NMR spectrum (acetone-d_6, CCl_4), δ, ppm: 0.96–1.38 m (6H, CH_3), 2.02–1.48 m (4H, CH_2), 5.19 d (2H, CH_2, $^3J_{PH}$ 8.1 Hz), 7.69 d and 8.23 d (4H, C_6H_4, $^3J_{HH}$ = $^3J_{HH}$ = 8.6 Hz). ^{31}P NMR spectrum: δ_P 60.4 ppm. Found, %: N 5.10, 4.95; P 12.65, 12.41. $C_{11}H_{16}NO_4P$. Calculated, %: N 5.45; P 12.04.

b. A mixture of 2.23 g (0.013 mol) of 4-nitrobenzyl chloride **Ib** and 3.54 g (0.026 mol) of methyl diethylphosphinate **II** was kept in a sealed ampoule at 180ºC for 5 h and then distilled. Yield 1.58 g (47%), bp 133–135ºC (0.2 mm Hg).

4-Nitrobenzyl ethyl ether (VII). *a.* A mixture of 4.76 g (0.022 mol) of 4-nitrobenzyl bromide **Ia** and 3.56 g (0.024 mol) of triethyl orthoformate **VIa** was kept in a sealed ampule at 220ºC for 18 h and then distilled. Yield 1.60 g (40%), bp 110ºC (0.2 mm Hg), {bp 134ºC (1.0 mm Hg) [4]}. ^{1}H NMR spectrum (acetone-d_6, CCl_4), δ, ppm: 1.30 t (3H, CH_3, $^3J_{HH}$ 7.1 Hz), 3.62 q (2H, CH_2, $^3J_{HH}$ 7.1 Hz), 4.61 s (2H, CH_2), 7.52 d and 8.16 d (4H, C_6H_4, $^3J_{HH}$ = $^3J_{HH}$ = 8.7 Hz).

b. A mixture of 2.16 g (0.010 mol) of 4-nitrobenzyl bromide **Ia** and 2.11 g (0.013 mol) of triethyl orthoacetate **VIb** was kept in a sealed ampule at 180ºC for 5 h and distilled. Yield 0.5 g (27%), bp 124ºC (0.4 mm Hg).

The ^{1}H NMR spectra were registered on a Tesla BS-567A spectrometer operating at 100 MHz, internal referenceTMS. The ^{31}P NMR spectra were recorded on a Bruker MSL-400 instrument (162 MHz) relative to 85% H_3PO_4.

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