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LETTERS TO THE EDITOR

Reduction of Arylmethyl Chlorides with a Phosphine–Hydrogen Mixture in the KOH–DMSO System

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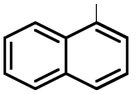
Arylalkyl halides are reduced either under rigid conditions or under the action of fairly expensive reagents and complex systems.

We used the example of benzyl chloride (**Ia**) and 1-chloromethylnaphthalene (**Ib**) to show for the first time that arylalkyl chlorides can be reduced with phosphine generated together with hydrogen from red phosphorus in the KOH–water–organic solvent (dioxane, toluene) system [1]. The reaction is accomplished by bubbling the phosphine–hydrogen mixture through the arylmethyl chloride **I**–KOH–DMSO system heated to 85–90°C. The yields of toluene **IIa** and 1-methylnaphthalene **II** were 27 and 77%, respectively.

$$\underset{\textbf{Ia, Ib}}{ArCH_2Cl} \xrightarrow{PH_3\text{–}H_2\text{–}KOH\text{–}DMSO} \underset{\textbf{IIa, IIb}}{ArMe},$$

Ar = Ph (**a**),  (**b**).

Expected phosphorylation products of benzyl chloride (benzyl- and dibenzylphosphines [2]) are formed in the reaction studied in 6 and 32% yields, respectively, while in the case of 1-chloromethylnaphthalene the total yield of organophosphorus compounds is no higher than 6%. In the PH_3–DMSO system without KOH, arylmethyl chlorides **Ia** and **Ib** are scarcely reduced or phosphorylated. The mechanism of the reaction is under study.

Reaction of 1-chloromethylnaphthalene with the PH_3–H_2–KOH–DMSO system. To a suspension of 5 g of $KOH \cdot 0.5H_2O$ in 25 ml of DMSO and 3.4 ml of water, purged with argon and saturated with the phosphine–hydrogen mixture, a solution of 3.26 g of 1-chloromethylnaphthalene in 5 ml of DMSO was added dropwise over the course 2.5 h at 85–90°C with stirring and continuous bubbling of the phosphine–hydrogen mixture. The reaction mixture was cooled and extracted with benzene. The extract was washed with water, dried with potassium carbonate, the solvent was removed, and the residue was fractionated in a vacuum to give 2.02 g (77%) of 1-methylnaphthalene, bp 94°C (5 mm Hg) (identified by the ^1H and ^{13}C NMR spectra). Found, %: C 92.49, H 7.51. $C_{11}H_{10}$. Calculated, %: C 92.91: H 7.09. In the undistillable residue (0.13 g) by contained ^{31}P NMR using authentic samples [3], there were identified bis(1-naphthylmethyl)phosphine oxide (δ_P 36.8 ppm, $^1J_{PH}$ 470 Hz) and tris(1-naphthylmethyl)phosphine oxide (δ_P 42.4 ppm) (total yield ca. 1%). The aqueous alkaline layer was acidified with HCl to pH 4–5 and extracted with chloroform. The extracts were washed with water, dried with calcium chloride, and the solvent was distilled off to give 0.21 g of a product that, according to the ^{31}P NMR spectrum, contained a 7 : 1 mixture of organophosphorus compounds which were assigned the structures of (1-naphthylmethyl)phosphinic (δ_P 33.4 ppm, $^1J_{PH}$ 557 Hz) and bis(1-naphthylmethyl)phosphinic (δ_P 51.7 ppm) acids, respectively (total yield 5%).

The reaction of benzyl chloride with the PH_3–H_2–KOH– DMSO system was carried out under the analogous conditions. The reaction mixture was extracted with hexane, the extract was washed with water, dried with potassium carbonate and analyzed by GLC (reference decane) to identify toluene (27%). The solvent was removed, and the residue was fractionated in a vacuum to give 0.71 g of a product that, according to the ^{31}P NMR spectrum, contained a 1 : 4.2 mixture of benzylphosphine (t, δ_P –120.15 ppm, $^1J_{PH}$ 194 Hz) and dibenzylphosphine (d, δ_P –47.48 ppm, $^1J_{PH}$ 198.2 Hz) [2] (yields 6 and 32%, respectively). The chloroform extract from the acidified aqueous alkaline solution contained no organophosphorus compounds.

The ^1H, ^{13}C, and ^{31}P NMR spectra were obtained

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on a Bruker DPX-400 spectrometer (400, 100, and 161.98 MHz, respectively) in $CDCl_3$ against internal HMDS. Gas chromatography was performed on a PAKhV chromatograph, column 1200 × 10 mm, packing 15% of Carbowax 6000 on Chromaton N-AW-DMGS (0.25–0.36 mm), carrier gas helium.

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