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LETTERS TO THE EDITOR

Phosphorus Trihalides in Reactions with 2-(Adamantan-1-yl)imidazo[1,2-*a*]pyridines

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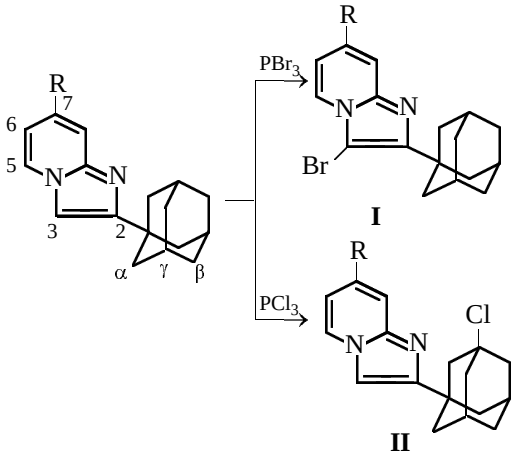
It was recently found [1, 2] that the reaction of adamantane derivatives with phosphorus trichloride in sulfuric acid involves substitution of the leaving group either by a dichlorophosphoryl group or a chlorine atom, depending on the nature of substituents in the adamantane nucleus [1], whereas the reaction with phosphorus tribromide always leads to corresponding brominated adamantanes [2].

In the present work we found that the reactions of 2-(adamantan-1-yl)- and 2-(adamantan-1-yl)-7-methylimidazo[1,2-*a*]pyridines with phosphorus trichloride fail to occur under the conditions described in [1], and the starting compounds are recovered. At the same time, in the reactions with phosphorus tribromide, like in those with elemental bromine [3], 2-(adamantan-1-yl)imidazo[1,2-*a*]pyridine converts into 2-(adamantan-1-yl)-3-bromoimidazopyridine **I**. Under more rigid conditions, the reaction pathway with phosphorus tribromide does not alter, while with phosphorus trichloride, 2-(3-chloroadamantan-1-yl)imidazopyridines **IIa** and **IIb** are formed.



I, R = H, **II**, R = H (**a**), CH_3 (**b**).

Reaction of 2-(adamantan-1-yl)imidazo[1,2-*a*]-pyridine with phosphorus tribromide was carried out as described in [2] with 0.002 mol of 2-(adamantan-1-yl)imidazo[1,2-*a*]pyridine and 0.0014 mol of phosphorus tribromide. The next day the reaction mixture was poured onto ice and neutralized with sodium bicarbonate. The precipitate that formed was filtered off, treated with 20% aqueous NaOH, and washed with water to neutral. The melting point and spectral data of the sample were identical to those of 2-(adamantan-1-yl)-3-bromoimidazo[1,2-*a*]pyridine described in [3].

2-(3-Chloroadamantan-1-yl)imidazo[1,2-*a*]-pyridine (IIa) and 2-(3-chloroadamantan-1-yl)-7-methylimidazo[1,2-*a*]pyridine (IIb). 2-(Adamantan-1-yl)imidazo[1,2-*a*]pyridine, 0.002 mol, was added in portions to a cold (0–5°C) and stirred mixture of 2 ml of conc. H_2SO_4 and 2 ml of 20% oleum, maintaining the temperature at 45–50°C, after which 0.014 mol of phosphorus trichloride was added. The reaction mixture stirred at 65–70°C for 2 h and then poured onto ice. The next day it was neutralized with sodium bicarbonate, the precipitate that formed was filtered off, treated with 20% aqueous NaOH, and washed with water to neutral. Compound **IIa**, yield 66%, mp 132–134°C (from aquoeus ethanol). ^{1}H NMR spectrum (DMSO-d_6 + CCl_4), δ, ppm: 1.70–2.33 m (14H, Ad), 6.84 t (1H, ^3J 10 Hz, H^7), 7.19 t (1H, ^3J 8 Hz, H^6), 7.49 d (1H, ^3J 10 Hz, H^8), 7.69 s (1H, H^3), 8.45 (1H, ^3J 8 Hz, H^5). Found, %: Cl 12.24. $C_{17}H_{19}ClN_2$. Calculated, %: Cl 12.36. Compound **IIb**, yield 70%, mp 94–96°C (from aqueous ethanol). ^{1}H NMR spectrum (DMSO-d_6 + CCl_4), δ, ppm: 1.70–2.36 m (14H, Ad), 2.39 s (3H, CH_3), 6.70 d (1H, ^3J 7 Hz, H^6), 7.28 s (1H, H^3), 7.60 s (1H, ^3J 7 Hz, H^5). Found, %: Cl 12.0. $C_{18}H_{21}ClN_2$. Calculated, %: Cl 11.79.

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The ^{1}H NMR spectra were recorded on a Bruker WR-200 spectrometer (200 MHz) against internal TMS.

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