

LETTERS  
TO THE EDITOR

Unexpected Reaction Pathway of *tert*-Butyl Tetraethylphosphorodiamidite with Benzyl Chloride

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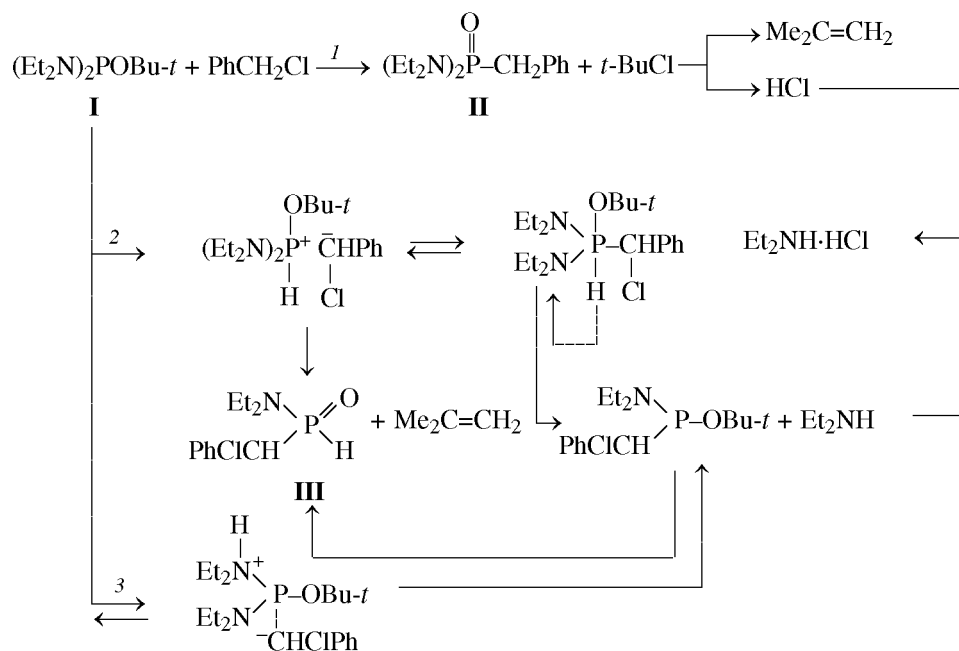
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Amides and amidoesters of P(III) acids react with alkyl halides with participation of the unshared electron pair of the phosphorus atom and formation of quasiphosphonium compounds. In the presence of alkoxy groups on phosphorus, the products are capable to undergo transformation according to the second stage of the Arbuzov reaction [1, 2].

We are the first to find that *tert*-butyl tetraethylphosphorodiamidite (**I**) reacts with benzyl chloride in different ways depending on reaction conditions. The reaction in the absence of solvent involves primarily the Arbuzov reaction leading to benzylphosphonic bis-

(diethylamide) (**II**). In nonpolar and polar solvents, much diethylamine hydrochloride is formed along with compound **II**. Other reaction products are isobutylene and ( $\alpha$ -chlorobenzyl)phosphonous diethylamide (**III**),  $\delta_p$  8 ppm,  $J_{PH}$  580 Hz. The IR spectrum of compound **III** contains a P–H absorption band at  $2370\text{ cm}^{-1}$ . Evidently, this reaction is described by a scheme involving the Arbuzov rearrangement competing with the initial protonation of the phosphorus atom, leading to an ionic or a pentacovalent quasiphosphonium compound which can further transform along several pathways.



**Benzylphosphonic bis(diethylamide) (II)**, bp 153–154°C (0.5 mm), mp 80–81°C. Published data [3]: mp 82–83.5°C.

**( $\alpha$ -Chlorobenzyl)phosphonous diethylamide (III)**, mp 137–138°C.  $^{31}P$  NMR spectrum:  $\delta_p$  8 ppm ( $J_{PH}$  580 Hz). IR spectrum,  $\nu$ ,  $cm^{-1}$ : 2370 (P–H),

1220 (P=O). Found, %: C 53.29; H 7.15; N 5.23; P 12.48; Cl 14.78.  $C_{11}H_{17}ClOP$ . Calculated, %: C 53.77; H 6.92; N 5.70; P 12.63; Cl 14.46.

The IR spectra were recorded on a Specord IR-75 spectrometer in thin layer. The  $^1H$  NMR spectra were measured on a Bruker WP-80 spectrometer (32.44 MHz) against external  $H_3PO_4$

## REFERENCES

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2. Hudson, R.F. and Searle, R.J.G., *Chimia*, 1966, vol. 20, no. 4, p. 117.
3. JP Patent 48-40740, *Ref. Zh. Khim.*, 1974, 18N684P.