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LETTERS TO THE EDITOR

Reaction of *tert*-Butyl Tetraethylphosphorodiamidite with Bromomalonic Ester

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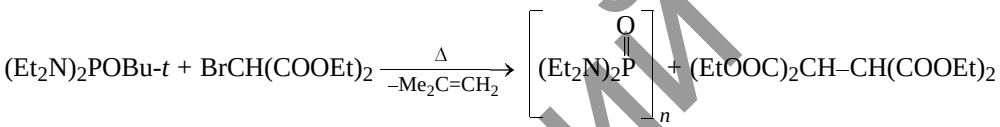
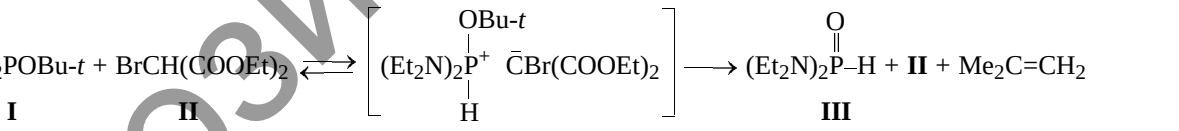
Previously we showed that *tert*-butyl tetraethylphosphorodiamidite (**I**) reacts with CH acids by way of protonation of the phosphorus atom to form a hydrogen phosphite [1].

While studying the reaction of phosphite **I** with bromomalonic ester (**II**) which contains, on the one hand, a very labile hydrogen atom and, on the other, an acidic proton, we found that in the absence of solvent an exothermal reaction occurs accompanied by vigorous isobutylene evolution and leading to polyaminophosphine and tetraethyl ethanetetracarboxylate.



This reaction pathway agrees with the results of Arbuzov [2] for reactions of sodium dialkyl phosphites with bromomalonic ester. The reaction in solvents yields phosphorous bis(diethylamide) (**III**). The latter reaction is accompanied by vigorous isobutylene evolution and regeneration of bromomalonic ester (**II**).



The formation of compound **III** can be explained in no other way than by initial protonation of the phosphorus atom.

Phosphorous bis(diethylamide) (III), bp 54–55°C (0.04 mm), d_4^{20} 0.9621, n_D^{20} 1.4540. IR spectrum, ν, cm^{-1}: P=O (1225), P–H (2470). ^{31}P NMR spectrum: δ_P 19 ppm (J_{HP} 570 Hz). Published data [3]: bp 76–80°C (0.5 mm), d_D^{20} 1.4545, δ_P 18 ppm (J_{HP} 570 Hz).

The IR spectra were recorded on a Specord IR-75 spectrometer in thin layer. The ^{31}P NMR spectra were measured on a Bruker WP-80 spectrometer (32.44 MHz) against external 85% phosphoric acid.

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