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LETTERS TO THE EDITOR

New Data on the Malonic Ester Phosphorylation

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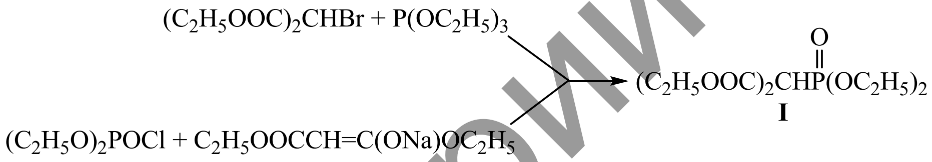
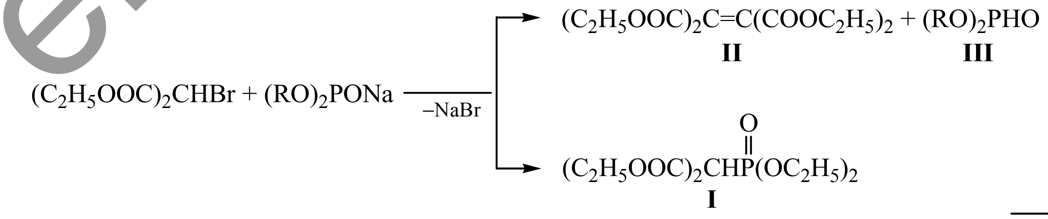
Phosphorylation reaction of malonic ester so far attracts the researchers attention that is obviously associated with a possibility of its wide chemical modifications for the synthesis of compounds with the practically useful properties. Previously was shown [1] that the reaction of diethyl bromomalonate with triethyl phosphite and the reaction of diethyl chlorophosphate with sodium malonic ester proceed to afford the *C*-phosphorylation product.



Later was shown [2] that the reaction of chlorophosphate with sodium malonic ester occurs by an *O*-phosphorylation scheme. The phosphorylation of malonic ester with diethyl chlorophosphite in the presence of triethylamine was shown to give a *C*-phosphorylation product, which was converted into diethyl dicarboethoxymethylphosphonate **I** [3].

In view of these conflicting literature data, we studied the reaction of bromomalonic ester with diethyl sodium phosphite by the scheme of Michaelis–Becker reaction. The direction of this process was found to be essentially dependent on the methods of reagents mixing and dilution. Thus, at the slow adding bromomalonic ester to a benzene solution of diethyl sodium phosphite the reaction proceeds by an elimination scheme. A significant exothermic effect was observed together with the NaBr precipitating. After the precipitate separation, white crystals of the compound **II** formed. Identification of the latter showed that they are ethyl ethylenetetracarboxylate, mp 53–54°C (literature data: mp 53–54°C). Distillation of the remaining filtrate yields diethyl hydrogen phosphite **III**.



At the reverse order of mixing the reagents the NaBr precipitation was also observed. After distillation, ester **I** was isolated, whose structure and physicochemical constants are identical to those described previously [1]: bp 160–161 (10 mm Hg), n_D^{20} 1.4453.

A small amount of the compound **II** crystals (mp 55–56°C) was isolated as a by-product. At a high dilution of the reagents, the compound **II** formation was not practically observed.

The IR spectrum of the ester **I** contains the absorption bands at 1744 and 1731 cm^{-1} belonging to the carbonyl groups. The absorption band of P=O bond was observed at 1202 cm^{-1}, which corresponds to the data [3].

The IR spectra were recorded on a Nicolet Avatar-360 spectrometer from KBr pellets (measurement error ±0.2 cm^{-1}). The melting point was determined on a Boetius device (measurement error ±0.1°C). The reaction progress and individuality of the obtained compounds were monitored by TLC on Silufol UV-254 plates, eluting with a benzene–ethanol mixture (6:1) and detecting with iodine vapors.

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