

## Flame Retardant Properties of Phosphorylated Derivatives of Malonic Ester

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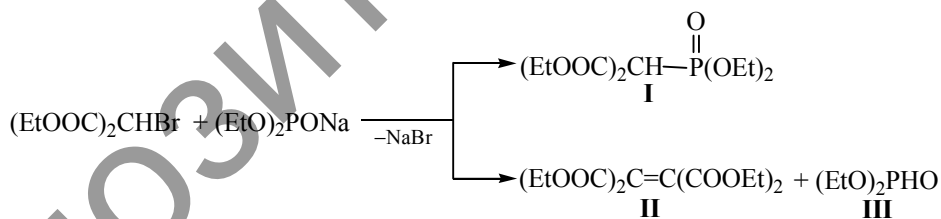
**Abstract**—Thermal stability of the phosphorylated derivatives of malonic ester synthesized by the Michaelis–Becker reaction was studied. The flame-retardant efficiency of the phosphonomalonic ester was assessed by the flame-tube technique measuring the weight loss of wood samples impregnated with the studied compound.

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Earlier we showed [1] that the reaction route of bromomalonic ester with sodium diethyl phosphite by the Michaelis–Becker reaction scheme was strongly dependent of the order of mixing and degree of dilution of the reagents. When a benzene solution of sodium diethyl phosphite was slowly added to bromomalonic ester, NaBr precipitation was observed; after its separation diethyl (diethoxyphosphinoyl) malonate (**I**) was isolated by distillation. A little tetraethyl ethylenetetra-carboxylate (**II**) was isolated as

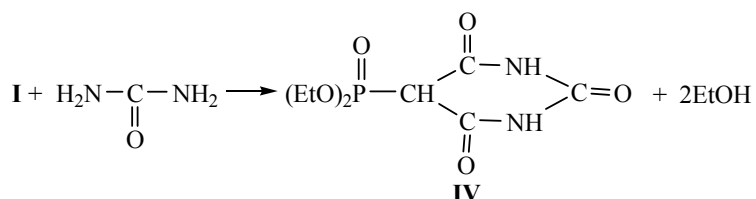
a by-product, white crystals, mp 55–56°C (published data: mp 53–54°C). With stronger diluted reagent solutions, ester **II** hardly formed.

If the reagents were mixed in the reverse order strong heat release was observed and NaBr precipitated; after separation of the NaBr precipitate, ester **II** precipitated as white crystals, mp 55–56°C. Distillation of the mother liquor gave diethyl hydrogen phosphite (**III**).



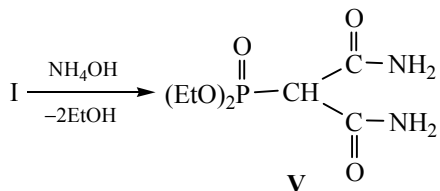
The IR spectrum of compound **I** contains absorption bands characteristic of the C=O group at 1744 and 1731 cm<sup>-1</sup> and a P=O band at 1202 cm<sup>-1</sup>, which is consistent with published data [2].

To confirm the structure of compound **I** we performed its reaction with urea and isolated phosphonobarbituric acid **IV**, mp 97°C, whose parameters, too, were consistent with published data [2].

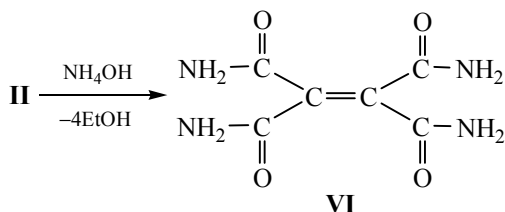


Ester **I** was further subjected to chemical modification to prepare diamides. The latter may be interesting for practical applications, in particular, as flame retardants.

(Diethoxyphosphinoyl)malonic diamide (**V**) was synthesized in high yield by the ammonolysis of ester **I** with an excess of aqueous ammonia.



By the same procedure we prepared enthylenetetracarboxylic acid tetramide (**VI**) which was used as reference in the thermal stability study on organophosphorus compounds **V**.



As known, over the past years the problem of imparting fire-retardant properties to materials of different nature and uses is gaining in importance. This is due to the fact that various materials are hazardous during fires, since they are flammable, favor fire propagation, and release much smoke and gases.

Even though at present a wide range of flame retardants is available, including nitrogen-, phosphorus, and halogen-containing organic and inorganic compounds, yet they are unable to meet all demands of vigorously developing industry. This encourages further R&D and implementation of fire-retardant means, among which a particular place belongs to organophosphorus compounds.

Traditionally, wood and other cellulose materials are the most widespread building materials. But, although a number of advantages sets them apart from other building materials, wood and cellulose materials have certain drawbacks, the main of which are easy ignitability and flammability. One of the most efficient ways of flame protection of wood and cellulose materials is their impregnation with flame retardants.

Phosphorous acids and their esters and amidoesters are highly reactive compounds which present both practical and theoretical interest. However, the flame-

retardant properties of phosphites and phosphonates, as well as amides of phosphonic acids have scarcely been studied [3].

Aiming at a search for new flame retardants and assessing their efficiency, we chose as objects for the study phosphonomalonic diamide **V** and full amide of ethylenetetracarboxylic acid **VI**.

The efficiency of the potential flame retardants for wood was assessed according to State Standard 16363-76 (Comecon Standard 4686-84) by a procedure involving measurement of the weight loss of wood samples treated with impregnating compositions in flame resistance tests and comparison of the results with those for untreated samples.

Impregnating compositions containing 5% solutions of compounds **V** and 5 or 10% solutions of compound **VI** were applied on all sides of dry and weighed samples (three tests for each impregnating solution). The concentrations were chosen taking into account that our goal was to find an optimal flame-retardant agent efficient at as low concentrations as possible. The concentrations of known and widely used flame-retardant solutions are generally no higher than 50%. Use of more concentrated flame-retardant solutions is economically inexpedient, since it hinders drying of objects and deteriorates their performance characteristics and increases toxicity.

The known solvents for impregnating solutions are water, ethanol, benzene, diethyl ether, etc. We dissolved compound **V** in distilled water and compound **VI** in benzene. The choice of solvents was motivated by their chemical inertness with respect to the solutes, as well as accessibility.

The treated samples were dried for 21 days until complete dryness. After exposure to flame, untreated wood samples lost their shape completely, whereas the wood samples treated with impregnating solutions completely or partially retained the shape.

The flame-retardant efficiency was estimated from the weight loss of a sample after exposure to flame, using the following formula:

$$m = [(m_1 - m_2)/m_1] \times 100.$$

Here  $m_1$  is the sample weight before test, g, and  $m_2$ , sample weight after test, g.

The result was taken as an arithmetic mean of three test runs for each compound. The resulting data are listed in the table.

## Weight losses of treated and untreated wood samples

Compound no.	Sample weight before impregnation, g	Sample weight after impregnation, g	Sample weight after combustion, g	Weight loss, %	
VI	1.651	1.735	1.015	41.5	41.0
	1.583	1.652	0.981	40.6	
	1.585	1.657	0.979	40.9	
V <sup>a</sup>	1.831	1.891	1.349	28.7	27.7
	1.784	1.848	1.331	27.9	
	1.483	1.523	1.125	26.1	
VI <sup>b</sup>	1.663	1.780	0.913	48.7	49.1
	1.592	1.712	0.835	48.8	
	1.846	1.972	0.991	49.7	
Untreated sample	1.912	–	0.790	58.7	59.3
	1.726	–	0.709	58.9	
	1.397	–	0.556	60.2	

<sup>a</sup> Concentration in the impregnating solution, %: 5. <sup>b</sup> Concentration in the impregnating solution, %: 10.

According to the above-mentioned standards, if the weight loss is less than 9%, the substance is related to group I efficiency flame retardants providing production of nonflammable wood. If the weight loss is more than 9% but less than 30%, the substance is related to group II efficiency flame retardants providing production of nonflammable wood. If the weight loss is equal to or more than 30%, the substance is considered as not providing protection from flame (group III).

Compound VI, with which the weight loss was more than 30%, should be related to the III group. This compound at chosen concentrations proved to be an inefficient flame retardant.

The weight loss for the wood sample impregnated with a solution of compound V was less than 30%, which allows it to be related to the II group.

Thus, our search for new cheap and sufficiently efficient organophosphorus flame retardants resulted in the synthesis of compound V in very mild conditions and with an almost quantitative yield.

## EXPERIMENTAL

The IR spectra were measured on a Nicolet Avatar-360 spectrometer in pellets with KBr (measurement error 0.2 cm<sup>-1</sup>). <sup>1</sup>H NMR spectra were obtained on a Bruker DRX500 spectrometer (500 MHz) in CDCl<sub>3</sub> relative to internal TMS (measurement error ±0.1–

0.2 ppm). The <sup>31</sup>P NMR spectra were obtained on a Bruker AC-200 spectrometer (80.014 MHz) in CDCl<sub>3</sub>. The melting point was determined on a Boetius heating block (measurement error ±0.1°C). The reaction progress and product purity were controlled by TLC on Silufol UV-254 plates in benzene–ethanol, 6:1. The chromatograms were developed in iodine vapor.

**Diethyl (diethoxyphosphinoyl)malonate (I).** *a.* Sodium diethyl phosphite, 16.0 g (0.1 mol) was added dropwise with stirring to 23.9 g (0.1 mol) of diethyl bromomalonate in benzene. The NaBr precipitate that formed was filtered off, and the residue was distilled in a vacuum. Yield 25.8 g (87%), bp 159–160°C (10 mm),  $n_D^{20}$  1.4457 {published data: bp 160–161°C (10 mm),  $n_D^{20}$  1.4420 [2]}. IR spectrum (KBr),  $\nu$ , cm<sup>-1</sup>: 1202 (P=O), 1744, 1731 (C=O). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 1.371 t (CH<sub>3</sub>CH<sub>2</sub>,  $J_{HH}$  7.2 Hz), 1.20 t (CH<sub>3</sub>CH<sub>2</sub>OP,  $J_{HH}$  7.2 Hz), 4.18 q (CH<sub>3</sub>CH<sub>2</sub>OOC,  $J_{HH}$  7.2 Hz), 4.08 q (CH<sub>2</sub>OP,  $J_{HH}$  7.2,  $J_{HP}$  14.4 Hz), 3.97 d (CHP,  $J_{HP}$  20.5 Hz). NMR spectrum <sup>31</sup>P:  $\delta_P$  12.81 ppm.

*b.* Diethyl bromomalonate, 23.9 g (0.1 mol), was added dropwise to 16.0 g (0.1 mol) of sodium diethyl phosphite under constant stirring. The NaBr precipitate that formed was filtered off. As the solvent was distilled off, compound II precipitated as white crystals, mp 55–56°C (published data: mp 53–54°C). IR spectrum (KBr),  $\nu$ , cm<sup>-1</sup>: 1737 (C=O), 1627 (C=C), 1147 (C–O). NMR spectrum <sup>1</sup>H (CDCl<sub>3</sub>),  $\delta$ , ppm: 1.37 t

( $\text{CH}_3\text{CH}_2$ ,  $J_{\text{HH}}$  7.0 Hz), 4.22 q ( $\text{CH}_3\text{CH}_2$ ,  $J_{\text{HH}}$  7.0 Hz). Acid **III** was isolated from the residual mother liquor, bp 80–81°C (10 mm),  $n_{\text{D}}^{20}$  1.4072,  $d_4^{20}$  1.0714 (published data: bp 72–73°C (9 mm),  $n_{\text{D}}^{20}$  1.4086,  $d_4^{20}$  1.0742.  $^{31}\text{P}$  NMR spectrum:  $\delta_{\text{P}}$  8.149 ppm.

**5-(Diethoxyphosphinoyl)barbituric acid (IV).**

Urea, 6.0 g (0.1 mol), and 29.6 g (0.1 mol) of compound **I** were added to a solution of 0.3–0.4 mol of sodium ethylate in 20–30 ml of anhydrous ethanol. The reaction mixture was heated under reflux for 6–7 h. Sodium barbiturate that was dissolved in water, and the solution was acidified with dilute HCl. The crystals that formed were recrystallized from ethanol. Yield 22.4 g (85%), mp 97°C (published data: mp 97°C [2]). IR spectrum (KBr),  $\nu$ ,  $\text{cm}^{-1}$ : 1174 (P=O), 1740, 1628 (C=O), 3435 (NH).  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.191 t ( $\text{CH}_3\text{CH}_2$ ,  $J_{\text{HH}}$  6.8 Hz), 3.84 d (CHP,  $J_{\text{HP}}$  20.4 Hz), 4.19 q ( $\text{CH}_2\text{OP}$ ,  $J_{\text{HH}}$  6.8,  $J_{\text{HP}}$  14.0 Hz), 8.33 br.s (NH).  $^{31}\text{P}$  NMR spectrum:  $\delta_{\text{P}}$  14.01 ppm.

**(Diethoxyphosphinoyl)malonic diamide (V).**

To 29.6 g (0.1 mol) of compound **I** was added 28.0 g of 25% aqueous ammonia. The reaction mixture was stirred for 24 h at room temperature till crystals precipitated which were filtered off and dried at 50–80°C till the constant weight. Yield 18.8 g (79%), mp

124–125°C. IR spectrum (KBr),  $\nu$ ,  $\text{cm}^{-1}$ : 1693, 1670 (C=O), 1263 (P=O), 3391, 3651 ( $\text{NH}_2$ ).  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 1.18 t ( $\text{CH}_3\text{CH}_2$ ,  $J_{\text{HH}}$  7.4 Hz), 3.22 d (CHP,  $J_{\text{HP}}$  20.8 Hz), 4.06 q ( $\text{CH}_2\text{OP}$ ,  $J_{\text{HH}}$  7.4,  $J_{\text{HP}}$  14.0 Hz), 5.46 br.s ( $\text{NH}_2$ ).  $^{31}\text{P}$  NMR spectrum:  $\delta_{\text{P}}$  14.02 ppm.

**Ethylenetetracarboxylic acid tetraamide (VI).**

Compound **II**, 31.6 g (0.1 mol), and 56.0 g of 25% aqueous ammonia were placed in a flask. The reaction mixture was stirred for 0.5 h under cooling and then left to stand for 1 h until crystals formed. The crystals were filtered off and dried to constant weight. Yield 16.6 g (83%), mp 70°C. IR spectrum (KBr),  $\nu$ ,  $\text{cm}^{-1}$ : 1627 (C=C), 1720 (C=O), 3392, 3655 ( $\text{NH}_2$ ).

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