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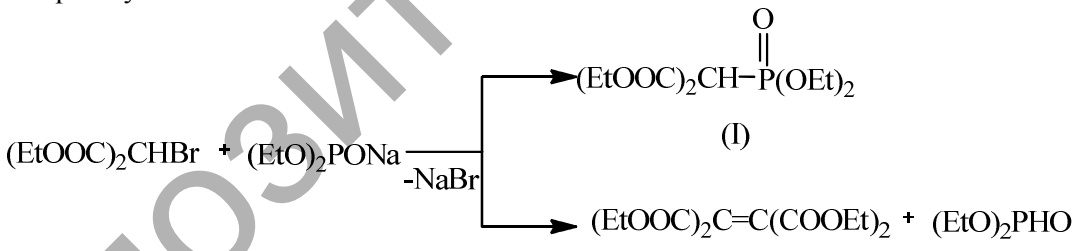
Investigation of flame retardant properties of malonic ester phosphorylated derivatives

Flame retardant properties of malonic ester phosphorylated derivatives synthesized by the Michaelis-Becker reaction according to the mechanism of nucleophilic substitution at the reverse mixing of reagents were studied. Fire-retardant efficiency of phosphonmalonic ester was investigated by the method of «fire tube» by determining weight loss of wood samples impregnated with the test substance.

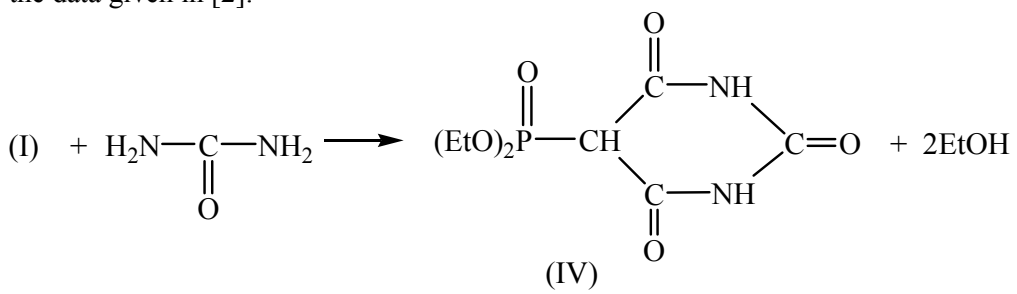
Key words: flame retardants, a method of «fire tube», malonic ester phosphorylated derivatives, diethyl ester of dicarboethoxymethylphosphonic acid, diethylphosphonbarbituric acid, diamide of phosphonmalonic acid, ethylenetetracarbonic acid amide.

The direction of a reaction of brommalonic ester with diethylphosphoric acid sodium salt according to the scheme of Michaelis-Becker reaction was shown to depend significantly on the method of mixing and dilution of reagents [1]. Precipitation of NaBr was observed at slow addition of the benzene solution of diethylphosphoric acid sodium salt to brommalonic ester. After filtration of NaBr precipitate diethyl ester of dicarboethoxymethylphosphonic acid (I) was isolated. The structure and physical-chemical constants of (I) are identical to those of the product described in the literature. It was isolated a small amount of white crystals of ethylenetetracarbonic acid ethyl ester (II) with melting point 55–56 °C (reference data: melting point is 53–54 °C) as a by-product. At more high dilution of reagents the compound (II) was not isolated. However the elimination reaction took place at reverse mixing of reagents. A significant exothermic effect and sodium bromide precipitation were observed. After separation of sodium bromide precipitate white crystals of the compound (II) with m.p. 55–56 °C was isolated. Diethylphosphoric acid (III) was isolated from the remaining mother liquor by distillation.



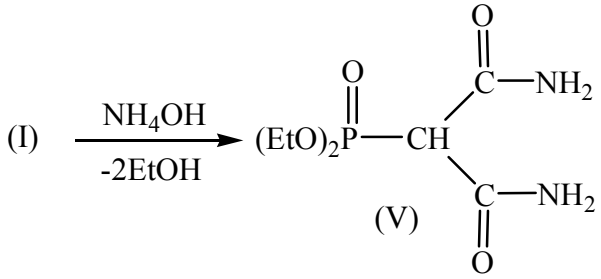
The IR spectrum of (I) contains absorption bands characteristic for carbonyl group 1744 and 1731 cm^{-1}; the absorption of P=O group is observed at 1202 cm^{-1} and correspond to the data given in [2].

It was carried out the reaction of the compound (I) with urea, confirming the structure of the compound (I). As a result phosphorylated barbituric acid (IV) with melting point 97 °C was isolated. It also corresponds to the data given in [2].

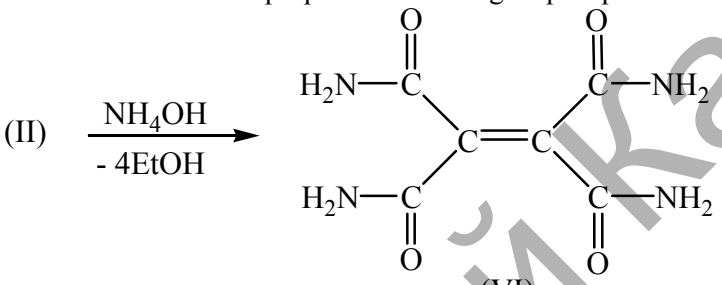


The compound (I) synthesized in accordance with the proposed scheme was subsequently used in the reaction of chemical modification to produce diamides with valuable properties, in particular, fire retardant properties.

Phosphonmalonic acid diamide was synthesized with high yield by ammonolysis of (I) with excess of ammonia.



Amide of ethylenetetracarbonic acid (VI) was obtained by the same method. This compound was used as an object for comparison of flame retardant properties of the organophosphorus compound (V).



The problem of giving fire protection to the different construction materials is known to become increasingly relevant in recent years. This is due to the fact that many of them are flammable, contribute to the spread of flame and produce a large amount of smoke and gases.

The current range of nitrogen-, phosphorus-, halogen-containing organic and inorganic flame retardants with diverse chemical structure are not capable enough to fully meet the needs of the rapidly growing industry. Therefore research on the development, creation and implementation of fire protection of a variety of materials is intensified. Organophosphorus compounds occupy a special place among flame retardants.

The most common construction material is traditionally wood and other cellulose materials and products made from them. However wood and cellulose materials along with the advantages have disadvantages which are the combustibility and flammability. One of the most effective ways of fire protection of wood and cellulose materials is impregnation with retardants.

A well-known class of organophosphorus compounds with high reactivity and theoretical and practical interest are phosphoric acids, their esters and etheramides. However the flame retardant properties of phosphates, phosphonates and phosphonic acid amides are less studied [3].

Diamide of phosphonmalonic ester (V) and amide of ethylenetetracarbonic acid (VI) were selected as objects of study in order to find new flame retardants and estimate their fire-resistance properties.

Estimation of the effectiveness of the selected potential fire retardants is carried out according to the all-union state standard 16363–76. The method consists in determining mass loss of wood samples impregnated with a studied solution in comparison with an untreated sample in a fire test.

The impregnating compositions, 5 % solution of phosphonmalonic acid diamide (V) and 5 and 10 % solutions of ethylenetetracarbonic acid amide (VI), were applied to the dry and weighted samples (three for each of the impregnating solution) on all sides. The choice of concentrations depends on the finding of the best fire retardant which is effective at low concentrations. The use of fire retardant solutions with higher concentrations is not economically feasible. Drying facilities is hampered and toxicity is increased.

The solvents for impregnating solutions of fire retardants are known to be water, ethanol, benzene, ether and others. Distilled water and benzene were used as solvents to prepare solutions of (V) and (IV), correspondingly. The choice of solvents is driven by their chemical inertness to the solute and affordability. Drying the samples was processed within 21 days to complete dry of objects. After a firing test the sample which had not been impregnated with the solutions investigated lost its shape completely. Wood samples treated with the impregnating solutions retained their shapes fully or partially.

Evaluation of fire-resistance was determined by weight loss after combustion of the sample by the formula:

$$m = \frac{(m_1 - m_2)}{m_1} \cdot 100,$$

where m_1 is mass of the sample before the test, g; m_2 is mass of the sample after the test.

Table 1

Weight loss of the samples treated and untreated after burning at the concentration of 5 %

Substance	Weight of wood samples before impregnation, g	Weight of wood samples after impregnation, g	Weight of the samples after combustion, g	Mass 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)	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	
Sample of untreated wood	1.912	-	0.790	58.7	59.3
	1.726	-	0.709	58.9	

Table 2

Weight loss of the samples treated and untreated after burning at the concentration of 10 %

Substance	Weight of wood samples before impregnation, g	Weight of wood samples after impregnation, g	Weight of the samples after combustion, g	Mass loss, %	
(VI)	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	

If weight loss is not more than 9 % substances refer to the group I of fire-resistance in accordance with the all-union state standard 16363–76. If weight loss is more than 9 % but less than 30 % the substances refer to the group II. If weight loss is 30 % or more, these agents do not provide fire protection and belong to the Group III.

The compound (VI), for which mass loss at the chosen concentrations is more than 30 %, belongs to the group III. This compound was not effective as a flame retardant in the given concentrations.

Mass loss of wood samples treated with the solution of the compound (V) is less than 30 % and it belongs to the flame retardants of the group II.

Thus, the search for new cheap and quite effective organophosphorus flame retardants has led us to the synthesis of (V) which is obtained under mild conditions with quantitative yield.

Experimental part

FT-IR spectra of the synthesized compounds were recorded with a «Nicolet Avatar-360» spectrometer by using the KBr technique with an accurancy of measurements 0.2 cm^{-1}. ^1H NMR spectra were recorded on a Bruker DRX500 spectrometer (500 MHz) with tetramethylsilane with an accurancy of measurements ±0.1–0.2 ppm. The melting points were determined on a Boetius device with an accurancy of measurements ±0.1 °C. The reaction course and the purity of synthesized compounds were monitored using TLC on Silufol UV-254 plates in the system benzene-ethanol (6:1). Chromatograms were developed with iodine vapours.

Diethyl ester of dicarboethoxymethylphosphonic acid (I)

a) A benzene solution of sodium diethylphosphite (16.0 g (0.1 mol)) was added dropwise to brommalonoic ester (23.9 g (0.1 mol)) at constant stirring. NaBr precipitate was filtered off. The residue was distilled in a vacuum. Purification gave 8.25 g (87 %) of (I); bp 159–160 ºC (10 mmHg) and n_D^{20} 1.4457. Reference bp is 160–161 ºC (10 mmHg) and n_D^{20} is 1.4420 [2]. IR spectrum (KBr), ν, cm^{-1}: 1202 (P=O), 1744, 1731 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.371 t (CH_3CH_2, J_{HH} 7.2 Hz), 1.20 t (CH_3CH_2OP,

J_{HH} 7.2 Hz), 4.183 m (CH_3CH_2OOC, J_{HH} 7.2 Hz), 4,082 m (CH_2OP, J_{HH} 7.2, J_{HP} 14.4 Hz), 3.975 d (CHP J_{HP} 20.5 Hz). ^{31}P NMR spectrum: δ_p 12.809 ppm.

b) Brommalonic ester (23.9 g (0.1 mol)) was added dropwise to a stirred solution of sodium diethylphosphite (16.0 g (0.1 mol)) in benzene. NaBr precipitate is filtered off. After removal of the solvent white crystals of (II) were precipitated (mp 55–56 °C). Reference mp is 53–54 °C. IR spectrum (KBr), ν, cm^{-1}: 1737 (C=O), 1627 (C=C), 1147 (CO). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.373 t (CH_3CH_2, J_{HH} 7.0 Hz), 4.224 m (CH_3CH_2, J_{HH} 7.0 Hz). Acid (III) was isolated from the remaining mother liquor (bp 80–81 ºC (10 mmHg), n_D^{20} 1.4072, d_4^{20} 1.0714). ^{31}P NMR spectrum: δ_p 8,149 ppm. Reference bp is 72–73ºC, n_D^{20} is 1.4086, d_4^{20} is 1.0742.

Diethylphosphonbarbituric acid (IV)

6.0 g (0.1 mol) of urea and 29.6 g (0.1 mol) of (I) were added to a solution of 0.3–0.4 mole of sodium ethylate in 20–30 ml of dry ethanol. The reaction mixture was heated under reflux for 6–7 hours. The precipitated sodium salt of barbituric acid is dissolved in water; the solution is acidified with dilute hydrochloric acid. The precipitated crystals (IV) were recrystallized from ethanol to yield 4.22 g (85 %) of (IV); mp 97 ºC. Reference mp is 97 ºC [2]. IR spectrum (KBr), ν, cm^{-1}: 1174 (P=O), 1740, 1628 (C=O), 3435 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.191 t (CH_3CH_2, J_{HH} 6.8 Hz), 3.845 d (CHP J_{HP} 20.4 Hz), 4.190 m (CH_2OP, J_{HH} 6.8, J_{HP} 14.0 Hz), 8.327 broad singlet (NH). ^{31}P NMR spectrum: δ_p 14.009 ppm.

Diamide of phosphonmalonic acid (V)

25 % solution of aqueous ammonia (28.0 g) was added to the compound (I) (29.6 g (0.1 mol)). The reaction mixture was stirred overnight at room temperature until precipitation of crystals which were filtered and dried at 50–80 ºC until a constant weight. The yield is 8.18 g (79 %); mp 124–125°C. IR spectrum (KBr), ν, cm^{-1}: 1693, 1670 (C=O), 1263 (P=O), 3391, 3651 (NH_2). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.185 t (CH_3CH_2, J_{HH} 7.4 Hz), 3.218 d (CHP J_{HR} 20.8 Hz), 4.064 m (CH_3CH_2OP, J_{HH} 7.4, J_{HR} 14.0 Hz), 5.456 broad singlet (NH_2). ^{31}P NMR spectrum: δp 14.018 ppm.

Ethylenetetracarbonic acid amide (VI)

31.6 g (0.1 mol) of (II) and 56.0 g of 25 % aqueous ammonia were placed into the flask. The reaction mixture was stirred for 30 minutes and kept at room temperature until the crystals precipitation. Crystals formed were filtered off and dried to a constant weight. The yield is 16.6 g (83 %); mp 70 ºC. IR spectrum (KBr), ν, cm^{-1}: 1627 (C=C), 1720 (C=O), 3392, 3655 (NH_2).

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Малон эфирінің фосфорилденген туындыларының антипирендік қасиеттерін зерттеу

Михаэлис-Беккер реакциясы бойынша реагенттерді кері араластыруда нуклеофилді орынбасу механизміне сәйкес синтезделген малон эфирінің фосфорилденген туындыларының антипирендік қасиеттері анықталды. Фосфонмалон эфирінің оттан қорғау тиімділігі «от құбыры» тәсілімен, зерттелетін затпен сіңірілген атом үлгілерінің массасын жоғалтуын анықтау арқылы зерттелді.

Л.К.Салькеева, П.Войтишек, Е.К.Тайшибекова, Е.В.Минаева,
К.А.Жумашева, Л.А.Смакова, А.К.Салькеева, Е.Т.Сагатов

Исследование антипиреновых свойств фосфорилированных производных малонового эфира

Изучены антипиреновые свойства фосфорилированных производных малонового эфира, синтезированных по схеме реакции Михаэлиса-Беккера, согласно механизму нуклеофильного замещения при обратном смешении реагентов. Огнезащитная эффективность фосфонмалонового эфира исследована методом «огневой трубы» путем определения потери массы образцов древесины, пропитанных исследуемым веществом.