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Reaction of (Ethoxycarbonylfuryl)methanephosphonates with Diethyl Carbonate in Presence of Sodium Foil

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Abstract—Reaction of (ethoxycarbonylfuryl)methanephosphonates with diethyl carbonate in presence of sodium foil is studied. It is shown that if the acidifying group is conjugated with the carbanion center of 2-furylmethanephosphonate, addition of the carbanion to the carbonyl group of diethyl carbonate takes place to give 2-furylacetic acid derivatives in high yield. Sodium salts of these CH-acids are synthesized, isolated, and characterized. Their alkylation with alkyl bromoacetates is carried out. If ethoxycarbonyl group is not conjugated with the carbanion center, conversion of starting phosphonate and yield of adduct sharply decreases. Alkyl (2- and 4-ethoxycarbonylfur-3-yl)methanephosphonates immediately after acylation with diethyl carbonate are reduced with sodium–diethyl carbonate system to form alkyl 1-(2- and 4-ethoxycarbonylfur-3-yl)-ethanephosphonates. Formation of intermediate reduction product, the phosphorylated furylacetic aldehyde is also fixed spectroscopically. Simultaneously with the reduction dealkylation of ester group of starting phosphonates and alkyl 1-(3-furyl)ethanephosphonates takes place leading to the carboxylic acid salts. Alkyl (2-methyl-5-ethoxycarbonylfur-3-yl)methanephosphonate does not take part in condensation. It gives only the products of dealkylation under the action of sodium ethylate forming from diethyl carbonate.

Keywords: CH-acids, furylmethanephosphonates, diethyl carbonate, Claisen condensation

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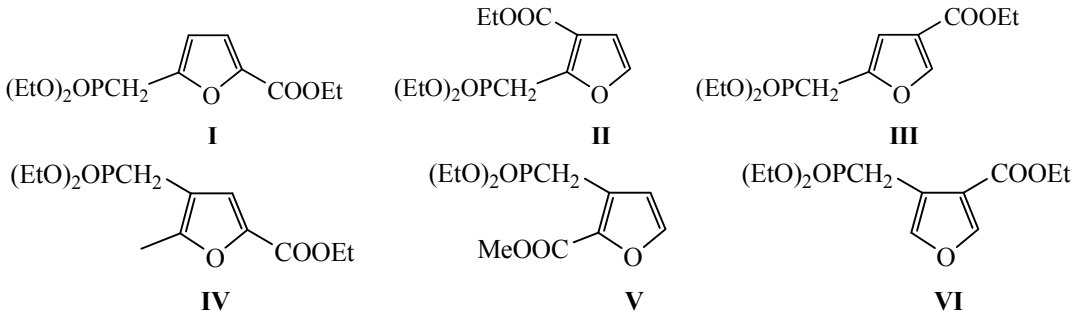
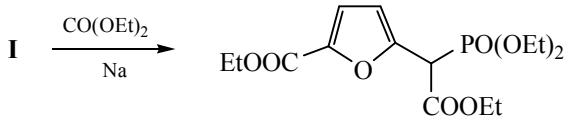
Recently [1–3] we have studied condensation of furylmethanephosphonates with such highly active carbonyl components as ethyl formate, ethyl trifluoroacetate, and diethyl oxalate leading to formation of phosphorylated derivatives of furylacetic aldehyde, 1,1,1-trifluoro-3-(2-furyl)propan-2-one and ethyl furylpyruvate. In the work presented we tried to involve in this reaction diethyl carbonate which is significantly less active in the Claisen reaction. The final goal of our studies was to develop synthetic approaches to phosphorylated derivatives of furyl-acetic acids which up to now were not reported about. Basing on our previous studies it was possible to propose that CH-acid involving in the reaction with diethyl carbonate must be sufficiently strong, that is to have the acidifying electron-accepting substituent in the furan ring. That is why furylmethanephosphonates **I–VI** were chosen as starting substances. This set of compounds includes all six possible variants of relative location of substituents in the furan ring (Scheme 1).

Scheme 1.



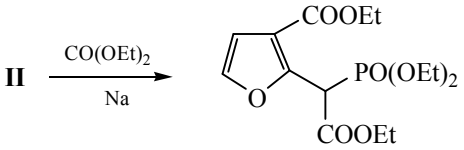
Condensation of furylmethanephosphonates with diethyl carbonate was carried out in toluene in presence of freshly prepared sodium foil at phosphonate : sodium : diethyl carbonate ratio 1 : 1.2 : 2.

Reaction of phosphonate **I** proceeds with heat evolution. Temperature of the reaction mixture increases from 15 to 28°C. Complete dissolution of sodium is achieved in the course of 4–5 h. Conversion of starting substance under these conditions is complete. The product formed is the significantly weaker CH-acid than ketophosphonates, and while extraction of its sodium salt from the reaction mixture with water the equilibrium is strongly shifted to the side of formation of free acid which remains in toluene layer. Besides, in the course of the reaction significant dealkylation of ester groups and also formation of phosphates (δ_P 0.5 to –0.6 ppm) takes place. That is why for isolation of the target product reaction mixture was treated with the equivalent amount of acetic acid, and then washed with sodium bicarbonate solution and water. Under these conditions the target phosphonate remained in the toluene layer, while all the salt-like products were removed to water phase. After removing of solvent and evacuation of residue the syrup-like product **Ia** was obtained. Its ^{31}P NMR spectrum contained only one signal at 15.05 ppm. In the ^{1}H NMR spectrum there appears a signal at 4.56 ppm (J_{PH} 24.8 Hz) characterizing CHP fragment. In the ^{13}C NMR spectrum the signals at 46.61 ppm ($^{1}J_{PC}$ 133.4 Hz) and 165.00 ppm ($^{2}J_{PC}$ 4.2 Hz) appear. They tell about the formation of P–CH-C=O fragment. Basing on these data the reaction under study may be described by the following scheme. Yield of phosphonate **Ia** was 64%.



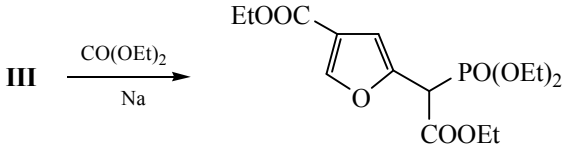
Ia

Condensation of phosphonate **II** with diethyl carbonate proceeded analogously. Reaction proceeded with heat evolution. Temperature of the reaction mixture increased from 18 to 29°C. Isolation of the condensation product was carried our analogously to the previous case by treating with acetic acid and subsequent extraction of acidic products with potassium bicarbonate solution. Conversion of phosphonate **II** was complete. The condensation product **IIa** was light brown syrup. In its ^{31}P NMR spectrum a signal of phosphorus atom was observed at 15.45 ppm, and a doublet at 5.56 ppm (J_{PH} 25.2 Hz) in the ^{1}H NMR spectrum characterized CHP fragment. Strong downfield shift as compared to the corresponding signal in the spectrum of phosphonate **Ia** may be explained by formation of strong hydrogen bond between the proton and the carbonyl of ester group in the furan ring. Signals at 44.96 ppm ($^{1}J_{PC}$ 133.9 Hz) and 165.15 ppm ($^{2}J_{PC}$ 3.1 Hz) in the ^{13}C NMR spectrum characterize P–C–C=O fragment. Reaction of phosphonate **II** may be presented as follows. Conversion of phosphonate **II** was complete, while the yield of the condensation product **IIa** was 74%.



IIa

Condensation of phosphonate **III** with diethyl carbonate at the same reagent ratio proceeded only while heating to 60°C. Dissolution of sodium completed in 1.5 h. The product **IIIa** was traced spectroscopically in a mixture with starting phosphonate. According to the ^{1}H and ^{31}P NMR spectral data conversion of compound **III** was 56% and the yield of the product **IIIa** 11%. CHP fragment was characterized with a doublet at 4.419 ppm (J_{PH} 24.8 Hz) in the ^{1}H NMR spectrum. Signal of phosphorus atom was observed at 15.30 ppm. Signals of carbon atoms of the CHP–C=O fragment were observed at 46.46 ppm ($^{1}J_{PC}$ 133.7 Hz) and 165.30 ppm ($^{2}J_{PC}$ 3.1 Hz).

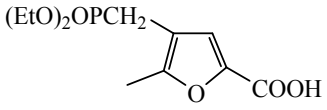


IIIa

Hence, yield of the product of 2-furylmethanephosphonate acylation strongly depends on the location of the acidifying ethoxycarbonyl group in the furan ring. Besides, from spectral characteristics of the products **Ia–IIIa** it follows that between the hydrogen atom of CHP fragment and the carbonyl oxygen atom of the ester group in the adjacent position of the furan ring strong hydrogen bond is formed. It causes downfield shift of the proton signal approximately on 1 ppm. In the starting substances **I–III** this effect is absent.

Contrary to the esters previously used by us [1–3] diethyl carbonate can react with sodium to form

sodium ethylate and evidently carbon monoxide. When condensation of phosphonate with ester is slow or does not proceed at all, large amount of sodium ethylate is accumulated in the system. It causes dealkylation of ethoxycarbonyl group in the furan ring. This pathway of the reaction becomes especially noticeable in the reactions of 3-furylmethanephosphonates **IV–VI**. When sodium foil is added to the solution of phosphonate **IV** and diethyl carbonate in toluene its dissolution in the course of 7 h is observed. Proceeding of this reaction causes the increase in temperature of the reaction mixture from 19 to 26°C. After washing with water the organic layer contained the non-reacted starting substance, and from water phase the acid **VII** was isolated. It is slightly possible to form in the course of development of the reaction mixture because hydrolysis of alkyl furoates proceeds at elevated temperature and needs significantly longer time [4].



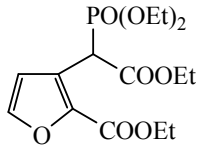
VII

Spectral characteristics of the acid **VII** agree with the reported data [4], and its melting point (111–112°C) was to some extent higher (mp 92°C [4]). No product of the phosphonate **IV** acylation was found.

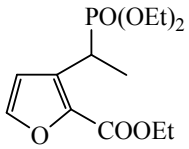
In the reactions of phosphonates **V, VI** formation of the significantly more complex set of products was observed. In the toluene solution of phosphonate **V** and diethyl carbonate at the 1 : 2 molar ratio of reagents no reaction with sodium foil is observed at room temperature. Noticeable dissolution of sodium begins at 65–70°C and completes at this temperature for 4 h. The salt-like products were extracted with water, the extract was acidified to pH 3 and extracted with methylene chloride. After drying of toluene solution and extract solvents were removed, and the mixtures of neutral substances and the compounds exhibiting acidic properties were obtained.

Main component of the preparation isolated from the toluene solution is the ethoxyl analog of phosphonate **V**. Corresponding signals of protons of the CH_2P fragment and the furan ring were observed in ^1H NMR spectrum, and in ^{31}P NMR spectrum a signal of phosphonate at 24.98 ppm was presented. Signal of the methoxyl group in the ^1H NMR spectrum of the mixture was absent. That means that transesterification of the carboxyl group in the furan ring takes place.

Signals of the minor products can be divided in two sets differing by intensity. One of them included the doublet at 5.41 ppm (O=C–CH–P, J_{PH} 24.8 Hz) in the ^1H NMR spectrum and a signal of phosphorus atom at 17.61 ppm. These signals most probably characterize the acylation product **Va**. Second set of signals consisted of a doublet of doublets at 1.90 ppm ($\underline{CH_3}$-CHP, J_{HH} 6.6 Hz, J_{PH} 2.0 Hz), a doublet of quartets at 6.22 ppm (CH_3-$\underline{CH}$P, J_{HH} 6.6 Hz, J_{PH} 16.0 Hz), and a signal of phosphorus atom at 26.25 ppm which was attributed to 1-(3-furyl)ethanephosphonate **Vb**. Its analog, does not containing ethoxycarbonyl group in the furan ring was obtained by us previously [5]. It was characterized by following spectral data, δ, ppm: 1.26 d.d ($\underline{CH_3}$-CHP, J_{HH} 7.0 Hz, J_{PH} 16.0 Hz), 3.16 d.q (CH_3-$\underline{CH}$P, J_{HH} 7.0 Hz, J_{PH} 22.0 Hz), δ_P 29.9 ppm.



Va

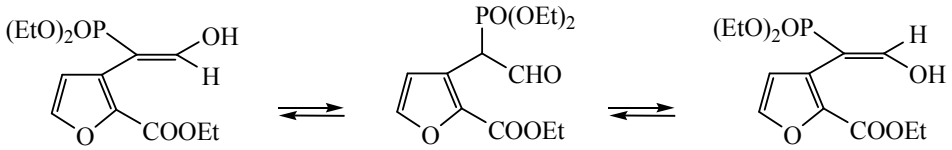


Vb

Downfield shift of a signal of proton of the CHP fragment on 3 ppm as compared to the non-substitued analog may be probably explained by the formation of strong intramolecular hydrogen bond. One more analogous case confirming this proposal will be described below.

In the ^{31}P spectrum of the residue obtained from water extract signals at 22.93, 17.67, and 16.79 ppm were observed. In the ^1H NMR spectrum the doublet of doublets at 5.50 ppm (O=C–CH-P, J_{PH} 28.8 Hz), the signals of furan protons at 6.82 and 7.55 ppm, and a signal of aldehyde group at 9.78 ppm correspond to the last of phosphopus signals. Presented spectral data permit to characterize this product by the structure **Vc**. This aldehyde must exist in equilibrium with its *Z*- and *E*-enolic forms. Signal of the enolic hydroxyl proton is observed at 11.34 ppm. Signals of the furan ring protons at 6.73 ppm (H^4) and 7.10 ppm (H^5) are evidently common for *Z*-and *E*-forms. The doublet at 6.56 ppm (J_{PH} 24.8 Hz) belongs to *Z*-form, and a doublet at 7.22 ppm (J_{PH} 24.8 Hz) is characteristic of *E*-form. Basing on the intensity ratio of the above-presented sets of signals the signal of phosphorus atom at 17.67 ppm may be attributed to *Z*-enol **Vd**, while the signal at 22.93 ppm must characterize *E*-isomer **Ve**. Such attribution agrees with the previously obtained data [1, 2]. These workers have shown that sodium salt of this aldehyde can be extracted from toluene to water

Scheme 2.



Vd **Vc** **Ve**

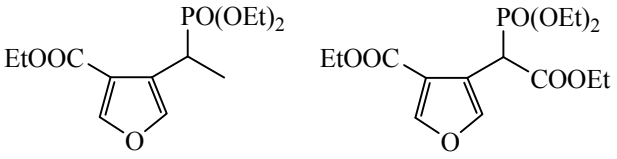
without the cleavage of ester groups. The same result may be probably observed in the case under investtigation (Scheme 2).

Presented data permit to propose the pathways of the process. First act of one of them must be acylation of phosphonate **V** with diethyl carbonate leading to formation of compound **Va**. It quickly reduces with the sodium–diethyl carbonate system to furylethanephosphonate **Vb** through the intermediate formation of the aldehyde **Vc**. Just a mixture of sodium and diethyl carbonate must be the reducing agent because no reducing effect was marked for the previously studied mixtures of sodium with ethyl formate and diethyl oxalate. Besides the above-described reactions also the processes leading to formation of phosphorus-free substances take place. Regretfully, we failed to identify these products because the attempts of their chromatographic isolation were not successful.

Reaction of phosphonate **VI** with diethyl carbonate and sodium foil was carried out as described above. Dissolution of sodium proceeded with small heat evolution and completed in 8 h. Similarly to the case of phosphonate **V** by means of water extraction the fraction of neutral compounds and the fraction of compounds, extracted from the reaction mixture as sodium salts were obtained. Main component of a mixture of esters was phosphonate **VI** which did not take part in the reaction. Its presence was confirmed by the signal of protons at 3.32 ppm (CH_2P, J_{PH} 20.8 Hz), the signals of furan protons, the signal of carbon atom at 20.81 ppm ($^1J_{PC}$ 141.9 Hz), and a signal of phosphorus atom at 26.34 ppm.

Minor components of the mixture were characterized by two sets of signals. One of them included the doublet of doublets at 1.81 ppm ($\underline{CH_3}$-CHP, J_{HH} 6.8 Hz, J_{PH} 1.6 Hz), a doublet of quartets at 6.03 ppm (CH_3-$\underline{CH}$P, J_{HH} 6.8 Hz, J_{PH} 15.6 Hz), and a signal of phosphorus atom at 27.65 ppm. Detailed spectral characteristics of this product are presented in the Experimental. They permit to subscribe this product the structure of 1-(3-furyl)ethanephosphonate **VIa**. As is seen, in this case strong hydrogen bond between the proton of CHP fragment and the carbonyl of ester group occupying the neighboring position of the furan ring is formed. It causes downfield shift of the signal of proton on ~3 ppm as compared to 1-(3-furyl)ethanephosphonate having no substituents in the furan ring.

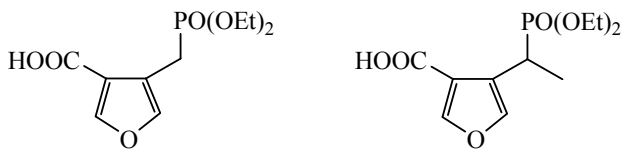
Second, less intense, set of signals included a doublet at 5.91 ppm (J_{PH} 24 Hz) and a signal of phosphorus atom at 18.61 ppm. These signals may be probably subscribed to the acylation product **VIb.**



VIa **VIb**

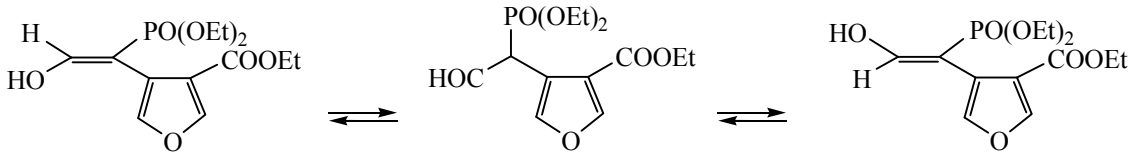
Main component of a mixture of acids extracted from the reaction mixture as salts was the acid **VIc**. Its presence was proved by the signal of CH_2P protons at 3.39 ppm (J_{PH} 20.8 Hz), the signal of carbon atom at 20.70 ppm (CH_2P, $^1J_{PC}$ 141.8 Hz), and a signal of phosphorus atom at 26.85 ppm.

The second component by content was the acid **VId** formed by dealkylation of the ester **VIb**. It is characterized by the signals of protons at 1.74 ppm ($\underline{CH_3}$-CHP, J_{HH} 7.0 Hz, J_{PH} 2.8 Hz) and 7.03 ppm (CH_3-$\underline{CH}$P, J_{HH} 7.0 Hz, J_{PH} 22.0 Hz), the signals of carbon atoms at 16.18 ppm (($\underline{CH_3}$-CHP, $^2J_{PC}$ 8.1 Hz) and 31.52 ppm (CH_3-$\underline{CH}$P, $^1J_{PC}$ 132.3 Hz), and also the signal of phosphorus atom at 26.69 ppm. Note that the signal of CHP fragment proton in the spectrum of the acid **VId** is shifted downfield on 1 ppm as compared to the ester **VIa**. Evidently bonding of this proton by the adjacent carbonyl group is still stronger. Detailed spectral characteristics of the products **VIc, VId** are presented in the experimental.



VIc **VId**

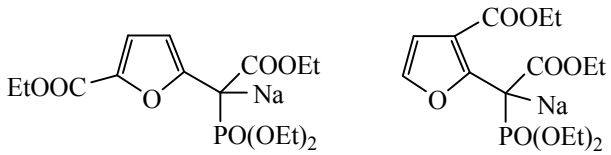
Besides the above-mentioned signals ^{31}P NMR spectrum of a mixture of acidic compounds contained three minor signals at 17.74, 17.25, and 15.41 ppm. Basing on the intensity ratio of these signals and the minor signals in the ^{1}H NMR spectrum following attribution can be made. First of these signals may be corresponded to the doublet at 5.33 ppm (CHP, J_{PH} 29.2 Hz) and a broadened signal at 9.78 ppm (CHO). The third signal of phosphorus corresponds to the doublet at 7.21 ppm [=C(O)-H-*trans*, 28.8 Hz], and the second one to the doublet at 7.26 ppm [=C(O)-H-*cis*, 7.2 Hz]. Basing on the sum of intensities of these signals and the intensity of quartet of the esterial methylene group at 4.27 ppm (CH_2OC, J_{HH} 7.0 Hz) it is possible to attribute them to one and the same substance. Comparison with the data [1, 2] and the above-delivered one permits to conclude that these spectral characteristics belong to the aldehyde **VIe** which is in the equilibrium with *Z*-**VIf** and *E*-enol **VIg.** Due to the presence of large amount of free acids in the mixture separate signal of the enol hydroxyl group is not observed, and common exchange signal is marked at 9.01 ppm. Detailed characteristics of all reaction products are listed in the Experimental.



VIg **VIe** **VIf**

Hence, similarly to the case of phosphonate **V** compound **VI** is acylated with diethyl carbonate to form the ester **VIb** which is immediately reduced to furylethanephosphonate **VIa** through the intermediate aldehyde. The latter was traced spectroscopically in the equilibrium with its enol forms. Parallel dealkylation of esters under the action of sodium ethylate leads to formation of salts at the carboxyl group of the furan ring. Increase in the amount of sodium and diethyl carbonate in 5 times in relation to phosphonate **VI** did not alter principally the ratio of the reaction products, and practically did not increase the conversion of starting substance. Note that the amount of substances do not containing phosphorus which are formed in this reaction is significantly lower than in the case of phosphonate **V**, but we failed to isolate and identify them as well.

Hence, among six isomers of (ethoxycarbonylfuryl)(diethoxyphosphoryl)acetates only the compounds **Ia** and **IIa** occurred to be available. In the reactions with sodium ethylate or hydride they form salts **Ib** and **IIb** which were isolated and characterized spectroscopically. They are crystalline compounds very sensitive to the action of air moisture and oxygen, but comparatively stable in DMSO and dioxane solutions.

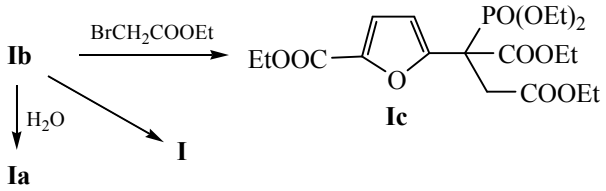


Ib **IIb**

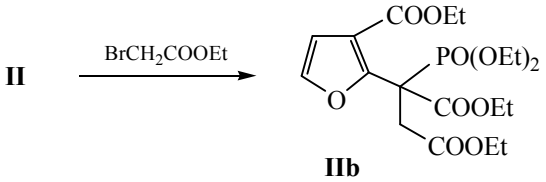
Alkylation of salts **Ib, IIb** with ethyl bromoacetate was carried out in dioxane. It was found that while metallization with sodium ethylate these compounds are deactivated evidently due to the presence of ethanol, and alkylation does not proceed. Synthesis of sodium salts by treating with the suspension of sodium hydride in mineral oil permitted to carry out alkylation. In both cases the reaction was carried out in anhydrous dioxane at 80°C. The control point of the reaction completion was the achievement of pH 7–8 in water solution of the reaction mixture.

In the ^{31}P NMR spectrum of reaction mixture obtained after alkylation of sodium salt **Ib** three signals at 21.63, 16.55, and 14.88 ppm were observed. First signal belongs to phosphonate **I**, and the third one to phosphonate **Ia**. Presence of these compounds was confirmed also by means of ^{1}H and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectrum also a doublet of doublets at 3.49 ppm (CH_2P, J_{HH} 6.8 Hz, J_{PH} 6.8 Hz) and the signals of furan ring protons corresponding to it by intensity were observed. In the ^{13}C NMR spectrum the signals at 35.82 ppm (CH_2) and 53.13 ppm (C–P, $^{1}J_{PC}$ 127.1 Hz) were presented as well as two signals of carbonyl group at 169.78 ppm and 169.97 ppm corresponding to the $CH_2\underline{C}$=O fragment. Obtaining of the ^{13}C NMR spectrum in DMSO-d_6 instead of chloroform gave very close difference in chemical shifts of these signals. Most probably here reveals the interaction with phosphorus with the coupling constant ~19.0 Hz, though for $^{3}J_{PC}$ this value is abnormally high. Presented spectral characteristics must be sub-

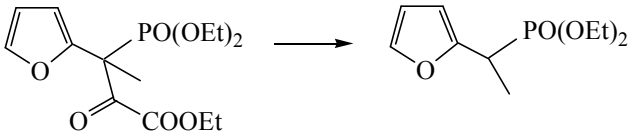
scribed to the alkylation product **Ic**. Hence, observed process may be described by following scheme.



In the ^{31}P NMR spectrum of the mixture obtained after alkylation of sodium salt **IIb** signals of phosphonate **IIa** at 15.45 ppm and the alkylation product **IIc** at 17.22 ppm were found. In the ^{1}H NMR spectrum the product **IIc** is characterized by a doublet of doublets at 4.02 ppm (CH_2, J_{HH} 7.2 Hz, J_{PH} 1.2 Hz). In the ^{13}C NMR spectrum of this substance the signals at 37.26 ppm (CH_2, $^{2}J_{PC}$ 3.9Hz), 53.70 ppm (C–P, $^{1}J_{PC}$ 130.5 Hz), and 167.07 ppm ($CH_2\underline{C}=O$ $^{3}J_{PC}$ 5.6 Hz) were observed.



Alkylation of tertiary carbanions **Ib**, **IIb** is rather complicated. At the same time it must be noted that the obtained alkylation products are stable, and abstraction of functional group from the side chain characteristic of alkylation of the unsubstituted 2-furyl(diethoxyphosphorylpiruvate [3] was not observed.



Hence, ability of furylmethanephosphonates to take part in Claisen condensation with diethyl carbonate strongly depends on the position of diethoxyphosphorylmethyl group and the acidifying ethoxycarbonyl substituent in the furan ring. 2-Furylmethanephosphonates are easily acylated if the carbanion center is conjugated with the acceptor substituent. When conjugation is absent conversion of starting phosphonate and yield of the condensation product strongly decrease. In the case of 3-furylmethanephosphonate Claisen condensation proceeds only when ethoxycarbonyl substituent is located in the adjacent position of the furan ring. In this case entering acyl residue unexpectedly undergoes gradual reduction to methyl group. In both cases among the intermediates aldehyde is traced spectroscopically. Ester group of the furan ring does not take part in these transformations. Proton of the CHP fragment forms strong hydrogen bond with the carbonyl oxygen atom of the ester group located in the neighboring position of the furan ring. In the case of phosphonoacetic acid esters it causes the downfield shift of signal on 1 ppm. In the case of furylethanephosphonates the downfield shift of signal reaches 3 ppm as compared to the compound having no substituents in the furan ring. Transformation of ester group to the carboxyl one in the furan ring leads to additional downfield shift of signal on 1 ppm. In this case it is observed at ~7 ppm.

(Ethoxycarbonylfur-2-yl)(diethoxyphosphoryl)-acetates occur to be comparatively weak CH-acids. They form sodium salts which are rather stable at room temperature. Contrary to formyl derivatives of furylmethanephosphonates while treating with water these salts undergo complete hydrolysis, and free CH-acid transforms to the organic phase. In presence of small amount of alcohol these salts do not undergo alkylation. They can be involved in the reaction even with active alkyl halides only after metallization of CH-acids with sodium hydride in anhydrous dioxane, but even in this case the reaction is complicated by side processes.

EXPERIMENTAL

^{1}H, ^{13}C, and ^{31}P NMR spectra were taken on a Bruker DPX-400 [400.13 MHz (^{1}H), 161.97 MHz (^{31}P), 100.61 MHz (^{13}C)]. Spectra of sodium salts were obtained in deuterated DMSO. In all the other cases $CDCl_3$ was used as a solvent.

Ethyl (5-ethoxycarbonylfur-2-yl)(diethoxyphosphoryl)acetate (Ia). To a solution of 2.1 g of phosphonate **I** and 1.8 mL of diethyl carbonate in 15 mL of toluene 0.2 g of freshly prepared sodium foil was added under the intense stirring. Temperature of the reaction mixture gradually increased from 15 to 28°C, and then returned to the starting value. Dissolution of sodium took place in 5 h. After that 0.6 mL of acetic acid and 15 mL of ethyl acetate was added. The mixture obtained was washed with 15 mL of 5% potassium bicarbonate, 15 mL of water, and dried over sodium sulfate. After removing of solvent and evacuation 1.7 g (64%) of phosphonate **Ia** was obtained as a light brown oil. ^{1}H NMR spectrum, δ, ppm: 1.23–1.36 m (CH_3-ester), 4.05–4.25 m (CH_2OP), 4.32 q (CH_2OC, J_{HH} 7.2 Hz), 4.56 d (CHP, J_{PH} 24.8 Hz), 6.70 d.d (H^3-furan, J_{HH} 3.2 Hz, J_{PH} 3.2 Hz), 7.27 d (H^4-furan, J_{HH}

3.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.94 (CH_3-ester), 14.27 (CH_3-ester), 15.98 (CH_3-phosphonate, $^3J_{PC}$ 7.0 Hz), 16.20 (CH_3-phosphonate, $^3J_{PC}$ 4.2 Hz), 46.61 (CHP, $^1J_{PC}$ 133.4 Hz), 60.94 (CH_2OC), 62.46 (CH_2OC), 63.65 (CH_2OP, $^2J_{PC}$ 5.4 Hz), 63.89 (CH_2OP, $^2J_{PC}$ 6.8 Hz), 64.09 (CH_2OP, $^2J_{PC}$ 6.5 Hz), 112.05 (C^3, $^3J_{PC}$ 5.1 Hz), 119.03 (C^4), 144.39 (C^5, $^4J_{PC}$ 1.8 Hz), 148.69 (C^2, $^2J_{PC}$ 7.5 Hz), 158.47 (C=O-furan), 165.00 (C=O, $^2J_{PC}$ 4.3 Hz). ^{31}P NMR spectrum, δ_P 15.05 ppm.

Sodium salt of ethyl (5-ethoxycarbonylfur-2-yl)(diethoxyphosphoryl)acetate (Ib). To a solution of sodium ethylate obtained by dissolution of 0.12 g of sodium in 5 mL of absolute ethanol a solution of 1.8 g of ester **Ia** in absolute ethanol was added, and the mixture obtained was evaporated to dryness in a vacuum. The residue was triturated with anhydrous ether to form light brown crystals immediately darkening and agglutinating on air. ^{1}H NMR spectrum, δ, ppm: 1.13 t (CH_3-ester, J_{HH} 7.0 Hz), 1.15 t (CH_3-ester, J_{HH} 7.0 Hz), 1.23 t (CH_3-ester, J_{HH} 7.0 Hz), 3.84 m (CH_2OP, J_{HH} 7.0 Hz, J_{PH} 14.0 Hz), 3.91 q (CH_2OC, J_{HH} 7.0 Hz), 4.16 q (CH_2OC, J_{HH} 7.0 Hz), 6.19 d (H^3-furan, J_{HH} 3.6 Hz), 7.074 (H^4-furan, J_{HH} 3.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.92 (CH_3-ester), 15.42 (CH_3-ester), 16.74 (CH_3-phosphonate, $^3J_{PC}$ 7.1 Hz), 57.08 (CH_2OC), 59.94 (CH_2OC), 60.11 (CH_2OP, $^2J_{PC}$ 4.9 Hz), 102.63 (C^3, $^3J_{PC}$ 7.2 Hz), 122.16 (C^4), 135.56 (C^5), 165.99 (C^2, $^2J_{PC}$ 9.5 Hz), 159.41 (C=O-furan), 168.14 (C=O, $^2J_{PC}$ 14.7 Hz), signal of P–C fragment was not found. Probably it can overlap with DMSO. ^{31}P NMR spectrum, δ_P 29.13 ppm.

Alkylation of sodium salt Ib with ethyl bromoacetate. To a solution of 3.21 g of phosphonate **Ia** in 30 mL of anhydrous dioxane 0.4 g of 60% suspension of sodium hydride in the mineral oil was added. The mixture obtained was kept for 30 min at 40°C, and 1.1 mL of ethyl bromoacetate was added in one portion. The reaction mixture was heated for 4 h at 80°C. Liberation of sodium bromide was observed, and pH of water solution of a batch of the reaction mixture became neutral. Dioxane was removed on a rotor evaporator, the residue was dissolved in 30 mL of ethyl acetate, washed with 10 mL of 5% potassium bicarbonate solution, with 10 mL of water, and dried over sodium sulfate. Solvent was removed on a rotor evaporator, and the residue was evacuated at room temperature and the residual pressure 1 mm for 1 h. A mixture, 2.24 g, consisting of phosphonates **I**, **Ia**, and diethyl 2-(5-ethoxycarbonylfur-2-yl)-2-(diethoxyphosphoryl)butanedioate **Ic** was obtained. ^{1}H NMR spectrum, δ, ppm: common signals: 1.15–1.35 m (CH_3), 3.99–4.12 m (CH_2OP), 4.24–4.34 m (CH_2OC); **I**: 3.28 d (CH_2P, J_{PH} 21.2 Hz), 6.38 d.d (H^3-furan, J_{HH} 3.0 Hz, J_{PH} 3.0 Hz), 7.091 d (H^4-furan, J_{HH} 3.0 Hz); **Ia**: 4.509 d (CHP, J_{PH} 24.8 Hz), 6.03 d.d (H^3-furan, J_{HH} 3.2 Hz, J_{PH} 3.0 Hz), 7.13 d (H^4-furan, J_{HH} 3.2 Hz); **Ic**: 3.49 d.d (–$\underline{CH_2}$C=O, J_{HH} 6.8 Hz, J_{PH} 6.8 Hz), 6.88 d.d (H^3-furan, J_{HH} 3.2 Hz, J_{PH} 3.4 Hz), 7.133d (H^4-furan, J_{HH} 3.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: common signals: 13.84 (CH_3-ester), 14.00 (CH_3-ester), 14.26 (CH_3-ester), 16.21 (CH_3-phosphonate, $^3J_{PC}$ 5.6 Hz), 16.26 (CH_3-phosphonate, $^3J_{PC}$ 5.6 Hz), 60.61 (CH_2OC), 60.79 (CH_2OC), 60.90 (CH_2OC), 62.42 (CH_2OC), 63.56 (CH_2OP, $^2J_{PC}$ 5.1 Hz), 63.62 (CH_2OP, $^2J_{PC}$ 6.3 Hz), 63.83 (CH_2OP, $^2J_{PC}$ 6.7 Hz), 64.14 (CH_2OP, $^2J_{PC}$ 7.1 Hz), 64.26 (CH_2OP, $^2J_{PC}$ 7.Hz); **I**: 26.99 (CH_2P, $^1J_{PC}$ 142.0 Hz), 110.54 (C^3, $^3J_{PC}$ 6.2 Hz), 118.99 (C^4), 144.08 (C^5, $^4J_{PC}$ 2.7 Hz), 150.53 (C^2, $^2J_{PC}$ 9.5 Hz), 158.493 (C=O); **Ia**: 46.69 (CHP, $^1J_{PC}$ 132.6 Hz), 111.95 (C^3, $^3J_{PC}$ 4.9 Hz), 117.24 (C^4), 144.33 (C^5, $^4J_{PC}$ 2.6 Hz), 149.13 (C^2, $^2J_{PC}$ 7.3 Hz), 158.49 (C=O-furan), 165.00 (C=O); **Ic**: 35.82 (CH_2), 53.13(CP, $^1J_{PC}$ 1 27.1 Hz), 113.09 (C^3, $^3J_{PC}$ 5.9 Hz), 119.01 (C^4), 143.52 (C^5, $^4J_{PC}$ 3.7 Hz), 151.49 (C^2, $^2J_{PC}$ 10.6 Hz), 158.37 (C=O-furan), 166.52 (P–C–$\underline{C}$=O, $^2J_{PC}$ 5.7 Hz), 169.78 (CH_2–$\underline{C}$=O), 169.97 (CH_2–$\underline{C}$=O). ^{31}P NMR spectrum, δ_P, ppm: 21.63 (**I**), 16.55 (**Ic**), 14.88 (**Ia**), intensity ratio 0.34 : 1.00 : 0.24.

Ethyl (3-ethoxycarbonylfur-2-yl)(diethoxyphosphoryl)acetate (IIa). To a solution of 2.5 g of phosphonate **II** and 2.1 mL of diethyl carbonate in 25 mL of toluene 0.23 g of freshly prepared sodium salt was added with stirring. Temperature of the reaction mixture gradually rose from 18 to 29°C, and then gradually returned back. Dissolution of sodium completed in 3 h. After that 0.6 mL of acetic acid and 25 mL of ethyl acetate was added. The mixture obtained was washed with 15 mL of 5% potassium bicarbonate, with 15 mL of water, and dried over sodium sulfate. Solvent was removed on a rotor evaporator, and the residue was evacuated at room temperature and the residual pressure 1 mm for 1 h to give 2.3 g (74%) of phosphonate **IIa** as the light brown syrup. ^{1}H NMR spectrum, δ, ppm: 1.22–1.33 m (CH_3), 4.01–4.32 m (CH_2OC + CH_2OP), 5.56 d (CHP, J_{PH} 25.2 Hz), 6.69 br.s (H^4-furan), 7.41 br.s (H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: 13.96 (CH_3-ester), 16.00 (CH_3-phosphonate, $^3J_{PC}$ 6.6 Hz), 16.23 (CH_3-phosphonate, $^3J_{PC}$ 5.5 Hz), 44.96 (CHP, $^1J_{PC}$ 133.9 Hz), 60.59 (CH_2OC), 62.21 (CH_2OC), 63.32 (CH_2OP, $^2J_{PC}$

6.6 Hz), 63.46 (CH_2OP, $^2J_{PC}$ 7.4 Hz), 110.48 (C^4), 116.44 (C^3, $^3J_{PC}$ 7.3 Hz), 142.67 (C^5), 150.64 (C^2, $^2J_{PC}$ 12.2 Hz), 163.16 (C=O-furan), 165.15 (C=O, $^2J_{PC}$ 3.1 Hz). ^{31}P NMR spectrum, δ_P 15.45 ppm.

Sodium salt of ethyl (3-ethoxycarbonylfur-2-yl)(diethoxyphosphoryl)acetate (IIb). To a solution of sodium ethylate prepared by dissolution of 0.12 g of sodium in 5 mL of absolute ethanol a solution of 1.9 g of the ester **IIa** in absolute ethanol was added, and the mixture obtained was evaporated to dryness in a vacuum. The residue was triturated with 15 mL of anhydrous ether, the mixture formed was diluted with 15 mL of hexane, and light brown crystals of the salt **IIb** were quickly filtered off. When exposed to air these crystals darken and melt in the course of 2–3 min. ^{1}H NMR spectrum, δ, ppm: 1.17–1.33 m (CH_3), 3.66 m (CH_2OP, J_{HH} 7.2 Hz, J_{PH} 14.4 Hz), 3.76 q (CH_2OC, J_{HH} 7.2 Hz), 4.05 q (CH_2OC, J_{HH} 7.0 Hz), 6.45 d (H^4-furan, J_{HH} 1.6 Hz), 7.21 br.s (H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: 14.81 (CH_3-ester), 15.45 (CH_3-ester), 16.74 (CH_3-phosphonate, $^3J_{PC}$ 7.3 Hz), 58.90 (CH_2OC), 59.63 (CH_2OP, $^2J_{PC}$ 3.6 Hz), 59.792 (CH_2OP, $^2J_{PC}$ 5.0 Hz), 110.81 (C^3, $^3J_{PC}$ 7.3 Hz), 111.36 (C^4), 137.83 (C^5), 163.56 (C^2, $^2J_{PC}$ 9.9 Hz), 164.55 (C=O-furan), 169.14 (C=O, $^2J_{PC}$ 19.4 Hz), signal of C–P fragment was not found. It probably overlaps with DMSO. ^{31}P NMR spectrum, δ_P 31.91 ppm.

Alkylation of sodium salt IIb with ethyl bromoacetate. To a solution of 1.6 g of phosphonate **IIa** in 10 mL of anhydrous dioxane 0.2 g of 60% suspension of sodium hydride in mineral oil was added. The mixture obtained was kept for 30 min at 40°C, and 0.6 mL of ethyl bromoacetate was added in one portion. Reaction mixture was heated for 4 h at 80°C. Liberation of sodium bromide precipitate was observed, and pH of water solution of a batch of the reaction mixture became equal to 7. Dioxane was removed on a rotor evaporator, the residue was dissolved in 30 mL of ethyl acetate, washed with 10 mL of 5% potassium bicarbonate solution, with 10 mL of water, and dried over sodium sulfate. The drying agent was filtered off, solvent was removed on a rotor evaporator, and the residue was evacuated at room temperature and the residual pressure 1 mmHg for 1 h to give 1.84 g of a mixture consisting of phosphonate **IIa** and diethyl 2-(3-ethoxycarbonylfur-2-yl)-2-(diethoxyphosphoryl)butanedioate **IIc**. ^{1}H NMR spectrum, δ, ppm: common signals: 1.13–1.35 m (CH_3), 4.08–4.27 m (CH_2OP + CH_2OC); **IIa**: 5.58 d (CHP, J_{PH} 25.6 Hz), 6.71 br.s (H^4-furan), 7.43 br.s (H^5-furan); **IIc**: 4.02 d.d ($\underline{CH_2}$–C=O, J_{HH} 7.2 Hz, J_{PH} 1.2 Hz), 6.75 br.s (H^4-furan), 7.40 br.s (H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: common signals: 13.79 (CH_3-ester), 13.98 (CH_3-ester), 14.23 (CH_3-ester), 16.27 (CH_3-phosphonate, $^3J_{PC}$ 6.6 Hz), 60.49 (CH_2OC), 62.30 (CH_2OC), 63.32 (CH_2OP, $^2J_{PC}$ 7.0 Hz), 63.39 (CH_2OP, $^2J_{PC}$ 7.1 Hz), 63.60 (CH_2OP, $^2J_{PC}$ 7.2 Hz), 63.77 (CH_2OP, $^2J_{PC}$ 6.9 Hz); **IIa**: 45.01 (CHP, $^1J_{PC}$ 133.6 Hz), 110.68 (C^4), 116.43 (C^3, $^3J_{PC}$ 7.1 Hz), 142.66 (C^5), 150.74 (C^2, $^2J_{PC}$ 12.1 Hz), 163.18 (C=O-furan), 165.20 (C=O, $^2J_{PC}$ 3.0 Hz); **IIc**: 32.26 (–CH_2–, $^2J_{PC}$ 3.9 Hz), 53.70 (CP, $^1J_{PC}$ 130.5 Hz), 111.87 (C^4), 115.86 (C^3, $^3J_{PC}$ 6.5 Hz), 140.86 (C^5), 154.41 (C^2, $^2J_{PC}$ 9.7 Hz), 162.95 (C=O-furan), 167.07 (P–C–$\underline{C}$=O, $^2J_{PC}$ 5.6 Hz), 169.31 (CH_2-C=O, $^3J_{PC}$ 5.9 Hz). ^{31}P NMR spectrum, δ_P, ppm: 15.45 (**IIa**), 17.276 (**IIc**), intensity ratio 1.56 : 1.00.

Condensation of phosphonate III with diethyl carbonate. To a solution of 2.2 g of phosphonate **III** and 1.9 mL of diethyl carbonate in 20 mL of toluene 0.2 g of freshly prepared sodium foil was added in one portion under the intense stirring. Dissolution of sodium began after heating of reaction mixture to 60°C, and its temperature rose spontaneously to 70°C. After the completion of heat evolution the reaction mixture temperature was maintained at 60–62°C for 1.5 h until the complete dissolution of sodium. Then 0.6 mL of acetic acid was added, and the mixture obtained was diluted with 20 mL of ethyl acetate. After washing with 10 mL of 5% potassium bicarbonate solution and 10 mL of water it was dried over sodium sulfate. Solvent was removed on a rotor evaporator, and the residue was evacuated at room temperature and the residual pressure 1 mmHg for 1 h to give 1.3 g of a mixture of phosphonates **III** and **IIIa**. ^{1}H NMR spectrum, δ, ppm: common signals: 1.23–1.31 m (CH_3), 4.05–4.12 m (CH_2OP, J_{HH} 7.2 Hz, J_{PH} 14.4 Hz), 4.26 q (CH_2OC-furan, J_{HH} 7.2 Hz); **III**: 3.21 d (CH_2P, J_{PH} 20.8 Hz), 6.57 d (H^3-furan, J_{PH} 3.6 Hz), 7.90 s (H^5-furan); **IIIa**: 4.17 q (CH_2O, J_{HH} 7.2 Hz), 4.42 d (CHP, J_{PH} 24.8 Hz), 6.87 d (H^3-furan, J_{PH} 2.8 Hz), 7.94 s (H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: **III**: 14.26 (CH_3-ester), 16.34 (CH_3-phosphonate, $^3J_{PC}$ 5.8 Hz), 26.65 (CH_2P, $^1J_{PC}$ 143.0 Hz), 60.34 (CH_2OC), 62.44 (CH_2OP, $^2J_{PC}$ 6.5 Hz), 108.18 (C^3, $^3J_{PC}$ 7.2 Hz), 120.63 (C^4) 146.87 (C^5), 147.42 (C^2, $^2J_{PC}$ 9.4 Hz), 162.93 (C=O-furan); **IIIa**: 13.98 (CH_3-ester), 14.07 (CH_3-ester), 16.09 (CH_3-phosphonate, $^3J_{PC}$ 6.5 Hz), 46.46 (CHP, $^1J_{PC}$ 133.7 Hz), 60.47 (CH_2OC), 62.33 (CH_2OP, $^2J_{PC}$ 7.8 Hz), 109.73 (C^3), 120.74 (C^4) 146.29 (C^2, $^2J_{PC}$

8.0 Hz) 147.21(C^5), 162.77 (C=O-furan), 165.30 (PC–C=O, $^2J_{PC}$ 3.1 Hz). ^{31}P NMR spectrum, δ_P, ppm: 22.16 (**III**), 15.30 (**IIIa**), intensity ratio 1.00 : 0.19.

Reaction of phosphonate IV with diethyl carbonate. To a solution of 3.2 g of phosphonate **IV** and 2.5 mL of diethyl carbonate in 20 mL of toluene 0.3 g of freshly prepared sodium foil was added in one portion. Temperature of the reaction mixture rose from 19 to 26°C. Dissolution of sodium completed after 7 h of stirring. The reaction mixture was extracted with water (2 × 15 mL), and toluene layer was dried over sodium sulfate. Water extract was acidified to pH 3, extracted with chloroform (3 × 15 mL), and the obtained organic layer was dried over sodium sulfate. According to the ^{1}H and ^{31}P NMR data toluene layer contained only the starting phosphonate **IV**. Chloroform extract was evaporated on a rotor evaporator, and the residue was triturated with 10 mL of hexane. After handling the mixture for 3 days crystals of the acid **VII** precipitated. Yield 0.2 g, mp 111–112°C (mp 91–92°C [4]). ^{1}H NMR spectrum, δ, ppm: 1.31 t (CH_3, J_{HH} 7.2 Hz), 2.35 br.s (CH_3-furan), 2.94 d (CH_2P, J_{PH} 20.8 Hz), 4.13 m (CH_2OP, J_{HH} 6.8 Hz, J_{PH} 14.2 Hz), 7.19 s (H^4-furan), 9.00 br.s (OH). ^{13}C NMR spectrum, δ_C, ppm: 12.09 (CH_3-furan), 16.38 (CH_3-phosphonate, $^3J_{PC}$ 5.6 Hz), 22.68 (CH_2P, $^1J_{PC}$ 143.9 Hz), 62.68 (CH_2OP, $^2J_{PC}$ 6.6 Hz), 112.06 (C^3, $^2J_{PC}$ 9.4 Hz), 121.45 (C^4) 142.21 (C^5), 154.97 (C^2, $^3J_{PC}$ 10.3 Hz), 161.31 (C=O-furan). ^{31}P NMR spectrum, δ_P: 26.26 ppm.

Reaction of phosphonate V with diethyl carbonate. To a solution of 2.4 g of phosphonate **V** and 2 mL of diethyl carbonate in 25 mL of toluene 0.3 g of freshly prepared sodium foil was added with stirring. Dissolution of sodium proceeded at 65–70°C for 3.5 h. After dissolution was complete, the reaction mixture was extracted with water (2 × 15 mL), and toluene layer was dried over sodium sulfate. After removing of toluene on a rotor evaporator and evacuation of the residue for 1 h at room temperature and the residual pressure 1 mm, 1.1 g of brown oil was obtained. Its main component was the ethyl analog of phosphonate **V**. ^{1}H NMR spectrum, δ, ppm: common signals 1.22–1.33 m (CH_3), 1.32–1.41 m (CH_3), 4.06–4.14 m (CH_2OP), 4.18 q (CH_2OC, J_{HH} 7.2 Hz); **V**: 3.485 d (CH_2P, J_{PH} 22.0 Hz), 6.63 d (H^4-furan, J_{HH} 2.0 Hz), 7.41 d (H^5-furan, J_{HH} 2.0 Hz). ^{31}P NMR spectrum, δ_P: 24.98 ppm.

Minor products: ^{1}H NMR spectrum, δ, ppm: **Va**: 5.41 d (O=C–CH–P, J_{PH} 24.8 Hz); **Vb**: 1.90 d.d (CH_3-CHP, J_{HH} 6.6 Hz, J_{PH} 2.0 Hz), 6.22 d.q (CH_3-CHP, J_{HH} 6.6 Hz, J_{PH} 16.0 Hz); ^{31}P NMR spectrum, δ_P, ppm: 17.617 (**Va**), 26.25 (**Vb**).

Water extract was acidified with hydrochloric acid to pH 3 and extracted with methylene chloride (3 × 10 mL). After drying over sodium sulfate solvent was removed on a rotor evaporator, and the residue was evacuated for 1 h at room temperature and the residual pressure 1 mmHg to give light brown oil. ^{1}H NMR spectrum, δ, ppm: common signals: 1.16–1.38 m (CH_3), 3.98-4.37 m (CH_2OP + CH_2OC); (**Vc**): 5.50 d (CHP, J_{PH} 28.8 Hz), 6.82 br.s (H^4-furan), 7.55 br.s (H^5-furan), 9.79 s (CHO); **Vd**: 6.65 d (=CH-O, J_{PH} 24.8 Hz); **Ve**: 7.22 d (=CH–O, J_{PH} 7.2 Hz); common signals: 6.73 br.s (H^4-furan), 7.10 br.s (H^5-furan), 11.34 (OH-enol). ^{31}P NMR spectrum, δ_P, ppm: 16.73 (**Vc**), 17.66 (**Vd**), 22.93 (**Ve**).

Reaction of phosphonate VI with diethyl carbonate. To a solution of 2.8 g of phosphonate **VI** and 2.5 mL of diethyl carbonate in 30 mL of toluene 0.3 g of freshly prepared sodium foil was added in one portion under the intense stirring. Reaction proceeded at room temperature, dissolution of sodium completed after 8 h. Reaction mixture was extracted with water (2 × 15 mL), and the organic layer was dried over sodium sulfate. Solvent was removed on a rotor evaporator, and the residue was evacuated for 1 h at room temperature and the residual pressure 1 mmHg. Light brown oil was obtained. Its main component was phosphonate **VI**. ^{1}H NMR spectrum, δ, ppm: 1.25 t (CH_3-phosphonate, J_{HH} 7.2 Hz), 1.31 t (CH_3-ester, J_{HH} 7.2 Hz), 3.32 d (CH_2P, J_{PH} 20.8 Hz), 4.41 m (CH_2OP, J_{HH} 7.2 Hz, J_{PH} 14.4 Hz), 4.26 q (CH_2OC, J_{HH} 7.2 Hz), 7.48 br.d (H^2-furan, J_{PH} 2.4 Hz), 7.94 br.s (H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: 14.23 (CH_3), 16.30 (CH_3, $^3J_{PC}$ 6.0 Hz), 20.805 (CH_2P, $^1J_{PC}$ 141.9 Hz), 60.23 (CH_2O), 62.01 (CH_2OP, $^2J_{PC}$ 6.4 Hz), 115.18 (C^3, $^2J_{PC}$ 8.7 Hz), 118.23 (C^4, $^3J_{PC}$ 6.6 Hz), 142.74 (C^2, $^3J_{PC}$ 7.5 Hz), 148.37 (C^5), 163.24 (C=O-furan). ^{31}P NMR spectrum, δ_P: 26.34 ppm.

Minor products: ^{1}H NMR spectrum, δ, ppm: **VIa**: 1.81 d.d (CH_3-CHP, J_{HH} 6.8 Hz, J_{PH} 1.6 Hz), 6.03 d.d (CH_3-CHP, J_{HH} 6.8 Hz, J_{PH} 15.6 Hz), 7.44 br.s (H^2-furan), 7.70 br.s (H^5-furan); **VIb**: 5.91 d (O=C–CH–P, J_{PH} 124.0 Hz); ^{31}P NMR spectrum, δ_P, ppm: 27.65 (**VIa**), 18.61 (**VIb**).

Water extract was acidified with hydrochloric acid to pH 4, extracted with chloroform (3 × 15 mL), and dried over sodium sulfate. Solvent was removed on a rotor evaporator, and the residue was evacuated for 1 h

at room temperature and the residual pressure 1 mmHg. Brown syrup was obtained. Its main component was the acid **VIc**. ^{1}H NMR spectrum, δ, ppm: 1.26–1.36 m (CH_3-phosphonate), 4.06–4.14 m (CH_2OP), 9.006 br.s (OH) (these three signals overlap with the corresponding signals of the other components of the mixture), 3.39 d (CH_2P, J_{PH} 20.8 Hz), 7.51 br.d (H^2-furan), 8.030 br.s (H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: common signals: 15.99 (CH_3, $^3J_{PC}$ 7.0 Hz), 16.26 (CH_3, $^3J_{PC}$ 6.4 Hz), 16.32 (CH_3, $^3J_{PC}$ 7.0 Hz), 62.36 (CH_2OP, $^2J_{PC}$ 5.3 Hz), 62.51 (CH_2OP, $^2J_{PC}$ 6.8 Hz), 63.593 (CH_2OP, $^2J_{PC}$ 5.3 Hz); **VIc**: 20.70 (CH_2P, $^1J_{PC}$ 141.8 Hz), 114.69 (C^3, $^2J_{PC}$ 8.9 Hz), 118.51 (C^4, $^3J_{PC}$ 6.2 Hz), 142.21 (C^2, $^3J_{PC}$ 7.8 Hz), 149.35 (C^5), 149.78 (C^5), 166.39 (C=O-furan). ^{31}P NMR spectrum, δ_P: 26.85 ppm.

Minor products: ^{1}H NMR spectrum, δ, ppm: **VId**: 1.74 d.d ($\underline{CH_3}$-CHP, J_{HH} 6.8 Hz, J_{PH} 3.2 Hz), 7.03 d.q (CH_3-$\underline{CH}$P, J_{HH} 6.8 Hz, J_{PH} 22.0 Hz), 7.37 br.s (H^2-furan), 8.12 br.s (H^5-furan); aldehyde, common signals: 4.27 q (CH_2OC, J_{HH} 7.0 Hz), 7.50 s (H^2-furan), 7.97 br.s (H^5-furan); **VIe**: 5.33 d (CHP, J_{PH} 29.2 Hz), 9.78 br.s (CHO); **VIf**: 7.21 d (=CH-O, J_{PH} 28.8 Hz); **VIg**: 7.26 d (=CH-O, J_{PH} 7.2 Hz); ^{13}C NMR spectrum, δ_C, ppm: **VId**: 16.18 ($\underline{CH_3}$-CHP, $^2J_{PC}$ 5.3 Hz), 31.52 (PC, $^1J_{PC}$ 132.3 Hz), 117.55 (C^3, $^2J_{PC}$ 12.2 Hz), 118.82 (C^4, $^3J_{PC}$ 4.2 Hz), 142.66 (C^2, $^3J_{PC}$ 5.3 Hz), 148.44(C^5), 165.75 (C=O-furan); aldehyde, common signals: 14.42 (CH_3-ester), 60.32 (CH_2OC); 31P NMR spectrum, δ_P, ppm: 26.69 (**VId**), 17.64 (**VIe**), 17.25 (**VIf**), 15.41 (**VIg**).

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