ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 12, pp. 1938–1950. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © L.M. Pevzner, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 12, pp. 1983–1995.

Acylation of Diethyl (Ethoxycarbonylfuryl)methanephosphonates under the Conditions of Claisen Reaction

L. M. Pevzner

St. Petersburg State Technological Institute, Moskovskii pr. 26, St. Petersburg, 190031 Russia
e-mail: pevzner_lm@list.ru

Received June 3, 2012

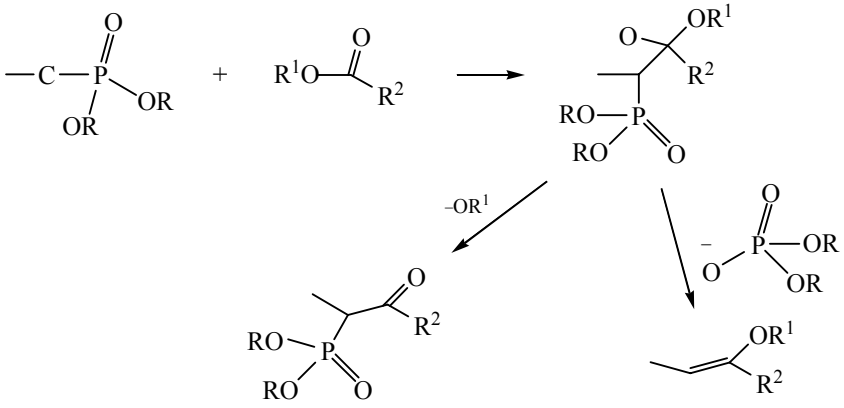
Abstract—*O,O*-Diethyl (ethoxycarbonylfuryl)methanephosphonates are formylated with ethyl formate in the presence of sodium foil at the methylene group adjacent to phosphorus atom to form sodium salts of phosphonoacetic aldehyde. When the substituents in the furan ring are remote from one another, and also in the case of 3, 4-disubstituted isomer these salts in DMSO solution exist in the carbanion form. Anions of salts of (2-ethoxycarbonylfur-3-yl)phosphonoacetic aldehyde and the isomer with the reversed location of substituents in DMSO solution take part in the dynamic equilibrium between the carbanion and the enolate form. The alkylation of all salts obtained with allyl bromide and dimethyl sulfate proceeds exclusively at the oxygen to form a mixture of *Z*- and *E*-isomers of phosphorylated vinyl ethers.

DOI: 10.1134/S1070363212120067

The addition of anions of phosphorus-containing CH-acids to the carbonyl group of aldehyde with the subsequent elimination of phosphate anion and formation of an olefin (Horner reaction) is a thoroughly investigated process [1–3]. Meanwhile, the similar reaction of phosphonates analogous to the Claisen condensation is not practically studied. We found only several works dealing with the reaction of benzylphosphonates with ethyl formate and diethyl oxalate in the presence of strong bases [4–6]. Reports concerning analogous studies in heterocyclic series are absent.

It is expectable that the reaction of α-phosphorylated carbanions with esters might proceed according to several pathways. In the first stage similarly to the Horner reaction an adduct to the carbonyl group of ester is formed. The elimination of the phosphate anion will lead to vinyl ether, while the liberation of an alcoholate should give the corresponding β-carbonyl-containing phosphonates. Just this pathway was observed in [4–6] for benzylphosphonates. The above-described reaction is of great value because β-formyl- and β-ketophosphonates are often difficultly available by the reaction of trialkyl phosphites with α-halocarbonyl compounds due to the competing formation of enol phosphates (Perkov reaction).

Hence, the dependence of the reaction pathway of heterylphosphonates with esters on the structure of

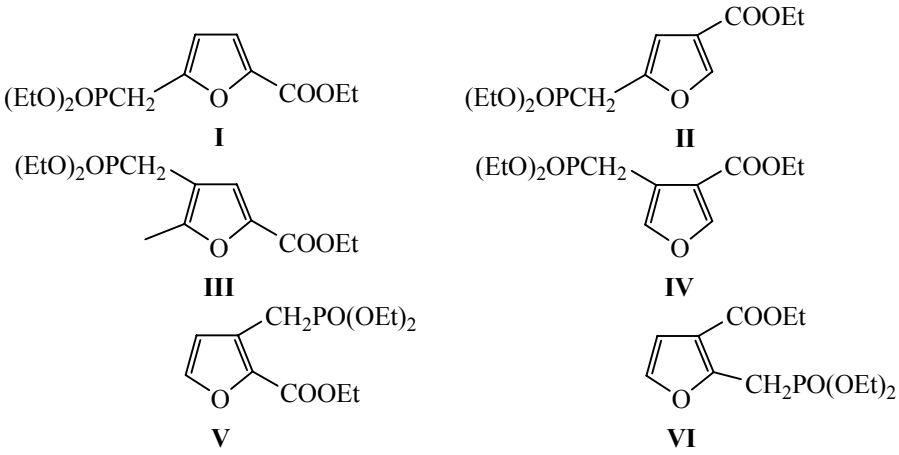


substrate and reagent presents a theoretical as well as a practical interest.

As known, the furan ring is the pharmacophoric structural fragment, but its introduction in the molecule of compound synthesized is often complicated. That is why the placing of a highly reactive functional group in the side chain of furan derivative may be a convenient synthetic strategy. One of the ways of its formation can be the above-described reaction.

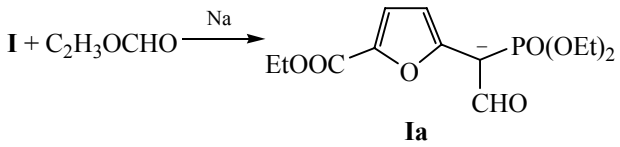
Among the furan derivatives we have chosen diethyl (ethoxycarbonylfuryl)methanephosphonates **I–VI**. This set of compounds includes all six versions of relative location of substituents in the furan ring and permits to establish the dependence of the reaction pathway on the type of substitution in the heterocycle. Besides, carbonyl group favors the increase in the CH-acidity of the methylene group adjacent to the phosphorus and to some extent stabilizes the labile furan ring. Highly reactive ethyl formate was chosen as the acylating agent whose reactions with ketones and esters are well studied [7]. We suggested that the process under investigation would lead either to phosphorylated derivatives of furylacetic aldehyde or to furylvinyl ethers, i.e., to compounds having a reactive functional group in the side chain.

Phan Hieu et al. [4, 5] have carried out this reaction in two steps. In the first step the phosphonates were metallated with butyllithium or lithium diisopropylamide, and then the carbanions obtained were involved in the reaction with ester. As the substrates chosen by us are stronger CH-acids than the above-mentioned oxybenzylphosphonates [8] we decided that sodium ethylate must be sufficiently strong base for generation of carbanions. If the reaction is carried out according to the classical Claisen procedure in the presence of sodium foil, the liberated ethanol would give sodium ethylate shifting the process to the side of formation of the condensation products and simultaneously generating the catalyst. Besides, the evolving hydrogen must to some degree prevent the oxidation of carbanions.



The reaction of compounds **I–VI** with ethyl formate in the presence of sodium foil was carried out in toluene at 1:1.2:2 molar ratio of phosphonate, sodium, and ethyl formate analogously to the procedure [9]. In the case of compounds **I–VI** the addition of a solution of a mixture of phosphonate and ethyl formate in toluene to the vigorously stirred suspension of sodium foil in toluene results in an exothermic reaction with the liberation of hydrogen and dissolution of sodium. Reaction products were extracted with water, the water solution was evaporated in a vacuum to dryness, the residue was dissolved in ethanol, the insoluble sodium formate was filtered off, and the filtrate was evaporated to dryness and evacuated. Toluene layer was dried, evaporated, and evacuated. After that the composition of residue was studied by spectral methods. It occurred that by this way good separation of the reaction products and starting substances was achieved permitting the evaluation of the phosphonates conversion.

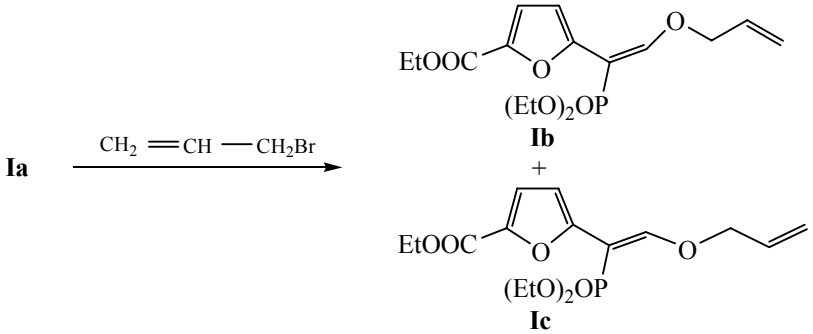
The products of condensation isolated from the ethanol solution are white or light brown crystalline substances having clear melting points. Their structure was established by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.



Ia

In the case of formylation of phosphonate **I** its conversion was 89%. In ^{31}P NMR spectrum of yellowish brown crystalline reaction product (mp 108–109°C from ethanol) in DMSO-d_6 one signal at δ_P 29.304 ppm was observed. With respect to the starting substance **I** (δ_P 20.378 ppm) it is shifted upfield. In the ^{1}H NMR spectrum signals of the furan ring protons give doublets at 6.052 ppm (H^4, J_{HH} 3.6 Hz) and 7.216 ppm (H^3, J_{HH} 3.6 Hz), and the downfield doublet is observed at 8.777 ppm (J_{HP} 2.4 Hz). Signals of CH_2P fragment at ~3 ppm are absent proving the participation of this group in the reaction. In the ^{13}C NMR spectrum a doublet at 81.207 ppm ($^1J_{CP}$ 199.7 Hz) is observed. Signals of the furan ring carbon atoms are revealed at 102.386 ppm (C^3, $^3J_{CP}$ 6.6 Hz), 121.500 ppm (C^4), 136.368 ppm (C^2), and 161.796 ppm (C^5, $^2J_{CP}$ 11.5 Hz). Signal of the carbonyl carbon atom of the ester group is observed at 159.110 ppm. Besides, the spectrum of the product obtained contains a doublet at 177.971 ppm ($^2J_{CP}$ 19.1 Hz). Hence, the product **Ia** is the ester of 2-furoic acid containing the residue of phosphonoacetic aldehyde in the position 5. Judging from the location of signals and the value of J_{HP} it exists in solution in the carbanion form. The salt-like character of compound **Ia** was proved by its alkylation with allyl bromide. The reaction was carried out in dioxane in the presence of small excess of allyl bromide at boiling. In the course of the process the liberation of sodium bromide was observed, and from the reaction mixture the oily product was isolated. It decomposed below its boiling point at the attempt to distill it in a vacuum. In its ^{31}P NMR spectrum in $CDCl_3$ the signal of the salt **Ia** was absent, and two signals at 17.306 ppm and 13.512 ppm in 1:4 ratio were observed. In the upfield area of the ^{1}H NMR spectrum the signals of ethoxy groups of the phosphonate and the ester were present, and among the downfield signals two sets of sigals can be marked. The main product was characterized by the signal at 4.662 ppm (CH_2-allyl, J_{HH} 5.2 Hz) and by the signals at 5.460 ppm (H^A, J_{AB} 17.2 Hz), and 5.344 ppm (H$^{A'}$, $J_{A'B}$ 10.4 Hz) belonging to the terminal protons at the double bond. The latter signal was common for both products. Signals of the =CH-fragment of allyl group of both products are strongly overlapped which made impossible the accurate calculation of their parameters. Signals of the furan ring protons of the main product appeared at 6.665 ppm (H^3) and 7.180 ppm (H^4). At 7.439 ppm a doublet (J_{HP} 10.8 Hz) was observed characteristic of the proton at the double bond occupying *cis*-position with respect to phosphorus. It follows from these findings that the main product of alkylation of salt **Ia** may be characterized by the structure **Ib**. Signals of carbon atoms of the enol fragment in this compound are characterized by the values 96.654 ppm ($^1J_{CP}$ 193.1 Hz) and 160.499 ppm ($^2J_{CP}$ 21.0 Hz).

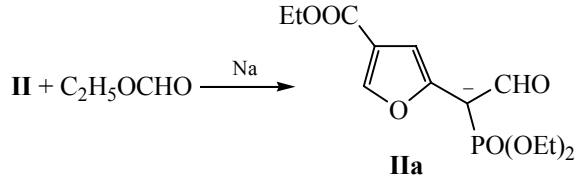
Signals of the allyl group protons belonging to the second set were observed at 4.732 ppm (CH_2-allyl, J_{HH} 5.2 Hz) and 5.437 ppm (H^A, J_{AB} 17.2 Hz). The other signals overlapped with the corresponding signals of compound **Ib**. The signals of furan protons of the minor product were observed at 6.716 ppm (H^3) and 7.114 ppm (H^4). Besides, the downfield doublet is observed at 7.584 ppm (J_{HP} 32.0 Hz) which is characteristic of the double bond proton trans-located with respect to phosphorus. Hence, the minor product can be characterized by the structure **Ic**. Signals of carbon atom of the enol fragment appeared at 96.654 ppm ($^1J_{CP}$ 193.1 Hz) and 160.262 ppm ($^2J_{CP}$ 22.4 Hz).



Ib + **Ic**

It follows from these findings that though the salt **Ia** exists in solution mainly in the carbanion form, its alkylation proceeds at the oxygen atom with the formation of *E*- and *Z*-isomers of the enol ether.

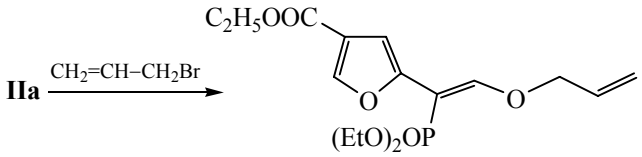
The formylation of phosphonate **II** was carried out analogously. The conversion of this compound was 63%, and the isolated sodium salt of the formylation product **IIa** was crystallized from 10:1 hexane-ethyl acetate. The product **IIa** forms white crystals of mp 153–154°C stable while handling in air.



IIa

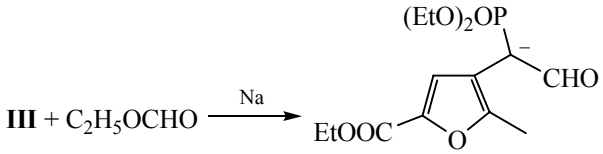
In ^{31}P NMR spectrum of this compound in DMSO-d_6 one signal with δ_P 31.262 ppm was observed. The protons of the furan ring of salt **IIa** were characterized by the signals at 6.623 ppm (H^3) and 7.822 ppm (H^5). At 8.537 ppm the doublet with J_{HP} 2.4 Hz belonging to the aldehyde proton was observed. In the ^{13}C NMR spectrum signals of carbon atoms of phosphonoacetic aldehyde residue gave doublets at 79.095 ppm ($^1J_{CP}$ 201.5 Hz) and 176.572 ppm ($^2J_{CP}$ 17.5 Hz). Hence, analogously to the previous case, the condensation product **IIa** in solution exists in the carbanion form. The yield of this compound is 90%.

Alkylation of salt **IIa** with the allyl bromide excess in dioxane is accompanied by the liberation of sodium bromide, and from the reaction mixture the oily product was isolated. In ^{31}P NMR spectrum of this compound in $CDCl_3$ only one signal at 13.529 ppm was observed. The methylene group protons of the allyl fragment gave rise to two signals at 4.554 ppm (J_{HH} 5.2 Hz) and 4.624 ppm (J_{HH} 5.6 Hz) in 6:1 ratio. Signals of the other protons of the allyl fragment practically coincided, therefore the calculation of spectral characteristics was carried out by means of the subspectum method neglecting small broadening of spectral lines. Probably, the allyl group in the alkylation product exists in two conformations. Signals of the furan ring protons were observed at 6.781 ppm (H^3) and 7.827 ppm (H^5). At 7.272 ppm a doublet with J_{PH} 32.4 Hz characteristic of the vinyl ether proton trans-located with respect to the phosphorus is observed. In the ^{13}C NMR spectrum carbon atoms of the vinyl fragment were characterized by doublets at 98.399 ppm ($^1J_{CP}$ 186.6 Hz) and 150.559 ppm ($^2J_{CP}$ 17.6 Hz). The spectral data prove that the alkylation of salt **IIa** proceeds at the oxygen atom to form the product having a *Z*-configuration.



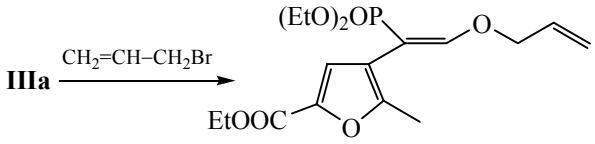
IIb

The formylation of phosphonate **III** yielded yellowish brown crystalline substance (mp 132°C). The conversion of the starting phosphonate was 56%. In ^{31}P NMR spectrum of the product in DMSO one signal at 33.921 ppm was observed. The signal of the methyl group protons at the furan ring was found at 2.216 ppm, signal of the furan ring proton appeared at 7.036 ppm, and at 8.196 ppm a doublet with J_{PH} 3.6 Hz was observed. In the ^{13}C NMR spectrum two doublets at 78.902 ppm ($^1J_{CP}$ 162.1 Hz) and 172.360 ppm ($^2J_{CP}$ 24.4 Hz) were present. The obtained data permit characterizing the product as sodium derivative **IIIa** existing in DMSO in the carbanion form.



IIIa

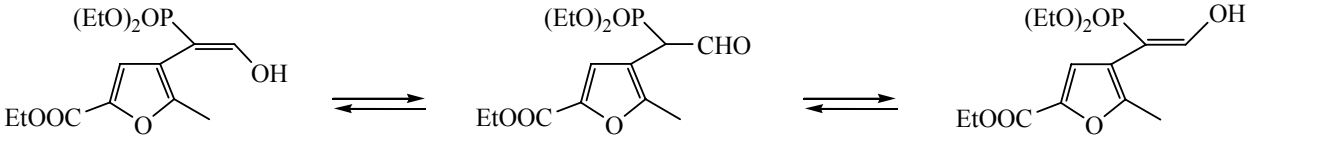
The alkylation of salt **IIIa** with allyl bromide in dioxane was accompanied by the liberation of sodium bromide and resulted in isolation of an oily product. Its ^{31}P NMR spectrum in $CDCl_3$ contained two signals at 6.119 ppm and 5.921 ppm with practically equal intensity. In the ^{1}H NMR spectrum one set of signals of the allyl group was observed, the furan ring proton H^4 gave rise to a signal at 7.065 ppm, and at 6.612 ppm a doublet with J_{PH} 34.4 Hz was found. Carbon atoms of the vinyl fragment were characterized by signals at 98.195 ppm ($^1J_{CP}$ 187.0 Hz) and 158.887 ppm ($^2J_{CP}$ 23.9 Hz). Hence, the alkylation of salt **IIIa** proceeds selectively at the oxygen atom with the formation of one product of *Z*-configuration **IIIb** existing as two conformers differing in the shifts of phosphorus atoms.



IIIb

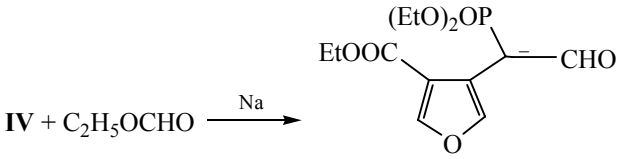
We tried to prepare also trimethylsilyl enolate of the above-described phosphonoacetic aldehyde. With this purpose salt **IIIa** was boiled in dioxane with trimethylchlorosilane. After removing sodium chloride precipitate and keeping the residue in a vacuum the crystalline product of mp 88–89°C was obtained. In its ^{1}H NMR spectrum in $CDCl_3$ signal of trimethylsilyl group was absent. In the range of chemical shifts typical of the methyl group at the furan ring a broadened singlet at 2.274 ppm and two doublets at 2.313 ppm (J_{PH} 2.0 Hz) and at 2.339 ppm (J_{PH} 1.6 Hz) were observed with the ratio ~1:0.3:1.2.

The signal at 3.662 ppm was attributed to dioxane. In the ^{13}C NMR spectrum in $CDCl_3$ typical signal of dioxane was observed at 67.016 ppm. The ratio of summary intensities of signals of protons of the methyl groups by the furan ring and dioxane gave the value 1:2.8. It permitted to characterize the isolated crystals as the molecular complex of furan derivative with dioxane in 1:1 ratio. The downfield region of the ^{1}H NMR spectrum contained two signals of the furan ring proton at 6.967 and 7.035 ppm, broadened doublets at 7.237 ppm (J_{PH} 13.6 Hz) and 7.572 ppm (J_{PH} 6.8 Hz), a singlet at 9.712 ppm, and the exchange signal at 11.052 ppm. These data permit to establish that the furan derivative is aldehyde **IIIc** which in solution is in dynamic equilibrium with the enolic forms of *Z*- **IIId** and *E*-configuration **IIIe**, form **IIId** prevailing. ^{13}C NMR spectrum of aldehyde **IIIc** is characterized by the signals at 50.527 ppm (CHP, $^1J_{CP}$ 131.1 Hz) and 192.213 ppm (CHO). Basing on the ratio of intensities of signals at 92.692 ppm (PC=, $^1J_{CP}$ 205.0 Hz) and at 158.236 ppm (=CHOH, $^2J_{CP}$ 27.8 Hz) they can be attributed to *Z*-enol **IIId**. *E*-enol **IIIe** is characterized by signals at 90.560 ppm ($^1J_{PC}$ 180.6 Hz) and 158.782 ppm ($^2J_{CP}$ 15.9 Hz). In ^{31}P NMR spectrum of solution under investigation two signals at 18.262 ppm and 23.170 ppm in 0.18:1 ratio were present. Considering that the chemical shift of the phosphorus signal in starting phosphonate **III** is 24 ppm, and in the above-described vinyl ethers the signal of phosphorus in the compounds having *Z*-configuration is located downfield as compared to the isomers of *E*-configuration it must be accepted that chemical shifts of phosphorus atoms in the compounds **IIIc, e** are equal, and the downfield signal belongs to *Z*-enol **IIId**. Just the same attribution agrees with the ratio of intensities of finely resolved signals of methyl groups at the furan ring in the ^{1}H NMR spectrum.



IIIe **IIIc** **IIId**

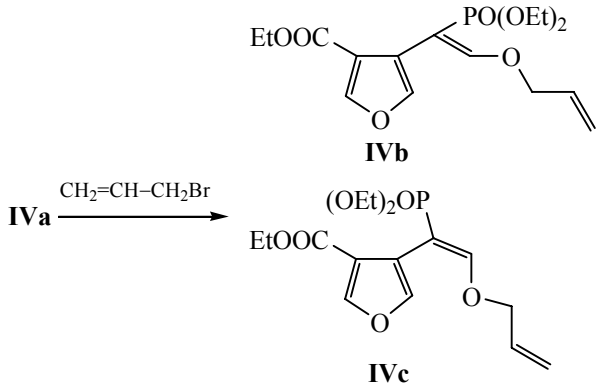
The formylation of phosphonate **IV** led to isolation of the crystalline substance of mp 167–168°C. In ^{31}P NMR spectrum in DMSO-d_6 of the product obtained one signal at 32.281 ppm was observed. Signals of the furan protons appeared at 7.881 ppm (H^5) and 8.267 ppm (H^2, J_{PH} 2.4 Hz). In the downfield region two broad signals at 8.360 ppm and 8.491 ppm were observed. They were attributed to two forms of aldehyde taking part in slow exchange with one another. In the ^{13}C NMR spectrum two signals at 72.732 ppm ($^1J_{CP}$ 207.7 Hz) and 175.290 ppm ($^2J_{CP}$ 24.2 Hz) characterizing the fragment of phosphonoacetic aldehyde were observed. Hence, the formylation product is sodium salt of phosphonoacetic aldehyde existing in DMSO in the carbanion form.



IVa

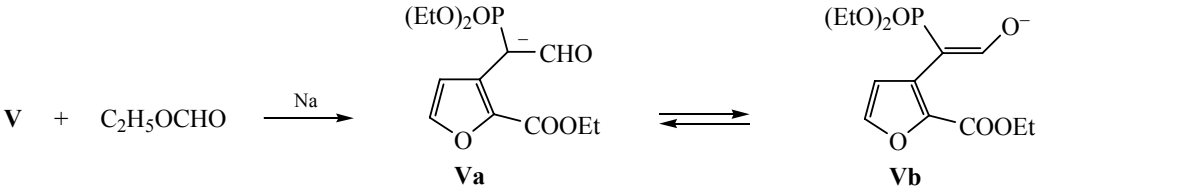
The alkylation of salt **IVa** with allyl bromide in dioxane was accompanied by the liberation of sodium bromide and led to formation of oily product. In its ^{31}P NMR spectrum in $CDCl_3$ two signals at 20.614 ppm and 15.836 ppm in the 1:6 ratio were observed. The signals of protons of methylene groups of the allyl fragment gave two doublets at 4.385 ppm (J_{HH} 5.6 Hz) and 4.437 ppm (J_{HH} 5.6 Hz) with the intensity ratio 1:6.2. Two sets of signals of the furan ring protons included the signals at 7.318 ppm (H^2, J_{PH} 2.0 Hz), 7.860 ppm (H^5), and 7.324 ppm (H^2, J_{PH} 2.4 Hz), 7.860 ppm (H^5). The ratio of intensities of the corresponding signals was also 6:1. Two doublets at 6.779 ppm (J_{PH} 34.0 Hz) and 7.110 ppm (J_{PH} 10.0 Hz)

characterized the protons at the double bond of vinyl fragment. The ratio of intensities of these signals was also close to 6:1. In the ^{13}C NMR spectrum the signals of carbon atoms of the phosphorylated enol ether gave signals at 95.889 ppm ($^1J_{CP}$ 189.0 Hz) and 160.212 ppm ($^2J_{CP}$ 26.6 Hz). Hence, the alkylation of sodium salt **IVa** proceeds only at the oxygen with the formation of products of *Z*- **IVb** and *E*-configuration **IVc** in the 6:1 ratio. They differ by spectral characteristics of protons not only of the vinyl fragment and of the furan ring, but also of the allyl group.



In the course of formylation of phosphonate **V** sodium salt precipitated directly from the reaction mixture. After purification it was a white crystalline substance of mp 164–166°C stable while handling in air.

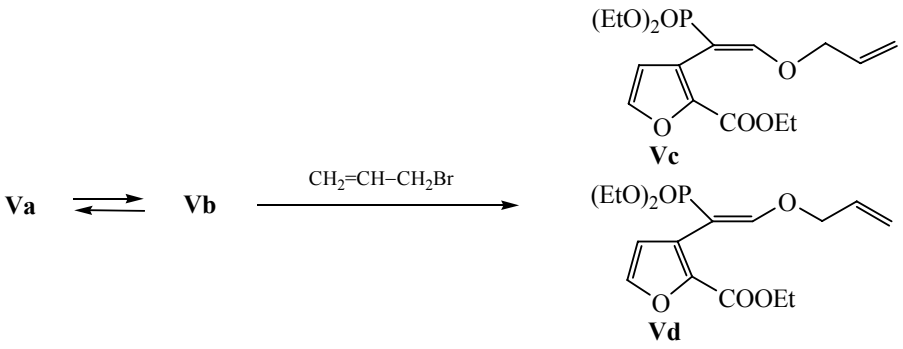
In the ^{31}P NMR spectrum of the evaporated reaction mixture in DMSO-d_6 the signal of phosphorus atom at 26.515 ppm belonging to the starting phosphonate **V** and two signals at 35.287 ppm and 29.215 ppm with the ratio of intensities 0.64:1 were observed. In ^{31}P NMR spectrum of solution of crystalline substance in DMSO-d_6 two signals at 35.463 ppm and 29.415 ppm with the ratio of intensities 1.7 :1 appeared. Therefore in the solution the sodium salt of the formylation product exists in two forms in dynamic equilibrium depending on the composition of solution. ^1H NMR spectrum of the crystalline product contained two sets of signals. More intense signals were observed at 6.365 ppm (H^4-furan), 7.515 ppm (H^5-furan), and 8.362 ppm (CHO, J_{PH} 2.4 Hz). The second set included signals at 6.430 ppm (H^4-furan), 7.538 ppm (H^5-furan) and 8.561 ppm (J_{PH} 38.0 Hz). The latter signal of the second set is characteristic of the protons at the double bond having trans-location with respect to phosphorus. Hence, the formylation of phosphonate **V** leads to the product which in DMSO solution exists as a mixture of carbanion **Va** and *Z*-enolate **Vb** taking part in dynamic equilibrium. The signal of phosphorus atom in compound **Va** is located upfield as compared to that in compound **Vb.**



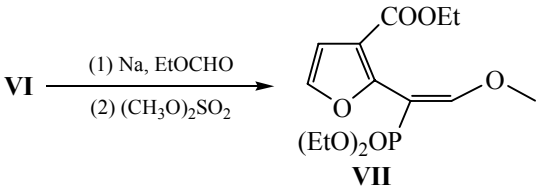
In the ^{13}C NMR spectrum signals of carbon atoms of phosphonoacetic aldehyde in compound **Va** were observed at 76.323 ppm ($^2J_{CP}$ 204.1 Hz) and 174.785 ppm ($^2J_{CP}$ 22.8 Hz) which were common for all the previous cases. The second pair of signals at 74.846 ppm ($^1J_{CP}$ 192.7 Hz) and 182.260 ppm ($^2J_{CP}$ 7.5 Hz) we have attributed to the enolate fragment of compound **Vb**. Note the unusually large shift of signal of the =CHO carbon atom and its small coupling constant with phosphorus nuclei.

Treating of the salt obtained with allyl bromide was accompanied by the liberation of sodium bromide, and as a result of the reaction a yellow oil-like product was obtained. In its ^{31}P NMR spectrum in $CDCl_3$ two signals at 19.901 ppm and 15.228 ppm were observed in the ratio 1:0.62, while the signals we attributed to compounds **Va, Vb** disappeared. This fact is a chemical confirmation of validity of the suggestion about the existence of the enolate form **Vb**. In the ^1H NMR spectrum two sets of signals were observed. Their relative intensities corresponded to the intensities of phosphorus signals. More intense signals were observed at 6.581 ppm (H^4-furan), 7.441 ppm (H^5-furan), and 6.985 ppm (H-vinyl, J_{PH} 33.6 Hz). Minor product was characterized by the signals at 6.440 ppm (H^4-furan), 7.441 ppm (H^5-furan), and 7.510 ppm (H-vinyl, J_{PH} 10.2 Hz). Allyl group protons also gave two sets of signals, but their intensities did not correspond to the intensities of the above-presented sets. Evidently,

allyl fragment of the products obtained was not conformationally homogeneous. Hence, the alkylation of salt **Va, Vb** proceeds exclusively at the oxygen with the formation of enol ethers of *E*- **Vc** and *Z*-configuration **Vd**.

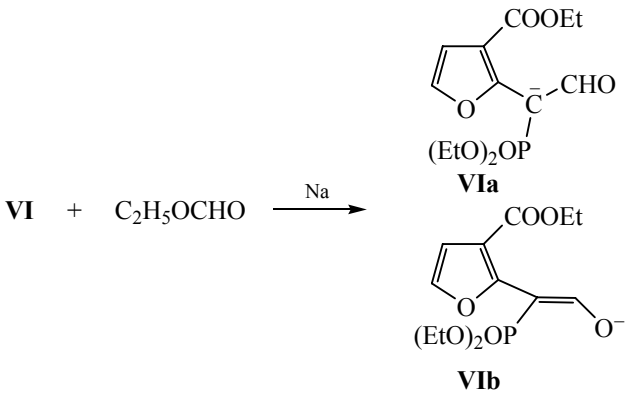


Signals of carbon atoms of the vinyl fragment of ether **Vc** are located at 96.160 ppm ($^1J_{CP}$ 200.4 Hz) and 160.321 ppm ($^2J_{CP}$ 25.9 Hz). In compound **Vd** the corresponding signals were observed at 96.091 ppm ($^1J_{CP}$ 187 Hz) and 160.321 ppm ($^2J_{CP}$ 25.9 Hz). The comprehensive spectral characteristics of these products are presented in the Experimental.



The formylation of phosphonate **VI** leads to the formation of sodium salt which is more labile while treating with water than the above-described ones. Therefore for evaluation of the conversion and the composition of the formylation products the reaction mixture was directly treated with dimethyl sulfate, and the product formed was investigated. ^{31}P NMR spectrum of the mixture of phosphonates obtained contained three signals at 21.766 ppm (compound **VI**), 17.866 ppm, and 17.526 ppm in 1:0.28:0.63 ratio. It follows from these data that the conversion of starting compound is ~50%. In the ^{1}H NMR spectrum of the obtained product besides the signals of compound **VI** the signals of furan protons at 6.713 ppm (H^4) and 7.313 ppm (H^5), and the the signal of a methoxy group at 3.844 ppm were observed. Signals at 7.278 ppm (J_{PH} 9.6 Hz) and 7.298 ppm (J_{PH} 12.0 Hz) correspond to the fragment of enol ether having *E*-configuration and existing in two stabile conformations. The absence of *Z*-isomer is proved by J_{PH} values and small difference in chemical shifts of phosphorus atoms. Hence, the structure of methylation product is described by formula **VII**. This substance exists as a mixture of stable structurally distinguishable conformers in 2.3:1 ratio. In the ^{13}C NMR spectrum the signals of the vinyl fragment of conformers were observed at 95.471 ppm ($^1J_{CP}$ 196.3 Hz), 165.294 ppm ($^2J_{CP}$ 24.2 Hz), and 94.688 ppm ($^1J_{CP}$ 195.5 Hz), 164.171 ppm ($^2J_{CP}$ 24.2 Hz). Detailed spectral data are listed in the Experimental.

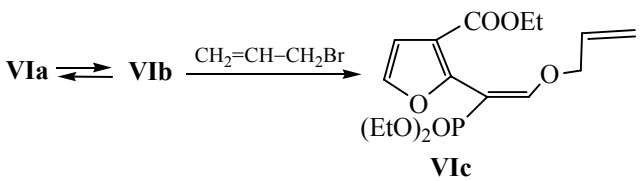
After the evaporation of water extract of the reaction obtained after formylation of phosphonate **VI** the syrup-like product was obtained. Its ^{31}P NMR spectrum in DMSO-d_6 contained the signals at 32.291 ppm, 26.255 ppm, 23.861 ppm, and 0.600 ppm. The last two signals belong to compound **VI** and the phosphate formed at the decomposition of the sodium salt of the formylation product in the course of treatment with water. In the ^{1}H NMR spectrum of this mixture in DMSO-d_6 the total intensity of downfield signals is much smaller than the intensity of signals of alkyl substituents. Therefore the phosphate does not contain the furan fragment. The downfield proton signals according to their intensities can be divided in three sets. One of them corresponds to phosphonate **VI** while the other two include the signals at 6.483 ppm (H^4-furan), 7.298 ppm (H^5-furan), 8.460 ppm (CHO, J_{PH} 1.6 Hz), and at 6.529 ppm (H^4-furan), 7.312 ppm (H^5-furan), 8.558 ppm (J_{PH} 36.8 Hz). The last signal of the second set basing on the coupling constant value we attributed to the proton at the double bond of *Z*-enolate form having *trans*-location with respect to phosphorus. Hence, the sodium salt of the formylation product in DMSO solution exists as a mixture of carbanion **VIa** and *Z*-enolate **VIb** taking part in the dynamic equilibrium. This salt is methylated with dimethyl sulfate only at the oxygen with the formation of *E*-isomer.



In the ^{13}C NMR spectrum signals of phosphonoacetic aldehyde fragment are characterized by the signals at 76.653 ppm ($^1J_{CP}$ 194.2 Hz) and 177.636 ppm ($^2J_{CP}$ 20.2 Hz). The signals of enolate fragment of compound **VIb** are observed at 76.647 ppm ($^1J_{CP}$ 197.2 Hz) and 183.038 ppm ($^2J_{CP}$ 5.7 Hz). Note a good agreement of spectral characteristics of enolate fragment in compounds **Vb, VIb**. In both cases the formation of *Z*-isomer takes place.

Treating a mixture of phosphonates **VI, VIa, VIb** with allyl bromide in dioxane was accompanied by the liberation of sodium bromide and the formation of yellowish brown oily product. Its ^{31}P NMR spectrum in $CDCl_3$ contained a signal of phosphonate **VI** at 20.710 ppm and two signals at 18.013 ppm and 16.573 ppm with the intensity ratio 1:0.35:0.37. The signal of phosphate at –1.998 ppm was negligible though it was the strongest in the starting mixture. This means that only the salt of formylation product took part in the alkylation, while the phosphate did not enter the reaction.

^1H NMR spectrum contained two sets of signals of the alkylation products. One of them included the signals of furan protons at 6.884 ppm (H^4), 7.248 ppm (H^5) and the proton of vinyl fragment at 7.053ppm (J_{PH} 10.4 Hz). Basing on its intensity it corresponds to the signal of phosphorus at 16.573 ppm. Signals of the second set were observed at 6.671 ppm (H^4), 7.321 ppm (H^5) and 7.452 ppm (J_{PH} 10.0 Hz). The allyl fragment also gave several sets of signals whose intensity does not correspond to any of the above-presented ones. This means that the alkylation product



VIc has *E*-configuration and exists as a mixture of spectroscopically distinguishable stable conformers.

Hence, dialkyl (ethoxycarbonylfuryl)methanephosphonates are formylated with ethyl formate in the presence of sodium foil with the formation of sodium salts of (ethoxycarbonyl)(diethoxyphosphoryl)acetic aldehyde. If the substituents in the furan ring are remote from one another and also in the case of 3,4-disubstituted derivative these salts in DMSO solution exist exclusively in the carbanion form. In the case of 2,3-disubstituted compounds dynamic equilibrium between the carbanion and *Z*-enolate shifts to the side of the latter and both forms can be registered spectroscopically. The alkylation of the obtained salts with allyl bromide and dimethyl sulfate proceeds exclusively at the oxygen. This means that in all cases the enolate anion is the reacting species. The obtained enol ethers may have *Z*- as well as *E*-configurantion. No definite dependence on the structure of substrate is observed.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were taken on a Bruker DPX-400 spectrometer (400.13 and 100.61 MHz respectively) and ^{31}P NMR spectra were obtained on a Bruker AC-200 device (81.014 MHz).

Reaction of diethyl (ethoxycarbonylfuryl) methanephosphonates with ethyl formate *(general procedure)*. Fresh sodium foil (0.024 g-at) prepared by rolling sodium pieces between two layers of polyethylene film was suspended in 30 ml of toluene, and a solution of 0.02 mol of phosphonate and 0.04 mol of ethyl formate in 20 ml of toluene was added dropwise under vigorous stirring. After the addition was complete the reaction mixture was stirred until the dissolution of sodium and left overnight. On the next day the obtained solution was extracted with water [(2–3)×15 ml], the water extract was washed with 10 ml of ether and evaporated to dryness on a rotory evaporator. The residue was dissolved in ethanol, the insoluble part was filtered off, and the filtrate was once more evaporated to dryness on a rotory evaporator. The obtained crystalline mass was ground and dried for 1 h in a vacuum (1 mm Hg) at room temperature. After that the crystals obtained were analyzed by spectral methods.

Sodium salt of (5-ethoxycarbonylfur-2-yl)(diethoxyphosphoryl)acetic aldehyde Ia. Conversion of phosphonate **I** 80%, yield of the salt **Ia** 86%, yellowish

brown crystals of mp 108–109°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.164 t (CH_3-phosphonate, J_{HH} 7.0 Hz), 1.250 t (CH_3-carboxyl, J_{HH} 7.0 Hz), 3.867 m (CH_2OP, J_{HH} 7.0 Hz, J_{HP} 14.2 Hz), 4.196 q (CH_2OOC, J_{HH} 7.0 Hz), 6.502 d (H^3-furan, J_{HH} 3.6 Hz), 7.216 d (H^4-furan, J_{HH} 3.6 Hz), 8.666 d (CHO, J_{HP} 2.4 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.837 (CH_3-carboxyl); 16.704 d (CH_3-phosphonate $^3J_{CP}$ 6.5 Hz); 59.834 (CH_2OOC); 60.207 d (CH_2OP, $^2J_{CP}$ 4.4 Hz); 81.271 d (P–C, $^1J_{CP}$ 199.7 Hz); 102.368 d (C^3, $^3J_{CP}$ 6.5 Hz); 121.500 (C^4); 136.296 (C^5); 159.110 (C=O); 161.796 d (C^2, $^2J_{CP}$ 11.5 Hz); 177.971 d (CHO, $^2J_{CP}$ 19.1 Hz). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 29.304.

Sodium salt of (4-ethoxycarbonylfur-2-yl)(diethoxyphosphoryl)acetic aldehyde IIa. Conversion of phosphonate **II** 63%, yield of the salt **IIa** 90%, white crystals of mp 153–154°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.125 t(CH_3-phosphonate, J_{HH} 7.2 Hz), 1.253 t (CH_3-carboxyl, J_{HH} 7.2 Hz), 3.815 m (CH_2OP, J_{HH} 7.2 Hz, J_{HP} 14.4 Hz), 4.187 q (CH_2OOC, J_{HH} 7.2 Hz), 6.623 s (H^3-furan), 7.822 s (H^5-furan), 8.537 d (CHO, J_{HP} 2.4 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.732 (CH_3-carboxyl); 16.723 d (CH_3-phosphonate $^3J_{CP}$ 6.5 Hz); 59.736 d (CH_2OP, $^2J_{CP}$ 4.0 Hz); 59.844 (CH_2OOC); 79.095 d (P–C, $^1J_{CP}$ 201.5 Hz); 98.776 d (C^3, $^3J_{CP}$ 7.6 Hz); 119.716 (C^4); 141.641 (C^5); 157.434 d (C^2, $^2J_{CP}$ 8.8 Hz); 163.966 (C=O); 176.572 d (CHO, $^2J_{CP}$ 18.5 Hz). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 31.262.

Sodium salt of (2-methyl-5-ethoxycarbonylfur-3-yl)(diethoxyphosphoryl)acetic aldehyde IIIa. Conversion of phosphonate **III** 56%, yield of the salt **IIIa** 81%, yellowish brown crystals of mp 132°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.137 t (CH_3-phosphonate, J_{HH} 7.0 Hz), 1.266 t (CH_3-carboxyl, J_{HH} 7.0 Hz), 2.216 br.s (CH_3-furan), 3.796 m (CH_2OP, J_{HH} 7.0 Hz, J_{HP} 14.0 Hz), 4.218 q (CH_2OOC, J_{HH} 7.0 Hz), 7.037 s (H^4-furan), 8.196 d (CHO, J_{HP} 3.6 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.438 (CH_3-furan); 14.741 (CH_3-carboxyl); 16.746 d (CH_3-phosphonate $^3J_{CP}$ 6.4 Hz); 59.582 d (CH_2OP, $^2J_{CP}$ 4.1 Hz); 60.166 (CH_2OOC); 78.920 d (P–C, $^1J_{CP}$ 162.1 Hz); 119.419 d (C^3, $^2J_{CP}$ 12.1 Hz); 122.920 (C^4); 140.253 (C^5), 153.249 d (C^2, $^3J_{CP}$ 8.8 Hz); 158.854 (C=O); 172.360 d (CHO, $^2J_{CP}$ 24.4 Hz). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 33.921.

Sodium salt of (4-ethoxycarbonylfur-3-yl)(diethoxyphosphoryl)acetic aldehyde IVa. Conversion of phosphonate **IV** 70%, yield of the salt **IVa** 65%, white crystals of mp 167–168°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.109 t (CH_3-phosphonate, J_{HH} 7.2 Hz), 1.179 t (CH_3-carboxyl, J_{HH} 7.2 Hz), 3.808 m (CH_2OP, J_{HH} 7.2 Hz, J_{HP} 14.4 Hz), 4.135 q (CH_2OOC, J_{HH} 7.2 Hz), 7.881 s (H^5-furan), 8.267 d (H^2-furan, J_{HP} 2.4 Hz), 8.360 br.s, 8.491 br.s (CHO exchanging). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.460 (CH_3-carboxyl); 16.834 d (CH_3-phosphonate $^3J_{CP}$ 6.8 Hz); 59.255 d (CH_2OP, $^2J_{CP}$ 3.4 Hz); 59.510 (CH_2OOC); 72.732 d (P–C, $^1J_{CP}$ 207.7 Hz); 121.723 (C^3, $^2J_{CP}$ 8.8 Hz); 121.833 d (C^3, $^2J_{CP}$ 13.2 Hz); 139.044 (C^4); 145.385 (C^2); 148.183 (C^5); 164.640 (C=O); 175.290 d (CHO, $^2J_{CP}$ 24.2 Hz). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 32.281.

Sodium salt of (2-ethoxycarbonylfur-3-yl)(diethoxyphosphoryl)acetic aldehyde Va, Vb. Conversion of phosphonate **V** 72%, yield of sodium salt 62%, white crystals of mp 164–166°C, crystallized directly from the reaction mixture. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: common signals of compounds **Va, Vb**: 1.130 t (CH_3-phosphonate, J_{HH} 7.2 Hz); 1.189 t (CH_3-carboxyl, J_{HH} 7.2 Hz); 3.764-3.860 m (CH_2OP); 4.062–4.175 m (CH_2OOC); **Va**: 6.365 s (H^4-furan); 7.515 s (H^5-furan); 8.362 d (CHO, J_{HP} 2.4 Hz); **Vb**: 6.430 s (H^4-furan); 7.538 s (H^5-furan); 8.561 d (=CH–O, J_{HP} 38.0 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: common signal of compounds **Va, Vb**: 14.653, 14.827 (CH_3-carboxyl); 16.834 d (CH_3-phosphonate $^3J_{CP}$ 7.0 Hz); 59.309, 59.672 (CH_2OOC + CH_2OP); **Va**: 76.323 d (P–C, $^1J_{CP}$ 204.1 Hz); 115.033 (C^4); 129.716 d (C^3, $^2J_{CP}$ 13.8 Hz); 139.356 d (C^2, $^3J_{CP}$ 15.3 Hz); 143.451 (C^5); 160.448 (C=O); 174.785 d (CHO, $^2J_{CP}$ 22.8 Hz); **Vb**: 74.846 d (P–C, $^1J_{CP}$ 192.4 Hz); 115.107 d (C^3, $^2J_{CP}$ 14.9 Hz); 115.503 (C^4); 144.594 (C^5); 158.981 (C^2); 167.340 (C=O); 182.260 d (=CH–O, $^2J_{CP}$ 7.5 Hz). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 35.463 **Va**, 29.417 **Vb**. Ratio of forms **Va**:**Vb** 1.7:1.

Reaction of phosphonate VI with ethyl formate. *a.* To a suspension of 0.4 g of sodium foil in 30 ml of toluene a solution of 4.0 g of phosphonate **VI** and 2.5 ml of ethyl formate in 10 ml of toluene was added dropwise with vigorous stirring. Reaction proceeded with heat evolution. Temperature of the reaction mixture rose to 54°C, and sodium gradually dissolved. Two hours after the complete dissolution of sodium the reaction mixture was treated with 2.5 ml of dimethyl sulfate in one portion which caused its heating to 33°C. The reaction mixture was stirred until cooling to room temperature, and then was heated at 90°C for 1.5 h.

After that it was cooled, washed two times with water, and dried by boiling with the Dean-Stark trap. After complete separation of water the solvent was distilled off at a reduced pressure and the residue was kept in a vacuum (1 mm Hg) at room temperature for 1 h. ^{31}P NMR spectrum ($CDCl_3$) δ_P, ppm: 21.766 (1), 17.866 (0.28), 17.526 (0.63). First signal belongs to phosphonate **VI**, and the other two, to the conformers of the enol methyl ether **VII.** From the data obtained it follows that the conversion of phosphonate **VI** is ~50%.

***E*-Diethyl 1-(3-ethoxycarbonylfur-2-yl)-2-methoxyethylenephosphonate VII**. This substance exists as a mixture of two conformers in 2.25:1 ratio. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: common signals: 1.257 t (CH_3-phosphonate, J_{HH} 7.2 Hz); 1.330 (CH_3-carboxyl, J_{HH} 7.2 Hz); 3.844 s (CH_3O); 4.040–4.112 (CH_2OP); 4.229 q (CH_2OOC, J_{HH} 7.2 Hz); 6.713 s (H^4-furan); 7.313 s (H^5-furan); main conformer: 7.278 d (=CH–O, J_{HP} 9.6 Hz); minor conformer: 7.298 d (=CH–O, J_{HP} 12.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.429 (CH_3-carboxyl); 16.265 d (CH_3-phosphonate, $^3J_{CP}$ 5.7 Hz); 16.127 d (CH_3-phosphonate, $^3J_{CP}$ 6.6 Hz); 60.100, 60.352 (CH_2OOC); 61.941 d (CH_2OP, $^2J_{CP}$ 4.6 Hz), 62.348 d (CH_2OP, $^2J_{CP}$ 5.9 Hz); 71.038 (CH_3O); 95.471 d (P–C=, $^1J_{CP}$ 196.3 Hz major); 94.688 d (P–C=, $^1J_{CP}$ 193.5 Hz minor); 110.873 (C^4 major); 110.644 (C^4 minor); 117.011 d (C^3, $^3J_{CP}$ 6.7 Hz); 149.796 (C^5), 157.912 (C^2), 162.922 (C=O); 164.174 d (=CH–O, $^2J_{CP}$ 24.2 Hz, major); 165.294 d (=CH–O, $^2J_{CP}$ 24.2 Hz, minor). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 17.526 (major), 17.855 (minor).

b. To a suspension of 0.8 g of sodium foil in 50 ml of toluene a solution of 8.5 g of phosphonate **VI** and 5 ml of ethyl formate was added dropwise with stirring. The temperature of the reaction mixture gradually rose to 54°C, and the complete dissolution of sodium was achieved in 40 min. The reaction mixture was stirred for additional 2 h and left overnight. On the next day it was extracted with water (2×20 ml), the water extract was washed with 10 ml of ether and evaporated to dryness on a rotory evaporator. The residue was kept in a vacuum (1 mm Hg) at room temperature for 1 h. Syrup, 4.9 g, was obtained. It consisted of phosphonate **VI**, sodium salt of phosphonoacetic aldehyde **VIa, VIb**, and phosphate whose structure was not established.

Sodium salt of (3-ethoxycarbonylfur-2-yl)(diethoxyphosphoryl)acetic aldehyde VIa, VIb. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: common signals of compounds **VIa, VIb**: 1.115 t (CH_3-phosphonate, J_{HH} 7.2 Hz); 1.177 t (CH_3-phosphonate, J_{HH} 7.2 Hz); 1.267 t (CH_3-carboxyl, J_{HH} 7.2 Hz); 4.093 m (CH_2OP, J_{HH} 7.2 Hz, J_{HP} 14.8 Hz), 4.226 q (CH_2OOC, J_{HH} 7.2 Hz); **VIa**: 6.483 s(H^4-furan); 7.298 s (H^5-furan); 8.470 d (CHO, J_{HP} 1.6 Hz); **VIb**: 6.599 s (H^4-furan); 7.312 d (H^5-furan, J_{HP} 1.2 Hz); 8.558 d (=CH–O, J_{HP} 36.8 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: common signals of compounds **VIa, VIb**: 14.703 (CH_3-carboxyl); 16.460 d (CH_3-phosphonate, $^3J_{CP}$ 5.3 Hz); 16.834 d (CH_3-phosphonate, $^3J_{CP}$ 7.0 Hz); 58.995, 59.159 (CH_2OOC + CH_2OP); **VIa**: 76.653 d (P–C, $^1J_{CP}$ 194.2 Hz); 111.209 (C^4); 111.855 d (C^3, $^3J_{CP}$ 7.4 Hz); 138.838 (C^5); 161.314 d (C^2, $^2J_{CP}$ 13.5 Hz); 164.592 (C=O); 177.636 (CHO, $^2J_{CP}$ 20.2 Hz); **VIb**: 76.647 d (=C–P, $^1J_{CP}$ 197.2 Hz); 108.151 d (C^3, $^3J_{CP}$ 7.9 Hz); 112.183 (C^4); 138.536 (C^5); 164.284 d (C^2, $^2J_{CP}$ 7.5 Hz); 170.736(C=O); 183.038 (=CH–O, $^2J_{CP}$ 5.7 Hz). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 32.291 **VIa**; 26.255 **VIb**, **VIa**:**VIb** intensity ratio 1:1.75.

Reaction of sodium salts of phosphonoacetic aldehyde with allyl bromide *(general procedure)*. Sodium salt of phosphonoacetic acid (10 mmol) was suspended in 20 ml of dioxane and 18 mmol of freshly distilled allyl bromide was added in one portion. The reaction mixture was refluxed with stirring until the disappearance of the signal of sodium salt in ^{31}P NMR spectrum (7–8 h), the solvent was removed on a rotory evaporator. The residue was dissolved in chloroform, the solution obtained was washed with brine and dried over calcium chloride. After that the solvent was removed and the residue was kept in a vacuum (1 mm Hg) at room temperature for 1 h.

Diethyl 1-(5-ethoxycarbonylfur-2-yl)-2-(allyloxy)ethylenephosphonate. Yield 86%, syrup. ***E*-isomer Ib:** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.310 t (CH_3-phosphonate, J_{HH} 7.2 Hz); 1.355 t (CH_3-carboxyl, J_{HH} 7.2 Hz); 4.116 m (CH_2OP, J_{HH} 7.2 Hz, J_{HP} 14.4 Hz), 4.331 q (CH_2OOC, J_{HH} 7.2 Hz); 4.662 d (CH_2-allyl, J_{HH} 5.2 Hz); 5.406 d (H_A, J_{AB} 17.2 Hz); 5.334 d ($H_{A'}$, $J_{A'B}$ 10.4 Hz); 5.933-6.025 m (H_B); 6.665 br.s (H^3-furan); 7.180 br.s (H^4-furan); 7.439 d (–O–CH=, J_{HP} 10.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C ppm: 14.311 (CH_3-carboxyl); 16.221 d (CH_3-phosphonate, $^3J_{CP}$ 6.6 Hz); 60.635 (CH_2OOC); 62.413 d (CH_2OP, $^2J_{CP}$ 5.4 Hz); 96.754 d (P–C=, $^1J_{CP}$ 193.1 Hz); 111.218 d (C^3, $^3J_{CP}$ 5.8 Hz); 119.247 (H_2C=); 119.854 (C^4); 131.801 (=CH–); 142.794 (C^5); 151.202 d (C^2, $^2J_{CP}$ 6.5 Hz); 158.729 (C=O); 160.499 d (=CH–O, $^2J_{CP}$

21.0 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 17.306. ***Z*-isomer Ic:** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.310 t(CH_3-phosphonate, J_{HH} 7.2 Hz); 1.355 t (CH_3-carboxyl, J_{HH} 7.2 Hz); 4.177 m (CH_2OP, J_{HH} 7.2 Hz, J_{HP} 14.4 Hz), 4.331 q (CH_2OOC, J_{HH} 7.2 Hz); 4.632 d (CH_2-allyl, J_{HH} 5.2 Hz); 5.437 d (H_A, J_{AB} 17.2 Hz); 5.334 d ($H_{A'}$, $J_{A'B}$ 10.4 Hz); 5.933-6.025 m (H_B); 6.716 br.s (H^3-furan); 7.114 br.s (H^4-furan); 7.584 d (–O–CH=, J_{HP} 32.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.311 (CH_3-carboxyl); 16.221 d (CH_3-phosphonate, $^3J_{CP}$ 6.6 Hz); 60.635 (CH_2OOC); 62.110 d (CH_2OP, $^2J_{CP}$ 5.3 Hz); 96.754 d (P–C=, $^1J_{CP}$ 193.1 Hz); 111.218 d (C^3, $^3J_{CP}$ 5.8 Hz); 119.134 (H_2C=); 119.854 (C^4); 132.071 (=CH–); 142.321 (C^5); 151.202 d (C^2, $^2J_{CP}$ 6.5 Hz); 160.170 (C=O); 160.282 d (=CH–O, $^2J_{CP}$ 22.4 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 13.512. Signal of CH_2-O carbon atom of the allyl fragment overlaps with the signal of deuterochloroform.

***Z*-Diethyl 1-(4-ethoxycarbonylfur-2-yl)-2-(allyloxy)-ethylenephosphonate IIb.** Yield 87%, syrup. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.293 t (CH_3-phosphonate, CH_3-carboxyl, J_{HH} 7.0 Hz); 4.014–4.160 m (CH_2OP), 4.243 q (CH_2OOC, J_{HH} 7.0 Hz); 4.296 q (CH_2OOC, J_{HH} 7.0 Hz); 4.554 d (CH_2-allyl, J_{HH} 5.6 Hz); 4.624 d (CH_2-allyl, J_{HH} 5.2 Hz); 5.306 d (H_A, J_{AB} 10.4 Hz); 5.412 d ($H_{A'}$, $J_{A'B}$ 17.2 Hz); 5.914 m (H_B, J_{HH} 5.2 Hz, 5.6 Hz; J_{AB} 10.4 Hz, $J_{A'B}$ 17.2 Hz); 6.781 s (H^3-furan); 7.272 d (–O–CH=, J_{HP} 32.4 Hz); 7.827 s (H^5-furan). Compound **IIb** exists as a mixture of two conformers having different shifts of the allyl group protons. While calculating the spectral parameters of the double bond protons this difference was not considered. ^{13}C NMR spectrum ($CDCl_3$), δ_c, ppm: 14.255 (CH_3-carboxyl); 16.221 d (CH_3-phosphonate, $^3J_{CP}$ 6.6 Hz); 60.318 (CH_2OOC); 62.040 d (CH_2OP, $^2J_{CP}$ 5.1 Hz); 75.523 (O–CH_2-allyl); 98.399 d (P–C=, $^1J_{CP}$ 186.8 Hz); 105.951 (C^3); 119.371 (C^4); 120.552, 121.016 (H_2C=); 132.124 (=CH–); 145.776 (C^5); 150.559 d (=CH–O, $^2J_{CP}$ 16.6 Hz) 158.860 (C^2); 163.064 (C=O). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 13.529.

***Z*-Diethyl 1-(2-methyl-5-ethoxycarbonylfur-3-yl)-2-(allyloxy)ethylenephosphonate IIIb.** Yield 83%, syrup**.** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.254 t (CH_3-phosphonate, J_{HH} 7.2 Hz); 1.331 t (CH_3-carboxyl, J_{HH} 6.8 Hz); 2.320 d (CH_3-furan, J_{HH} 2.0 Hz); 3.993–4.106 m (CH_2OP), 4.290 q (CH_2OOC, J_{HH} 6.8 Hz); 4.482 d (CH_2-allyl, J_{HH} 5.4 Hz); 5.287 d (H_A, J_{AB} 11.6 Hz); 5.382 d ($H_{A'}$, $J_{A'B}$ 17.2 Hz); 5.917 m (H_B, J_{HH} 5.4 Hz, 5.6 Hz; J_{AB} 11.6 Hz, $J_{A'B}$ 17.2 Hz); 6.612 d (–O–CH=, J_{HP} 34.4 Hz); 7.065 s (H^3-furan). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.566 (CH_3-furan); 14.304 (CH_3-carboxyl); 16.254 d (CH_3-phosphonate, $^3J_{CP}$ 6.5 Hz); 60.660 (CH_2OOC); 68.785 d (CH_2OP, $^2J_{CP}$ 5.6 Hz); 74.834 (O–CH_2-allyl); 98.195 d (P–C=, $^1J_{CP}$ 187.0 Hz); 117.212 d (C^3, $^2J_{CP}$ 7.9 Hz); 119.204 (H_2C=); 121.382 (C^4); 132.419 (=CH–); 142.067 (C^5); 154.191 d (C^2, $^3J_{CP}$ 8.4 Hz); 158.887 d (=CH–O, $^2J_{CP}$ 23.9 Hz); 159.007 (C=O). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 5.921, 6.119, intensity ratio 1:1.

Diethyl 1-(4-ethoxycarbonylfur-3-yl)-2-(allyloxy)-ethylenephosphonate. Yield 42%, syrup. It exists as a mixture of ***Z*-isomer IVb** and ***E*-isomer IVc** in 6:1 ratio. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: common signals of compounds **IVb, IVc**: 1.188 t (CH_3-phosphonate, J_{HH} 7.0 Hz); 1.241 t (CH_3-carboxyl, J_{HH} 7.2 Hz); 3.959-4.067 m (CH_2OP), 4.185 q (CH_2OOC, J_{HH} 7.2 Hz); **IVb**: 4.432 d (CH_2-allyl, J_{HH} 5.6 Hz); 5.208 d (=CH_2, H_A, J_{AB} 10.4 Hz); 5.337 d (=CH_2, $H_{A'}$, $J_{A'B}$ 17.2 Hz); 5.730–5.918 m (=CH–, H_B); 6.779 d (–O–CH=, J_{HP} 34.0 Hz); 7.318 d (H^2-furan, J_{HP} 2.0 Hz); 7.860 s (H^5-furan); **IVc**: 4.385 d(CH_2-allyl, J_{HH} 5.6 Hz); 5.156 d ((=CH_2, H_A, J_{AB} 10.8 Hz); 5.337 d (=CH_2, $H_{A'}$, $J_{A'B}$ 17.2 Hz); 5.730–5.918 m (=CH–, H_B); 7.110 d (–O–CH=, J_{HP} 10.0 Hz); 7.324 d (H^2-furan, J_{HP} 2.4 Hz); 7.864 s (H^5-furan). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: Common signals of compounds **IVb, IVc**: 14.174 (CH_3-carboxyl); 16.173 d (CH_3-phosphonate, $^3J_{CP}$ 6.6 Hz); 60.112 (CH_2OOC); 61.697 d (CH_2OP, $^2J_{CP}$ 12.5 Hz); 74.632 (O–CH_2-allyl); 95.889 d (P–C=, $^1J_{CP}$ 189.0 Hz); 118.840 (H_2C=); 132.474 (=CH–); 160.212 d (=CH–O, $^2J_{CP}$ 26.6 Hz); 164.470 (C=O); **IVb**: 119.037 d (C^3, $^2J_{CP}$ 3.4 Hz); 132.434 (C^4); 142.815 d (C^2, $^3J_{CP}$ 6.6 Hz); 148.446 (C^5); **IVc**: 119.321 d (C^3, $^2J_{CP}$ 4.1 Hz); 132.173 (C^4); 142.296 d (C^2, $^3J_{CP}$ 3.4 Hz); 147.842 (C^5). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 20.614 **IVb**, 15.836 **IVc**.

Diethyl 1-(2-ethoxycarbonylfur-3-yl)-2-(allyloxy)-ethylenephosphonate. Yield 57%, syrup. It exists as a mixture of ***E*-isomer Vc** and ***Z*-isomer Vd** in 1:0.62 ratio. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: common signals of compounds **Vc, Vd**: 1.198 m (CH_3-phosphonate + CH_3-carboxyl) 4.031 m (CH_2OP, J_{HH} 7.0 Hz, J_{HP} 14.0 Hz), 4.262 q (CH_2OOC, J_{HH} 7.0 Hz); 5.663–5.969 m (=CH–, H_B); **Vc**: 4.450 d (CH_2-allyl, J_{HH} 5.8 Hz); 5.170 d (=CH_2, H_A, J_{AB} 10.2 Hz); 5.232 d (=CH_2, $H_{A'}$, $J_{A'B}$ 14.6 Hz); 6.581 s (H^4-furan); 6.985 d (–O–CH=, J_{HP} 33.6 Hz); 7.441 s (H^5-furan); **Vd**: 4.485

d (CH_2-allyl, J_{HH} 8.0 Hz); 5.170 d (=CH_2, H_A, J_{AB} 10.2 Hz); 5.354 d (=CH_2, $H_{A'}$, $J_{A'B}$ 17.4 Hz); 6.440 s (H^4-furan); 7.399 s (H^5-furan); 7.510 d (–O–CH=, J_{HP} 10.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **Vc**: 14.285 (CH_3-carboxyl); 16.215 (CH_3-phosohonate); 60.594 d (CH_2OP, $^2J_{CP}$ 8.1 Hz); 61.772 (CH_2OOC); 74.740 (O–CH_2-allyl); 96.160 d (P–C=, $^1J_{CP}$ 200.4 Hz); 114.322 (C^4); 118.728 (H_2C=); 125.331 d (C^3, $^2J_{CP}$ 9.6 Hz); 132.238 (=CH–); 141.216 d (C^2, $^3J_{CP}$ 10.0 Hz); 144.638(C^5); 160.321 d (=CH–O, $^2J_{CP}$ 25.9 Hz); 161.372 (C=O); **Vd**: 14.052 (CH_3-carboxyl); 16.215 (CH_3-phosphonate); 60.818 (CH_2OOC); 62.178 d (CH_2OP, $^2J_{CP}$ 6.0 Hz); 75.122 (O–CH_2-allyl); 96.091 d (P–C=, $^1J_{CP}$ 186.7 Hz); 115.988 (C^4); 119.015 (H_2C=); 129.058 d (C^3, $^2J_{CP}$ 8.8 Hz); 132.302 (=CH–); 139.702 d (C^2, $^3J_{CP}$ 10.7 Hz); 144.438 (C^5); 159.030 (C=O); 160.321 d (=CH–O, $^2J_{CP}$ 25.9 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 19.901 **Vc**, 15.228 **Vd**.

***E*-Diethyl 1-(3-ethoxycarbonylfur-2-yl)-2-(allyloxy)-ethylenephosphonate.** Syrup. It exists as a mixture of conformers differing in spectral characteristics of the allyl group, of the furan ring, and of phosphorus atom. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.181-1.324 m (CH_3-caroxyl + CH_3-phosphonate); 3.975–4.081 m (CH_2OP); 4.246 q (CH_2OOC, J_{HH} 7.4 Hz); 4.367 d (CH_2-allyl, J_{HH} 5.2 Hz); 4.506 d (CH_2-allyl, J_{HH} 5.6 Hz); 5.184 d (=CH_2, H_A, J_{AB} 10.6 Hz); 5.187 d (=CH_2, H_A, J_{AB} 9.6 Hz); 5.254 d (=CH_2, $H_{A'}$, $J_{A'B}$ 17.2 Hz); 5.306 d (=CH_2, $H_{A'}$, $J_{A'B}$ 17.2 Hz); 5.822–5.971 m (=CH–, H_B); first conformer:6.884 s (H^4-furan); 7.248 s (H^5-furan); 7.503 d (–O–CH=, J_{HP} 10.4 Hz); second conformer: 6.671 s (H^4-furan); 7.321 s (H^5-furan); 7.452 d (–O–CH=, J_{HP} 10.0 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 16.523 (first conformer), 18.013 (second conformer).

Molecular complex of (2-methyl-5-ethoxycarbonylfur-3-yl)(diethoxyphosphoryl)acetaldehyde with dioxane. Sodium salt **IIIa** (2 g) was suspended in 10 ml of dioxane, 1 ml of trimethylchlorosilane was added, and the reaction mixture was refluxed with stirring for 4 h. Sodium chloride precipitate was removed on a centrifuge, solvent was removed from the fugate under the reduced pressure, and the residue was kept in a vacuum (1 mm Hg) at room temperature for 1 h. The obtained syrup gradually crystallized, mp 88–89°C. In the $CDCl_3$ solution this complex decomposes to dioxane and aldehyde **IIIc** which exists in the solution in the equilibrium with *Z*- **IIId** and *E*-enol **IIIe**.

(2-Methyl-5-ethoxycarbonylfur-3-yl)(diethoxyphosphoryl)acetaldehyde IIIc. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.230–1.350 m (CH_3-carboxyl + CH_3-phosphonate); 2.274 s (CH_3-furan); 3.986–4.134 m (CH_2OP); 4.275–4.338 m (CH_2OOC); 7.161 s (H^4-furan); 9.720 s (CHO). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.367 (CH_3-furan); 14.317 (CH_3-carboxyl); 16.300 d (CH_3-phosphonate, $^3J_{CP}$ 5.5 Hz); 50.527 d (CHP, $^1J_{CP}$ 131.1 Hz); 60.646 (CH_2OOC); 63.416 d (CH_2OP, $^2J_{CP}$ 6.8 Hz); 63.624 d (CH_2OP, $^2J_{CP}$ 6.5 Hz); 113.378 d (C^3, $^3J_{CP}$ 5.8 Hz); 120.336 (C^4); 142.998 (C^5); 153.754 d (C^2, $^3J_{CP}$ 9.4 Hz); 163.074 (C=O); 192.213 (CHO). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 23.170.

***Z*-Diethyl 1-(2-methyl-5-ethoxycarbonylfur-3-yl)-2-hydroxyethylenephosphonate IIId.** ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.230–1.350 m (CH_3-carboxyl + CH_3-phosphonate); 2.313 d (CH_3-furan, J_{HH} 2.0 Hz); 3.986–4.134 m (CH_2OP); 4.275–4.338 m (CH_2OOC); 6.978 s (H^4-furan); 7.237 d (=CH–O, J_{HP} 13.6 Hz); 11.029 br.s (OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.268 (CH_3-furan); 14.317 (CH_3-carboxyl); 16.138 d (CH_3-phosphonate, $^3J_{CP}$ 6.0 Hz); 60.866 (CH_2OOC); 61.996 d (CH_2OP, $^2J_{CP}$ 3.5 Hz); 90.560 d (P–C=, $^1J_{CP}$ 180.6 Hz); 115.611 d (C^3, $^3J_{CP}$ 7.0 Hz); 120.634 (C^4); 142.360 (C^5); 155.207 d (C^2, $^3J_{CP}$ 10.2 Hz); 158.236 d (=C-OH, $^2J_{CP}$ 27.8 Hz); 163.012 (C=O). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 18.262.

***E*-Diethyl 1-(2-methyl-5-ethoxycarbonylfur-3-yl)-2-hydroxyethylenephosphonate IIIe.** ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.230–1.350 m (CH_3-carboxyl + CH_3-phosphonate); 2.339 d (CH_3-furan, J_{HH} 1.6 Hz); 3.986–4.134 m (CH_2OP); 4.275–4.338 m (CH_2OOC); 7.049 s (H^4-furan); 7.572 d (=CH–O, J_{HP} 6.8 Hz); 11.029 br.s (OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.480 (CH_3-furan); 14.317 (CH_3-carboxyl); 16.138 d (CH_3-phosphonate, $^3J_{CP}$ 6.0 Hz); 60.818 (CH_2OOC); 62.477 d (CH_2OP, $^2J_{CP}$ 6.8 Hz); 92.692 d (P–C=, $^1J_{CP}$ 205.0 Hz); 115.611 d (C^3, $^3J_{CP}$ 7.0 Hz); 120.608 (C^4); 142.408 (C^5); 155.207 d (C^2, $^3J_{CP}$ 10.2 Hz); 158.782 d (=C-OH, $^2J_{CP}$ 15.9 Hz); 163.012 (C=O). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 23.170.

REFERENCES

1. Dombrovskii, A.V. and Dombrovskii, V.A., *Usp. Khim*., 1966, vol. 35, p. 1771.
2. Mikolajzyk, M., *Reviews on Heteroatomic Chem*., 1989, Tokyo, vol. 2, p. 19.
3. Kabachnik, M.I. and Mastryukova, T.A., *Mezhfaznyi kataliz v fosfororganicheskoi khimii* (Interphase

Catalysis in the Organophosphorus Chemistry), Moscow, URSS, 2002.

4. Phan Hieu, Trung, Nguyen, Lan Mong, Vinh, Van, Azoulay, R., Eschenhof, H., Nesor, E.J., Bentzen, C.L., and Ife, R.J., USA Patent 114421A1, 2003.
5. Phan Hieu, Trung, Nguyen, Lan Mong, Vinh, Van, Azoulay, R., Eschenhof, H., Nesor, E.J., Bentzen, C.L., and Ife, R.J., USA Patent 111332A1, 2002.
6. Aboujaoude, E.E., Collignon, N., and Savijnac, P., *J. Organomet. Chem*., 1984, vol. 264, nos. 1–2, p. 9.
7. *Organicheskie reaktsii* (Organic Reactions), Moscow: Inostrannaya Literatura, 1956, vol. 8, p. 288.
8. Pevzner, L.M., Terekhova, M.I., Ignat'ev, V.M., Petrov, E.S., and Ionin, B.I., *Zh. Obshch. Khim*., 1984, vol. 54, no. 9, p. 1990.
9. Boyd, M.R., Harris, T.M., and Wilson, B.J., *Synthesis*, 1971, p. 545.