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Reaction of 2- and 3-Furylmethanephosphonates with Esters

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Abstract—2- and 3-furylmethanephosphonates are acylated with ethyl formate, diethyl oxalate, and ethyl trifluoroacetate in toluene in the presence of sodium foil to afford five phosphorylated derivatives of furylacetic aldehyde, furylpyruvic acid, and 1,1,1-trifluoro-1-(2-furyl)propan-2-one. In a chloroform solution these compounds exist in the equilibrium with their enolic forms. When treated with sodium ethylate they form sodium salts which were isolated and characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. It was shown that in DMSO solutions sodium salts of formyl and oxalyl derivatives of 2-furylmethanephosphonate exist as mixtures of the carbanion and enolate forms. In the first case the carbanion form is predominant, while in the second one the enolate forms prevail. Sodium salt of formylated 3-furylmetanephosphonate exists only in the carbanion form, while the salt of 3-furylpyruvate is enolate. The alkylation of these salts with iodomethane proceeds at the carbon atom as well as at the oxygen one. First reaction pathway is often preferred.

Keywords: furylmethanephosphonates, condensation with esters, sodium salts, keto-enol tautomerism, O- and C-alkylation

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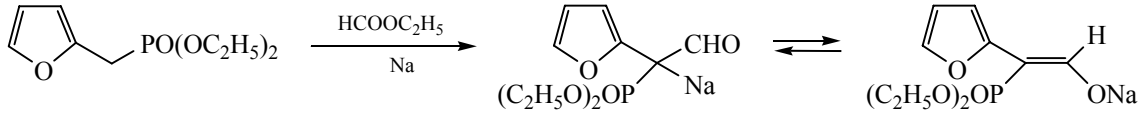
We have shown previously that furylmethanephosphonates containing ethoxycarbonyl or cyano group in the furan ring react with ethyl formate in the presence of sodium foil according to the scheme analogous to the Claisen condensation [1, 2]. In this presented we have attempted to establish whether the presence of the acceptor group in the furan ring is necessary for proceeding of this reaction, in other words, whether 2- and 3-furylmethane phosphonates are sufficiently strong CH-acids to generate the carbanion under the conditions used. Besides, we decided to broaden the range of acylating agents by using diethyl oxalate and ethyl trifluoroacetate in this reaction. These esters have a reactive carbonyl group, and, besides, they cannot form carbanions. Due to that in these cases Claisen condensation always proceeds unambiguously.

The formylation of diethyl (2-furyl)methanephosphonate **I** with ethyl formate was carried out similarly to [1, 2] in toluene in the presence of sodium foil at the 1 : 1.2 : 2 molar ratio of phosphonate, sodium, and formate. The reaction proceeded with heat evolution (reaction temperature rose to 70°C). Sodium salt of phosphonoacetic aldehyde partially precipitated from the reaction mixture, and after dilution with hexane the reaction product was obtained as white crystals in 84% yield. The conversion of phosphonate **I** was 93%. In the ^{31}P NMR spectrum of this salt in DMSO-d_6 two signals were observed at 31.910 ppm and 26.541 ppm in 1 : 0.14 ratio. In the ^{1}H NMR spectrum of this product in DMSO-d_6 two sets of signals were observed. Most intense of them included the signals of the furan protons at 6.219 ppm (H^3, d.d, J_{HH} 3.2Hz, J_{PH} 1.6 Hz), 6.322 ppm (H^4, d, J_{HH} 3.2Hz), and 7.161 ppm (H^5, br.s). The signal at 8.454 ppm we attributed to the aldehyde proton which splits from coupling with phosphorus, J_{PH} 2.8 Hz. In the ^{13}C NMR spectrum the carbon atom directly bound to phosphorus gave a signal at 79.769 ppm ($^{1}J_{PC}$ 200.0 Hz), and the signal of the aldehyde carbonyl carbon atom was observed at 175.435 ppm ($^{2}J_{PC}$ 19.6 Hz). Hence, the main product **Ia** is the carbanion form of sodium salt of the phosphorylated furylacetic aldehyde. Less intense set of signals in the ^{1}H NMR spectrum includes broadened singlets at 6.235 ppm (H^4), 7.198 ppm (H^3), and 7.237 ppm (H^5), and also a doublet at 8.734 ppm (J_{PH} 38.8 Hz). Phosphorus-containing fragment of the side chain is characterized by the signals at 82.421 ppm ($^{1}J_{PC}$ 216.0 Hz) and 179.081 ppm ($^{2}J_{PC}$ 8.8 Hz) in the ^{13}C NMR spectrum. These spectral data permit to ascribe to the minor product the structure of *Z*-enolate

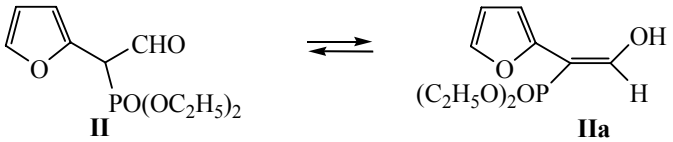
Ib. Detailed spectral characteristics of the substances **Ia, Ib** are presented in the Experimental. Hence, the formylation of phosphonate **I** is described by the following equation:



I **Ia** **Ib**

Free aldehyde **II** can be isolated by water extraction of the reaction mixture, followed by acidifying the water extract to pH 3–4 and extraction of the isolated oil with ether. The distillation of the ether extract in a vacuum gave aldehyde **II** as a viscous liquid crystallizing on storage, bp 121°C (1 mmHg), mp 61–62°C. Yield of the product was 43%, the conversion of starting phoshonate **I** being 93%. In the chloroform solution aldehyde **II** exists in the equilibrium with its *E*-enol **IIa** in 1 : 0.27 ratio. Signals of protons of the side chain of the aldehyde **II** are observed at 7.763 ppm (CHP, J_{HH} 13.3, J_{PH} 39.2 Hz) and 11.274 ppm (CHO, J_{HH} 13.3 Hz). Note the unusually high coupling constant of the vicinal protons which we have not observed previously or have not found in the literature. Carbon atoms of this fragment had usual values of 92.010 ppm (PC, $^1J_{PC}$ 177.7 Hz) and 161.625 ppm (CHO). The chemical shift of phosphorus in compound **II** is equal to 21.782 ppm what is characteristic of furylmethanephosphonates.

The proton of the double bond in enol **IIa** gives rise to a signal at 7.616 ppm (J_{PH} 10.8 Hz) what indicates its *cis*-location with respect to phosphorus. The proton of the enol hydroxy group appears as a broad signal at 10.178 ppm. Carbon atoms of the double bond are characterized by signals at 94.172 ppm (=C–P, $^1J_{PC}$ 197.0 Hz) and 156.779 ppm (=CH–OH, $^2J_{PC}$ 19.7 Hz). Values of chemical shifts and coupling constants of the enol carbon atoms well agree with the corresponding values of enol ethers of *E*-configuration [2]. Chemical shift of phosphorus in compound **IIa** is equal to 20.048 ppm.



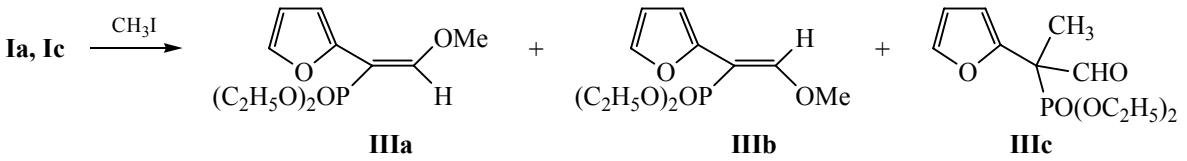
II **IIa**

Sodium salt **Ia, Ib** was brought into alkylation with methyl iodide. The reaction was carried out in acetonitrile at 50–60°C for 8 h, and the reaction products were isolated by vacuum distillation. It proved that the composition of the alkylation products of this salt was more complicated than in the case of previously studied substances [1, 2]. Besides the enol ethers **IIIa, IIIb** a significant amount of C-alkylation product **IIIc** was formed.

In the ^{31}P NMR spectrum of the mixture of products **IIIa–IIIc** three signals were observed at 19.481, 18.637, and 13.700 ppm with the intensity ratio 1 : 1.65 : 1.09. In the ^{1}H NMR spectrum two sets of signals corresponded by intensity to the last two phosphorus signals. One of them included the singlet at 3.938 ppm (OCH_3) and a doublet at 7.118 ppm (=CH–O, J_{PH} 10.8 Hz). These signals characterize methyl enolate of *E*-configuration **IIIa**. In the ^{13}C NMR spectrum the corresponding signals of carbon atoms were observed at 61.891 ppm (CH_3O), 96.768 ppm (=C–P, $^1J_{PC}$ 190.1 Hz), and 159.547 ppm (=CH–O, $^2J_{PC}$ 21.4 Hz). Methyl enolate having Z-configuration **IIIb** was characterized by the signals of protons at 3.874 ppm (OCH_3) and 7.216 ppm (=CH, J_{PH} 32.8 Hz). In the ^{13}C NMR spectrum carbon atoms of this fragment give signals at 62.292 ppm (OCH_3), 98.633 ppm (=C–P, $^1J_{PC}$ 182.9 Hz), and 159.850 ppm (=C–O).

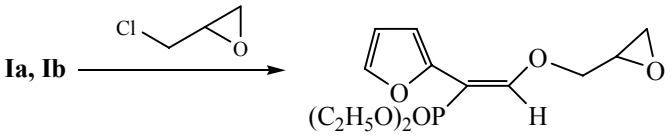
Signals of protons at 1.671 ppm (CH_3, J_{PH} 16.0 Hz) and 9.797 ppm (CHO) belong to the C-alkylation product **IIIc**. In the ^{13}C NMR spectrum signals of the corresponding carbon atoms are observed at 14.190 ppm (CH_3, $^2J_{PC}$ 5.2 Hz), 55.838 ppm (PC, $^1J_{PC}$ 132.2 Hz), and 194.253 ppm (CHO). The signal of phosphorus atom in this compound is characterized by a value 19.481 ppm typical of phosphonates. Spectral parameters of all three products are presented in Experimental.

Hence, in the absence of electron-acceptor substituents in the furan ring C-alkylation of the ambident anions is possible. The proportion of this reaction pathway is sufficiently high (~27%).



IIIa **IIIb** **IIIc**

With the purpose of introduction of the reactive functional group in the peripheral part of the molecule we have made an attempt to alkylate salts **IIa, IIb** with epichlorohydrin. The reaction was carried out in acetonitrile at 80°C during 7 h in the presence of the catalytic amount of potassium iodide. In this case the alkylation proceeded regio- and stereoselectively to give enol ether of *E*-configuration **IV**. The chemical shift of phosphorus in this compound was 18.251 ppm. The signal of the double bond proton was characterized by the chemical shift value of 7.158 ppm (J_{PH} 10.8 Hz), and the signals of carbon atoms of this fragment were observed at 97.499 ppm (=C–P, $^{1}J_{PC}$ 189.8 Hz) and 157.868 ppm (=CH–O, $^{2}J_{PC}$ 21.7 Hz).



IV

The phosphonate obtained may serve a convenient precursor in the synthesis of phospholipids analogs.

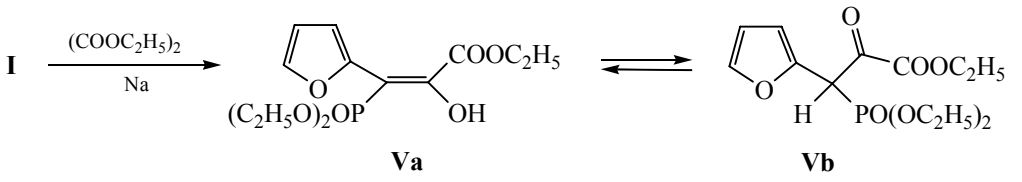
Up to now we have studied acylation of furylmethanephosphonates only with ethyl formate. In this work we made an attempt to broaden the range of acylating agents by using diethyl oxalate and ethyl trifluoroacetate.

A successful attempt at oxalylation of benzylphosphonates was reported in [3], but heterylmethylphosphonates were not involved in this reaction. In [3] the generation of carbanions was carried out using butyl lithium, but our experience showed that the reaction proceeds successfully in the presence of sodium ethylate, which formed from ethanol in the course of condensation, and sodium foil.

The oxalylation of phosphonate **I** was carried out in toluene, the molar ratio of phosphonate, sodium, and diethyl oxalate being 1 : 1.1 : 1.3. The dissolution of sodium proceeded with heat evolution, the temperature of the reaction mixture rose to 36°C. The complete dissolution of sodium took place within 1 h. The reaction product was isolated by extraction with water, subsequent acidifying of the extract, and extracting of the target product from water by methylene chloride. After removing the solvent and keeping the residue in a vacuum light brown syrup was obtained. In ^{31}P NMR spectrum of this preparation two signals of phosphorus nuclei were observed at 21.564 and 14.225 ppm with the intensity ratio 1 : 0.35. In the ^{1}H NMR spectrum first phosphonate was characterized by a broad signal at 12.199 ppm attributed by us to the enol hydroxy group. Signals of the side chain carbon atoms of this substance were observed at 91.287 ppm (=C–P, $^{1}J_{PC}$ 176.2 Hz), 163.007 ppm (=C–OH, $^{2}J_{PC}$ 23.0 Hz), and 161.583 ppm (COOEt, $^{3}J_{PC}$ 7.0 Hz). The observed significantly large $^{3}J_{PC}$ coupling constant indicate that in the compound obtained the phosphoryl and ethoxycarbonyl groups are *trans*-located with respect to the double bond, though it cannot be regarded as a completely strict evidence.

In the ^{1}H NMR spectrum of minor compound the doublet at 5.683 ppm is observed (CHP, J_{PH} 26.4 Hz). In the ^{13}C NMR spectrum the side chain of this product is characterized by the signals at 47.666 ppm (HCP, $^{1}J_{PC}$ 130.8 Hz), 186.806 ppm (C=O), and 160.240 ppm (COOEt). Note that no signal of carbonyl carbon atoms is split.

Hence, the product of oxalylation of phosphonate **I** in chloroform exists as a mixture of enol **Va** and ketoester **Vb**. Note specially that the signal of phosphorus atom in enol is located upfield from the ketoester one, while in the case of compounds **II**, **IIa** and the previously studied formyl derivatives [1, 2] reversed pattern was observed. Detailed spectral characteristics of compounds **Va, Vb** are presented in Experimental.

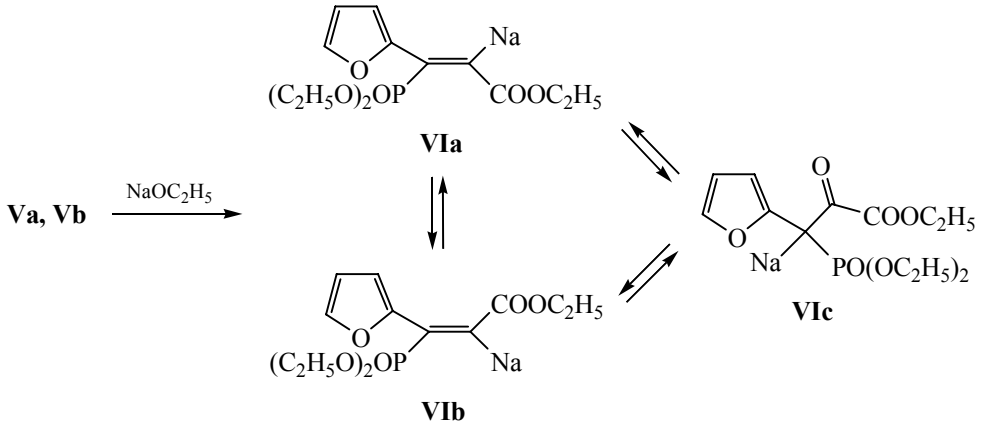


Va **Vb**

The product synthesized can be distilled in a vacuum [bp 142–145°C (1 mmHg)], but according to the ^{1}H NMR data the distillate is more contaminated than the initial preparation. It must be also marked specially that no decarbonylation takes place in the course of distillation.

Treating of ethanol solution of the oxalyl derivative **Va, Vb** with sodium ethylate leads to the formation of sodium salt. The latter forms yellowish brown crystals after evaporation of ethanol in a vacuum and treating of the residue with 2 : 1 hexane–diethyl ether mixture. During evaporation of residual solvent after filtration these crystals quickly cover with a brown syrup-like film, but according to the spectral data immediate dissolution in anhydrous DMSO prevented the accumulation of decomposition products for several days.

In the ^{31}P NMR spectrum of sodium salt three signals at 28.250 ppm, 26.438 ppm, and 23.277 ppm in the 1 : 1.06 : 0.16 ratio were observed. First signal corresponds to the signals at 74.431 ppm (P–C=, $^1J_{PC}$ 203.0 Hz), 176.657 ppm (=C–ONa, $^2J_{PC}$ 11.9 Hz), and 169.787 ppm (C=O) in the ^{13}C NMR spectrum. Signals of carbon atoms corresponding to the second signal of phosphorus are located at 74.219 ppm (P–C=, $^1J_{PC}$ 196.0 Hz), 175.465 ppm (=C–ONa, $^2J_{PC}$ 21.7 Hz), and 169.329 ppm (C=O, $^3J_{PC}$ 25.9 Hz). These spectral data permit ascribing the first set of signals to structure **VIa** with the *cis*-location of the phosphoryl and carboxy groups, and the second set, to the corresponding *trans*-isomer **VIb**. The minor product is characterized by the signals of carbon atoms at 88.566 ppm (PCNa, $^1J_{PC}$ 217.8 Hz), 199.356 ppm (C=O), and 176.216 ppm (O=COEt). It may be regarded as the carbanion form of sodium salt **VIc**.



VIa **VIb** **VIc**

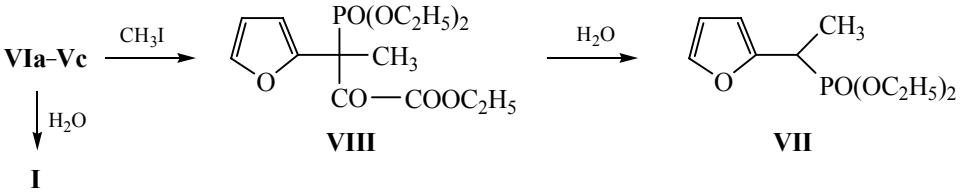
^{1}H NMR spectra of the products **VIa–VIc** are not very informative, but we managed to attribute the furan proton signals for all three compounds. Detailed spectral data are listed in the Experimental.

The sodium salt obtained alkylated with excess iodomethane in acetonitrile. The reaction proceeded for 10 h at 60°C. After removing acetonitrile, dissolving the residue in methylene chloride, extracting the water-soluble products with water and keeping the preparation in a vacuum we obtained a syrup-like substance which subjected to molecular distillation in a vacuum at 90–110°C. In ^{31}P NMR spectrum of this substance three signals at 23.106, 26.618, and 18.992 ppm with the intensity ratio 0.64 : 1.00 : 0.56 were observed. First signal belonged to the starting phosphonate **I**, and the corresponding signals of protons and carbon atoms were found in the NMR spectra. Signals of protons at 1.479 ppm (CH_3, J_{HH} 7.6 Hz, J_{PH} 17.6 Hz) and 3.271 ppm (CHP, J_{HH} 7.7 Hz, J_{PH} 24.8 Hz) corresponded to the most intense signal of phosphorus. In the ^{13}C NMR spectrum this product

was characterized by the signals at 13.526 ppm (CH_3, $^2J_{PC}$ 4.7 Hz) and 32.342 ppm (CHP, $^1J_{PC}$ 141.9 Hz). These data permit to ascribe structure **VII** to the compound under study.

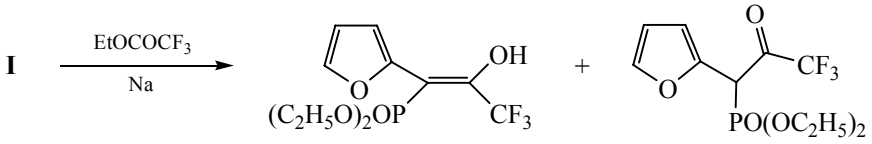
The last signal of phosphorus corresponds to the doublet at 1.09 ppm (CH_3, J_{PH} 16.0 Hz) in the ^{1}H NMR spectrum. In the ^{13}C NMR spectrum signals of the same substance are observed at 13.819 ppm (CH_3), 54.134 ppm (CP, $^1J_{PC}$ 142.1 Hz), 190.881 ppm (C=O) and 161.329 ppm (O=C–OEt). These spectral data characterize ketoester **VIII**.

Establishing the structure of the reaction products permits suggesting the following reaction pathway. Sodium salt **VIa–VIc** is alkylated with methyl iodide at the carbon atom to give compound **VIII**. Simultaneously under the action of air moisture and (or) residual water in acetonitrile the elimination of the oxalyl residue leading to phosphonates **I**, **VII** takes place. Note that no signs of alkylation at the oxygen were found though in DMSO the enolate form of the salt **VIa–VIc** prevails.



The reaction of phosphonate **I** with ethyl trifluoroacetate was carried out in toluene at the phosphonate : sodium : ester ratio 1 : 1.2 : 2. While mixing the reagents an increase in temperature of the reaction mixture by ~10°C was observed but no sodium dissolution was marked. After heating the reaction mixture to 55–60°C an exothermic reaction took place, and the complete dissolution of sodium foil was achieved in the course of ~2 h at 65–70°C. The condensation product was isolated by extraction with water, acidifying, and extraction of the obtained oil with chloroform. In the toluene layer phosphonate **I** was found which was not involved in the reaction. On the basis of this data it was established that the conversion of starting substance was 51%. The reaction product was distilled in a vacuum to give a single fraction with bp 111–112°C (1 mmHg). In the ^{31}P NMR spectrum of the preparation obtained three signals at 23.208, 20.343, and 12.986 ppm with the intensity ratio 1 : 0.8 : 0.3 were observed. Most intense signal belonged to phosphonate **I**. The corresponding signals of protons and carbon atoms were found in the ^{1}H and ^{13}C NMR spectra. In the ^{19}F NMR spectra two signals at –68.033 and –77.422 ppm with the intensity ratio 2.5 : 1 were found. They agree with the intensity ratio of phosphorus atom signals providing a possibility to make attribution of proton and carbon atom signals. Detailed spectral data are presented in Experimental. Here we note only that in the ^{1}H NMR spectrum of the major product among the phosphorus-containing ones a broad signal at 12.433 ppm typical of an enol form is observed. In the ^{13}C NMR spectrum this substance is characterized by the signals at 92.051 ppm (P–C=, $^1J_{PC}$ 176.3 Hz), and a doublet of quartets at 159.273 ppm with the coupling constants 9.9 and 34.0 Hz. The character of signal and the values of coupling constants [4] show that the largest one is $^2J_{FC}$, while the smallest is $^2J_{PC}$. Signals of carbon atoms of CF_3 groups are quartets at 119.072 ppm ($^1J_{FC}$ 277 Hz) and 118.808 ppm ($^1J_{FC}$ 276.5 Hz). Due to their small intensities we have failed to attribute any of them to enol, but note, that neither of them is split due to coupling with phosphorus. Hence, regardless of the attribution of signals it can be stated that in the enol form the phosphoryl and trifluoromethyl groups are *cis*-located with respect to the double bond, and the compound under consideration may be characterized by the structure **IX**. In the ^{1}H NMR spectrum of the minor product the doublet at 5.041 ppm (CHR, J_{PH} 24.0 Hz) is observed. In the ^{13}C NMR spectrum it is characterized by the signals at 43.515 ppm ($^1J_{PC}$ 136.6 Hz) and 45.994 ppm ($^1J_{PC}$ 135.2 Hz) belonging to CHP fragment and a singlet at 165.334 ppm attributed by us to the carbonyl group. Note that this signal is not split from coupling either with phosphorus or with fluorine. It must be also mentioned that the signals of carbon atoms of P–OCH_2 fragment, and of the C^2 and C^3 atoms of the furan ring are also doubled. Evidently, the ketophosphonate characterized by the structure **X** is a mixture of

spectroscopically dis-tinguishable conformers. From the presented data it follows that trifluoroacetylation of phosphonate **I** proceeds according to the following equation:



IX **X**

Enol form **IX** prevails in chloroform solution.

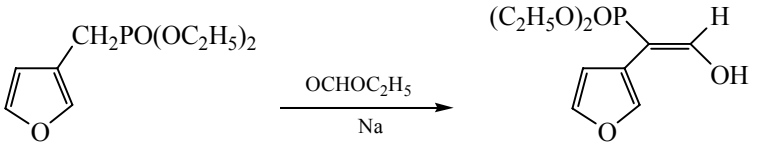
Trifluoroacetylation products are very hydrolytically unstable. All the attempts to carry out methylation of this compound with methyl iodide failed despite treating the freshly prepared sodium salt of the pure trifluoroacetyl derivative or the reaction mixture directly after the condensation. In all cases only the liberation of phosphonate **I** was observed.

Hence, 2-furylmethanephosphonate **I** is a sufficiently strong CH-acid to give the carbanion in the presence of sodium foil. This carbanion can add to the carbonyl group of esters most active in the Claisen reaction. The metallation agent is the most probably sodium ethylate forming from the traces of ethanol initially present as an admixture to the ester, and later evolving in the course of condensation. The process is limited by the hydrolytic lability of the obtained carbonyl derivatives.

We have also tried to involve in this reaction still weaker CH-acid, diethyl 3-furylmethane phosphonate **XI**. The reaction with ethyl formate was carried out also in toluene, molar ratio of phosphonate, sodium, and ethyl formate being 1 : 1.2 : 2. It was found that the dissolution of sodium proceeds at 60°C within 6 h. After water extraction of the reaction mixture and fast drying of toluene layer the starting phosphonate **XI** was found in it. Its amount permitted evaluating the conversion of starting substance at 56%. The water extract was acidified to pH 4–5, and the liberating oil was extracted with dichloromethane, dried, and kept in a vacuum. In the ^{31}P NMR spectrum of the preparation isolated the signal at 26.475 ppm belonging to the starting phosphonate **XI**, the broadened signal at 23.789 ppm attributed by us to the product of hydrolysis of phosphonate **XI** at the ester group, and a signal at 18.026 ppm were observed. In the ^{1}H NMR spectrum the signals belonging to the protons of phosphonate **XI** and a one more doublet of CH_2P fragment at 2.909 ppm (J_{PH} 20.4 Hz) were found. The intensity of the latter corresponds to the second signal in ^{31}P NMR spectrum. These data prove that in the course of water extraction the hydrolysis not only of formyl group, but also of the phosphonic acid ester takes place. This fact is quite unexpected because as a rule phosphonates are stable in alkaline medium at room temperature.

Besides the above-mentioned signals ^{1}H NMR spectrum of the preparation under consideration contained also one more set of signals including those belonging to the furan ring at 6.763 ppm (H^3), 7.359 ppm (H^5), and 7.776 ppm (H^2), a doublet at 7.542 ppm (=CH–O, J_{PH} 10.4 Hz), and a broad signal at 11.071 ppm (OH, enol). These data characterize structure **XII**.

Hence, the formylation of phosphonate **XI** proceeds according to the usual scheme [1, 2], formyl derivative is hydrolytically unstable, and in chloroform solution it exists in the enol form of *E*-configuration.



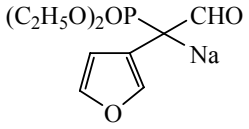
XI **XII**

After evaporation to dryness in a vacuum of the reaction mixture formed after dissolution of sodium in toluene solution of phosphonate **XI** and ethyl formate, and treating of the residue with anhydrous ether, yellow crystals were obtained which immediately covered with a syrup-like film at exposure to air. In the course of 5–7 min in air the crystals melted. The substance obtained dissolved in DMSO, but just in the

course of recording the NMR spectra the decomposition of the product took place. Nevertheless we managed to obtain spectral characteristics of the compounds formed though their ratio in solution constantly altered.

^{31}P NMR spectrum contained a signal at 34.400 ppm attributed by us to the carbanion form of sodium salt on the basis of the data [1, 2]. The signal at 26.575 ppm belonged to phosphonate **XI**, and the signal at 16.333 ppm characterized the enol form of sodium salt (or the enol resulting from its hydrolysis). In the ^{1}H and ^{13}C NMR spectra signals of phosphonate **XI** and sodium formate [δ 8.484 ppm (CHO), δ_C 167.252 (C=O)] were found. The latter is poorly soluble in DMSO and in the course of accumulation it precipitates from the solution. Besides, ^{1}H NMR spectrum contained the furan proton signals at 6.593 ppm (H^4), 7.995 ppm (H^5), and 8.342 ppm (H^2), and a doublet at 8.381 ppm (CHO, J_{PH} 2.8 Hz). Signals of the side chain carbon atoms of this substance were observed at 84.318 ppm (PC, $^{1}J_{PC}$ 224.5 Hz) and 177.199 ppm (CHO, $^{2}J_{PC}$ 24.4 Hz). Signals of corresponding carbon atoms of the furan ring are presented in Experimental. We failed to establish the signals of protons and carbon atoms belonging to the enol form.

Hence, spectral data show that in the course of the reaction the formation of sodium salt **XIII** takes place which in DMSO is detected in more stable carbanion form.

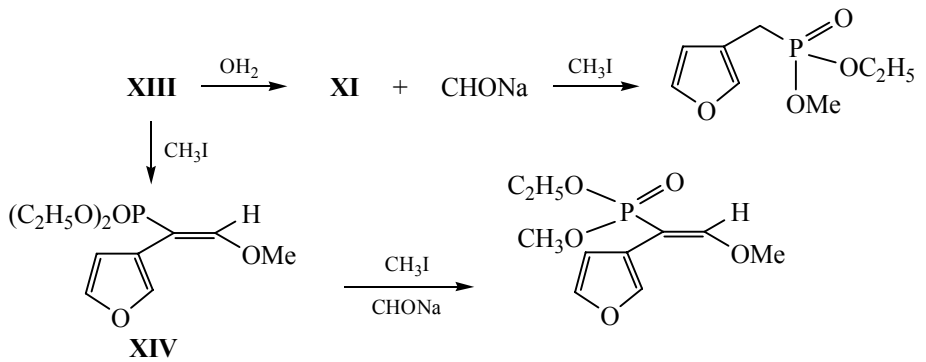


XIII

Yield of salt **XIII** was evaluated to be 58% calculated on the conversion of starting phosphonate equal to 56%, as was found from the parallel experiment.

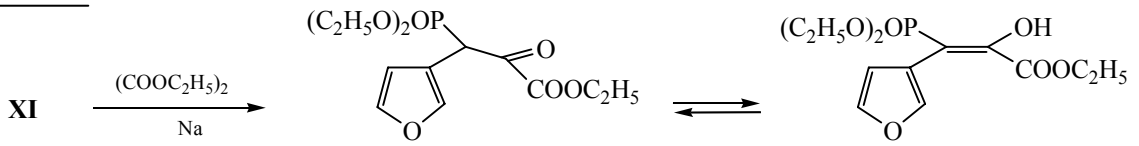
Directly after isolation salt **XIII** was subjected to alkylation with methyl iodide in acetonitrile at 60°C for 10 h. After removing water-soluble components of reaction mixture, drying, and evaporation in a vacuum the syrup-like preparation was obtained. In its ^{31}P NMR spectrum four signals at 27.650, 26.398, 21.434, and 21.627 ppm were present. In the upfield part of the ^{1}H NMR spectrum the multiplet of non-equivalent methyl groups of phosphonate, two signals of CH_2P fragment at 2.946 ppm (J_{PH} 20.8 Hz) and 2.956 ppm (J_{PH} 20.8 Hz), and a doublet at 3.698 ppm (CH_3OP, J_{PH} 10.8 Hz) were observed. Singlet at 3.933 ppm belongs to the metoxy group of enol ether, and the doublet at 7.125 ppm (=CH–O, J_{PH} 10.4 Hz) shows that this ether has *E*-configuration. Corresponding signals of the enol side chain carbon atom are found at 96.464 ppm (PC=, $^{1}J_{PC}$ 191.0 Hz) and 156.632 ppm (=CH–O, $^{2}J_{PC}$ 24.7).

These data show that in the course of the process several reactions occur. First of all, sodium salt **XIII** reacts with methyl iodide to give ether **XIV**. The same salt simultaneously undergoes the hydrolysis with the traces of water to form phosphonate **XI** and sodium formate. The latter plays the role of a base in the reaction of ester groups of phosphonates with methyl iodide leading to formation of mixed esters. It explains the appearance of two pairs of signals in the ^{31}P NMR spectrum, two signals of CH_2P fragments, and a doublet of CH_3OP group. At the formation of mixed esters the location of the furan proton signals and the carbon atom signals of the main skeleton of the molecules **XI** and **XIV** does not alter. From the comparison of intensities of signals in the ^{1}H and ^{31}P NMR spectra it follows that the proportion of mixed ester in phosphonate **XI** is about 30%, and in the compound **XIV** it is ~20%. The process can be described by the following scheme:



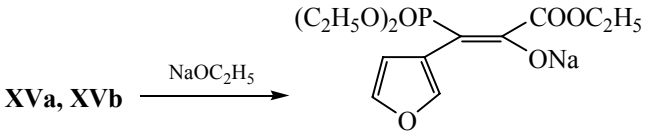
Main pathway of the process under the described conditions is the decomposition of the salt **XII** to the phosphonate **XI**.

Oxalylation of phosphonate **II** was carried out in toluene. Molar ratio of phosphonate, sodium, and diethyl oxalate was 1 : 1.1 : 1.3. The reaction proceeded with heat evolution. The temperature of the reaction mixture rose from 19 to 32°C, and a complete dissolution of sodium foil proceeded within 2 h. Treating at room temperature and change of toluene for ether did not cause the crystallization of sodium salt. Therefore the condensation product was extracted with water, neutralized, and the liberating oil was extracted with chloroform. After evaporation and keeping in a vacuum a very viscous oil was obtained. In ^{31}P NMR spectrum of this preparation three signals were observed at 26.625 ppm (phosphonate **XI**), 22.791 ppm, and 16.512 ppm. The presence of phosphonate **XI** was confirmed also by the ^{1}H and ^{13}C NMR spectra. Hence, the condensation product is easily split by water with the liberation of starting compound. In the ^{1}H NMR spectrum of the preparation obtained a doublet at 5.441 ppm (J_{PH} 27.8 Hz) and the furan proton signals at 6.236 ppm (H^4), 7.386 ppm (H^5), and 7.661 ppm (H^2) of the corresponding intensity were observed. These data suggested that ketoester **XVa** was present among the reaction products. Signals in the ^{13}C NMR spectrum at 44.683 ppm ($^{1}J_{PC}$ 129.5 Hz), 186.766 ppm ($^{2}J_{PC}$ 5.0 Hz), and 160.428 ppm corresponding to P–C fragment, and the ketone and ester carbonyl carbon atoms respectively confirm this suggestion. One more set of proton signals consisting of a broad singlet at 9.753 ppm (OH), and singlets at 6.274 ppm (H^4-furan), 7.295 ppm (H^5-furan) and 7.343 ppm (H^2-furan) characterize the enol form **XVb**. In the ^{13}C NMR spectrum the corresponding signals are observed at 90.753 ppm (P–C=, $^{1}J_{PC}$ 176.0 Hz), 163.102 ppm (=C–O, $^{2}J_{PC}$ 24.6 Hz), and 160.290 ppm (C=O, $^{3}J_{PC}$ 8.3 Hz). A considerable coupling constant between the phosphorus atom and the carbonyl group shows that these structural fragments are *trans*-located with respect to the double bond. The comparison of the intensities of signals of the protons and phosphorus atoms permits assignment of the signal at δ_P 16.512 ppm to the ketoester **XVa**. The signal of phosphorus atom in the enol form **XVb** is located at 22.791 ppm. Molar ratio of tautomers **XVa, XVb** in chloroform is 1 : 0.3.



XVa **XVb**

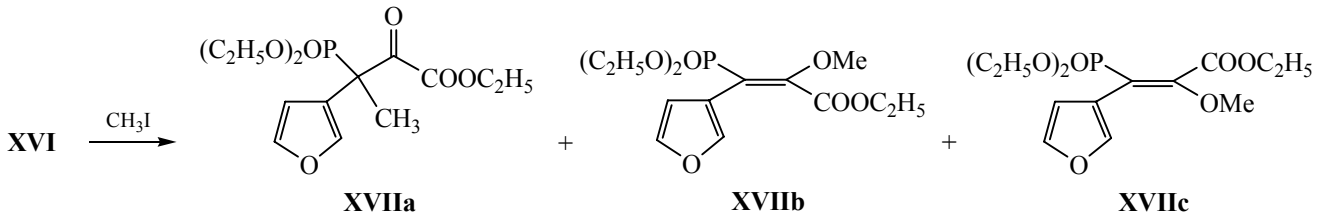
Treating the compound obtained with the calculated amount of sodium ethylate led to formation of sodium salt **XVI** isolated in crystalline state from the 1 : 3 ether–hexane mixture. Under the layer of solvent these crystals are light yellow, but when subjected to air they quickly darken and melt. In DMSO this salt gradually decomposes to give phosphonate **XI**. Chemical shift of phosphorus in this compound is 30.947 ppm. Signals of the side chain carbon atoms are observed at 72.385 ppm (P–C=, $^{1}J_{PC}$ 199.5 Hz), 175.154 (=C–ONa, $^{2}J_{PC}$ 22.1 Hz), and 170.078 ppm (C=O). These data show that salt **XVI** exists in DMSO in the enol form with *cis*-location of the phosphoryl and ethoxycarbonyl groups with respect to the double bond.



XVI

Alkylation of freshly isolated compound **XVI** with methyl iodide was carried out at 60°C in the course of 7 h. We could not avoid the decomposition of salt, and significant amount of phosphonate **XI** was found in the reaction mixture. Besides, among the reaction products three substances were found with the signals of phosphorus atom at 20.981, 17.257, and 14.218 ppm. The intensity ratio of these signals was 1 : 0.42 : 0.18. In the ^{1}H NMR spectrum the main reaction product was characterized by a doublet at 1.891 ppm (CH_3, J_{PH}

16.0 Hz) and the furan proton signals with the corresponding intensity. Signals of the side chain carbon atom of the compound under consideration are observed at 18.675 ppm (CH_3, $^2J_{PC}$ 5.8 Hz), 51.081 ppm (P–C, $^1J_{PC}$ 139.5 Hz), 162.865 ppm (C=O, ester), and 193.023 ppm (C=O, ketone). From these data it follows that the main methylation product is ketophosphonate **XVIIa**. The second reaction product is characterized by the carbon atom signals at 57.326 ppm (OCH_3), 157.808 ppm (=C–O, $^2J_{PC}$ 26.6 Hz), and 162.155 ppm (C=O, $^3J_{PC}$ 5.9 Hz). These data permit assignment to it structure **XVIIb** with *trans*-location of the ester and phosphoryl groups. Signals of the side chain carbon atoms of the minor reaction product are located at 58.246 ppm (OCH_3), 162.645 ppm (=C–O), and 162.185 ppm (C=O). These spectral data correspond to the structure **XVIIb** with *cis*-location of the ester and phosphoryl groups. The carbon atom signals of the P–C= fragment are observed at 97.944 ppm ($^1J_{PC}$ 219.8 Hz) and 99.692 ppm ($^1J_{PC}$ 192.0 Hz), but their intensity is so small that is impossible to establish reliably which of them is more intense on the background of noises. Hence, methylation of sodium salt **XVI** can be described by the following scheme.



Summarizing the above data the following conclusions can be made. 2– And 3-furylmethanephosphonates possess sufficiently high CH-acidity to form the carbanions under the action of sodium ethylate. These carbanions are capable of addition to the ester carbonyl groups of ethyl formate, diethyl oxalate, and ethyl trifluoroacetate leading to the formation of phosphorylated derivatives of furylacetic aldehyde, ethyl furylpyruvate, and 1,1,1-trifluoro-3-(1-furyl)propan-2-one. In the chloroform solutions these compounds exist as mixtures of tautomers. While treating with bases these substances give salts similarly to 1,3-dicarbonyl derivatives. The salts of formyl and oxalyl derivatives of 2-furylmethanephosphonate in DMSO solutions give an equilibrium mixture of the carbanion and the enol forms. In the first case the carbanion form prevails, while in the second one the mixture of enol forms is the main product. Sodium salt of the formyl derivative of 3-furylmethanephosphonate exists only in the carbanion form, while the salt of its oxalyl analog is pure enolate. Alkylation of these salts with methyl iodide proceeds at the carbon as well as at the oxygen atom. First reaction pathway is often preferred. In contrast, the salts containing electron-acceptor substituent in the furan ring in the majority of cases exist in the carbanion form. Their alkylation proceeds exclusively at the oxygen atom.

EXPERIMENTAL

^1H, ^{13}C, and ^{31}P NMR spectra were taken on a Bruker DPX-400 spectrometer [400.13 (^1H), 161.97 (^{31}P) 100.16 MHz (^{13}C)]. Spectra of sodium salts were recorded in deuterated DMSO, in all the other cases $CDCl_3$ was used as a solvent.

(2-Furyl)(diethoxyphosphoryl)acetic aldehyde sodium salt (Ia, Ib). To the suspension of 0.8 g of sodium foil in 40 mL of toluene a mixture of 5.7 g of diethyl (2-furyl)methanephosphonate **I** and 4.2 mL of ethyl formate was added in one portion under the intense stirring. Dissolution of sodium proceeded in the course of 1 h, temperature of the reaction mixture rose to 70°C. After the completion of heat evolution and dissolution of sodium a precipitate began to form separate the reaction mixture. On the next day the reaction mixture was diluted with 40 mL of hexane, the crystals were filtered off and washed with hexane until the disappearance of coloration. Yield of the salt 5.5 g (84%), decomposition temperature 178°C. ^1H NMR spectrum, δ, ppm: common signals: 1.121 t (CH_3-ethyl, J_{HH} 7.2 Hz), 3.763-4.842 m (CH_2OP); **Ia**: 6.322 d (H^4-furan, J_{HH} 3.2 Hz), 6.219 d.d ((H^3-furan, J_{HH} 3.2 Hz, J_{PH} 1.6 Hz), 7.156 br.s (H^5-furan), 8.454 d (CHO, J_{PH} 2.8 Hz); **Ib**: 6.235 br.s (H^4-furan), 7.188 br.s (H^3-furan), 7.237 br.s (H^5-furan), 8.734 d (=CH–O,

J_{PH} 38.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: common signals: 16.779 (CH_3, $^3J_{PC}$ 6.6 Hz), 59.562 (CH_2OP, $^2J_{PC}$ 4.1 Hz); **Ia**: 79.790 (CP, $^1J_{PC}$ 200.0 Hz), 100.108 (C^3, $^3J_{PC}$ 7.2 Hz), 110.534 (C^4), 135.769 (C^5), 155.468 (C^2, $^2J_{PC}$ 4.1 Hz), 175.435 (CHO, $^2J_{PC}$ 19.6 Hz); **Ib**: 82.421 (=CP, $^1J_{PC}$ 216.0 Hz), 102.913 (C^3, $^3J_{PC}$ 8.0 Hz), 110.007 (C^4), 125.769 (C^5), 155.468 (C^2, $^2J_{PC}$ 9.0 Hz), 179.081 (=C–O, $^2J_{PC}$ 8.8 Hz). ^{31}P NMR spectrum, δ_P, ppm: 31.910 (**Ia**), 26.541 (**Ib**), intensity ratio of the signals 1 : 0.14.

(2-Furyl)(diethoxyphosphoryl)acetic aldehyde (II, IIa). To the suspension of 0.6 g of sodium foil in 40 mL of toluene a mixture of 4.1 g of phosphonate **I** and 3 mL of ethyl formate was added in one portion under the intense stirring. After the completion of heat evolution and dissolution of sodium the reaction mixture was left overnight. On the next day it was washed with water (3 × 10 mL), combined water extracts were washed with 10 mL of ether and acidified with dilute sulfuric acid to pH 3–4. The liberated oil was extracted with ether, dried over sodium sulfate, and distilled in a vacuum to give 2.0 g (43%) of aldehyde, bp 121°C (1 mmHg), mp 61–62°C. ^1H NMR spectrum, δ, ppm: common signals: 1.310 t (CH_3-ethyl, J_{HH} 7.2 Hz), 3.999–4.180 m (CH_2OP); **II**: 6.131 d (H^3-furan, J_{HH} 3.2 Hz), 6.335 d.d (H^4-furan, J_{HH} 3.2 Hz, 1.2 Hz), 7.291 d (H^5-furan, J_{HH} 1.2 Hz), 7.763 d.d (CHP, J_{HH} 13.3 Hz, J_{PH} 39.6 Hz), 11.274 (CHO, J_{HH} 13.3 Hz); **IIa**: 6.424 d.d (H^4-furan, J_{HH} 3.2 Hz, 1.2 Hz), 6.553 d (H^3-furan, J_{HH} 3.2 Hz), 7.401 d (H^5-furan, J_{HH} 1.2 Hz), 7.616 d (=CH, J_{PH} 10.8 Hz), 10.178 br.s (OH). ^{13}C NMR spectrum, δ_C, ppm: **II**: 16.053 (CH_3, $^3J_{PC}$ 6.7 Hz), 62.633 (CH_2OP, $^2J_{PC}$ 4.1 Hz), 92.010 (CHP, $^1J_{PC}$ 177.7 Hz), 105.049 (C^3), 110.050 (C^4), 140.740 (C^5), 148.066 (C^2, $^2J_{PC}$ 6.1 Hz), 161.626 (CHO); **IIa**: 16.132 (CH_3, $^3J_{PC}$ 6.9 Hz), 62.122 (CH_2OP, $^2J_{PC}$ 4.6 Hz), 94.172 (=C–P, $^1J_{PC}$ 197.0 Hz), 108.235 (C^3, $^3J_{PC}$ 3.7 Hz), 110.050 (C^4), 140.385 (C^5), 148.066 (C^2, $^2J_{PC}$ 13.1 Hz), 156.779 (=C–OH, $^2J_{PC}$ 19.7 Hz). ^{31}P NMR spectrum, δ_P, ppm: 21.782 (**II**), 20.048 (**IIa**), intensity ratio of the signals 1 : 0.27.

After drying of toluene layer and evaporation in a vacuum 0.3 g of starting phosphonate **I** was obtained.

Alkylation of sodium salt Ia, Ib with methyl iodide. To the suspension of 3 g of sodium salt **Ia, Ib** in 30 mL of acetonitrile 1.4 mL of methyl iodide was added, and the mixture obtained was stirred at 50–60°C for 8 h. On the next day the precipitate formed was filtered off, the filtrate was evaporated to dryness on a rotary evaporator, the residue was dissolved in methylene chloride, washed with water, dried over sodium sulfate, and distilled in a vacuum to give 1.4 g of the fraction with bp 146–18°C (1 mmHg). ^1H NMR spectrum, δ, ppm: non-attributed signals: 1.238 t (CH_3-ethyl, J_{HH} 7.2 Hz), 1.260 t (CH_3-ethyl, J_{HH} 7.2 Hz), 1.281 t (CH_3-ethyl, J_{HH} 7.2 Hz), 3.988–4.130 m (CH_2OP); **IIIa**: 3.938 s (CH_3O), 6.314 d.d (H^4-furan J_{HH} 3.2 Hz, 2.0 Hz), 6.541 d (H^3-furan, J_{HH} 3.2 Hz), 7.372 d (H^5-furan, J_{HH} 2.0 Hz), 7.118 d (=CH–O, J_{PH} 10.8 Hz); **IIIb**: 3.874 s (CH_3O), 6.374 d.d (H^4-furan, J_{HH} 3.0 Hz, 1.4 Hz), 6.448 d (H^3-furan, J_{HH} 3.0 Hz), 7.250 br.s (H^5-furan), 7.216 d (=CH–O, J_{PH} 32.8 Hz); **IIIc**: 1.671 d (CH_3, J_{PH} 16.0 Hz), 6.392 d.d (H^4-furan, J_{HH} 3.4 Hz, 1.8 Hz), 6.454 d (H^3-furan, J_{HH} 3.4 Hz), 7.440 br.s (H^5-furan), 9.797 s (CHO). ^{13}C NMR spectrum, δ_C, ppm: non-attributed signals: 16.167 (CH_3, $^3J_{PC}$ 6.4 Hz), 16.218 (CH_3, $^3J_{PC}$ 6.4 Hz), 61.912 (CH_2OP, $^2J_{PC}$ 4.2 Hz), 62.874 (CH_2OP, $^2J_{PC}$ 4.6 Hz), 63.412 (CH_2OP, $^2J_{PC}$ 7.2 Hz); **IIIa**: 61.891 (CH_3O), 96.768 (=C–P, $^1J_{PC}$ 190.1 Hz), 109.414 (C^3, $^3J_{PC}$ 6.2 Hz), 110.817 (C^4), 141.041 (C^5), 147.041 (C^2, $^2J_{PC}$ 6.1 Hz), 159.547 (=C–OH, $^2J_{PC}$ 21.4 Hz); **IIIb**: 62.292 (CH_3O), 98.633 (=C–P, $^1J_{PC}$ 182.9 Hz), 109.173 (C^3, $^3J_{PC}$ 6.1 Hz), 111.277 (C^4), 140.740 (C^5), 148.014 (C^2, $^2J_{PC}$ 8.3 Hz), 159.805 (=C–OH); **IIIc**: 14.190 (CH_3, $^2J_{PC}$ 5.2 Hz), 55.838 (CP, $^1J_{PC}$ 132.2 Hz), 107.474 (C^4), 110.737 (C^3, $^3J_{PC}$ 3.5 Hz), 142.984 (C^5), 148.961 (C^2, $^2J_{PC}$ 7.5 Hz), 194.253 (CHO). ^{31}P NMR spectrum, δ_P, ppm: 18.637 (**IIIa**), 13.700 (**IIIb**), 19.481 (**IIIc**), intensity ratio of the signals 1.65 : 1.09 : 1.

Alkylation of sodium salt Ia, Ib with epichlorohydrin. To the suspension of 2.4 g of sodium salt **Ia, Ib** in 20 mL of acetonitrile 1 mL of epichlorohydrin and 0.2 g of potassium iodide was added. The mixture obtained was heated with intense stirring for 7 h at 80°C and left overnight. On the next day the precipitate formed was filtered off, and acetonitrile was removed on a rotary evaporator. The residue was dissolved in chloroform, washed with brine, and dried over sodium sulfate. After removing the solvent and keeping for 1 h in a vacuum (1 mmHg) at room temperature light brown syrup was obtained. ^1H NMR spectrum, δ, ppm: 1.281 t (CH_3-ethyl, J_{HH} 7.0 Hz), 2.694–2.712 m (CH_2-oxirane), 2.850 t (CH_2–O, J_{HH} 4.8 Hz), 3.247–3.284 m (–CH–O-oxirane), 3.986 m (CH_2OP), 4.372 d (OCH_2-ether, J_{HH} 2.8 Hz), 4.401 d (OCH_2-ether, J_{HH} 2.8 Hz), 6.393 br.s (H^4-furan), 6.590 d (H^3-furan, J_{PH} 3.0 Hz), 7.158 d (=CH–O, J_{PH} 10.8 Hz), 7.387 br.s (H^5-furan). ^{13}C NMR spectrum,

δ_C, ppm: 16.175 (CH_3, $^3J_{PC}$ 6.5 Hz), 44.073 (CH_2-oxirane), 49.931 (CH-oxirane), 62.072 (CH_2OP, $^2J_{PC}$ 4.6 Hz), 74.826 (OCH_2), 97.499 (=C–P, $^1J_{PC}$ 189.8 Hz), 109.797 (C^3, $^3J_{PC}$ 6.4 Hz), 110.906 (C^4), 141.158 (C^5), 146.834 (C^2, $^2J_{PC}$ 5.4 Hz), 157.868 (=C–OH, $^2J_{PC}$ 21.7 Hz). ^{31}P NMR spectrum, δ_P, ppm: 18.251.

Reaction of phosphonate I with diethyl oxalate. The mixture of 3.4 g of phosphonate **I** and 2.8 mL of diethyl oxalate was added in one portion to the suspension of 0.4 g of freshly prepared sodium foil in 20 mL of toluene. Temperature of the reaction mixture in the course of 10 min rose from 19 to 36°C. Complete dissolution of sodium was achieved in the course of 1 h. On the next day the reaction mixture was extracted with water (3 × 15 mL), combined extracts were acidified to pH 2 with dilute sulfuric acid, extracted with methylene chloride, and dried over sodium sulfate. After removing the solvent, 3.4 g of light brown syrup was obtained. ^{1}H NMR spectrum, δ, ppm: common signals: 1.198 t (CH_3-ethyl, J_{HH} 7.2 Hz), 1.273 t (CH_3-ethyl, J_{HH} 7.2 Hz), 1.312 t (CH_3-ethyl, J_{HH} 7.2 Hz), 4.119 m (CH_2OP, J_{HH} 7.2 Hz, J_{PH} 14.0 Hz), 4.211 q (CH_2OCO, J_{HH} 7.2 Hz), 4.342 q (CH_2OCO, J_{HH} 7.2 Hz); **Va**: 6.243 d.d (H^4-furan, J_{HH} 3.2 Hz, 2.0 Hz), 6.371 d.d (H^3-furan, J_{HH} 3.2 Hz, J_{PH} 2.0 Hz), 7.361 d (H^5-furan, J_{HH} 2.0 Hz), 12.199 br.s (OH); **Vb**: 5.683 d (CHP, J_{PH} 26.4 Hz), 6.394 d.d (H^4-furan, J_{HH} 3.2 Hz, 1.6 Hz), 6.595 d.d (H^3-furan, J_{HH} 3.2 Hz, J_{PH} 3.2 Hz), 7.413 br.s (H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: common signals: 13.848 (CH_3-ester), 13.903 (CH_3-ester), 16.015 (CH_3-phosphonate, $^3J_{PC}$ 6.6 Hz), 16.172 (CH_3-phosphonate, $^3J_{PC}$ 5.6 Hz), 62.205 (CH_2O-ester), 63.164 (CH_2O-ester), 63.265 (CH_2OP, $^2J_{PC}$ 4.6 Hz), 63.739 (CH_2OP, $^2J_{PC}$ 6.9 Hz), 63.328 (CH_2OP, $^2J_{PC}$ 6.9 Hz); **Va**: 91.287 (=C–P, $^1J_{PC}$ 176.2 Hz), 109.194 (C^3, $^3J_{PC}$ 3.7 Hz), 111.196 (C^4), 142.160(C^5), 145.634 (C^2, $^2J_{PC}$ 8.3 Hz), 161.583 (C=O-ester, $^3J_{PC}$ 7.0 Hz), 163.007 (=C–O, $^2J_{PC}$ 23.0 Hz); **Vb**: 47.666 (CH–P, $^1J_{PC}$ 130.8 Hz), 110.691 (C^3, $^3J_{PC}$ 5.7 Hz), 111.076 (C^4), 142.840(C^5), 143.007 (C^2, $^2J_{PC}$ 7.9 Hz), 160.240 (C=O-ester), 186.806 (C=O). ^{31}P NMR spectrum, δ_P, ppm: 21.564 (**Va**), 14.225 (**Vb**), intensity ratio 1 : 0.35.

Oxalyl phosphonate sodium salt VIa–VIc. Oxalyl phosphonate **Va, Vb** (1.8 g) was dissolved in 15 mL of anhydrous ethanol, and a solution of sodium ethylate prepared from 0.15 g of sodium and 5 mL of anhydrous ethanol was added in one portion. The mixture obtained was evaporated to dryness and treated with 2 : 1 mixture of hexane and ether. Yellowish brown crystals were obtained which under the action of air covered with a red-brown film within 2–3 min. Yield 1.2 g. ^{1}H NMR spectrum, δ, ppm: common signals: 1.010 t (CH_3-ethyl, J_{HH} 7.2 Hz), 1.094 t (CH_3-ethyl, J_{HH} 7.2 Hz), 1.126 t (CH_3-ethyl, J_{HH} 7.2 Hz), 1.183 t (CH_3-ethyl, J_{HH} 7.2 Hz), 3.729–3.999 m (CH_2O-ester, CH_2OP); **VIa**: 6.230 br.s (H^3-furan), 6.324 br.d (H^4-furan, J_{HH} 2.8 Hz), 7.208 br.s (H^5-furan); **VIb**: 5.787 d.d (H^3-furan, J_{HH} 2.6 Hz, J_{PH} 2.6 Hz), 6.219–6.240 m (H^4-furan, overlap), 7.315 br.s (H^5-furan); **VIc**: 6.219–6.240 m (H^4-furan, overlap), 6.402 d.d (H^3-furan, J_{HH} 2.4 Hz, J_{PH} 2.4 Hz), 7.503 br.s (H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: common signals: 14.448 (CH_3-ester), 16.660 (CH_3-phosphonate, $^3J_{PC}$ 6.5 Hz), 16.689 (CH_3-phosphonate, $^3J_{PC}$ 6.0 Hz); **VIa**: 59.084 (OCH_2), 60.174(CH_2OP, $^2J_{PC}$ 4.6 Hz), 74.431 (=C–P, $^1J_{PC}$ 203.3 Hz), 106.832 (C^3, $^3J_{PC}$ 5.3 Hz), 110.778 (C^4), 140.223 (C^5), 155.002 (C^2, $^2J_{PC}$ 6.8 Hz), 169.787 (C=O-ester), 176.657 (=C–O, $^2J_{PC}$ 11.9 Hz); **VIb**: 59.248 (OCH_2), 59.595 (CH_2OP, $^2J_{PC}$ 3.6 Hz), 74.912 (=C–P, $^1J_{PC}$ 196.0 Hz), 102.110 (C^3, $^3J_{PC}$ 6.8 Hz), 110.493 (C^4), 136.752 (C^5), 154.800 (C^2, $^2J_{PC}$ 10.8 Hz), 169.329 (C=O-ester, $^3J_{PC}$ 25.9 Hz), 175.465 (=C–O, $^2J_{PC}$ 21.7 Hz); **VIc**: 17.077 (CH_3-phosphonate, $^3J_{PC}$ 6.3 Hz), 59.672 (OCH_2), 62.069 (CH_2OP, $^2J_{PC}$ 6.3 Hz), 88.566 (C–P, $^1J_{PC}$ 217.8 Hz), C^3 overlaps with one of the main products, 111.274 (C^4), 138.275 (C^5), 152.846 (C^2, $^2J_{PC}$ 5.4 Hz), 176.216 (C=O-ester), 193.356 (C=O). ^{31}P NMR spectrum, δ_P, ppm: 28.250 (**VIa**), 26.438 (**VIb**), 23.257 (**VIc**), intensity ratio 1 : 1.06 : 0.16.

Alkylation of sodium salt VIa–VIc with methyl iodide. Sodium salt **VIa–VIc** (1.2 g) was dissolved in 15 mL of acetonitrile, 1 mL of methyl iodide was added, and the reaction mixture was heated with stirring for 10 h at 60°C. The mixture obtained was evaporated on a rotary exaporator, dissolved in methylene chloride, washed with water (2 × 5 mL), and dried over sodium sulfate. After that the solution was evaporated to dryness on the rotary evaporator. The residue was dissolved in ether, and the crystals formed were filtered off. Ether was evaporated, and the residue was recondensated for 2 h in a vacuum (1 mmHg) at 90–110°C to give a light brown oil. ^{1}H NMR spectrum, δ, ppm: common signals: 1.073–1.319 m (CH_3-ethyl), 3.874–4.126 m (CH_2O-ester, CH_2OP); **I**: 3.180 d (CH_2P, J_{PH} 20.8 Hz), 6.175 br.s (H^3-furan), 6.268 br.s (H^4-furan), 7.288 br.s (H^5-furan); **VII**: 1.479 d.d (CH_3, J_{HH} 7.6 Hz, J_{PH} 17.6 Hz), 3.271 d.q (CH, J_{HH} 7.6 Hz, J_{PH} 24.8 Hz), 6.175 br.s (H^3-furan), 6.268 b.s

(H^4-furan), 7.288 br.s (H^5-furan); **VIII**: 1.909 d (CH_3, J_{PH} 16.0 Hz), 6.350 d.d (H^4-furan, J_{HH} 3.2 Hz, 2.0 Hz), 6.432 d.d (H^3-furan, J_{HH} 3.2 Hz, J_{PH} 3.2 Hz), 7.378 br.s (H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: common signals: 16.020 (CH_3-phosphonate, $^3J_{PC}$ 6.6 Hz), 17.660 (CH_3-phosphonate, $^3J_{PC}$ 5.9 Hz), 62.053, 62.143, 62.220, 62.286, 62.319, 62.390 (CH_2O + CH_2OP); **I**: 26.653 (CH_2P, $^1J_{PC}$ 149.2 Hz), 108.145 (C^3, $^3J_{PC}$ 7.3 Hz), 110.738 (C^4), 141.831(C^5, $^4J_{PC}$ 2.7 Hz), 145.550 (C^2, $^2J_{PC}$ 9.4 Hz); **VII**: 13.526 (CH_3, $^2J_{PC}$ 4.7 Hz), 32.342 (CHP, $^1J_{PC}$ 141.9 Hz), 106.924 (C^3, $^3J_{PC}$ 7.2 Hz), 110.524 (C^4), 141.544 (C^5, $^4J_{PC}$ 2.7 Hz), 151.347 (C^2, $^2J_{PC}$ 8.5 Hz); **VIII**: 13.718 (CH_3-ester), 13.819 (CH_3-CP, broad), 54.134 (CP, $^1J_{PC}$ 141.2 Hz), 109.731 (C^3, $^3J_{PC}$ 5.0 Hz), 111.206 (C^4), 142.849(C^5), 147.881 (C^2, $^2J_{PC}$ 5.3 Hz), 161.329 (C=O-ester), 190.881 (C=O ketone). ^{31}P NMR spectrum, δ_P, ppm: 26.618 (**VII**), 23.108 (**I**), 18.922 (**VIII**), intensity ratio 1 : 0.64 : 0.56.

Reaction of phosphonate I with ethyl trifluoroacetate. To the suspension of 0.7 g of freshly prepared sodium foil in 30 mL of toluene a mixture of 5.1 g of phosphonate **I** and 6 mL of ethyl trifluoroacetate was added dropwise with stirring. In the course of this operation the temperature of the reaction mixture rose from 19 to 29°C, but then the heat evolution ceased. After the addition was complete the reaction mixture was heated to 55–60°C, and at this temperature heat evolution took place again. The temperature of the reaction mixture reached 65–70°C. When heat evolution stopped, the temperature of the reaction mixture was maintained at 65-70°C until the complete dissolution of sodium which was achieved in the course of 2 h. After that the reaction products were extracted with water (3 × 7 mL), the extract was acidified with hydrochloric acid to pH 2–3 and extracted with chloroform (3 × 15 mL). Combined organic layers were dried over sodium sulfate, the solvent was removed and the residue was distilled in a vacuum. The fraction with bp 111–112°C (1 mmHg) was collected. ^1H NMR spectrum, δ, ppm: common signals: 1.224–1.284 m (CH_3-ethyl), 4.002–4.113 m (CH_2OP); **I**: 3.208 d (CH_2P, J_{PH} 20.8 Hz), 6.202 d.d (H^3-furan, J_{HH} 3.4 Hz, J_{PH} 3.4 Hz), 6.353 d.d (H^4-furan, J_{HH} 3.4 Hz, 1.8 Hz), 7.283 br.s (H^5-furan); **IX**: 6.252 d.d (H^3-furan, J_{HH} 3.2 Hz, J_{PH} 3.2 Hz), 6.353 d.d (H^4-furan, J_{HH} 3.2 Hz, 1.8 Hz), 7.392 br.s (H^5-furan), 12.433 br.s (OH); **X**: 5.041 d (CHP, J_{PH} 24.0 Hz), 6.381 d.d (H^3-furan, J_{HH} 3.2 Hz, J_{PH} 4.0 Hz), 6.543 d.d (H^4 -furan , J_{HH} 3.2 Hz, 1.8 Hz), 7.392 br.s (H^5-furan). ^{13}C NMR spectrum, δ_C, ppm: **I**: 16.197 (CH_3, $^3J_{PC}$ 7.3 Hz), 26.525 (CH_2P, $^1J_{PC}$ 143.0 Hz), 62.380 (CH_2OP, $^2J_{PC}$ 6.6 Hz), 108.199 (C^3, $^3J_{PC}$ 7.4 Hz), 110.730 (C^4, $^4J_{PC}$ 2.4 Hz), 141.861 (C^5, $^4J_{PC}$ 2.9 Hz), 145.474 (C^2, $^2J_{PC}$ 9.4 Hz); **IX**: 15.871 (CH_3, $^3J_{PC}$ 6.5 Hz), 63.637 (CH_2OP, $^2J_{PC}$ 5.1 Hz), 92.051 (P-C=, $^1J_{PC}$ 176.3 Hz), 111.030 + 111.213 (C^3,C^4), 143.070 (C^5), 142.710 (C^2, $^2J_{PC}$ 1.9 Hz), 149.379 (C^2, $^2J_{PC}$ 2.2 Hz) (probably the conformers), 159.273 d.q (=C–CF_3, $^2J_{PC}$ 9.9 Hz, $^2J_{FC}$ 34 Hz); **X**: 16.069 (CH_3, $^3J_{PC}$ 5.7 Hz), 43.515 (CHP, $^1J_{PC}$ 136.6 Hz), 46.994 (CHP, $^1J_{PC}$ 135.2 Hz), 63.840 (CH_2OP, $^2J_{PC}$ 6.7 Hz), 64.114 (CH_2OP, $^2J_{PC}$ 6.9 Hz), 98.171 (C^4), 110.429 (C^3, $^3J_{PC}$ 5.9 Hz), 110.898 (C^3, $^3J_{PC}$ 6.0 Hz), 142.281 (C^5), 141.661 (C^2, $^2J_{PC}$ 8.7 Hz), 165.334 (C=O); CF_3 group (not attributed): 118.808 ($^1J_{FC}$ 271.5 Hz), 119.072 ($^1J_{FC}$ 277.0 Hz). ^{19}F NMR spectrum, δ_F, ppm: –68.033 (**IX**), –77.422 (**X**), signal intensity ratio 2.5 : 1. ^{31}P NMR spectrum, δ_P, ppm: 20.434 (**IX**), 12.986 (**X**), signal intensity ratio 2.6 : 1.

Reaction of phosphonate XI with ethyl formate. *a*. To the suspension of 0.12 g of freshly prepared sodium foil in 10 mL of toluene the mixture of 0.9 g of phosphonate **XI** and 0.7 mL of ethyl formate was added in one portion. The mixture obtained was heated for 6 h at 60°C until the complete dissolution of sodium. The reaction products were extracted with water (2 × 5 mL), the water extract was washed with ether and acidified with the diluted hydrochloric acid to pH 3. The liberated oil was extracted with methylene chloride (3 × 10 mL) and dried over sodium sulfate. The solvent was removed on a rotary evaporator, the residue was kept in a vacuum for 1 h at room temperature and the residual pressure 1 mm. Light brown oil, 0.4 g, was obtained. ^1H NMR spectrum, δ, ppm: common signals: 1.263 m (CH_3-ethyl), 4.048 m (CH_2OP), **XI**: 2.937 (CH_2P, J_{PH} 20.8 Hz), 6.298 br.s (H^4-furan), 7.256, 7.259 br.s ($H^{2,5}$-furan), **XII**: 6.763 br.s (H^4-furan), 7.354 br.s (H^5), 7.542 d (CH=, J_{PH} 10.4 Hz), 7.776 s (H^2-furan), 11.071 br.s (OH). The signal at 2.909 ppm, br.d (CH_2P, J_{PH} 20.4 Hz) belonged evidently to monoester formed in the course of hydrolysis of phosphonate **XI**. ^{31}P NMR spectrum, δ_P, ppm: 26.657 (**XI**), 23.789 (monoester), 18.026 (**XII**), signal intensity ratio 10.6 : 5.9 : 1. The toluene layer obtained after extraction was dried by azeotropic distillation with the Dean-Stark trap, toluene was removed at the reduced pressure, and the residue was kept in a vacuum for 1 h (room temperature, 1 mm Hg) to give 0.4 g of phosphonate **XI**. ^1H NMR spectrum, δ, ppm: 1.166 t (CH_3-ethyl, J_{HH} 7.2 Hz), 2.837 d (CH_2P,

J_{PH} 20.8 Hz), 3.964 m (CH_2OP J_{HH} 7.2 Hz, J_{PH} 14.8 Hz), 6.294 br.s (H^4-furan), 7.256 br.s, 7.259 br.s ($H^{2,5}$ -furan). ^{13}C NMR spectrum, δ_C, ppm: 16.504 (CH_3, $^3J_{PC}$ 5.9 Hz), 22.863 (CH_2P, $^1J_{PC}$ 143.1 Hz), 61.957 (CH_2OP, $^2J_{PC}$ 6.5 Hz), 111.738 (C^4, $^3J_{PC}$ 4.5 Hz), 114.617 (C^3, $^2J_{PC}$ 9.1 Hz), 140.577 (C^2, $^3J_{PC}$ 11.0 Hz), 142.835 (C^2). ^{31}P NMR spectrum, δ_P, ppm: 26.282.

b. The mixture of 1.0 g of phosphonate **XI** and 0.8 mL of ethyl formate was added in one portion to the suspension of 0.13 g of sodium foil in 10 mL of toluene. The mixture obtained was heated for 6 h at 60°C. After the complete dissolution of sodium the reaction mixture was evaporated to dryness on a rotary evaporator and treated with anhydrous ether. Yellow crystals of sodium salt **XIII**, 0.4 g, were obtained. At the exposure to air they immediately darkened and melt. In the NMR spectra in DMSO signals of the salt **XIII** are observed together with the signals of starting phosphonate formed by the hydrolysis of salt with the traces of water. ^1H NMR spectrum, δ, ppm: common signals: 1.051–1.125 m (CH_3-ethyl), 4.002–4.113 m (CH_2OP); **XIII**: 6.593 s (H^4-furan), 7.995 br.s (H^5-furan), 8.342 br.s (H^2-furan), 8.381 d (CHO, J_{PH} 2.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.832 (CH_3, $^3J_{PC}$ 6.9 Hz), 59.393 (CH_2OP, $^2J_{PC}$ 2.1 Hz), 84.318 (CP, $^1J_{PC}$ 224.5 Hz), 110.521 (C^4), 124.875 (C^3, $^2J_{PC}$ 5.5 Hz), 142.111 (C^5), 148.564 (C^2, $^3J_{PC}$ 13.7 Hz), 177.199 (CHO, $^2J_{PC}$ 24.4 Hz). 31P NMR spectrum: 34.400 (**XIII**).

Reaction of salt XIII with methyl iodide. Freshly prepared sodium salt, 0.4 g, was suspended in 8 mL of acetonitrile, 1 mL of methyl iodide was added, and the mixture obtained was heated for 10 h at 60–70°C. After that the reaction mixture was evaporated to dryness on a rotary evaporator and treated with a mixture of 5 mL of water and 15 mL of methylene chloride with the addition of 0.2 g of sodium sulfite. Water layer was removed, and the organic layer was washed with 5 ml of water and dried over sodium sulfate. After that the solvent was removed at a reduced pressure, and the residue was evacuated for 1 h at room temperature and the residual pressure 1 mmHg. Light brown oil was obtained. ^1H NMR spectrum, δ, ppm: common signals: 1.250–1.301 m (CH_3-ethyl), 3.698 d (CH_3OP, J_{PH} 10.8 Hz), 4.018–4.130 m (CH_2OP); **XI**: 2.956 d (CH_2P, J_{PH} 20.8 Hz), 6.404 br.s (H^4-furan), 7.367 br.s ($H^{2,5}$-furan), signals of methyl ester 2.946 d (CH_2P, J_{PH} 20.8 Hz), 3.698 d (CH_3OP, J_{PH} 10.8 Hz); **XIV**: 3.933 s (OCH_3), 6.731 br.s (H^4-furan), 7.125 d (=CH–O, J_{PH} 10.4 Hz), 7.367 br.s (H^5-furan), 7.737 br.s (H^2-furan). ^{13}C NMR spectrum, δ_C, ppm: common signals: 16.229 (CH_3-phosphonate, $^3J_{PC}$ 6.8 Hz), 16.375 (CH_3-phosphonate, $^3J_{PC}$ 5.8 Hz), 61.613 (CH_2OP, $^2J_{PC}$ 4.5 Hz), 62.096 (CH_2OP, $^2J_{PC}$ 6.5 Hz), 62.331 (CH_2OP, $^2J_{PC}$ 6.5 Hz), 63.301 (CH_2OP, $^2J_{PC}$ 5.5 Hz); **XI** + mixed ester: 22.568 (CH_2P, $^1J_{PC}$ 143.3 Hz), 111.773 (C^4, $^3J_{PC}$ 4.8 Hz), 111.822 (C^4, $^3J_{PC}$ 5.1 Hz), 114.509 (C^3, $^2J_{PC}$ 9.0 Hz), 114.686 (C^3, $^2J_{PC}$ 9.2 Hz), 140.700 (C^2, $^3J_{PC}$ 11.0 Hz), 142.938 (C^5), 143.012 (C^5); **XIV** + mixed ester: 61.654 (OCH_3), 96.464 (P–C=, $^1J_{PC}$ 191.1 Hz), 110.393 (C^4, $^3J_{PC}$ 6.6 Hz), 116.559 (C^3, $^2J_{PC}$ 7.6 Hz), 141.319 (C^5), 141.398 (C^2, $^3J_{PC}$ 10.3 Hz), 153.632 (=CH–O, $^2J_{PC}$ 24.7 Hz). ^{31}P NMR spectrum, δ_P, ppm: 27.650 (**XI**), 26.398 (mixed ester); 21.434 (**XIV**), 21.627 (mixed ester); signal intensity ratio 1 : 0.46 : 0.39 : 0.11.

Reaction of phosphonate XI with diehyl oxalate. To the solution of 2.2 g of phosphonate **XI** and 1.8 mL of diethyl oxalate in 25 mL of toluene 0.3 g of freshly prepared sodium foil was added. The temperature of the reaction mixture rose from 19 to 32°C, and then in the course of 2 h it gradually decreased to 25°C. Complete dissolution of sodium was achieved in the course of 6 h. Toluene was removed from the reaction mixture, the residue was dissolved in ether and extracted with water (2 × 10 mL). The extract obtained was acidified with diluted hydrochloric acid to pH 3, the liberated oil was extracted with chloroform (3 × 15 mL) and dried over sodium sulfate. Solvent was removed at a reduced pressure, and the residue was evacuated (1 mmHg) for 1 h at room temperature to give 1.8 g of brown oil. ^1H NMR spectrum, δ, ppm: common signals: 1.129–1.367 m (CH_3-ethyl), 3.977–4.173 m (CH_2OP); **XI**: 2.947 d (CH_2P, J_{PH} 20.8 Hz), 6.376 br.s (H^4-furan), 7.343 br.s ($H^{2,5}$-furan), **XVa**: 4.316 q (CH_2OOC, J_{HH} 7.2 Hz), 5.441 d (CHP, J_{PH} 27.2 Hz), 6.536 s (H^4-furan), 7.386 s (H^5-furan), 7.611 s (H^2-furan); **XVb**: 6.274 s (H^4-furan), 7.295 s (H^5-furan), 7.434 s (H^2-furan), 9.753 br.s (OH). ^{13}C NMR spectrum, δ_C, ppm: **XI**: 16.301 (CH_3-phosphonate, $^3J_{PC}$ 5.9 Hz), 22.728 (CH_2P, $^1J_{PC}$ 143.3 Hz), 62.314 (CH_2OP, $^2J_{PC}$ 6.6 Hz), 111.788 (C^4, $^3J_{PC}$ 4.8 Hz), 114.457 (C^3, $^2J_{PC}$ 9.0 Hz), 140.738 (C^2, $^3J_{PC}$ 10.5 Hz), 142.964 (C^5); **XVa**: 13.893 (CH_3-ester), 16.154 (CH_3-phosphonate, $^3J_{PC}$ 5.9 Hz), 44.683 (CHP, $^1J_{PC}$ 129.5 Hz), 63.068 (CH_2O-ester), 63.683 (CH_2OP, $^2J_{PC}$ 7.0 Hz), 63.784 (CH_2OP, $^2J_{PC}$ 7.3 Hz), 111.444 (C^4, $^3J_{PC}$ 3.5 Hz), 113.506 (C^3, $^2J_{PC}$ 9.4 Hz), 141.900 (C^2, $^3J_{PC}$ 8.9 Hz), 142.898 (C^5), 160.438 (C=O ester), 186.766 (C=O

ketone, $^2J_{PC}$ 5.0 Hz), **XVb**: 13.655 (CH_3-ester), 16.068 (CH_3-phosphonate, $^3J_{PC}$ 7.7 Hz), 61.876 (CH_2O-ester), 62.976 (CH_2OP, $^2J_{PC}$ 5.0 Hz), 90.753 (=C–P, $^1J_{PC}$ 176.0 Hz), 111.660 (C^4, $^3J_{PC}$ 3.6 Hz), 116.371 (C^3, $^2J_{PC}$ 4.6 Hz), 140.821 (C^2, $^3J_{PC}$ 6.0 Hz), 142.812 (C^5), 160.029 (C=O-ester, $^3J_{PC}$ 8.3 Hz), 163.102 (=C–O, $^2J_{PC}$ 24.6 Hz). ^{31}P NMR spectrum, δ_P, ppm: 26.625 (**XI**), 22.791 (**XVb**), 16.512 (**XVa**), signal intensity ratio 0.5 : 0.29 : 1.

Ethyl (3-furyl)(diethoxyphosphoryl)pyruvic acid sodium salt (XVI). A mixture of phosphonates **XI, XV** (1.5 g) obtained by condensation was treated with the sodium ethylate solution prepared from 0.1 g of sodium and 10 mL of anhydrous ethanol. The mixture obtained was evaporated to dryness on a rotary evaporator, and the residue was immediately treated with 1 : 3 hexane–ether mixture. Light yellow crystals of sodium salt **XVI** were formed. At the exposure to air they quickly covered with brown film and melt. Freshly prepared product containing significant amount of residual solvent which prevented it from coloration was used in further transformations. ^{1}H NMR spectrum, δ, ppm: **XVI**: 1.075–1.128 m (CH_3-phosphonate), 1.175 t (CH_3-ester J_{HH} 7.2 Hz), 3.687–3.838 m (CH_2OP), 3.912 q (CH_2OOC, J_{HH} 7.2 Hz), 6.596 s (H^4-furan), 7.295 s (H^5-furan), 8.023 s (H^2-furan). ^{13}C NMR spectrum, δ_C, ppm: **XVI**: 15.603 (CH_3-ester), 16.732 (CH_3-phosphonate, $^3J_{PC}$ 6.7 Hz), 59.001 (CH_2O-ester), 59.371 (CH_2OP, $^2J_{PC}$ 3.2 Hz), 72.385 (P–C=, $^1J_{PC}$ 199.5 Hz), 111.020 (C^4, $^3J_{PC}$ 3.1 Hz), 122.624 (C^3, $^2J_{PC}$ 11.6 Hz), 137.082 (C^2, $^3J_{PC}$ 13.8 Hz), 139.651 (C^5), 170.078 (C=O), 175.154 (=C–O, $^2J_{PC}$ 22.1 Hz). ^{31}P NMR spectrum, δ_P, ppm: 30.947 (**XVI**). Signals of phosphonate **XI** accumulating in solution due to hydrolysis of the salt **XVI** are not presented.

Reaction of the salt XVI with methyl iodide. About 2 g of salt **XVI** containing residual solvent was suspended in 20 mL of acetonitrile, 2 mL of methyl iodide was added, and the mixture obtained was stirred for 7 h at 60°C. Then reaction mixture was evaporated on a rotary evaporator, the residue was dissolved in methylene chloride, washed with water, and dried over sodium sulfate. After that the solvent was distilled off, and the residue was kept in a vacuum (1 mmHg) for 1 h at room temperature. Yellow oil was obtained. ^{1}H NMR spectrum, δ, ppm: common signals: 1.172–1.275 m (CH_3), 3.922–4.178 m (CH_2OOC + CH_2OP); **XVIIa**: 1.891 d (CH_3, J_{PH} 16.0 Hz), 6.503 s (H^4-furan), 7.380 s (H^5-furan), 7.505 s (H^2-furan); **XVIIb**: 3.789 s (CH_3O), 6.6576 s (H^4-furan), 7.329 s (H^5-furan), 7.701 s (H^2-furan); **XVIIc**: 3.271 s (CH_3O), 6.6576 s (H^4-furan), 7.329 s (H^5-furan), 7.701 s (H^2-furan). ^{13}C NMR spectrum, δ_C, ppm: common signals: 13.516, 13.735, 13.855, 14.030 (CH_3-ester), 16.096 (CH_3-phosphonate, $^3J_{PC}$ 6.6 Hz), 16.212 (CH_3-phosphonate, $^3J_{PC}$ 5.2 Hz), 16.264 (CH_3-phosphonate, $^3J_{PC}$ 5.2 Hz), 16.313 (CH_3-phosphonate, $^3J_{PC}$ 5.6 Hz), 62.024, 62.189 (CH_2O-ester), 61.824 (CH_2OP, $^2J_{PC}$ 4.2 Hz), 62.059 (CH_2OP, $^2J_{PC}$ 7.0 Hz), 63.429 (CH_2OP, $^2J_{PC}$ 7.5 Hz), 63.504 (CH_2OP, $^2J_{PC}$ 7.9 Hz); **XVIIa**: 18.675 (CH_3, $^2J_{PC}$ 5.8 Hz), 51.083 (PC, $^1J_{PC}$ 139.5 Hz), 110.615 (C^4, $^3J_{PC}$ 3.7 Hz), 119.865 (C^3, $^2J_{PC}$ 6.5 Hz), 141.603 (C^2, $^3J_{PC}$ 7.3 Hz), 143.016 (C^5), 162.865 (C=O ester), 193.023 (C=O ketone); **XVIIb**: 57.326 (CH_3O), 111.126 (C^4, $^3J_{PC}$ 5.0 Hz), 116.529 (C^3, $^2J_{PC}$ 6.6 Hz), 141.460 (C^5), 142.521 (C^2, $^3J_{PC}$ 9.8 Hz), 157.808 (=C–O, $^2J_{PC}$ 26.6 Hz), 162.155 (C=O, $^3J_{PC}$ 5.9 Hz); **XVIIc**: 58.246 (CH_3O), 112.455 (C^4), 116.529 (C^3), 142.375 (C^5), 145.415 (C^2, $^3J_{PC}$ 9.8 Hz), 162.185 (C=O), 162.645 (=C–O). ^{31}P NMR spectrum, δ_P, ppm: 20.981 (**XVIIa**), 17.257 (**XVIIb**), 14.218 (**XVIIc**), signal intensity ratio 1.00 : 0.42 : 0.18.

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