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Formylation of Alkyl Cyanofurylmethanphosphonates at the Active Methylene Group

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Abstract—Alkyl cyanofurylmethanephosphonates are formylated with ethyl formate in the presence of sodium foil to form sodium derivatives of phosphonoacetic aldehyde. If phosphonoacetic aldehyde and nitrile groups occupy remote positions in the furan ring, the sodium derivative in DMSO solution exists in the form of carbanion carrying charge on the carbon atom adjacent to the aldehyde group. If the substituents are located at the adjacent carbons of furan ring, the solution equilibrium between the carbanionic (major product) and *Z*-enolate forms of salts is established. Alkylation of the formed salts with methyl iodide occurs exclusively at the oxygen atom to give methyl enolates. In most cases, a mixture of *E*-and *Z*-isomers is formed, the E one being prevailing. In the case of 2,5-location of the substituents in furan ring, the sodium salt is inactive, and the alkylation does not occur.

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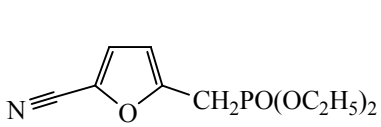
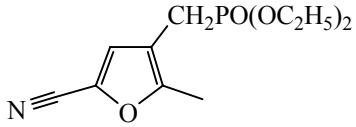
It has been shown that alkyl (ethoxycarbonylfuryl)-methanephosphonates can be formylated with ethyl formate under the conditions of the Claisen reaction, thus giving phosphonoacetaldehyde derivatives [1]. Extending that study, the derivatives of furylmethanephosphonic acid carrying the acidifying acceptor substituent, cyano group, in the furan ring have been tested as substrate of the same reaction. A similar modification of the Claisen reaction has been recently mentioned with *p*-cyanobenzylphosphonate as the substrate [2], however, the reaction has not been thoroughly studied.

The aim of this work was to investigate the effect of the substituents positions in the furan ring on the above-mentioned formylation reaction pathway and the structure of its products; the features of the so formed sodium salts alkylation was in the focus of the study as well. The latter issue was of special interest: it was shown that the sodium salts of (ethoxycarbonylfuryl)methanephosphonates formyl derivatives existed in solution majorly in the carbanion form and were alkylated exclusively at the oxygen atom to give alkyl enolates [1]. It was of practical importance to clear out whether such behavior was a special case, or it was a reflection of general feature of α-phosphorylated aldehydes as compared with 1,3-dicarbonyl compounds.

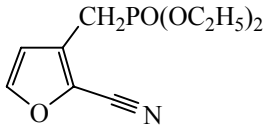
The studied substrates of the formylation reaction were nitrile derivatives of furylmethanephosphonic acids **I–VI** covering all the possible locations of phosphonomethyl and nitrile groups in the furan ring.



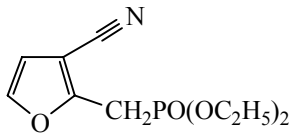
I



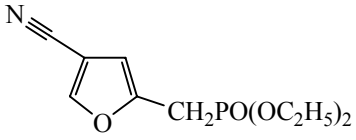
II



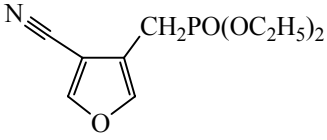
III



IV

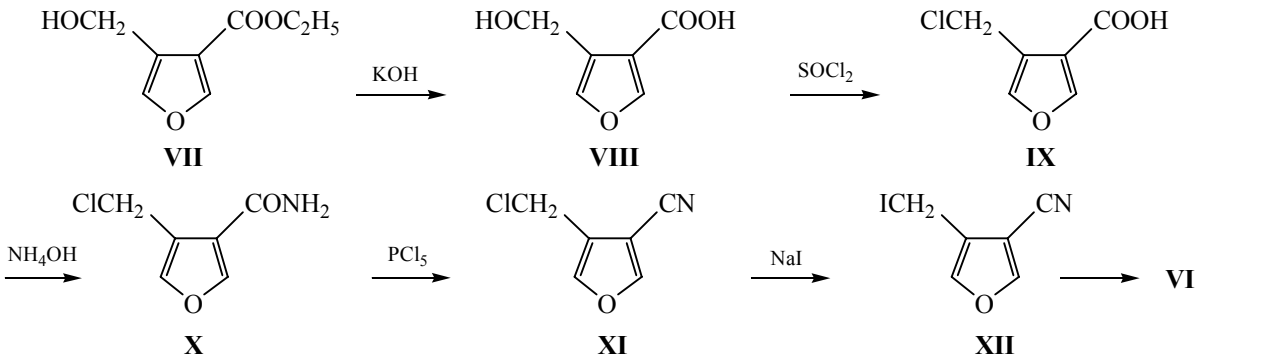


V



VI

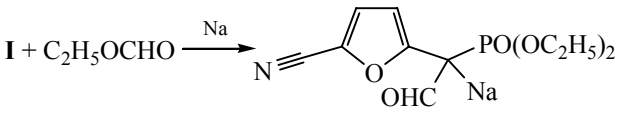
Synthesis of compounds **I–V** was reported previously [3], whereas **VI** was prepared via a newly designed pathway starting from alkyl 4-hydroxymethylfuran-3-carboxylate **VII** described in [4].



Using of the iodide **XII** was necessary because chloride **XI** did not participate smoothly in the Arbuzov and the Michaelis–Becker reactions, thus the target com-pound **VI** could be obtained only in poor yield. On the contrary, under the conditions of the Arbuzov reaction iodide **XII** within 7–8 min gave the target phosphonate **VI** which was isolated by vacuum distillation with 62% yield. Details of the synthesis are given in the Experimental part.

Similarly to reported previously, formylation of phosphonates **I–VI** was performed in the toluene medium at phosphonate : sodium : ethyl formate ratio of 1:1.2:2. Formylation of **I** proceeded exothermically, and the reaction mixture temperature grew up to 50–55°C. The product was extracted with water, the extract was evaporated in a vacuum to dryness, and the residue was dissolved in ethanol to remove insoluble sodium formate. Evaporation of the ethanol solution in vacuum to dryness and further rubbing up of the residue with hexane gave sodium salt **Ia**, light yellow crystals, which blurred in air within several minutes. In ^{31}P NMR spectrum of **Ia** in DMSO-d_6, two signals at δ_P of 30.064 and 28.991 ppm in the ratio of 3:1 were observed. In the ^{1}H NMR spectrum of **Ia**, two sets of signals with the same ratio of intensities were observed in the range characteristic of furan protons signals. The first set contained a broad exchanged signal at 6.642 ppm, a doublet at 6.680 ppm (J = 2.8 Hz), and a doublet at 8.550 ppm (J = 2.8 Hz). The second set contained a doublet at 6.657 ppm (J = 3.8 Hz), a doublet of doublets at 7.294 ppm (J = 3.8, 1.6 Hz), and a doublet at 8.676 ppm (J = 2.8 Hz). From the spectral data it followed that **Ia** existed in the form of carbanion, as no large coupling constants characteristic of enolates were found. The doublet of doublets from the weaker set of signals was assigned to the furan H^3 proton interacting with H^4 and with phosphorus atom. Another doublet with the same coupling constant of 3.8 Hz corresponded to H^4, and the downfield signal was assigned to the aldehyde proton, split at phosphorus atom with the characteristic constant of 2.8 Hz. The nearby intense doublet with the same coupling constant of 2.8 Hz was assigned to the aldehyde proton signal of the set of stronger signals. The signal at 6.680 ppm (J = 2.8 Hz) from the same set was assigned to H^4, whereas intense exchange signal at 6.642 ppm corresponded to H^3. Due to whatever reason, the signals of both furan protons of that product were shifted upfield as compared with the signals of the second form of the aldehyde salt **Ia**, and the proton H^3 was exchanged.

In the downfield part of ^{13}C NMR spectrum of **Ia**, both forms of the salt were also clearly revealed. The major form gave a doublet at 80.608 ppm ($^1J_{PC}$ = 202.8 Hz) assigned to the carbanion carbon atom. The signal of nitrile group carbon atom was observed at 113.892 ppm. Other signals observed were as follows: C^3 doublet (102.048 ppm, $^3J_{PC}$ = 6.8 Hz), ring carbon atom C^4 singlet (116.582 ppm), C^5 singlet (125.876 ppm), C^2 doublet (159.478 ppm, $^2J_{PC}$ = 8.9 Hz), and the aldehyde proton doublet (177.235 ppm, $^2J_{PC}$ = 18.8 Hz). The weaker set included the signals at 81.027 (PC=, $^1J_{PC}$ = 200.7 Hz), 101.093 (C^3, $^3J_{PC}$ = 8.5 Hz), 115.297 (C^4), 162.748 ppm (C^2, $^2J_{PC}$ = 6.3 Hz), and 178.564 ppm ($^2J_{PC}$ = 18.0 Hz, doublet of the aldehyde proton). The signals of C^5 carbon atom and the nitrile group in both forms of **Ia** evidently coincided. Hence, the three nuclei NMR spectral data for **Ia** were in mutual agreement, as well as were supported by data for similar ethoxycarbonyl derivative described in [1]. Thus, the formylation of phosphorylated nitrile **I** could be represented as follows.



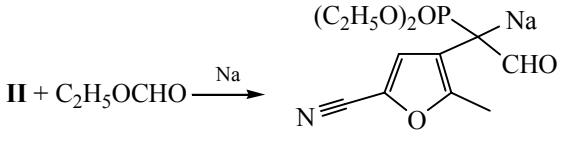
Ia

In the course of the reaction, phosphonate **I** was consumed completely. Yield of the salt **Ia** was of 73%. In the solution, that salt existed in the two forms clearly distinguished by NMR spectroscopy. Its chemical properties differed from those of its ethoxycarbonyl analog, and of other salts to be described below. **Ia** could not be alkylated neither with methyl iodide nor with dimethyl sulfate when directly treating the reaction mixture just after the synthesis (in that case, minimal effect of water was expected). No reaction was observed as well in the case of the isolated **Ia**.

Formylation of phosphonate **II** proceeded notably less vigorously. Complete dissolution of the sodium foil was observed within 2 h at 65°C. The sodium salt **IIa** partially precipitated directly from the reaction mixture as yellowish powder. After dilution of the reaction mixture with hexane, the product was isolated quantitatively. **IIa** was a comparatively stable compound with mp of 166–167°C.

Sodium formate was not formed in the reaction. In ^{31}P NMR spectrum of the isolated product in DMSO-d_6, a singlet at δ_P = 33.472 ppm was observed. Protons of methyl group in the furan ring, H^4, and aldehyde proton gave signals at 2.218, 7.206, and 8.320 ppm (J_{PH} = 2.8 Hz), respectively.

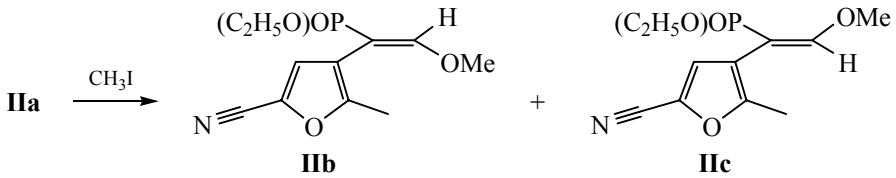
In the ^{13}C NMR spectrum, the signal of carbanion carbon atom was observed at 74.445 ppm ($^1J_{PC}$ = 204.1 Hz). Carbon atoms of the furan ring gave signals at 119.837 (C^3, $^2J_{PC}$ = 12.5 Hz), 120.789 (C^4), 125.225 (C^5), and 154.220 ppm (C^2). The signal of nitrile group appeared at 113.555 ppm, and doublet of aldehyde carbon atom was found at 173.513 ppm ($^2J_{PC}$ = 23.6 Hz). Thus, in the solution, **IIa** existed in the form of aldehyde carbanion, and phosphonate **II** formylation could be described by the following scheme.



IIa

Phosphonate **II** was completely consumed in the course of reaction. Yield of the salt **IIa** reached 97%.

The sodium salt **IIa** could be alkylated with methyl iodide in acetonitrile at 50–60°C to form *E*-**IIb** and *Z*-**IIc** alkyl enolates in the ratio of 2:1. In ^{31}P NMR spectrum, the corresponding signals were observed at 19.352 and 14.388 ppm. In the ^{1}H NMR spectrum, the vinyl protons of **IIb** were observed at 3.832 (OCH_3) and 7.122 ppm (HC=, J_{PH} = 10.4 Hz). The signals of **IIb** furan fragment protons appeared of at 2.216 (CH_3, J_{PH} = 1.6 Hz) and 6.980 ppm (H^4). The signals of the vinyl fragment carbon atoms of **IIb** were observed at 61.179 (OCH_3), 95.895 (P=C, $^1J_{PC}$ = 199.6 Hz), and 160.349 ppm (=CO, $^2J_{PC}$ = 26.9 Hz). The isomer **IIc** ^{1}H NMR spectrum revealed the signals of protons at 3.845 (OCH_3), 6.752 (HC=, J_{PH} = 33.6 Hz), 2.320 (CH_3, J_{PH} = 2.0 Hz), and 6.980 ppm (H^4). In the ^{13}C NMR spectrum, **IIc** gave signals at 62.056 (OCH_3), 97.054 (PC=, $^1J_{PC}$ = 188.6 Hz), and 161.117 ppm (=CHO). The total yield of compounds **IIb** and **IIc** was of 45%.

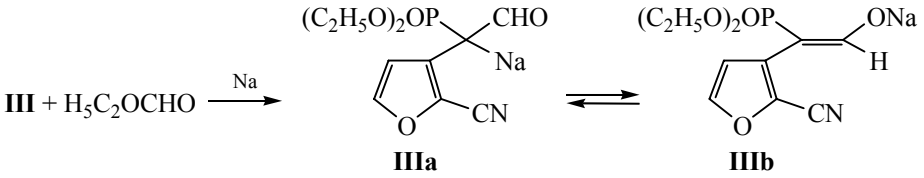


IIb **IIc**

Formylation of phosphonate **III** proceeded with negligible exothermal effect. The reaction mixture temperature increased from 19 to 29°C, and sodium was completely dissolved within 5 h; significant amount of sodium formate was formed. The reaction product was isolated by water extraction, evaporation to dryness, dissolution in ethanol to remove sodium formate, additional evaporation, and finally crystallization from the ethyl acetate–ether (1:4) mixture. The sodium salt formed yellowish-brown crystals with mp of 174°C (with decomposition). In ^{31}P NMR spectrum of this product in DMSO-d_6, two signals were observed at 31.600 and 25.335 ppm at 15:1 ratio. In the downfield part of the ^{1}H NMR spectrum, two sets of signals with nearly the same intensity ratio were found. In the first of the sets, the furan ring protons gave signals at 6.790 (H^4) and 7.588 ppm (H^5), whereas aldehyde proton singlet was observed at

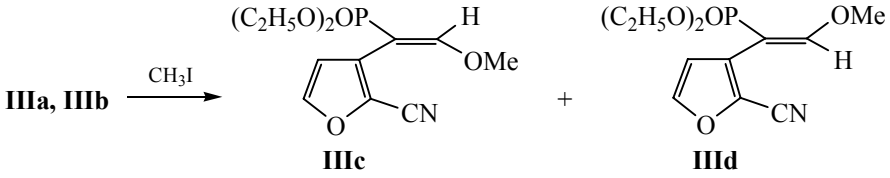
8.651 ppm. In the ^{13}C NMR spectrum, that structural fragment was assigned to the signals at 77.144 (PC, $^1J_{PC}$ = 202.7 Hz), 111.951 (C^4, $^3J_{PC}$ = 4.9 Hz), 119.398 (C^3, $^2J_{PC}$ = 11.8 Hz), 133.814 (C^2, $^3J_{PC}$ = 14.6 Hz), 145.943 (C^5), and 178.219 ppm (CHO, $^2J_{PC}$ = 21.4 Hz). The signal of nitrile group carbon atom was found at 115.895 ppm. Thus, in the DMSO solution, the carbanion form of sodium salt **IIIa** prevailed.

The second set of protons signals contained singlets at 6.652 (H^4) and 7.660 ppm (H^5). The doublet at 8.975 ppm (J_{PH} = 38.0 Hz) was assigned to the hydrogen atom at the double bond in the *trans* location with respect to the phosphoryl group. In the ^{13}C NMR spectrum, the signals at 78.545 (PC=, $^1J_{PC}$ = 219.2 Hz), 112.819 (C^4), 119.378 (C^3, $^2J_{PC}$ = 11.8 Hz), 133.714 (C^2, $^3J_{PC}$ = 14.6 Hz), 147.436 (C^5), and 179.398 ppm (=CHO, $^2J_{PC}$ = 7.3 Hz) were observed. The signal at 116.164 ppm was assigned to the carbon atom of nitrile group. Taking into account the data from [1] (describing the structurally similar ester compounds) the second set of signals was assigned to the *Z*-configuration of enolate **IIIb**. Thus, formylation of phosphonate **III** proceeded according to the following scheme.



In the course of the reaction, phosphonate **III** was completely consumed. Yield of the sodium salt was of 63%.

The salt **IIIa,b** was alkylated with methyl iodide in acetonitrile at 50°C to give a mixture of alkyl enolates with *E*-**IIIc** and *Z*-**IIId** configurations in 3:1 ratio.

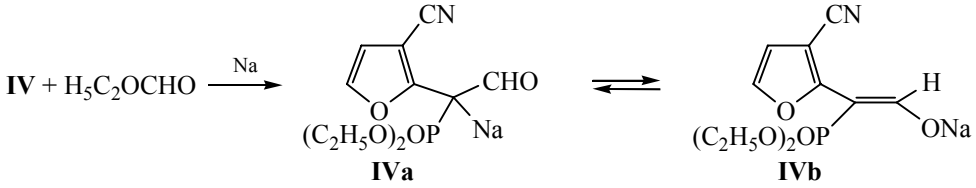


In the case of **IIIc**, the signal of phosphorus atom was observed at 18.054 ppm, the proton at double bond gave a doublet at 7.111 ppm (J_{PH} = 10.4 Hz), whereas the signals of vinyl fragment carbon atoms appeared at 93.814 (PC=, $^1J_{PC}$ = 199.7 Hz) and 162.791 ppm (=CHO, $^2J_{PC}$ = 24.1 Hz). The methyl carbon signal was located at δ_c 62.622 ppm. In the ^1H NMR spectrum, the corresponding singlet of methoxyl protons was observed at 3.759 ppm. Compound **IIId** was characterized by the signal of phosphorus atom at 12.777 ppm, the double bond proton doublet at 6.876 ppm (J_{PH} = 33.2 Hz), and the signals of vinyl fragment carbon atoms at 95.528 (PC=, $^1J_{PC}$ = 199.7 Hz) and 162.035 ppm (=CHO). In the case, $^2J_{PC}$ was not revealed. The signal of methoxyl carbon was observed at 62.529 ppm, and methoxyl protons in the ^1H NMR spectrum gave a singlet at 3.748 ppm. The total yield of alkyl enolates was of 75%.

Formylation of phosphonate **IV** proceeded significantly faster, the reaction mixture temperature grew up from 19 to 38°C, and complete dissolution of sodium foil took 30 min. The formed sodium salt was isolated similarly to the above-described. The product crystallized from the 2:1 ether – ethyl acetate mixture to give light brown crystals with mp of 165–166°C. In ^{31}P NMR spectrum in DMSO-d_6, two signals at 29.399 and 23.570 ppm at the intensity ratio of 8:1 were observed. In the downfield part of the ^1H NMR spectrum, two sets of signals with the intensity ratio close to the above-mentioned one were revealed. The more intense set included signals at 6.520 (H^4), 7.390 (H^5), and 8.621 ppm (CHO). In the ^{13}C NMR spectrum, signals of the corresponding isomer were found at 78.317 (PC, $^1J_{PC}$ = 202.9 Hz), 87.237 (C^3, $^3J_{PC}$ = 8.8 Hz), 112.211 (C^4), 138.118 (C^5), 169.960 (C^2, $^2J_{PC}$ = 7.5 Hz), and 178.154 ppm (CHO, $^2J_{PC}$ = 19.1 Hz). Thus, the recorded spectral data should be attributed to the carbanion form of sodium salt **IVa**.

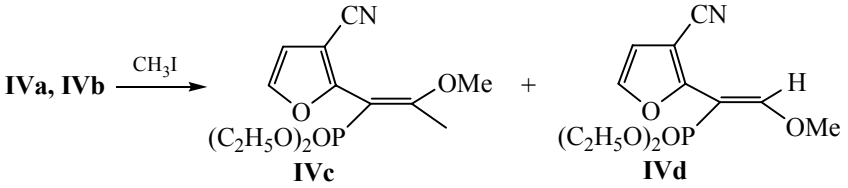
The weaker set of protons signals included singlets at 6.576 (H^4) and 7.412 ppm (H^5), and a doublet at 8.924 ppm (HC=, J_{PH} = 35.6 Hz). In the ^{13}C NMR spectrum, the corresponding signals of carbon atoms

were observed at 76.881 (PC=, $^1J_{PC}$ = 253.1 Hz), 111.743 (C^4), 138.589 (C^5), 162.960 (C^2, $^2J_{PC}$ = 7.5 Hz), and 180.268 ppm (=CHONa, $^2J_{PC}$ = 3.7 Hz). That set of signals indicated the presence of *Z*-enolate form of **IVb**. Thus, formylation of phosphonate **IV** proceeded according to following scheme.



In DMSO solution, the carbanion form prevailed. In the course of formylation, phosphonate **IV** was completely consumed. Yield of sodium salt reached 65%.

Alkylation of the sodium salt **IVa,b** with methyl iodide in acetonitrile at 50–60°C also led to mixture of alkyl enolates *E*-**IVc** and *Z*-**IVd** in the ratio of 1:0.8.



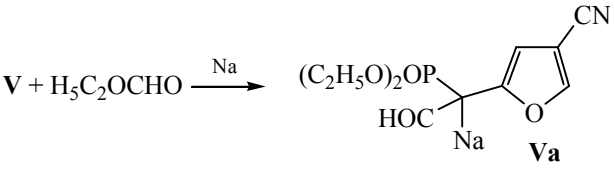
E-Enolate **IVc** was characterized by the signal of phosphorus atom at 15.537 ppm. Vinyl proton of double bond gave a doublet at 7.194 ppm (J_{PH} = 9.6 Hz), and the methoxyl group signal was observed at 3.948 ppm. In the ^{13}C NMR spectrum, the following signals of carbon atoms were revealed: at 61.183 (OCH_3), 94.433 (PC=, $^1J_{PC}$ = 196.4 Hz), 96.065 (C^3, $^3J_{PC}$ = 7.5 Hz), 112.367 (CN), 113.586 (C^4), 142.433 (C^5), 157.532 (C^2, $^2J_{PC}$ = 5.7 Hz), and 164.979 ppm (=CO, $^2J_{PC}$ = 21.9 Hz).

The phosphorus atom signal at 10.575 ppm was assigned to *Z*-enolate **IVd**. Its vinyl proton was characterized by a doublet at 7.071 ppm (J_{PH} = 31.6 Hz), whereas the signal of methoxyl protons was observed at 3.927 ppm. In the ^{13}C NMR spectrum, signals assigned to this isomer were revealed at 63.088 (OCH_3), 93.987 (C^3, $^2J_{PC}$ = 5.6 Hz), 96.288 (PC=, $^1J_{PC}$ = 187.7 Hz), 111.892 (CN), 114.183 (C^5), 153.680 (C^2), and 164.936 ppm (=CO). Total yield of the alkylation products was 51%.

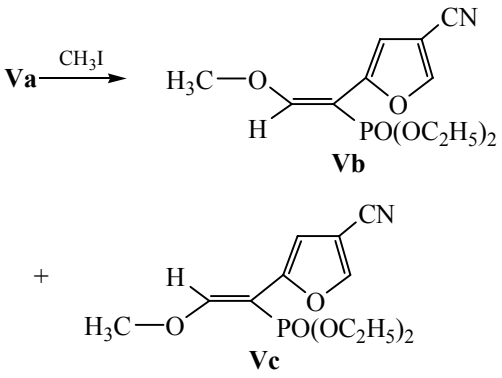
Formylation of phosphonate **V** with the distant substituents occurred slower than in the case of phosphonate **IV**, but faster than in the cases of phosphonates **II** and **III** bearing diethoxyphosphorylmethyl group in β-position of the furan ring. In the course of the reaction, temperature grew up from 19 to 40°C, and sodium foil was completely dissolved within 1 h. The product was isolated by water extraction and filtering off insoluble sodium formate from ethanol solution. The salt product precipitated upon dilution of its acetone solution with ethyl acetate or ether. The crystals formed quickly stuck together in air, and then formed the syrup-like mass.

^{31}P NMR spectrum of this product in DMSO-d_6 contained the only signal, at 29.858 ppm. In the downfield part of the ^1H NMR spectrum, signals at 6.647 (H^3), 8.055 (H^5), and 8.553 ppm (CHO, J_{PH} 2.4 Hz) were observed. ^{13}C NMR spectrum contained the signals of carbon atoms at 79.184 (PC, $^1J_{PC}$ = 202.9 Hz), 79.672 (C^4), 98.783 (C^3, $^3J_{PC}$ = 8.7 Hz), 115.616 (CN), 144.476 (C^5), 157.978 (C^2, $^2J_{PC}$ = 7.5 Hz), and 174.201 ppm (CHO, $^2J_{PC}$ = 18.4 Hz). Thus, the isolated sodium salt existed in the carbanion form **Va** in DMSO solution.

The toluene solution remaining after extraction of water-soluble products contained initial unreacted phosphonate. Conversion of **V** was of 77%, and sodium salt **Va** was obtained with 61% yield. The condensation proceeded as follows.



Methylation of **Va** with methyl iodide at 50°C in acetonitrile led to the mixture of *E*-**Vb** and *Z*-**Vc** alkyl enolates in the ratio of 2:1.



The phosphorus atom signal in ^{31}P NMR spectrum of **Vb** was observed at 16.768 ppm. The downfield part of **Vb** ^{1}H NMR spectrum contained signals at 6.675 (H^3), 7.873 (H^4), and a doublet at 7.190 ppm (=CH, J_{PH} = 10.8 Hz). In the ^{13}C NMR spectrum, the following signals were found: at 93.323 (PC=, $^1J_{PC}$ = 194.5 Hz), 99.010 (C^4), 109.404 (C^3, $^3J_{PC}$ = 6.8 Hz), 147.640 (C^5), 147.671 (C^2, $^2J_{PC}$ = 6.8 Hz), and 161.878 ppm (=CO, $^2J_{PC}$ 20.7 Hz). The methoxyl carbon atom signal, common for **Vb** and **Vc**, was observed at 62.812 ppm.

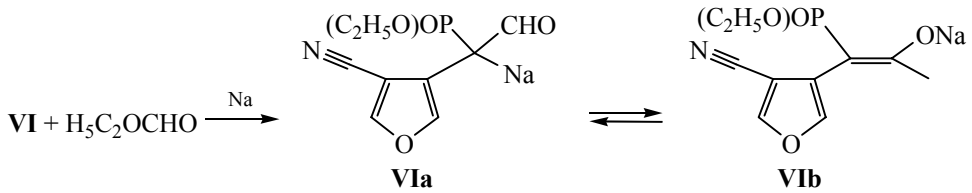
The chemical shift of phosphorus atom in **Vc** was of 12.143 ppm. In the downfield part of the ^{1}H NMR spectrum, signals at 6.628 (H^3), 7.284 ppm (H^5), and a doublet at 7.795 ppm (=CHO, J_{PH} 32.4 Hz) were observed. In the ^{13}C NMR spectrum, **Vc** was characterized by the signals at 93.323 (PC=, $^1J_{PC}$ = 194.5 Hz), 97.997 (C^4), 109.404 (C^3, $^3J_{PC}$ = 6.8 Hz), 149.161 (C^5), 149.191 (C^2, $^2J_{PC}$ = 5.3 Hz), and 161.519 ppm (=CO). The total yield of alkylation products **Vb** and **Vc** was of 60%.

Formylation of **VI** occurred exothermally, the reaction mixture temperature grew up from 19 to 33°C. Sodium foil was completely dissolved within 5 h. Major part of sodium salt precipitated directly from the reaction mixture. Sodium formate was only formed as trace admixture. The product obtained was a yellowish crystalline substance decomposing at 170–172°C. It was comparatively stable in air; at room temperature it was not changed during several days.

In ^{31}P NMR spectrum of the prepared salt in DMSO-d_6, phosphorus atoms signals at 32.228 and 26.516 ppm were observed in the ratio of 7.5:1. The downfield part of the ^{1}H NMR spectrum contained a set of intense signals at 7.616 ppm (broad singlet, H^2), 8.285 ppm (d, H^5, J_{PH} = 1.2 Hz), and 8.451 ppm (CHO). In the ^{13}C NMR spectrum, that structural fragment was characterized by the signals at 73.301 (PC, $^1J_{PC}$ = 207.2 Hz), 100.298 (C^4, $^3J_{PC}$ = 7.1 Hz), 123.209 (C^3, $^2J_{PC}$ = 13.4 Hz), 139.215 (C^2, $^3J_{PC}$ = 7.2 Hz), 159.514 (C^5), and 175.975 ppm (CHO, $^2J_{PC}$ = 22.4 Hz). The described set of signals was assigned to the carbanion form of **VIa** salt.

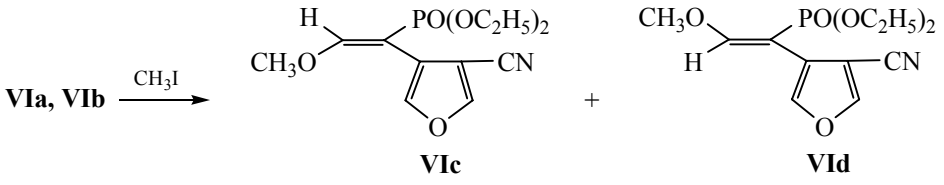
Signals of the minor product protons included singlets at 7.310 (H^2) and 8.384 ppm (H^5), and a doublet at 8.563 ppm (=CHO, J_{PH} = 40.0 Hz). In the ^{13}C NMR spectrum, the signals of carbon atoms of this structure were observed at 73.311 (PC=, $^1J_{PC}$ = 193.4 Hz), 99.440 (C^4, $^3J_{PC}$ = 7.3 Hz), 125.560 (C^3, $^2J_{PC}$ = 13.4 Hz), 138.933 (C^2), 151.333 (C^5), and 178.668 ppm (=CHO). According to the spectral data, the minor product was *Z*-enolate **VIb**.

Thus, formylation of phosphonate **VI** occurred according to the following scheme.



The initial phosphonate **VI** was completely consumed in the reaction. Yield of sodium salt was of 94%.

Methylation of **VIa** and **VIb** with methyl iodide in acetonitrile at 50°C led to formation of methyl enolates *E*-**VIc** and *Z*-**VId** in the ratio of 2:1.



In ^{31}P NMR spectrum of the ether **VIc**, a signal at 18.458 ppm was observed. In the downfield part of ^{1}H NMR spectrum, the signals of **VIc** furan protons were found at 7.446 (H^2) and 7.890 ppm (H^5). Doublet of the vinyl group proton appeared at 7.159 ppm (J_{PH} 9.6 Hz). In the ^{13}C NMR spectrum, *E*-isomer **VIc** was characterized by signals at 98.389 (PC=, $^1J_{PC}$ = 200.0 Hz), 99.807 (C^4, $^3J_{PC}$ = 7.9 Hz), 117.445 (C^3, $^2J_{PC}$ = 7.3 Hz), 141.946 (C^2, $^3J_{PC}$ = 3.1 Hz), 150.039 (C^5), and 162.261 ppm (=CHO, $^2J_{PC}$ = 25.0 Hz).

^{31}P NMR signal of the *Z*-isomer **VId** was observed at 13.869 ppm. In the downfield part of the ^{1}H NMR spectrum, the furan ring protons singlets were located at 7.586 (H^2) and 7.868 ppm (H^5). A doublet of vinyl proton appeared at 7.159 ppm (=CHO, J_{PH} = 33.2 Hz). Signals of carbon atoms were observed at 95.125 (PC=, $^1J_{PC}$ = 186.2 Hz), 98.677 (C^4, $^3J_{PC}$ = 6.6 Hz), 119.933 (C^3, $^2J_{PC}$ = 9.7 Hz), 142.501 (C^2, $^3J_{PC}$ = 3.6 Hz), 150.207 (C^5), and 160.972 ppm (=CHO).

Thus, similarly to ethoxycarbonyl derivatives, the cyano-substituted furylmethanephosphonates reacted with ethyl formate via ester condensation. Conversions of initial cyanophosphonates and yields of the sodium salts were higher as compared with the case of structurally similar esters. Both in the cases of ester and nitrile derivatives, the structure of sodium salt product depended on the nature of phosphonate. In the cases of furans with distant substituents, the sodium salt existed in a form of carbanion in DMSO solution. In the cases of furans with adjacent substituents, in most cases the anion of *Z*-enolate was found as well.

In contrast with β-dicarbonyl compounds, anions of phosphorylated furylacetic aldehydes in all the cases were alkylated exclusively at the oxygen atom, to give alkyl enolates. In the case of esters derivatives, the regular stereoselectivity was not revealed, whereas in the case of nitriles, *E*-isomer always prevailed.

The spectra of carbanion and enolate forms of the sodium salts were clearly different. Phosphorus atom shift varied within δ_P 29.3–35.5 ppm in the cases of carbanion forms, whereas the similar signal of *Z*-enolates was located between 23 and 28 ppm. Aldehyde proton signal was observed in the range of 8.3–8.9 ppm with the coupling constant J_{PH} of 0–3.6 Hz in the carbanion form. In *Z*-enolate spectra, signal of vinyl proton was also located between 8.5 and 8.9 ppm, but its *trans*-constant was of J_{PH} 35–40 Hz. The furan ring and the anionic oxygen atom at the double bond tended to spatially separate as much as possible. The enolate ion of *E*-configuration was not observed in the products, even though in the case of alkyl enolates, products with *E*-configuration prevailed. That meant that methoxyl group tended to move away from the phosphorus-containing group, rather than from the furan ring.

The signal of the aldehyde group carbon of anion appeared at 175–178 ppm. It was split with phosphorus, the coupling constant being of 18–24 Hz. The signal of the respective carbon atom of *Z*-enolate was shifted downfield (δ_C 178–183 ppm) and was characterized by the coupling constant of $^2J_{PC}$ 0–7.5 Hz.

The chemical shift of phosphorus atom in *E*-isomers of alkyl enolates of phosphonoacetic aldehyde was of 15–19 ppm. In the case of *Z*-isomers, that signal shifted to 10–14 ppm. Signals of vinyl protons in *E*-isomer were found at 7.2–7.5 ppm, and were split with a typical *cis*-constant of J_{PH} 9–11 Hz. In *Z*-isomers spectra, vinyl proton signal was located upfield (6.8–7.3 ppm) and was split with a typical *trans*-constant of J_{PH} 32–34 Hz. The signal of carbon atom of =CHO fragment in *E*-isomers was observed at 160–165 ppm. It was a doublet with a coupling constant of $^2J_{PC}$ 21–25 Hz. In *Z*-isomers, the signal of the vinyl carbon atom had the same shift, usually was not split.

Noteworthily, the spectral features assigned to protons, phosphorus and carbon atoms of *Z*-enolate forms of salts and of alkyl *Z*-enolates were similar. This additionally supported the elucidation of enolate anion structure. No data on spectral characteristics of ambident phosphorus-containing anions was found in the literature; likely, this issue was systematically considered for the first time.

EXPERIMENTAL

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker DPX-400 spectrometer [400.13 MHz (^{1}H),

161.97 MHz (^{31}P), 100.61 MHz (^{13}C)]. Spectra of sodium salts were recorded in deuterated DMSO, for other compounds $CDCl_3$ was used.

4-Hydroxymethyl-furan-3-carboxylic acid (VIII). Potassium hydroxide, 2.2 g, was dissolved in 50 ml of ethanol, and 5.5 g of ethyl 4-hydroxymethylfuran-3-carboxylate **VII** was added to it in a single portion. The reaction mixture was refluxed upon stirring for 3 h. In the course of the reaction precipitate of potassium salt poorly soluble in ethanol was formed. When the reaction mixture pH became constant, the mixture was cooled down and treated with one equivalent of hydrogen chloride solution in ethanol. Potassium chloride was filtered off and the filtrate was evaporated to dryness and kept in vacuum (1 mm Hg) for 1 h at room temperature. Yield of the acid **VIII** was 4.1 g (96%), mp 122–123°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.549 s (CH_2O), 7.586 d (H^5, J_{HH} 1.2 Hz), 8.216 d (H^2, J_{HH} 1.2 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 55.50 (CH_2O), 118.152 (C^4), 127.513 (C^3), 141.964 (C^5), 149.675 (C^2), 164.802 (C=O).

4-Chloromethylfuran-3-carbonyl chloride (IX). The acid **VIII,** 4.1 g, was suspended in 50 ml of carbon tetrachloride, and 12 g of finely pulverized phosphorus pentachloride was added upon intense stirring. After vigorous liberation of hydrogen chloride stopped, the reaction mixture was refluxed for 7 h, cooled, treated with 5 ml of anhydrous acetone to remove excess of PCl_5, and distilled in vacuum to give 2.9 g (56%) of acid chloride **IX** with bp 72–74°C (1 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.629 s (CH_2Cl), 7.613 br.s (H^5), 8.243 d (H^2, J_{HH} 1.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 36.177 (CH_2Cl), 108.992 (C^4), 122.522 (C^3), 144.397 (C^5), 159.378 (COCl).

4-Chloromethylfuran-3-carboxamide (X). Acid chloride **IX,** 9.8 g, was dissolved in 50 ml of toluene and 10 ml of 25% ammonium hydroxide was added upon intense stirring and cooling in the ice bath. The resulting mixture was stirred for 2 h at 10–12°C, and the precipitate formed was filtered off with thorough sucking on a filter. Amide **X** was well soluble in water and its washing would cause considerable losses. Yield 8.3 g (95%), mp 103°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.815 s (CH_2Cl), 7.828 br.s (H^5), 8.216 d (H^2, J_{HH} 1.5 Hz), 6.404 br.s + 7.367 br.s (NH_2). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 36.291 (CH_2Cl), 119.878 (C^4), 122.575 (C^3), 142.477 (C^5), 145.765 (C^2), 164.388 ($CONH_2$).

4-Chloromethyl-3-cyanofuran (XI). Chloromethylamide **X**, 10.1 g, was suspended in 50 ml of carbon tetrachloride, and 13.2 g of finely pulverized phosphorus pentachloride was added in small portions. Obtained suspension was heated carefully, gradually increasing the temperature of reaction mixture to 80°C. The rate of heating was adjusted according to the intensity of liberation of hydrogen chloride. After reaching 80°C heating was ceased, the reaction mixture was cooled and treated with acetone to remove excess of phosphorus pentachloride. Then volatile substances were removed at reduced pressure, and the residue was distilled in vacuum to give 5.7 g (64%) of nitrile **XI**, bp 81°C (1 mm Hg), mp 62°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.532 s (CH_2Cl), 7.571 s (H^5), 7.954 s (H^2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 34.227 (CH_2Cl), 98.806 (C^3), 111.535 (CN), 123.323 (C^4), 142.419 (C^5), 150.777 (C^2).

4-Iodomethyl-3-cyanofuran (XII). One equivalent of saturated solution of sodium iodide monohydrate in acetone was added to a solution of 5.6 g of chloride **XI** in 30 ml of acetone, and the reaction mixture was kept for a day at room temperature protected from light. Then the mixture was poured in 300 ml of water, the product was extracted with chloroform, and the extract was washed with sodium sulfite solution until discoloration. Then it was washed with water and dried over sodium sulfate in a flask protected from light. Chloroform was removed at reduced pressure, and the residue was kept in a vacuum (1 mm) protecting the product from light. Iodide **XII**, 7 g (76%) was obtained as white crystals, mp 79°C. In air, under the action of light they gradually became yellow. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.276 s (CH_2I), 7.584 br.s (H^5), 7.946 d (H^2, J_{HH} 1.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –11.974 (CH_2I), 99.499 (C^3), 111.476 (CN), 124.552 (C^4), 141.639 (C^5), 150.489 (C^2).

Diethyl (4-cyanofur-3-yl)methanephosphonate (VI). Iodide **XII**, 7 g, was dissolved in 7 ml of triethyl phosphite and heated upon stirring. At 105°C liberation of ethyl iodide from the reaction mixture began. The reaction mixture was heated gradually to 160°C. The rate of heating was adjusted according to ethyl iodide release intensity. After reaching 160°C, the reaction mixture was distilled in vacuum to give 4.5 g (62%) of phosphonate **VI**, bp 151°C (1 mm Hg). Total reaction time was 7–8 min. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.237 m (CH_3-ethyl), 2.948 d (CH_2P, J_{PH} 20.8 Hz), 4.042 m (CH_2OP), 7.459 br.s (H^2-furan), 7.872 br.s (H^5-furan). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.270

(CH_3, $^3J_{PC}$ 5.8 Hz), 21.509 (CH_2P, $^1J_{PC}$ 143.7 Hz), 62.411 (CH_2OP, $^2J_{PC}$ 6.5 Hz), 100.190 (C^4, $^3J_{PC}$ 6.5 Hz), 112.070 (CN), 116.424 (C^3, $^2J_{PC}$ 8.9 Hz), 142.390 (C^2, $^3J_{PC}$ 7.8 Hz), 149.779 (C^5). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 23.684.

Reaction of diethyl (cyanofuryl)methanephosphonates with ethyl formate *(general procedure).* Freshly prepared sodium foil, 0.024 mol, 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 upon intense stirring to this suspension. The reaction mixture was stirred until the dissolution of sodium and left overnight. If sodium salt precipitated, it was filtered off and washed with toluene. When no precipitate was formed, the reaction mixture was extracted with water 2–3 times; the extract was washed with ether and evaporated to dryness, and the residue was dissolved in ethanol, insoluble sodium formate was filtered off, the filtrate was evaporated to dry state, and the residue was kept in vacuum (1 mm Hg) for 1 h at room temperature.

Sodium salt of (5-cyanofur-2-yl)(diethoxyphosphoryl)acetic aldehyde (Ia) was isolated by extraction with water from the reaction mixture. Conversion of phosphonate **I** was 100%. After rubbing up of the evaporated ethanol solution with hexane, yellow crystals were formed blurring in air within 3–4 min. Yield 3 g (73%). ^1H NMR spectrum (DMSO-d_6), δ, ppm: common signals: 1.257 t (CH_3-ethyl, J_{HH} 7.0 Hz), 3.753–3.903 m (CH_2OP); major form: 6.642 br.s (H^3), 6.680 d (H^4, J_{HH} 2.8 Hz), 8.550 d (CHO, J_{PH} 2.8 Hz); minor form: 6.657 d (H^4, J_{HH} 3.8 Hz), 7.294 d.d (H^3, J_{HH} 3.8 Hz, J_{PH} 1.6 Hz), 8.676 d (CHO, J_{PH} 2.8 Hz). Ratio of major and minor forms 3:1. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: major form: 16.711 (CH_3, $^3J_{PC}$ 6.8 Hz), 60.016 (CH_2OP, $^2J_{PC}$ 4.2 Hz), 80.608 (P–C–, $^1J_{PC}$ 202.8 Hz), 102.048 (C^3, $^3J_{PC}$ 6.8 Hz), 113.892 (CN), 116.582 (C^4), 125.876 (C^5), 159.478 (C^2, $^2J_{PC}$ 8.9 Hz), 177.325 (CHO, $^2J_{PC}$ 18.8 Hz); minor form: 16.642 (CH_3, $^3J_{PC}$ 6.8 Hz), 60.143 (CH_2OP, $^2J_{PC}$ 4.5 Hz), 81.027 (P–C–, $^1J_{PC}$ 200.7 Hz), 101.093 (C^3, $^3J_{PC}$ 8.5 Hz), 113.892 (CN), 115.297 (C^4), 125.876 (C^5), 162.748 (C^2, $^2J_{PC}$ 6.3 Hz), 178.564 (CHO, $^2J_{PC}$ 18.0 Hz). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 30.064, 28.991, intensity ratio 3:1

Sodium salt of (2-methyl-5-cyanofur-3-yl)(diethoxyphosphoryl)acetic aldehyde (IIa). To completely dissolve sodium, the reaction mixture was heated for 2 h at 65°C. Conversion of phosphonate **II** was 100%. The salt was isolated by filtration after dilution of reaction mixture with hexane. Yield 97%, mp 166–167°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.128 t (CH_3-ethyl, J_{HH} 7.2 Hz), 2.218 s (CH_3-furan), 3.746–3.318 m (CH_2OP), 7.206 s (H^4), 8.320 d (CHO, J_{PH} 2.8 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.507 (CH_3-furan), 16.774 (CH_3, $^3J_{PC}$ 6.4 Hz), 59.460 (CH_2OP, $^2J_{PC}$ 3.6 Hz), 74.445 (P–C–, $^1J_{PC}$ 204.1 Hz), 113.555 (CN), 119.837 (C^3, $^2J_{PC}$ 12.5 Hz), 120.789 (C^4), 125.775 (C^5), 154.220 (C^2, $^3J_{PC}$ 11.5 Hz), 173.513 (CHO, $^2J_{PC}$ 23.6 Hz). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 33.472.

Sodium salt of (2-cyanofur-3-yl)(diethoxyphosphoryl)acetic aldehyde (IIIa, IIIb). Conversion of phosphonate **III** was 100%. The salt was isolated by extraction with water and crystallization from ethyl acetate–ether mixture (1:4). Yield 63%, mp 174°C (with decomposition). ^1H NMR spectrum (DMSO-d_6), δ, ppm: common signals: 1.142 t (CH_3-ethyl, J_{HH} 7.2 Hz), 3.767 m (CH_2OP, J_{HH} 7.2 Hz, J_{PH} 14.8 Hz); **IIIa**: 6.790 s (H^4), 7.588 c (H^5), 8.651 s (CHO); **IIIb**: 6.552 s (H^4), 7.660 s (H^5), 8.945 d (CH=CP, J_{PH} 38.0 Hz); ratio of intensities of signals **IIIa**:**IIIb** 15:1. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: **IIIa**: 16.693 (CH_3, $^3J_{PC}$ 6.6 Hz), 59.704 (CH_2OP, $^2J_{PC}$ 4.3 Hz), 77.144 (P–C–, $^1J_{PC}$ 202.7 Hz), 111.951 (C^4, $^2J_{PC}$ 4.9 Hz), 115.895 (CN), 119.398 (C^3, $^2J_{PC}$ 14.8 Hz), 133.714 (C^2, $^3J_{PC}$ 14.6 Hz), 145.943 (C^5), 178.219 (CHO, $^2J_{PC}$ 21.4 Hz); **IIIb**: 17.009 (CH_3, $^3J_{PC}$ 7.0 Hz), 59.948 (CH_2OP, $^2J_{PC}$ 4.6 Hz), 78.545 (=C–P, $^1J_{PC}$ 219.2 Hz), 112.815 (C^4), 116.164 (CN), 119.378 (C^3, $^2J_{PC}$ 14.8 Hz), 133.714 (C^2, $^3J_{PC}$ 14.6 Hz), 147.436 (C^5), 179.385 (=C–O, $^2J_{PC}$ 7.3 Hz). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 31.600 (**IIIa**), 25.335 (**IIIb**), ratio of intensities of signals **IIIa**: **IIIb** 15:1.

Sodium salt of (3-cyanofur-2-yl)(diethoxyphosphoryl)acetic aldehyde (IVa, IVb). Conversion of phosphonate **IV** was 100%. The salt was isolated by extraction with water and crystallization from ethyl acetate – ether mixture (1:2). Yield 65%, mp 165–166°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: **IVa**: 1.124 t (CH_3-ethyl, J_{HH} 7.2 Hz), 3.776–3.886 m (CH_2OP, J_{HH} 7.2 Hz, J_{PH} 14.4 Hz); 6.250 s (H^4), 7.390 s (H^5), 8.621 s (CHO); **IVb**: 1.135 t (CH_3-ethyl, J_{HH} 7.2 Hz), 3.776–3.886 m (CH_2OP, J_{HH} 7.2 Hz, J_{PH} 14.4 Hz), 6.576 s (H^4), 7.412 s (H^5), 8.924 d (HC=CP, J_{PH} 35.6 Hz), ratio of intensities of signals **IVa**:**IVb** 8:1. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: **IVa**: 16.679 (CH_3, $^3J_{PC}$ 6.7 Hz), 59.911 (CH_2OP, $^2J_{PC}$ 4.1 Hz), 78.317 (P–C–,

$^1J_{PC}$ 202.9 Hz), 87.327 (C^3, $^3J_{PC}$ 8.8 Hz), 112.211 (CN), 117.147 (C^4), 138.118 (C^5), 162.960 (C^2, $^2J_{PC}$ 7.5 Hz), 178.154 (CHO, $^2J_{PC}$ 19.1 Hz); **IVb**: 17.043(CH_3, $^3J_{PC}$ 7.0 Hz), 60.325 (CH_2OP, $^2J_{PC}$ 4.4 Hz), 76.881 (=C–P, $^1J_{PC}$ 253.1 Hz), 87.327 (C^3, $^3J_{PC}$ 8.8 Hz), 111.743(CN), 117.949 (C^4), 138.589 (C^5), 162.960 (C^2, $^2J_{PC}$ 7.5 Hz), 180.268 (=CH–O, $^2J_{PC}$ 3.7 Hz). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 29.399 (**IVa**), 23.510 (**IVb**), ratio of intensities of signals **IVa**: **IVb** 8:1.

Sodium salt of (4-cyanofur-2-yl)(diethoxyphosphoryl)acetic aldehyde (Va). Conversion of phosphonate **V** was 100%. Sodium salt was isolated by extraction with water and crystallization from acetone–ethyl acetate mixture (1:1). The crystals almost immediately blurred in air. Yield 61%. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.115 t (CH_3-ethyl, J_{HH} 7.2 Hz), 3.747–3.861 m (CH_2OP), 6.647 s (H^3), 8.055 s (H^5), 8.553 d (CHO, J_{PH} 2.4 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 16.794 (CH_3, $^3J_{PC}$ 6.6 Hz), 59.954 (CH_2OP, $^2J_{PC}$ 4.3 Hz), 76.672 (C^4), 79.184 (P–C, $^1J_{PC}$ 202.9 Hz), 98.783 (C^3, $^3J_{PC}$ 8.7 Hz), 115.616 (CN), 144.576 (C^5), 157.978 (C^2, $^2J_{PC}$ 7.5 Hz), 174.201 (CHO, $^2J_{PC}$ 18.4 Hz). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm : 29.858.

Sodium salt of (4-cyanofur-3-yl)(diethoxyphosphoryl)acetic aldehyde (VIa, VIb). Conversion of phosphonate **VI** was 100%. The salt was isolated by filtration of the reaction mixture diluted with equal volume of hexane. Yield 94%, yellow crystals, temperature of decomposition 170–172°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: common signals: 1.137 t (CH_3-ethyl, J_{HH} 7.5 Hz), 3.756–3.864 m (CH_2OP); **VIa**: 7.615 br.s (H^2), 8.285 d (H^5, J_{HH} 1.2 Hz), 8.451 d (CHO, J_{PH} 2.0 Hz). **VIb**: 7.310 s (H^2), 8.384 s (H^5), 8.563 d (HC=CP, J_{PH} 40 Hz), ratio of intensities **VIa**:**VIb** 7.5:1. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: **VIa**: 16.732 (CH_3, $^3J_{PC}$ 6.7 Hz), 59.453 (CH_2OP, $^2J_{PC}$ 4.3 Hz), 73.301 (P–C–, $^1J_{PC}$ 207.2 Hz), 100.298 (C^4, $^3J_{PC}$ 7.1 Hz), 115.122 (CN), 123.209 (C^3, $^2J_{PC}$ 13.4 Hz), 139.215 (C^2, $^3J_{PC}$ 7.2 Hz), 150.514 (C^5), 175.975 (CHO, $^2J_{PC}$ 22.4 Hz); **VIb**: 16.732 (CH_3, $^3J_{PC}$ 6.7 Hz), 59.838 (CH_2OP, $^2J_{PC}$ 3.5 Hz), 72.321 (=C–P, $^1J_{PC}$ 193.4 Hz), 99.440 (C^4, $^3J_{PC}$ 7.3 Hz), 115.122 (CN), 125.560 (C^3, $^2J_{PC}$ 13.4 Hz), 138.933 (C^2), 151.333 (C^5), 178.668 (=CH–O). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 32.228 (**VIa**), 26.516 (**VIb**), ratio of intensities **VIa**:**VIb** 7.5:1.

Methylation of sodium salts of phosphonoacetic aldehydes with methyl iodide *(general procedure).* Sodium salt of phosphonoacetic aldehyde, 0.01 mol, was suspended in 20 ml of acetonitrile, and 0.015 mol of methyl iodide was added in one portion. Reaction mixture was stirred at 50–60°C for 8–9 h and left overnight. Next day, the obtained precipitate was filtered off; the filtrate was evaporated to dryness at reduced pressure, dissolved in 20 ml of chloroform, and washed with water (2×10 ml). After drying over sodium sulfate, the solvent was distilled off at reduced pressure, and the residue was kept for 1 h in vacuum (1 mm Hg) at room temperature. The products were viscous oils or syrups.

Diethyl 1-(2-methyl-5-cyanofur-3-yl)-2-methoxyethylenephosphonate (IIb, IIc). Yield 45%, viscous oil. Ratio of *E*-**IIb** and *Z*-**IIc** isomers 2:1. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: common signals: 1.264 t (CH_3-ethyl, J_{HH} 7.0 Hz), 3.950–4.101 m (CH_2OP), **IIb**: 2.216 d (CH_3-furan, J_{PH} 1.6 Hz), 3.832 s (OCH_3), 6.989 s (H^4), 7.122 d (HC=CP, J_{PH} 10.4 Hz); **IIc**: 2.320 d (CH_3-furan, J_{PH} 2.0 Hz), 3.845 s (OCH_3), 6.572 d (HC=CP, J_{PH} 33.6 Hz) 6.980 s (H^4). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **IIb**: 13.357 (CH_3-furan), 16.261 (CH_3, $^3J_{PC}$ 6.3 Hz), 61.179 (CH_3O), 61.883 (CH_2OP, $^2J_{PC}$ 5.1 Hz), 95.895 (P–C=, $^1J_{PC}$ 199.6 Hz), 111.815 (CN), 113.263 (C^3, $^2J_{PC}$ 6.0 Hz), 123.702 (C^4), 124.453 (C^5), 155.989 (C^2, $^3J_{PC}$ 10.3 Hz), 160.349 (=CH–OCH_3, $^2J_{PC}$ 26.9 Hz); **IIc**: 12.519 (CH_3-furan), 16.261 (CH_3, $^3J_{PC}$ 6.3 Hz), 61.157 (CH_3O), 61.881 (CH_2OP, $^2J_{PC}$ 4.6 Hz), 97.054 (P–C=, $^1J_{PC}$ 188.6 Hz), 111.711 (CN), 116.763 (C^3, $^2J_{PC}$ 7.6 Hz), 123.569 (C^4), 125.525 (C^5), 155.351 (C^2, $^3J_{PC}$ 8.6 Hz), 161.117 (=CH–OCH_3). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 19.352 (**IIb**), 14.388 (**IIc**).

Diethyl 1-(2-cyanofur-3-yl)-2-methoxyethylenephosphonate (IIIc, IIId). Yield 75%, *E*-**IIIc** : *Z*-**IIId** = 3:1. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: common signals: 1.274 t (CH_3-ethyl, J_{HH} 7.0 Hz), 3.804–3.952 m (CH_2OP); **IIIc**: 3.759 s (OCH_3), 6.439 d (H^4, J_{HH} 2.0 Hz), 7.113 d (HC=CP, J_{PH} 10.4 Hz); 7.358 d (H^5, J_{HH} 2.0 Hz); **IIId**: 3.748 s (OCH_3), 6.491 d (H^4, J_{HH} 1.6 Hz), 6.876 d (HC=CP, J_{PH} 33.2 Hz); 7.332 d (H^5, J_{HH} 1.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **IIIc:** 16.356 (CH_3, $^3J_{PC}$ 6.4 Hz), 61.906 (CH_2OP, $^2J_{PC}$ 5.1 Hz), 62.622 (CH_3O), 93.914 (P–C=, $^1J_{PC}$ 199.7 Hz), 112.657, 113.903 (CN, C^4), 124.404 (C^3, $^2J_{PC}$ 12.6 Hz), 128.001 (C^2, $^3J_{PC}$ 7.5 Hz), 146.659 (C^5), 162.791 (=CH–OCH_3, $^2J_{PC}$ 24.1 Hz); **IIId:** 16.163 (CH_3, $^3J_{PC}$ 6.2 Hz), 62.042 (CH_2OP, $^2J_{PC}$ 5.4 Hz), 62.529 (CH_3O), 95.528 (P–C=, $^1J_{PC}$ 187.6 Hz), 111.642, 111.884 (CN, C^4), 122.068 (C^3, $^2J_{PC}$ 10.5 Hz), 132.556 (C^2, $^3J_{PC}$

8.8 Hz), 147.063 (C^5), 162.035 (=CH–OCH_3). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 18.054 **(IIIc)**, 12.777 **(IIId)**.

Diethyl 1-(3-cyanofur-2-yl)-2-methoxyethylenephosphonate (IVc, IVd). Yield 51%, *E*-**IVc** : *Z*-**IVd** = 1:0.8. ^1H NMR spectrum ($CDCl_3$), δ, ppm: common signals: 3.904–3.971 m (CH_2OP); **IVc**: 1.111 t (CH_3-ethyl, J_{HH} 7.2 Hz), 3.948 s (CH_3O), 6.404 d (H^4, J_{HH} 1.6 Hz), 7.194 d (HC=CP, J_{PH} 9.6 Hz); **IVd**: 1.124 t (CH_3-ethyl, J_{HH} 7.2 Hz); 3.927 s (CH_3O), 6.449 d (H^4, J_{HH} 1.2 Hz), 7.071 d (HC=CP, J_{PH} 31.6 Hz), 7.262 d (H^5, J_{HH} 1.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: common signals: 16.059 (CH_3, $^3J_{PC}$ 6.2 Hz); **IVc**: 61.183 (OCH_3), 62.155 (CH_2OP, $^2J_{PC}$ 5.6 Hz), 94.433 (P–C=, $^1J_{PC}$ 196.4 Hz), 96.065 (C^3, $^3J_{PC}$ 7.5 Hz), 112.367, 113.586 (C^4, CN), 142.433 (C^5), 157.532 (C^2, $^3J_{PC}$ 5.7 Hz), 164.979 (=CH–OCH_3, $^2J_{PC}$ 21.9 Hz); **IVd**: 62.275 (CH_2OP, $^2J_{PC}$ 6.3 Hz), 63.088 (OCH_3), 93.987 (C^3, $^3J_{PC}$ 5.6 Hz); 96.288 (P–C=, $^1J_{PC}$ 187.7 Hz), 111.829, 114.183 (C^4, CN), 142.835 (C^5), 153.680 (C^2), 164.936 (=CH–OCH_3). ^{31}P NMR spectrum ($CDCl_3$) δ_P, ppm: 15.537 (**IVc**), 10.575 (**IVd**).

Diethyl 1-(4-cyanofur-2-yl)-2-methoxyethylenephosphonate (Vb, Vc). Yield 60%, *E*-**Vb** : *Z*-**Vc** = 2:1. ^1H NMR spectrum ($CDCl_3$), δ, ppm: common signals: 1.210–1.227 m (CH_3-ethyl), 3.979–4.069 m (CH_2OP); **Vb**: 3.979 s (OCH_3), 6.675 s (H^3), 7.190 d (HC=CP, J_{PH} 10.8 Hz), 7.877 s (H^5); **Vc**: 3.897 (OCH_3), 6.628 s (H^3), 7.284 (H^5), 7.795 d (HC=CP, J_{PH} 32.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **Vb**: 16.293 (CH_3-ethyl, $^3J_{PC}$ 5.7 Hz, 62.073 (CH_2OP, $^2J_{PC}$ 4.4 Hz), 62.812 (OCH_3), 93.324 (P–C=, $^1J_{PC}$ 194.5 Hz), 99.010 (C^4), 109.404 (C^3, $^3J_{PC}$ 6.8 Hz), 113.135 (CN), 147.640 (C^5), 147.671 (C^2, $^2J_{PC}$ 6.8 Hz), 161.878 (=CH–OCH_3, $^2J_{PC}$ 20.7 Hz); **Vc**: 16.164 (CH_3-ethyl, $^3J_{PC}$ 6.3 Hz), 62.812 (OCH_3), 63.461 (CH_2OP, $^2J_{PC}$ 6.0 Hz), 93.324 (P–C=, $^1J_{PC}$ 194.5 Hz), 97.997 (C^4), 109.404 (C^3, $^3J_{PC}$ 6.8 Hz), 113.065 (CN), 149.165 (C^5), 149.191 (C^2, $^2J_{PC}$ 5.3 Hz), 161.519 (=CH–OCH_3). ^{31}P NMR spectrum ($CDCl_3$) δ_P : 16.768 (**Vb**), 12.143 (**Vc**).

Diethyl 1-(4-cyanofur-3-yl)-2-methoxyethylenephosphonate (VIc, VId). Yield 62%. *E*-**VIc** : *Z*-**VId** = 2:1. . ^1H NMR spectrum ($CDCl_3$), δ, ppm: common signals: 1.226 t CH_3-ethyl J_{HH} 7.0 Hz), 3.979–4.111 m (CH_2OP); **VIc**: 3.860 (CH_3O), 7.159 d (HC=CP, J_{PH} 9.6 Hz), 7.446 s (H^2), 7.890 s (H^5); **VId**: 3.851 (CH_3O), 7.006 d (HC=CP, J_{PH} 33.2 Hz), 7.586 s (H^2), 7.868 s (H^5). ^{31}P NMR spectrum ($CDCl_3$) δ_P, ppm: 18.458 (**VIc**), 13.869 (**VId**). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: **VIc**: 16.167 (CH_3-ethyl, $^3J_{PC}$ 6.4 Hz), 61.633 (OCH_3), 61.925 (CH_2OP, $^2J_{PC}$ 5.1 Hz), 93.338 (P–C=, $^1J_{PC}$ 200.0 Hz), 99.807 (C^4, $^3J_{PC}$ 7.9 Hz), 112.728 (CN), 117.445 (C^3, $^2J_{PC}$ 7.3 Hz), 141.946 (C^2, $^3J_{PC}$ 3.1 Hz), 150.039 (C^5), 162.261 (=CH–OCH_3, $^2J_{PC}$ 25.0 Hz); **VId**: 16.167 (CH_3-ethyl, $^3J_{PC}$ 6.4 Hz), 62.049 (CH_2OP, $^2J_{PC}$ 5.5 Hz), 62.228 (OCH_3), 95.125 (P–C=, $^1J_{PC}$ 186.2 Hz), 98.677 (C^4, $^3J_{PC}$ 6.6 Hz), 113.024 (CN), 119.933 (C^3, $^2J_{PC}$ 9.7 Hz), 142.501 (C^2, $^3J_{PC}$ 3.6 Hz), 150.207 (C^5), 160.972 (=CH–OCH_3).

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