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Synthesis and Wittig Reaction of Formylated (Trifluoromethylfuryl)methanephosphonates

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Abstract—Methods of synthesis of 4-functionalyzed (5-trifluoromethylfur-2-yl)methanephosphonates and (5-methyl-2-trifluoromethylfur-3-yl)methanephosphonate are developed. Their formylation with ethyl formate in the presence of sodium foil is studied. Spectral characteristics of tautomers of obtained derivatives of phosphonoacetic aldehyde are evaluated. It is shown that interaction of obtained formyl derivatives with ethoxycarbonylmethylenetriphenylphosphorane regardless of the structure of the furan fragment leads to 4-furylsubstituted alkyl 4-(diethoxyphosphoryl)but-3-enoate, the abnormal product of Wittig reaction.

Keywords: trifluoromethylfuranes, methanephosphonates, formylation, tautomerism, Wittig reaction

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Recently we have found that diethyl (5-trifluoromethylfur-2-yl)methanephosphonate prepared from the corresponding bromomethylfuran via the Arbuzov reaction can be formylated at the active methylene group to give trifluoromethylfuryl derivative of phosphonoacetic aldehyde. This compound is completely enolized. Despite of this fact the above-mentioned compound reacts with ethoxycarbonylmethylenetriphenylphosphorane to give the abnormal product of Wittig reaction, ethyl 4-(5-trifluoromethylfur-2-yl)-4-(diethoxyphosphoryl)but-3-enoate [1, 2]. This reaction was thoroughly studied by an example of ethoxycarbonylfuryl and cyanofuryl derivatives of (diethoxyphosphoryl)acetic aldehyde [3]. It occurred that in all cases the abnormal product was preferable, but if the electron-acceptor group and phosphorus-containing substituent occupy neighboring positions of the furan ring the formation of usual product of the Wittig reaction, 4-furylsubstituted 4-(diethoxyphosphoryl)but-2-enoate was also observed.

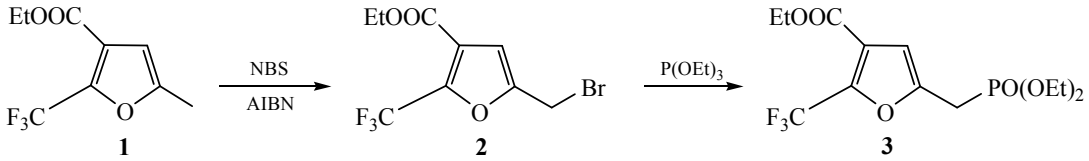
In this work we have continued studies of this reaction range with the participation of derivatives of diethyl (5-trifluoromethylfur-2-yl)methanephosphonate containing additional electron-acceptor substituent that is the ester or nitrile group in the furan ring, and also diethyl (2-trifluoromethylfur-3-yl)methanephosphonate. In the last case trifluoromethyl group was adjacent to the active methylene one. Evaluation of its effect on the Claisen formylation and the subsequent Wittig reaction presented special interest.

First step in solving these problems was the synthesis of alkyl (5-trifluoromethylfur-2-yl)methanephosphonates containing ethoxycarbonyl or cyano group in the furan ring. Evidently their presence would increase CH-acidity of the furan-CH_2P fragment and facilitate its participation in ester condensation.

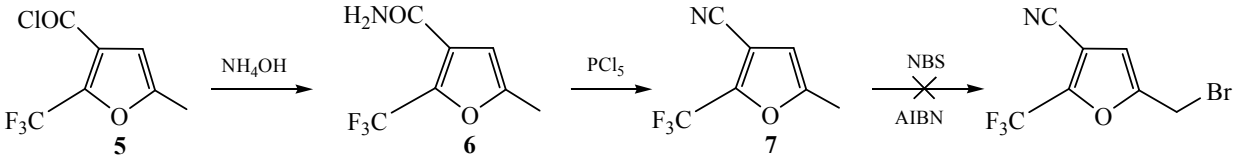
Ethyl 2-trifluoromethyl-5-methyl-3-furoate **1** was chosen as the starting substance. By bromination with NBS in the presence of AIBN it was converted to the known bromide **2** [4]. Phosphorylation of the latter with triethyl phosphite via the Arbuzov reaction gave phosphonate **3** in 63% yield (Scheme 1). In NMR spectra of this compound the signal of phosphorus nucleus was observed at 20.76 ppm, the doublet of protons of P–CH_2-furan fragment was located at 3.20 ppm (J_{PH} = 20.8 Hz), and the signal of the corresponding carbon atom, at 20.42 ppm ($^1J_{PC}$ = 142.8 Hz). The signal of fluorine nuclei was registered at –61.18 ppm.

We presumed that diethyl (4-cyano-5-trifluoromethylfur-2-yl)methanephosphonate **4** must be the most available via the sequence of transformations

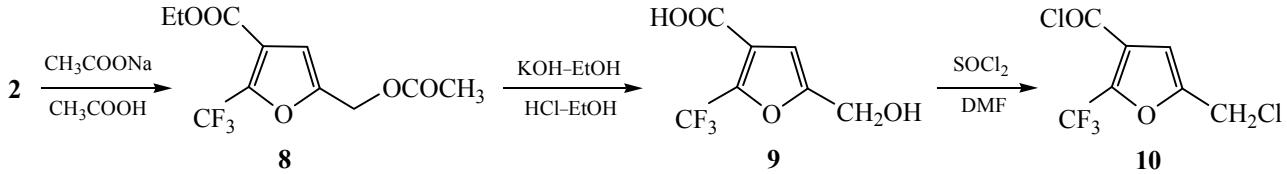
Scheme 1.



Scheme 2.



Scheme 3.



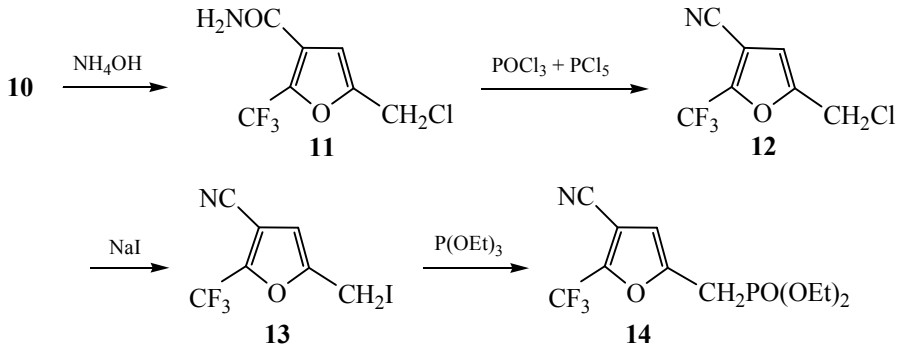
including the dehydration of amide **6** to nitrile **7**, the bromination of the latter at methyl group and prosphorylation of bromide **8** using the Arbuzov reaction (Scheme 2).

Starting acid chloride **5** was prepared according to a described protocol [4] from ester **1**. Treating its cold benzene solution with 25% ammonia gave the corresponding amide **6** in 68% yield. In the ^{1}H NMR spectrum of this substance two broad signals at 7.48 and 7.81 ppm were present. That proves the formation of a primary amide group. Amide **6** was converted to nitrile **7** by treating with phosphorus pentachloride by boiling in tetrachloromethane for 2.5 h. The target product was isolated by a vacuum distillation in a 62% yield. The formation of a nitrile group was confirmed by the appearance of a characteristic signal of carbon atom at 110.44 ppm (CN), the disappearance of the carbonyl group signal at 162.12 ppm and by the upfield shift of the signal of C^3 carbon atom of the furan ring from 125.68 ppm in the starting amide to 99.67 ppm in the reaction product. All attempts to brominate nitrile **7** with NBS failed. Regardless of used amount of AIBN only starting substance was isolated from the reaction mixture.

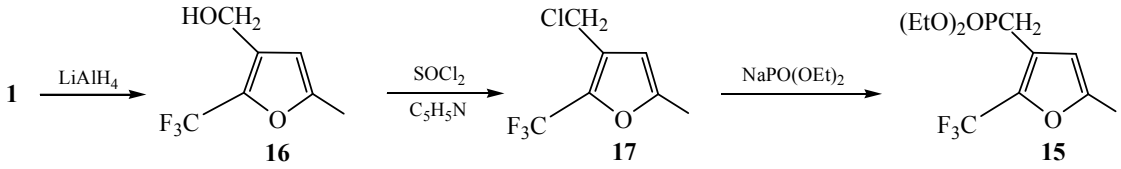
Because of that another pathway beginning from transformation of methyl group in the furan ring was developed (Scheme 3). By treating bromide **2** with sodium acetate in acetic acid according to the protocol [5] acetate **8** was obtained. Its hydrolysis with ethanol solution of potassium hydroxide at room temperature gave hydroxyl acid **9** in a 94% yield. By boiling this acid with thionyl chloride in benzene in the presence of DMF the chloride of 2-trifluoromethyl-5-chloromethyl-3-furoic acid **10** was synthesized in a 48% yield. The singlet of chloromethyl group protons in its ^{1}H NMR spectrum was located at 4.61 ppm. The signal of the corresponding carbon atom appeared at 35.45 ppm, and of the carbonyl carbon atom, at 158.85 ppm. The signal of fluorine nuclei was found at –62.79 ppm.

Treating benzene solution of acid chloride **10** with ammonia at 4–5°C lead to amide **11** in 48% yield (Scheme 4). Under these conditions the chloromethyl group did not take part in the reaction. Dehydration of amide **11** to nitrile was carried out by treating with phosphorus pentachloride in phosphorus oxychloride-carbon tetrachloride mixture. This system was found to be much more efficient than phosphorus pentachloride in tetrachloromethane or benzene. Instead of usually observed 50–60% yield nitrile **12** was obtained in 92% yield. Its isolation was also simple. As a rule, dehydrochlorination of the majority of imidoyl chloride formed in the reaction of phosphorus pentachloride with amide proceeds while distillation at about 100°C. In the case under consideration this process takes place directly in the reaction mixture. It is proved by more intense evolution of hydrogen chloride and absence of

Scheme 4.



Scheme 5.



solid phase after removing the solvent. Evidently, phosphorus oxychloride also reacts with amide and forming phosphoric acid dichloride catalyzes dehydrochlorination of imidoyl chloride. Simultaneously reaction of phosphorus pentachloride with phosphoric acid dichloride takes place, its only product being phosphorus oxychloride. Signal of the nitrile group carbon atom in the ^{13}C NMR spectrum of compound **12** was observed at 109.64 ppm.

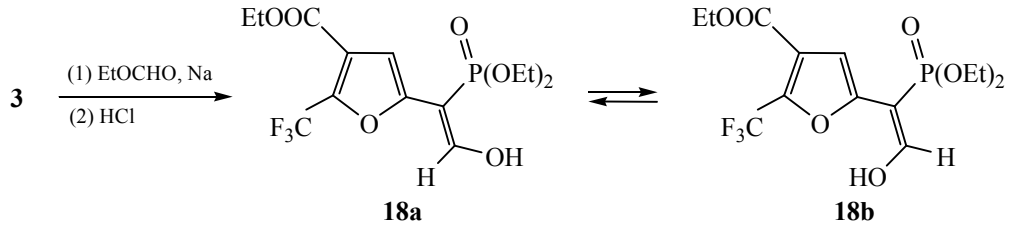
Chloromethyl derivative **12** had the desired structure, but such compounds enter the Arbuzov reaction only at 160–170°C what may provoke their decomposition. Therefore we tried to prepare much more active iodomethyl derivative **13** by means of the Finkelstein reaction. The substitution of chlorine for iodine was carried out at room temperature in the dark using saturated acetone solution of sodium iodide dihydrate. The target product **13** was obtained in 57% yield. The signal of iodomethyl group protons was observed at 4.38 ppm, that of the corresponding carbon atom, at –11.88 ppm, and of the nitrile group carbon atom, at 109.72 ppm. As compared to another known iodomethylfurans compound **13** is relatively stable towards light.

Phosphorylation of amide **13** was carried out by treating with triethyl phosphite under heating and distillation of evolving ethyl iodide from the reaction mixture (Scheme 4). Phosphonate **14** was isolated by a vacuum distillation in a 51% yield. The signal of the phosphorus atom in this compound was observed at 19.71 ppm, the doublet of phosphonomethyl group protons was found at 3.29 ppm (J_{PH} = 21.2 Hz), and the signal of the corresponding carbon atom, at 26.66 ppm ($^1J_{PC}$ = 142.9 Hz).

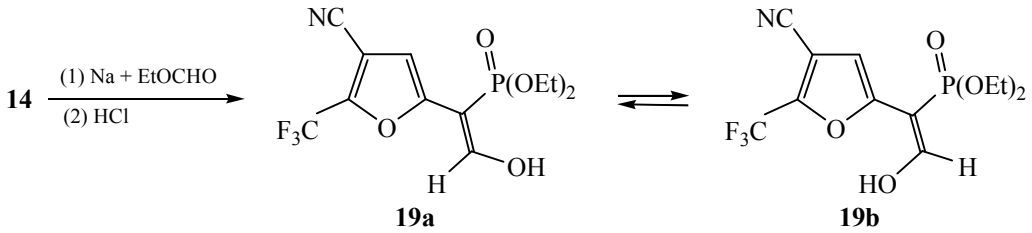
The synthesis of diethyl (2-trifluoromethyl-5-methylfur-3-yl)methanephosphonate **15** began by reduction of ester **1** to alcohol **16** with lithium aluminum hydride (Scheme 5). The target product was isolated by vacuum distillation in a 70% yield. The signal of hydroxymethyl group protons in this substance was observed at 4.59 ppm and of the corresponding carbon atom, at 55.10 ppm. 3-Chloromethylfuran **17** was prepared in a 48% yield by treating ethyl acetate solution of alcohol **16** and pyridine with thionyl chloride. The formation of chloromethyl fragment was confirmed by the signal of chloromethyl group protons at 4.51 ppm and of the corresponding carbon atom, at 34.89 ppm. Phosphorylation of chloride **17** was carried out under conditions of the Michaelis–Becker reaction with sodium diethyl phosphite in benzene at 80°C for 16 h. Phosphonate **15** was isolated by vacuum distillation in a 69% yield.

Hence, two new phosphonates **3** and **14** were synthesized. In these substances phosphonomethyl group is located in the position 2 of the furan ring. It is exposed to combined acidifying action of trifluoromethyl and ethoxycarbonyl or cyano groups. New phosphonate **15** contained phosphonomethyl group in

Scheme 6.



Scheme 7.



the position 3 of the furan ring which was acidified only by the action of 2-trifluoromethyl group. Next step of our work was the formylation of these compounds under the conditions of Claisen reaction.

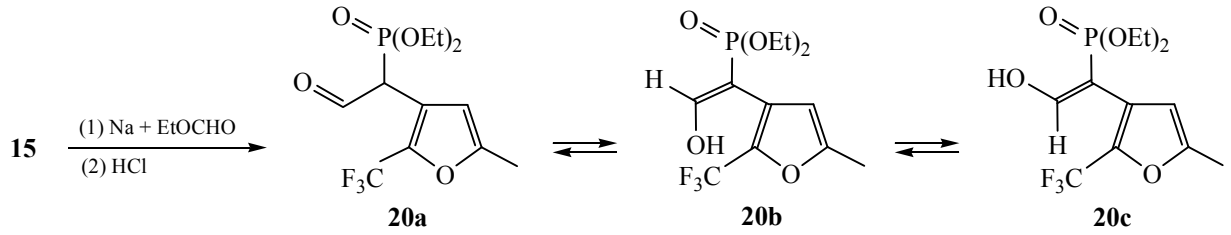
The formylation of phosphonate **3** was carried out according to protocol [1] in benzene at phosphonate : sodium : ethyl formate molar ratio 1.0 : 1.2 : 2.0 (Scheme 6). In the course of the reaction the dissolution of sodium and insignificant heat evolution in the course of ~4 h was observed. Sodium enolate was not isolated from the reaction mixture. After extraction of reaction products with water and acidifying of extract with hydrochloric acid to pH 2–3 formyl derivative **18** was isolated in a 48% yield.

In the ^{31}P NMR spectrum of the obtained preparation two signals at 18.42 and 19.88 ppm with the intensity ratio 0.2 : 1.0 were observed. ^{19}F NMR spectrum contained two signals at –61.36 and –61.33 ppm with the same ratio of intensities. In the ^{1}H NMR spectrum two doublets at 7.73 (J_{PH} = 10.4 Hz) and 7.87 ppm (J_{PH} = 38.4 Hz) with the intensity ratio 0.2 : 1.0 and the broadened signal at 11.58 ppm are present. These data show that formyl derivative **18** is completely enolyzed in solution. It exists as a mixture of isomers with *Z*- (**18a**) and *E*-location (**18b**) of diethoxyphosphoryl and hydroxy groups, *Z*-isomer being the main form. Signals of H^3 proton of the furan ring in these compounds also differ. They appear at 6.54 ppm for *Z*-enol and at 7.03 ppm for *E*-enol. In the ^{13}C NMR spectrum signals of carbon atom directly bound with phosphorus are located at 91.09 ppm ($^{1}J_{PC}$ = 180.5 Hz) (**18a**) and at 92.02 ppm ($^{1}J_{PC}$ = 202.8 Hz) (**18b**). Signals of carbon atom bound with oxygen are found at 160.83 and 161.03 ppm ($^{2}J_{PC}$ = 20.6 Hz) respectively [6–8].

The formylation of phosphonate **14** was carried out analogously. Formyl derivative **19** was isolated in a 39% yield (Scheme 7). In ^{31}P NMR spectrum of obtained compound two signals at 17.37 and 19.06 ppm with the intensity ratio 0.2 : 1.0 are presented. In ^{19}F NMR spectrum the signals of trifluoromethyl groups with the same ratio of intensities are located at –63.56 and –63.48 ppm. In the ^{1}H NMR spectrum of this preparation two doublets at 7. 79 ppm (J_{PH} = 10.4 Hz) and 7.92 ppm (J_{PH} = 39.2 Hz) with the intensity ratio 0.2 : 1.0 and the broadened signal at 11.75 ppm are found. Hence, compound **19** is also a mixture of *Z*-enol **19a** and *E*-enol **19b** [6–8]. Similarly to the previous case *Z*-enol is the main product. In the ^{13}C NMR spectrum signals of carbon atoms directly bound with phosphorus are located at 91.09 ppm ($^{1}J_{PC}$ = 180.5 Hz) (**19a)** and 91.75 ppm ($^{1}J_{PC}$ = 179.1 Hz) (**19b**). Signals of carbon atoms bound with oxygen are registered at 164.87 pm ($^{2}J_{PC}$ = 1.1 Hz) and 162.30 ppm ($^{2}J_{PC}$ = 20.7 Hz) respectively [7]. Nucleus of the carbon atom of the nitrile group resonates at 110.18 ppm.

By the formylation of phosphonate **15** according to the above-described protocol formyl derivative **20** (Scheme 8) was obtained. In ^{31}P NMR spectrum of this preparation three signals at 16.19, 22.04, and 21.44 ppm with the intensity ratio 0.3 : 0.7 : 1.0 were

Scheme 8.



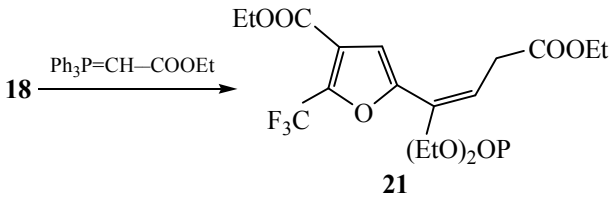
observed. In ^{19}F NMR spectrum three signals at –61.27, –60.11, and –63.43 ppm with the same intensity ratio were present. In the ^{1}H NMR spectrum a doublet at 4.53 ppm (J_{PH} = 28.0 Hz) and a singlet of the same intensity at 9.76 ppm were registered. In the ^{13}C NMR spectrum signals of the corresponding carbon atoms were located at 50.12 ppm ($^{1}J_{PC}$ = 129.6 Hz) and 191.75 ppm ($^{2}J_{PC}$ = 4.3 Hz). These spectral data show that not only *E*- and *Z*-enols, but also the aldehyde form containing PCH–CHO fragment is present [7]. The signal of the furan ring proton corresponding by intensity to the aldehyde proton signal was located at 6.40 ppm, and of methyl group, at 2.37 ppm. The described set of signals characterizes aldehyde **20a** which is present in the mixture in the smallest amount. More intense set of proton signals includes a singlet at 6.01 ppm (H^4-furan) and a doublet at 7.61 ppm (J_{PH} = 10.0 Hz). These signals can be attributed to *E*-enol **20b**. Hydroxyl proton of this enol form evidently easily exchanges with deuterium because the residual signal of chloroform in the ^{1}H NMR spectrum of phosphonate **20** is much more intense, than in all the other cases. Signal of carbon atom directly bound with phosphorus belonging to **20b** form was located at 89.90 ppm ($^{1}J_{PC}$ = 181.4 Hz). Doublet of =CH–O carbon atom of this form was observed at 159.55 ppm with the characteristic coupling constant 25.9 Hz [7]. All components of the signal are broadened due to the coupling with fluorine nuclei. Third set of signals of protons with relative intensity 0.7 included broad doublet at 11.17 ppm and a doublet of doublets at 7.24 ppm. A large coupling constant of the last signal (40.0 Hz) is characteristic of the olefin proton *trans*-located to phosphorus which belongs to *Z*-enol **20b**. This proton interacts with the exchange proton of enol hydroxyl group. As the signals are broadened, the convergence of the coupling constant values is not strict its average meaning being 12.0 Hz. In the ^{13}C NMR spectrum the signal of the carbon atom directly bound with phosphorus appears at 91.34 ppm ($^{1}J_{PC}$ = 205.7 Hz). Its components are broadened because of coupling with fluorine. Quartet of =CH–O fragment is located at 163.77 ppm ($^{5}J_{FC}$ = 2.4 Hz). This signal is not split from phosphorus what is characteristic of *Z*-enol forms [7, 8]. Signal of H^4 proton of the furan ring of *Z*-enol **20b** is located at 6.50 ppm.

Hence, the structure of trifluoromethylfuryl derivatives of phosphonoacetic aldehyde strongly depends on the structure of substituents in the furan ring. If the substituents in the furan ring are remote from the phosphorus-containing fragment as in 5-trifluoromethylfuryl derivative [1] or in 4,5-disubstituted phosphonates **18**, **19**, these substances are completely enolized in chloroform. In all the cases *Z*-isomer prevails. CH-acidity of 2-trifluoromethyl-5-methylfur-3-yl derivative is evidently lower. Therefore in the equilibrium mixture in chloroform a significant amount of aldehyde form appears there though enol ones still prevail. Probably because of sterical factors *E*-isomer becomes the main one, but its prevalence is not large.

Formyl derivatives **18–20** were involved in Wittig reaction with ethoxycarbonylmethylenetriphenylphosphorane analogously to [3]. The reaction was carried out in benzene at boiling at phosphonate : phosphorane molar ratio = 1 : 1.2 (Scheme 9). The reaction progress was monitored by means of ^{31}P NMR spectroscopy.

In the reaction of compound **18** the abnormal product of Wittig reaction, ethyl *E*-4-(4-ethoxycarbonyl-5-trifluoromethylfur-2-yl)-4-(diethoxyphosphoryl)-but-3-enoate is formed in 80% yield (Scheme 9). In the ^{1}H NMR spectrum of this substance two doublets of

Scheme 9.

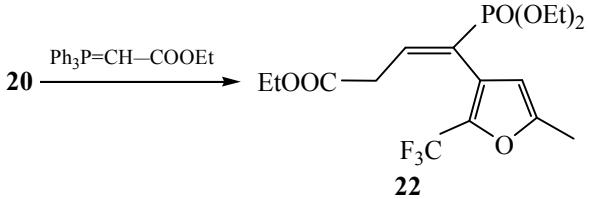


doublets at 3.60 (J_{HH} = 7.0, J_{PH} = 3.2 Hz) and 3.89 ppm (J_{HH} = 7.0, J_{PH} = 3.2 Hz) with the intensity ratio 1 : 0.4 and total intensity 2H were present. A doublet of triplets with total intensity corresponding to 1H was located at 7.13 ppm (J_{HH} = 7.0, J_{PH} = 23.2 Hz). These data show the formation of olefin fragment with phosphorus *trans*-located with respect to ethoxycarbonylmethylene group [8]. The compound probably exists as a mixture of two spectroscopically different conformers. It is confirmed also by the presence of two phosphorus signals at 11.87 and 14.03 ppm (0.4 : 1.0) in ^{31}P NMR spectrum and two signals of fluorine at –61.55 and –61.68 ppm (0.4 : 1.0) in ^{19}F NMR spectrum. At the same time the side chain is characterized in the ^{13}C NMR spectrum by one set of signals including doublets at 35.71 ppm (PC=CH$\underline{C}^{\alpha}$H$_2$, $^3J_{PC}$ = 18.0 Hz), 121.79 ppm (=CP, $^1J_{PC}$ = 185.6 Hz), and 142.10 ppm (=CH, $^2J_{PC}$ = 7.2 Hz).

The reaction of nitrile **19** with ethoxycarbonylmethylenetriphenylphosphorane was carried out analogously, but only triphenylphosphine oxide was isolated from the reaction mixture. Evidently, the product of condensation of this substance with phosphorane still more eagerly undergoes polymerization than the compounds containing no trifluoromethyl group [3].

In the reaction of formyl derivative **20** the abnormal product **22** is also formed in a 61% yield (Scheme 10). It has *E*-configuration as is well confirmed by spectral data. Hence, despite of the presence of aldehyde **20a** in the equilibrium mixture of tautomers of phosphonate **20** and the occupation of position 2 of the furan ring with substituent, Wittig condensation proceeds unambiguously. As there is no strong base in the reaction mixture, but-3-enoate derivative is formed directly in the course of the reaction and not as a result of subsequent prototropic isomerization. Note that neighboring position of trifluoromethyl group and the reaction center does not influence the result of the reaction. It characterizes the difference of its effect from that provided by the ester and nitrile group as found previously [3].

Scheme 10.



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Hence, the formation of alkyl *E*-4-(furyl)-4-(diethoxyphosphoryl)but-3-enoates in the reaction of phosphorylated derivatives of furylacetic aldehyde is a general rule for a broad range of 2- and 3-substituted furan derivatives containing ester, nitrile, or trifluoromethyl group in the ring.

EXPERIMENTAL

^{1}H, ^{13}C, and ^{31}P NMR spectra were taken on a Bruker DPX-400 spectrometer [400.13 (^{1}H), 161.97 (^{31}P), 100.16 MHz (^{13}C) respectively]. Melting points were measured on a Boëtius apparatus.

Ethyl 5-[(diethoxyphosphoryl)methyl]-2-(trifluoromethyl)-3-furoate (3). To 4.0 g (13.29 mmol) of bromide **2**, 2.8 mL of triethyl phosphite was added. The reaction mixture was heated to 160°C until the end of ethyl bromide evolution. Vacuum distillation of reaction mixture gave 3.02 g (63%) of phosphonate **3** as yellow oil of bp 154°C (1 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.25 t (3H, CH_3-ester, J_{HH} = 7.2), 1.28 t (6H, CH_3-phosphonate, J_{HH} = 7.2), 3.20 d (2H, CH_2P, $^1J_{PH}$ = 20.8), 4.08 q (2H, OCH_2-ester, J_{HH} = 7.6), 4.09–4.11 m (4H, OCH_2-phosphonate), 6.66 d (1H, H^4-furan, $^3J_{PH}$ = 3.6). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 13.78 (CH_3-ester), 16.15 d (CH_3-phosphonate, $^3J_{PC}$ = 3.2), 20.42 d (CH_2P, $^1J_{PC}$ = 142.8), 61.35 (OCH_2-ester), 62.58 d (OCH_2-phosphonate, $^2J_{PC}$ = 6.1), 62.61 (OCH_2-phosphonate, $^2J_{PC}$ = 6.0), 110.94 d (C^3-furan, $^3J_{PC}$ = 6.7), 118.35 q (CF_3, $^1J_{FC}$ = 267.4), 120.72 (C^4-furan), 142.47 d.q (C^5-furan, $^2J_{CF}$ = 42.6, $^3J_{PC}$ = 2.7), 148.16 d (C^2-furan, $^2J_{PC}$ = 8.7), 160.50 (C=O). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –61.18(CF_3). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 20.76.

5-Methyl-2-(trifluoromethyl)furan-3-carboxamide (6). In 10 mL of benzene was dissolved 1.39 g (6.4 mmol) of acid chloride **5**, the solution was cooled on an ice bath and was treated with 3 mL of 25% ammonia. The reaction mixture was stirred for 1h at 10°C. The obtained precipitate was filtered off and dried in air until the constant mass. Yield 0.8 g (68%), white powder. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.35 s (1H, CH_3), 6.62 s (1H, H^4-furan), 7.48 s (1H, NH_2), 7.81 s (1H, NH_2). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm (*J*, Hz): 13.47 (CH_3), 108.29 (C^4-furan), 119.39 q (CF_3, $^1J_{FC}$ = 266.3), 125.68 br.s (C^3-furan), 135.19 q (C^2-furan, $^2J_{FC}$ = 43.3), 154.32 (C^5-furan), 162.12 (C=O). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: –60.13 (CF_3).

5-Methyl-2-(trifluoromethyl)-3-cyanofuran (7). To the suspension of 2.8 g (15.6 mmol) of amide **6** in 40 mL of carbon tetrachloride 3.26 g (15.6 mmol) of phosphorus pentachloride was added in small portions at vigorous stirring. The mixture formed was refluxed with stirring for 2.5 h. Vacuum distillation gave 1.7 g (62%) of nitrile **7** as a colorless oil with sweet scent, bp 102–104°C (10 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.43 s (1H, CH_3), 6.37 s (1H, H^4-furan). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 13.33 (CH_3), 99.67 (C^3-furan), 108.74 (C^4-furan), 110.44 (CN), 117.70 q (CF_3, $^1J_{FC}$ = 267.6), 145.22 q (C^2-furan, $^2J_{FC}$ = 42.9), 156.74 (C^5-furan). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –63.75 (CF_3).

5-(Hydroxymethyl)-2-(trifluoromethyl)-3-furoic acid (9). A mixture of 12.83 g (46 mmol) of acetoxymethylfuran **8** and 5.7 g (101.2 mmol) of potassium hydroxide in 50 mL of ethanol was stirred at room temperature for a day. At the beginning a small heat evolution was observed, the temperature of the reaction mixture rose to 30°C. On the next day the reaction mixture was acidified with saturated ethanol solution of hydrogen chloride until pH 2, potassium chloride precipitate was filtered off and washed with 15 mL of ethanol. Joined filtrates were evaporated to dryness, the crystals formed were suspended in chloroform, filtered, and dried in air until constant mass. Yield 9.06 g (94%), light yellow crystals, mp 157°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 4.47 s (2H, CH_2), 6.76 s (1H, H^3-furan). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm (*J*, Hz): 55.56 (CH_2OH), 110.06 (C^4-furan), 119.05 q (CF_3, $^1J_{FC}$ = 267.0), 121.95 q (C^3-furan, $^3J_{FC}$ = 2.5), 140.81 q (C^2-furan, $^2J_{FC}$ = 41.5), 158.31 (C^5-furan), 162.15 (C=O). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: –60.27 (CF_3).

5-(Chloromethyl)-2-(trifluoromethyl)-3-furoyl chloride (10). To the suspension of 9.06 g (43 mmol) of hydroxyl acid **9** in 30 mL of benzene the solution of 6.3 mL (86 mmol) of thionyl chloride in 20 mL of benzene and 3 drops of DMF were added. The mixture obtained was refluxed with stirring for a day. On the next day vacuum distillation of reaction mixture gave 5.12 g (48%) of acid chloride **10** as yellow liquid of bp 88°C (1 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 4.61 s (2H, CH_2Cl), 6.99 q (1H, H^4-furan, J_{HF} = 0.8). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 35.45 (CH_2Cl), 113.03 (C^4-furan), 117.56 q (CF_3, $^1J_{FC}$ = 269.3), 123.83 q (C^3-furan, $^3J_{FC}$ = 2.1), 144.19 q (C^2-furan, $^2J_{FC}$ = 44.0), 152.33 (C^5-furan), 158.85 (C=O). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –62.79 (CF_3).

5-(Chloromethyl)-2-(trifluoromethyl)furan-3-carboxamide (11). To the cooled solution of 5.1 g (21.9 mmol) of acid chloride **10** in 30 mL of benzene 4 mL of 25% ammonia was added. Five minutes later the formation of white precipitate was observed. The reaction mixture was stirred for 1.5 h at 5°C, the precipitate was filtered off and dried in air until constant mass. Yield 2.18 g (48%), white crystals, mp 60–62°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 4.91 s (2H, CH_2Cl), 7.07 s (1H, H^4-furan), 7.69 s (1H, NH_2), 8.07 s (1H, NH_2). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm (*J*, Hz): 36.78 (CH_2Cl), 111.66 (C^4-furan), 119.07 q (CF_3, $^1J_{FC}$ = 266.8), 125.83 q (C^3-furan, $^3J_{FC}$ = 2.4), 139.71 q (C^2-furan, $^2J_{FC}$ = 41.8), 152.67 (C^5-furan), 161.68 (C=O). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: –60.44 (CF_3).

5-(Chloromethyl)-2-(trifluoromethyl)-3-cyanofuran (12). To a solution of 1.96 g (8.61 mmol) of amide **11** in 7 mL of phosphorus oxychloride 30 mL of carbon tetrachloride and 1.8 g (8.63 mmol) of phosphorus pentachloride were added. The reaction mixture was refluxed with stirring for 3 h, volatile products were removed at a reduced pressure, and the residue was distilled in a vacuum to give 1.65 g (92%) of compound **12,** light yellow liquid with bp 78–80°C (1 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 4.59 s (2H, CH_2Cl), 6.75 s (1H, H^4-furan). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 36.25 (CH_2Cl), 100.06 q (C^3-furan, $^3J_{FC}$ = 2.2), 109.64 (C≡N), 111.68 (C^4-furan), 117.33 q (CF_3, $^1J_{FC}$ = 268.7), 146.91 q (C^2-furan, $^2J_{FC}$ = 43.2), 154.32 (C^5-furan). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –63.77 (CF_3).

5-(Iodomethyl)-2-(trifluoromethyl)-3-cyanofuran (13). To a solution of 3.24 g (17.41 mmol) of sodium iodide dihydrate in 20 mL of acetone the solution of 1.83 g (8.74 mmol) of chloride **12** in 10 mL of acetone was added. The reaction mixture was kept in the dark for a day and then poured in 50 mL of 10% sodium sulfite solution. The solution formed was extracted with chloroform (25, 10, 10 mL), the extract was washed with brine and dried over calcium chloride in the dark. Chloroform was removed at a reduced pressure, and the residue was kept in a vacuum (1 mmHg) in the dark at room temperature for 1 h. Yield 1.38 g (54%), yellow syrup. Liberation of iodine under the action of light is rather slow. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 4.38 s (2H, CH_2I), 6.70 s (1H, H^4-furan). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): –11.88 (CH_2I), 100.45 q (C^3-furan, $^3J_{FC}$ = 2.2), 109.72 (C≡N), 110.10 (C^4-furan), 117.44 q (CF_3,

$^{1}J_{FC}$ = 268.4), 146.05 q (C^{2}-furan, $^{2}J_{FC}$ = 43.2), 155.97 (C^{5}-furan). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –63.67 (CF_3).

Diethyl [5-(trifluoromethyl)-4-cyanofur-2-yl]methanephosphonate (14). A mixture of 1.38 g (4.59 mmol) of nitrile **13** and 2 mL of triethyl phosphite was heated with stirring. The liberation of ethyl iodide began at 110°C and completed at 160°C. Total reaction time was 8 min. Vacuum distillation gave 0.73 g (51%) of phosphonate **14** with bp 144–145°C (1 mmHg), light yellow viscous oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.34 t (6H, CH_3, J_{HH} = 7.2), 3.29 d (2H, CH_2P, $^{2}J_{PH}$ = 21.2), 4.12–4.19 m (4H, OCH_2), 6.63 d (1H, H^{3}-furan, $^{3}J_{PH}$ = 3.2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 16.32 d (CH_3, $^{3}J_{PC}$ = 4.0), 26.66 d (CH_2P, $^{1}J_{PC}$ = 142.9), 62.92 d (OCH_2, $^{2}J_{PC}$ = 5.9), 100.22 q (C^{4}-furan, $^{3}J_{FC}$ = 2.5) 109.99 (C≡N), 110.95 d (C^{3}-furan, $^{3}J_{PC}$ = 6.6), 117.54 q (CF_3, $^{1}J_{FC}$ = 268.2), 145.93 q (C^{5}-furan, $^{2}J_{FC}$ = 42.6), 151.27 d (C^{2}-furan, $^{2}J_{PC}$ = 8.0). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –63.73 (CF_3). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 19.71.

[2-(Trifluoromethyl)-5-methylfur-3-yl]methanol (16). To a suspension of 1 g (26.3 mmol) of lithium aluminum hydride in 20 mL of diethyl ether the solution of 3.92 g (17.7 mmol) of ester **1** in 10 mL of diethyl ether was added at vigorous stirring at a rate providing a slight boiling of the solvent. After that the reaction mixture was stirred for a day. On the next day 15 mL of ethyl acetate was added dropwise with stirring, and then saturated water solution of ammonium chloride was added in small portions until coagulation of grey inorganic precipitate. The organic phase was decanted and dried over sodium sulfate. Vacuum distillation gave 2.22 g (69%) of alcohol **16** as colorless oil of bp 89–91°C (1 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.31 s (3H, CH_3), 2.62 s (1H, OH), 4.59 s (2H, CH_2O), 6.16 s (1H, H^{4}-furan). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 13.27 (CH_3), 55.10 (CH_2O), 107.93 (C^{4}-furan), 119.87 q (CF_3, $^{1}J_{FC}$ = 266.7), 128.02 (C^{3}-furan), 134.94 q (C^{2}-furan, $^{2}J_{FC}$ = 40.9), 154.61 (C^{5}-furan). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –61.58 (CF_3).

2-(Trifluoromethyl)-3-(chloromethyl)-5-methylfuran (17). To a solution of 2.22 g (12.2 mmol) of alcohol **16** and 1.2 mL of pyridine in 20 mL of ethyl acetate the solution of 0.9 mL of thionyl chloride in 10 mL of ethyl acetate was added dropwise with stirring and cooling. The reaction mixture was stirred for a day and left overnight. On the next day it was washed with 7 mL of 5% hydrochloric acid, with 10 mL of saturated sodium hydrogen carbonate solution, and then with 10 mL of brine. The solution obtained was dried over sodium sulfate and distilled in a vacuum to give 1.17 g (48%) of chloride **17** as colorless oil with bp 57°C (1 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 2.34 s (3H, CH_3), 4.51 s (2H, CH_2Cl), 6.20 s (1H, H^{4}-furan). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 13.28 (CH_3), 34.89 (CH_2Cl), 108.67 (C^{4}-furan), 119.58 q (CF_3, $^{1}J_{FC}$ = 266.0), 124.92 (C^{3}-furan), 135.93 q (C^{2}-furan, $^{2}J_{FC}$ = 40.8), 155.01 (C^{5}-furan). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –61.95 (CF_3).

Diethyl [2-(trifluoromethyl)-5-methylfur-3-yl] methanephosphonate (15). To a solution of sodium diethyl phosphite prepared from 1.5 mL of diethyl hydrogen phosphite and 0.2 g of sodium in 20 mL of benzene the solution of 1 g (5.03 mmol) of chloride **17** in 5 mL of benzene was added. The reaction mixture was refluxed with stirring for 16 h, washed with 5 mL of water, and dried over sodium sulfate. Vacuum distillation gave 0.99 g (69%) of phosphonate **15** as light yellow liquid of bp 115°C (1 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.27 t (3H, CH_3-phosphonate, J_{HH} = 7.2), 1.28 t (3H, CH_3-phosphonate, J_{HH} = 7.2), 2.29 s (3H, CH_3), 3.04 d (2H, CH_2P, J_{PH} = 21.6), 4.05–4.10 m (4H, OCH_2), 6.16 s (1H, H^{4}-furan). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 13.40 (CH_3), 16.23 d (CH_3-phosphonate, $^{3}J_{PC}$ = 5.3), 22.95 d (CH_2P, $^{1}J_{PC}$ = 142.2), 62.26 d (OCH_2-phosphonate, $^{2}J_{PC}$ = 6.2), 109.88 d (C^{4}-furan, $^{3}J_{PC}$ = 3.0), 119.94 q (CF_3, $^{1}J_{FC}$ = 267.1), 118.78 d (C^{3}-furan, $^{2}J_{PC}$ = 8.6), 136.45 d.q (C^{2}-furan, $^{2}J_{FC}$ = 40.0, $^{3}J_{CP}$ 11.7), 154.38 (C^{5}-furan). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –61.54 (CF_3). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 24.22.

Ethyl 5-[1-(diethoxyphosphoryl)-2-oxoethyl]-2-(trifluoromethyl)-3-furoate (18). To a solution of 3.0 g (8.38 mmol) of phosphonate **3** and 1.35 mL of ethyl formate in 20 mL of benzene 0.23 g (10 mg-at) of sodium foil was added. The reaction mixture was stirred until complete dissolution of sodium and left overnight. On the next day it was extracted with water (2×10 mL), the water extract was washed with 10 mL of ethyl acetate, acidified to pH 2–3 with hydrochloric acid, and saturated with sodium chloride. The reaction product was extracted with chloroform (3×10 mL) and dried over sodium sulfate. Solvent was removed on a rotary evaporator, and the residue was kept in a vacuum (1 mmHg) at room temperature for 1 h. Yield

1.44 g (46%), light yellow viscous oil. In chloroform compound **18** exists as a mixture of *Z*-enol **18a** and *E*-enol **18b** in 1 : 0.2 ratio. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): common signals: 1.27–1.33 m (9H, CH_3-ester, CH_3-phosphonate) 4.06–4.21 m (6H, OCH_2-ester, OCH_2-phosphonate), 11.58 br.s (1H, OH); **18a**: 6.54 s (1H, H^3-furan), 7.87 d (1H, =CH–O, $^2J_{PH}$ = 38.4); **18b**: 7.03 (1H, H^3-furan), 7.73 d (1H, =CH–O, $^2J_{PH}$ = 10.4). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): common signals: 13.89 (CH_3-ester), 16.04 d (CH_3-phosphonate, $^3J_{PC}$ = 6.4), 61.5 (OCH_2-ester), 63.07 d (OCH_2-phosphonate, $^2J_{PC}$ = 4.7), 118.57 q (CF_3, $^1J_{FC}$ = 267.5), 141.05 q (C^5-furan, $^2J_{FC}$ = 42.2), 149. 85 d (C^2-furan, $^2J_{PC}$ = 16.5), 163.99 (C=O); **18a**: 91.09 d (CP, $^1J_{PC}$ = 180.5), 110.57 d (C^3-furan, $^3J_{PC}$ = 7.6), 121.02 (C^4-furan), 160. 83 (=C–OH); **18b**: 92.02 d (CP, $^1J_{PC}$ = 202.8), 110.08 d (C^3-furan, $^3J_{PC}$ = 5.9), 120.75 (C^4-furan), 161. 03 d (=C–OH, $^2J_{PC}$ = 20.6). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –61.33 (CF_3, **18a**), –61.36 (CF_3, **18b**). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 18.42 (**18b**), 19.88 (**18a**).

Diethyl 1-[4-cyano-5-(trifluoromethyl)fur-2-yl]-2-oxoethylphosphonate (19). To a solution of 0.68 g (2.18 mmol) of phosphonate **14** and 0.4 mL of ethyl formate in 20 mL of benzene 0.06 g (2.6 mg-at) of sodium foil was added, and the reaction mixture was stirred for 6 h. Dissolution of sodium proceeded with slight heat evolution. On the next day the reaction mixture was extracted with water (2×10 mL), water extract was washed with 5 mL of ethyl acetate and acidified with hydrochloric acid to pH 3. The mixture formed was saturated with sodium chloride and extracted with chloroform (3×8 mL). The extract was dried with sodum sulfate, the solvent was removed on a rotary evaporator, and the residue was kept in a vacuum (1 mmHg) at room temperature for 1 h. Yield 0.29 g (39%), light yellow viscous oil. In chloroform compound **19** exists as a mixture of *Z*-enol **19a** and *E*-enol **19b** in 1 : 0.2 ratio. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): common signals: 4.08–4.24 m (4H, OCH_2), 11.75 br.s (1H, OH); **19a**: 1.37 t (6H, CH_3, J_{HH} = 7.0), 6.30 s (1H, H^3-furan), 7.92 d (1H, =CH–O, J_{PH} = 39.2); **19b**: 1.27 t (6H, CH_3, J_{HH} = 7.0), 6.93 (1H, H^3-furan), 7.78 d (1H, =CH–O, J_{PH} = 10.4). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): common signals: 100.59 q (C^4-furan, $^3J_{CF}$ = 2.2), 110.18 (CN), 117.69 q (CF_3, $^1J_{FC}$ = 267.6), 144.14 q (C^5-furan, $^2J_{FC}$ = 42.9), 152. 81 d (C^2-furan, $^2J_{PC}$ = 17.2); **19a**: 16.11 d (CH_3, $^3J_{PC}$ = 6.4), 63.31 d (OCH_2, $^2J_{PC}$ = 4.9), 90.09 d (CP, $^1J_{PC}$ = 180.5), 106.12 (C^3-furan), 164.87 d (=C–OH, $^2J_{PC}$ = 1.1); **19b**: 16.40 d (CH_3, $^3J_{PC}$ = 5.9), 62.75 d (OCH_2, $^2J_{PC}$ = 5.7), 91.75 d (CP, $^1J_{PC}$ = 179.1), 110.01 d (C^3-furan, $^3J_{PC}$ = 8.3), 162.30 d (=C–OH, $^2J_{PC}$ = 20.7). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –61.48 (CF_3, **19a**), –61.56 (CF_3, **19b**). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 17.37 (**19b**), 19.06 (**19a**).

Diethyl 1-[5-methyl-2-(trifluoromethyl)fur-3-yl]-2-oxoethylphosphonate (20). To a solution of 1.14 g (4.01 mmol) of phosphonate **15** and 0.7 mL of ethyl formate in 10 mL of benzene 0.1 g (4.34 mg-at) of sodium foil was added. The reaction mixture was stirred until complete dissolution of sodium and left overnight. On the next day the reaction mixture was extracted with water (3×5 mL), water extract was washed with 5 mL of ethyl acetate, saturated with sodium chloride, and acidified with hydrochloric acid to pH 2–3. The reaction product was extracted with chloroform and dried over sodium sulfate, the solvent was removed on a rotary evaporator, and the residue was kept in a vacuum (1 mmHg) at room temperature for 1 h. Yield 0.36 g (26%), yellow viscous oil. In the solution compound **20** exists as a mixture of aldehyde **20a**, *E*-enol **20b** and *Z*-enol **20c** in 0.3 : 1.0 : 0.7 ratio. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): common signals: 1.29 t (3H, CH_3-phosphonate, J_{HH} = 7.2), 1.35 t (3H, CH_3-phosphonate, J_{HH} = 7.0), 3.99–4.23 m (4H, OCH_2-phosphonate); **20a**: 2.37 s (3H, CH_3), 4.53 d (1H, PCH, $^1J_{PH}$ = 28.0), 6.40 s (1H, H^4-furan), 9.76 s (1H, CHO); **20b**: 2.32 s (3H, CH_3), 6.01 s (1H, H^4-furan), 7.61 d (1H, =CH, $^2J_{PH}$ = 10.0). **20c**: 2.32 s (3H, CH_3), 6.50 s (1H, H^4-furan), 7.24 d.d (1H, =CH–O, J_{PH} = 40.0, J_{HH} = 12.0), 11.17 d (OH, J_{HH} = 12.0). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): common signals: 16.06 d (CH_3-phosphonate, $^3J_{PC}$ = 6.9), 16.10 d (CH_3-phosphonate, $^3J_{PC}$ = 6.8), 16.24 d (CH_3-phosphonate, $^3J_{PC}$ = 5.8), 16.39 d (CH_3- phosphonate, $^3J_{PC}$ = 5.9), 63.49 d (OCH_2-phosphonate, $^2J_{PC}$ = 7.0), 63.77 d (OCH_2-phosphonate, $^2J_{PC}$ = 7.0), 61.95 d (CH_2O-phosphonate, $^2J_{PC}$ = 5.1), 62.54 d (CH_2O-phosphonate, $^2J_{PC}$ = 4.9); **20a**: 13.55 (CH_3), 50.12 d (PC, $^1J_{PC}$ = 129.6), 109.28 d (C^4-furan, $^3J_{PC}$ = 2.2), 118.39 d.q (C^3-furan, $^2J_{PC}$ = 7.7, $^3J_{FC}$ = 3.0), 119.72 q (CF_3, $^1J_{FC}$ 265.7), 136.68 d.q (C^2-furan, $^2J_{FC}$ = 40.0, $^3J_{CP}$ 10.3), 154. 92 (C^5-furan), 191.75 (C=O); (**20b**): 13.50 (CH_3), 88.90 d (PC=, $^1J_{PC}$ = 181.4), 110.10 s (C^4-furan), 119.86 (CF_3, $^1J_{FC}$ = 267.2), 121.56 d.q (C^3-furan, $^2J_{PC}$ = 7.9, $^3J_{FC}$ = 2.3), 135.72 (C^2-furan, $^2J_{FC}$ = 39.9, $^3J_{PC}$ = 10.9), 154.11 (C^5-furan), 159.55 br.d (=C–OH, $^2J_{PC}$ = 25.9); (**20c**): 13.50 (CH_3), 91.34 br.d (PC, $^1J_{PC}$ = 205.7), 110.10 s (C^4-furan), 119.86 q (CF_3, $^1J_{FC}$ =

267.2), 121.56 d.q (C^3-furan, $^2J_{PC}$ = 7.9, $^3J_{FC}$ = 2.3), 135.72 (C^2-furan, $^2J_{FC}$ = 39.9, $^3J_{PC}$ = 10.9), 154.11 (C^5-furan), 163.77 q (=C–OH, $^4J_{FC}$ = 2.4). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –60.11 (CF_3, **20c**), –61.27 (CF_3, **20a**), –63.43 (CF_3, **20b**). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 16.19 (**20a**), 21.44 (**20b**), 22.04 (**20c**).

Ethyl *E*-4-[4-carbethoxy-5-(trifluoromethyl)fur-2-yl)]-4-(diethoxyphosphoryl)but-3-enoate (21). A mixture of 0.65 g (1.86 mmol) of ethoxycarbonylmethylenetriphenylphosphorane, 0.6 g (1.35 mmol) of formyl derivative **18**, and 10 mL of benzene was stirred for 8 h at 70°C, diluted with 25 mL of light petroleum ether, and left overnight for crystallizaton of triphenylphosphine oxide. The precipitate formed was filtered off, and the solvent was removed from filtrate at a reduced pressure. The residue was kept in a vacuum (1 mmHg) at room temperature for 1 h. Yield 1.11 g (80%), yellow oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.25–1.37 m (12H, CH_3-ester, CH_3-phosphonate), 3.60 d.d (1.4H, CP=CH$\underline{CH}_2$, J_{HH} = 7.0, J_{PH} = 3.2), 3.89 d.d (0.6H, PC=CH$\underline{CH}_2$, J_{HH} = 7.0, J_{PH} = 3.2), 4.08–4.21 m (8H, OCH_2-ester, OCH_2-phosphonate), 7.06 s (1H, H^3-furan), 7.13 d.t (1H, PC=C$\underline{H}$, $^1J_{PH}$ = 23.2, J_{HH} = 7.0). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 13.91 (CH_3-ester), 14.07 (CH_3-ester), 16.2 d (CH_3-phosphonate, $^3J_{PC}$ = 6.2), 35.71 d (PC=CH$\underline{C}^{\alpha}H_2$, $^3J_{PC}$ = 18.0), 61.31 (CH_2O-ester), 61.65 (CH_2O-ester), 62.49 d (CH_2OP, $^2J_{PC}$ = 4.7), 62.78 d (CH_2OP, $^2J_{PC}$ = 5.3), 113.74 (C^3-furan), 120.82 br.s (C^4-furan), 118.40 q (CF_3, $^1J_{FC}$ = 267.9), 121.79 d (=CP, $^1J_{PC}$ = 185.6), 142.10 d (=CH, $^2J_{PC}$ = 7.2), 142.82 q (C^5-furan, $^2J_{FC}$ = 42.9), 149.75 d (C^2-furan, $^2J_{PC}$ = 21.6), 160.43 (furan-C=O), 169.57 (C=O). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –61.55 (CF_3, 0.4), –61.68 (CF_3, 1.0). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 11.87 (0.4), 14.03 (1.0).

Ethyl *E*-4-[5-methyl-2-(trifluoromethyl)fur-3-yl]-4-(diethoxyphosphoryl)but-3-enoate (22). This compound was prepared analogously from 0.33 g (0.94 mmol) of ethoxycarbonylmethylenetriphenylphosphorane and 0.26 g (0.80 mmol) of formyl derivative **20**. Yield 0.19 g (61%), light brown oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.19 t (3H, CH_3-ester, J_{HH} = 7.2), 1.25 t (6H, CH_3-phosphonate, J_{HH} = 7.0), 2.29 s (3H, CH_3-furan), 3.06 d.d (2H, CP=CH$\underline{CH}_2$, J_{HH} = 7.0, J_{PH} = 3.4), 4.00–4.08 m (4H, OCH_2-phosphonate), 4.09 q (2H, OCH_2-ester, J_{HH} = 7.2), 5.97 s (1H, H^4-furan), 6.99 d.t (1H, PC=C$\underline{H}$, $^1J_{PH}$ = 21.6, J_{HH} = 7.0). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 13.41 (CH_3-furan), 13.99 (CH_3-ester), 16.12 d (CH_3-phosphonate, $^3J_{PC}$ = 6.4), 35.28 d (PC=CH$\underline{C}^{\alpha}H_2$, $^3J_{PC}$ = 18.1), 61.05 (CH_2O-ester), 62.29 d (CH_2OP, $^2J_{PC}$ = 5.5), 109.60 d (C^4-furan, $^3J_{PC}$ = 1.8), 119.36 d.q (CF_3, $^1J_{FC}$ = 266.6, $^4J_{PC}$ = 1.5), 120.99 d.q (C^3-furan, $^2J_{PC}$ = 10.1, $^3J_{FC}$ = 2.4), 124.69 d (=CP, $^1J_{PC}$ = 188.1), 135.96 d.q (C^2-furan, $^3J_{PC}$ 8.9, $^2J_{FC}$ 43.1), 141.97 d (=CH, $^2J_{PC}$ = 10.9), 154.89 (C^5-furan), 169.37 (C=O). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –62.59 (CF_3). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 14.37.

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