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Reactions of Aldoketeniminophosphonates with CH-Acids

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Abstract—Aiming to obtain new polyfunctional organophosphorus compounds, we studied the reactions of aldoketeniminophosphonates with different CH-acids. The reactions were shown to proceed efficiently in anhydrous acetonitrile medium in the presence of the catalytic amounts of potassium carbonate to form the products of the addition of CH-acids to a multiple carbon-carbon bond followed by the prototropic isomerization to the corresponding γ-substituted β-functional alkylaminoethenephosphonates. The reaction of aldoketeniminophosphonates with CH-acids is found to depend significantly on the strength and nature of the acid. The formation of the carbon–carbon bond is possible mainly in the case of the CH-acids whose pK_a values lie within 10–14.

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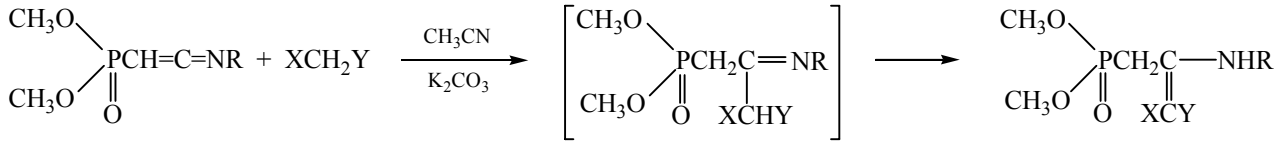
Stable aldoketeniminophosphonates formed in the reaction of chloroacetylenephosphonates with the sterically hindered primary amines (*tert*-butyl-, 1-adamantylamine) [1] are highly reactive compounds whose structure contains several reaction centers, which makes them attractive for the study of their chemical properties. The addition to them of various electrophilic and nucleophilic reagents is known [2]. However, aldoketenimines have not been brought into the reactions with CH-acids, although the expected adducts can be used as precursors for the synthesis of open-chain and heterocyclic structures with biological activity.

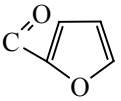
We found that aldoketeniminophosphonates react readily with CH-acids in the presence of the catalytic amount of K_2CO_3 with the quantitative formation of the corresponding phosphonates of enamine structure. Probably, the reaction proceeds as regioselective nucleophilic addition to the multiple carbon–carbon bond with an initial attack of the carbanion on the diagonal carbon atom of aldoketenimine and the subsequent prototropic imino-enamine isomerization.

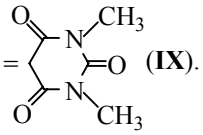
The reaction occurs in the medium of anhydrous acetonitrile at heating the equimolar amounts of the initial reactants in the presence of the catalytic amount of anhydrous potassium carbonate (~ 5 mol %) for 3–5 h.



Ia, Ib **IIa, IIb–IXa, IXb**

R = *t*-Bu (**a**), 1-Ad (**b**); X = Y = CN (**II**); X = Y = COOEt (**III**); X = CN, Y = COOEt (**IV**); X = CN, Y = SO_2Ph (**V**);

X = CN, Y = $(CH_3O)_2P(O)$ (**VI**); $XCH_2Y=CH_3C(O)NHCH(COOEt)_2$ (**VII**); X = CN,Y =  (**VIII**);

$XCH_2Y =$  (**IX**).

After the reaction completion, in the $^{1}H–\{^{31}P\}$ NMR spectrum of the reaction mixture the signal of the starting aldoketeniminophosphonate at $\delta_P \sim 25$ ppm disappears. An intense signal at $\delta_P \sim 21–23$ ppm appears, which indicates the formation of the adduct with the assumed stucture. The obtained compounds **II**–**IX** were purified from the minor tarring by the column liquid chromatography on silica gel (MN Kieselgel, 60/0.025–0.004 mm, eluent acetone–petroleum ether, 1:3). The yield is almost quantitative. The compounds **II**, **V**, and **IX** are colorless crystalline substances, the others are very viscous colored liquids which eventually crystallize.

The structure of the compounds was confirmed by the ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. Thus, in the ^{1}H NMR spectrum of dimethyl 2-(1,3-dimethyl-2,4,6-trioxohexahydro-5-pyrimidinylidene)-2-tricyclo-[3.3.1.1^{3},^{7}]dec-1-ylaminoethanephosphonate **IXb** (Fig.1) 1), the methylene protons of the carbon atom directly attached to the phosphorus appear as a doublet signal in the strong field at δ_H 2.74 ppm ($^{2}J_{HP}$ 20.8 Hz). The signals of α-, β-, and γ-protons of the adamantane fragment are observed upfield of other signals. The methoxy protons resonate in the expected region, their chemical shift is δ_H 3.77 ppm and the coupling constant is $^{3}J_{HP}$ 11.2 Hz. An intense singlet in the region of δ_H 3.27 ppm belongs to the protons of methyl groups at the nitrogen atoms of barbituric acid. The NH-proton resonates downfield at δ_H 9.12 ppm.

In the ^{13}C NMR spectrum of dimethyl 2-(1,3-dimethyl-2,4,6-trioxohexahydro-5-pyrimidinylidene)-2-tricyclo-[3.3.1.1^{3},^{7}]dec-1-ylaminoethanephosphonate **IXb** (Fig. 2) the carbon atom directly attached to the phosphorus resonates as a doublet signal at δ_C 31.21 ppm with a large coupling constant with the phosphorus nucleus ^{1}J 137.9 Hz. The carbon atom at the double bond (C^2) resonates downfield at δ_C 167.56 ppm with a small spin–spin coupling with the phosphorus nucleus ^{2}J 5.2 Hz. The signal of the second carbon atom at the double bond (C^3) appears upfield at δ_C 90.73 ppm.

In the upfield region of the spectrum there are intense singlet signals of the carbon atoms of the adamantane fragment (δ_C 29–43 ppm) and a singlet signals of the carbon atoms of two nonequivalent methyl groups ($\delta_C \sim 27$ ppm). The methoxy carbon atoms appear at δ_C 53.19 ppm with a constant of spin–spin coupling with the phosphorus nucleus $^{2}J_{CP}$ 6.0 Hz. The quaternary carbon atom of adamantyl moiety is recorded at δ_C 57.39 ppm. The carbonyl carbon atoms C^4, $C^{4'}$, and C^5 resonate in a weak field with the chemical shifts δ_C 163.15, 166.17, and 151.05 ppm, respectively.

The ^{31}P NMR spectrum of dimethyl 2-(1,3-dimethyl-2,4,6-trioxohexahydro-5-pyrimidinylidene)-2-tricyclo-[3.3.1.1^{3},^{7}]dec-1-ylaminoethanephosphonate **IXb** contains a single signal at δ_P 22.93 ppm. The IR spectra of the synthesized γ-functionally substituted β-aminoalkenephosphonates **II**–**IX** contain intense bands

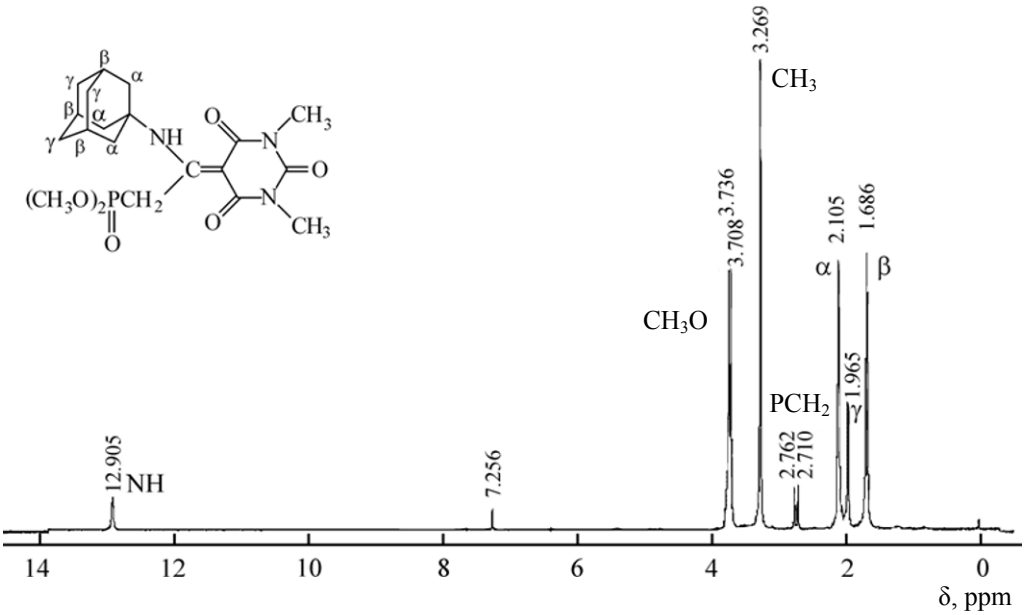


Fig. 1. The ^{1}H NMR spectrum of dimethyl 2-(1,3-dimethyl-2,4,6-trioxohexahydro-5-pyrimidinylidene)-2-tricyclo[3.3.1.1^{3,7}]dec-1-ylaminoethanephosphonate **IXb**.

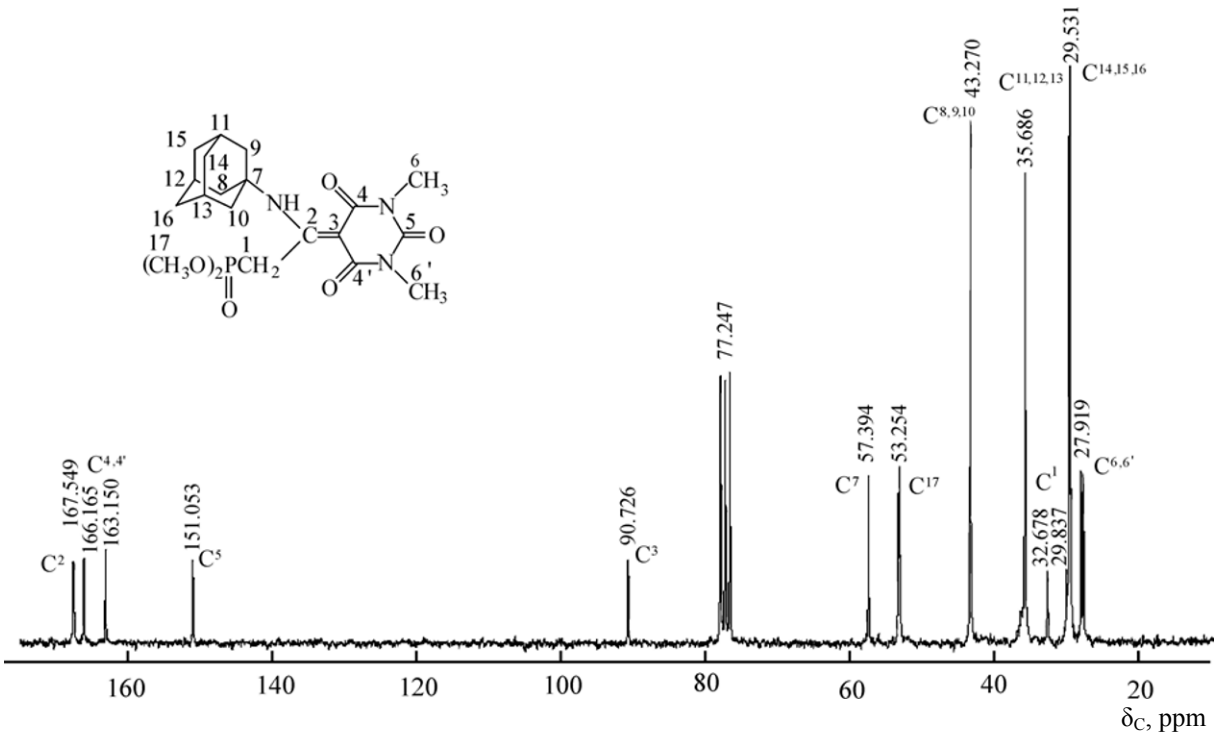


Fig. 2. The ^{13}C NMR spectrum of dimethyl 2-(1,3-dimethyl-2,4,6-trioxohexahydro-5-pyrimidinylidene)-2-tricyclo[3.3.1.1^{3,7}]dec-1-ylaminoethanephosphonate **IXb**.

at 1550–1600 cm^{-1} corresponding to the carbon-carbon double bond vibrations.

Note that in the case of the addition of diethyl acetamidomalonate to *N*-*tert*-butyl- and *N*-adamantyl (dimethoxyhosphoryl)ketenimine in the ^{13}C NMR spectrum of the product there are two duplicate signals in the region of 125–130 ppm with constants of spin–spin coupling with the phosphorus nucleus $^2J_{CP}$ 10–12 Hz related to the resonance of the carbon atom at the double bond (C^2), which probably indicates the formation of a mixture of *syn*- and *anti*-isomers.

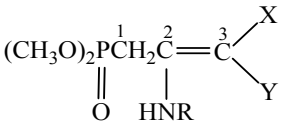
In addition, the ^{13}C NMR spectra of the adducts of diethyl acetamidomalonate with *N*-*tert*-butyl- and *N*-adamantyl(dimethoxyphosphoryl)ketenimines (**VIIa**, **VIIb**) contain a peak of the carbon atom C^3 of the CH-acid residue as a signal of low intensity in the region ~ 60 ppm. Its location is confirmed by the fact that in the case of such adduct of diethyl acetamidomalonate to acetylenediphosphonate the carbon atom of CH-acid appears as a doublet of doublets with a chemical shift δ_C 69.0 ppm and spin–spin coupling constants with two phosphorus nuclei $^2J_{CP}$ 15.2, $^3J_{CP}$ 20.9 Hz.

The structure of the substituted β-aminoalkenephosphonates was also confirmed by the X-ray diffraction analysis. The X-ray analysis of the crystal of dimethyl 2-*tert*-butylamino-3,3-dicyanoprop-2-enephosphonate **IIa** (Fig. 3) was performed on a SMART-1000 CCD diffractometer (MoK_α-irradiation, θ/2θ-scanning, graphite monochromator). The crystals are monoclinic, $C_{11}H_{18}N_3O_3P$; size 0.40×0.23×0.22 mm^3; unit cell parameters: *a* 8.6247(7), *b* 18.3866(16), *c* 9.6208(9) Å, α 90, β 111.289(2), γ 90°, *V* 778.4(3) Å^3, space group *P*21/c, *Z* 4, d_{calc} 1.267 mg m^{-3}. The structure was solved by the direct method, the values of *R*-factor are 0.0520, R_W 0.0959 [2349 reflections with $I > 2\sigma(I)$]. The hydrogen atoms were refined in the isotopic approximation. All calculations were performed using SHELXTL PLUS program package. Some bond lengths and angles are given in Fig 3.

It should be noted that, unlike aminoacetylenephosphonates [3], in the case aldoketeniminophosphonates we were able to extend the range of the CH-acids involved into the reaction. This fact confirms the greater reactivity of the ketenimine in the reactions with nucleophiles compared with ynamines.

The study showed that the reaction of aldoketeniminophosphonates with the CH-acids is affected by a number of factors, depending on the nature of the CH-acid. We have found that the reaction occurs mainly with the CH-acids with the pK_a values

Table 1. Parameters of the ^{1}H, ^{13}C, ^{31}P NMR spectra of the 3-substituted 2-amino-2-propenephosphonates **II**–**IX**



Comp. no.	^{1}H NMR spectrum, δ (CH_2P), ppm, ($^{2}J_{HP}$, Hz)	^{13}C NMR spectrum			^{31}P NMR spectrum, δ_P, ppm
		δ_{C1}, ppm, ($^{1}J_{CP}$, Hz)	δ_{C2}, ppm, ($^{2}J_{CP}$, Hz)	δ_{C3}, ppm, ($^{3}J_{CP}$, Hz)	
IIa	3.20 (22.4)	31.51 (135.3)	162.25 (5.7)	50.63	21.34
IIb	3.19 (22.0)	31.59 (137.4)	162.65 (8.9)	52.34	21.78
IIIa	–	27.47 (134.7)	158.84 (6.7)	93.87 (5.6)	23.56
IIIb	–	28.01 (139.1)	158.44 (7.1)	93.61 (3.9)	24.59
IVa	3.33 (22.8)	30.42 (135.1)	163.82 (6.1)	73.12	20.81
IVb	3.34 (22.8)	30.91 (136.1)	163.39 (6.7)	73.00 (4.6)	20.87
Va	3.27 (22.8)	31.11 (133.4)	160.37 (5.5)	83.36 (6.9)	20.08
Vb	2.76 (20.0)	35.28 (130.6)	162.64 (4.2)	80.72 (2.7)	20.37
VIa	3.29 (22.8, $^{4}J_{HP}$ 1.8)	31.14 (134.3, $^{3}J_{CP}$ 12.5)	166.89 (6.2, 7.5)	60.22 (5.6, $^{1}J_{CP}$ 199.8)	21.16 (7.4), 22.32 (7.4)
VIb	3.37 (23.2, $^{4}J_{HP}$ 1.9)	31.80 (134.9, $^{3}J_{CP}$ 11.7)	166.456 (6.8, 5.8)	60.24 (7.5, $^{1}J_{CP}$ 204.9)	23.28 (5.3), 22.12 (4.8)
VIIa	2.74 (22.4) 2.78 (22.6)	31.65 (137.0)	125.11 (12.2) 131.32 (10.92)	60.85	29.09
VIIb	2.73 (20.41) 2.77 (22.0)	32.56 (137.0)	123.77 (12.43) 132.46 (8.9)	61.64	28.17
VIIIa	3.45 (22.8)	30.84 (139.8)	165.96 (7.2)	80.80	21.35
VIIIb	3.48 (24.0)	31.33 (134.9)	165.33 (6.7)	80.74 (2.7)	20.55
IXa	2.79 (22.4)	30.34 (135.3)	168.06 (4.7)	90.13	22.88
IXb	2.74 (20.8)	31.21 (138.0)	167.56 (5.2)	90.73	22.93

in the range of 10–14. Thus, an attempt to introduce benzyl cyanide into the reaction does not lead to any results that can be attributed to its low thermodynamic CH-acidity (pK_a 20.81), which is several orders of magnitude lower than the acidity of the malonate (pK_a 11–13). For the same reason, methylmalonic ester, which has also a low ionization rate, does not react. However, a similar result was obtained also in the reaction of aldoketeniminophosphonates with the nitro CH-acids (nitromalonic ester, ethyl nitroacetate, and *p*-nitrobenzylcyanidemethane), whose thermodynamic CH-acidity is very high; the inertness of the nitro compounds in these reactions is associated with the known fact of an abnormally low ionization rate, which depends on the mechanism of the resonance stabilization of the nitro carbanion. In the CH-acid carbanion the charge is mainly localized on the more electronegative atoms. As a result, both the proton elimination and attachment to the carbon is slower than in the case of CH-acids, where the carbanion charge is mainly located on the carbon atom [4].

The acidity of the studied CH-acids was evaluated using a program Marvin Sketch, Version 5.4.1 (ChemAxon.Ltd, http://chemaxon.com/marvin). The pK_a values calculated by this program for the CH-acids correlate well with the published ones [4, 5] (Table 2).

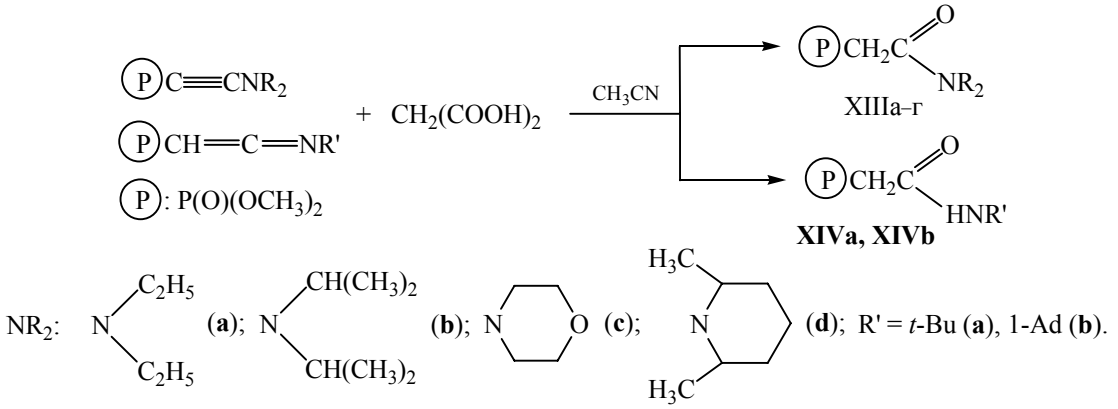
Under these conditions we failed to perform the reaction of aldoketeniminophosphonates with malonic acid amide due to the low solubility of the latter in the most organic solvents. The use of anhydrous dimethylformamide and dimethyl sulfoxide for the reaction was undesirable because of the possible involvement of the solvent into the reaction and the difficulties associated with the adducts isolation.

The reaction of aldoketeniminophosphonates with malonic acid proceeds in another way. In this case malonic acid reacts as an OH-acid (pK_a 2.73) and aldo-

Table 2. pK_a Values of CH-acids, calculated by Marvin Sketch program, Version 5.4.1

CH-Acid	pK_a	CH-Acid	pK_a
$O_2NCH(COOEt)_2$	4.22	$CH_2(CN)_2$	12.52
1,3-Dimethylbarbituric acid	4.47	$CH_2(CN)SO_2Ph$	12.72
		$CH_2(CONH_2)_2$	12.85
$CH_2(NO_2)COOEt$	5.99	$CH_2(COOEt)_2$	13.05
2-Furoylacetonitrile	11.02	$(CH_3O)_2P(O)CH_2CN$	13.40
$CH_3C(O)NHCH(COOEt)_2$	11.28	$CH_2(CN)COOEt$	13.82
$CH_2(COOH)_2$	11.32	$CH_3CH(COOEt)_2$	14.68
	(2.73 O–H)	$PhCH_2CN$	20.81

keteniminophosphonate acts as a strong dehydrating agent. The reaction occurs predominantly as the hydration of acetylenic substrates. The reaction proceeds at room temperature with a noticeable exothermic effect to form the phosphonacetic acid alkylamides **XIIIa–XIIId**, **XIVa**, **XIVb**.



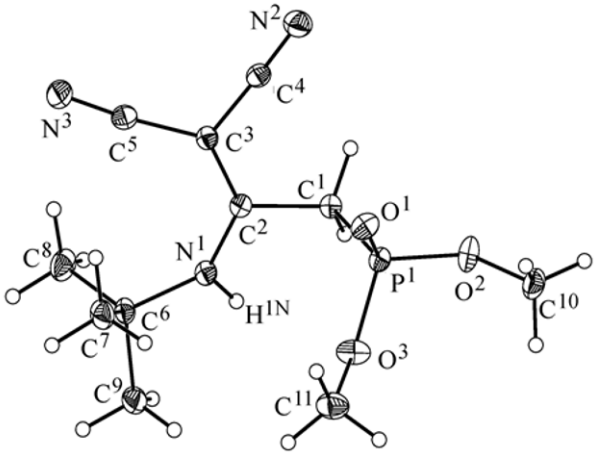


Fig. 3. The general view of the molecule of dimethyl 2-*tert*-butylamino-3,3-dicyanoprop-2-enephosphonate **IIa**. Selected bond lengths (Å) and angles (deg): P^1–C^1 1.789, N^1–C^2 1.327(2), C^1–C^2 1.513(3), C^2–C^3 1.390(3), N^3–C^5 1.148(3), C^3–C^5 1.436(3), $C^2N^1C^6$ 133.40(18), $C^2C^1P^1$ 111.77(13), $N^1C^2C^3$ 129.75(19), $N^1C^2C^1$ 112.90(17), $C^3C^2C^1$ 117.34(17), $C^2C^3C^5$ 127.92(19).

In the course of the reaction in the ^1H–{^{31}P} NMR spectrum of the reaction mixture we observed the appearance and growth of the signals of the products of amide structure and the disappearance of the signals of malonic acid. Thus, in the case of the reaction of dimethyl morpholylethynephosphonate with malonic acid in the NMR spectra of the reaction mixture taken after the reaction completion and the solvent removal there are only the signals corresponding to the dimethoxyphosphorylacetic acid morpholylamide **XIIIc**. The ^1H NMR spectrum of the reaction mixture contains the upfield doublet signal of methylene protons of the CH_2P fragment at δ_H 3.30 ppm ($^2J_{HP}$ 22.0 Hz).

The methoxy protons appear at δ_H 3.75 ppm as a doublet signal ($^3J_{HP}$ 11.2 Hz). The protons of morpholine moiety are unequal with respect to the carbonyl oxygen atom and appear as two pairs of the triplet signals with chemical shifts δ_H 3.50 and 3.58 ppm (CH_2N) and δ_H 3.60 and 3.66 ppm (CH_2O) ($^3J_{HH}$ 5.6 Hz), respectively.

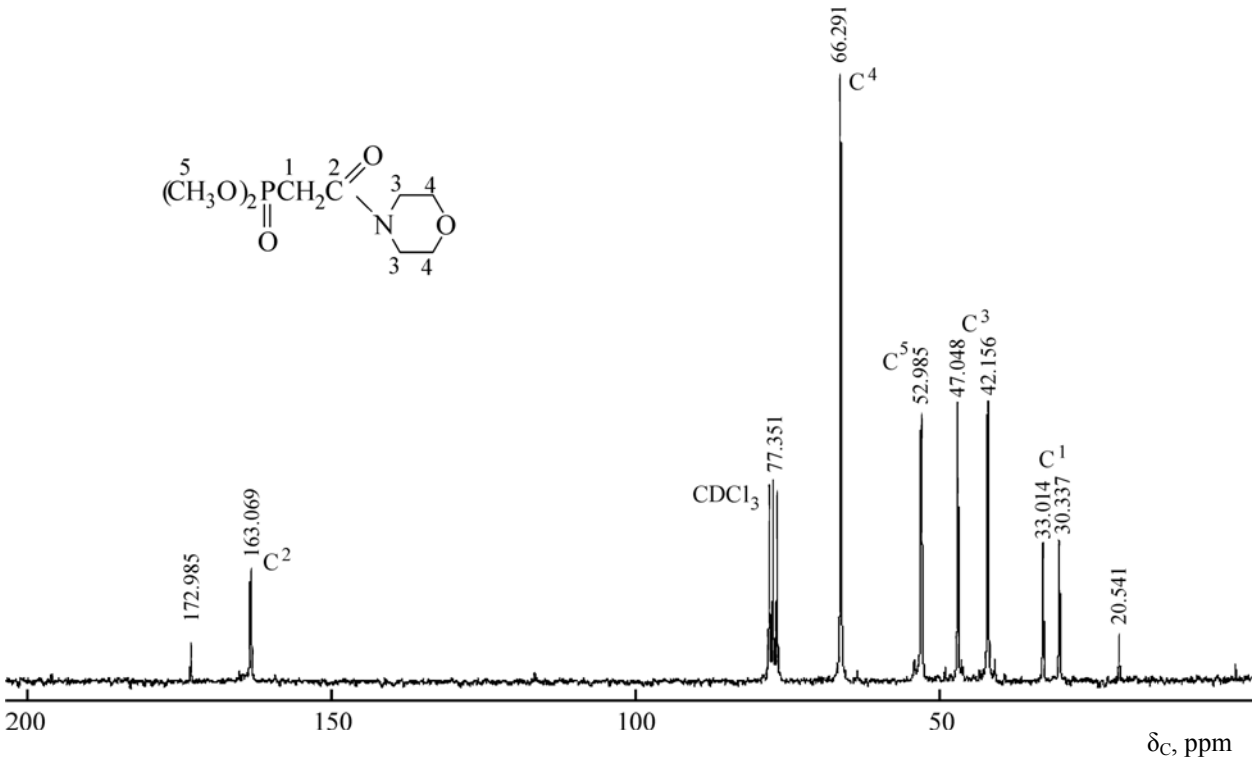


Fig. 4. The ^{13}C NMR spectrum of the reaction mixture of morpholylethynedimethylphosphonate with malonic acid.

The ^{13}C NMR spectrum of the reaction mixture contains a characteristic doublet signal of the carbon atom C^1 directly bonded to the phosphorus atom located in a strong field at δ_C 31.68 ppm with a constant of spin–spin coupling with the phosphorus nucleus $^1J_{CP}$ 134.7 Hz (Fig. 4). Two singlet signals of equal intensity in the region of δ_C 42.16 and 47.05 ppm correspond to the unequal carbon atoms of the morpholine fragment attached directly to the nitrogen atom. The carbons of CH_2O-morpholine group are recorded as an intense singlet signal with the chemical shift δ_C 66.29 ppm. The CH_3OP-carbon atoms resonate with the chemical shift δ_C 53.40 ppm ($^2J_{CP}$ 5.4 Hz). The carbonyl carbon atom appears downfield at δ_C 163.10 ppm ($^2J_{CP}$ 3.4 Hz).

Note that in the NMR spectra of the reaction mixture there are no signals corresponding to the initial malic acid, but in the ^{13}C NMR spectrum in the strong and weak field there are two low-intensity singlet signals with the chemical shifts δ_C 20.54 and 172.98 ppm, respectively, which can probably be attributed to the dehydration product of malonic acid. But we have not succeeded to establish structure of these products unequivocally.

A similar course is observed in the reaction between aldoketeniminophosphonates and nitromalonates or nitroacetates. Owing to the high pK_a values of the nitro compounds the reaction occurs almost immediately after the reagents mixing. The ^1H, ^{13}C, and ^{31}P NMR spectroscopy could detect reliably in the reaction mixture the formation of the products of amide structure. As with malonic acid, we failed to determine the structure of the end-products of dehydration of the nitro-containing CH-acids.

It should be noted that in the reaction of nitromalonates and nitroacetates with *N-tert*-butyl (dimethoxyphosphoryl)ketenimine we observed the preferential formation of the phosphonoacetic acid nitrile together with the corresponding amide, which was confirmed by the ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Thus, after the removal of the solvent and the starting CH-acid the ^1H NMR spectrum of the reaction mixture contained the upfield doublet signal of the CH_2P-protons (δ_H 2.72 ppm, $^2J_{HP}$ 20.8 Hz) of the amide product along with the intense doublet with chemical shift δ_H 2.89 ppm ($^2J_{HP}$ 20.41 Hz) belonging to the CH_2P-protons of the second product, the phosphonoacetic acid nitrile.

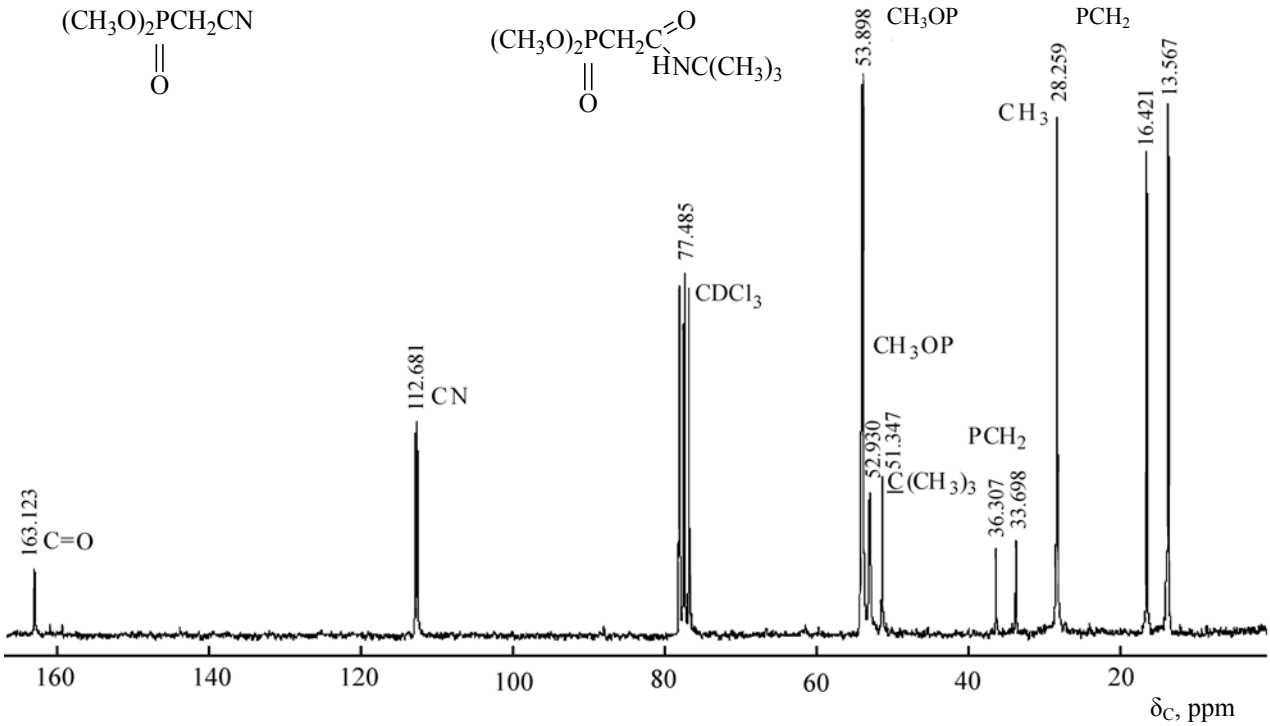


Fig. 5. The ^{13}C NMR spectrum of the reaction mixture of *N-tert*-butyl(dimethoxyphosphoryl)ketenimine with diethyl nitromalonate.

The ^{13}C NMR spectrum of the reaction mixture (Fig. 5) contains the characteristic doublet signals of the carbon atoms C^1 directly attached to the phosphorus atom in both reaction products: In a strong field there is an intense doublet at δ_C 14.99 ppm ($^1J_{CP}$ 143.6 Hz) corresponding to the nitrile carbon resonance, the amide carbon C^1 resonates with the chemical shift δ_C 35.00 ppm ($^1J_{CP}$ 131.3 Hz). The signals of *tert*-butyl group appear upfield: An intense singlet signal at δ_C 28.26 ppm corresponds to the resonance of the methyl groups, and a singlet signal at δ_C 51.35 ppm belongs to the quaternary carbon atom. In the region of ~ 53 ppm there are two doublet signals corresponding to the resonance of CH_3OP-carbon atoms. The doublet of lower intensity δ_C 52.99 ppm ($^2J_{CP}$ 5.5 Hz) is assigned to the reaction product of amide structure. The methoxy groups of phosphonoacetic acid nitrile appear as the more intense doublet with the chemical shift δ_C 53.96 ppm ($^2J_{CP}$ 7.8 Hz). An intense doublet signal downfield (δ_C 112.79 ppm, $^2J_{CP}$ 10.6 Hz) corresponds to the resonance of the carbon atom of nitrile group. The carbonyl carbon of *N-tert*-butylamide is registered downfield at δ_C 163.18 ppm ($^2J_{CP}$ 5.7 Hz).

The ^{31}P NMR spectrum of the reaction mixture is represented by two signals at δ_P 17.33 (nitrile) and 25.27 ppm (amide). The integral intensities ratio is 5:1.

A similar result, the nitrile formation, was observed in the reaction of *N-tert*-butyl(dimetilphosphono)ketenimine with mineral acids, such as hydrogen chloride. As noted in [6], the reaction proceeds through the proton attack of the imine nitrogen of ketenimino-phosphonate to form the adduct at the double nitrogen-carbon bond followed by stabilization via the *tert*-butyl group elimination (*t*-BuCl or isobutylene) to give phosphonoacetic acid nitrile.

Thus, aldoketeniminophosphonates were established to react with the CH-acids, the pK_a values of which lie within 10–14, to afford the γ-functionally substituted β-aminoalkenephosphonates.

EXPERIMENTAL

The NMR spectra were recorded on spectrometers Bruker AC-200 operating at 200.132 (^1H), 50.328 (^{13}C), and 81.014 (^{31}P) MHz, Bruker AC-400 operating at 400.133 MHz (^1H), and Tesla BS-497 (100 MHz) using the double magnetic resonance ^1H–{^{31}P} technique. In the ^1H NMR spectra hexamethyldisiloxane (HMDS) was used as an internal reference. The phosphorus chemical shifts were determined relative to external 85% phosphoric acid (Bruker AC-200) and trimethylphosphate (Tesla BS-497). The ^{13}C spectra

were recorded relative to the internal $CDCl_3$ and DMSO-d_6. The IR spectra were recorded on a Shimadzu FTIR-8400S instrument from KBr pellets.

The standard laboratory techniques were used in purifying and drying the organic solvents and reagents [7–9].

***N*-*tert*-Butyl(dimethoxyphosphoryl)ketenimine (Ia).** To a solution of 2.9 g of *tert*-butylamine in 50 ml of anhydrous diethyl ether was added dropwise 3.4 g of dimethyl chloroacetylenephosphonate at stirring and cooling in the range of –5 to –10°C. The reaction mixture was kept at room temperature for 2 h, then *tert*-butylamine hydrochloride was filtered off and washed with ether (5×5 ml). The filtrate was concentrated and distilled in a vacuum. Yield 4.3 g (98%), bp 65–66°C (1 mm Hg) [2]. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.17 s (9H, CH_3), 3.21 d (1H, PCH, $^2J_{HP}$ 3.2 Hz), 3.61 d (6H, CH_3OP, $^3J_{HP}$ 12.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 30.00 [C(*C*H_3)$_3$], 34.89 d (PCH, $^1J_{CP}$ 211.9 Hz), 52.41 q (CH_3OP, $^2J_{CP}$ 4.5 Hz), 59.92 [*C*(CH_3)$_3$], 167.90 d (C=N, $^2J_{CP}$ 6.8 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 26.47 ppm.

***N*-Adamantyl(dimethoxyphosphoryl)ketenimine (Ib).** To a solution of 4.3 g of 1-adamantylamine in 60 ml of anhydrous diethyl ether was added dropwise 1.7 g of dimethyl chloroacetylenephosphonate at stirring and cooling to 0–5°C. The reaction mixture was kept at room temperature for 24 h. The precipitate was filtered off and washed with ether (5×5 ml). The filtrate was concentrated to oil. Yield 2.79 g (99%) [2]. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.64–1.87 m (12H, CH_2, adamant.), 2.00–2.12 m (3H, CH, adamant.), 3.36 d (PCH, $^2J_{CP}$ 2.0 Hz), 3.70 d (6H, CH_3OP, $^3J_{HP}$ 8.10 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 29.26 (CH, adamant.), 34.26 d (PCH, $^1J_{CP}$ 212.9 Hz), 35.40 γ-CH_2, adamant.), 43.04 (α-CH_2, adamant.), 52.07 d (CH_3OP, $^2J_{CP}$ 5.6 Hz), 59.74 (C–N, adamant.), 167.88 d (C=N, $^2J_{CP}$ 8.4 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 26.18 ppm.

Functional γ-substituted β-*tert*-butyl(1-adamantyl)aminoalkenephosphonates (IIa–IXa, IIb–IXb). General procedure. To a solution of 0.0049 mol of the corresponding aldoketeniminophosphonate in 5 ml of anhydrous acetonitrile was added 0.0049 mol of CH-acid and catalytic amount (0.03 g) of anhydrous potassium carbonate. The reaction mixture was kept for several hours at 80°C at exclusion of the air moisture. The solvent was evaporated under the vacuum of a water-jet pump, the residue was a viscous colored liquid. The target products were chromatographed by the liquid chromatography on silica gel (MN Kieselgel, 60/0.025–0.004 mm), eluent carbon tetrachloride–acetone, 4:1. The product yield was almost quantitative.

Dimethyl 2-*tert*-butylamino-3,3-dicyano-2-propenephosphonate (IIa) was prepared according to the general procedure from 1 g of *N*-*tert*-butyl(dimethoxyphosphoryl)ketenimine and 0.32 g of malonic acid dinitrile. The product was isolated by recrystallization from benzene. IR spectrum, ν, cm^{-1}: 1238 (P=O), 1569 (C=C), 2190 and 2206 (C≡N). ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.51 s (9H, CH_3), 3.20 d (2H, CH_2P, $^2J_{HP}$ 22.4 Hz), 3.82 d (6H, CH_3OP, $^3J_{HP}$ 11.2 Hz), 6.61 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 30.77 [*C*(CH_3)$_3$], 31.51 d (CH_2P, $^1J_{PC}$ 135.3 Hz), 50.63 [=*C*(CN)$_2$], 53.66 d (CH_3OP, $^2J_{CP}$ 5.1 Hz), 56.32 [*C*(CH_3)$_3$], 116.13 (C≡N), 162.25 d (=CN, $^2J_{CP}$ 5.7 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 21.34 ppm. Found, %: C 49.01; H 6.90; N 15.88. $C_{11}H_{18}N_3O_3P$. Calculated, %: C 48.71; H 6.69; N 15.49.

Dimethyl 2-(1-adamantylamine)-3,3-dicyano-2-propenephosphonate (IIb) was prepared according to the general procedure from 1 g of *N*-(1-adamantyl)-(dimethoxyphosphoryl)ketenimine and 0.23 g of malonic acid dinitrile. The product was isolated by recrystallization from benzene. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.69 m (6H, γ-CH_2, adamant.), 2.10 m (6H, α-CH_2, adamant.), 2.36 m (3H, β-CH, adamant.) 3.19 d (2H, CH_2P, $^2J_{HP}$ 22.0 Hz), 3.77 d (6H, CH_3OP, $^3J_{HP}$ 10.8 Hz), 6.60 br.sc (1H, NH). (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 29.52 (CH, adamant.), 31.59 d (CH_2P, $^1J_{PC}$ 137.4 Hz), 35.37 γ-CH_2, adamant.), 42.98 α-CH_2, adamant.), 52.34 [=*C*(CN)$_2$], 53.67 d (CH_3OP, $^2J_{CP}$ 3.6 Hz), 57.56 (C–N, adamant.), 116.13 (C≡N), 162.65 d (=CN, $^2J_{CP}$ 8.9 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 21.78 ppm.

Dimethyl 2-*tert*-butylamino-3-cyano-3-ethoxycarbonyl-2-propenephosphonate (IIIa) was prepared according to the general procedure from 1 g of *N*-*tert*-butyl(dimethoxyphosphoryl)ketenimine and 0.55 g of ethyl cyanoacetate. IR spectrum, ν, cm^{-1}: 1276 (P=O), 1608 (C=C), 1659 (C=O), 2205 (C≡N). ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.27 m (3H, C*H*$_3$CH$_2$O, $^3J_{HN}$ 7.4 Hz), 1.45 s [9H, C(C*H*$_3$)$_3$], 3.33 d (2H, CH_2P, $^2J_{HP}$ 22.8 Hz), 3.80 d (6H, CH_3OP, $^3J_{HP}$ 11.2 Hz), 4.15 q (2H, OC*H*$_2$CH$_3$, $^3J_{HH}$ 7.4 Hz), 10.44 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.13 (*C*H$_3$CH$_2$O), 30.42 d (CH_2P, $^1J_{PC}$ 135.1 Hz), 30.88

[$C(CH_3)_3$], 53.18 d (CH_3OP, $^2J_{CP}$ 6.0 Hz), 55.18 [$C(CH_3)_3$], 60.18 (OCH_2CH_3), 73.12 [=C(CN)COO·CH_2CH_3], 118.61 (C≡N), 163.82 d (=CN, $^2J_{CP}$ 6.1 Hz), 168.67 (C=O). ^{31}P NMR spectrum ($CDCl_3$): δ_P 20.81 ppm. Found, %: C 49.41; H 7.16; N 8.52. $C_{13}H_{23}N_2O_5P$. Calculated, %: C 49.05; H 7.28; N 8.80.

Dimethyl 2-(1-adamantylamino)-3-cyano-3-ethoxycarbonyl-2-propenephosphonate (IIIb) was prepared according to the general procedure from 1 g of *N*-(1-adamantyl)(dimethyphosphono)ketenimine and 0.40 g of ethyl cyanoacetate. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.24 m (3H, CH_3CH$_2$O, $^3J_{HH}$ 7.2 Hz), 1.62 m (6H, γ-CH_2, adamant.) 1.97 m (6H, α-CH_2, adamant.), 2.09 m (3H, β-CH, adamant.), 3.19 d (2H, CH_2P, $^2J_{HP}$ 22.8 Hz), 3.78 d (6H, CH_3OP, $^3J_{HP}$ 10.8 Hz), 4.12 q (2H, OCH_2CH$_3$, $^3J_{HH}$ 7.2 Hz), 10.28 br.sc (1H, NH). (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.11 (CH_3CH_2O), 29.34 (CH, adamant.), 31.91 d (CH_2P, $^1J_{PC}$ 13.1 Hz), 35.42 γ-CH_2, adamant.), 43.39 α-CH_2, adamant.), 53.19 d (CH_3OP, $^2J_{CP}$ 7.2 Hz), 56.57 (C–N, adamant.), 60.15 (OCH_2CH_3), 73.00 [=C(CN)COO·CH_2CH_3], 118.69 (C≡N), 163.39 d (=CN, $^2J_{CP}$ 6.7 Hz), 168.67 (C=O). ^{31}P NMR spectrum ($CDCl_3$): δ_P 20.87 ppm.

Dimethyl 2-*tert*-butylamino-3,3-diethoxycarbonyl-2-propenephosphonate (IVa) was prepared according to the general procedure from 1 g of *N*-*tert*-butyl (dimethoxyphosphoryl)ketenimine and 0.78 g of diethyl malonate. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.25 br.s (3H, CH_3CH$_2$O, $^3J_{HH}$ 7.2 Hz), 1.47 s [9H, C(CH_3)$_3$], 3.70 d (6H, CH_3OP, $^3J_{HP}$ 10.8 Hz), 4.12 br.q (2H, OCH_2CH$_3$, $^3J_{HH}$ 7.2 Hz), 10.18 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 03.14 (CH_3CH_2O), 27.47 d (CH_2P, $^1J_{PC}$ 134.7 Hz), 31.48 [$C(CH_3)_3$], 53.02 d (CH_3OP, $^2J_{CP}$ 5.3 Hz), 53.59 [$C(CH_3)_3$], 59.82 (OCH_2CH_3), 93.87 [=C($COOCH_2CH_3$)$_2$, $^3J_{CP}$ 5.7 Hz], 158.84 d (=CN, $^2J_{CP}$ 6.7 Hz), 169.11 (C=O). ^{31}P NMR spectrum ($CDCl_3$): δ_P 23.56 ppm.

Dimethyl 2-(1-adamantylamino)-3,3-diethoxycarbonyl-2-propenephosphonate (IVb) was prepared according to the general procedure from 1 g of *N*-(1-adamantyl)(dimethyphosphono)ketenimine and 0.56 g of diethyl malonate. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.22 m (3H, CH_3CH$_2$O, $^3J_{HH}$ 7.6 Hz), 1.62 m (6H, γ-CH_2, adamant.) 1.96 m (6H, α-CH_2, adamant.), 2.25 m (3H, β-CH, adamant.), 3.71 d (6H, CH_3OP, $^3J_{HP}$ 11.2 Hz), 4.14 q (2H, OCH_2CH$_3$, $^3J_{HH}$ 7.6 Hz), 5.10 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.93 (CH_3CH_2O), 28.01 d (CH_2P, $^1J_{PC}$ 139.1 Hz), 29.39 (CH, adamant.), 35.65 γ-CH_2, adamant.), 43.90 α-CH_2, adamant.), 52.91 d (CH_3OP, $^2J_{CP}$ 5.6 Hz), 54.80 (C–N, adamant.), 59.68 (OCH_2CH_3), 93.58 [=C($COOCH_2CH_3$)$_2$, $^3J_{CP}$ 4.4 Hz], 158.54 d (=CN, $^2J_{CP}$ 7.3 Hz), 168.98 (C=O). ^{31}P NMR spectrum ($CDCl_3$): δ_P 24.59 ppm.

Dimethyl 2-*tert*-butylamino-3-cyano-3-phenylsulfonyl-2-propenephosphonate (Va) was prepared according to the general procedure from 1 g of *N*-*tert*-butyl(dimethoxyphosphoryl)ketenimine and 0.89 g of phenylsulfonylacetonitrile. The reaction product was isolated by recrystallization from benzene. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.50 s [9H, C(CH_3)$_3$], 3.27 d (2H, CH_2P, $^2J_{HP}$ 22.8 Hz), 3.69 d (6H, CH_3OP, $^3J_{HP}$ 12.0 Hz), 7.55 m (2H, CH^m, $^3J_{HH}$ 7.4 Hz), 7.63 m (1H, CH^p, $^3J_{HH}$ 7.4 Hz), 8.00 d (2H, CH^o, $^3J_{HH}$ 7.4 Hz), 8.95 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 31.11 d (CH_2P, $^1J_{PC}$ 133.4 Hz), 31.21 [$C(CH_3)_3$], 53.34 d (CH_3OP, $^2J_{CP}$ 6.7 Hz), 56.34 [$C(CH_3)_3$], 83.36 [=C(CN)SO_2Ph, $^3J_{CP}$ 6.9 Hz], 116.51 (C≡N), 126.43 (CH^m), 129.17 (CH^o), 133.34 (C^p), 141.93 (SO_2C, Ph), 160.37 d (=CN, $^2J_{CP}$ 5.5 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 20.08 ppm.

Dimethyl 2-(1-adamantylamine)-3-cyano-3-phenylsulfonyl-2-propenephosphonate (Vb) was prepared according to the general procedure from 1 g of *N*-(1-adamantyl)(dimethyphosphono)ketenimine and 0.63 g of phenylsulfonylacetonitrile. The reaction product was isolated by recrystallization from benzene. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.67 m (6H, γ-CH_2, adamant.), 1.99 m (6H, α-CH_2, adamant.), 2.06 m (3H, β-CH, adamant.), 2.76 d (2H, CH_2P, $^2J_{HP}$ 20.4 Hz), 3.78 d (6H, CH_3OP, $^3J_{HP}$ 11.6 Hz), 7.64 t (2H, CH^m, $^3J_{HH}$ 7.6 Hz), 7.77 t (1H, CH^p, $^3J_{HH}$ 7.6 Hz), 8.02 d (2H, CH^o, $^3J_{HH}$ 7.6 Hz), 6.22 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 29.45 (CH, adamant.), 35.28 d (CH_2P, $^1J_{PC}$ 130.6 Hz), 35.46 (γ-CH_2, adamant.), 43.27 (α-CH_2, adamant.), 52.23 d (CH_3OP, $^2J_{CP}$ 5.4 Hz), 57.30 (C–N, adamant.), 80.72 [=C(CN)SO_2Ph, $^3J_{CP}$ 2.7 Hz], 118.65 (C≡N), 126.06 (CH^m, arom.), 130.61 (CH^o, arom.), 135.16 (C^p, arom.), 142.25 (SO_2C, arom.), 162.64 d (=CN, $^2J_{CP}$ 4.2 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 21.35 ppm.

Dimethyl 2-*tert*-butylamino-3-cyano-4-(2-furyl)-4-oxo-2-butenephosphonate (VIa) was prepared according to the general procedure from 1 g of *N*-*tert*-butyl(dimethoxyphosphoryl)ketenimine and 0.66 g of furoylacetonitrile. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.51 s [9H, C(CH_3)$_3$], 3.45 d (2H, CH_2P, $^2J_{HP}$ 22.8 Hz), 3.82 d (6H, CH_3OP, $^3J_{HP}$ 11.6 Hz), 6.45–6.49

m (2H, β-CH, furan.), 7.54 d (1H, α-CH, furan., $^{3}J_{HH}$ 3.2 Hz), 13.05 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 30.81 [C(CH_3)$_3$], 30.84 d (CH_2P, $^{1}J_{PC}$ 139.8 Hz), 53.36 d (CH_3OP, $^{2}J_{CP}$ 5.7 Hz), 56.15 [C(CH_3)$_3$], 80.80 [=C(CN)C(O)Fu], 111.76 (C≡N), 117.51 (β'-CH, furan.), 120.62 (β-CH, furan.), 145.60 (α'-CH, furan.), 150.62 (α-C, furan.), 165.96 d (=CN, $^{2}J_{CP}$ 7.2 Hz), 177.28 (C=O). ^{31}P NMR spectrum ($CDCl_3$): δ_P 21.35 ppm.

Dimethyl 2-(1-adamantylamino)-3-cyano-4-(2-furyl)-4-oxo-2-butenephosphonate (VIb) was prepared according to the general procedure from 1 g of *N*-(1-adamantyl)(dimethyphosphono)ketenimine and 0.47 g of 2-furoylacetonitrile. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.69 m (6H, γ-CH_2, adamant.), 2.08 m (6H, α-CH_2, adamant.), 2.16 m (3H, β-CH, adamant.), 3.48 d (2H, CH_2P, $^{2}J_{HP}$ 24.0 Hz), 3.83 d (6H, CH_3OP, $^{3}J_{HP}$ 11.2 Hz), 6.49 t (1H, β'-CH, furan., $^{3}J_{HH}$ 3.4 Hz), 6.82 t (1H, β-CH, furan., $^{3}J_{HH}$ 3.4 Hz), 7.55 d (1H, α-CH, furan., $^{3}J_{HH}$ 3.4 Hz), 12.93 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 29.34 (CH, adamant.), 31.33 d (CH_2P, $^{1}J_{PC}$ 134.9 Hz), 35.46 (γ-CH_2, adamant.), 43.26 (α-CH_2, adamant.), 53.39 d (CH_3OP, $^{2}J_{CP}$ 6.3 Hz), 59.39 (C–N, adamant.), 80.74 [=C(CN)C(O)Fu, $^{3}J_{CP}$ 2.7 Hz], 111.76 (C≡N), 117.44 (β'-CH, furan.), 120.77 (β-CH, furan.), 145.52 (α'-CH, furan.), 150.68 (α-C, furan.), 165.33 d (=CN, $^{2}J_{CP}$ 6.7 Hz), 177.25 (C=O). ^{31}P NMR spectrum ($CDCl_3$): δ_P 20.55 ppm.

Dimethyl 2-*tert*-butylimino-3-methylcarboxamido-3,3-diethoxycarbonylpropenephosphonate (VIIa) was prepared according to the general procedure from 1 g of *N*-*tert*-butyl(dimethoxyphosphoryl)ketenimine and 1.06 g of diethyl acetamidomalonate. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.25 br.t (3H, CH_3CH$_2$O, $^{3}J_{HH}$ 7.2 Hz), 1.42 s [9H, C(CH_3)$_3$], 2.07 s (3H, CH_3C=O), 2.73 d (2H, CH_2P, $^{2}J_{HP}$ 22.8 Hz), 3.82 d (6H, CH_3OP, $^{3}J_{HP}$ 11.6 Hz), 4.12 br.q (2H, OCH_2CH$_3$, $^{3}J_{HH}$ 7.2 Hz), 9.46 br.s [1H, NHC(O)CH$_3$]. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.89 and 14.26 (CH_3CH_2O), 22.56 (CH_3C=O), 27.99 [C(CH_3)$_3$], 30.53 d (CH_2P, $^{1}J_{PC}$ 133.5 Hz), 53.36 d (CH_3OP, $^{2}J_{CP}$ 5.7 Hz), 57.31 [C(CH_3)$_3$], 60.38 (CH_3CH_2O), 60.85 [C(COOEt)$_2$], 125.11 (C=N, $^{2}J_{HP}$ 12.2 Hz) and 131.32 (C=N, $^{2}J_{HP}$ 10.2 Hz), 153.18 and 163.30 (C=O), 168.32 (CH_3C=O).^{31}P NMR spectrum ($CDCl_3$): δ_P 29.09 ppm.

Dimethyl 2-(1-adamantylimino)-3-methylcarboxamido-3,3-diethoxycarbonylpropenephosphonate (VIIb) was obtained according to the general procedure from 1 g of *N*-(1-adamantyl)(dimethyphosphono)ketenimine and 0.76 g of diethyl acetamidomalonate. ^{1}H NMR spectrum (DMSO-d_6), δ_H, ppm: 1.20 t (3H, CH_3CH$_2$O, $^{3}J_{HH}$ 7.6 Hz), 1.24 t (3H, CH_3CH$_2$O, $^{3}J_{HH}$ 7.6 Hz), 1.63 m (6H, γ-CH_2, adamant.), 1.97 m (6H, α-CH_2, adamant.), 2.08 m (3H, β-CH, adamant.), 2.04 s (3H, CH_3C=O), 2.73 d (2H, CH_2P, $^{2}J_{HP}$ 20.4 Hz), 2.77 d (2H, CH_2P, $^{2}J_{HP}$ 22.0 Hz), 3.75 d (6H, CH_3OP, $^{3}J_{HP}$ 10.8 Hz), 3.77 d (6H, CH_3OP, $^{3}J_{HP}$ 11.2 Hz), 4.16 br.q (2H, OCH_2CH$_3$, $^{3}J_{HH}$ 7.6 Hz), 4.23 br.q (2H, OCH_2CH$_3$, $^{3}J_{HH}$ 7.6 Hz), 9.53 br.s [1H, NHC(O)CH$_3$]. ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 14.07 and 14.40 (CH_3CH_2O), 22.70 (CH_3C=O), 30.22 (CH, adamant.), 32.56 d (CH_2P, $^{1}J_{PC}$ 137.0 Hz), 36.38 (γ-CH_2, adamant.), 39.72 (α-CH_2, adamant.), 53.27 d (CH_3OP, $^{2}J_{CP}$ 5.8 Hz), 59.39 (C–N, adamant.), 61.19 (CH_3CH_2O), 61.64 [C(COOEt)$_2$], 125.77 (C=N, $^{2}J_{HP}$ 12.4 Hz) and 132.46 (C=N, $^{2}J_{HP}$ 8.9 Hz), 153.53 and 163.51 (C=O), 169.20 (CH_3C=O). ^{31}P NMR spectrum (DMSO-d_6): δ_P 28.17 ppm.

Tetramethyl 2-*tert*-butylamino-1-cyano-1-propenephosphonate (VIIIa) was prepared according to the general procedure from 1 g of *N*-*tert*-butyl(dimethoxyphosphoryl)ketenimine and 0.73 g of dimethoxyphosphorylacetic acid nitrile. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.36 s [9H, C(CH_3)$_3$], 3.29 d (2H, CH_2P, $^{2}J_{HP}$ 22.8, $^{4}J_{HP}$ 1.8 Hz), 3.65 d (6H, CH_3OP, $^{3}J_{HP}$ 11.2 Hz), 3.75 d (6H, CH_3OP, $^{3}J_{HP}$ 11.6 Hz), 9.26 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 30.85 [C(CH_3)$_3$], 31.14 d.d (CH_2P, $^{1}J_{CP}$ 134.3, $^{3}J_{CP}$ 12.5 Hz), 52.92 d (CH_3OP, $^{2}J_{CP}$ 5.3 Hz), 53.36 d (CH_3OP, $^{2}J_{CP}$ 5.9 Hz), 54.99 [C(CH_3)$_3$], 60.22 d. d (=CCN, $^{1}J_{CP}$ 199.8, $^{3}J_{CP}$ 5.6 Hz), 118.84 (C≡N, $^{2}J_{CP}$ 7.9 Hz), 166.89 t (=CN, $^{2}J_{CP}$ 6.2, 7.5 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 21.16 d ($^{4}J_{PP}$ 7.4 Hz), 22.33 d ($^{4}J_{PP}$ 7.4 Hz).

Tetramethyl 2-(1-adamantylamino)-1-cyano-1-propenephosphonate (VIIIb) was prepared according to the general procedure from 1 g of *N*-(1-adamantyl)-(dimethyphosphono)ketenimine and 0.52 g of dimethoxyphosphorylacetic acid nitrile. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.62 m (6H, γ-CH_2, adamant.), 1.95 m (6H, α-CH_2, adamant.), 2.09 m (3H, β-CH, adamant.), 3.37 d (2H, CH_2P, $^{2}J_{HP}$ 23.2, $^{4}J_{HP}$ 1.9 Hz), 3.74 d (6H, CH_3OP, $^{3}J_{HP}$ 11.2 Hz), 3.80 d (6H, CH_3OP, $^{3}J_{HP}$ 11.6 Hz), 9.15 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 29.43 (CH, adamant.), 31.80 d. d (CH_2P, $^{1}J_{CP}$ 134.9, $^{3}J_{CP}$ 11.7 Hz), 36.17 (γ-CH_2, adamant.), 43.44 (α-CH_2, adamant.), 52.15 d (CH_3OP, $^{2}J_{CP}$ 4.2 Hz), 53.05 d (CH_3OP, $^{2}J_{CP}$ 5.6 Hz), 56.50 (C–N, adamant.), 60.24 d.d (=CCN, $^{1}J_{CP}$ 204.9,

$^3J_{CP}$ 7.5 Hz), 119.14 (C≡N, $^2J_{CP}$ 6.7 Hz), 166.46 t (=CN, $^2J_{CP}$ 6.8, 7.8 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 22.11 d ($^4J_{PP}$ 4.8 Hz), 23.28 d ($^4J_{PP}$ 4.8 Hz).

Dimethyl 2-(1,3-dimethyl-2,4,6-trioxohexahydro-5-pyrimidinylidene)-2-*tert*-butilaminoethanephosphonate (IXa) was prepared according to the general procedure from 1 g of *N*-*tert*-butyl(dimethoxyphosphoryl)ketenimine and 0.76 g of 1,3-dimethylbarbituric acid. ^{1}H NMR spectrum (DMSO-d_6), δ_H, ppm: 1.51 s [9H, C(CH_3)$_3$], 2.79 d (2H, CH_2P, $^2J_{HP}$ 22.4 Hz), 3.17 s (6H, NCH_3), 3.64 d (6H, CH_3OP, $^3J_{HP}$ 11.2 Hz), 12.98 br.s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 27.44 and 27.73 (NCH_3), 30.34 d (CH_2P, $^1J_{PC}$ 135.3 Hz), 30.37 [C(CH_3)$_3$], 52.76 d (CH_3OP, $^2J_{CP}$ 6.3 Hz), 55.63 [C(CH$_3$)$_3$], 90.13 [=C(C=O)$_2$], 150.56 [NC(O)N], 162.65 and 165.37 [=C(C=O)$_2$], 168.06 d (=CN, $^2J_{CP}$ 4.7 Hz). ^{31}P NMR spectrum (DMSO-d_6): δ_P 22.88 ppm.

Dimethyl 2-(1,3-dimethyl-2,4,6-trioxohexahydro-5-pyrimidinylidene)-2-tricyclo[3.3.1.1^{3,7}]dec-1-ylaminoethanephosphonate (IXb) was prepared according to the general procedure from 1 g of *N*-(1-adamantyl)(dimethyphosphono)ketenimine and 0.55 g of 1,3-dimethylbarbituric acid. ^{1}H NMR spectrum (DMSO-d_6), δ_H, ppm: 1.69 m (6H, γ-CH_2, adamant.), 1.97 m (6H, α-CH_2, adamant.), 2.11 m (3H, β-CH, adamant.), 2.74 d (2H, CH_2P, $^2J_{HP}$ 20.8 Hz), 3.27 s (6H, NCH_3), 3.72 d (6H, CH_3OP, $^3J_{HP}$ 11.2 Hz), 12.91 br.s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 27.61 and 27.92 (NCH_3), 29.53 (CH, adamant.), 31.21 d (CH_2P, $^1J_{PC}$ 138.0 Hz), 35.69 (γ-CH_2, adamant.), 43.28 (α-CH_2, adamant.), 53.19 d (CH_3OP, $^2J_{CP}$ 6.0 Hz), 57.39 (C–N, adamant.), 90.73 [=C(C=O)$_2$], 151.05 [NC(O)N], 163.15 and 166.17 [=C(C=O)$_2$], 167.56 d (=CN, $^2J_{CP}$ 5.2 Hz). ^{31}P NMR spectrum (DMSO-d_6): δ_P 22.93 ppm.

Dimethoxyphosphorylacetic acid *N*-*tert*-butylamide (Xa). ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.28 s [9H, C(CH_3)$_3$], 2.73 d (2H, CH_2P, $^2J_{HP}$ 21.2 Hz), 3.66 d (6H, CH_3OP, $^3J_{HP}$ 11.6 Hz), 6.52 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 28.20 [C(CH_3)$_3$], 34.84 d (CH_2P, $^1J_{PC}$ 132.7 Hz), 51.20 [C(CH$_3$)$_3$], 52.79 d (CH_3OP, $^2J_{CP}$ 5.9 Hz), 163.08 d (C=O, $^2J_{CP}$ 4.6 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 25.30 ppm.

Dimethoxyphosphorylacetic acid *N*-(1-adamantyl)-amide (Xb). ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 1.64 m (6H, γ-CH_2, adamant.), 1.97 m (6H, α-CH_2, adamant.), 2.05 m (3H, β-CH, adamant.), 2.82 d (2H, CH_2P, $^2J_{HP}$ 20.81 Hz), 3.77 d (6H, CH_3OP, $^3J_{HP}$ 11.2 Hz), 6.39 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 29.21 (CH, adamant.), 35.14 d (CH_2P, $^1J_{PC}$ 130.6 Hz), 36.12 (γ-CH_2, adamant.), 40.98 (α-CH_2, adamant.), 52.44 (C–N, adamant.), 53.28 d (CH_3OP, $^2J_{CP}$ 4.7 Hz), 162.88 d (C=O, $^2J_{CP}$ 4.3 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 25.63 ppm.

Dimethoxyphosphorylacetonitrile. ^{1}H NMR spectrum ($CDCl_3$), δ_H, ppm: 2.89 d (2H, CH_2P, $^2J_{HP}$ 20.4 Hz), 3.81 d (6H, CH_3OP, $^3J_{HP}$ 11.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.99 d (CH_2P, $^1J_{PC}$ 143.6 Hz), 53.96 d (CH_3OP, $^2J_{CP}$ 7.8 Hz), 112.79 d (C≡N, $^2J_{CP}$ 4.6 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 17.33 ppm.

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