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Dedicated to the memory of Correspondent Member of the Russian Academy of Sciences M.Yu. Antipin

Synthesis of Alkyl Tetraphosphonates: First Example of Nickel Catalyst for H-Phosphonates Addition to Diynes

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Abstract—Efficient algorithm was developed for the analysis of products of the catalytic reaction of diynes multiphosphorylation based on combined application of ^{31}P NMR DOSY spectra and HPLC-MS method. Using this analytical approach the reaction of H-phosphonates addition to diynes was investigated and a simple synthetic procedure got alkyl tetraphosphonates preparation was developed.

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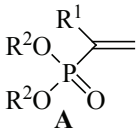
A special attention is directed to the creation of selective procedures of carbon–phosphorus bond formation due to the outstanding importance of organophosphorus compounds in chemistry, medicine, and materials science. Phosphorus-containing alkene derivatives are biologically active components [1–5], important compounds for the chemistry of nucleic acids [6–10], convenient reagents for a number of synthetic transformations [15–17]. Among the multiple organophosphorus molecules special attention is lately drown to vinylphosphonates **A** that exhibit a wide range of biologic activity [18–21].



A

The practical application of organophosphorus compounds includes their use in the membranes of fuel elements [22], in optical materials [23–25], as flame retardants (antipyrenes) [26–29], and as ligands in catalytic reactions [30–33]. The growing demand for the preparation of new ligands for highly efficient catalytic systems is among the driving forces in the field of the organophosphorus chemistry.

The intensive development of the transition metal complex catalysis in the recent years advanced a new stage in the study of the catalytic reactions of the carbon–phosphorus bond formation based on acetylene hydrocarbons thus introducing quite a number of promising routes [34]. In particular, the application of addition of molecules containing a phosphorus–hydrogen bond to unsaturated organic compounds catalyzed by the transition metal complexes made it possible to develop a convenient synthetic method of carbon-phosphorus bonds formation [35–39]. 100% atomic efficiency of the addition reaction combined with a high regioselectivity permitted a development of economical and environmentally safe synthetic procedures.

The first example of alkynes hydrophosphorylation catalyzed by transition metal complexes was described under 1972 [40]. The reaction carried out in severe conditions was characterized by low selectivity and low to medium yields.

Tanaka et al. for the first time carried out the hydrophosphorylation catalyzed with palladium complexes in 1996 [41]. The addition of $(MeO)_2P(O)H$ to alkynes in the presence of palladium catalyst under mild conditions (67°C, 15–20 h) afforded vinylphosphonates in high yields (Scheme 1).

We had formerly developed a catalytic system Pd_2dba_3–PPh_3–CF_3COOH [42] that was successfully tested on

a hydrophosphorylation of a series of alkynes (Scheme 2).

The high regio- and stereoselectivity allowed the preparation of addition products with excellent yields and purity. The study of the reaction mechanism showed that the addition of CF_3COOH to the catalytic system was a necessary condition of the suppression for the side reactions.

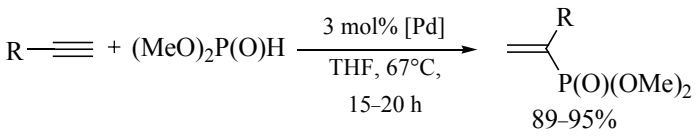
In the course of further research we found that the use of $Ni(acac)_2$ as the catalyst precursor made it possible to carry out the reaction in the absence of the acid without a decrease in the yield and the selectivity of the process. We succeeded to apply the developed catalytic system to carry out the addition of H-phosphonates both to terminal and internal alkynes with an excellent regio- and stereoselectivity [43, 44].

Up till now catalytic hydrophosphorylation of various classes of unsaturated compounds (alkenes, dienes, alkynes) has been studied [34]. However only scanty examples exist for the catalytic hydrophosphorylation of diynes (Scheme 3) [41, 45, 46]. It should be mentioned as well that only the addition of the simplest H-phosphonates {$(MeO)_2P(O)H$ [41, 46], $(Me_2CO)_2P(O)H$ [45, 46], and $(EtO)_2P(O)H$ [46]} was known furnishing branched and linear adducts, and also cyclic derivatives of vinylphosphonates.

The scanty published data on the diynes hydrophosphorylation, the latter being very interesting not only for the synthesis of divinyldiphosphonates but for the preparation of multiphosphorylated products, as well prompted us to investigate these reactions. Here we present the catalytic system $Ni(acac)_2$–$(i\text{-}Bu)_2AlH$ that we have developed for the hydrophosphorylation of diynes. The developed synthetic procedure excludes the application of organic solvents and toxic phosphine ligands in keeping with the requirements of the "green chemistry".

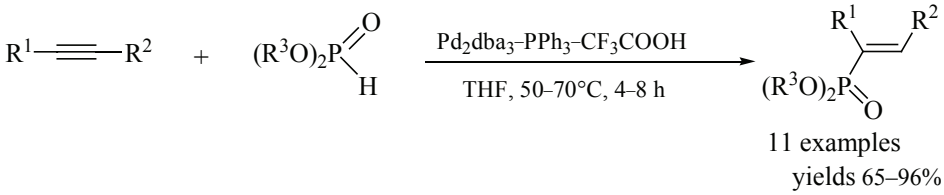
As a model reaction we chosen the addition of diisopropyl-H-phosphonate (**Ia**) to 1,6-heptadiyne (**IIa**) using $Ni(acac)_2$ as catalyst precursor (Scheme 4). The stable in air and cheap $Ni(acac)_2$ has obvious advantages over the expensive palladium complexes and unstable compounds of Ni(0).

Scheme 1.



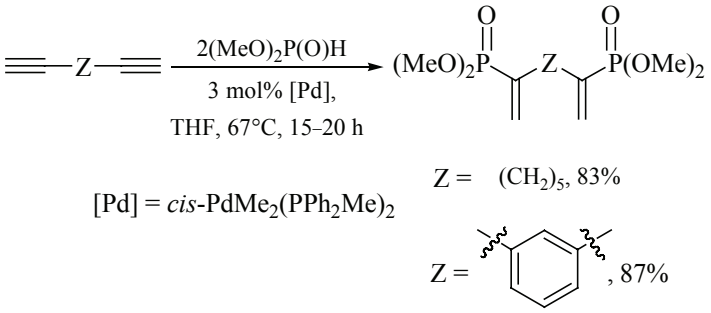
[Pd] = *cis*-$PdMe_2(PPh_2Me)_2$; R = Ar, Alk.

Scheme 2.



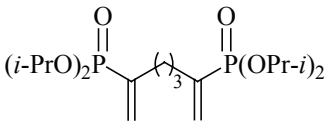
R^1 = Alk; R^2 = H, Et; R^3 = Alk, Ar.

Scheme 3.



[Pd] = *cis*-$PdMe_2(PPh_2Me)_2$

The ratio being reagents **Ia** and **IIa** of 2 : 1 was chosen initially aiming at selective synthesis of divinyldiphosphonate **B** as a result of the addition of two molecules of H-phosphonate **Ia** to both triple bonds of diyne **IIa**.



B

In the absence of a phosphine ligand the formation of product **B** was not observed, and the only signal registered in the $^{31}P\{^{1}H\}$ NMR spectrum belonged to the initial H-phosphonate **Ia** (Table 1, run no. *1*). The introduction of bidentate phosphine ligands (Table 1, runs nos. *2–4*) to the system also did not result in the formation of the target divinyldiphosphonate **B**. In particular, the system $Ni(acac)_2$–DPPE (Table 1, run no. *3*) which high efficiency in the hydrophosphorylation of alkynes, including 1-heptyne, was demonstrated earlier [44], was inactive in the case of diynes.

It turned out that the application of diisobutylaluminum hydride led to the 100% conversion of H-phosphonate **Ia** within 24 h at 120°C (Table 1, run no. *5*). In the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture after the completion of the reaction two main signals accompanied by the signals of side products of unknown nature were observed. However in the ^{1}H NMR spectrum of the reaction mixture the characteristic divinyldiphosphonate signals of vinyl protons in the region 4–6 ppm were lacking. To establish the number of formed products the reaction mixture in the first stage was subject to 31P DOSY NMR [47].

Table 1. Variation of promoters in the addition reaction of diisopropyl-*H*-phosphonate (**Ia**) to 1,6-heptadiyne (**IIa**)

Run no.	Ligand	Additive	Conversion of **Ia**, %[a]	Yield, %[a]	
				IIIa	**IVa**
1	–	–	0	0	0
2[b]	DPPM	–	0	0	0
3[b]	DPPE	–	0	0	0
4[b]	DPPB	–	0	0	0
5[c]	–	$(i\text{-Bu})_2AlH$	100	79	19

[a] Calculated from $^{31}P\{^{1}H\}$ NMR spectrum;
[b] Conditions: 1 mmol of **Ia**, 0.5 mmol of **IIa**, 4 h, 100°C, 6 mol% of $Ni(acac)_2$, 12 mol% of ligand;
[c] Conditions: 1 mmol of **Ia**, 0.5 mmol of **IIa**, 24 h, 120°C, 9 mol% of $Ni(acac)_2$, 18 mol% of $(i\text{-Bu})_2AlH$.

The analysis of the DOSY spectrum allowed the separation of the main components present in the ^{31}P NMR spectrum by their self-diffusion coefficients. Two doublets at 28.8 and 30.9 ppm proved to belong to the same component, $\log(D) = -10.22 \pm 0.07$ **IIIa**, whereas the singlet at 26.1 ppm corresponded to another molecule with higher mobility [$\log(D) = -10.07 \pm 0.05$ **IVa**]. In the DOSY spectrum the signals of the initial diisopropyl-*H*-phosphonate (**Ia**), $\log(D) = -9.78 \pm 0.16$ ($^{1}J_{PH}$ 687 Hz) and

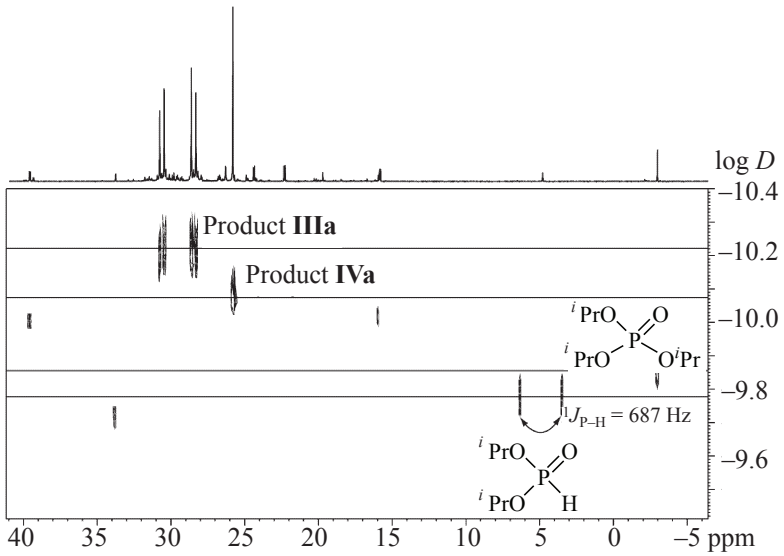
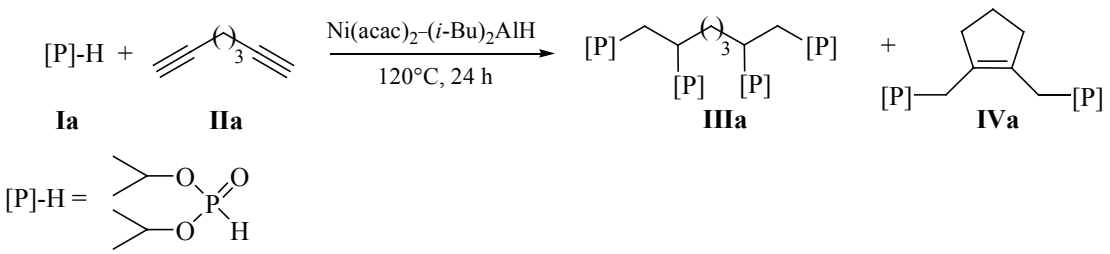


Fig. 1. ^{31}P NMR DOSY spectrum of the reaction mixture.

Scheme 4.



of a side product of the reaction, triisopropyl phosphate, log(D) = –9.86 ± 0.07, were also identified (Fig. 1).

Regretfully, we failed to separate completely the mixture obtained by the dry column chromatography. The purest fraction contained a mixture of compounds **IIIa** and **IVa** in 1 : 1 ratio. The establishment of the structure of individual compounds was performed using ^{1}H–^{31}P HMBC, ^{1}H–^{13}C HSQC, and ^{1}H–^{13}C HMBC NMR method. It turned out that compound **IVa** was a product of the intramolecular cyclization of diyne with two phosphorus-containing substituents (Fig. 2).

Analogous cyclization product of heptadiyne with a pinacol-H-phosphonate was described earlier [46]. In this study we have performed a complete assignment of the signals in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **IVa**. The data of the chemical shifts and the multiplicity of signals are listed in Table 2. The strong overlapping of signals in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra impeded their complete assignment for compound **IIIa**, but the characteristic pattern of the signals in the $^{31}P\{^{1}H\}$NMR spectrum allowed an assumption that adduct **IIIa** formed via the addition of four molecules of diisopropyl-H-phosphonate to the molecule of 1,6-heptadiyne (Fig. 3).

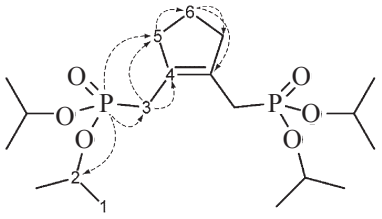


Fig. 2. Structure of compound **IVa** according to the NMR spectroscopy. The arrows indicate the key ^{1}H–^{13}C and ^{1}H–^{31}P HMBC correlations.

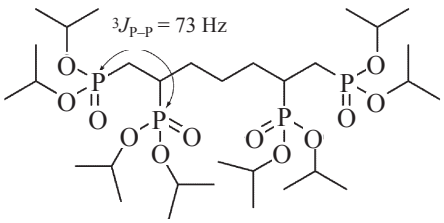


Fig. 3. Assumed structure of multiphosphorylation product **IIIa**.

The observed spin-spin coupling constant J_{P-P} in the spectrum of compound **IIIa** equals 73 Hz. It corresponds to typical values of $^{3}J_{P-P}$ for phosphate residues in similar fragments [48, 49]. Yet the values $^{2}J_{P-P}$ and $^{4}J_{P-P}$ usually do not exceed 10 Hz [50], therefore it is possible to assign to compound **IIIa** the structure presented in Fig. 3. This assumption is in agreement with the data of diffusion NMR presented in Fig. 1: The tetraphosphorylation product owing to the large mass and steric load is less mobile in solution which corresponds to the observed smaller self-diffusion coefficient.

To get an independent confirmation of the assumed structures of compounds **IIIa** and **IVa** the reaction mixture was subjected to HPLC-MS analysis. The mixture contained two prevailing substances **IIIa** and **IVa** with retention time 1.2 and 1 min respectively, and also several side products (Fig. 4). Found *m/z* 757.3743 (**IIIa**). $C_{31}H_{68}O_{12}P_4$. Calculated $[M + H]^+$ 757.3734, Δ 1.2 ppm. Found *m/z* 425.2222 (**IVa**). $C_{19}H_{38}O_6P_2$. Calculated $[M + H]^+$ 425.2216, Δ 1.4 ppm.

The method HPLC-MS in contrast to HPLC-UV makes

Table 2. Chemical shifts in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **IVa** (for numeration of atoms, see Fig. 2)

Atom no.	δ(^{1}H)	δ($^{13}C\{^{1}H\}$)
1	1.28	24.18
2	4.67	70.28
3	2.67 d ($^{2}J_{PH}$ 18 Hz)	28.42 dd ($^{1}J_{PC}$ 143, $^{4}J_{PC}$ 6 Hz)
4	–	130.11
5	2.49	37.39
6	1.82	21.92

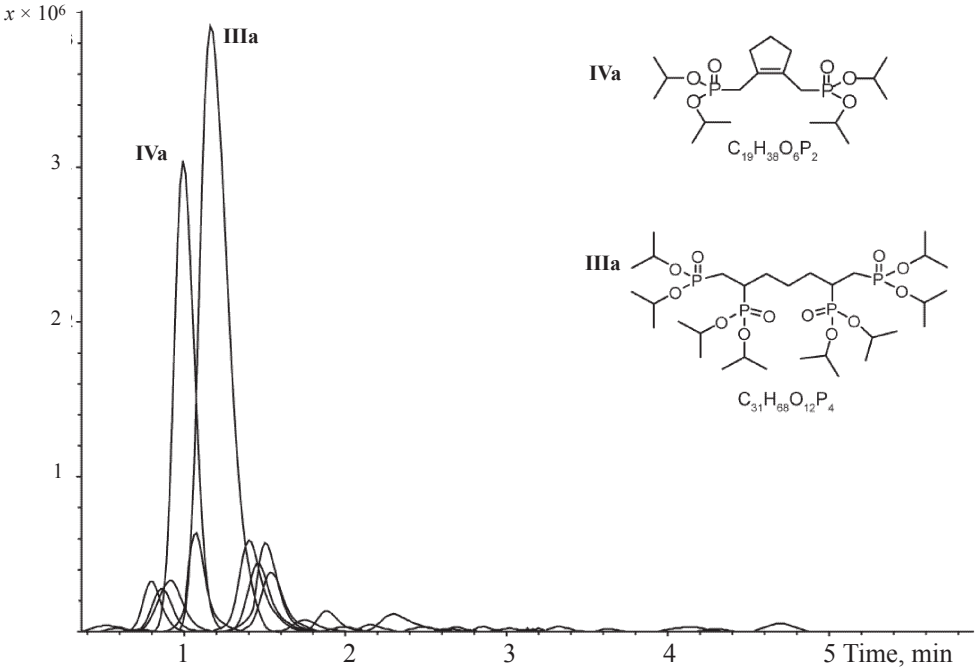


Fig. 4. HPLC-MS chromatogram of the reaction mixture of model reaction.

it possible to independently detect all components simultaneously due to the variation in the intensity of each definite *m*/*z* value with time. This feature of the detection provides a possibility to avoid the laborious grading of eluent composition, parameters of the chromatographic column, and the separation conditions and permits obtaining complete information on the composition of a multicomponent mixture in one run (in this case the time of analysis not exceeds 5 min). According to HPLC-MS data compounds **IIIa** and **IVa** were the main components of the obtained mixture; therewith the system contained quite a number of the other impurity products with phosphorus atoms in their composition which were registered as small peaks in the ^{31}P NMR DOSY spectrum (Fig. 1, 4).

Hence the structure of compound **IVa** and the assumed structure of compound **IIIa** were confirmed by the data of diffusion, heteronuclear correlation NMR spectroscopy, and HPLC-MS analysis.

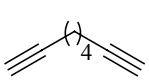
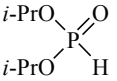
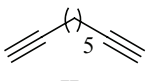
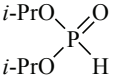
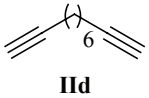
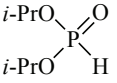
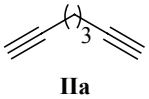
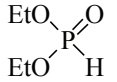
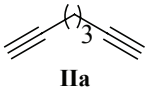
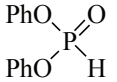
It is noteworthy that the examples of the formation of alkyl tetraphosphonates in catalytic reactions of H-phosphonates with diynes were not known up today. The catalytic system developed by us based on $Ni(acac)_2$–(*i*-$Bu)_2AlH$ allowed a hydrophosphorylation of diyne with H-phosphonate with a 100% conversion of the latter and a prevailing formation of alkyl tetraphosphonate **IIIa**.

We carried out a series of experiments on the optimization of the conditions of the model reaction aiming at increasing the yield of compound **IIIa**. Decreasing the temperature from 120 to 100°C resulted in the reduction of compound **IIIa** yield from 79 to 51%, the yield of compound **IVa** decreased insignificantly (from 19 to 15%), yet about 20% of H-phosphonate **Ia** did not react. The use of 1 mol% of $Ni(acac)_2$ at 120°C caused a sharp decrease in the yield of compound **IIIa** from 79 to 36%, whie the yield of compound **IVa** remained on the same level (17%).

In accordance with the stoichiometry of adduct **IIIa** formation the most favorable ratio of the reagents H-phosphonate–diyne would be 4 : 1. However the increased excess of the H-phosphonate in the reaction to three- and fourfold did not result in a considerable increase in the yield of the tetraaddition product. Therefore for the subsequent experiments we chose the ratio H-phosphonate–diyne 2 : 1.

We carried out under the optimized conditions the hydrophosphorylation of various diynes **IIb–IId** with diisopropyl-H-phosphonate (**Ia**) (Table 3, runs nos. *1–3*), and also the hydrophosphorylation of 1,6-heptadiyne (**IIa**) with various H-phosphonates **Ib, Ic** (Table 3, runs nos. *4*, *5*). The performed experiments confirmed the high efficiency of the catalytic system $Ni(acac)_2$–(*i*-$Bu)_2AlH$ for the synthesis of the product of multiphosphorylation. In all cases the complete conversion of H-phosphonate **I** was attained, and the corresponding alkyl tetraphospho-

Table 3. Hydrophosphorylation of diynes **II** with *H*-phosphonates **I**

Run no.	Diyne **II**	H-phosphonate **I**	Conversion of **I**,%[a]	Yield of **III**,%[a]	Yield of **IV**,%[a]
1	 **IIb**	 **Ia**	100	91 **IIIb**	9[b]
2	 **IIc**	 **Ia**	100	70 **IIIc**	30[b]
3	 **IId**	 **Ia**	100	90 **IIId**	10[b]
4	 **IIa**	 **Ib**	97	45 **IIIe**	30[c]
5[e]	 **IIa**	 **Ic**	100	56 **IIIf**	8[d]

[a] Calculated from the data of $^{31}P\{^{1}H\}$NMR spectra. Conditions: 2 mmol of **I**, 1 mmol of **II**, 24 h, 120°C, 9 mol% of $Ni(acac)_2$, 18 mol% of $(i\text{-}Bu)_2AlH$.

[b] Overall yield of compound **IV** and the other side products.

[c] Overall yield of phosphorus-containing products of unknown structure 25%.

[d] Overall yield of phosphorus-containing products of unknown structure 36%.

[e] 12 mol% $Ni(acac)_2$, 24 mol% $(i\text{-}Bu)_2AlH$.

nates **IIIa–IIId** were obtained in high yields.

The catalyst based on $Ni(acac)_2$–$(i\text{-}Bu)_2AlH$ proved to be equally efficient for multiphosphorylation of diynes with diverse lengths of the carbon chains (Table 1, run no. *5*; Table 3, runs nos. *1–3*). In the case of diyne **IIb** the corresponding cyclic compound **IV** formed in trace amounts and the overall yield of side products did not exceed 9% (Table 3, run no. *1*).

The developed catalytic system $Ni(acac)_2$–$(i\text{-}Bu)_2AlH$ turned out to be suitable for the reactions with H-phosphonates containing the other substituents **Ib, Ic**, although the selectivity of the process and the yield of the corresponding compounds **III** were considerably lower in this case (Table 3, runs nos. *4*, *5*). Such high sensitivity to the variations in the structure of the substituent is characteristic of this type of processes. The obtained compounds **IIIa–IIIe, IVa** were characterized by the NMR spectroscopy and high resolution mass spectrometry.

The main attention in this research we directed to the development of an efficient physicochemical approach to the study of the catalytic hydrophosphorylation of diynes. The applied combination of the methods of NMR spectroscopy and HPLC-MS made it possible to determine the structure of compounds **III** and **IV** by the direct analysis of the reaction mixture without preliminary separation. The analysis of the data of diffusion ^{31}P NMR spectroscopy provides in a short time the fundamental information on the number and type of the components in the studied mixture of compounds. The existence of this information allows carrying out further purposeful analysis of the interesting components of the mixture with the help of HPLC-MS and the other analytic methods. It should be noted that such approach is especially suitable to the study of the processes of synthesis of phosphorus-containing hydrocarbons where often a large number of reaction products are formed.

The system $Ni(acac)_2$–$(i\text{-}Bu)_2AlH$ that we have developed is the first example of a nickel-based catalyst for the addition of H-phosphonates to diynes. The addition occurs without solvent, does not require the presence of a phosphorus-containing ligand and permits the synthesis of alkyl tetraphosphonates in high yields. The utilization of catalytic amounts of cheap and stable against the air oxygen and moisture $Ni(acac)_2$ makes the procedure of the synthesis cheap and easily available. The developed catalytic system made it possible to prepare a series of

new multiphosphorylated alkanes, valuable organophosphorus compounds.

The detailed study of the mechanism of the reaction described here is the object of further research. In particular, the important problems are discovering the role of the metal in the stages of hydrophosphorylation of the triple and double bonds, and also the nature of catalysis and of the strong effect of the substituents in the diyne and the H-phosphonate on the yield and the selectivity of the reaction.

EXPERIMENTAL

1D NMR spectra were registered on a spectrometer Bruker DRX500 at operating frequencies 500.1, 125.8, 202.5 MHz for nuclei ^{1}H, ^{13}C, and ^{31}P respectively. The solvents for NMR experiments were stored over molecular sieves. Chemical shifts are reported in the scale δ, ppm. As internal reference for ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra tetramethylsilane (^{1}H) and solvent signals (^{13}C) were used. Chemical shifts in $^{31}P\{^{1}H\}$ NMR spectra are reported with respect to external reference 85% water solution of H_3PO_4. The error in the evaluation of the yield from the $^{1}P\{^{1}H\}$ NMR spectra did not exceed 2% [51]. All spectra were processed with Bruker Topspin 2.1 software package.

2D spectra were registered with a Bruker Avance II 600 NMR spectrometer equipped with a 5 mm BBO probehead with Z-gradient coil. Standard pulse programs were used for the registration of COSY, HSQC and HMBC NMR spectra. 2D ^{31}P DOSY spectra were obtained with a Bruker Avance II 600 NMR spectrometer operating at 242.9 MHz for ^{31}P. A standard 5 mm BBO probehead with Z-gradient coil was used. Gradient field strength was calibrated with 1% H_2O/D_2O sample (known diffusion coefficient 1.90×10^{-9} m^2s^{-1} at 25°C) and appeared to be 6.50 G cm^{-1} A^{-1}. The spectra were acquired with air flow switched off to prevent convection artifacts. Standard pulse program *stegp1*s (stimulated echo with one spoil gradient) was used. ^{31}P DOSY NMR spectra were registered without proton decoupling. The duration of gradient pulse and diffusion time were set to 1500 μs and 400 ms, respectively. 128 diffusion points were acquired with 32 scans per point and linear gradient increment from 5 to 95%. 2D DOSY spectra were generated using Bruker Topspin 2.1 software package.

The separation by the method HPLC was carried out on a chromatograph Agilent 1200 equipped with a chromatographic column ZORBAX SB-C18 (2.1 × 50.0 mm); the size of the particles of the stationary phase 1.8 μm, mobile phase acetronitrile–0.1% water solution of formic acid, 9:1, elution in the isocratic mode, flow rate 0.25 ml min^{-1}, temperature 25°C, the volume of injected sample 0.01 μl. The analyzed mixture was dissolved in acetonitrile (Merck, HPLC grade).

Mass spectrometric detection was performed on an instrument Bruker maXis equipped with ESI ion source. The measurements were carried out by registering the positive ions (the voltage on the capillary 4500 V). The range of mass scanning *m/z* 50–3000 Da, external calibration (Electrospray Calibrant Solution, Fluka). The eluate from the analytic column of the chromatograph was directly introduced into the ion source of the mass spectrometer, flow rate 0.25 ml min^{-1}, spraying gas nitrogen (8 l min^{-1}), interface temperature 200°C.

High resolution mass spectra were measured on an instrument Bruker micrOTOF II equipped with ESI ion source. The measurements were carried out by registering the positive ions (the voltage on the capillary 4500 V). The range of mass scanning *m/z* 50–3000 Da, external calibration (Electrospray Calibrant Solution, Fluka). The acetonitrile (Merck, HPLC grade) solutions of substances were injected by a syringe, flow rate 3 μl min^{-1}, spraying gas nitrogen (4 l min^{-1}), interface temperature 180°C.

All reagents were commercial products and were used after spectral testing their purity (^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR spectroscopy). $Ni(acac)_2$ before use was dried in a vacuum (3 Pa, 70°C, 2 h).

All reactions were carried out in PTFE screw capped tubes, equipped with a magnetic stirrer bar. In all cases reaction vessels were flushed with argon before heating.

Hydrophosphorylation in the system $Ni(acac)_2$–$(i\text{-Bu})_2AlH$. The mixture of diyne **II** (1×10^{-3} mol), H-phosphonate **I** (2×10^{-3} mol), and $Ni(acac)_2$ 23.1 mg (9×10^{-5} mol), was stirred for 5 min. To the formed homogeneous green solution at stirring and constant argon flow was added 0.18 ml of 1 M solution of $(i\text{-Bu})_2AlH$ in THF; at the moment of the addition the color of the solution changed from green to black. The reaction was carried out at 120°C over 24 h.

The experiments with the use of phosphine ligands (Table 1) were carried out along procedure [44].

The purification of the products was carried out by vacuum chromatography on a dry column with a gradient elution [52]; silica gel 0.015–0.040 mm (Merck); eluent ethyl acetate–ethanol, 1.5 : 1 (**IIIa, IVa**); hexane–metha-

nol, 1.5 : 1 (**IIIb–IIIe**). The solvents were purified by known procedures [53].

Octaisopropyl (heptane-1,2,6,7-tetrayl)tetrakisphosphonate (IIIa). Yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.18–2.25 m (60H), 4.60–4.78 m (8H). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), δ, ppm: 28.8 d ($^3J_{P–P}$ 73.0 Hz), 30.9 d ($^3J_{P–P}$ 73.0 Hz). Mass spectrum: *m*/*z* 757.3744 $[M + H]^+$. $C_{31}H_{68}O_{12}P_4$. Calculated: 757.3734, Δ 1.3 ppm

Tetraisopropyl [cyclopent-1-ene-1,2-diyldi(methylene)]bisphosphonate (IVa). Yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.26–1.29 m (24H), 1.78–1.86 m (2H), 2.46–2.52 m (4H), 2.67 d (4H, *J* 18 Hz), 4.64–4.69 m (4H). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), δ, ppm: 26.1. Mass spectrum: *m*/z 425.2216 $[M + H]^+$. $C_{19}H_{38}O_6P_2$. Calculated: 425.2216, Δ 0 ppm

Octaisopropyl (octane-1,2,7,8-tetrayl)tetrakisphosphonate (IIIb). Yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.16–2.27 m (62H), 4.61–4.76 m (8H). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), δ, ppm: 28.8 d ($^3J_{P–P}$ 76.5 Hz), 31.0 d ($^3J_{P–P}$ 76.5 Hz). Mass spectrum: *m*/*z* 793.3687 $[M + Na]^+$. $C_{32}H_{70}O_{12}P_4$. Calculated: 793.3710, Δ 2.9 ppm

Octaisopropyl (nonane-1,2,8,9-tetrayl)tetrakisphosphonate (IIIc). Yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.22–2.25 m (64H), 4.58–4.85 m (8H). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), δ, ppm: 28.8 d ($^3J_{P–P}$ 77.6 Hz), 31.1 d ($^3J_{P–P}$ 77.6 Hz). Mass spectrum: *m*/*z* 807.3867 $[M + Na]^+$. $C_{33}H_{72}O_{12}P_4$. Calculated: 807.3866, Δ 0.1 ppm

Octaisopropyl (decane-1,2,9,10-tetrayl)tetrakisphosphonate (IIId). Yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.16–2.24 m (66H), 4.64–4.74 m (8H). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), δ, ppm: 28.8 d ($^3J_{P–P}$ 78.1 Hz), 31.1 d ($^3J_{P–P}$ 78.1 Hz). Mass spectrum: *m*/*z* 821.4012 $[M + Na]^+$. $C_{34}H_{74}O_{12}P_4$. Calculated: 821.4023, Δ 1.3 ppm

Octaethyl (heptane-1,2,6,7-tetrayl)tetrakisphosphonate (IIIe). Yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.27–2.30 m (36H), 4.02–4.18 m (16H). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), δ, ppm: 30.6 d ($^3J_{P–P}$ 65.2 Hz), 32.8 d ($^3J_{P–P}$ 65.2 Hz). Mass spectrum: *m*/*z* 667.2312 $[M + Na]^+$. $C_{23}H_{52}O_{12}P_4$. Calculated: 667.2301, Δ 1.7 ppm.

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