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One-Step Synthesis of Phosphorylated Vinylacethylene Derivatives

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Abstract—A one-step method for the preparation of 3-substituted 2-(diethylphosphoryl)but-1-en-3-ynes was developed based on the reaction of phosphorylated α-allene alcohols with methanesulfonic anhydride in the presence of triethylamine. The obtained vinylacetylene derivatives are of interest as promising precursors for the creation of organophosphorus heterocyclic compounds.

Keywords: organophosphorus compounds, unsaturated compounds, vinylacetylene

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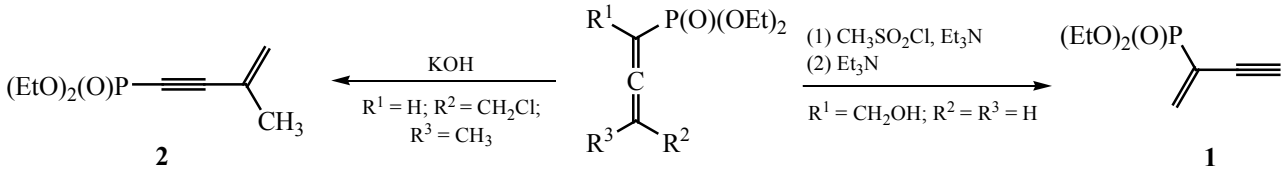
Interest in the organophosphorus chemistry is due to the wide practical application of phosphorus-containing compounds. Organophosphorus derivatives have long been used in the development of effective biologically active compounds [1–3], non-combustible polymer compositions [4, 5], extractants [6–8], light-emitting materials [9, 10], and metal complex catalysts [11, 12]. Among the many organophosphorus compounds, unsaturated compounds are of special interest. This is due to the fact that the presence of an electron-withdrawing phosphorus-containing fragment and multiple bonds in the molecule leads to favorable conditions for the interaction of compounds of this class with reagents of various nature, both electrophilic and nucleophilic. At present, phosphorylated alkynes [13–16], alkenes [4, 17], 1,2- [18–22] and 1,3-alkadienes [23–26] are widely used in the construction of cyclic, acyclic, and heterocyclic organophosphorus derivatives.

In continuation of previously initiated studies in the chemistry of 1,2- and 1,3-alkadiene with electron-withdrawing groups [27, 28], a convenient method was developed for the preparation of new phosphorylated vinylacetylene derivatives. It should be noted that organophosphorus compounds containing double and triple bonds, i.e., the vinylacetylene fragment, have been little studied, although they may potentially be of interest as synthons with great synthetic capabilities. There is data on the synthesis of phosphorylated derivatives of vinylacetylene [29–34], while functionally substituted phosphorylated allens can be used as versatile starting compounds. As a result of simple chemical transformations, they can easily be transformed into phosphorus-containing enyne systems of different structure with a phosphorus-containing fragment attached to *sp*- or sp^2-hybridized carbon atom (Scheme 1).

The location of the phosphorus atom in the molecule dramatically affects the reactivity of the enyne system. In particular, it was shown that the reaction of [2 + 4] cycloaddition of nitrile oxides using phosphonate **2** proceeds exclusively at the double bond, and no products of cycloaddition at the triple bond were detected [31]. In the case of 2-(diethylphosphoryl)but-1-en-3-yne **1**, under the same conditions, both double and triple bonds are involved into the cycloaddition reaction [34]. Despite the simplicity and ease of obtaining phosphonate **1** [34], the reaction has some disadvantages associated with the difficulty in isolation of the intermediate mesylate in pure form. Due to its high reactivity towards various nucleophiles, 3-chloro-1,3-butadienylphosphonate, a product of the reaction of 2-(diethoxyphosphoryl)buta-2,3-dien-1-ylmethanesulfonate with triethylamine hydrochloride, is formed as a side compound.

In order to improve the synthesis of phosphonate **1** and to obtain its new derivatives, 3-substituted 2-(diethylphosphoryl)but-1-en-3-ynes were obtained using phosphorylated α-allene alcohols as starting compounds. Allenic alcohols **9–14** were synthesized using standard procedure [30] from acetylene alcohols [28] (Scheme 2).

Scheme 1.



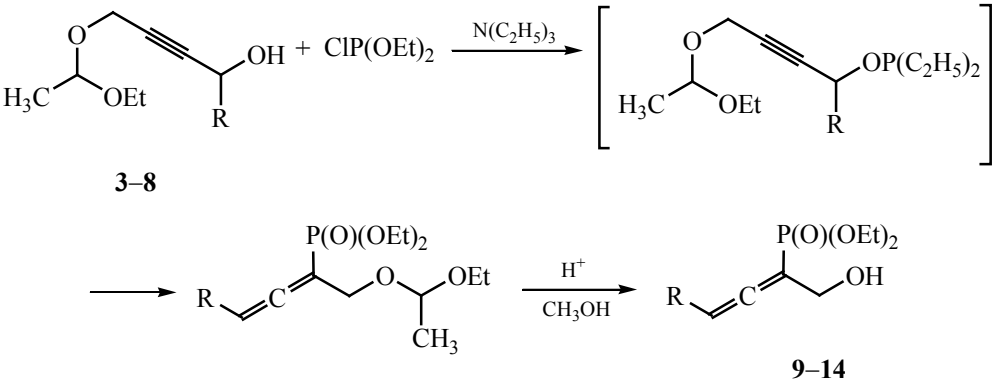
The obtained phosphonates **9–14** were isolated individually using column chromatography. Their structures were confirmed by ^{1}H, ^{13}C, and ^{31}P NMR. Spectroscopy. The presence in the ^{1}H NMR spectra of compounds **9–14** of proton signals of ethoxyl groups and groups associated with the 1,2-alkadiene system confirms the presence of an allene fragment. In addition, the data of ^{13}C NMR spectroscopy are an unambiguous proof of the structure of compounds **9–14**. It is known that the presence of weakly field signals in the 200 ppm region in the ^{13}C NMR spectra is typical for compounds of the cumulene structure, which indicates the presence of a diagonal carbon atom =C= [30]. In the ^{13}C NMR spectra of compounds **9–14**, the weak-field signal of diagonal carbon atom is registered in the region of 206–210 ppm as a doublet with the spin-spin coupling constant J_{CP} = 5–6 Hz.

Since the methodology for the synthesis of 3-substituted 2-(diethylphosphoryl)but-1-en-3-ynes involves the preparation of α-allene mesylates as intermediates that can react with nucleophiles, methanesulfonic acid anhydride was used as a mesitylation reagent. The reaction was carried out at room temperature in the presence of 2–2.5 eq. of triethylamine using methylene chloride as a solvent (Scheme 3). It is obvious that the reaction of alcohols **9–14** with methanesulfonic anhydride proceeds through the stage of formation of mesylates **1a**, **15a**–**18a**. This fact was confirmed by the example of the reaction of alcohol **12** with methanesulfonic anhydride in the presence of 1 eq. of triethylamine. 2-(Diethoxyphosphoryl)-4-phenylbuta-2,3-dien-1-ylmethanesulfonate **17a** was isolated individually and characterized by NMR spectral methods.

An interesting result was obtained for allenic alcohol **14**, in which the substituent R corresponded to the CH(Cl)CH_3 fragment. So, when using more than 3 eq. of triethylamine in the reaction with methanesulfonic anhydride phosphonate **19** containing two double and one triple bond was obtained as the major product.

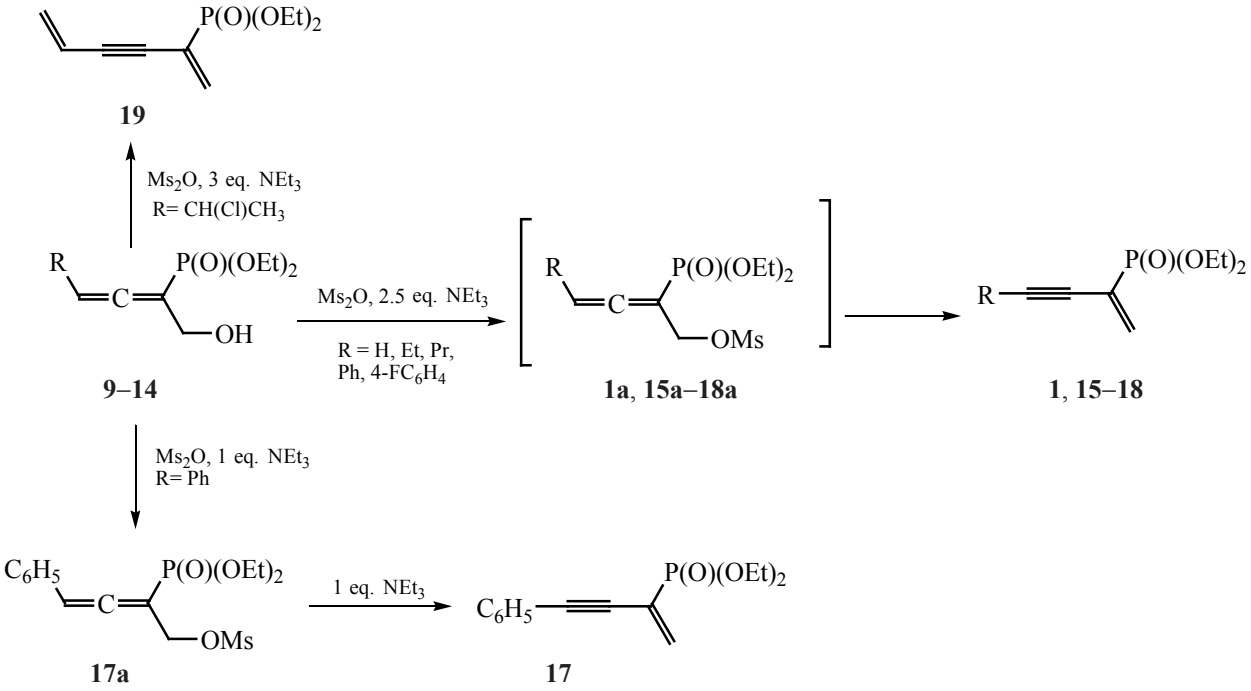
All the synthesized compounds **1**, **15–19** were isolated in an individual form; their structure and composition were determined by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy methods and elemental analysis data. The ^{1}H NMR spectra contain the signals indicating the presence of ethoxyl groups and corresponding substituents located at the triple bond. The presence of vinylphosphonate fragment in compounds **15–18** is indicated by the doublet proton signals of in the 6.1–6.5 ppm region with the spin-spin coupling constants J_{HP} = 44–48 Hz (*trans*) and J_{HP} = 20 Hz (*cis*). In the case of compound **19**, the spectra additionally contain two doublet and one triplet signals of

Scheme 2.



R = H, C_2H_5, C_3H_7, C_6H_5, 4-FC_6H_4, CH(Cl)CH_3.

Scheme 3.



the protons of the vinyl group at 5.54 (J_{HH} = 12.0 Hz), 5.68 (J_{HH} = 16.0 Hz) and 5.91 ppm (J_{HH} = 12.0, 16.0, J_{HP} = 4.0 Hz). Since a 1,4-cleavage of the methanesulfonic acid molecule in α-allene mesylates results in a cardinal change in the carbon skeleton of the molecule, the ^{13}C NMR spectral data are the most informative. The presence of vinyl acetylene fragment in compounds **1**, **15–19** is indicated by the presence of the signals from two *sp*-hybridized carbon atoms in the ranges of 75–84 and 92–96 ppm with a coupling constant of about 10 Hz and two sp^2-hybridized carbon atoms at 122–123 (J_{CP} = 186.0 Hz) and 137–138 ppm (J_{CP} = 7.0 Hz).

In summary, a convenient method was developed for the preparation of new 3-substituted 2-(diethylphosphoryl)but-1-en-3-ynes based on the available phosphorylated α-allene alcohols. The obtained compounds can be used as precursors for the creation of various organophosphorus heterocycles.

EXPERIMENTAL

NMR spectra were recorded on a Bruker AV-400 instrument from $CDCl_3$ solutions using the signal of residual protons of a deuterated solvent as an internal standard (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P) as an external standard. ^{13}C NMR spectra were recorded in the JMODECHO mode, the signals of carbon atoms with even and odd number of protons have opposite polarity. The reaction progress was monitored by TLC on Alumina TLC Plates w/UV254 plates. Chromatographic purification of substances was carried out using Macherey-Nagel silica gel (MN Kieselgel 60, 70–230 mesh).

General procedure for the synthesis of compounds 9–14. A solution of 0.01 mol of diethyl chlorophosphite in 10 mL of abs. diethyl ether was added to a solution of a mixture of the corresponding acetylene alcohol **3–8** (0.01 mol) and triethylamine (0.015 mol) in 100 mL of abs. diethyl ether at a temperature of –20 to –25°C. The reaction mixture was stirred for 1 h, then the temperature was slowly brought to room temperature and stirred for another 4 h. The mixture was filtered and kept for 12 h. After removal of the solvent, 15 mL of methanol, 2–3 drops of hydrochloric acid were added (until pH < 7) and kept for 30 min. After removing the solvent in vacuum, the residue was chromatographed on silica gel using a mixture $CHCl_3$–MeOH (10 : 07) as eluent.

2-(Diethoxyphosphoryl)buta-2,3-dien-1-ol (9). Yield 1.55 g (75%), colorless viscous liquid. The spectral data are identical to those described previously [32].

2-(Diethoxyphosphoryl)hexa-2,3-dien-1-ol (10). Yield 1.83 g (78%), colorless oil. ^1H NMR spectrum, δ, ppm: 1.0 t (3H, CH_3, J_{HH} = 8.0 Hz), 1.26 t (6H, OCH_2CH_3, J_{HH} = 8.0 Hz), 2.07 d. q (2H, CH_2, J_{HH} = 7.0, J_{HP} =

7.5 Hz), 3.74 br. s (1H, OH), 3.98–4.09 m (4H, $POCH_2$), 4.16 d (2H, CH_2OH, J_{HP} = 12.2 Hz), 5.47–5.58 m (1H, =CH). ^{13}C NMR spectrum, δ_C, ppm: 13.12 l (CH_3, J_{CP} = 3.0 Hz), 16.12 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 16.15 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 20.91 d (CH_2, J_{CP} = 7.0 Hz), 60.78 d (CH_2OH, J_{CP} = 16.0 Hz), 62.35 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 62.39 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 95.11 d (CP, J_{CP} = 187.0 Hz), 96.72 d (=CH, J_{CP} = 15.0 Hz), 207.77 d (=C=, J_{CP} = 6.0 Hz). ^{31}P NMR spectrum: δ_P 17.2 ppm. Found, %: C 51.17; H 8.09; P 13.17. $C_{10}H_{19}O_4P$. Calculated, %: C 51.28; H 8.18; P 13.22.

2-(Diethoxyphosphoryl)hepta-2,3-dien-1-ol (11). Yield 1.81 g (73%), colorless oil. ^1H NMR spectrum, δ, ppm: 0.9 t (3H, CH_3, J_{HH} = 8.0 Hz), 1.28 t (6H, OCH_2CH_3, J_{HH} = 8.0 Hz), 1.42 m (2H, CH_2), 2.06 d. t (2H, CH_2, J_{HH} = 8.0, J_{HP} = 8.0 Hz), 3.47 br. s (1H, OH), 4.0–4.23 m (4H, $POCH_2$), 4.21 d. d (2H, CH_2OH, J_{HH} = 4.0, J_{HP} = 12.2 Hz), 5.42–5.48 m (1H, =CH). ^{13}C NMR spectrum, δ_C, ppm: 13.49 (CH_3), 16.19 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 22.16 d (CH_2, J_{CP} = 8.0 Hz), 29.73 d (CH_2, J_{CP} = 2.0 Hz), 61.10 d (CH_2OH, J_{CP} = 16.0 Hz), 62.46 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 62.51 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 93.8 d (=CH, J_{CP} = 16.0 Hz), 94.17 d (CP, J_{CP} = 188.0 Hz), 207.03 d (=C=, J_{CP} = 6.0 Hz). ^{31}P NMR spectrum: δ_P 17.25 ppm. Found, %: C 53.16; H 8.58; P 12.40. $C_{11}H_{21}O_4P$. Calculated, %: C 53.22; H 8.53; P 12.48.

2-(Diethoxyphosphoryl)-4-phenylbuta-2,3-dien-1-ol (12). Yield 1.92 g (68%), yellow oil. ^1H NMR spectrum, δ, ppm: 1.27 t (3H, OCH_2CH_3, J_{HH} = 8.0 Hz), 1.34 t (3H, OCH_2CH_3, J_{HH} = 8.0 Hz), 3.32 br. s (1H, OH), 4.07–4.16 m (2H, $POCH_2$), 4.18 d. q (2H, $POCH_2$, J_{HH} = 8.0, J_{HP} = 8.0 Hz), 4.42 d (2H, $\underline{CH_2}OH$, J_{HP} = 16.0 Hz), 6.41 d (1H, =CH, J_{HP} = 12.0 Hz), 7.24–7.35 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 16.23 d (OCH_2CH_3, J_{CP} = 3.0 Hz), 16.29 d (OCH_2CH_3, J_{CP} = 3.0 Hz), 61.25 d (CH_2OH, J_{CP} = 7.0 Hz), 62.92 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 97.2 d (=CH, J_{CP} = 15.0 Hz), 98.75 d (CP, J_{CP} = 186.0 Hz), 127.24 d (C_{Ph}, J_{CP} = 2.0 Hz), 127.99 (C_{Ph}), 128.887 d (C_{Ph}, J_{CP} = 1.0 Hz), 131.75 d (C_{Ph}, J_{CP} = 8.0 Hz), 209.98 d (=C=, J_{CP} = 4.0 Hz). ^{31}P NMR spectrum: δ_P 15.4 ppm. Found, %: C 59.50; H 6.70; P 10.88. $C_{14}H_{19}O_4P$. Calculated, %: C 59.57; H 6.79; P 10.97.

2-(Diethoxyphosphoryl)-4-(4-fluorophenyl)buta-2,3-dien-1-ol (13). Yield 2.00 g (70%), yellow oil. ^1H NMR spectrum, δ, ppm: 1.23 t (3H, OCH_2CH_3, J_{HH} = 8.0 Hz), 1.31 t (3H, OCH_2CH_3, J_{HH} = 8.0 Hz), 3.30 br. s (1H, OH), 4.02–4.11 m (2H, $POCH_2$), 4.12 d. q (2H, $POCH_2$, J_{HH} = 8.0, J_{HP} = 8.0 Hz), 4.37 d. d (2H, CH_2OH, J_{HP} = 12.0, J_{HH} = 4.0 Hz), 6.46 d. t (1H, =CH, J_{HH} = 4.0, J_{HP} = 12.0 Hz), 6.97–7.01 m (2H, C_6H_4F), 7.23–7.27 m (2H, C_6H_4F). ^{13}C NMR spectrum, δ_C, ppm: 16.23 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 16.24 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 60.95 d (CH_2OH, J_{CP} = 8.0 Hz), 62.89 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 96.39 d (=CH, J_{CP} = 16.0 Hz), 99.23 d (=CP, J_{CP} = 185.0 Hz), 115.78 d (C_{Ar}, J_{CP} = 21.0 Hz), 127.80 d. d (C_{Ar}, J_{CP} = 3.0, J_{CF} = 8.0 Hz), 128.78 d. d (C_{Ar}, J_{CP} = 2.0, J_{CF} = 8.0 Hz), 162.39 d. d (CF_{Ar}, J_{CP} = 1.0, J_{CF} = 249.0 Hz), 208.91 d (=C=, J_{CP} = 5.0, J_{CF} = 1.0 Hz). ^{31}P NMR spectrum: δ_P 15.2 ppm. Found, %: C 56.12; H 6.17; P 10.39. $C_{14}H_{18}FO_4P$. Calculated, %: C 56.00; H 6.04; P 10.32.

2-(Diethoxyphosphoryl)-5-chlorohexa-2,3-dien-1-ol (14). Yield 1.69 g (63%, diastereomers mixture), yellow oil. ^1H NMR spectrum, δ, ppm: 1.32 t (3H, OCH_2CH_3, J_{HH} = 8.0 Hz), 1.34 t (3H, OCH_2CH_3, J_{HH} = 8.0 Hz), 1.64 t (3H, CH_3, J_{HH} = 4.0 Hz), 3.45 br. s (1H, OH), 4.11–4.16 m (4H, $POCH_2$), 4.28 d (2H, CH_2OH, J_{HP} = 16.0 Hz), 4.60–4.67 m (1H, CHCl), 5.72–5.78 m (1H, =CH). ^{13}C NMR spectrum, δ_C, ppm: 15.91 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 15.96 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 24.36 d (CH_3, J_{CP} = 2.0 Hz), 24.71 d (CH_3, J_{CP} = 1.0 Hz), 52.87 d (CHCl, J_{CP} = 6.0 Hz), 53.22 d (CHCl, J_{CP} = 6.0 Hz), 59.98 d (CH_2OH, J_{CP} = 9.0 Hz), 60.5 d (CH_2OH, J_{CP} = 8.0 Hz), 62.63 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 62.65 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 98.32 d (J_{CP} = 14.0 Hz), 98.33 d (J_{CP} = 183.0 Hz), 98.39 d (J_{CP} = 16.0 Hz), 98.63 d (J_{CP} = 184.0 Hz), 206.03 d (=C=, J_{CP} = 5.0 Hz), 206.09 d (=C=, J_{CP} = 6.0 Hz). ^{31}P NMR spectrum: δ_P 14.85 ppm. Found, %: C 44.79 H 6.82; P 11.32. $C_{10}H_{18}ClO_4P$. Calculated, %: C 44.71; H 6.75; P 11.53.

General procedure for the synthesis of compounds 1, 15–19. A solution of 0.01 mol of triethylamine (0.015 mol in the case of allene alcohol **14**) was added with stirring to a solution of a mixture of the corresponding allene alcohol **9–13** (0.005 mol) in 10 mL of methylene chloride at room temperature. The reaction mixture was stirred until the starting compound disappeared (control by TLC) for about 1 h, and then washed with water. The organic layer was separated, and the solvent was distilled off. The residue was chromatographed on silica gel using a mixture of $CHCl_3$–MeOH (10 : 0.2) as eluent.

2-(Diethoxyphosphoryl)but-2-en-4-yne (1). Yield 0.69 g (70%), colorless liquid. The spectral data are identical to those described previously [34].

2-(Diethoxyphosphoryl)hex-2-ene-4-yne (15). Yield 0.76 g (70%), colorless liquid.

2-(Diethoxyphosphoryl)hex-2-ene-4-yne (15). Yield 0.76 g (70%), colorless liquid. ^{1}H NMR spectrum, δ, ppm: 1.49 t (3H, CH_3, J_{HH} = 8.0 Hz), 1.32 t (6H, OCH_2CH_3, J_{HH} = 8.0 Hz), 2.32 d. q (2H, CH_2, J_{HH} = 8.0, J_{HP} = 4.0 Hz), 4.03–4.14 m (4H, $POCH_2$), 6.14 d (1H, HC=CHP, J_{HP} 48.0 Hz, *trans*), 6.30 d (1H, HC=CHP, J_{HP} = 20.0 Hz, *cis*). ^{13}C NMR spectrum, δ_C, ppm: 13.15 d (CH_2, J_{CP} = 2.0 Hz), 13.46 d (CH_3, J_{CP} = 2.0 Hz), 16.24 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 62.68 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 75.29 d (C≡, J_{CP} = 11.0 Hz), 96.71 d (C≡, J_{CP} = 8.0 Hz), 122.98 d (=CP, J_{CP} = 186.0 Hz), 137.38 d (=CH_2, J_{CP} = 7.0 Hz). ^{31}P NMR spectrum: δ_P 13.4 ppm. Found, %: C 55.68; H 7.83; P 14.18. $C_{10}H_{17}O_3P$. Calculated, %: C 55.55; H 7.93; P 14.33.

2-(Diethoxyphosphoryl)hept-2-ene-4-yne (16). Yield 0.9 g (79%), colorless liquid. ^{1}H NMR spectrum, δ, ppm: 0.97 t (3H, CH_3, J_{HH} = 8.0 Hz), 1.32 t (6H, OCH_2CH_3, J_{HH} = 8.0 Hz), 1.54 m (2H, CH_2), 2.29 d. t (2H, CH_2, J_{HH} = 4.0, J_{HP} = 4.0 Hz), 4.04–4.17 m (4H, $POCH_2$), 6.14 d (1H, HC=CP, J_{HP} = 44.0 Hz, *trans*), 6.31 d (1H, HC=CP, J_{HP} = 20.0 Hz, *cis*). ^{13}C NMR spectrum, δ_C, ppm: 13.37 (CH_3), 16.24 d (CH_3, J_{CP} = 6.0 Hz), 21.20 d (CH_2, J_{CP} = 3.0 Hz), 21.83 d (CH_2, J_{CP} = 3.0 Hz), 62.66 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 76.09 d (C≡, J_{CP} = 11.0 Hz), 95.44 d (C≡, J_{CP} = 8.0 Hz), 123.06 d (=CP, J_{CP} = 186.0 Hz), 137.32 d (=CH_2, J_{CP} = 7.0 Hz). ^{31}P NMR spectrum: δ_P 13.5 ppm. Found, %: C 57.59; H 8.25; P 13.19. $C_{11}H_{19}O_3P$. Calculated, %: C 57.38; H 8.32; P 13.45.

2-(Diethoxyphosphoryl)-4-phenylbut-2-ene-4-yne (17). Yield 1.0 g (76%), colorless liquid. ^{1}H NMR spectrum, δ, ppm: 1.35 t (6H, OCH_2CH_3, J_{HH} = 8.0 Hz), 4.13–4.20 m (4H, $POCH_2$), 6.31 d (1H, HC=CP, J_{HP} = 44.0 Hz, *trans*), 6.46 d (1H, HC=CP, J_{HP} = 20.0 Hz, *cis*), 7.29–7.31 m (3H, C_6H_5), 7.42–7.44 m (2H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 16.32 d (CH_3, J_{CP} = 6.0 Hz), 62.89 d ($POCH_2$, J_{CP} = 6.0 Hz), 84.53 d (C≡, J_{CP} = 10.0 Hz), 93.81 d (C≡, J_{CP} = 11.0 Hz), 122.35 d (C_{Ph}, J_{CP} = 2.0 Hz), 122.76 d (=CP, J_{CP} =186.0 Hz), 128.37 (C_{Ph}), 128.87 (C_{Ph}), 131.63 d (C_{Ph}, J_{CP} = 3.0 Hz), 138.40 d (=CH_2, J_{CP} = 7.0 Hz). ^{31}P NMR spectrum: δ_P 12.6 ppm. Found, %: C 63.60 H 6.38; P 11.77. $C_{14}H_{17}O_3P$. Calculated, %: C 63.63; H 6.48; P 11.72.

2-(Diethoxyphosphoryl)-4-(4-fluorophenyl)but-2-ene-4-yne (18). Yield 0.97 g (69%), colorless liquid. ^{1}H NMR spectrum, δ, ppm: 1.41 t (6H, OCH_2CH_3, J_{HH} = 8.0 Hz), 4.13–4.27 m (4H, $POCH_2$), 6.35 d (1H, HC=CP, J_{HP} = 44.0 Hz, *trans*), 6.50 d (1H, HC=CP, J_{HP} = 20.0 Hz, *cis*), 7.03–7.07 m (2H, C_6H_4F), 7.45–7.48 m (2H, C_6H_4F). ^{13}C NMR spectrum, δ_C, ppm: 16.30 d (CH_3, J_{CP} = 7.0 Hz), 62.62 d ($POCH_2$, J_{CP} = 6.0 Hz), 84.31 d. d (C≡, J_{CP} = 11.0, J_{CF} = 1.0 Hz), 92.62 d (C≡, J_{CP} = 9.0 Hz), 115.65 d (C_{Ar}, J_{CF} = 22.0 Hz), 118.50 d. d (C_{Ar}, J_{CP} = 3.0, J_{CF} = 3.0 Hz), 122.81 d (=CP, J_{CP} = 186.0 Hz), 133.56 d. d (C_{Ar}, J_{CP} = 2.0, J_{CF} = 8.0 Hz), 138.17 d (=CH_2, J_{CP} = 7.0 Hz), 162.74 d (CF, J_{CF} = 250.0 Hz). ^{31}P NMR spectrum: δ_P 12.6 ppm. Found, %: C 58.69; H 5.78; P 10.69. $C_{14}H_{16}FO_3P$. Calculated, %: C 59.58; H 5.71; P 10.97.

2-(Diethoxyphosphoryl)-4-phenylbuta-2,3-dien-1-yl methanesulfonate (17a). Compound **17a** was prepared similarly to **1**, **15**–**19** using 1 eq. of triethylamine. Yield 0.39 g (89%), yellow oil. ^{1}H NMR spectrum, δ, ppm: 1.28 t (3H, OCH_2CH_3, J_{HH} = 8.0 Hz), 1.33 t (3H, OCH_2CH_3, J_{HH} = 8.0 Hz), 3.06 s (3H, CH_3S), 4.05–4.21 m (4H, OCH_2), 4.18 d. q (2H, $POCH_2$, J_{HH} = 8.0, J_{HP} = 8.0 Hz), 4.94 d (2H, CH_2OMs, J_{HP} = 12.0 Hz), 6.63 d (1H, =CH, J_{HP} 12.0 Hz), 7.25–7.36 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 16.31 d (OCH_2CH_3, J_{CP} = 3.0 Hz), 16.32 d (OCH_2CH_3, J_{CP} = 3.0 Hz), 61.41 d (CH_2OH, J_{CP} = 7.0 Hz), 62.45 d (OCH_2CH_3, J_{CP} = 6.0 Hz), 98.8 d (=CH, J_{CP} = 15.0 Hz), 98.84 d (CP, J_{CP} = 186.0 Hz), 127.27 d (C_{Ph}, J_{CP} = 2.0 Hz), 127.99 (C_{Ph}), 128.90 d (C_{Ph}, J_{CP} = 1.0 Hz), 131.78 d (C_{Ph}, J_{CP} = 8.0 Hz), 210.01 d (=C=, J_{CP} = 4.0 Hz). ^{31}P NMR spectrum: δ_P 12.5 ppm. Found, %: C 49.86; H 5.84; P 8.52. $C_{15}H_{21}O_6PS$. Calculated, %: C 49.99 H 5.87; P 8.60.

2-(Diethoxyphosphoryl)hexa-2,6-diene-4-yne (19). Yield 0.7 g (73%), colorless liquid. ^{1}H NMR spectrum, δ, ppm: 1.33 t (6H, OCH_2CH_3, J_{HH} = 8.0 Hz), 4.05–4.19 m (4H, $POCH_2$), 5.54 d (1H, =CH, J_{HH} = 12.0 Hz), 5.68 d (1H, =CH, J_{HH} = 16.0 Hz), 5.91 t. d (1H, =CH, J_{HH} = 12.0, J_{HH} = 16.0, J_{HP} = 4.0 Hz), 6.24 d (1H, HC=CP, J_{HP} = 48.0 Hz, *trans*), 6.41 d (1H, HC=CP, J_{HP} = 20.0 Hz, *cis*). ^{13}C NMR spectrum, δ_C, ppm: 16.24 d (CH_3, J_{CP} = 7.0 Hz), 62.85 d ($POCH_2$, J_{CP} = 5.0 Hz), 84.95 d (C≡, J_{CP} = 10.0 Hz), 92.41 d (C≡, J_{CP} = 10.0 Hz), 116.61 d (CH=, J_{CP} = 3.0 Hz), 122.24 d (=CP, J_{CP} = 186.0 Hz), 128.24 d (=CH_2, J_{CP} = 3.0 Hz), 138.54 d (=CH_2, J_{CP} = 7.0 Hz). ^{31}P NMR spectrum: δ_P 12.59 ppm. Found, %: C 56.18; H 7.09; P 14.42. $C_{10}H_{15}O_3P$. Calculated, %: C 56.07; H 7.06; P 14.46.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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