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To the 80th Anniversary of B.I. Ionin

A New Approach Towards Synthesis of Phosphorylated Alkenes

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Abstract—New method of synthesis of *trans*-vinylphosphonates via reaction of trimethylsilyl(methyl)phosphonites with carbonyl compounds in the presence of carbon tetrachloride has been developed. The reaction involves formation of C-trimethylsilyl substituted ylides and 2-chloro-1,2λ^5-oxaphosphetanes as intermediates.

Keywords: C-silylated tertiary phosphine, vinylphosphonate, diene phosphonate, C-trimethylsilyl substituted ylide, 1,2λ^5-oxaphosphetane

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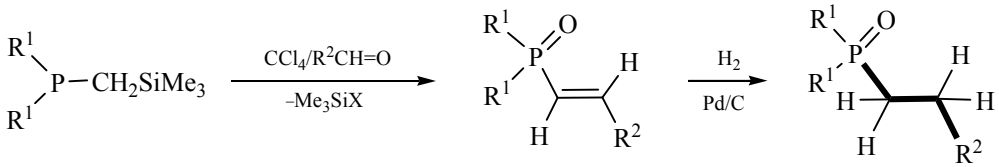
Phosphonic acids have been recognized as isosteres of some biologically important phosphates such as nucleotides, phospholipids, and polyphosphates of nucleosides and carbohydrate-containing phosphates [1–4]; they also exhibit biological activity as regulators, mediators, or inhibitors of enzymes [1]. Moreover, phosphonates have been applied in general organic synthesis as the Horner–Emmons reagents in the reactions with aldehydes and ketones yielding olefins [2].

Substituted vinylphosphonates are of interest as building blocks in the synthesis of anticancer and antiviral agents [3–5], immunosuppressants, various metabolites [6–11], and insecticides as well as antibacterial and antifungal drugs. Vinylphosphonates are used as substrates of the Michael reaction to give aziridine phosphonates, aminophosphonates, and aminophosphonic acids derivatives [12–17]. Vinylphosphonates serve as monomers leading to non-inflammable phosphorus-containing polymers [18, 19] and are thus applied as fire-retardants [20–22].

In view of the above, development of new approaches to prepare phosphonates and vinylphosphonates is of definite interest. In this work we describe a convenient method of vinylphosphonates synthesis; the procedure is based on the reaction of C-trimethylsilyl-(methyl)phosphonates with easily accessible carbonyl compounds and carbon tetrachloride. Subsequent reduction of the prepared vinylphosphonates can yield alkylphosphonates. The approach may be considered as a new method of modification and extension of alkyl chain of tertiary phosphines and phosphonates (Scheme 1).

Reaction of trimethylsilylphosphonates **I** with carbonyl compounds and CCl_4 was performed via stirring of equimolar amounts of the reagents in diethyl

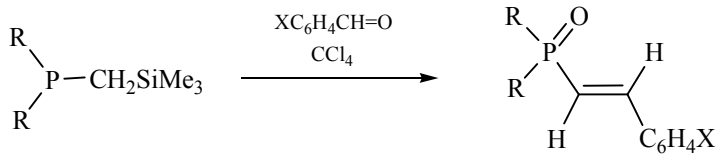
Scheme 1.



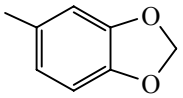
I **II** **III**

R^1 = Alk, AlkO, Et_2N; R^2 = Ar, Alk, AlkCH=CH.

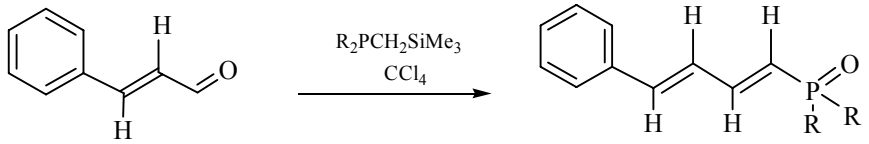
Scheme 2.



Ia–Ic **IIa–IIf**

R = OEt (**Ia**), O*i*-Pr (**Ib**), Et_2N (**Ic**); R = Et_2N, X = Ph (**IIa**); R = OEt, X = Ph (**IIb**); R = O*i*-Pr, X = Ph (**IIc**); R = OEt, X = 2-BrC_6H_4 (**IId**); R = Et_2N, X = 2-FC_6H_4 (**IIe**); R = Et_2N, X =  (**IIf**).

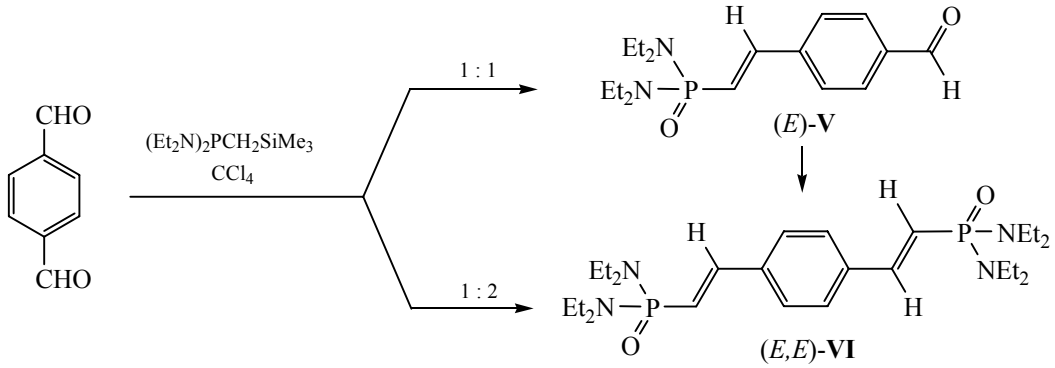
Scheme 3.



IV

R = EtO, Et_2N.

Scheme 4.

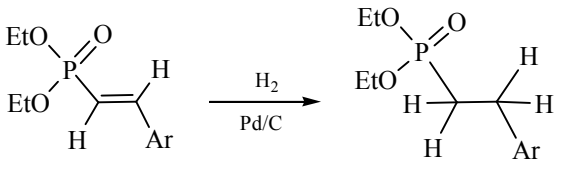


ether or in bulk during few hours. The reaction progress was monitored via TLC or ^{31}P NMR spectroscopy. The target olefins **IIa**–**IIf** were isolated by column chromatography in 60–82% yield. According to the ^{31}P NMR spectroscopy data, the reactions proceeded stereoselectively with formation of of *trans*-vinylphosphonates **IIa**–**IIf** (Scheme 2).

Configuration of the olefins **IIa**–**IIf** was elucidated from NMR spectroscopy data. In particular, in the ^1H NMR spectra two doublets of doublets of the olefinic protons were observed at 6–8 ppm with spin-spin coupling constants $^3J_{HH}$ 17 and $^2J_{PH}$ 19 Hz, corresponding to the *trans*-location of hydrogen atoms with respect to the double bond. Structures of vinylphosphonates **IIb**–**IId** were additionally confirmed by comparison of their physical and chemical parameters with those for the reference vinylphosphonates prepared via other methods.

The reaction with unsaturated aldehydes gave diene phosphonates **IVa** and **IVb**. Strong absorption at 1560 and 1620 cm^{-1} was observed in IR spectrum of diene **IVa**, assigned to asymmetric and symmetric stretching of the transoid bonds; the absorption bands at 3010, 3030, 3090–3100, and 930–940 cm^{-1} (stretching and out-of-plane deformations of unsubstituted vinyl group) were also observed. A group of signals was observed at 6–8 ppm in the ^1H NMR spectrum, the integral intensity corresponding to four protons of the diene system (Scheme 3).

Scheme 5.



II **VII, VIII**

The reactions with aldehydes proceeded regioselectively. In particular, depending on the ratio of the reagents, the reaction of trimethylsilylphosphonate **Ic** with terephthalic aldehyde occurred with sequential substitution of one or two carbonyl groups leading to formation of (phosphonovinyl)benzaldehyde **V** and bis(vinylphosphono)benzene **VI**. The reaction was performed at 20°C in THF (Scheme 4).

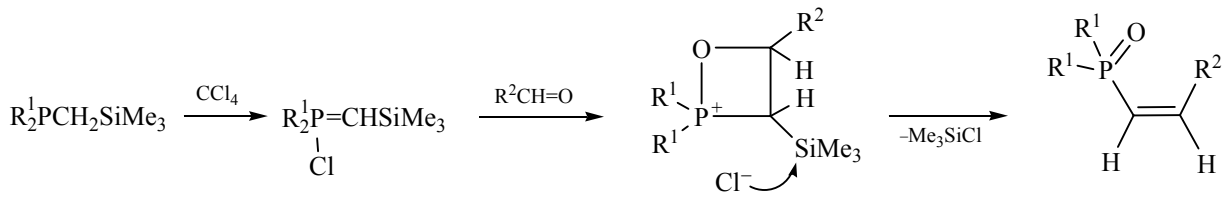
Compounds **V** and **VI** were stable and readily crystallized from nonpolar solvents. The results of elemental analysis and spectroscopy study of compounds **V** and **VI** coincided with their structure. In particular, IR spectrum of compound **V** contained absorption bands at 2700 cm^{-1} (CH) and 1690 cm^{-1} (C=O), pointing at appearance of aldehyde group; other characteristic bands at 1550 cm^{-1} (C=C) as well as at 1205 and 1215 cm^{-1} (P=O) were observed in the spectrum. IR spectrum of compound **VI** contained absorption bands at 1560 (C=C) and 1200 cm^{-1} (P=O). In ^1H NMR spectrum of compound **V**, a singlet signal assigned to aldehyde group was observed at 11.5 ppm. Two doublets of doublets assigned to vinyl protons were found at 6.5 (PCH=C) and 7.7 ppm (PC=CH), the spin-spin coupling constants being of $^3J_{HH}$ 17.0, $^3J_{PH}$ 19.0, and $^2J_{PH}$ 17.5 Hz; the spectral data thus confirmed the *trans*-location of hydrogen atoms with respect to the C=C bond. Doublet of doublets of the *ortho*-protons of unsymmetrically 1,4-disubstituted aromatic ring was also observed. In ^1H NMR spectrum of compound **VI**, the protons of the aromatic ring resonated as finely resolved singlet, coinciding with high symmetry of the molecule.

Catalytic hydrogenation of the vinylphosphonates with hydrogen at low pressure over Pd/C gave alkylphosphonates **VII** and **VIII** (Scheme 5).

Mechanism of the vinylphosphonates **IIa**–**IIf** formation coincided with the results of our previous studies [23–27]. The tertiary phosphine reacted with carbon tetrachloride at the first stage to give P-chloro ylide **IV**; the product further reacted with the carbonyl compound to form 1,2λ^5-oxaphosphetane **V**. The latter is the P-chlorine-containing analog of the Wittig reaction intermediate; however, due to its special structural features it decomposed with elimination of trimethylsilyl chloride to yield vinylphosphonate instead of tertiary phosphine oxide and alkene formation (Scheme 6).

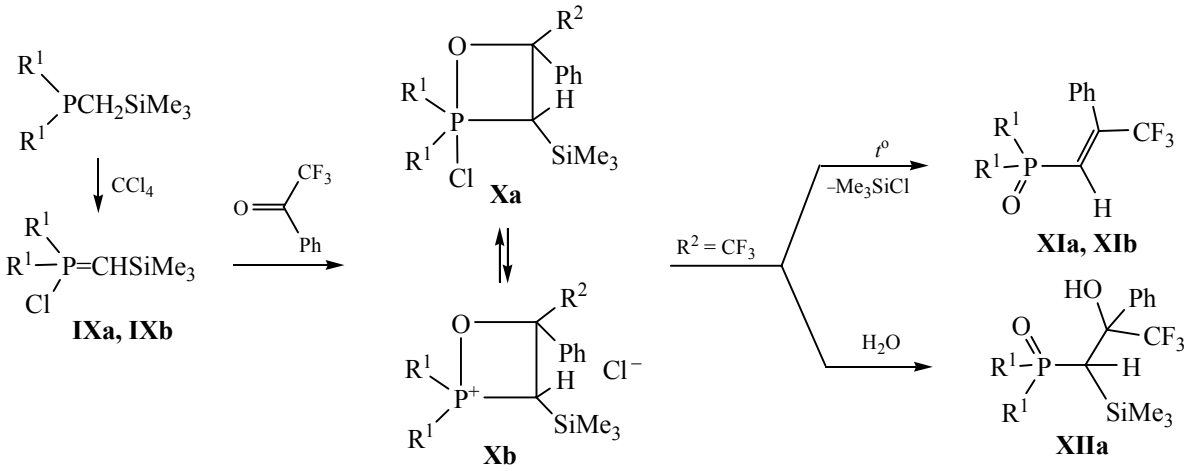
Formation of C-silyl substituted P-chloro ylides **IV** was confirmed with ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The doublet signal of the P=CH group proton was observed at 0 to –5 ppm, $^2J_{PH}$ 7–8 Hz; the ylide carbon atom resonated as doublet at 30 ppm ($^1J_{PC}$ 100–120 Hz), confirming carbanion character of the atom. Chemical shift δ_P of the P-chloro ylides **IV** was of 70–90 ppm, corresponding to the "onium" nature of the phosphorus atom. 2-Chloro-1,2λ^5-oxaphosphetanes **V**, unstable four-membered intermediates formed at the second stage of the reaction, were registered by spectroscopy techniques only in the case of the reaction of tertiary phosphines **I** with trifluoroacetophenone. As we demonstrated earlier, the electron-acceptor bulky trifluoromethyl group at C^3 atom of oxaphosphetane increased its stability; hence, such oxaphosphetanes could be detected by physicochemical methods and in certain cases even isolated [27]. 2-Chloro-1,2λ^5-oxaphosphetane **X** containing CF_3 and Ph substituents at C^3 atom was a transparent oily substance. At room temperature compound **X** was gradually converted into alkenephosphonate **XI** with elimination of trimethylsilyl chloride. Heating increased the conversion rate, and the oxaphosphetane was completely transformed into alkenephosphonate

Scheme 6.



IV **V** **II**

Scheme 7.



R^1 = *i*-PrO, R^2 = CF_3 (**a**); R^1 = Et_2N, R^2 = CF_3 (**b**).

XI that was isolated in good yield via vacuum distillation. The other 2-chlorooxaphosphetanes (not containing CF_3 group) were converted into the vinylphosphonates even below 0°C, but in some cases their formation was registered in ^{31}P NMR spectra. For example, formation of oxaphosphetane **X** with R^1 = *i*-PrO and R^2 = H was confirmed by observation of the signal at 40 ppm which gradually vanished with appearance of another signal at 15 ppm, assigned to diisopropyl 2-styryl phosphonate **IIc**; the latter was isolated and characterized. Oxaphosphetane **X** was easily hydrolyzed to yield crystalline 2-trifluoromethyl-2-hydroxy(ethyl)phosphonate **XI**; compound **X** was converted into the corresponding vinylphosphonate **II** upon heating at 40°C or after prolonged incubation at room temperature. Hydrolysis of oxaphosphetane **X** in the presence of trimethylamine yielded 2-hydroxy(alkyl)phosphonate **XII**. Structure of 2-chloro-1,2λ^5-oxaphosphetane **X** was confirmed by NMR spectroscopy: the signals of trimethylsilyl group at 0.2 ppm, C^3H protons at 2.0 ppm ($^2J_{PH}$ 18.0 Hz), and C^4H at 4.5 ppm were observed in the ^1H NMR spectrum. ^{31}P chemical shift of compound **X** was of 48.0 ppm, typical of the phosphonium atom in four-membered phosphetane ring.

The δ_P value in oxaphosphetanes **X** spectra depended on the solvent polarity. Upfield shift of the signals (≈30 ppm) in less polar solvents (hexane or CCl_4) was observed, whereas in more polar solvents (chloroform or acetonitrile) downfield shift of the signals occurred (up to 50 ppm); that was possibly due to the P–Cl bond dissociation and the change of the equilibrium ratio of the covalent and ionic forms **Xa** ↔ **Xb**. The downfield shifted δ_P values observed in the case of chloroform solutions indicated significant degree of ionization of the P–Cl bond and the tetracoordinated nature of the phosphorus atom. Possibility of 2-chloro-1,2λ^5-oxaphosphetanes dissociation via the P–Cl bond has been discussed earlier in [27] (Scheme 7).

To conclude, the reaction of trimethylsilyl(methyl)phosphonates with aldehydes in the presence of CCl_4 is a convenient approach to stereoselective synthesis of phosphorus-containing olefins, suitable for application in fine organic synthesis.

EXPERIMENTAL

NMR spectra were recorded with a Varian VXR-300 spectrometer at 300 MHz (^1H), 60 MHz (^{13}C), 126.16 MHz(^{31}P), or 225.8 MHz (^{19}F) referenced to Me_4Si (^1H and ^{13}C), 85% H_3PO_4 (^{31}P), or $CFCl_3$ (^{19}F). The chemicals, silica gel, and TLC plates (Poligram SIL G/UV254) from Fluka and Acros suppliers were used. The solvents were distilled before use. The starting trimethylsilyl(methyl)phosphonates **Ia**–**Ic** were synthesized as described elsewhere [24].

Bis(diethylamido) (*E*)-styrylphosphonate (IIa). Carbon tetrachloride (2 mL) (or 0.012 mol of bromotrichloromethane) was added to a solution of 0.01 mol of tetraethyldiaminotrimethylsilyl(methyl)phosphine **Ic** at –70°C. The reaction mixture was allowed to warm up to 0°C and was stirred during 15 min. After addition of benzaldehyde (0.015 mol), the reaction

mixture was stirred during 14 h at room temperature. Then the solvent was removed, and the residue was kept in vacuum (0.05 mmHg) at 100°C during 15 min in order to remove excess of benzaldehyde; then the residue was recrystallized from hexane. Yield 80% (75% in the case of bromotrichloromethane), mp 103.5°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.38 t (12H, CH_3CH_2, $^3J_{HH}$ 7.0 Hz), 1.38 d.q (8H, CH_2N, $^3J_{HH}$ 7.0, $^3J_{PH}$ 11.0 Hz), 6.60 d.d (1H, PCH=C, $^3J_{HH}$ 17.2, J_{PH} 18.0 Hz), 7.75 d.d (1H, C=CH, $^3J_{HH}$ 17.5, $^3J_{PH}$ 19 Hz), 7.65 m (5H, C_6H_5). ^{13}C NMR spectrum (C_6D_6), δ_C, ppm: 13.70, 41.85, 114.50 d (PCH=C, $^1J_{PC}$ 152.0 Hz), 128.70, 131.66 d (PC=C, $^2J_{PC}$ 24.0 Hz), 144.17, 161.90 d ($^3J_{PC}$ 30.0 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 24.50 ppm.

Diethyl (*E*)-styrylphosphonate (IIb) was prepared similarly. Yield 60%, mp 122°C (0.06 mmHg) [28–30]. ^{1}H NMR spectrum ($CDC1_3$), δ, ppm: 1.28 t (3H, $^3J_{HH}$ 7.0 Hz), 1.30 t (3H, CH_3, $^3J_{HH}$ 7.0 Hz), 4.15 d.q (4H, OCH_2, $^3J_{HH}$ 7.0, $^3J_{PH}$ 11.0 Hz), 6.30 d.d (1H, CH=C, $^3J_{HH}$ 17.2, $^2J_{PH}$ 17.2 Hz), 7.10 d.d (1H, C=CH, $^3J_{HH}$ 17.2, $^3J_{PH}$ 22.0 Hz), 7.10–7.40 m (5H, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.30, 61.6 d ($^2J_{PC}$ 6.0 Hz), 110.70 d (CH, $^1J_{PC}$ 190.0 Hz), 128.00, 129.00, 131.10, 136.10, 149.20 d (CH, $^2J_{PC}$ 6.1 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 18.00 ppm.

Diisopropyl (*E*)-styrylphosphonate (IIc) was prepared similarly. Yield 60%, bp 122°C (0.06 mmHg) [28]. ^{1}H NMR spectrum ($CDC1_3$), δ, ppm: 1.24 d.d (12H, CH_3C, $^3J_{HH}$ 6.0, $^3J_{PH}$ 2.5 Hz), 4.33 m (2H, OCH), 6.10 d.d (1H, PCH=C, $^3J_{HH}$ 17.5, $^2J_{PH}$ 18.0 Hz), 7.70 d.d (1H, PC=CH, $^3J_{HH}$ 17.5, $^3J_{PH}$ 19.0 Hz), 7.10 m (5H, C_6H_5). ^{13}C NMR spectrum (C_6D_6), δ_C, ppm: 23.60, 23.80, 70.21 d (OCH, $^2J_{PC}$ 6.0 Hz), 120.80 d (CH, $^1J_{PC}$ 180.0 Hz), 128.35, 129.00, 131.10, 136.10, 149.20 d (CH, $^2J_{PC}$ 6.1 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 16.00 ppm.

Diethyl (*E*)-2-bromostyrylphosphonate (IId) was prepared similarly. Yield 75%, mp 82°C (mp 82°C [31]). ^{1}H NMR spectrum ($CDC1_3$), δ, ppm: 1.29 t (6H, CH_3, $^3J_{HH}$ 7.0 Hz), 4.07 m (4H, CH_2O, $^3J_{HH}$ 7.5 Hz), 6.18 d.d (1H, PCH=C, $^3J_{HH}$ 17.5, $^2J_{PH}$ 17.0 Hz), 7.30 d (2H, C_6H_4, $^3J_{HH}$ 8.5 Hz), 7.37 d.d (1H, PC=CH, $^3J_{HH}$ 17.5, $^3J_{PH}$ 18.2 Hz), 7.46 d (2H, *o*-BrC_6H_4, $^3J_{HH}$ 8.5 Hz). ^{13}C NMR spectrum (C_6D_6), δ_C, ppm: 16.40 d (CH_3, $^2J_{PC}$ 7.0 Hz), 61.90 d (CH_2O, $^2J_{PC}$ 5.6 Hz), 114.80 d (PC=C, $^2J_{PC}$ 192.0 Hz), 124.40, 128.50, 132.60, 133.70 d ($^3J_{PC}$ 24.0 Hz), 147.30 d (PC=C, $^2J_{PC}$ 6.9 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 19.06 ppm.

Bis(diethylamido)-(*E*)-2-(*o*-fluorophenyl)ethenylphosphonate (IIe) was prepared similarly. Yield 60%, bp 130°C (0.1 mmHg), mp 114°C. ^{1}H NMR spectrum ($CDC1_3$), δ, ppm: 1.08 t (6H, CH_3, $^3J_{HH}$ 7.0 Hz), 3.08 m (4H, CH_2O, $^3J_{HH}$ 7.5 Hz), 6.25 d.d (1H, PCH=C, $^3J_{HH}$ 17.5, $^2J_{HP}$ 17.0 Hz), 7.03 m (2H, C_6H_4), 7.40 d.d (1H, PC=CH, ^3J 17.5, $^3J_{HP}$ 18.0 Hz), 7.46 d (2H, C_6H_4, ^3J 8.5 Hz). ^{13}C NMR spectrum (C_6D_6), δ_C, ppm: 13.77, 37.90, 114.50, 118.10 d (P–CH=C, $^2J_{PC}$ 152.0 Hz), 128.70, 131.66 d (PC=C, $^2J_{PC}$ 24.0 Hz), 144.17, 161.90 d ($^2J_{CF}$ 247.5 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 19.06 ppm. Found, %: C 61.81; H 8.42; P 9.61. $C_{16}H_{26}FN_2OP$. Calculated, %:C 61.52; H 8.39; P 9.92.

Bis(diethylamido)-(*E*)-2-(1,3-benzodioxol-5-yl)-vinylphosphonate (IIf) was prepared similarly. Yield 60%, bp 115–135°C (0.1 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.08 t (12H, CH_3, $^3J_{HH}$ 7.0 Hz), 3.07 m (4H, CH_2N), 5.96 s (2H, OCH_2O), 6.14 d.d (1H, PCH=C, $^3J_{HH}$ 17.0, $^2J_{PH}$ 17.5 Hz), 6.78–7.32 m (6H, PC=CH, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.86, 38.00, 100.94, 105.63, 107.97, 115.39, 116.63, 122.69, 129.93, 130.03, 145.00, 147.76, 148.32. ^{31}P NMR spectrum ($CDCl_3$): δ_P 24.00 ppm. Found, %: C 60.66; H 8.21; P 9.05. $C_{17}H_{27}N_2O_3P$. Calculated, %: C 60.34; H 8.04; P 9.15.

Bis(diethylamido)-4-phenyl-(1*E*,3*E*)-1,3-butadienylphosphonic acid (IV). Carbon tetrachloride (0.03 mol) was added to a solution of 0.02 mol of diethylaminotrimethylsilyl methylphosphonite **Ic** in 10 mL of diethyl ether at –70°C followed by increasing of temperature to 0–5°C and stirring of the reaction mixture for 15 min. Then cinnamaldehyde (0.02 mol) was added, and the reaction mixture was incubated during 18 h at room temperature. Yield 70%, bp 170–175°C (0.06 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.4 t (12H, CH_3, $^3J_{HH}$ 7.0), 3.30 d.q (8H, CH_2N, $^3J_{PH}$ 10.0 Hz), 6.30 m and 7.30 m (4H, CH=CH), 7.80 m (5H, C_6H_5). ^{31}P NMR spectrum ($CDCl_3$): δ_P 23.30 ppm. Found, %: C 67.77; H 9.20; P 9.66. $C_{18}H_{29}N_2OP$. Calculated, %: C 67.47; H 9.12; P 9.67.

Bis(diethylamido)-4-formylphenyl-(*E*)-vinylphosphonic acid (V) was prepared similarly from 0.02 mol of diethylaminotrimethylsilyl methylphosphonite **Ic**, 0.03 mol of carbon tetrachloride, and 0.02 mol of terephthalic aldehyde. After removal of the solvent, the residue was recrystallized from diethyl ether–pentane mixture. Yield 50%, mp 92.5–94°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.40 t (12H, CH_3CH, $^3J_{HH}$ 7.0 Hz), 3.41 d.d (8H, CH_2N, $^3J_{HH}$ 7.0, $^3J_{PH}$ 10.5 Hz),

8.10 d.d (4H, C_6H_4), 6.80 d.d (1H, PCH=C, $^2J_{HH}$ 17.5, $^2J_{PH}$ 17.5 Hz), 7.85 d.d (1H, C=CH, $^3J_{HH}$ 17.5, $^3J_{PH}$ 19.0 Hz), 8.00 d and 8.10 d (4H, C_6H_4, $^4J_{HH}$ 9.0 Hz), 10.30 s [1H, C(O)H]. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.01, 41.7 d (*J* 6.0 Hz), 105.2 d (PC, $^2J_{PC}$ 160.0 Hz), 130.1, 131.5, 136.0, 142.5, 154.2 d ($^3J_{PC}$ 32.0 Hz), 191.5. ^{31}P NMR spectrum ($CDCl_3$): δ_P 23.7 ppm. Found, %: C 63.13; H 8.41; P 9.52. $C_{17}H_{27}N_2O_2P$. Calculated, %: C 63.34; H 8.44; P 9.61.

Bis[(1*E*,1'*E*)-2-tetraethyldiamidophosphonovinyl]benzene (VI) was prepared similarly from 0.02 mol of diethylaminotrimethylsilyl methylphosphonite **Ic**, 0.03 mol of carbon tetrachloride, and 0.01 mol of terephthalic aldehyde. After removal of the solvent, the residue was recrystallized from pentane. Yield 50%, yellow crystals, mp 188.5–190°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.05 t (24H, CH_3CH, $^3J_{HH}$ 7.0 Hz), 3.03 d.q (16H, NCH_2, $^3J_{HH}$ 7.0, $^3J_{PH}$ 11.0 Hz), 6.33 d.d (2H, PCH=C, $^3J_{HH}$ 17.0, $^2J_{PH}$ 17.0 Hz), 7.30 d.d (2H, C=CH, $^3J_{HH}$ 17.0, $^3J_{PH}$ 19.0 Hz), 7.44 m (4H, C_6H_4). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.00 d ($^3J_{PC}$ 8.0 Hz), 41.80 d ($^2J_{PC}$ 6.0 Hz), 105.70 d (PCH=, $^1J_{PC}$ 180.0 Hz), 129.80, 137.70, 154.20 d ($^2J_{PC}$ 32.0 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 24.80 ppm. Found, %: C 61.31; H 9.66; N 10.85. $C_{20}H_{48}H_2O_2P_2$. Calculated, %: C 61.16; H 9.47; N 10.97.

Diethyl (*E*)-(2-bromophenylethyl)phosphonate (VII). A solution of 120 mg of vinylphosphonate **II** in 10 mL of ethanol was subject to hydrogenation over 10% Pd/C (20 mg) at atmospheric pressure. The mixture was vigorously stirred at room temperature for 3 h, and the catalyst and solvent were removed. Yield 120 mg (99%), colorless oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 t (6H, $^3J_{HH}$ 7.1 Hz), 2.10 m (2H, CH_2), 2.91 m (2H, CH_2), 4.04–4.10 m (4H, CH_2O), 7.16–7.30 m (4H, C_6H_5). ^{31}P NMR spectrum ($CDCl_3$): δ_P 32.00 ppm. Found, %: C 44.88; H 5.65; P 9.64. $C_{12}H_{18}BrO_3P$. Calculated, %: C 44.88; H 5.65; P 9.64.

Diethyl (*E*)-(2-phenylethyl)phosphonate (VIII) was prepared similarly from compound **IIb**. Yield 90%. ^{1}H NMR ($CDCl_3$), δ, ppm: 1.32 t (6H, CH_3, $^3J_{PH}$ 7.1 Hz), 2.11 m (2H, CH_2), 2.85 m (2H, CH_2), 4.09 q (4H, OCH_2, $^3J_{HH}$ 7.4 Hz), 7.21–7.29 m (5H, C_6H_5). ^{31}P NMR spectrum ($CDCl_3$): δ_P 32.00 ppm. Found, %: C 59.50; H 7.91; P 12.79. $C_{12}H_{19}O_3P$. Calculated, %: C 59.50; H 7.91; P 12.79.

Diisopropoxychlorophosphonium (trimethylsilyl)methylide (IXa). Carbon tetrachloride (0.04 mol) was added dropwise to a solution of diisopropyl trimethylsilyl(methyl)phosphonite [32] (0.02 mol) in 20 mL of diethyl ether at stirring and cooling to –70°C. Then temperature was increased to ambient, the reaction mixture was stirred during 3 h, and the solvent was evaporated. Yield 80%, bp 65°C (0.06 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.01 d (9H, CH_3Si, $^4J_{PH}$ 0.3 Hz), 0.48 d (1H, P=CH, $^3J_{PH}$ 3.0 Hz), 1.25 d.d (6H, $(CH_3)_2CH$, $^3J_{PH}$ 3.0 Hz), 4.62 m (2H, OCH). ^{13}C NMR spectrum (C_6D_6), δ_C, ppm: 0.89 d (CH_3Si, $^3J_{PC}$ 6.0 Hz), 15.00 d (P=C, $^1J_{PC}$ 155.0 Hz), 21.30 d (CH_3C, $^3J_{PC}$ 6.0 Hz), 71.55 d (OCH, $^2J_{PC}$ 9.0 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 59.00 ppm.

Bis(diethylamido)-3,3,3-trifluoro-2-phenylpropenephosponate (IXb) was prepared similarly. Yield 70%, bp 150°C (0.07 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.38 t (12H, CH_3, $^3J_{HH}$ 7.0 Hz), 3.27 d.q (8H, CH_2N, $^3J_{PH}$ 10.0 Hz), 6.80 d.q (1H, C=CH, $^2J_{PH}$ 12.0, $^4J_{HF}$ 1.5 Hz), 7.60 m (5H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ_F –68.11 ppm. ^{31}P NMR spectrum ($CDCl_3$): δ_P 23.50, 16.20 ppm. Found, %: C 56.35; H 7.23; P 8.55. $C_{17}H_{26}F_3N_2OP$. Calculated, %: C 56.35; H 7.23; P 8.55.

2-Chloro-2,2-diisopropoxy-2,2-dihydro-4-phenyl-4-trifluoromethyl-3-trimethylsilyl-1,2λ^5-oxaphosphetane (X). Carbon tetrachloride (0.04 mol) was added dropwise to a solution of 0.02 mol of diisopropyl trimethylsilyl(methyl)phosphonate in 20 mL of diethyl ether at stirring and cooling to –70°C. Then temperature was increased to ambient, and the reaction mixture was stirred during 2–3 h; the reaction progress was monitored by ^{31}P NMR spectroscopy. Then 0.025 mol of 2,2,2-trifluoroacetophenone was added and the mixture was stirred during 2–4 h, and the solvent was evaporated in vacuum. Yield 90%, oily unstable substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.20 s (9H, CH_3Si), 0.90 d (12H, CH_3C, $^3J_{HH}$ 6.0 Hz), 1.95 d (1H, PCH, $^2J_{PH}$ 18.0 Hz), 4.20 m (2H, OCH), 7.30 m and 7.80 m (5H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ_F –68.40 ppm. ^{31}P NMR spectrum ($CDCl_3$): δ_P 48.0 ppm.

Diisopropyl 2-phenyl-3,3,3-trifluoroprop-1-enyl-1-phosphonate (XIa). Oxaphosphetane **X** was heated at 60°C during 0.5 h and distilled in vacuum. Yield 77% (*E* : *Z* = 7 : 1), bp 115°C (0.07 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *E*-isomer, 1.03 d (6H, CH_3C, $^3J_{HH}$ 6.4 Hz), 1.12 d (6H, CH_3C, $^3J_{HH}$ 6.2 Hz), 4.45 m (2H, OCH), 6.44 d.q (1H, PCH=C, $^4J_{FH}$ 1.5, $^2J_{PC}$ 12.0 Hz), 7.30 m (5H, C_6H_5); *Z*-isomer, 1.28 d (6H, CH_3C, $^3J_{HH}$ 6.5 Hz), 1.32 d (6H, CH_3C, $^3J_{HH}$ 6.0 Hz),

4.75 m (2H, OCH), 6.20 d (1H, C=CH, $^2J_{PH}$ 8.8 Hz), 7.30 m (5H, C_6H_5). ^{31}P NMR spectrum ($CDCl_3$): δ_P 9.30 (*E*), 7.68 (*Z*) ppm. Found, %: C 53.57; H 5.99; P 9.21. $C_{15}H_{20}F_3O_3P$. Calculated, %: C 53.57; H 5.99; P 9.21.

Diisopropyl 1-(trimethylsilyl-2-hydroxyphenyl-3,3,3-trifluoro)propylphosphonate (XIIa). Yield 80%, bp 118°C (0.04 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.5 s (9H, CH_3Si), 0.92 m (12H, CH_3C), 2.87 d (1H, PCH, $^2J_{PH}$ 20.0 Hz), 4.48 m and 4.85 m (3H, CHO, OH), 7.17–7.51 m (5H, C_6H_5). ^{31}P NMR spectrum ($CDCl_3$): δ_P 18.70 ppm. ^{19}F NMR spectrum ($CDCl_3$): δ_F –77.60 ppm. Found, %: C 49.97; H 6.89. $C_{18}H_{30}F_3O_4P$. Calculated, %: C 50.69; H 7.09.

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