Heteroatom Chemistry
Volume 20, Number 2, 2009

Cycloaddition Reaction of Phosphonyl Nitrile Oxides to Phosphaacetylene and Alkene

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Received 26 January 2008; revised 18 June 2008, 28 August 2008

ABSTRACT: *Here, we report the cycloaddition reaction of phosphonyl nitrile oxides and the formation of an unexpected 2:1 cycloaddition product. It provides a direct route to triphosphonyl-substituted dihydroisoxazolyl dihydroisoxazoles and diphosphonyl-substituted dihydroisoxazolyl dihydroisoxazoles with excellent levels of regiocontrol product. Density functional theory studies of the reactions between nitrile oxides and acrylonitrile are used to propose a possible reaction mechanism.* © 2009 Wiley Periodicals, Inc. Heteroatom Chem 20:95–100, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20518

INTRODUCTION

,3-Dipolar cycloaddition reactions are among the most important synthetic methods for the preparation of five-membered ring carbocycles and heterocycles [1,2]. The reaction between nitrile oxides and alkenes is of considerable interest in organic synthesis, as the resulting heterocycles are versatile intermediates for the syntheses of natural products and biologically active compounds [3]. Intensive investigations of 1,3-dipolar cycloaddition reactions between nitrile oxide and electron-deficient alkenes have been undertaken, and in most cases, 4,5-dihydroisoxazoles were obtained. Although there are several examples of 1,3-dipolar cycloaddition of an electron-deficient nitrile oxide with an unsaturated alkene, the scope and generality of nitrile oxides remain insufficient. Here, we report the cycloaddition of phosphonyl nitrile oxides and the formation of an unexpected 2:1 cycloaddition product. This method provides a direct route to triphosphonyl-substituted dihydroisoxazolyl dihydroisoxazoles and diphosphonyl-substituted dihydroisoxazolyl dihydroisoxazoles with excellent levels of regiocontrol. We believe that this strategy provides a potentially facile route to a wide range of dihydroisoxazolyl dihydroisoxazoles–based targets.

RESULTS AND DISCUSSION

Cycloaddition Reaction of Phosphonyl Nitrile Oxides with Phosphaacetylene

The requisite nitrile oxides **1** were prepared according to literature routes starting with the corresponding hydroxymoyl bromides via base-induced dehydrobromidination [4]. We first investigated the 1,3-dipolar cycloaddition of nitrile oxide and

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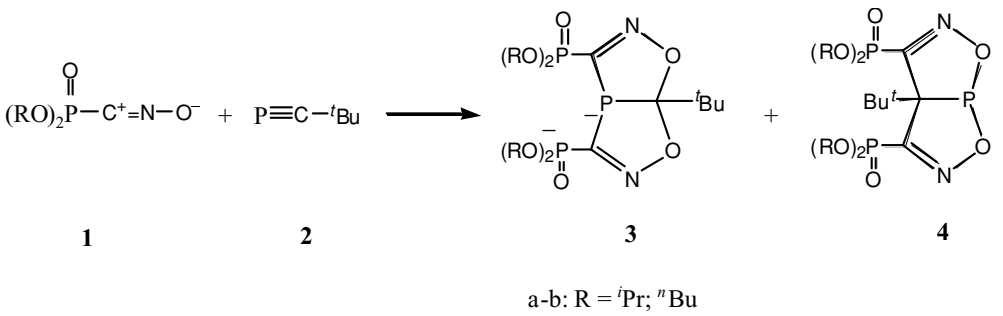
Contract grant sponsor: Natural Science Foundation of China.
Contract grant numbers: 20602032, 20572061, 10376024, and 20373048.



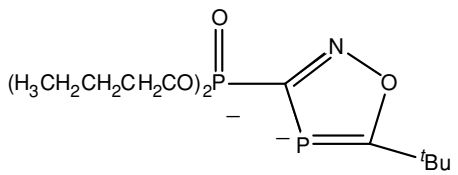
1 2 3 4

SCHEME 1 Cycloaddition of phosphonyl nitrile oxides with phosphaacetylene.

phosphaacetylene **2**, as shown in Scheme 1. In our initial attempts, we failed to isolate the pure nitrile oxide **1**. Therefore, unpurified nitrile oxide was directly used for the cycloaddition reaction. *tert*-Butyl phosphaacetylene 2 can react with nitrile oxides **1** to give heterocyclic compounds. However, we found that when phosphonyl nitrile oxides are treated with a threefold excess of *tert*-butyl phosphaacetylene, an unexpected 2:1 cycloaddition product **3** is achieved. Its regioisomer **4** is not obtained. This is probably a consequence of the sterically demanding *tert*-butyl groups on phosphaacetylene 2 and the bulky phosphonyl groups on the nitrile oxides so that only one regioisomer is obtained.

When a onefold excess of dibutoxyphosphonyl nitrile oxides **1** was used, a 1:1 cycloaddition product **5** was detected in the ^{1}H and ^{31}P NMR spectra (the structure is shown in Scheme 2). From ^{31}P NMR spectroscopy (Fig. 1), a doublet at 85.9–86.7 ppm is observed, which suggests a typical bivalent phosphorus [5] and is consistent with a phosphorus atom in isoxazole. Another doublet resonance at 7.1–7.9 ppm is assigned to a phosphorus atom in the phosphonate group. The ^{31}P NMR coupling constant is 67.7 Hz.

In addition, the integrated area of hydrogen in the ^{1}H NMR spectrum is consistent with a 1:1 cycloaddition product. By this method, we can draw the conclusion that this cycloaddition reaction is completed in two steps. In the first step, a 1:1 cycloaddition product **5** is formed. In the second step, a second phosphonyl nitrile oxide **1** adds to the P=C double bond of **5** to form the 2:1 product **3**.



5

SCHEME 2 Cycloaddition product structure of phosphonyl nitrile oxides with phosphaacetylene.

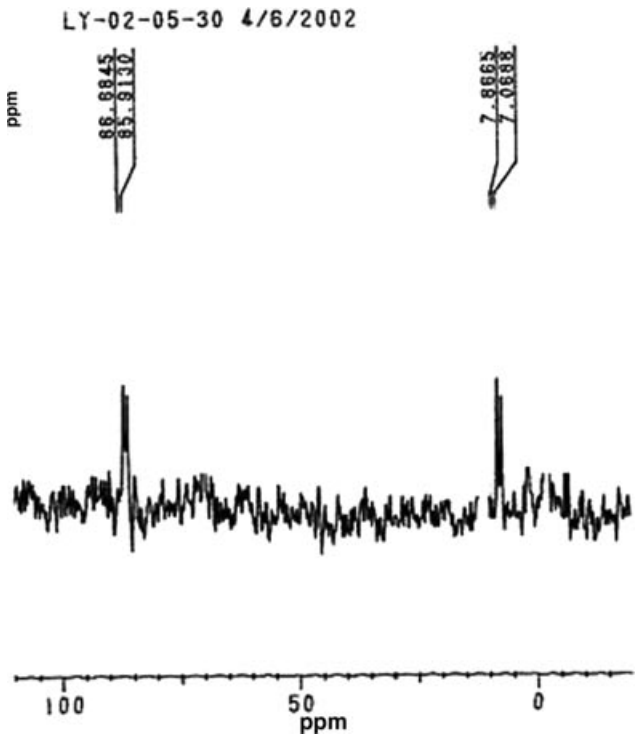


FIGURE 1 ^{31}P NMR of compound **5**.

The proposed structure of the 2:1 cycloaddition product **3a** was confirmed by ^{1}H and ^{31}P NMR spectroscopy. Figure 2 shows the ^{31}P spectrum of compound 3a. Since the middle-group phosphorus ($^{\beta}P$) is attached to two chemically different phosphorus atoms ($^{\alpha}P$), spin–spin coupling leads to a 1:2:1 triplet between 16.1 and 17.6 ppm. Coupling constants of 56.1 Hz are observed. Likewise, the attachment of the two end-group phosphorus atoms to the lone middle-group phosphorus gives spin–spin splitting into a 1:1 doublet at 1.05–1.75 ppm.

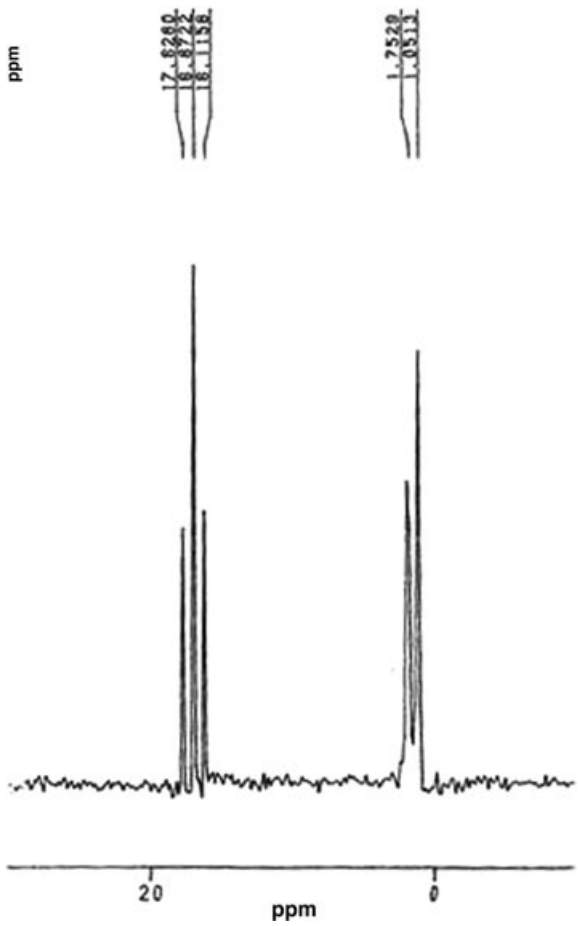


FIGURE 2 ^{31}P NMR of compound **3a**.

Cycloaddition of Phosphonyl Nitrile Oxides with Alkene

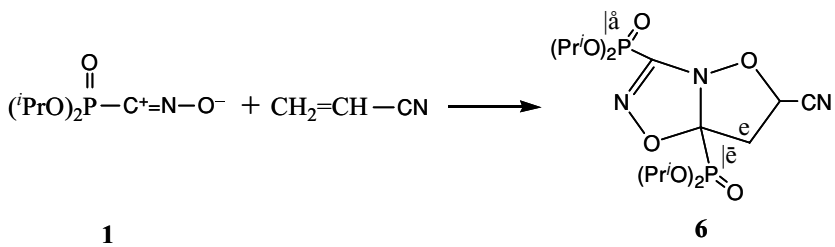
We also examined the reaction of phosphonyl nitrile oxides with electron-deficient alkenes. When reacted with acrylonitrile, diisopropoxy phosphonyl nitrile oxides **1** showed analogous behavior. Nitrile oxide **1** reacted regioselectively with acrylonitrile to give an unexpected 2:1 product **6** (Scheme 3).

When treated with *trans*-vinylphosphonate, phosphonyl nitrile oxides **1** also showed analogous behavior (Scheme 4). Vinylphosphonate **7** was prepared according to the procedures described previously [2h]. When diisopropoxy phosphonyl nitrile oxides **1** are treated with β-substituted vinylphosphonate **7**, only the regioselective 2:1 addition product **8** was obtained. Meanwhile, when excessive β-substituted vinylphosphonate **7** was added, only 2:1 cycloadduct was obtained.

Theoretical Calculations

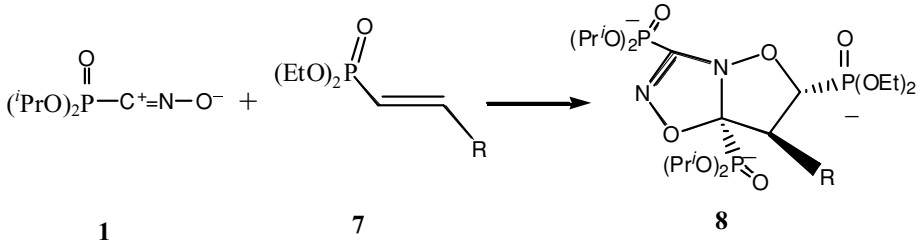
In the current case, the detailed mechanism has been explored with the density functional theory method. Each structure was fully optimized with the B3LYP (B3LYP calculations give relative energies of the various structural transitions to be within ~5 kcal/mol of the actual energies) [7–11] method by using the 6-31G* basis set for C, O, and H atoms. Harmonic vibrational frequencies were calculated for each structure. The bond orders reported were the Wiberg bond, calculated by means of natural bond orbitals. The charges reported were the Mulliken atomic charges. The structures of ts_1 and ts_2 are shown in the supporting information. All calculations were performed with the Gaussian 03 program package. All relative energies discussed within this context are free energies at 298 K. To make the calculations easier, we used the methyl group instead of the propyl group.

A plausible reaction pathway has been proposed to account for the high reactivity and selectivity of diisopropoxy phosphonyl nitrile oxide. First, a regiospecific 1:1 product was formed. Second, highly reactive diisopropoxy phosphonyl nitrile oxide can continue reacting with C=N double bond and give the corresponding cycloadduct. From Fig. 3, we can see that the free energy barriers for the first and second steps are 11.7 and −14.6 kcal/mol, respectively. The free energy of the second stepis quite low. So, the cycloaddition stops at this step.



1 **6**

SCHEME 3 Cycloaddition of phosphonyl nitrile oxides with acrylonitrile.



1 **7** **8**

A-F: R = C_6H_5, C_6H_{13}, *p*-$O_2NC_6H_4$, 2,4-$Cl_2C_6H_3$, *m*-$O_2NC_6H_4$,CO_2CH_3

SCHEME 4 Cycloaddition of phosphonyl nitrile oxides with β-substituted vinylphosphonate.

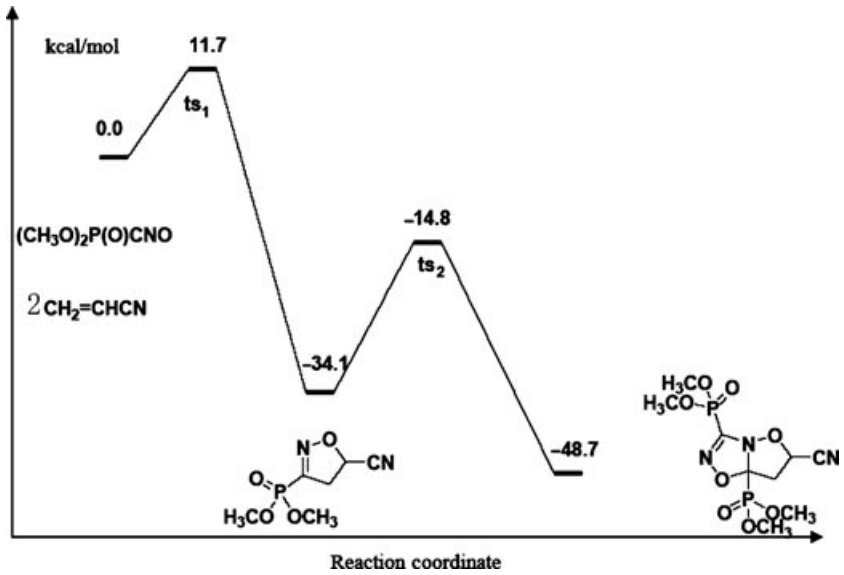


FIGURE 3 Potential energy surface of the reaction with the B3LYP method. All energies are electronic energies without zero point energy corrections with respect to the reactants. ts_1 and ts_2 stand for the transition state of the first and second steps.

EXPERIMENTAL

General Procedures

Elemental analyses were carried on a Yanaco CHN Corder MT-3 apparatus. ^1H, ^{13}C, and ^{31}P NMR spectra were measured with a Bruker 300 spectrometer using TMS and 85% H_3PO_4 as the internal and external references, respectively, and $CDCl_3$ as the solvent. Solvents used were purified and dried by standard procedures. Compounds **1** and **2** were synthesized according to refs. [4] and [6], respectively.

Procedure for the Synthesis of **3**

To a rapidly stirred solution of *tert*-butyl phosphaacetylene **2** (0.2 mL, 1 M in $Me_3SiOSiMe_3$) and Et_3N (0.15 g) in dry ether (10 mL) under N_2, a solution of compound **1** (0.288 g, 1 mmol) in dry ether (6 mL) was added dropwise at −10°C. The mixture was stirred at room temperature for 24 h. Then, the reaction mixture was filtered to remove triethylamine hydrobromides and the solvent was evaporated in vacuum. The residue was chromatographed on a silica gel column with petroleum ether/ethyl acetate (1:1, v/v) to give pure **3a–b** as an oil.

*[7a-tert-Butyl-5-(diisopropoxy-phosphoryl)-[1,2,4]oxazaphospholo[4,5-d][1,2,4]oxazaphosphol-3-yl]-phosphonic Acid Diisopropyl Ester (***3a***).* This compound was obtained in 50.4% yield as an oil. Elemental analysis found (calcd): C 44.27 (44.36), H 7.32 (7.25), N 5.44 (5.44). ^1H NMR: 4.78 (m, 4H, *CH*Me_2), 1.26–1.33 (t, 24H, CH*Me*$_2$), 1.03 (s, 9H, Me); ^{13}C NMR: 20.1 (d, CH_3), 50 (d, CH), 26.3 (d, $^3J_{cp}$ = 5.9 Hz, *Me*C), 36.6 (d, $^2J_{cp}$ = 16 Hz, Me_3C), 130 ($^1J_{cp}$ = 30 Hz, P—C), 156 ($^1J_{cp}$ = 45 Hz, C=N); ^{31}P NMR: 1.4 ($^{\alpha}$P), 16.87 ($^{\beta}$P).

*[7a-tert-Butyl-5-(dibutoxy-phosphoryl)-[1,2,4]-oxazaphospholo[4,5-d][1,2,4]oxazaphosphol-3-yl]-phosphonic Acid Dibutyl Ester (***3b***).* This compound was obtained in 76.4% yield as an oil. Elemental analysis found (calcd): C 48.46 (48.42), H 7.92 (7.95), N 4.88 (4.91). ^{1}H NMR: 4.66 (m, 4H, CH), 1.67 (m, 8H, CH_2), 1.28–1.36 (m, 12H, CH_3), 1.08 (s, 9H, CMe_3), 0.88–0.95 (t, 12H, Me); ^{31}P NMR: 1.71 ($^{\alpha}$P), 17.57 ($^{\beta}$P).

Procedure for the Synthesis of **5**

The procedure is similar to the synthesis of **3**. When 0.04 mL solution of *tert*-butyl phosphaacetylene **2** (1 M in $Me_3SiOSiMe_3$) was used, compound **5** was obtained as an oil. Yield 43.2%. ^{1}H NMR: 0.87–0.94 (m, 6H), 1.19–1.44 (m, 13H), 1.67–1.68 (m, 4H), 4.17 (m, 4H); ^{31}P NMR: 85.9–86.7 (d, J = 67.7 Hz, $^{\alpha}$P), 7.1–7.9 (d, J = 67.7 Hz, $^{\beta}$P).

*Procedure for the Synthesis of [6-Cyano-3-(diisopropoxy-phosphoryl)-6,7-dihydro-isoxazolo[2,3-d][1,2,4]oxadiazol-7a-yl]phosphonic Acid Diisopropyl Ester (***6***)*

To a stirred solution of compound **1** (0.432 g, 1.5 mmol) and acrylonitrile (0.53 g, 10 mmol) in dry ether (10 mL), a solution of Et_3N (0.2 g, 2 mmol) in dry ether (10 mL) was added dropwise at −10°C°fter half an hour, the solution rises to ambient temperature. The reaction mixture was stirred continuously for 3 days. After filtration, the solvent was evaporated in vacuum. The residue was chromatographed on a silica gel column with petroleum ether/ethyl acetate 3:1 (v/v) to give pure **6** in 22% yield as an oil.

Elemental analysis found (calcd): C 43.64 (43.69), H 6.63 (6.68), N 8.95 (8.99). ^{1}H NMR: 5.03–5.12 (dd, 1H, *CH*CN), 4.53–4.61 (m, 4H, O*CH*Me_2), 3.53–3.59 (t, 2H, CH_2CHCN), 0.99–1.23 (m, 24H, OCHMe_2); ^{13}C NMR: 22 (CH_3CH), 50 (d, CH_3*CH*), 70 (CH_2), 128 ($^1J_{cp}$ = 31 Hz, CP), 131 (CH), 148 ($^1J_{cp}$ = 42 Hz, PC=N), 151 (CN); ^{31}P NMR: 0.57 ($^{\alpha}$P), −3.37 ($^{\beta}$P).

General Procedure for the Synthesis of **8**

To a stirred solution of compound **1** (0.432 g, 1.5 mmol) and β-substituted vinylphosphonate (15 mmol) in dry ether (10 mL), a solution of Et_3N (0.2 g, 2 mmol) in dry ether (10 mL) was added dropwise at −10°C. After half an hour, the solution rises to ambient temperature. The reaction mixture was stirred continuously for 3 days. After filtration, the solvent was evaporated in vacuum. The residue was chromatographed on a silica gel column with petroleum ether/ethyl acetate (1:3) to give pure **8a–e** as an oil.

*[3,7a-Bis(diisopropoxy-phosphoryl)-7-phenyl-7,7a-dihydro-6H-isoxazolo[2,3-d][1,2,4]oxadiazol-6-yl]-phosphonic Acid Diethyl Ester (***8a***).* The compound was obtained in 19.6% yield. Elemental analysis found (calcd): C 47.72 (47.71), H 6.79 (6.93), N 4.29 (4.28). ^{1}H NMR: 7.32 (m, 5H), 5.89–6.03 (dd, 1H), 4.69 (m, 4H), 4.12–4.22 (m, 5H), 1.20–1.39 (m, 30H); ^{13}C NMR: 22.3 (d, CH_3), 16 (CH_2CH_3), 49 (CPh), 50 (d, CH), 56 (CH_2CH_3), 82 ($^1J_{cp}$ = 30 Hz, CHP), 92 ($^1J_{cp}$ = 50 Hz, PC—N), 160 ($^1J_{cp}$ = 37 Hz, PC=N), 126–130 (C_{arom}); ^{31}P NMR: 0.89 ($^{\alpha}$P), −3.25 ($^{\beta}$P), 18.53 ($^{\gamma}$P).

*[3,7a-Bis(diisopropoxy-phosphoryl)-7-hexyl-7,7a-dihydro-6H-isoxazolo[2,3-d][1,2,4]oxadiazol-6-yl]-phosphonic Acid Diethyl Ester (***8b***).* The compound was obtained in 31.4% yield. Elemental analysis found (calcd): C 46.98 (47.13), H 8.13 (8.06), N 4.28 (4.23). ^{1}H NMR: 4.65–4.75 (m, 5H), 3.99–4.10 (m, 5H), 1.08–1.41 (m, 40H), 0.73–0.76 (m, 3H); ^{31}P NMR: 1.08 ($^{\alpha}$P), 3.14 ($^{\beta}$P), 19.2 ($^{\gamma}$P).

*[3,7a-Bis(diisopropoxy-phosphoryl)-7-(4-nitro-phenyl)-7,7a-dihydro-6H-isoxazolo[2,3-d][1,2,4]oxadiazol-6-yl]phosphonic Acid Diethyl Ester (***8c***).* The compound was obtained in 56.1% yield. Elemental analysis found (calcd): C 44.59 (44.64), H 6.35 (6.34), N 5.98 (6.01). ^{1}H NMR: 8.19–8.23 (d, 2H), 7.51–7.55 (d, 2H), 6.06 (dd, 1H), 4.83 (m, 4H), 4.21 (m, 5H), 1.23–1.37 (m, 30H); ^{31}P NMR: 0.53 ($^{\alpha}$P), −3.32 ($^{\beta}$P), 17.68 ($^{\gamma}$P).

*[7-(2,4-Dichloro-phenyl)-3,7a-bis(diisopropoxy-phosphoryl)-7,7a-dihydro-6H-isoxazolo[2,3-d][1,2,4]oxadiazol-6-yl]phosphonic Acid Diethyl Ester (***8d***).* The compound was obtained in 56.1% yield. Elemental analysis found (calcd): C 43.1 (43.16), H 5.96 (5.99), N 3.85 (3.87). ^{1}H NMR: 7.24–7.37 (m, 3H), 6.19–6.32 (dd, 1H), 4.67–4.87 (m, 4H), 4.15–4.31 (m, 5H), 1.20–1.39 (m, 30H); ^{31}P NMR: 0.93 ($^{\alpha}$P), −3.25 ($^{\beta}$P), 18.53 ($^{\gamma}$P).

*[3,7a-Bis(diisopropoxy-phosphoryl)-7-(3-nitro-phenyl)-7,7a-dihydro-6H-isoxazolo[2,3-d][1,2,4]oxadiazol-6-yl]phosphonic Acid Diethyl Ester (***8e***).* The compound was obtained in 35.3% yield. Elemental analysis found (calcd): C 44.65 (44.64), H 6.37 (6.34), N 6.03 (6.01). ^{1}H NMR: 8.14–8.18 (d, 2H), 7.54–7.66 (dd, 2H), 5.95–6.09 (dd, 1H), 4.69 (m, 4H), 4.14–4.36 (m, 5H), 1.21–1.35 (m, 30H); ^{31}P NMR: 0.54 ($^{\alpha}$P), −3.35 ($^{\beta}$P), 17.61 ($^{\gamma}$P).

*6-(Diethoxy-phosphoryl)-3,7*a-*bis(diisopropoxy-phosphoryl)-7,7*a-*dihydro-6*H-*isoxazolo[2,3-*d*][1,2,4]oxadiazole-7-carboxylic Acid Methyl Ester (***8f***).* The compound was obtained in 78.8% yield. Elemental analysis found (calcd): C 47.79 (47.71), H 7.0 (6.97), N 4.28 (4.31). ^{1}H NMR: 5.31–5.45 (dd, 1H), 4.77 (m, 4H), 4.13–4.20 (m, 5H), 3.75–3.77 (s, 3H), 1.27–1.37 (m, 30H); ^{31}P NMR: 0.03 ($^{\alpha}$P), −3.27 ($^{\beta}$P), 17.7 ($^{\gamma}$P).

Isolated yields of 8 are based on substituted vinylphosphonate.

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