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Reaction of Tri(2-pyridyl)phosphine with Electron-Deficient Alkynes in Water: Stereoselective Synthesis of Functionalized Pyridylvinylphosphine Oxides

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The reaction of tri(2-pyridyl)phosphine with electron-deficient alkynes in water proceeds under mild conditions (40–45 °C, without catalyst, 4–5 h) with liberation of pyridine to give (*E*)-pyridylvinylphosphine oxides in 45–56 % yields, the only exception being the reaction with cyanophenylacetylene, which affords the corresponding vinylphosphine oxide of *Z*-configuration in 40 % yield. The reaction is likely triggered by the zwitterion, the adduct of tri(2-pyridyl)-phosphine to the electrophilic acetylenes, the carbanionic center of which is then neutralized by a proton from water. The intermediate phosphonium hydroxide finally decomposes to the product.

Introduction

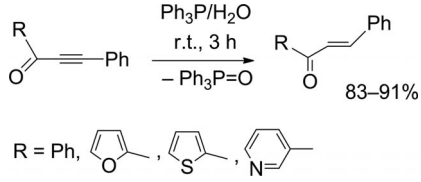
Generating zwitterionic species by the addition of tertiary phosphines to electron-deficient acetylenes and their further transformations is a general and convenient strategy for the synthesis of a diverse range of organic compounds.[1] In these reactions, tertiary phosphines behave as both catalysts and reactants.

Thus, nucleophilic phosphine organocatalysis is successfully employed in Michael β-addition of C-,[1c] N-,[2] O-,[1c,3] and S-[1c] centered nucleophiles to electron-deficient acetylenes. This strategy has also been used to direct the nucleophilic attack to the α- and γ-positions of the alkynes.[1a–1c,4] The tertiary phosphines actively initiate isomerization of conjugated alkynes to conjugated dienes[1a–1c,5] as well as cycloaddition reactions of electron-deficient acetylenes with dipolarophiles leading to carbocycles and heterocycles.[1]

As reactants,[6] tertiary phosphines in most cases react with electron-deficient acetylenes to deliver stable phosphorus ylides.[6b–6j] Commonly, in all the above reactions, the set of tertiary phosphines is limited to the most available and stable triphenylphosphine and trialkylphosphines are involved quite rarely.

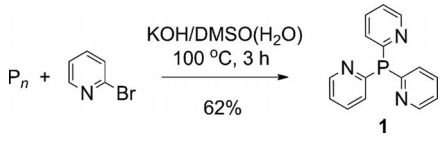
Results and Discussion

Recently, we have shown that 1-acyl-2-phenylacetylenes are stereoselectively reduced with triphenylphosphine in water at room temperature to afford (*E*)-1-acyl-2-phenylethenes in high yields (83–91 %; Scheme 1).[7]



Scheme 1. Synthesis of (*E*)-1-acyl-2-phenylethenes from 1-acyl-2-phenylacetylenes in the system Ph_3P/H_2O.

Recently, the close heteroanalogue of triphenylphosphine, tri(2-pyridyl)phosphine (**1**), has become available through the straightforward reaction between elemental phosphorus and 2-bromopyridine (Scheme 2).[8] This tetradentate phosphine might be expected to interact with electron-deficient alkynes in water in quite a different way to that of triphenylphosphine.



Scheme 2. Synthesis of tri(2-pyridyl)phosphine (**1**) from elemental phosphorus and 2-bromopyridine in the system KOH/DMSO.

Indeed, the reaction of **1** with a range of electron-deficient alkynes **2a**–**e** in water (40–45 °C, 4–5 h) takes an unusual direction to form stereoselectively functionalized (*E*)-pyridylvinylphosphine oxides **3a**–**d** in 45–56 % yields, except for cyanophenylacetylene (**2e**) which gives the corresponding vinylphosphine oxide **3e** of *Z*-configuration in 40 % yield. The reaction is accompanied by liberation of the pyridine molecule (Table 1).

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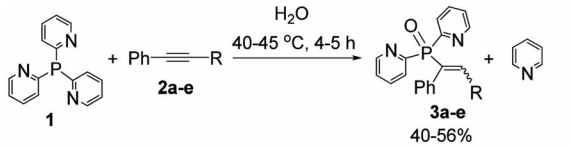
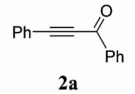
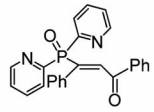
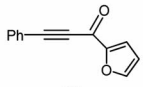
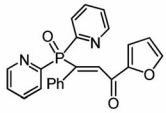
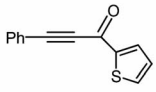
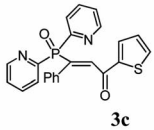
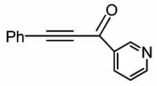
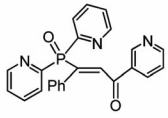
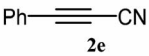
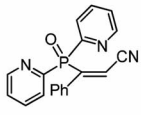
Table 1. Three-component reaction between **1**, electron-deficient alkyne **2** and water.[a]



Alkyne **2**	Vinylphosphine oxide **3**	Isolated yield [%][b]
 **2a**	 **3a**	56
 **2b**	 **3b**	45
 **2c**	 **3c**	53
 **2d**	 **3d**	49
 **2e**	 **3e**	40

[a] Reaction conditions: phosphine **1** (1 mmol), alkyne **2** (1 mmol), H_2O (8 mL), 40–45 °C, 4–5 h. [b] The yield was calculated on the basis of alkyne consumed.

Because both phosphine **1** and acetylene **2** are solids that are almost insoluble in water, the reaction actually initiates in the three-phase solid-solid-liquid system. The crude products are also insoluble in water, which allows them to be easily separated from the aqueous phase. The products are purified by the extraction of impurities by acetone.

Notably, homogenization of the reaction system with tetrahydrofuran (THF) resulted in lower yields (ca. 20%) of phosphine oxide **3a**, with the major product being tri(2-pyridyl)phosphine oxide (**4**; 55%), as exemplified by the reaction of phosphine **1** with acetylene **2a**.

Whereas the formation of the corresponding phosphonium hydroxide is expected (see below), a contribution of phase-transfer catalysis by this species to this reaction is plausible. The liberation of pyridine and the appearance of amphiphilic phosphine oxides may also autocatalyze the reaction.

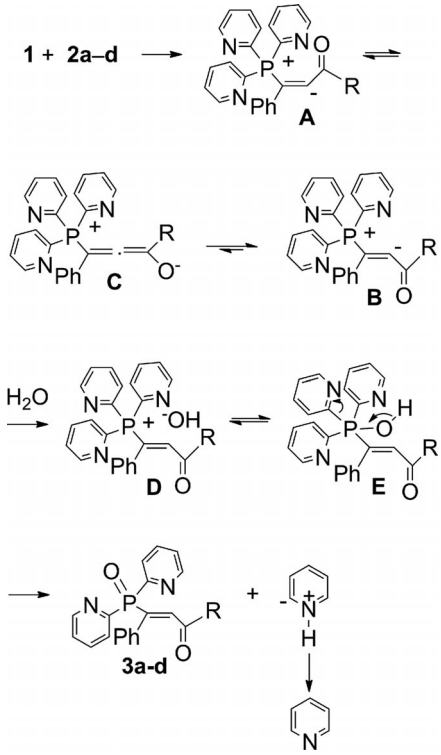
The reaction was monitored by ^{31}P NMR and IR spectroscopic analysis of the solid phase particles dissolved in $CDCl_3$ prior to the analysis because both reactants and products (except for pyridine) were almost insoluble in water (liquid phase). ^{31}P NMR spectra showed reduction in the intensity of peaks of the initial tri(2-pyridyl)phosphine (**1**) at –1 ppm and an increase in the intensity of new peaks at ca. 20 ppm corresponding to vinylphosphine oxides **3a–e**. In the IR spectra, a reduction in the intensity of the absorption band of the acetylenic C≡C bond (2198–2200 cm^{-1}) in the case of acylacetylenes **2a–d** or the intensity of the absorption band corresponding to C≡C and C≡N bonds of initial cyanophenylacetylene (**2e**) (2270 cm^{-1} with a shoulder) was observed. The optimal process duration was found to be 4–5 h; no change was observed in the spectra after additional heating of the reaction mixture for a further 1–2 h.

Configurational assignment of the synthesized vinylphosphine oxides **3** was performed on the basis of ^1H spectra and 2D NOESY data. Thus, doublets of ethenyl protons at 7.45–7.50 ppm with $^3J_{HP}$ ca. 20 Hz and the cross-peaks between the ethenyl and pyridine protons reliably support the *E*-configuration of phosphine oxides **3a–d**. A doublet at δ = 6.20 ppm with $^3J_{HP}$ 32 Hz and the cross-peak between the ethenyl and *ortho*-phenyl protons, observed in the spectra of phosphine oxides **3e**, indicate its *Z*-configuration.

A tentative mechanism for the reaction involves nucleophilic addition of **1** as a neutral nucleophile to the triple bond to give zwitterionic intermediate **A** with a carbanionic center *trans* to the phosphorus (according to classic nucleophilic addition to acetylenes[9]) (Scheme 3, Scheme 6). In the case of acylacetylenes, the equilibrium between zwitterions of *E*- (**A**) and *Z*- (**B**) configuration should exist, which interconvert via allenic intermediate **C** (Scheme 3). Evidently, the most stable intermediate should be zwitterion **B** due to the attractive intramolecular interaction between carbanionic center and the positively charged phosphorus atom. Therefore, the reaction is expected to proceed via intermediate **B** because the equilibrium (Scheme 3) should be shifted mostly to the right. After neutralizing the carbanionic center by a proton from water, phosphonium hydroxide **D** is formed, which is in equilibrium with intermediate hydroxyphosphorane **E**. The latter then decomposes to the final product to release the pyridine molecule.

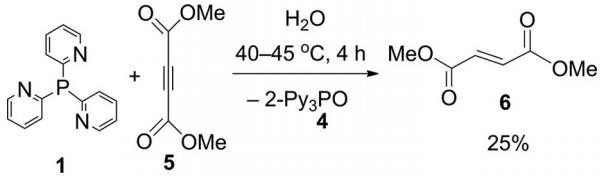
The elimination step (Scheme 3) could involve an intramolecular proton transfer from the OH group of phosphorane **E** to the basic nitrogen atom of the pyridine ring. This makes the latter a much better leaving group. Such a protonation would also explain the unexpected reaction outcome as compared to the reaction of PPh_3 with electron-deficient acetylenes in water. With PPh_3, no intramolecular protonation can occur (as there is no basic site) and the reaction thus proceeds through a different route.[7]

However, under similar conditions, in the case of dimethyl acetylene dicarboxylate (**5**), the elimination of pyr-



Scheme 3. Tentative scheme for the formation of (*E*)-vinylphosphine oxides **3a**–**d**.

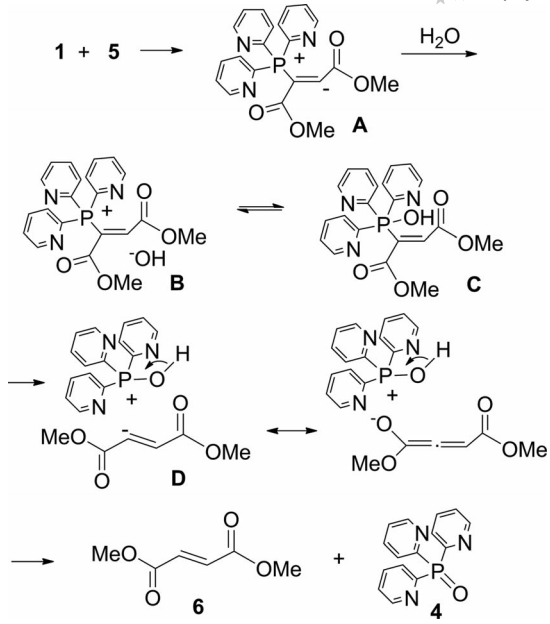
idine does not occur. Instead, competitive C–P bond cleavage in the intermediate phosphorane between tripyridylphosphine and the acetylene counterparts takes place followed by elimination of tri(2-pyridyl)phosphine oxide (**4**) and proton transfer from the hydroxyl group to the ethylenic moiety to afford dimethyl fumarate (**6**) in 25% yield (Scheme 4).



Scheme 4. Three-component reaction between tri(2-pyridyl)phosphine (**1**), dimethyl acetylene dicarboxylate (**5**), and water.

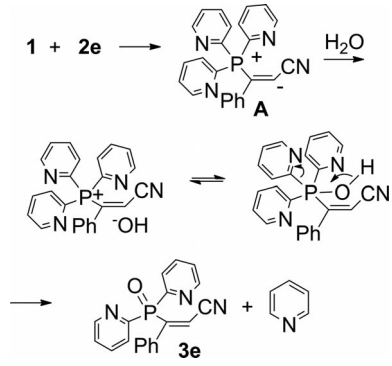
In other words, the stereoselective reduction of the triple bond under the action of the tri(2-pyridyl)phosphine/water system, as previously found for the reaction of acetylenes with PPh_3/water,[7] is observed. The different reactivity of electron-deficient acetylenes **2a**–**e** and acetylene **5** in this reaction is likely due to a better distribution of the negative charge of carbanion-like counterpart of the transition state **D** (Scheme 5) in the case of acetylene **5**.

The above stated *E*-stereochemistry of the products **3a**–**d** derived from acylacetylenes is consistent with the proposed mechanism (Scheme 3). However a puzzle remains regarding the *Z*-stereochemistry of the cyanoethenylphosphine



Scheme 5. Tentative scheme for the formation of dimethyl fumarate (**6**).

oxide, which does not comply with the above rationale. Clearly, the equilibrium between the zwitterions of **A** and **B** types (see Scheme 3) is not as fast as with acylacetylenes and, hence, this cyano derivative remains as the kinetic product (Scheme 6).



Scheme 6. Tentative scheme for the formation of (*Z*)-vinylphosphine oxide **3e**.

The stage of pyridine elimination from tri(2-pyridyl)phosphine oxides under the action of organometallic compounds, water, and alcohols has also been observed.[10]

Conclusions

The one-pot stereoselective synthesis of functionalized dipyridylphosphine oxides has been elaborated through the straightforward reaction of available tri(2-pyridyl)phosphine with electron-deficient alkynes in water. The reaction highlights novel facets of phosphine and acetylene chemistry that paves an ecologically benign way to a new family of promising ligands[11] and building blocks for organic synthesis.[12] Among such compounds are retardants,[13] drug

precursors,[14] and ligands for the design of metallocomplex catalysts applied particularly for hydrogenation of cyclohexene, acetone, and cyclohexanone.[11b]

Experimental Section

General Remarks: ^{1}H, ^{13}C, ^{15}N, ^{31}P NMR and 2D NMR spectra were recorded with an AV-400 Bruker BioSpin spectrometer and referenced to HMDS (^{1}H, ^{13}C), $MeNO_2$ (^{15}N) and H_3PO_4 (^{31}P). All 2D NMR spectra were recorded by using standard gradient Bruker pulse programs. IR spectra were recorded with a Bruker Vertex 70 instrument. GLC analysis was carried out with an Agilent 6890 N chromatograph, HP-5 column (5% phenyl methyl siloxane phase), column length of 30 m, vaporizer temperature 250 °C, column temperature 125–270 °C, temperature increase rate of 30 °C/min. Acetylenes **2a** and **2e** are commercial reagents (Alfa Aesar), acylacetylenes **2b**–**d** were prepared by reported methods.[15]

General Procedure for the Synthesis of Phosphine Oxides 3: A suspension of finely divided tri(2-pyridyl)phosphine **1** (1 mmol) and acetylene **2** (1 mmol) in water (8 mL) was blown with argon and stirred at 40–45 °C for 4–5 h. The aqueous layer was decanted from the dark solid obtained, the solid was solved in chloroform (3 mL) and the solution was dried with $MgSO_4$. After evaporation of the solvent, the crude product was washed with acetone (5 × 0.5 mL) and dried in vacuo to give vinylphosphine oxides **3** as white or yellowish powders.

The relative content of the *Z* isomers of **3a**–**d** or the *E* isomer of **3e** in the crude product did not exceed 10%, with the total conversion being 90–95% (^{1}H, ^{31}P NMR analysis; acetylene **2** could be recovered by extraction with hexane). Pyridine was quantified by titration of the aqueous layer against aqueous HCl or by GLC analysis (after extraction of the aqueous layer with chloroform).

(*E*)-3-(Di-2-pyridinylphosphoryl)-1,3-diphenyl-2-propen-1-one (3a): Yield 230 mg (56%); white powder; m.p. 159–161 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 6.98 (m, 3 H, H_m, H_p, PhC=), 7.09 (m, 2 H, H_o, PhC=), 7.28 (m, 2 H, H_m, PhC=O), 7.34 (m, 2 H, H-5, Py), 7.39 (m, 1 H, H_p, PhC=O), 7.45 (d, $^{3}J_{P,H}$ = 20.8 Hz, 1 H, =CH), 7.74 (m, 2 H, H-4, Py), 7.83 (m, 2 H, H_o, PhC=O), 8.11 (m, 2 H, H-3, Py), 8.77 (d, $^{3}J_{6-5}$ = 4.5 Hz, 2 H, H-6, Py) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 125.7 (d, $^{4}J_{P,C}$ = 3.1 Hz, C-5, Py), 127.8 (C_m, PhC=), 128.1 (C_p, PhC=), 128.4 (C_m, PhC=O), 129.2 (d, $^{2}J_{P,C}$ = 20.9 Hz, C-3, Py), 129.2 (C_o, PhC=O), 129.4 (d, $^{3}J_{P,C}$ = 4.5 Hz, C_o, PhC=), 133.4 (C_p, PhC=O), 133.9 (d, $^{2}J_{P,C}$ = 7.9 Hz, C_i, PhC=), 136.1 (d, $^{3}J_{P,C}$ = 9.3 Hz, C-4, Py), 136.3 (d, $^{4}J_{P,C}$ = 1.5 Hz, C_i, PhC=O), 140.8 (d, $^{2}J_{P,C}$ = 8.7 Hz, =CH), 143.8 (d, $^{1}J_{P,C}$ = 88.7 Hz, =CP), 150.3 (d, $^{3}J_{P,C}$ = 19.5 Hz, C-6, Py), 154.3 (d, $^{1}J_{P,C}$ = 132.5 Hz, C-2, Py), 193.1 (d, $^{3}J_{P,C}$ = 17.6 Hz, C=O) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 19.7 ppm. ^{15}N NMR (40.55 MHz, $CDCl_3$) δ = –57.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1665 (C=O), 1199 (P=O) cm^{-1}. $C_{25}H_{19}N_2O_2P$ (410.40): calcd. C 73.16, H 4.67, N 6.83, P 7.55; found C 73.55, H 4.97, N 6.69, P 7.52.

(*E*)-3-(Di-2-pyridinylphosphoryl)-1-(2-furanyl)-3-phenyl-2-propen-1-one (3b): Yield 180 mg (45%); white powder; m.p. 158–160 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 6.40 (m, 1 H, H-3, Fur), 7.08–7.14 (m, 6 H, H-4, Fur, Ph), 7.39 (m, 2 H, H-5, Py), 7.46 (d, $^{3}J_{P,H}$ = 20.1 Hz, 1 H, =CH), 7.47 (m, 1 H, H-5, Fur), 7.77 (m, 2 H, H-4, Py), 8.14 (m, 2 H, H-3, Py), 8.80 (d, $^{3}J_{6-5}$ = 4.3 Hz, 2 H, H-6, Py) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 112.4 (C-3, Fur), 119.9 (C-4, Fur), 125.8 (d, $^{4}J_{P,C}$ = 2.6 Hz, C-5, Py), 127.8 (d, $^{4}J_{P,C}$ = 1.3 Hz, C_m, Ph), 128.1 (d, $^{5}J_{P,C}$ = 1.8 Hz, C_p, Ph), 129.2 (d, $^{3}J_{P,C}$ = 4.6 Hz, C_o, Ph), 129.2 (d, $^{2}J_{P,C}$ = 21.1 Hz, C-3, Py), 134.0 (d, $^{2}J_{P,C}$ = 7.3 Hz, C_i, Ph), 136.2 (d, $^{3}J_{P,C}$ = 9.6 Hz, C-4, Py), 137.4 (d, $^{2}J_{P,C}$ = 9.2 Hz, =CH), 146.4 (d, $^{1}J_{P,C}$ = 87.0 Hz, =CP), 147.3 (C-5, Fur), 150.3 (d, $^{3}J_{P,C}$ = 19.2 Hz, C-6, Py), 152.5 (C-2, Fur), 154.1 (d, $^{1}J_{P,C}$ = 132.2 Hz, C-2, Py), 178.8 (d, $^{3}J_{P,C}$ = 18.8 Hz, C=O) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 19.8 ppm. ^{15}N NMR (40.55 MHz, $CDCl_3$) δ = –56.8 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1644 (C=O), 1197 (P=O) cm^{-1}. $C_{23}H_{17}N_2O_3P$ (400.37): calcd. C 69.00, H 4.28, N 7.00, P 7.74; found C 68.62, H 4.07, N 6.84, P 7.76.

(*E*)-3-(Di-2-pyridinylphosphoryl)-3-phenyl-1-(2-thienyl)-2-propen-1-one (3c): Yield 220 mg (53%); yellowish powder; m.p. 156–158 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.02 (dd, $^{3}J_{4-5}$ = 4.9, $^{3}J_{4-3}$ = 3.9 Hz, 1 H, H-4, thienyl), 7.09 (m, 1 H, H_p, Ph), 7.11 (m, 2 H, H_m, Ph), 7.17 (m, 2 H, H_o, Ph), 7.41 (m, 2 H, H-5, Py), 7.52 (d, $^{3}J_{P,H}$ = 20.3 Hz, 1 H, =CH), 7.58 (dd, $^{3}J_{5-4}$ = 4.9, $^{4}J_{5-3}$ = 1.0 Hz, 1 H, H-5, thienyl), 7.71 (dd, $^{3}J_{3-4}$ = 3.9, $^{4}J_{3-5}$ = 1.0 Hz, 1 H, H-3, thienyl), 7.80 (m, 2 H, H-4, Py), 8.15 (m, 2 H, H-3, Py), 8.83 (d, $^{3}J_{6-5}$ = 4.5 Hz, 2 H, H-6, Py) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 125.8 (d, $^{4}J_{P,C}$ = 2.9 Hz, C-5, Py), 127.9 (C_m, Ph), 128.2 (C_p, Ph), 128.2 (C-4, thienyl), 129.2 (d, $^{2}J_{P,C}$ = 21.3 Hz, C-3, Py), 129.2 (d, $^{3}J_{P,C}$ = 5.1 Hz, C_o, Ph), 133.9 (d, $^{2}J_{P,C}$ = 7.3 Hz, C_i, Ph), 134.5 (C-3, thienyl), 135.0 (C-5, thienyl), 136.2 (d, $^{3}J_{P,C}$ = 9.5 Hz, C-4, Py), 138.8 (d, $^{2}J_{P,C}$ = 8.8 Hz, =CH), 144.0 (d, $^{4}J_{P,C}$ = 2.9 Hz, C-2, thienyl), 144.9 (d, $^{1}J_{P,C}$ = 87.3 Hz, =CP), 150.4 (d, $^{3}J_{P,C}$ = 19.1 Hz, C-6, Py), 154.1 (d, $^{1}J_{P,C}$ = 132.8 Hz, C-2, Py), 184.3 (d, $^{3}J_{P,C}$ = 18.3 Hz, C=O) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 20.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1631 (C=O), 1196 (P=O) cm^{-1}. $C_{23}H_{17}N_2O_2PS$ (416.43): calcd. C 66.34, H 4.11, N 6.73, P 7.44; found C 65.96, H 4.09, N 6.72, P 7.42.

(*E*)-3-[Di(2-pyridinyl)phosphoryl]-3-phenyl-1-(3-pyridinyl)-2-propen-1-one (3d): Yield 200 mg (49%); white powder; m.p. 166–168 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.02 (m, 3 H, H_m, H_p, Ph), 7.08 (m, 2 H, H_o, Ph), 7.21 (m, 1 H, H-5, PyC=O), 7.41 (m, 2 H, H-5, PyP=O), 7.43 (d, $^{3}J_{P,H}$ = 20.1 Hz, 1 H, =CH), 7.80 (m, 2 H, H-4, PyP=O), 8.06 (m, 1 H, H-4, PyC=O), 8.13 (m, 2 H, H-3, PyP=O), 8.59 (m, 1 H, H-6, PyC=O), 8.83 (d, $^{3}J_{6-5}$ = 4.5 Hz, 2 H, H-6, PyP=O), 9.04 (d, $^{4}J_{2-4}$ = 2.5 Hz, 1 H, H-2, PyC=O) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 123.4 (C-5, PyC=O), 126.0 (d, $^{4}J_{P,C}$ = 3.0 Hz, C-5, PyP=O), 128.1 (C_m, Ph), 128.5 (C_p, Ph), 129.3 (d, $^{2}J_{P,C}$ = 21.0 Hz, C-3, PyP=O), 129.34 (d, $^{3}J_{P,C}$ = 4.4 Hz, C_o, Ph), 131.8 (d, $^{4}J_{P,C}$ = 1.8 Hz, C-3, PyC=O), 133.7 (d, $^{2}J_{P,C}$ = 7.6 Hz, C_i, Ph), 136.2 (C-4, PyC=O), 136.4 (d, $^{3}J_{P,C}$ = 9.6 Hz, C-4, PyP=O), 139.3 (d, $^{2}J_{P,C}$ = 8.8 Hz, =CH), 145.4 (d, $^{1}J_{P,C}$ = 87.7 Hz, =CP), 150.5 (d, $^{3}J_{P,C}$ = 19.2 Hz, C-6, PyP=O), 150.8 (C-2, PyC=O), 153.6 (C-6, PyC=O), 154.1 (d, $^{1}J_{P,C}$ = 132.2 Hz, C-2, PyP=O), 192.5 (d, $^{3}J_{P,C}$ = 18.0 Hz, C=O) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 20.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1671 (C=O), 1199 (P=O) cm^{-1}. $C_{24}H_{18}N_3O_2P$ (411.39): calcd. C 70.07, H 4.41, N 10.21, P 7.53; found C 69.87, H 4.30, N 10.13, P 7.30.

(*Z*)-3-[Di(2-pyridinyl)phosphoryl]-3-phenyl-2-propenenitrile (3e): Yield 132 mg (40%); yellowish powder; m.p. 176–178 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 6.20 (d, $^{3}J_{P,H}$ = 32.0 Hz, 1 H, =CH), 7.21 (m, 1 H, H_p, Ph), 7.23 (m, 2 H, H_m, Ph), 7.37 (m, 2 H, H-5, Py), 7.49 (m, 2 H, H_o, Ph), 7.80 (m, 2 H, H-4, Py), 8.21 (m, 2 H, H-3, Py), 8.76 (d, $^{3}J_{6-5}$ = 4.5 Hz, 2 H, H-6, Py) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 111.4 (d, $^{2}J_{P,C}$ = 3.1 Hz, =CH), 113.9 (d, $^{3}J_{P,C}$ = 9.2 Hz, CN), 126.2 (d, $^{4}J_{P,C}$ = 3.0 Hz, C-5, Py), 127.9 (d, $^{3}J_{P,C}$ = 4.6 Hz, C_o, Ph), 128.5 (C_m, Ph), 129.2 (d, $^{2}J_{P,C}$ = 21.4 Hz, C-3, Py), 129.5 (C_p, Ph), 136.3 (d, $^{3}J_{P,C}$ = 9.9 Hz, C-4, Py), 136.8 (d, $^{2}J_{P,C}$ = 6.9 Hz, C_i, Ph), 150.7 (d, $^{3}J_{P,C}$ = 20.3 Hz, C-6, Py), 153.4 (d, $^{1}J_{P,C}$ = 135.8 Hz, C-2, Py), 156.3 (d, $^{1}J_{P,C}$ = 86.4 Hz, =CP) ppm. ^{31}P NMR ($CDCl_3$): δ = 17.4 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2210 (C≡N), 1191 (P=O) cm^{-1}. $C_{19}H_{14}N_3OP$ (331.31): calcd. C 68.88, H 4.26, N 12.68, P 9.35; found C 68.55, H 4.21, N 12.73, P 9.69.

Reaction of Tri(2-pyridyl)phosphine (1) with Dimethyl Acetylenedicarboxylate (5) in Water: A mixture of phosphine **1** (150 mg, 0.56 mmol), acetylene **5** (80 mg, 0.56 mmol) and water (5 mL) was blown with argon and stirred at 40–45 °C for 4 h. The aqueous layer was decanted from the white solid obtained. The solid was dried in vacuo to give dimethyl fumarate (**6**), yield 20 mg (25%); m.p. 100–102 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, Me), 6.86 (s, 1 H, =CH) ppm.

The aqueous layer was extracted with chloroform (3 × 3 mL) and the extract was dried with $MgSO_4$. After removal of the extractant, the crude residue (120 mg) was analyzed by ^{1}H and ^{31}P NMR spectroscopy. Tri(2-pyridyl)phosphine oxide (**4**) was identified as the major product in this residue (^{1}H NMR spectra were consistent with reported data[16]).

Supporting Information (see footnote on the first page of this article): Spectroscopic data for all new products.

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