An Efficient Synthesis of Vinylphosphonates from Alkyl Cyanoformates, Activated Acetylenes, and Trialkyl Phosphites

Tayebeh Sanaeishoar,[1*] Tahereh Shojaee, Parvaneh Shabankareh, Mina Bashirpour

[1] *Young Researchers Club, Khouzestan Science and Research Branch, Islamic Azad University, Ahvaz, Iran*

[2] *Department of chemistry, College of Science, Khouzestan Science and Research Branch, Islamic Azad University, Ahvaz, Iran; Email: t.sanaei@khouzestan.srbiau.ac.ir*

Abstract- An efficient synthesis of vinylphosphonates is described. This involves the reaction of alkyl cyanoformates and dialkyl acetylendicarboxylates in the presence of trialkyl phosphites. The ^{1}H, ^{13}C NMR, and ^{31}P NMR spectra of vinylphosphonates having different substitution are consistent with the presence of two geometrical isomers.

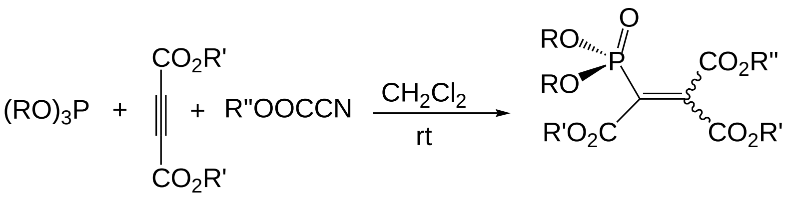
Keywords: Vinylphosphonates, Alkyl cyanoformates, Acetylenic esters, Trialkyl phosphites,

Introduction

Multicomponent reactions (MCRs) provide a powerful tool towards the one-pot synthesis of diverse and complex compounds due to their superior atom economy; simple experimental procedures, one-pot character, and high bond-forming efficiency [1]. Organophosphorus compounds are important in a variety of applications, from medicines to pesticides, from ligands in catalysis to extractants and flame-retardants [2]. In addition, they are widely used in agriculture as insecticides and, herbicides, and plant growth regulators [3-5].

Vinylphosphonates are a well known class of organophosphorus compounds which have proved to be very useful reagents in organic synthesis. They have attracted much interest in synthetic chemistry and their synthetic applications have been widely investigated in the last two decades [6,7]. Furthermore, they are frequently used as intermediates in the synthesis of many important acyclic, carbocyclic and especially heterocyclic compounds [8–10].

In this paper, we report the results of our studies involving the reactions of zwitterions derived from trialkyl phosphites **1** and dialkyl acetylenedicarboxylates **2** in the presence of alkyl cyanoformates **3**, which constitute a synthesis of trialkyl 2-(dialkoxyphosphoryl)ethene-1,1,2-tricarboxylates **4a-4d** and 1,2-dialkyl 1-alkyl 2-(dialkoxyphosphoryl)ethene-1,1,2-tricarboxylates **4e-4h**, as a mixture of two isomers, in 70-85% yields (Scheme 1).



1	R
a	Me
b	Et

2	R'
a	Me
b	Et

3	R''
a	Me
b	Et

4	R	R'	R''	Yield%
a	Me	Me	Me	70
b	Et	Me	Me	80
c	Me	Et	Et	80
d	Et	Et	Et	80
e	Me	Et	Me	73
f	Et	Et	Me	82
g	Me	Me	Et	75
h	Et	Me	Et	85

Scheme 1

Experimental

Elemental analyses for the C and H were performed using a Heraeus CHN-O-Rapid analyzer. The results agreed favorably with the calculated values. Mass spectra were recorded on a Finnigan-Mat 8430 spectrometer operating at an ionization potential of 70 eV. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured with a Bruker DRX-300 Avance spectrometer at 300.1, 75.5, and 121.5 MHz. Alkyl cyanoformates and alkyl isocyanides and acetylenic compounds were obtained From Fluka and were used without further purification.

General procedure for the preparation of compounds 4:

To a stirred solution of alkyl cyanoformate **3** (1 mmol) and acetylenic ester **2** (1 mmol) in CH_2Cl_2 (5 mL) was added $P(OR)_3$ **1** (1 mmol) at room temperature. The reaction mixture was then stirred for 12 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO_2; hexane/EtOAc 3:1) to afford the pure compounds.

Trimethyl 2-(dimethoxyphosphoryl)ethene-1,1,2-tricarboxylate (**4a**)

Pale yellow oil, yield: 0.21 g (70%). IR (KBr) (ν_{max} /cm^{-1}): 1732 (C=O), 1257 (P=O), 1022 (PO–Me). ^{1}H NMR: δ = 3.85 (6 H, d, $^{3}J_{HP}$ = 11.7 Hz, 2 MeO), 3.84 (3 H, s, MeO), 3.90 (3 H, s, MeO), 3.92 (3 H, s, MeO) ppm; ^{13}C NMR: δ_C = 53.8 (MeO), 53.9 (MeO), 54.0 (MeO), 54.3 (d, $^{2}J_{PC}$ = 5.0 Hz, 2 MeO), 136.2 (d, $^{2}J_{CP}$ = 166.6 Hz, CH), 139.8 (d, $^{2}J_{CP}$ = 6.6 Hz, CH), 161.7 (d, $^{3}J_{CP}$ = 23.7 Hz, C=O), 164.1 (d, $^{3}J_{CP}$ = 9.1 Hz, C=O), 165.0 (d, $^{2}J_{CP}$ = 9.7 Hz, C=O) ppm; ^{31}P NMR: δ = 10.12 ppm; MS: m/z (%) = 310 (M^{+}, 86), 279 (100), 250 (55), 219 (24), 193 (12), 109 (15), 93 (28), 59 (14). Anal Calcd for $C_{10}H_{15}O_9P$ (310.2): C, 38.72; H, 4.87%. Found: C, 38.66; H, 4.80%.

Trimethyl 2-(diethoxyphosphoryl)ethene-1,1,2-tricarboxylate (**4b**)

Pale yellow oil, yield: 0.27 g (80%). IR (KBr) (ν_{max} /cm^{-1}): 1741 (C=O), 1268 (P=O), 1020 (PO–Et). ^{1}H NMR: δ = 1.37 (6 H, t, $^3J_{HH}$ = 7.0 Hz, 2 Me), 3.82 (3 H, s, MeO), 3.86 (3 H, s, MeO), 3.89 (3 H, s, MeO), 4.18-4.27 (4 H, m, 2 CH_2O); ^{13}C NMR: δ_C = 16.5 (d, $^3J_{PC}$ = 6.5 Hz, 2 Me), 53.1 (MeO), 53.4 (MeO), 54.8 (MeO), 64.2 (d, $^2J_{PC}$ = 5.1 Hz, 2 CH_2O), 136.5 (d, $^1J_{CP}$ =165.0 Hz, CH), 139.9 (d, $^2J_{CP}$ = 6.9 Hz, CH), 161.5 (d, $^3J_{CP}$ = 23.5 Hz, C=O), 164.2 (d, $^2J_{CP}$ = 9.4 Hz, C=O), 165.1 (d, $^3J_{CP}$ = 8.2 Hz, C=O) ppm; ^{31}P NMR: δ = 10.56 ppm; MS: m/z (%) = 338 (M$^+$, 90), 307 (40), 293 (100), 279 (45), 263 (24), 233 (31), 221 (20), 137 (25), 93 (20), 59 (10). Anal Calcd for $C_{12}H_{19}O_9P$ (338.2): C, 42.61; H, 5.66%. Found: C, 42.51; H, 5.58%.

Triethyl 2-(dimethoxyphosphoryl)ethene-1,1,2-tricarboxylate (**4c**)

Pale yellow oil, yield: 0.28 g (80%); IR (KBr) (ν_{max} /cm^{-1}): 1745 (C=O), 1266 (P=O), 1036 (POMe); ^{1}H NMR: δ = 1.30 (3 H, t, $^3J_{HH}$ = 6.9 Hz, Me), 1.34 (3 H, t, $^3J_{HH}$ = 6.9 Hz, Me), 1.37 (3 H, t, $^3J_{HH}$ = 6.9 Hz, Me), 3.83 (6 H, d, $^3J_{HP}$ = 12.0 Hz, 2 MeO), 4.28 (2 H, q, $^3J_{HH}$ = 6.9 Hz, CH_2O), 4.34 (2 H, q, $^3J_{HH}$ = 6.9 Hz, CH_2O), 4.38 (2 H, q, $^3J_{HH}$ = 6.9 Hz, CH_2O) ppm; ^{13}C NMR: δ_C = 14.1(Me), 14.2 (Me), 14.3 (Me), 54.2 (d, $^2J_{PC}$ = 5.1 Hz, 2 MeO), 62.9 (CH_2O), 63.0 (CH_2O), 63.2 (CH_2O), 135.6 (d, $^1J_{CP}$ = 162.5 Hz, CH), 140.2 (d, $^2J_{CP}$ = 7.2 Hz, CH), 161.4 (d, $^3J_{CP}$ = 24.6 Hz, C=O), 163.8 (d, $^3J_{CP}$ = 9.4 Hz, C=O), 164.5 (d, $^2J_{CP}$ = 10.1 Hz, C=O) ppm; ^{31}P NMR: δ = 10.78 ppm; MS: m/z (%) = 352 (M$^+$, 85), 307 (45), 293 (100), 265 (19), 219 (22), 207 (13), 191 (20), 109 (35), 73 (15); Anal Calcd for $C_{13}H_{21}O_9P$ (352.2): C, 44.32; H, 6.01%. Found: C, 44.25; H, 5.95%.

Triethyl 2-(diethoxyphosphoryl)ethene-1,1,2-tricarboxylate (**4d**)

Pale yellow oil, yield: 0.30 g (80%); IR (KBr) (ν_{max} /cm^{-1}): 1730 (C=O), 1271 (P=O), 1034 (POEt); ^{1}H NMR: δ = 1.15-1.45 (15 H, m, 5 Me), 3.97-4.36 (10 H, m, 5 CH_2O); ^{13}C NMR: δ_C = 14.1 (Me), 14.2 (Me), 15.2 (Me), 16.4 (d, $^3J_{PC}$ = 6.1 Hz, 2 Me), 62.6 (CH_2O), 62.8 (CH_2O), 63.1 (CH_2O), 64.0 (d, $^2J_{PC}$ = 5.0 Hz, 2 CH_2O), 136.6 (d, $^1J_{CP}$ =164.6 Hz, CH), 139.5 (d, $^2J_{CP}$ = 6.5 Hz, CH), 161.4 (d, $^3J_{CP}$ = 24.5 Hz, C=O), 163.7 (d, $^2J_{CP}$ = 10.1 Hz, C=O), 166.1 (d, $^3J_{CP}$ = 7.9 Hz, C=O) ppm; ^{31}P NMR: δ = 10.56 ppm; MS: m/z (%) = 380 (M$^+$, 74), 335 (100), 307 (36), 291 (33), 235 (14), 137 (21), 90 (24), 73 (21); Anal Calcd for $C_{15}H_{25}O_9P$ (380.3): C, 47.37; H, 6.63%. Found: C, 47.30; H, 6.55%.

1,2-Diethyl 1-methyl 2-(dimethoxyphosphoryl)ethene-1,1,2-tricarboxylate (**4e**)

Pale yellow oil, yield: 0.24 g (73%); IR (KBr) (ν_{max} /cm^{-1}): 1748 (C=O), 1261 (P=O), 1028 (POMe); NMR data for the major isomer (64%); ^{1}H NMR: δ = 1.35 (3 H, t, $^3J_{HH}$ = 6.9 Hz, Me), 1.37 (3 H, t, $^3J_{HH}$ = 6.9 Hz, Me), 3.84 (6 H, d, $^3J_{HP}$ = 11.7 Hz, 2 MeO), 3.92 (3 H, s, MeO), 4.34 (2 H, q, $^3J_{HH}$ = 6.9 Hz, CH$_2$O), 4.37 (2 H, q, $^3J_{HH}$ = 6.9 Hz, CH$_2$O) ppm; ^{13}C NMR: δ_C = 14.1 (Me), 14.2 (Me), 53.8 (MeO), 54.3 (d, $^2J_{PC}$ = 5.0 Hz, 2 MeO), 62.9 (CH$_2$O), 63.4 (CH$_2$O), 135.9 (d, $^1J_{CP}$ = 165.5 Hz, CH), 140.0 (d, $^2J_{CP}$ = 6.9 Hz, CH), 161.2 (d, $^3J_{CP}$ = 23.8 Hz, C=O), 164.3 (d, $^2J_{CP}$ = 9.5 Hz, C=O), 164.5 (d, $^3J_{CP}$ = 8.7 Hz, C=O) ppm; ^{31}P NMR: δ = 10.41 ppm; NMR data for the minor isomer (36%); 1.30 (3 H, t, $^3J_{HH}$ = 6.9 Hz, Me), 1.32 (3 H, t, $^3J_{HH}$ = 6.9 Hz, Me), 3.85 (6 H, d, $^3J_{HP}$ = 11.7 Hz, 2 MeO), 3.94 (3 H, s, MeO), 4.27 (2 H, q, $^3J_{HH}$ = 6.9 Hz, CH$_2$O), 4.29 (2 H, q, $^3J_{HH}$ = 6.9 Hz, CH$_2$O); ^{13}C NMR: δ_C = 14.3 (Me), 14.5 (Me), 53.9 (MeO), 54.2 (d, $^2J_{PC}$ = 4.5 Hz, 2 MeO), 63.0 (CH$_2$O), 63.2 (CH$_2$O), 136.0 (d, $^1J_{CP}$ = 165.7 Hz, CH), 139.7 (d, $^2J_{CP}$ = 7.3 Hz, CH), 161.8 (d, $^3J_{CP}$ = 23.5 Hz, C=O), 163.7 (d, $^2J_{CP}$ = 9.4 Hz, C=O), 164.6 (d, $^3J_{CP}$ = 8.7 Hz, C=O); ^{31}P NMR: δ = 11.02 ppm; MS: m/z (%) = 338 (M$^+$, 80), 307 (44), 293 (100), 264 (37), 219 (28), 193 (16), 109 (24), 93 (18), 73 (18); Anal Calcd for $C_{12}H_{19}O_9P$ (338.2): C, 42.61; H, 5.66%. Found: C, 42.55; H, 5.60%.

1,2-Diethyl 1-methyl 2-(diethoxyphosphoryl)ethene-1,1,2-tricarboxylate (**4f**)

Pale yellow oil, yield: 0.27 g (82%); IR (KBr) (ν_{max} /cm^{-1}): 1739 (C=O), 1271 (P=O), 1023 (POEt); NMR data for the major isomer (64%); ^{1}H NMR: δ = 1.28-1.36 (12 H, m, 4 Me), 3.95 (3 H, s, MeO), 4.07- 4.25 (8 H, m, 4 CH$_2$O) ppm; ^{13}C NMR: δ_C = 14.1 (Me), 14.3 (Me), 16.5 (d, $^3J_{PC}$ = 6.7 Hz, 2 Me), 53.6 (MeO), 62.3 (CH$_2$O), 62.4 (CH$_2$O), 64.0 (d, $^2J_{PC}$ = 5.8 Hz, 2 CH$_2$O), 135.8 (d, $^1J_{CP}$ = 166.0 Hz, CH), 139.5 (d, $^2J_{CP}$ = 6.5 Hz, CH), 161.4 (d, $^3J_{CP}$ = 24.5 Hz, C=O), 163.5 (d, $^2J_{CP}$ = 9.4 Hz, C=O), 165.3 (d, $^3J_{CP}$ = 7.9 Hz, C=O) ppm; ^{31}P NMR: δ = 10.41 ppm; NMR data for the minor isomer (36%); 1.19-1.24 (12 H, m, 4 Me), 3.91 (3 H, s, MeO), 4.29- 4.42 (8 H, m, 4 CH$_2$O) ppm; ^{13}CNMR: δ_C = 14.2 (Me), 14.4 (Me), 16.4 (d, $^3J_{PC}$ = 6.6 Hz, 2 Me), 53.8 (MeO), 62.7 (CH$_2$O), 62.8 (CH$_2$O), 63.6 (d, $^2J_{PC}$ = 5.8 Hz, 2 CH$_2$O), 136.0 (d, $^1J_{CP}$ = 164.4 Hz, CH), 139.9 (d, $^2J_{CP}$ = 6.9 Hz, CH), 161.9 (d, $^3J_{CP}$ = 23.5 Hz, C=O), 164.2 (d, $^2J_{CP}$ = 9.4 Hz, C=O), 165.7 (d, $^3J_{CP}$ = 7.9 Hz, C=O) ppm; ^{31}P NMR: δ = 10.72 ppm; MS: m/z (%) = 366 (M$^+$, 78), 335 (37), 321 (100), 307 (43), 291 (30), 219 (25), 137 (15), 90 (34), 73 (22); Anal Calcd for $C_{14}H_{23}O_9P$ (366.3): C, 45.90; H, 6.33%. Found: C, 45.84; H, 6.25%.

1-Ethyl 1,2-dimethyl 2-(dimethoxyphosphoryl)ethene-1,1,2-tricarboxylate (**4g**)

Pale yellow oil, yield: 0.24 g (75%); IR (KBr) (ν_{max} /cm^{-1}): 1738 (C=O), 1244 (P=O), 1030 (POMe); NMR data for the major isomer (64%); ^{1}H NMR: δ = 1.34 (3 H, t, $^3J_{HH}$ = 7.1 Hz, Me), 3.80 (3 H, s, MeO), 3.81 (3 H, s, MeO), 3.85 (6 H, d, $^3J_{HP}$ = 11.7 Hz, 2 MeO), 4.35 (2 H, q, $^3J_{HH}$ = 7.1 Hz, CH_2O) ppm; ^{13}C NMR: δ_C = 14.1 (Me), 53.7 (MeO), 53.9 (MeO), 54.2 (d, $^2J_{PC}$ = 5.1 Hz, 2 MeO), 63.1 (CH_2O), 135.8 (d, $^1J_{CP}$ = 166.8 Hz, CH), 139.9 (d, $^2J_{CP}$ = 7.9 Hz, CH), 161.9 (d, $^3J_{CP}$ = 24.6 Hz, C=O), 163.5 (d, $^2J_{CP}$ = 9.5 Hz, C=O), 165.1 (d, $^3J_{CP}$ = 9.4 Hz, C=O), ppm; ^{31}P NMR: δ = 10.41 ppm; NMR data for the minor isomer (36%); 1.28 (3 H, t, $^3J_{HH}$ = 6.9 Hz, Me), 3.83 (3 H, s, MeO), 3.87 (3 H, s, MeO), 3.88 (6 H, d, $^3J_{HP}$ = 11.7 Hz, 2 MeO), 4.26 (2 H, q, $^3J_{HH}$ = 6.9 Hz, CH_2O); ^{13}C NMR: δ_C = 14.2 (Me), 53.7 (MeO), 53.9 (MeO), 54.3 (d, $^2J_{PC}$ = 4.4 Hz, 2 MeO), 63.4 (CH_2O), 135.6 (d, $^1J_{CP}$ = 164.6 Hz, CH), 140.2 (d, $^2J_{CP}$ = 7.9 Hz, CH), 161.2 (d, $^3J_{CP}$ = 20.2 Hz, C=O), 164.1 (d, $^3J_{CP}$ = 13.7 Hz, C=O), 165.0 (d, $^2J_{CP}$ = 13.9 Hz, C=O); ^{31}P NMR: δ = 10.50 ppm; MS: m/z (%) = 324 (M$^+$, 92), 293 (56), 279 (100), 265 (62), 248 (31), 221 (15), 207 (20), 109 (16), 93 (31), 59 (16); Anal Calcd for $C_{11}H_{17}O_9P$ (324.2): C, 40.75; H, 5.28%. Found: C, 40.65; H, 5.32%.

1-Ethyl 1,2-dimethyl 2-(diethoxyphosphoryl)ethene-1,1,2-tricarboxylate (**4h**)

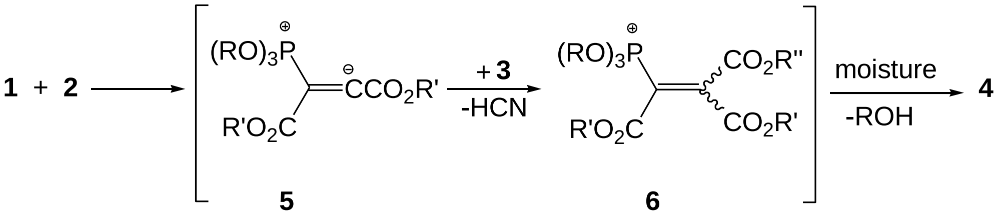
Pale yellow oil, yield: 0.30 g (85%); IR (KBr) (ν_{max} /cm^{-1}): 1725 (C=O), 1275 (P=O), 1051 (POEt); NMR data for the major isomer (64%); ^{1}H NMR: δ =1.26-1.41 (9 H, m, 3 Me), 3.84 (3 H, s, MeO), 3.90 (3 H, s, MeO), 4.15- 4.25 (6 H, m, 3 CH_2O); ^{13}C NMR: δ_C = 14.1 (Me), 16.4 (d, $^3J_{PC}$ = 6.5 Hz, 2 Me), 53.5 (MeO), 53.8 (MeO), 63.1 (CH_2O), 64.2 (d, $^2J_{PC}$ = 5.0 Hz, 2 CH_2O), 137.0 (d, $^1J_{CP}$ = 163.2 Hz, CH), 139.2 (d, $^2J_{CP}$ = 6.5 Hz, CH), 162.0 (d, $^3J_{CP}$ = 25.9 Hz, C=O), 163.6 (d, $^2J_{CP}$ = 10.8 Hz, C=O), 165.1 (d, $^3J_{CP}$ = 7.9 Hz, C=O) ppm; ^{31}P NMR: δ = 10.41 ppm; NMR data for the minor isomer (36%); 1.11-1.24 (9 H, m, 3 Me), 3.89 (3 H, s, MeO), 3.91 (3 H, s, MeO), 4.15- 4.25 (6 H, m, 3 CH_2O); ^{13}CNMR: δ_C = 14.2 (Me), 16.5 (d, $^3J_{PC}$ = 6.4 Hz, 2 Me), 53.4 (MeO), 53.6 (MeO), 63.3 (CH_2O), 64.0 (d, $^2J_{PC}$ = 5.8 Hz, 2 CH_2O), 136.8 (d, $^1J_{CP}$ = 162.4 Hz, CH), 139.5 (d, $^2J_{CP}$ = 5.8 Hz, CH), 161.4 (d, $^3J_{CP}$ = 23.1 Hz, C=O), 164.2 (d, $^2J_{CP}$ =10.8 Hz, C=O), 165.2 (d, $^3J_{CP}$ = 8.1 Hz, C=O) ppm; ^{31}P NMR: δ = 10.20 ppm; MS: m/z (%) = 352 (M$^+$, 95), 321 (43), 307 (100), 293 (36), 277 (35), 247(11), 235 (13), 137 (20), 90(16), 59(14); Anal Calcd for $C_{13}H_{21}O_9P$ (352.2): C, 44.32; H, 6.01%. Found: C, 44.22; H, 6.09%.

Result

The reaction of trialkyl phosphites **1** with dialkyl acetylenedicarboxylates **2** in the presence of alkyl cyanoformate**s** **3** at room temperature in dichloromethane, produced dialkoxy phosphoryl tricarboxylate derivatives **4** in 70–85% yields after 12 hours (Scheme 1). Structures of compounds **4a–4h** were assigned by IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and mass spectral data. The mass spectra of these compounds displayed molecular ion peaks at appropriate m/z values. The ^{1}H-NMR spectrum of **4a** displayed one sharp doublet at $\delta = 3.85$ ($^3J_{PH} = 11.7$ Hz) for the P–OMe protons, and three sharp singlets arising from the methoxy groups ($\delta = 3.84$, 3.90, and 3.92 ppm). The ^{1}H and ^{13}C NMR spectra of **4e–4h** are consistent with the presence of two geometrical isomers.

Although, in general, $^3J_{C-P}$-trans coupling is much larger than $^3J_{C-P}$-cis [11], But here identifying cis and trans isomers by the value of the ^{31}P–^{13}C coupling constant is difficult because of the complexity due to the three ester groups. The ^{1}H-decoupled ^{13}C NMR spectrum of **4a** showed 10 distinct resonances in agreement with the proposed structure. The ^{1}H- and ^{13}C-decoupled ^{31}P NMR spectrum of **4a** exhibited one sharp singlet readily recognized as arising from phosphonate ($\delta = 10.12$ ppm). Partial assignment of these resonances is given in the experimental section. The ^{1}H, ^{13}C and ^{31}P NMR spectra of compounds **4b**–**h** were similar to those of **4a** except for the alkoxy group, and ester groups, which exhibited characteristic signals with appropriate chemical shifts (see Experimental section).

Although, we have not yet established the mechanism of the reaction between activated acetylenes and phosphites in the presence of the alkyl cyanoformates in an experimental manner, a possible explanation is proposed in Scheme 2. On the basis of the well-established chemistry of phosphorus nucleophiles, it is reasonable to assume that compound **4** results from initial addition of the phosphite **1** to activated acetylene **2** and subsequent attack of the resulting zwitterion **5** on the cyanoformate **3** to generate **6**,which is converted to **4** by absorption of H_2O (moisture) and elimination of ROH.



Scheme 2

In summary, the reaction of activated acetylenes, trialkyl(aryl) phosphites, and alkyl cyanoformates provides a simple one-pot synthesis of stable vinylphosphonates derivatives of potential synthetic and pharmaceutical and biological interest. The present procedure has the advantage that the reaction is performed under neutral conditions, and the starting material can be used without any activation or modification.

REFERENCES

[1] L. F. Tietze, *Chem. Rev.* 1996, **96**, 115.

[2] M. I. Antczak, J.-L. Montchamp, *Tetrahedron Lett.* 2008, **49**, 5909.

[3] H. Morales-Rojas, R. A. Moss, *Chem. Rev.* 2002, **102**, 2497.

[4] J. Wu, H. R. Hudson, *Chin. J. Chem.* 2002, **20**, 1598.

[5] C.-Y. Yuan, Chin. *J. Org. Chem.* 2001, **21**, 862.

[6] T. Minami, J. Motoyoshiya, *Synthesis* 1992, 333.

[7] M. Mikołajczyk, P. Bałczewski, *Top. Curr. Chem.* 2003, **223**, 161.

[8] T. Minami, T. Okauchi, R. Kouno, *Synthesis* 2001, 349.

[9] T. Janecki, J. Ke˛dzia, T. Wa˛sek, *Synthesis* 2009, 1227.

[10] V. M. Dembitsky, A. A. A. Quntar, A. Haj-Yehia, M. Srebnik, *Mini-Rev. Org. Chem.* 2005, **2**, 91.

[11] Macomber, R. S.; Krudy, G. A. *J. Org.Chem.* 1981, **46**, 4038.