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Research Article

A Simple synthesis of vinylphosphonates from dialkyl(aryl) phosphites and alkyl(aryl) propiolates in aqueous acetone

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ABSTRACT

In this work, simple and mild efficient synthesis of various organophosphorus compounds based on the reaction of dialkyl(aryl) phosphites with alkyl(aryl) propiolates in the presence of NaCN in aqueous acetone, is described. Organophosphorus compounds are widely used in organic synthesis, such as agricultural chemicals, flame retardants, medicinal agents and the preparation of insecticides. Using this approach, to a solution of alkyl(aryl) propiolates and dialkyl(aryl) phosphite was added sodium cyanide in acetone/H_2O at room temperature, and the solution was stirred. The solvent was removed under reduced pressure, and the residue was dissolved in EtOAc, washed with aqueous $NaHCO_3$ and brine, dried (Na_2SO_4), and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel using *n*-hexane-EtOAc as eluent. Then, All organophosphorus compounds are obtained in excellent yields. The method offers several advantages including operational simplicity, high diversity via various functional groups and fairly good yields.

Keywords: Vinylphosphonates, Dialkyl(aryl) phosphites, Alkyl(aryl) propiolates, Sodium cyanide.

1. Introduction

In recent years there has been increasing interest in the synthesis of organophosphorus compounds [1-5], that is, those bearing a carbon atom bound directly to a phosphorus atom [6-12]. Organophosphorus compounds are widely used in organic synthesis [13-19]. This is a direct result of developing applications for phosphorus compounds in numerous synthetic procedures as well as an understanding of the role of the element in biological systems. The several "classical" efforts in regard to applications of organophosphorus compounds, the preparation of insecticides, agricultural chemicals, flame retardants, medicinal agents, and reagents for olefination reactions continue to be highly active topics in organophosphorus chemistry [20-26].

In continuation, we describe an efficient one-pot method for the direct synthesis of various vinylphosphonates compounds from the reaction of dialkyl phosphites and alkyl propiolates in aqueous acetone at room temperature.

2. Experimental

Chemicals and apparatus

All the chemicals used in this study were purchased from Merck and Sigma-Aldrich and were used without further purification. IR Spectra (ν/cm^{-1}) were recorded as KBr pellets with a Shimadzu IR-460 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a Bruker DRX-500 Avance instrument using $CDCl_3$ as the deuterated solvent containing TMS as internal standard, at 500.1, 125.8, and 202.4 MHz, respectively; δ in ppm, J in Hz. Elemental analyses(C, H) were obtained with a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN Scheme MATT 8430 spectrometer operating at an ionization potential of 70 eV.

General procedure for the preparation of compounds 3a-l

To a solution of alkyl(aryl) propiolates **1** (1 mmol) and dialkyl(aryl) phosphite **2** (1 mmol) was added sodium cyanide (0.001 g, 0.2 mmol) in acetone/H_2O (2:1,10 mL) at room temperature, and the solution was stirred for 2h. The solvent was removed under reduced pressure, and the residue was dissolved in EtOAc (10 mL), washed with aqueous $NaHCO_3$ (4 mL) and brine (4 mL), dried (Na_2SO_4), and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Merck 230–400 mesh) using *n*-hexane-EtOAc as eluent.

Methyl 3-phenyl-3-(dimethoxyphosphoryl)acrylate (3a) Pale yellow oil; yield: 0.30g (96%); IR(KBr)(ν_{max}/cm^{-1}) = 1748(C=O), 1259 (P=O), 1028(POMe); NMR data for the major isomer(64%); ^{1}H NMR: δ 3.39 (6 H, d, $^3J_{HP}$ 10.2 Hz, 2 MeO), 3.76(3H, s, OMe), 6.4(1H, d, $^3J_{HP}$ 7.2 Hz), 7.14(1H), 7.21(2H), 7.30(2H); ^{13}C NMR: δ 52.1(MeO), 53.8(d, $^2J_{CP}$ 3.8 Hz, 2 MeOP), 126.4(CH), 126.6(CH), 128(CH), 128.5(CH), 128.7(CH), 131.2(CH), 134.9(C), 140.2(C), 166.5(C=O); ^{31}P-NMR: δ 19.86 (P=O); NMR data for the minor isomer(36%): ^{1}H NMR: δ 3.41 (6 H, d, $^3J_{HP}$ 10.2 Hz, 2 MeO), 3.78(3H, s, OMe), 6.7(1H, d, $^3J_{HP}$ 7.2 Hz), 7.13(1H), 7.22(2H), 7.32(2H); ^{13}C NMR: δ 53.1 (MeO), 53.9 (d, $^2J_{CP}$ 3.8 Hz, 2 MeOP), 126.5(CH), 126.7(CH), 128.1(CH), 128.3(CH), 128.7(CH), 132.2(CH), 134.8(C), 140.4(C), 166.6(C=O); ^{31}P-NMR: δ 19.90 (P=O); Anal. Calcd.for $C_{12}H_{15}O_5P$ (270.22): C, 53.34; H, 5.60%; Found: C, 53.30; H, 5.62%.

Ethyl 3-phenyl-3-(dimethoxyphosphoryl)acrylate (3b) Pale yellow oil; yield: 0.27g (94%); IR(KBr)(ν_{max}/cm^{-1}) = 1746(C=O), 1260 (P=O), 1027(POMe); NMR data for the major isomer(62%); ^{1}H NMR: δ 1.30(3H, t, Me), 3.38 (6 H, d, $^3J_{HP}$ 10.2 Hz, 2 MeO), 4.19(2H, q, OCH_2), 6.5(1H, d, $^3J_{HP}$ 7.2 Hz), 7.14(1H), 7.21(2H), 7.30(2H); ^{13}C NMR: δ 14.2(Me), 53.9(d, $^2J_{CP}$ 3.8 Hz, 2 MeOP), 61.4(OCH_2), 126.5(CH), 126.7(CH), 128(CH), 128.4(CH), 128.8(CH),

129.4(CH), 134.9(C), 141.7(C), 166.7(C=O); ^{31}P-NMR: δ 19.85 (P=O); NMR data for the minor isomer(38%): ^{1}H NMR: δ 1.32(3H, t, Me), 3.37 (6 H, d, $^{3}J_{HP}$ 10.2 Hz, 2 MeO), 4.18(2H, q, OCH_2), 6.7(1H, d, $^{3}J_{HP}$ 7.2 Hz), 7.12(1H), 7.22(2H), 7.32(2H); ^{13}C NMR: δ 14.4(Me), 54.0(d, $^{2}J_{CP}$ 3.8 Hz, 2 MeOP), 61.7(OCH_2), 126.4(CH), 126.9(CH), 128.1(CH), 128.5(CH), 128.7(CH), 130.1 (CH), 134.4(C), 141.5(C), 166.6(C=O); ^{31}P-NMR: δ 19.90 (P=O); Anal. Calcd.for $C_{13}H_{17}O_5P$ (284.24): C, 54.93; H, 6.03%; Found: C, 54.90; H, 6.05%.

Methyl 3-phenyl-3-(diethoxyphosphoryl)acrylate (3c) Pale yellow oil; yield: 0.22g (90%); IR(KBr)(ν_{max}/cm^{-1}) = 1750(C=O), 1260 (P=O), 1030 ($POCH_2$); NMR data for the major isomer(63%); ^{1}H NMR: δ 1.11(6 H, dt, $^{3}J_{HH}$ 7.2 Hz, $^{4}J_{HP}$ 0.6 Hz, 2 Me), 3.76(3H, s, OMe), 4.07 (4H, dq, $^{3}J_{HP}$ 8.1 Hz, $^{3}J_{HH}$ 7.1 Hz 2 CH_2O), 7.06(1H, d, $^{3}J_{HP}$ 7.2 Hz), 7.14(1H), 7.21(2H), 7.30 (2H); ^{13}C NMR: δ 14.9 (2Me), 52.1 (MeO), 62.7(d, $^{2}J_{CP}$ 4.6 Hz, 2CH_2O), 126.5(CH), 126.7(CH), 128(CH), 128.4(CH), 128.8(CH), 131.2(CH), 134.9(C), 140.2 (C), 166.7 (C=O); ^{31}P-NMR: δ 19.85 (P=O); NMR data for the minor isomer (37%): ^{1}H NMR: δ 1.09 (6 H, dt, $^{3}J_{HH}$ 7.2 Hz, $^{4}J_{HP}$ 0.6 Hz, 2 Me), 3.73(3H, s, OMe), 4.10 (4H, dq, $^{3}J_{HP}$ 8.1 Hz, $^{3}J_{HH}$ 7.1 Hz 2 CH_2O), 7.08(1H, d, $^{3}J_{HP}$ 7.2 Hz), 7.15(1H), 7.20(2H), 7.32(2H); ^{13}C NMR: δ 15.0(2Me), 52.4 (OMe), 62.9(d, $^{2}J_{CP}$ 4.6 Hz, 2CH_2O), 126.3(CH), 126.6(CH), 128(CH), 128.2(CH), 128.5(CH), 131.5(CH), 135(C), 140.3(C), 166.8(C=O); ^{31}P-NMR: δ 19.83 (P=O); Anal. Calcd.for $C_{13}H_{17}O_5P$ (284.24): C, 54.93; H, 6.03%; Found: C, 54.90; H, 6.05%.

Ethyl-3-phenyl-3-(diethoxyphosphoryl)acrylate (3d) Pale yellow oil; yield: 0.28g (95%); IR(KBr)(ν_{max}/cm^{-1}) = 1726 (C=O), 1251 (P=O), 1027 ($POCH_2$); NMR data for the major isomer (65%); ^{1}H NMR: δ 1.11(6 H, dt, $^{3}J_{HH}$ 7.2 Hz, $^{4}J_{HP}$ 0.6 Hz, 2 Me), 1.30(3H, t, Me), 4.07 (4H, dq, $^{3}J_{HP}$ 8.1 Hz, $^{3}J_{HH}$ 7.1 Hz 2 CH_2O), 4.31 (2H, q, CH_2O), 6.6(1H, d, $^{3}J_{HP}$ 7.2 Hz), 7.26 (1H), 7.35 (2H), 7.45 (2H); ^{13}C NMR: δ 13.9(Me), 16.1(2Me), 61.4(CH_2O), 62.7(d, $^{2}J_{CP}$ 4.6 Hz, 2CH_2O), 127.6(CH), 127.8(CH), 128(CH), 128.4(CH), 128.8(CH), 131.2(CH), 134.9(C), 143.2(C), 166.0(C=O); ^{31}P-NMR: δ 19.85 (P=O); NMR data for the minor

isomer(35%): ^{1}H NMR: δ 1.13(6 H, dt, $^{3}J_{HH}$ 7.2 Hz, $^{4}J_{HP}$ 0.6 Hz, 2 Me), 1.32(3H, t, Me), 4.05 (4H, dq, $^{3}J_{HP}$ 8.1 Hz, $^{3}J_{HH}$ 7.1 Hz 2 CH_2O), 4.33(2H, q, CH_2O), 6.87(1H, d, $^{3}J_{HP}$ 7.2 Hz), 7.26(1H), 7.36(2H), 7.46(2H); ^{13}C NMR: δ 13.93(Me), 16.0(2Me), 62.4(CH_2O), 62.7(d, $^{2}J_{CP}$ 4.6 Hz, 2CH_2O), 127.7(CH), 127.9(CH), 128.1(CH), 128.6(CH), 130.7(CH), 132.4(CH), 135.0(C), 145.1(C), 165.0(C=O); ^{31}P-NMR: δ 19.85 (P=O); Anal. Calcd.for $C_{15}H_{21}O_5P$ (312.3): C, 57.69; H, 6.78%; Found: C, 57.60; H, 6.75%.

Methyl 3-phenyl-3-(diphenoxyphosphoryl)acrylate (3e) Pale yellow oil; yield: 0.22g (91%); IR(KBr)(ν_{max}/cm^{-1}) = 1739(C=O), 1277(P=O), 1180; NMR data for the major isomer(65%); ^{1}H NMR: δ 3.76(3H, s, OMe), 6.50 (1H, d, $^{3}J_{HP}$ 6.1 Hz, CH), 7.18 (2 H, t, $^{3}J_{HH}$ 8.1 Hz, 2 CH_{para} of 2 C_6H_5), 7.26(1H, t, CH), 7.28 (4 H, d, $^{3}J_{HH}$ 8.0 Hz, 4 CH_{ortho} of 2 C_6H_5), 7.34 (4 H, dd, $^{3}J_{HH}$ 8.1 Hz, $^{3}J_{HH}$ 7.8 Hz, 4 CH_{meta} of 2 C_6H_5), 7.35(2H, d, CH), 7.45(2H, dd, CH) ; ^{13}C NMR: δ 52.2 (OMe), 119.5 [d, $^{3}J_{CP}$ 8.1 Hz, 4 $CH_{ortho}$of $(C_6H_5O)_2PO$], 125.6 [d, $^{4}J_{PC}$ 2.3 Hz, 4 $CH_{meta}$of $(C_6H_5O)_2PO$], 127.6(CH), 127.8(CH), 128(CH), 128.4(CH), 128.7(CH), 129.8 [s, 2 CH_{para} of $(C_6H_5O)_2PO$], 131.2(CH), 134.9(C_{ipso}), 146.2(C), 150.0 [d, $^{2}J_{PC}$ 9.3 Hz, 2 $C_{ipso}$of $(C_6H_5O)_2PO$], 166.4 (C=O).; ^{31}P-NMR: δ 11.85 (P=O); NMR data for the minor isomer(35%): ^{1}H NMR: δ 3.77(3H, s, OMe), 6.53 (1H, d, $^{3}J_{HP}$ 6.1 Hz, CH), 7.2 (2 H, t, $^{3}J_{HH}$ 8.1 Hz, 2 CH_{para} of 2 C_6H_5), 7.25(1H, t, CH), 7.29 (4 H, d, $^{3}J_{HH}$ 8.0 Hz, 4 CH_{ortho} of 2 C_6H_5), 7.32 (4 H, dd, $^{3}J_{HH}$ 8.1 Hz, $^{3}J_{HH}$ 7.8 Hz, 4 CH_{meta} of 2 C_6H_5), 7.36(2H, d, CH), 7.44(2H, dd, CH); ^{13}C NMR: δ 52.3 (OMe), 119.7 [d, $^{3}J_{CP}$ 8.1 Hz, 4 $CH_{ortho}$of $(C_6H_5O)_2PO$], 125.8 [d, $^{4}J_{PC}$ 2.3 Hz, 4 $CH_{meta}$of $(C_6H_5O)_2PO$], 127.3(CH), 127.5(CH), 128.2(CH), 128.5(CH), 128.8(CH), 129.5[s, 2 CH_{para} of $(C_6H_5O)_2PO$], 131.0(CH), 134.7(C_{ipso}), 146.1(C), 150.2 [d, $^{2}J_{PC}$ 9.3 Hz, 2 $C_{ipso}$of $(C_6H_5O)_2PO$], 166.7 (C=O); ^{31}P-NMR: δ 11.87 (P=O); Anal. Calcd.for $C_{22}H_{19}O_5P$ (394.36): C, 67.00; H, 4.86%; Found: C, 67.03; H, 4.85%.

Ethyl 3-phenyl-3-(diphenoxyphosphoryl)acrylate (3f) Pale yellow oil; yield: 0.19g (88%); IR(KBr)(ν_{max}/cm^{-1}) = 1739(C=O), 1277(P=O), 1182; NMR data for the major

isomer(65%); ^{1}H NMR: δ 1.31(3H, t, CH_3), 4.21(2H, q, CH_2O), 6.50 (1H, d, $^{3}J_{HP}$ 6.1 Hz, CH), 7.18 (2 H, t, $^{3}J_{HH}$ 8.1 Hz, 2 CH_{para} of 2 C_6H_5), 7.26(1H, t, CH), 7.28 (4 H, d, $^{3}J_{HH}$ 8.0 Hz, 4 CH_{ortho} of 2 C_6H_5), 7.34 (4 H, dd, $^{3}J_{HH}$ 8.1 Hz, $^{3}J_{HH}$ 7.8 Hz, 4 CH_{meta} of 2 C_6H_5), 7.35(2H, d, CH), 7.45(2H, dd, CH) ; ^{13}C NMR: δ 14.3(Me), 61.52(CH_2O), 119.5 [d, $^{3}J_{CP}$ 8.1 Hz, 4 $CH_{ortho}$of $(C_6H_5O)_2PO$], 125.6 [d, $^{4}J_{PC}$ 2.3 Hz, 4 $CH_{meta}$of $(C_6H_5O)_2PO$], 127.6(CH), 127.8(CH), 128(CH), 128.4(CH), 128.7(CH), 129.8 [s, 2 CH_{para} of $(C_6H_5O)_2PO$], 131.2(CH), 134.9(C_{ipso}), 147.2(C), 150.0 [d, $^{2}J_{PC}$ 9.3 Hz, 2 $C_{ipso}$of $(C_6H_5O)_2PO$], 166.4 (C=O).; ^{31}P-NMR: δ 11.85 (P=O); NMR data for the minor isomer(35%): ^{1}H NMR: δ 1.29(3H, t, CH_3), 4.22(2H, q, CH_2O), 6.53 (1H, d, $^{3}J_{HP}$ 6.1 Hz, CH), 7.2 (2 H, t, $^{3}J_{HH}$ 8.1 Hz, 2 CH_{para} of 2 C_6H_5), 7.25(1H, t, CH), 7.29 (4 H, d, $^{3}J_{HH}$ 8.0 Hz, 4 CH_{ortho} of 2 C_6H_5), 7.32 (4 H, dd, $^{3}J_{HH}$ 8.1 Hz, $^{3}J_{HH}$ 7.8 Hz, 4 CH_{meta} of 2 C_6H_5), 7.36(2H, d, CH), 7.44(2H, dd, CH); ^{13}C NMR: δ 14.5(Me), 61.50(CH_2O), 119.7 [d, $^{3}J_{CP}$ 8.1 Hz, 4 $CH_{ortho}$of $(C_6H_5O)_2PO$], 125.8 [d, $^{4}J_{PC}$ 2.3 Hz, 4 $CH_{meta}$of $(C_6H_5O)_2PO$], 127.3(CH), 127.5(CH), 128.2(CH), 128.5(CH), 128.8(CH), 129.5 [s, 2 CH_{para} of $(C_6H_5O)_2PO$], 131.0(CH), 134.7(C_{ipso}), 146.1(C), 150.2 [d, $^{2}J_{PC}$ 9.3 Hz, 2 $C_{ipso}$of $(C_6H_5O)_2PO$], 166.7 (C=O).; ^{31}P-NMR: δ 11.87 (P=O); Anal. Calcd.for $C_{23}H_{21}O_5P$ (408.38): C, 67.64; H, 5.18%; Found: C, 67.63; H, 5.15%.

Methyl 3-(dimethoxyphosphoryl)acrylate (3g) Pale yellow oil; yield: 0.25g (95%); IR(KBr)(ν_{max}/cm^{-1}) = 1720(C=O), 1259 (P=O), 1028(POMe); NMR data for the major isomer(64%); ^{1}H NMR: δ 3.76(3H, s, OMe), 3.39(6 H, d, $^{3}J_{HP}$10.6Hz, 2 MeOP), 5.7(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{2}J_{HP}$ 10.8 Hz, CH), 6.0(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{3}J_{HP}$ 7.0 Hz, CH); ^{13}C NMR: δ 52.1(MeO), 53.8(d, $^{2}J_{CP}$ 3.8 Hz, 2 MeOP), 130.4(CH), 136.1(CH), 166.5(C=O); ^{31}P-NMR: δ 19.85 (P=O); NMR data for the minor isomer(36%); ^{1}H NMR: δ 3.73(3H, s, OMe), 3.40(6 H, d, $^{3}J_{HP}$10.6Hz, 2 MeOP), 5.8(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{2}J_{HP}$ 10.8 Hz, CH), 6.2(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{3}J_{HP}$ 7.0 Hz, CH); ^{13}C NMR: δ 52.3(MeO), 54.0(d, $^{2}J_{CP}$ 3.8 Hz, 2 MeOP), 130.5(CH), 136.3(CH), 166.6(C=O); ^{31}P-NMR: δ 19.87(P=O); Anal. Calcd.for $C_6H_{11}O_5P$ (194.12): C,

37.12; H, 5.71%; Found: C, 53.30; H, 5.62%.

Ethyl 3-(dimethoxyphosphoryl)acrylate (3h) Pale yellow oil; yield: 0.23g (94%); IR(KBr)(ν_{max}/cm^{-1}) = 1720(C=O), 1259 (P=O), 1028(POMe); NMR data for the major isomer(64%); ^{1}H NMR: δ 1.30(3H, t, Me), 3.39(6 H, d, $^{3}J_{HP}$10.6Hz, 2 MeOP), 4.19(2H, q, CH_2O), 5.8(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{2}J_{HP}$ 10.8 Hz, CH), 6.1(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{3}J_{HP}$ 7.0 Hz, CH); ^{13}C NMR: δ 14.2(Me), 53.8(d, $^{2}J_{CP}$ 3.8 Hz, 2 MeOP), 61.4(CH_2O), 132.4(CH), 134.3(CH), 166.5(C=O); ^{31}P-NMR: δ 19.85 (P=O); NMR data for the minor isomer(36%); ^{1}H NMR: δ 1.28(3H, t, Me), 3.40(6 H, d, $^{3}J_{HP}$10.6Hz, 2 MeOP), 4.20(2H, q, CH_2O), 5.6(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{2}J_{HP}$ 10.8 Hz, CH), 6.0(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{3}J_{HP}$ 7.0 Hz, CH); ^{13}C NMR: δ 14.4(Me), 54.0(d, $^{2}J_{CP}$ 3.8 Hz, 2 MeOP), 61.2(CH_2O), 132.3(CH), 134.5(CH), 166.7(C=O); ^{31}P-NMR: δ 19.87(P=O); Anal. Calcd.for $C_6H_{11}O_5P$ (208.15): C, 40.39; H, 6.50%; Found: C, 40.25; H, 6.48%.

Methyl 3-(diethoxyphosphoryl)acrylate (3i) Pale yellow oil; yield: 0.20g (89%); IR(KBr)(ν_{max}/cm^{-1}) = 1723(C=O), 1258 (P=O), 1025; NMR data for the major isomer(60%); ^{1}H NMR: δ 1.13(6 H, dt, $^{3}J_{HH}$ 7.2 Hz, $^{4}J_{HP}$ 0.6 Hz, 2 Me), 3.76(3H, s, OMe), 4.07 (4H, dq, $^{3}J_{HP}$ 8.1 Hz, $^{3}J_{HH}$ 7.1 Hz 2 CH_2O), 6.38(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{2}J_{HP}$ 10.8 Hz, CH), 6.70(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{3}J_{HP}$ 7.0 Hz, CH); ^{13}C NMR: δ 14.9(2Me), 52.1(OMe), 62.7(d, $^{2}J_{CP}$ 4.6 Hz, 2CH_2O), 130.5(CH), 136.3(CH), 166.8(C=O); ^{31}P-NMR: δ 20.45 (P=O); NMR data for the minor isomer(40%); ^{1}H NMR: δ 1.17(6 H, dt, $^{3}J_{HH}$ 7.2 Hz, $^{4}J_{HP}$ 0.6 Hz, 2 Me), 3.80(3H, s, OMe), 4.09 (4H, dq, $^{3}J_{HP}$ 8.1 Hz, $^{3}J_{HH}$ 7.1 Hz 2 CH_2O), 6.35(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{2}J_{HP}$ 10.8 Hz, CH), 6.72(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{3}J_{HP}$ 7.0 Hz, CH); ^{13}C NMR: δ 15.0(2Me), 52.3(OMe), 63.0(d, $^{2}J_{CP}$ 4.6 Hz, 2CH_2O), 130.7(CH), 136.5(CH), 167(C=O); ^{31}P-NMR: δ 20.43 (P=O); Anal. Calcd.for $C_8H_{15}O_5P$ (222.18): C, 43.25; H, 6.81%; Found: C, 43.27; H, 6.83%.

Ethyl 3-(diethoxyphosphoryl)acrylate (3j) Pale yellow oil; yield: 0.20g (88%); IR(KBr) (ν_{max}/cm^{-1}) = 1723(C=O), 1258 (P=O), 1023; NMR data for the major isomer (67%); ^{1}H

NMR: δ 1.12(6 H, dt, $^{3}J_{HH}$ 7.2 Hz, $^{4}J_{HP}$ 0.6 Hz, 2 Me), 1.30(3H, t, Me), 4.09 (4H, dq, $^{3}J_{HP}$ 8.1 Hz, $^{3}J_{HH}$ 7.1 Hz 2 CH_2O), 4.18(2H, q, CH_2O), 6.37(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{2}J_{HP}$ 10.8 Hz, CH), 6.71(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{3}J_{HP}$ 7.0 Hz, CH); ^{13}C NMR: δ 14.3(Me), 14.9(2Me), 61.4(OCH_2), 62.4(d, $^{2}J_{CP}$ 4.6 Hz, 2CH_2O), 132.5(CH), 134.3(CH), 166.5(C=O); ^{31}P-NMR: δ 20.33 (P=O); NMR data for the minor isomer(33%): ^{1}H NMR: δ 1.10(6 H, dt, $^{3}J_{HH}$ 7.2 Hz, $^{4}J_{HP}$ 0.6 Hz, 2 Me), 1.32(3H, t, Me), 4.10 (4H, dq, $^{3}J_{HP}$ 8.1 Hz, $^{3}J_{HH}$ 7.1 Hz 2 CH_2O), 4.15(2H, q, CH_2O), 6.39(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{2}J_{HP}$ 10.8 Hz, CH), 6.70(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{3}J_{HP}$ 7.0 Hz, CH); ^{13}C NMR: δ 14.5(Me), 15.1(2Me), 61.3(OCH_2), 62.6(d, $^{2}J_{CP}$ 4.6 Hz, 2CH_2O), 133.0(CH), 134.2(CH), 166.6(C=O); ^{31}P-NMR: δ 20.35 (P=O); Anal. Calcd.for $C_9H_{17}O_5P$ (236.2): C, 45.76; H, 7.25%; Found: C, 45.8; H, 7.23%.

Methyl 3-(diphenoxyphosphoryl)acrylate (3k) Pale yellow oil; yield: 0.26g (93%); IR(KBr)(ν_{max}/cm^{-1}) = 1735(C=O), 1280 (P=O), 1185; NMR data for the major isomer(56%); ^{1}H NMR: δ 3.77(3H, s, OMe), 5.72(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{2}J_{HP}$ 10.8 Hz, CH), 6.30(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{3}J_{HP}$ 7.0 Hz, CH); 7.15 (2 H, t, $^{3}J_{HH}$ 8.1 Hz, 2 CH_{para} of 2 C_6H_5), 7.23 (4 H, d, $^{3}J_{HH}$ 8.0 Hz, 4 CH_{ortho} of 2 C_6H_5), 7.35 (4 H, dd, $^{3}J_{HH}$ 8.1 Hz, $^{3}J_{HH}$ 7.8 Hz, 4 CH_{meta} of 2 C_6H_5); ^{13}C NMR: δ 52.0(OMe), 115.8 [d, $^{3}J_{CP}$ 8.1 Hz, 4 $CH_{ortho}$of $(C_6H_5O)_2PO$], 125.6 [d, $^{4}J_{PC}$ 2.3 Hz, 4 $CH_{meta}$of $(C_6H_5O)_2PO$], 129.8 [s, 2 CH_{para} of$(C_6H_5O)_2PO$], 135.8(CH), 136.5(CH), 150.3 [d, $^{2}J_{PC}$ 9.3 Hz, 2 $C_{ipso}$of $(C_6H_5O)_2PO$], 166.9 (C=O).; ^{31}P-NMR: δ 11.62 (P=O); NMR data for the minor isomer(44%); ^{1}H NMR: δ 3.75(3H, s, OMe), 5.74(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{2}J_{HP}$ 10.8 Hz, CH), 6.28(1H, dd, $^{3}J_{HH}$ 8.0 Hz, $^{3}J_{HP}$ 7.0 Hz, CH); 7.16 (2 H, t, $^{3}J_{HH}$ 8.1 Hz, 2 CH_{para} of 2 C_6H_5), 7.25 (4 H, d, $^{3}J_{HH}$ 8.0 Hz, 4 CH_{ortho} of 2 C_6H_5), 7.33 (4 H, dd, $^{3}J_{HH}$ 8.1 Hz, $^{3}J_{HH}$ 7.8 Hz, 4 CH_{meta} of 2 C_6H_5); ^{13}C NMR: δ 52.3(OMe), 115.6 [d, $^{3}J_{CP}$ 8.1 Hz, 4 $CH_{ortho}$of $(C_6H_5O)_2PO$], 125.8 [d, $^{4}J_{PC}$ 2.3 Hz, 4 $CH_{meta}$of $(C_6H_5O)_2PO$], 129.7 [s, 2 CH_{para} of $(C_6H_5O)_2PO$], 135.9(CH), 136.7(CH), 150.1 [d, $^{2}J_{PC}$ 9.3 Hz, 2 $C_{ipso}$of $(C_6H_5O)_2PO$], 166.7 (C=O).; ^{31}P-NMR: δ 11.64 (P=O); Anal. Calcd.for $C_{16}H_{15}O_5P$ (318.26): C, 60.38; H, 4.75%;

Found: C, 60.40; H, 4.76%.

Ethyl 3-(diphenoxyphosphoryl)acrylate (3l) Pale yellow oil; yield: 0.28g (92%); IR(KBr)(ν_{max}/cm^{-1}) = 1737(C=O), 1280 (P=O), 1183; NMR data for the major isomer(55%); ^{1}H NMR: δ 1.34(3H, t, Me), 4.22(2H, q, CH_2O), 5.75(1H, dd, $^3J_{HH}$ 8.0 Hz, $^2J_{HP}$ 10.8 Hz, CH), 6.23(1H, dd, $^3J_{HH}$ 8.0 Hz, $^3J_{HP}$ 7.0 Hz, CH); 7.18 (2 H, t, $^3J_{HH}$ 8.1 Hz, 2 CH_{para} of 2 C_6H_5), 7.26 (4 H, d, $^3J_{HH}$ 8.0 Hz, 4 CH_{ortho} of 2 C_6H_5), 7.34 (4 H, dd, $^3J_{HH}$ 8.1 Hz, $^3J_{HH}$ 7.8 Hz, 4 CH_{meta} of 2 C_6H_5); ^{13}C NMR: δ 14.6(Me), 62.7(CH_2O), 115.8 [d, $^3J_{CP}$ 8.1 Hz, 4 $CH_{ortho}$of $(C_6H_5O)_2PO$], 125.6 [d, $^4J_{PC}$ 2.3 Hz, 4 $CH_{meta}$of$(C_6H_5O)_2PO$], 129.8 [s, 2 CH_{para} of $(C_6H_5O)_2PO$], 134(CH), 138.5(CH), 150.3 [d, $^2J_{PC}$ 9.3 Hz, 2 $C_{ipso}$of $(C_6H_5O)_2PO$], 166.9 (C=O).; ^{31}P-NMR: δ 11.60 (P=O); NMR data for the minor isomer(45%); ^{1}H NMR: δ 1.33(3H, t, Me), 4.20(2H, q, CH_2O), 5.73(1H, dd, $^3J_{HH}$ 8.0 Hz, $^2J_{HP}$ 10.8 Hz, CH), 6.25(1H, dd, $^3J_{HH}$ 8.0 Hz, $^3J_{HP}$ 7.0 Hz, CH); 7.19 (2 H, t, $^3J_{HH}$ 8.1 Hz, 2 CH_{para} of 2 C_6H_5), 7.28 (4 H, d, $^3J_{HH}$ 8.0 Hz, 4 CH_{ortho} of 2 C_6H_5), 7.36 (4 H, dd, $^3J_{HH}$ 8.1 Hz, $^3J_{HH}$ 7.8 Hz, 4 CH_{meta} of 2 C_6H_5); ^{13}C NMR: δ 14.4(Me), 62.5(CH_2O), 115.6 [d, $^3J_{CP}$ 8.1 Hz, 4 $CH_{ortho}$of $(C_6H_5O)_2PO$], 125.8 [d, $^4J_{PC}$ 2.3 Hz, 4 $CH_{meta}$of $(C_6H_5O)_2PO$], 129.7 [s, 2 CH_{para} of $(C_6H_5O)_2PO$], 134.2(CH), 138.3(CH), 150.5 [d, $^2J_{PC}$ 9.3 Hz, 2 $C_{ipso}$of $(C_6H_5O)_2PO$], 166.7 (C=O); ^{31}P-NMR: δ 11.58 (P=O); Anal. Calcd.for $C_{17}H_{17}O_5P$ (332.29): C, 61.45; H, 5.16%; Found: C, 61.40; H, 5.18%.

3. Results and discussion

Initially, the reaction between ethyl phenylpropiolate **(1d)** and diethyl phosphite **(2d)** at room temperature, was chosen as the model reaction. As shown in (Fig. 1., Table 1), the best result was obtained with NaCN (20%) in H_2O/ acetone (1:2) (Table 1, Entry 7). Other solvents, gave lower yields (Table 1, Entry 1-6, 8-10). The reaction proceeded smoothly in aqueous acetone and afforded ethyl 3-phenyl-3-(diethoxyphosphoryl) acrylate**(3d)** in 95%

yield. When the reaction was carried out in other solvents, product **3d** was formed in 33-75% yields.

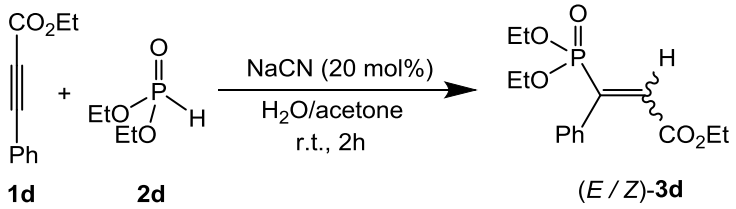

Fig. 1. Model reaction synthesis of various vinylphosphonates compounds

Table 1 Optimization of reaction conditions [a]

Entry	Catalyst (mol%)	Solvent	Yield[b](%)
1	NaCN (20)	MeCN	73
2	NaCN (30)	MeCN	75
3	NaCN (40)	MeCN	75
4	-	MeCN	0
5	NaCN (20)	EtOH	68
6	NaCN (20)	H_2O	35
7	**NaCN (20)**	**H_2O/ acetone**	**96**
8	NaCN (20)	THF	52
9	NaCN (20)	DMSO	33
10	NaCN (20)	DMF	65

[a] Reagents and conditions: diethyl phosphite(1mmol),ethyl phenylpropiolate(1mmol),solvent(10mL), r.t., 2h. [b] Isolated yield.

Thus, aqueous acetone was used as solvent for the preparation of functionalized vinylphosphonates **3a-l** see Fig. 2.

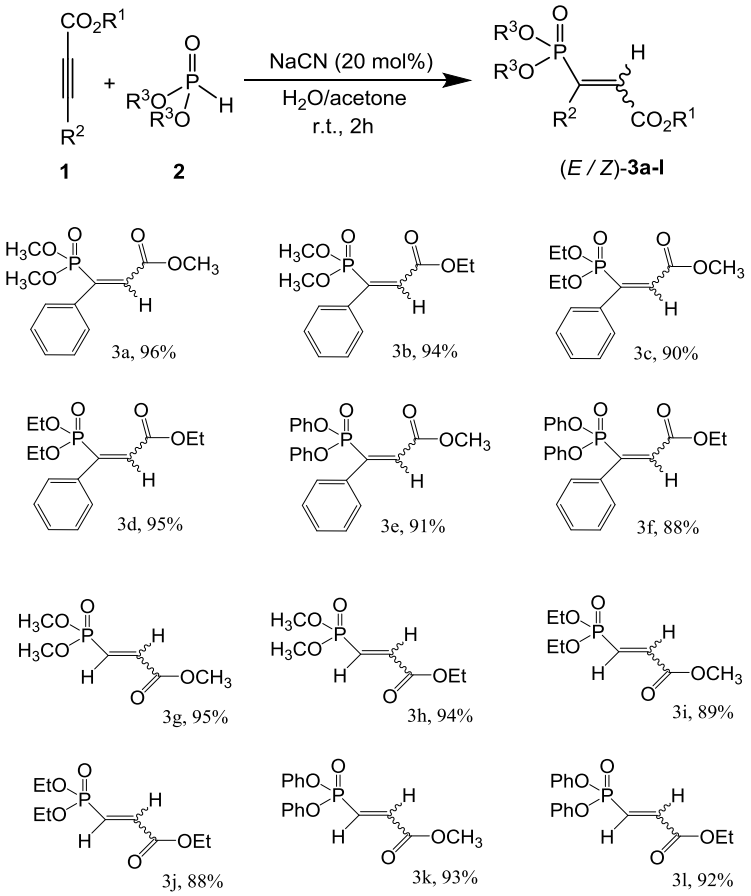

Fig. 2. Formation of vinylphosphonates derivatives 3a–l[a,b]

([a] Reaction conditions: alkyl(aryl) propiolates **1** (1mmol), dialkyl(aryl) phosphite **2** (1 mmol), NaCN (0.001 g, 0.2 mmol), acetone/H_2O (2:1, 10 mL), r.t., 2 h. [b] Isolated yield.)

The structures of organophosphorus **3a-l** were deduced from their elemental analyses and their IR, ^1H, ^{13}C, and ^{31}P NMR, and mass spectral data. Based on observed spectra, the obtained products have both ***E/Z*** isomers in their structure, but due to their complexity, the dominant isomer is not known Fig. 3. For example, the ^1H NMR spectrum of **3d** in $CDCl_3$ showed a triplet-doublet at δ 1.11 and a doublet-quartet at δ 4.07 for the ethoxy protons ($POCH_2CH_3$), a triplet at δ 1.30 and a quartet at δ 4.31 for the ethoxy protons (CO_2Et), a doublet at δ 6.50 for the methine proton(=CH), multiplets at δ 7.2-7.4 for aryl protons. The most noteworthy feature of the ^1H-decoupled ^{13}C NMR spectra of organophosphorus **3** showed 14 distinct resonances in agreement with the proposed structure.

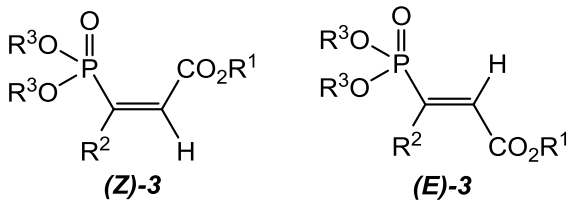

Fig. 3. The structure of (*E*)-3 and (*Z*)-3

Although the mechanistic details of the reaction are not known, a plausible rationalization may be advanced to explain the product formation Fig. 4. Presumably, the zwitterionic intermediate [27-31] formed from NaCN and alkyl propiolates, is protonated by **2** to furnish intermediate **5**, which is attacked by anion **6,** to afford **7**, which undergoes substitution reaction to produce product **3**.

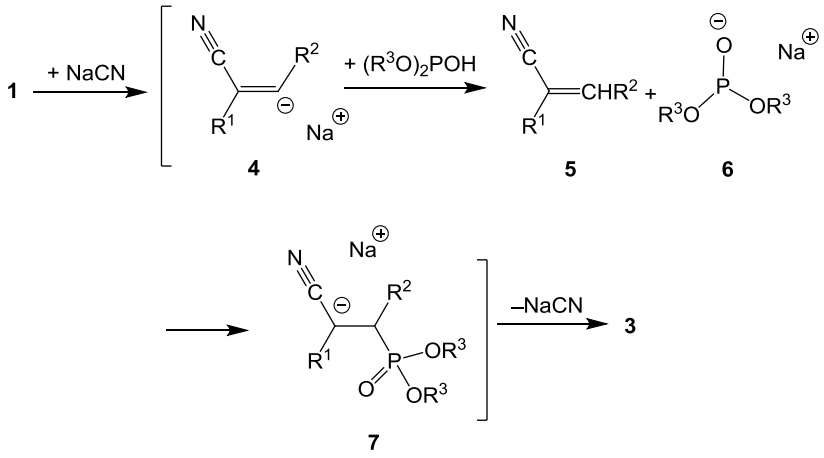

Fig. 4. A plausible mechanism for compound 3

4. Conclusions

In this work, simple and mild efficient synthesis of various organophosphorus compounds based on the reaction of dialkyl(aryl) phosphites with alkyl(aryl) propiolates in the presence of NaCN in aqueous acetone, is described. Using this approach, all organophosphorus compounds are obtained in excellent yields. The method offers several advantages including operational simplicity, high diversity *via* various functional groups and fairly good yields.

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