

A simple synthesis of stable phosphorus ylides containing cyano groups, from the reaction between triphenylphosphine and acetylenic esters in the presence of CH- acid compounds

Malek Taher Maghsoodlou,* Hamid Reza Shaterian, Ghasem Marandi, Fahimeh Shahraki Poor, and Jaber Salehzadeh

Department of Chemistry, The University of Sistan & Baluchestan, P. O. Box 98135-674, Zahedan, Iran

E-mail: mt_maghsoodlou@yahoo.com

Abstract

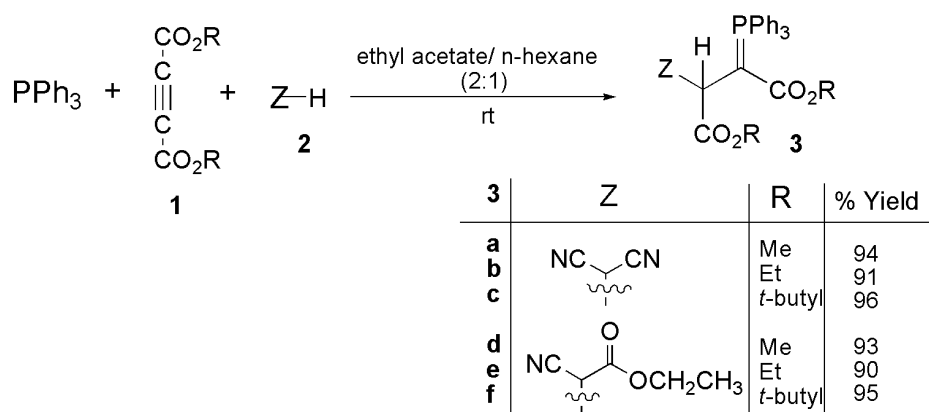
Stable crystalline phosphorus ylides were obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, in the presence of strong CH- acids such as malononitrile or ethyl cyanoacetate. These stable ylides exist in solution as a mixture of two geometrical isomers as a result of restricted rotation around the carbon-carbon partial double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group.

Keywords: Acetylenic ester, CH- acids, stable phosphorus ylides, triphenylphosphine, geometrical isomer

Introduction

The synthesis of phosphorus ylides is important in organic chemistry because of their applications in the synthesis of organic products,¹ especially the synthesis of naturally-occurring products with potentially useful biological and pharmacological properties.² Phosphorus ylides are reactive intermediates, which take part in many valuable reactions in organic synthesis,³⁻⁵ and several methods have been developed for their preparation. These ylides are usually prepared by treatment of a phosphonium salt with a base, and phosphonium salts are usually prepared from the phosphine and an alkyl halide.^{1,6-10} Among other methods, phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefins.⁶⁻²¹ We report here an efficient synthetic route for the generation of stable phosphoranes bearing cyano groups *via* the reaction of triphenylphosphine with dialkyl acetylenedicarboxylates (**1**) in the presence of

strong CH-acids such as malononitrile or ethyl cyanoacetate (**2**), which leads to the corresponding stable phosphorus ylides (**3**) in excellent yields (Scheme 1).

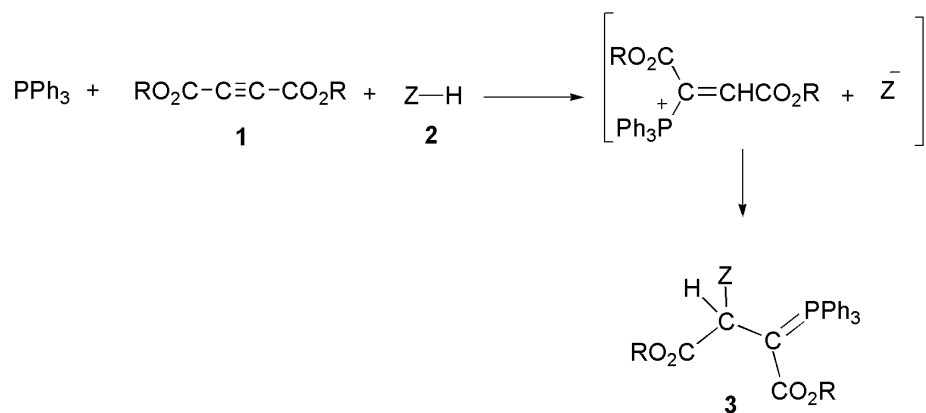


Scheme 1

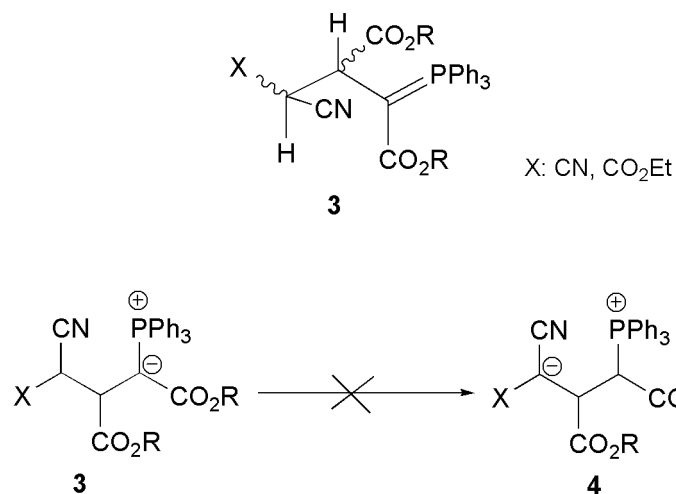
Result and Discussion

The reactions of malononitrile or ethyl cyanoacetate (**2**) with dialkyl acetylenedicarboxylates (**1**) in the presence of triphenylphosphine proceeded in a mixture of ethyl acetate and *n*-hexane (2:1) at room temperature and were complete within 1 hour. The ^1H - and ^{13}C - NMR spectra of the crude product clearly indicated the formation of stable phosphorus ylides, **3**. No products other than **3** could be detected by NMR spectroscopy. The structures of compounds **3a–f** were deduced from their IR-, ^1H -, ^{13}C - and ^{31}P - NMR spectra. The mass spectra of the products displayed molecular ion peaks at appropriate m/z values. Any initial fragmentations involved the loss of alkoxy, alkoxycarbonyl, and PPh_3 moieties.

The ^1H -, ^{13}C -, and ^{31}P - NMR spectra of ylides **3a–f** are consistent with the presence of two geometrical isomers. The ylide moiety of these compounds is conjugated with the adjacent carbonyl group, and rotation around the partial double bond of the (*E*)-**3** and (*Z*)-**3** geometrical isomers is slow on the NMR timescale at ambient temperature. Selected ^1H -, ^{13}C -, and ^{31}P - NMR chemical shifts and coupling constants in the major (M) and minor (m) geometrical isomers of compounds **3a–f** are shown in Table 1. On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,^{1,6,7} it is reasonable to assume that the phosphorus ylides (**3**) result from the initial addition of triphenylphosphine to the acetylenic ester and subsequent deprotonation of the 1:1 adduct (Scheme 2).



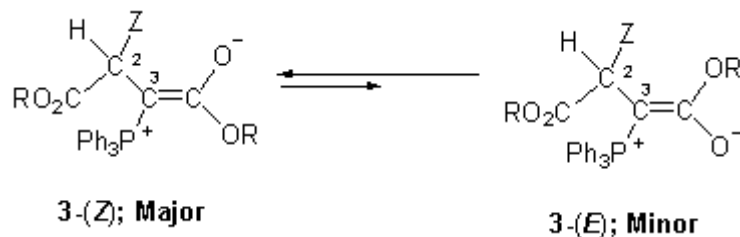
Scheme 2



Scheme 3

The ^1H -NMR spectra of compounds **3** verified that compound **4** had not been formed under these conditions, and the *anti*- conformation of the two vicinal protons in compounds **3** was supported by the value of $^3J_{\text{HH}}$: partial assignments are given in the Experimental Section (see Scheme 3 and Table 1).

Table 1. Selected ^1H -, ^{13}C -, and ^{31}P - NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for H-2, -OR, -CO₂R, C-2, and C-3, in the Major (M) and Minor (m) diastereoisomers of compounds **3a–f**.



Compd	Isomer (%)	^1H NMR data			^{13}C NMR data		
		H-2 ($^3J_{\text{PH}}$)	OR	CO ₂ R	C-2 ($^2J_{\text{PC}}$)	C-3 ($^1J_{\text{PC}}$)	^{31}P NMR
3a	M (74)	2.90 (16.0)	3.17	3.77	46.88 (14.5)	39.66 (128.8)	22.90
3a	m (26)	2.95 (15.6)	3.58	3.76	46.20 (14.2)	40.75 (137.3)	23.60
3b	M (75)	2.88 (16.1)	3.71	4.25	46.92 (15.1)	39.56 (129.1)	22.80
3b	m (25)	2.94 (17.7)	4.13	4.31	46.39 (14.2)	40.83 (137.4)	23.61
3c	M (79)	2.74 (16.2)	0.95	1.50	47.83 (15.1)	39.54 (129.8)	22.40
3c	m (21)	2.71 (16.3)	1.45	1.47	46.93 (14.7)	41.31 (137.5)	23.87
3d	M (64)	3.05 (16.6)	3.14	3.65	44.37 (14.4)	39.39 (128.3)	23.20
3d	m (36)	3.10 (16.5)	3.56	3.64	43.62 (14.5)	40.31 (136.9)	23.57
3e	M (67)	3.05 (16.5)	3.05–3.11	4.00–4.20	44.47 (14.5)	39.27 (128.5)	23.19
3e	m (33)	3.11 (16.6)	3.71–3.78	4.00–4.20	43.84 (14.3)	40.44 (136.9)	23.73
3f	M (70)	2.84 (18.7)	0.95	1.43	45.37 (14.8)	39.07 (129.1)	22.56
3f	m (30)	2.91 (17.1)	1.41	1.45	44.28 (14.7)	41.01 (136.3)	22.40

The assignment of **3-(E)-** and **3-(Z)-** rotamers as the major and minor components in phosphorus ylides have been reported previously in the literature.²²⁻²⁴ The ¹H- NMR spectrum of compound **3a** exhibits two sharp lines (δ 3.17 and 3.77) arising from the methoxy group in the *Z*-rotamer and two single sharp resonances at 3.58 and 3.76 ppm for methoxy groups in the *E*-rotamer. The shift at 3.21 of the methoxy group of the *Z*-rotamer is shielded, due to the anisotropic effect of the phenyl groups of triphenylphosphine. This effect confirms why the **3-E** and **3-Z** rotamers could appear as the minor and major forms, respectively, as reported in the Experimental Section. Also, the signals for methine protons at δ 2.90, 2.95, 4.91 and 5.46 ppm, appear as two doublets of doublets ($^3J_{PH}=16$ and $^3J_{HH}=10.5$ Hz) and ($^3J_{PH}=15.6$ and $^3J_{HH}=10.5$ Hz) and two doublets ($^3J_{HH}=10.5$ and $^3J_{HH}=10.5$ Hz) for the major and minor geometrical isomers, respectively. The ¹³C- NMR spectrum of **3a** exhibits 26 distinct resonances, which are in agreement with the mixture of two conformational isomers. Although the presence of the ³¹P nucleus complicated both the ¹H- and ¹³C- NMR spectra of phosphorane **3a**, it helps in assigning the signals by long-range spin-spin couplings with the ¹H- and ¹³C- nuclei. The ¹H- and ¹³C- NMR spectra of compounds **3b-c** are similar to those of **3a**, except for the signals from the ester group, which appear as characteristic resonance lines with the corresponding chemical shifts. The structural assignments made for phosphoranes **3a-f** on the basis of the ¹H- and ¹³C- NMR spectra were supported by their IR spectra. Of special interest is the absorption of the ester groups of such compounds at 1742–1614 cm⁻¹. The conjugation of one ester group with the negative charge is a plausible factor in the decrease in the wavenumbers of the corresponding carbonyl absorption bands.

In summary, we have prepared novel stable cyano-functional phosphorus ylides using a one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of strong CH-acids such as malononitrile or ethyl cyanoacetate. The present method has the advantage that not only is the reaction performed under neutral conditions, but also that the reagents can be mixed without any activation or modification.

Experimental Section

General Procedures. Melting points and IR spectra of all compounds were measured on an Electrothermal 9100 apparatus and a Shimadzu IR-460 spectrometer respectively. The ¹H-, ¹³C-, and ³¹P- NMR spectra were obtained from a BRUKER DRX-300 AVANCE instrument with CDCl₃ as a solvent at 300.1, 75.5, and 121.5 MHz, respectively. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on Shimadzu GCMS-QP5050A and Finnigan-MAT 8430 mass spectrometers operating at an ionization potential of 70 eV. Dialkyl acetylenedicarboxylates, triphenylphosphine, malononitrile, and ethyl cyanoacetate were purchased from Fluka (Buchs) and used without further purification. RT denotes room temperature.

General preparative procedure, exemplified by dimethyl 2-(dicyanomethyl)-3-(triphenylphosphanylidene)butanedioate (**3a**)

To a magnetically stirred solution of malononitrile (0.06 g, 1 mmol) and triphenylphosphine (0.26 g, 1 mmol) in a mixture of ethyl acetate and *n*-hexane (2:1, v/v) was added dropwise a mixture of dimethyl acetylenedicarboxylate (0.12 mL, 1 mmol) in 3 mL of ethyl acetate at -5°C over 10 min. After approximately 1 hour stirring at RT the product was filtered off and washed with cold diethyl ether (3 \times 5 mL), and was finally obtained as a white powder, 0.44 g, yield 94%, mp $182\text{--}185^{\circ}\text{C}$, IR (KBr) (ν_{max} , cm^{-1}): 2225 (CN), 1735 and 1618 (C=O). MS (m/z , %): 406 (30), 405 (100), 262 (8), 183 (27), 108 (15), 77 (13), 59 (8). Anal. Calcd for $\text{C}_{27}\text{H}_{23}\text{N}_2\text{O}_4\text{P}$ (470.46): C, 68.93; H, 4.93; N, 5.95. Found: C, 69.04; H, 4.93; N, 6.02%. **Major isomer (Z)-3a** (74%): ^1H NMR (300.1 MHz): δ 2.90 (1H, dd, $^3J_{\text{HH}}=10.5$ Hz, $^3J_{\text{PH}}=16.0$ Hz, P=C-CH), 3.17 and 3.77 (6H, 2s, 2xOCH₃), 5.46 (1H, d, $^3J_{\text{HH}}=10.5$ Hz, CH(CN)₂), 7.52–7.77 (15H, m, 3xC₆H₅). ^{13}C NMR (75.5 MHz): δ 24.80 (d, $^3J_{\text{PC}}=4.9$ Hz, CH(CN)₂), 39.66 (d, $^1J_{\text{PC}}=128.8$ Hz, P=C), 46.88 (d, $^2J_{\text{PC}}=14.5$ Hz, P=C-CH), 49.34 and 52.61 (2s, 2xOCH₃), 113.86 and 113.90 (2s, 2xCN), 125.64 (d, $^1J_{\text{PC}}=92.8$ Hz, C_{ipso}), 128.91 (d, $^3J_{\text{PC}}=12.3$ Hz, C_{meta}), 132.63 (d, $^4J_{\text{PC}}=2.6$ Hz, C_{para}), 139.91 (d, $^2J_{\text{PC}}=9.8$ Hz, C_{ortho}), 169.34 (d, $^2J_{\text{PC}}=12.3$ Hz, P-C=C), 171.11 (d, $^3J_{\text{PC}}=4.0$ Hz, C=O, ester). ^{31}P NMR (121.5 MHz): δ 22.90 (Ph₃P⁺-C). **Minor isomer (E)-3a** (26%): ^1H NMR (300.1 MHz): δ 2.95 (1H, dd, $^3J_{\text{HH}}=10.5$ Hz, $^3J_{\text{PH}}=15.6$ Hz, P=C-CH), 3.58 and 3.76 (6H, 2s, 2xOCH₃), 4.91 (1H, d, $^3J_{\text{HH}}=10.5$ Hz, CH(CN)₂), 7.52–7.77 (15H, m, 3xC₆H₅). ^{13}C NMR (75.5 MHz): δ 26.37 (d, $^3J_{\text{PC}}=5.3$ Hz, CH(CN)₂), 40.75 (d, $^1J_{\text{PC}}=137.3$ Hz, P=C), 46.20 (d, $^2J_{\text{PC}}=14.2$ Hz, P=C-CH), 50.35 and 52.58 (2s, 2xOCH₃), 113.53 and 113.63 (2s, 2xCN), 125.13 (d, $^1J_{\text{PC}}=92.9$ Hz, C_{ipso}), 128.98 (d, $^3J_{\text{PC}}=12.3$ Hz, C_{meta}), 132.63 (d, $^4J_{\text{PC}}=2.6$ Hz, C_{para}), 133.96 (d, $^2J_{\text{PC}}=9.8$ Hz, C_{ortho}), 169.59 (d, $^2J_{\text{PC}}=16.1$ Hz, P-C=C), 171.48 (d, $^3J_{\text{PC}}=4.8$ Hz, C=O, ester). ^{31}P NMR (121.5 MHz): δ 23.60 (Ph₃P⁺-C).

Diethyl 2-(dicyanomethyl)-3-(triphenylphosphanylidene)butanedioate (3b**).** The yield was 0.45 g, 91%, mp $169\text{--}172^{\circ}\text{C}$, IR (KBr) (ν_{max} , cm^{-1}): 2250 (CN), 1727 and 1620 (C=O). MS (m/z , %): 453 (M⁺-OEt, 5), 434 (9), 433 (100), 425 (7), 262 (11), 183 (39), 108 (18), 77 (13). Anal. Calcd for $\text{C}_{29}\text{H}_{27}\text{N}_2\text{O}_4\text{P}$ (498.51): C, 69.87; H, 5.46; N, 5.62. Found: C, 69.80; H, 5.49; N, 5.58%. **Major isomer (Z)-3b** (75%): ^1H NMR (300.1 MHz): δ 0.47 and 1.26 (6H, 2t, $^3J_{\text{HH}}=7.1$ Hz, 2xOCH₂CH₃), 2.88 (1H, dd, $^3J_{\text{HH}}=10.5$ Hz, $^3J_{\text{PH}}=16.1$ Hz, P=C-CH), 3.71 and 4.25 (4H, 2q, $J=7.1$ Hz, 2xOCH₂CH₃), 5.45 (1H, d, $^3J_{\text{HH}}=10.5$ Hz, CH(CN)₂), 7.48–7.80 (15H, m, 3xC₆H₅). ^{13}C NMR (75.5 MHz): δ 13.80 and 14.06 (2s, 2xCH₃), 24.83 (d, $^3J_{\text{PC}}=5.2$ Hz, CH(CN)₂), 39.56 (d, $^1J_{\text{PC}}=129.1$ Hz, P=C), 46.92 (d, $^2J_{\text{PC}}=15.1$ Hz, P=C-CH), 58.02 and 61.84 (2s, 2xOCH₂CH₃), 114.06 and 114.03 (2s, 2xCN), 125.83 (d, $^1J_{\text{PC}}=92.8$ Hz, C_{ipso}), 128.82 (d, $^3J_{\text{PC}}=12.1$ Hz, C_{meta}), 132.57 (d, $^4J_{\text{PC}}=2.2$ Hz, C_{para}), 134.0 (d, $^2J_{\text{PC}}=9.7$ Hz, C_{ortho}), 168.95 (d, $^2J_{\text{PC}}=12.1$ Hz, P-C=C), 170.68 (d, $^3J_{\text{PC}}=3.7$ Hz, C=O, ester). ^{31}P NMR (121.5 MHz): δ 22.80 (Ph₃P⁺-C). **Minor isomer (E)-3b** (25%): ^1H NMR (300.1 MHz): δ 1.20 and 1.30 (6H, 2t, $^3J_{\text{HH}}=7.1$ Hz, 2xOCH₂CH₃), 2.94 (1H, dd, $^3J_{\text{HH}}=10.3$ Hz, $^3J_{\text{PH}}=17.7$ Hz, P=C-CH), 4.13 and 4.31 (4H, 2m, 2xABX₃ system, 2xOCH₂CH₃), 4.93 (1H, d, $^3J_{\text{HH}}=10.3$ Hz, CH(CN)₂), 7.48–7.80 (15H, m, 3xC₆H₅). ^{13}C NMR (75.5 MHz): δ 14.14 and 14.91 (2s, 2xCH₃), 26.40 (d, $^3J_{\text{PC}}=5.2$ Hz, CH(CN)₂), 40.83 (d,

$^1J_{\text{PC}}=137.4$ Hz, P=C), 46.39 (d, $^2J_{\text{PC}}=14.2$ Hz, P=C-CH), 58.62 and 61.91 (2s, 2xOCH₂CH₃), 113.75 and 113.64 (2s, 2xCN), 125.31 (d, $^1J_{\text{PC}}=92.8$ Hz, C_{ipso}), 128.91 (d, $^3J_{\text{PC}}=12.1$ Hz, C_{meta}), 132.57 (d, $^4J_{\text{PC}}=2.2$ Hz, C_{para}), 134.0 (d, $^2J_{\text{PC}}=9.7$ Hz, C_{ortho}), 169.20 (d, $^2J_{\text{PC}}=17.3$ Hz, P-C=C), 171.04 (d, $^3J_{\text{PC}}=3.7$ Hz, C=O, ester). ^{31}P NMR (202.4 MHz): δ 23.61(Ph₃P⁺-C).

Di- *tert*-butyl 2-(dicyanomethyl)-3-(triphenylphosphanylidene)butanedioate (3c). The yield was 0.53 g, 96%, mp 158–160 °C, IR (KBr) (ν_{max} , cm⁻¹): 2247 (CN), 1723 and 1614 (C=O). MS (m/z , %): 554 (M⁺, 7), 490 (15), 489 (35), 337 (100), 262 (22), 183 (38), 108 (17), 77 (8), 57 (75). Anal. Calcd for C₃₃H₃₅N₂O₄P (554.62): C, 71.46; H, 6.36; N, 5.05. Found: C, 71.55; H, 6.37; N, 4.98%.

Major isomer (Z)-3c. (79%): ^1H NMR (300.1 MHz), δ 0.95 and 1.50 (18H, 2s, 2x CMe₃), 2.74 (1H, dd, $^3J_{\text{HH}}=10.4$ Hz, $^3J_{\text{PH}}=16.2$ Hz, P=C-CH), 5.44 (1H, d, $^3J_{\text{HH}}=10.4$ Hz, CH(CN)₂), 7.52–7.81 (15H, m, 3xC₆H₅). ^{13}C NMR (75.5 MHz), δ 24.91 (d, $^3J_{\text{PC}}=4.6$ Hz, CH(CN)₂), 28.00 and 28.22 (2s, 2x CMe₃), 39.54 (d, $^1J_{\text{PC}}=129.8$ Hz, P=C), 47.83 (d, $^2J_{\text{PC}}=15.1$ Hz, P=C-CH), 78.09 and 82.32 (2s, OCM₃), 114.46 and 114.27 (2s, 2xCN), 126.40 (d, $^1J_{\text{PC}}=92.4$ Hz, C_{ipso}), 128.61 (d, $^3J_{\text{PC}}=12.1$ Hz, C_{meta}), 132.34 (d, $^4J_{\text{PC}}=2.3$ Hz, C_{para}), 134.12 (d, $^2J_{\text{PC}}=9.7$ Hz, C_{ortho}), 168.48 (d, $^2J_{\text{PC}}=11.7$ Hz, P-C=C), 169.78 (d, $^3J_{\text{PC}}=4.5$ Hz, C=O). ^{31}P NMR (121.5 MHz): δ 22.40 (Ph₃P⁺-C).

Minor isomer (E)-3c. (21%): ^1H NMR (300.1 MHz), δ 1.45 and 1.47 (18H, 2s, 2x CMe₃), 2.71 (1H, dd, $^3J_{\text{HH}}=10.4$ Hz, $^3J_{\text{PH}}=16.3$ Hz, P=C-CH), 5.00 (1H, d, $^3J_{\text{HH}}=10.4$ Hz, CH(CN)₂), 7.52–7.81 (15H, m, 3xC₆H₅). ^{13}C NMR (75.5 MHz), δ 27.76 and 29.60 (2s, 2 CMe₃), 25.00 (d, $^3J_{\text{PC}}=5.3$ Hz, CH(CN)₂), 41.31 (d, $^1J_{\text{PC}}=137.5$ Hz, P=C), 46.93 (d, $^2J_{\text{PC}}=14.7$ Hz, P=C-CH), 78.49 and 82.30 (2s, OCM₃), 113.82 and 113.98 (2s, 2 CN), 125.80 (d, $^1J_{\text{PC}}=92.7$ Hz, C_{ipso}), 128.77 (d, $^3J_{\text{PC}}=11.2$ Hz, C_{meta}), 132.34 (d, $^4J_{\text{PC}}=2.3$ Hz, C_{para}), 133.99 (d, $^2J_{\text{PC}}=9.6$ Hz, C_{ortho}), 168.50 (d, $^2J_{\text{PC}}=11.1$ Hz, P-C=C), 169.56 (d, $^3J_{\text{PC}}=4.9$ Hz, C=O). ^{31}P NMR (121.5 MHz): δ 23.87 (Ph₃P⁺-C).

Dimethyl 2-(ethyl-1-cyanoethanoat-1-yl)-3-(triphenylphosphanylidene)butanedioate (3d). The yield was 0.48 g, 93%, mp 143–145 °C, IR (KBr) (ν_{max} , cm⁻¹): 2235 (CN), 1736 and 1621 (C=O). MS (m/z , %): 517 (M⁺, 4), 416 (20), 404 (22), 262 (100), 187 (72), 108 (15). Anal. Calcd for C₂₉H₂₈NO₆P (517.51): C, 67.31; H, 5.45; N, 2.71. Found: C, 67.39; H, 5.48; N, 2.65%.

Major isomer (Z)-3d. (64%): ^1H NMR (300.1 MHz): δ 1.21 (3H, t, $^3J_{\text{HH}}=7.1$ Hz, OCH₂CH₃), 3.05 (1H, dd, $^3J_{\text{HH}}=10.9$ Hz, $^3J_{\text{PH}}=16.6$ Hz, P=C-CH), 3.14 and 3.65 (6H, 2s, 2xOCH₃), 4.13 (2H, m, ABX₃ system, OCH₂CH₃), 5.02 (1H, d, $^3J_{\text{HH}}=10.9$ Hz, CH(CNCO₂Et)), 7.50–7.79 (15H_{arom}, m, 3xC₆H₅). ^{13}C NMR (75.5 MHz): δ 13.85 (s, OCH₂CH₃), 39.27 (d, $^3J_{\text{PC}}=3.9$ Hz, CH(CNCO₂Et)), 39.39 (d, $^1J_{\text{PC}}=128.3$ Hz, P=C), 44.37 (d, $^2J_{\text{PC}}=14.41$ Hz, P=C-CH), 49.10 and 52.15 (2s, 2xOCH₃), 62.23 (s, OCH₂), 117.32 (s, CN), 126.39 (d, $^1J_{\text{PC}}=92.4$ Hz, C_{ipso}), 128.68 (d, $^3J_{\text{PC}}=12.3$ Hz, C_{meta}), 132.25 (d, $^4J_{\text{PC}}=2.8$ Hz, C_{para}), 134.03 (d, $^2J_{\text{PC}}=9.7$ Hz, C_{ortho}), 166.26 (s, C=O, CO₂Et), 169.54 (d, $^2J_{\text{PC}}=12.8$ Hz, P-C=C), 173.24 (d, $^3J_{\text{PC}}=4.6$ Hz, C=O). ^{31}P NMR (202.4 MHz): δ 23.20 (Ph₃P⁺-C).

Minor isomer (E)-3d. (36%): ^1H NMR (300.1 MHz): δ 1.23 (3H, t, $^3J_{\text{HH}}=7.1$ Hz, OCH₂CH₃), 3.10 (1H, dd, $^3J_{\text{HH}}=11.2$ Hz, $^3J_{\text{PH}}=16.5$ Hz, P=C-CH), 3.56 and 3.64 (6H, 2s, 2xOCH₃), 4.13 (2H,

m, ABX₃ system, OCH₂CH₃), 4.63 (1H, d, ³J_{HH}=11.2 Hz, CH(CNCO₂Et)), 7.50–7.79 (15H, m, 3xC₆H₅). ¹³C NMR (75.5 MHz): δ 13.85 (s, OCH₂CH₃), 40.75 (d, ³J_{PC}=3.9 Hz, CH(CNCO₂Et)), 40.31 (d, ¹J_{PC}=136.9 Hz, P=C), 43.62 (d, ²J_{PC}=14.5 Hz, P=C-CH), 50.23 and 52.15 (2s, 2xOCH₃), 62.37 (s, OCH₂CH₃), 117.04 (s, CN), 125.80 (d, ¹J_{PC}=92.5 Hz, C_{ipso}), 128.76 (d, ³J_{PC}=12.4 Hz, C_{meta}), 132.25 (d, ⁴J_{PC}=2.8 Hz, C_{para}), 134.05 (d, ²J_{PC}=9.7 Hz, C_{ortho}), 166.02 (s, C=O, CO₂Et), 170.23 (d, ²J_{PC}=17.8 Hz, P-C=C), 173.69 (d, ³J_{PC}=5.1 Hz, C=O). ³¹P NMR (121.5 MHz): δ 23.57 (Ph₃P⁺-C).

Diethyl 2-(ethyl-1-cyanoethanoat-1-yl)-3-(triphenylphosphanylidene)butanedioate (3e). The yield was 0.49 g, 90%, mp 120–123 °C, IR (KBr) (ν_{max}, cm⁻¹): 2230 (CN), 1742, 1725 and 1619 (C=O). MS (*m/z*, %): 546 (M⁺+1, 2), 534 (15), 522 (23), 262 (65), 187 (79), 108 (100). Anal. Calcd for C₃₁H₃₂NO₆P (545.56): C, 68.25; H, 5.91; N, 2.57. Found: C, 68.57; H, 5.79; N, 2.65%.

Major isomer (Z)-3e. (67%): ¹H NMR (300.1 MHz): δ 0.46 (3H, t, ³J_{HH}=7.0 Hz, OCH₂CH₃), 1.17–1.24 (6H, m, 2xCH₃), 3.05 (1H, dd, ³J_{HH}=10.1 Hz, ³J_{PH}=16.5 Hz, P=C-CH), 3.05–3.11 and 4.00–4.20 (6H, 2m, 3xABX₃ system, 3xOCH₂CH₃), 5.01 (1H, d, ³J_{HH}=10.1 Hz, CH(CNCO₂Et)), 7.50–7.80 (15H, m, 3xC₆H₅). ¹³C NMR (75.5 MHz): δ 13.81, 14.08 and 15.02 (3s, 3xOCH₂CH₃), 39.27 (d, ¹J_{PC}=128.5 Hz, P=C), 39.35 (d, ³J_{PC}=3.9 Hz, CH(CNCO₂Et)), 44.47 (d, ²J_{PC}=14.5 Hz, P=C-CH), 57.67, 61.12 and 62.14 (3s, 3xOCH₂CH₃), 117.49 (s, CN), 126.66 (d, ¹J_{PC}=92.4 Hz, C_{ipso}), 128.56 (d, ³J_{PC}=12.3 Hz, C_{meta}), 132.14 (d, ⁴J_{PC}=2.6 Hz, C_{para}), 134.13 (d, ²J_{PC}=9.8 Hz, C_{ortho}), 166.39 (s, C=O, CO₂Et), 169.15 (d, ²J_{PC}=12.8 Hz, P-C=C), 172.83 (d, ³J_{PC}=4.7 Hz, C=O). ³¹P NMR (121.5 MHz): δ 23.19 (Ph₃P⁺-C). **Minor isomer (E)-3e** (33%): ¹H NMR (300.1 MHz): δ 0.46 (3H, t, ³J_{HH}=7.0 Hz, OCH₂CH₃), 1.17–1.24 (6H, m, 2xCH₃), 3.11 (1H, dd, ³J_{HH}=11.0 Hz, ³J_{PH}=16.6 Hz, P=C-CH), 3.71–3.78 and 4.00–4.20 (6H, 2m, 3xABX₃ system, 3xOCH₂CH₃), 4.64 (1H, d, ³J_{HH}=11.0 Hz, CH(CNCO₂Et)), 7.50–7.80 (15H, m, 3xC₆H₅). ¹³C NMR (75.5 MHz): δ 13.87, 14.15 and 14.95 (3s, 3xOCH₂CH₃), 40.44 (d, ¹J_{PC}=136.9 Hz, P=C), 40.80 (d, ³J_{PC}=3.9 Hz, CH(CNCO₂Et)), 43.84 (d, ²J_{PC}=14.3 Hz, P=C-CH), 58.30, 61.19 and 62.29 (3s, 3xOCH₂CH₃), 117.14 (s, CN), 126.03 (d, ¹J_{PC}=92.4 Hz, C_{ipso}), 128.67 (d, ³J_{PC}=12.2 Hz, C_{meta}), 132.14 (d, ⁴J_{PC}=2.6 Hz, C_{para}), 134.13 (d, ²J_{PC}=9.8 Hz, C_{ortho}), 166.13 (s, C=O, CO₂Et), 169.86 (d, ²J_{PC}=17.7 Hz, P-C=C), 173.24 (d, ³J_{PC}=5.1 Hz, C=O). ³¹P NMR (121.5 MHz): δ 23.73 (Ph₃P⁺-C).

Di-tert-butyl 2-(ethyl 1-cyanoethanoat-1-yl)-3-(triphenylphosphanylidene)butanedioate (3f). The yield was 0.57 g, 95%, mp 144–146 °C, IR (KBr) (ν_{max}, cm⁻¹): 2270 (CN), 1727, 1730 and 1616 (C=O). MS (*m/z*, %): 601 (M⁺, 10), 500 (22), 489 (20), 262 (23), 183 (59), 108 (18), 77 (9), 57 (100). Anal. Calcd for C₃₅H₄₀NO₆P (601.67): C, 69.87; H, 6.70; N, 2.33. Found: C, 69.75; H, 6.708; N, 2.41%. **Major isomer (Z)- 3f** (70%): ¹H NMR (300.1 MHz), δ 0.95 and 1.43 (18H, 2s, 2x CMe₃), 1.19 (3H, t, ³J_{HH}=7.1 Hz, OCH₂CH₃), 2.84 (1H, dd, ³J_{HH}=10.9 Hz, ³J_{PH}=18.7 Hz, P=C-CH), 4.10 (2H, m, ABX₃ system, OCH₂CH₃), 5.01 (1H, d, ³J_{HH}=10.9 Hz, CH(CNCO₂Et)), 7.46–7.85 (15H, m, 3xC₆H₅). ¹³C NMR (75.5 MHz), δ 13.75 (s, OCH₂CH₃), 28.05 and 28.29 (2s, 2x CMe₃), 39.07 (d, ¹J_{PC}=129.1 Hz, P=C), 39.41 (d, ³J_{PC}=3.9 Hz, CH(CNCO₂Et)), 45.37 (d, ²J_{PC}=14.8 Hz, P=C-CH), 61.85 (s, OCH₂CH₃), 77.38 and 80.92 (2s, 2x OCMe₃), 117.95 (s, CN), 126.49 (d, ¹J_{PC}=92.4 Hz, C_{ipso}), 128.36 (d, ³J_{PC}=11.9 Hz, C_{meta}), 131.96 (d, ⁴J_{PC}=2.4 Hz, C_{para}), 134.24 (d, ²J_{PC}=9.5 Hz, C_{ortho}), 166.40 (C=O, CO₂Et), 168.57 (d, ²J_{PC}=12.3 Hz, P-C=C), 171.96

(d, $^3J_{\text{PC}}=5.0$ Hz, C=O). ^{31}P NMR (121.5 MHz): δ 22.56 ($\text{Ph}_3\text{P}^+-\text{C}$). **Minor isomer (E)- 3f** (30%): ^1H NMR (300.1 MHz), δ 1.41 and 1.45 (18H, 2s, 2x CMe_3), 1.21 (3H, t, $^3J_{\text{HH}}=7.1$ Hz, OCH_2CH_3), 2.91 (1H, dd, $^3J_{\text{HH}}=10.8$ Hz, $^3J_{\text{PH}}=17.1$ Hz, $\text{P}=\text{C}-\text{CH}$), 4.10 (2H, m, ABX₃ system, OCH_2CH_3), 4.71 (1H, d, $^3J_{\text{HH}}=10.8$ Hz, $\text{CH}(\text{CNCO}_2\text{Et})$), 7.51–7.81 (15x H_{arom} , m, 3x C_6H_5). ^{13}C NMR (75.5 MHz), δ 13.75 (s, OCH_2CH_3), 28.17 and 28.84 (2s, 2x CMe_3), 40.48 (d, $^3J_{\text{PC}}=3.9$ Hz, $\text{CH}(\text{CNCO}_2\text{Et})$), 41.01 (d, $^1J_{\text{PC}}=136.3$ Hz, $\text{P}=\text{C}$), 44.28 (d, $^2J_{\text{PC}}=14.7$ Hz, $\text{P}=\text{C}-\text{CH}$), 62.08 (s, OCH_2), 77.63 and 80.86 (2s, 2x OCMe_3), 117.37 (s, CN), 127.16 (d, $^1J_{\text{PC}}=92.5$ Hz, C_{ipso}), 128.52 (d, $^3J_{\text{PC}}=11.5$ Hz, C_{meta}), 131.96 (d, $^4J_{\text{PC}}=2.4$ Hz, C_{para}), 134.11 (d, $^2J_{\text{PC}}=9.4$ Hz, C_{ortho}), 166.08 (C=O), 170.07 (d, $^2J_{\text{PC}}=17.9$ Hz, $\text{P}-\text{C}=\text{C}$), 171.79 (d, $^3J_{\text{PC}}=5.2$ Hz, C=O). ^{31}P NMR (121.5 MHz): δ 22.40 ($\text{Ph}_3\text{P}^+-\text{C}$).

Acknowledgements

The authors gratefully acknowledge financial support from the Research Council of the University of Sistan & Baluchestan.

References

1. (a) Engel, R. *Synthesis of Carbon–Phosphorus Bonds*; CRC: Boca Raton, FL, 1988. (b) Maryano, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, 89, 863. (c) Bestmann, H. J.; Vostrowsky, O. *Top. Curr. Chem.* **1983**, 109, 86. (d) Grayson, M.; Griffith, E. J. *Topics in Phosphorus Chemistry*; Interscience: New York, 1972; Vol. 7. (e) Yavari, I.; Maghsoodlou, M. T. *Tetrahedron Lett.* **1998**, 39, 4579. (f) Yavari, I.; Islami, M. R.; Bijanzadeh, H. R. *Tetrahedron Lett.* **1999**, 55, 5547.
2. (a) Ware, E. *Chem. Rev.* **1950**, 403. (b) Spinks, A.; Waring, W. S. *Prog. Med. Chem.* **1963**, 3, 313. (c) Mizuno, T.; Kino, T.; Ito, T.; Miato, T. *Synth. Commun.* **2000**, 30, 1675. (d) Engel, R. *Chem. Rev.* **1977**, 77, 349. (e) Wittig, G. *Science* **1980**, 210, 600.
3. Kolodiazny, O. I. *Russ. Chem. Rev.* **1997**, 66, 225.
4. Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, 94, 1375.
5. (a) Yavari, I.; Nasiri, F.; Djahaniani, H. *Phosphorus, Sulfur, and Silicon*, **2003**, 178, 2627. (b) Yavari, I.; Bayat, M. *Tetrahedron Lett.* **2003**, 59, 2001.
6. Cadogan, J. I. G. *Organophosphorus Reagents in Organic Synthesis*, Academic Press: New York, 1979.
7. Quin, L. D. *A Guide to Organophosphorus Chemistry*, Wiley–Interscience, New York, 2000.
8. Hudson, H. R. *The Chemistry of Organophosphorus Compounds, Primary, Secondary, and Tertiary Phosphates and Heterocyclic Organophosphorus (III) Compounds*, Hartley, F. R., Ed.; Wiley: New York, 1990; Vol. 1, pp 382–472.
9. Nicolaou, K. C.; Harter, M. W.; Gunzner, J. L.; Nadin, A. *Liebigs Annalen* **1997**, 7, 1283.

10. Johnson, A. W. *Ylide Chemistry*, Academic Press, London, 1966.
11. Corbridge, D. E. C. *Phosphorus: an Outline of Chemistry, Biochemistry and Uses*, 5th Edn.; Elsevier: Amsterdam, 1995.
12. Maghsoodlou, M. T.; Hazeri, N.; Habibi Khorassani, S. M.; Nassiri, M.; Marandi, G.; Afshari, G.; Niroumand, U. *J. Sulfur Chem.* **2005**, 26, 261.
13. Islami, M. R.; Mollazehi, F.; Badiei, A.; Sheibani, H. *ARKIVOC* **2005**, (xv), 25.
14. Maghsoodlou, M. T.; Hazeri, N.; Habibi Khorassani, S. M.; Afshari, G.; Nassiri, M.; *J. Chem. Res. (S)* **2005**, 727.
15. Hazeri, N.; Habibi Khorassani, S. M.; Maghsoodlou, M. T.; Marandi, G.; Nassiri, M.; Gulam-Shahzadeh, A. *J. Chem. Res. (S)*. **2006**, 215.
16. Maghsoodlou, M. T.; Saghatforoush, L.; Aminkhani, A.; Marandi, G.; Kabiri, R. *J. Sulfur Chem.* **2006**, 27, 583.
17. Maghsoodlou, M. T.; Hazeri, N.; Habibi Khorassani, S. M.; Kakaei, R.; Nassiri, M.; Marandi, G.; Moeeni, Z.; Niromand, U.; Z. Eskandari-Torbaghan, *Phosphorus, Sulfur, and Silicon* **2006**, 181, 865.
18. Kalantari, M.; Islami, M. R.; Hassani, Z.; Saidi, K. *ARKIVOC* **2006**, (x), 55.
19. Hassani, Z.; Islami, M. R.; Sheibani, H.; Kalantari, M.; Saidi, K. *ARKIVOC* **2006**, (i), 89.
20. Maghsoodlou, M. T.; Hazeri, N.; Habibi Khorassani, S. M.; Saghatforoush, L.; Rofouei, M. K.; Rezaie, M. *ARKIVOC* **2006**, (xiii), 117.
21. Maghsoodlou, M. T.; Habibi Khorassani, S. M.; Hazeri, N.; Nassiri, M. *Phosphorus, Sulfur, and Silicon* **2006**, 181, 1363.
22. Esmaili, A. A.; Ghoreghloo, M.; Islami, M. R.; Bijanzadeh, H. R. *Tetrahedron* **2003**, 59, 4785.
23. Bestmann, H. J.; Joachim, G.; Lengyel, T.; Oth, J. F.; Merenyi, R.; Weitkamp, H. *Tetrahedron Lett.* **1966**, 3355.
24. Islami, M. R.; Yavari, I.; Tikdari, A. M.; Ebrahimi, L.; Razee, S.; Bijanzadeh, H. R. *Russ. Chem. Bull.* **2002**, 51, 2244.