Efficient Synthesis of Stable Phosphonate Ylides and Phosphonate Esters: Reaction Between Activated Acetylenes and Triphenylphosphite in the Presence of Sulfonamide and Heterocyclic NH-Acids

Faramarz Rostami Charati[*,1], Malek Taher Maghsoodlou[2], Sayyed Mostafa Habibi-Khorassani[2], Nourallah Hazeri[2], Ali Ebrahimi[2], Zinatossadat Hossaini[3], Pouneh Ebrahimi[1], Nariman Maleki[2], Sayyed Reza Adhamdoust[2], Fatemeh Vasheghani-Farahani[2], Ghasem Marandi[2], Alexandre Sobolev[4] and Mohamed Makha[4]

[1]*Faculty of Basic Science, Gonbad Institutes of Higher Education, P.O. Box 163, Gonbad, Iran*

[2]*Department of Chemistry, The University of Sistan and Baluchestan, P.O. Box 98135-674, Zahedan, Iran*

[3]*Department of Chemistry, Islamic Azad University, Qaemshahr Branch, P.O.Box 163, Qaemshahr, Iran*

[4]*School of Biomedical, Biomolecular and Chemical Sciences, M310, University of Western Australia, Perth, WA 6009, Australia*

Abstract: An efficient synthesis of stable phosphonate ylides and phosphonate esters is described *via* a one-pot reaction between activated acetylenes and triphenylphosphite in the presence of sulfonamides and heterocyclic NH-acids. Single X-ray diffraction analysis and NMR studies were used in characterizing the ylides and phosphonate ester products. Dynamic NMR studies performed on a phosphonate ylide allowed the calculation of the free energy barrier for the inter-conversion between the geometrical isomers (*E*) and (*Z*).

Keywords: Dialkyl acetylenedicarboxylates, sulfonamide NH-acids, heterocyclic NH-acids, triphenylphosphite, phosphonate ylide, dynamic NMR.

1. INTRODUCTION

Phosphorus ylides are important class of organic compounds due to their applications in organic synthesis [1-6], especially for the preparation of naturally occurring products of biological and pharmacological activity [7-18]. Phosphorus ylides chemistry has contributed to the development of modern synthetic chemistry of naturally and physiologically active molecules [18]. These compounds are widely used reagents as synthetic building blocks in the formation of carbon-carbon double bonds. This has awakened interest in the study of the synthesis, structure and properties of phosphorus ylides and their derivatives [19]. In the course of our investigations to develop syntheses of organophosphorus compounds [20-30], we successfully synthesised a new class of stable phosphonate ylides, **4** which was undertaken from the reaction between triphenylphosphite **1** and acetylenic esters **2** in the presence of sulfonamides **3**. Subsequently, the hydrolysis of the phosphonate ylides, **4** afforded the corresponding phosphonate esters, **5** in excellent yields.

2. RESULTS AND DISCUSSION

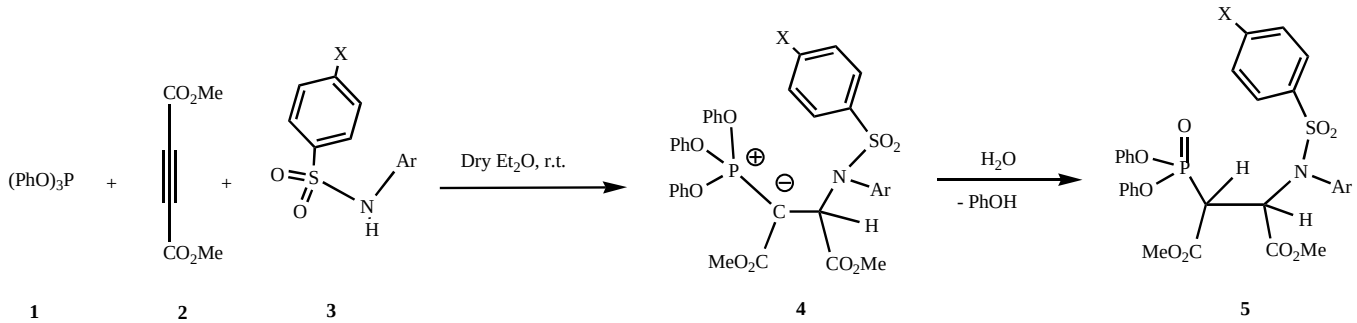
As part of our current studies on the development of new routes in heterocyclic synthesis, we report an efficient procedure for direct synthesis of stable phosphonate ylides, **4** from the reaction of triphenylphosphite **1** and acetylenic esters **2** in the presence of sulfonamides **3** at ambient temperature in diethyl ether as a solvent (Scheme **1**). The major product is the phosphonate ylide **4** and then followed by the hydrolysis reaction leads to the phosphonate esters **5**.

The structures of compounds **4** and **5** were assigned by IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and mass spectral data and confirmed by X-ray diffraction. The ^{1}H NMR spectrum of **4a** exhibited two singlets at 3.57 and 3.63 ppm arising from methoxy protons and a doublet at δ = 6.2 ($^3J_{PH}$ = 6.0 Hz) for the methine proton, along with multiplets at δ = 6.91-7.20 for the aromatic protons. The carbonyl groups resonances in the ^{13}C NMR spectra of **4a** appear at δ = 167.0 (d, $^3J_{PC}$ = 6.8 Hz) and 169.0 (d, $^2J_{PC}$ = 8.2 Hz) ppm. The mass spectrum of **4a** displayed the molecular ion peak at m/z = 685, which are consistent with the 1:1:1 adduct of dimethyl acetylenedicarboxylate, triphenylphosphite, and sulfonamide. The structure of **4a** was further confirmed by a single crystal X-ray diffraction analysis (Fig. **1**). The ^{1}H and ^{13}C NMR spectra of compounds **4b** and **4c** are similar to those of **4a**, except for the aromatic moiety, which exhibited characteristic signals with appropriate chemical shifts (see experimental). Moreover, The structure of **4b** was further confirmed by a single crystal X-ray diffraction analysis (Fig. **1**).

The ^{1}H NMR spectrum of **5c** exhibited two singlets at 3.54 and 3.60 ppm arising from methoxy protons, two doublet of doublet at the δ = 3.75 (dd, 1H, $^2J_{PH}$= 17 Hz, $^3J_{HH}$ = 12 Hz), and δ = 5.72 (dd, 1H, $^3J_{PH}$= 15 Hz, $^3J_{HH}$ = 1.5 Hz), for methine proton, along with multiplets at δ = 6.91-7.70

*Address correspondence to this author at the Faculty of Basic Science, Gonbad Institutes of Higher Education, P.O. Box 163, Gonbad, Iran;
Tel: 0172-2225021; Fax: 0172-2224060;
E-mails: f_rostami_ch@yahoo.com, frostami@gau.ac.ir

1386-2073/11 $58.00+.00



4, 5	Ar	X	%Yield of 4, 5
a	Phenyl	H	85, 80
b	Phenyl	CH_3	90, 85
c	2,6-dimethylphenyl	H	95, 90

Scheme 1. Reaction between triphenylphosphite and acetylenic esters in the presence of sulfonamides.

ppm for the aromatic protons. The carbonyl groups resonances in the ^{13}C NMR spectra of **5c** appear at δ = 165.3 (d, $^{2}J_{CP}$ = 5.5 Hz) and 169.3 (d, $^{2}J_{CP}$ = 2.5 Hz) ppm. The structure of **5c** was further confirmed by a single crystal X-ray diffraction analysis (Fig. **1**).

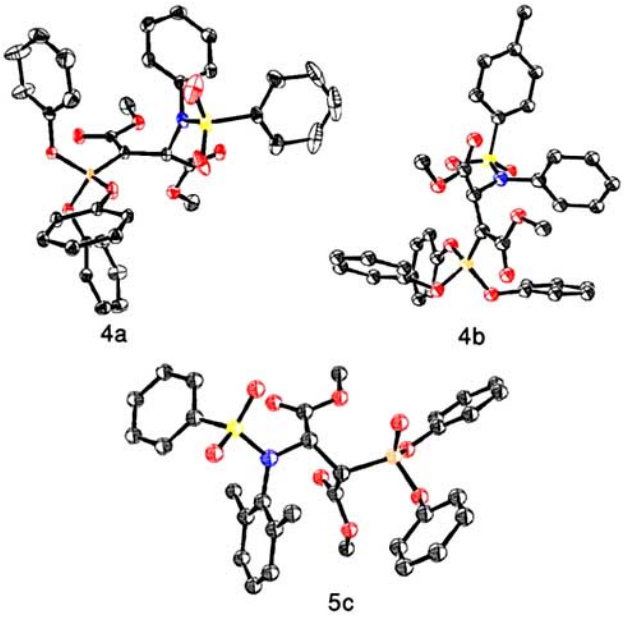


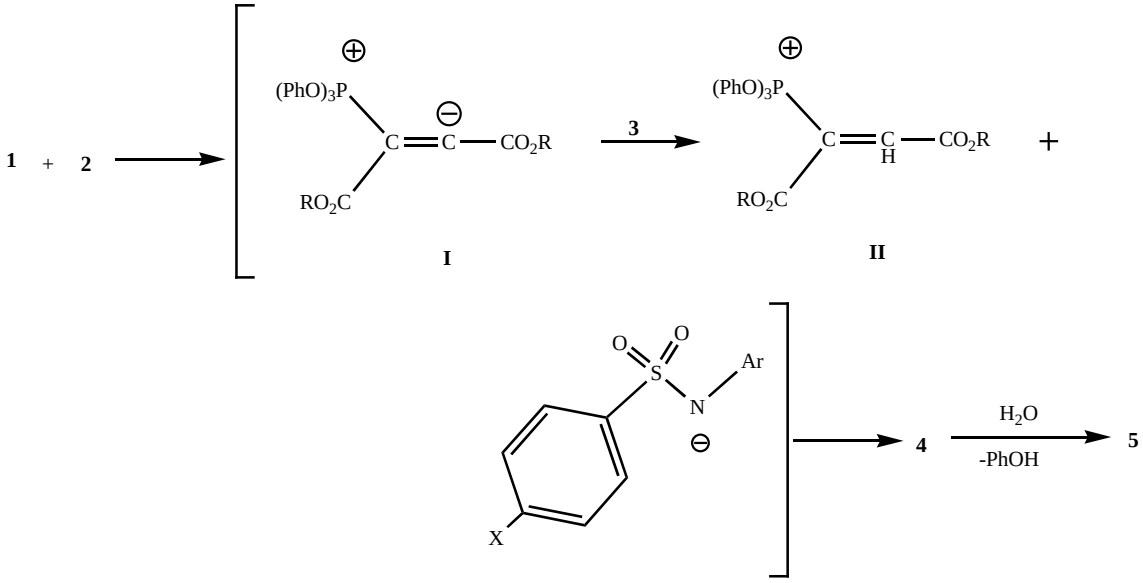
Fig. (1). ORTEP representation of the molecular structure of **4a**, **4b** and **5c**.

Although we have not established the mechanism of the reaction between the triphenylphosphite and the acetylenic esters in the presence of sulfonamide derivatives **3** experimentally, a possible explanation is proposed in Scheme **2**. The initial step may involve addition of triphenylphosphite to the acetylenic ester [31-33], and formation of the 1:1 adducts **I** which protonated by sulfonamide to give a transition state **II**. Subsequently, the positively charged ion **II** is attacked by the anion of the NH-acid **3** to produce ylide **4**, which is hydrolyzed to give phosphonate ester **5**. The hydrolysis of ylide **4** to the corresponding phosphonate ester **5** can be achieved by addition of water to the reaction mixture. Since the reactions were carried out under an ordinary atmosphere, the conversion of ylide **4** to phosphonate ester **5** can also be accomplished by hydrolysis from moisture in air or under chromatographic conditions.

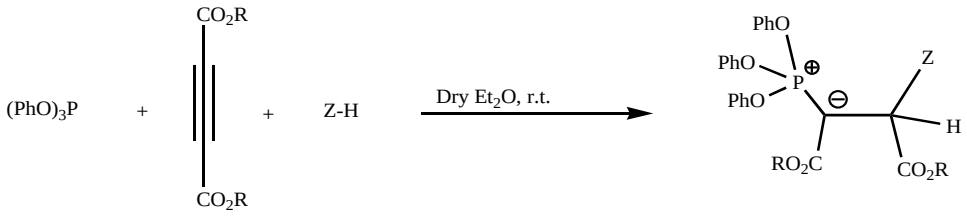
Under similar reaction conditions, the reaction between activated acetylenes **2** and heterocyclic NH-acids **6** in the presence of triphenylphosphite, **1** as a nucleophile leads to functionalized phosphonate ylides **7** in good yields (Scheme **3**).

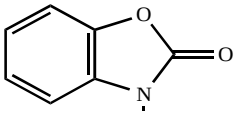
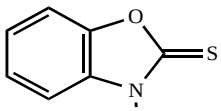
The ^{1}H NMR spectrum of **7a** in $CDCl_3$ shows two singlets at δ = 3.57 and 3.65 ppm for the methoxy protons and a doublet at δ = 6.02 ($^{3}J_{PH}$ = 16.9 Hz) for the methine proton, along with multiplets at δ = 6.98–9.20 for the aromatic protons. At ambient temperature, the ^{1}H NMR spectrum of **7a** in $CDCl_3$ exhibits two sets of methoxy resonances at 3.21 and 3.72 ppm and at 3.09 and 3.77 ppm with a relative intensity ratio of *ca.* 3:1. As the temperature was increased, broadening of the signals occurred (coalescence temperature, 295 ± 1 K). Although an extensive line-shape analysis in relation to the dynamic ^{1}H NMR effect observed for **7a** was not undertaken, the variable temperature spectra allowed the calculation of the free energy barrier for the dynamic NMR process in **7a**. From coalescence of the O-Me proton resonances and using the expression, $k = \pi\Delta\nu/\sqrt{2}$, the first-order rate constant (k) for the dynamic NMR effect in **7a** was calculated to be 55.53 s^{-1} at 295 K (Table **1**). Application of the absolute rate theory with a transmission coefficient of 1 gives a free-energy of activation ($\Delta G\#$) of 62.28 ± 2 $kJ.mol^{-1}$, where all known sources of errors are estimated and included [34].

The *E–Z* isomerism of ylides possessing a carbonyl group at the α-position has been observed previously [10, 35, 36]. Further evidence for the presence of the ylide ester group in **7a** was based on the observation of a strong low-frequency carbonyl absorption at 1667 cm^{-1} in the IR spectrum [10]. The other ester carbonyl absorption in **7a** appears at 1722 cm^{-1}. The ^{13}C and ^{31}P NMR spectra of **7a** also confirmed the presence of two rotational isomers at ambient temperature. Thus, the ^{13}C NMR spectrum consisted of two sets of signals that comprised more than 50 resonances in total. Characteristic carbonyl



Scheme 2. Proposed mechanism for the reaction of triphenylphosphite and acetylenic esters in the presence of sulfonamides.



7	Z	R	%Yield
a		Me	92
b		Et	90
c		Bu^t	85
d		Me	97

Scheme 3. Reaction between triphenylphosphite and acetylenic esters in the presence of NH-acids.

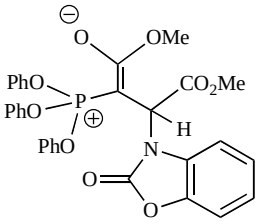
resonances appear clearly at δ = 173.1, 168.4 (d, $^2J_{PC}$ = 17 Hz) and 169.4 (d, $^2J_{PC}$ = 18 Hz) ppm, whereas the ylide carbon atom exhibits resonances at δ = 41.1 (d, $^1J_{PC}$ = 225 Hz) and 41.2 (d, $^1J_{CP}$ = 223 Hz) ppm. The observed $^1J_{CP}$ values are typical of an α-ylide ester [11]. The double bond character of the C–P bond and the presence of three electronegative oxo substituents on the phosphorus atom increases the $^1J_{CP}$ value [37].

3. CONCLUSION

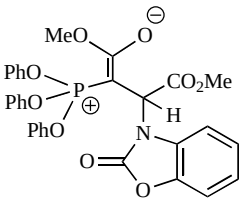
In conclusion, we have found that the reaction of Dialkyl acetylenedicarboxylates with triphenylphosphite in the presence of several NH-acid leads to a facile synthesis of some functionalized phosphonate ylieds and phosphonate esters. Also, dynamic NMR effect is observed in the 1H NMR spectra of some phosphonate ylides. The present

Table 1. Selected Proton Chemical Shifts (at 500.1 MHz, in ppm, Me_4Si) and Calculated Activation Parameters (kJ.mol^{-1}) for 7a in $CDCl_3$

Compound	Temp (˚C)	δ (OMe)	δ (CH)	Δν (Hz)	k (s^{-1})	T_C (K)	$\Delta G^{\neq}$ (kJ. mol^{-1})	$\Delta H^{\neq}$ (kJ. mol^{-1})	$\Delta S^{\neq}$ (kJ. mol^{-1})
7a	7	3.57 3.62	----	25	55.53	295	62.28 ± 2	48.82 ± 2	-0.376 ± 2
	2	----	5.94 6.01	35	77.74	290	60.37 ± 2		



(*E*)-**7a**



(*Z*)-**7a**

Scheme 4. Geometrical isomers (*E*)-**7a** and (*Z*)-**7a**.

method is advantageous because the reaction is performed under neutral conditions and the reagents can be used without prior activation or modification.

Material and Methods

Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MATT 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-500 AVANCE spectrometer at 500.1, 125.8, and 202.4 MHz, respectively. ^{1}H, ^{13}C, and ^{31}P spectra were obtained for solutions in CDCl3 using TMS as internal standard or 85% H_3PO_4 as external standard. All the chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification.

These results were rationalized on the basis of the presence of geometrical isomers (*E*)-**7a** and (*Z*)-**7a** (see Scheme **4**) that undergo rapid interconversion at 295 K.

General Procedure

To a magnetically stirred a solution of dialkyl acetylendicarboxylate **2** (2 mmol) and sulfonamide **3** (2 mmol) was added triphenylphosphite (0.62 g, 2 mmol) **1** slowly at room temperature in dry diethyl ether as a solvent. The reaction mixture was stirred for 2 hours at room temperature. The resultant precipitate was collected and washed with cooled *n*-Hexane and diethyl ether (3×5 mL) to yield the phosphonate ylide **4**. The phosphonate ester **5** is resulted if few drops of distilled water added to the reaction mixture after 2 hours reaction or by leaving the reaction mixture exposed to air for a week. The work-up followed removal of the solvent under reduced pressure and the resultant yellow residue was collected and crystallized from ether/*n*-Hexane (4:1).

Dimethyl 2-(2-Oxo-2,3-Dihydro-1,3-Benzoxazol-3-yl)-3-(Triphenoxyphosphanylidene) Butandioate (4a)

White powder, yield 85%, mp 140-142°C, IR (KBr) (ν_{max}, cm^{-1}): 1745, 1638 (C=O). MS, (*m/z*, %): 685 (M^+, 5), 592 (M^+- OPh, 90), 499(M^+-2Oph, 55), 406 (-P(OPh)$_3$), 60. Anal. Calcd for $C_{36}H_{32}NO_9PS$ C, 63.06; H, 4.70; N, 2.04, Found: C, 63.1; H, 4.77; N, 2.12. ^{1}H NMR (500.1 MHz, $CDCl_3$): 3.57 and 3.63 (6H, 2s, 2O*CH*$_3$), 6.2 (1H, d, $^{3}J_{PH}$ = 6.0 Hz, P^+-C$^-$-C*H*), 6.90-7.20 (25H$_{arom}$, 5C$_6$H$_5$). ^{13}C NMR (125.8 MHz, $CDCl_3$), δ_C 43.12 (d, $^{1}J_{PC}$ = 226.03 Hz P^+-C$^-$), 53.21 and 52.40 (2O*C*H$_3$), 55.20 (d, $^{2}J_{PC}$ = 15.01 Hz, P^+-C$^-$-*C*H), 113.5, 115.9, 121.02 (d, $^{3}J_{PC}$ = 4.5 Hz, C$_{ortho}$), 127.3 (C$_{para}$), 129.1 (C$_{metha}$), 130.2, 138.4, 139.7, 152.3 (d, $^{2}J_{PC}$ = 6.2 Hz, C$_{ipso}$), 167.0 (d, $^{3}J_{PC}$ = 6.8 Hz, C=O), 169.0 (d, $^{2}J_{PC}$ = 8.2 Hz, C=O): ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 40.70 [$(PhO)_3P^+$-C$^-$].

The X-ray diffracted intensities were measured from a single crystal 0.40 x 0.36 x 0.32 mm at about 100 K on an Oxford Diffraction Xcalibur-S CCD diffractometer using monochromatized Cu-K_α (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects and absorption correction applied using multiple symmetry equivalent reflections. The structure were solved by direct method and refined on F^2 using SHELX-97 crystallographic package. A full matrix least-squares refinement procedure was used, minimizing $w(F_o^2-F_c^2)$, with $w = [\sigma^2(F_o^2)+(AP)^2+BP]^{-1}$, where $P= (F_o^2+2F_c^2)/3$. Agreement factors ($R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ and GOF = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ are cited, where n is the number of reflections and p the total number of parameters refined). All non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms were localized from difference Fourier synthesis and their atomic parameters were constrained to the bonded atoms during the refinement.

Crystal/Refinement Details

$C_{36}H_{32}NO_9PS$, M = 685.66, F(000) = 2864 e, monoclinic, $C2/c$ (No. 15), Z = 8, T = 100(2) K, a = 22.7564(2), b = 21.5187(2), c = 15.4042(1) Å, β = 120.563(1) °, V = 6495.27(9) Å^3; D_c = 1.402 g cm^{-3}; $\sin\theta/\lambda_{max}$ = 0.7035; N(unique) = 9469 (merged from 102564, R_{int} = 0.0281, R_{sig} = 0.0199), N_o ($I > 2\sigma(I)$) = 7234; R = 0.0406, $wR2$ = 0.1119 (A,B = 0.08, 3.50), GOF = 1.007; $|\Delta\rho_{max}|$ = 0.47(6) e Å^{-3}. CCDC 729585

Dimethyl 2-(N-p-Toluenesulfonyl-N-Phenyl-3-yl)-3-(Triphenoxyphosphanylidene) Butandioate (4b)

White powder, yield 70, R (KBr) (ν_{max}, cm^{-1}): 1755, 1650(C=O). NMR (500.1 MHz, $CDCl_3$): 2.4 (s, -CH3), 3.50 and 3.68 (6H, 2s, 2O*CH*$_3$), 62.3 (1H, d, $^{3}J_{PH}$ = 7.4 Hz, P^+-C$^-$-C*H*), 6.80-7.30 (24H$_{arom}$, 5C$_6$H$_5$).

The X-ray diffracted intensities were measured from a single crystal (**4b**) of 0.26 x 0.15 x 0.07 mm at about 100 K on an Oxford Diffraction Gemini-R Ultra CCDC diffract meter using a Mo-K_α (λ = 0.71073 Å.) Data were corrected for Lorentz and polarization effects and analytical absorption correction. The structure were solved by direct method and

refined on F^2 using SHELX-97 crystallographic package. A full matrix least-squares refinement procedure was used, minimizing $w(F_o^2-F_c^2)$, with $w = [\sigma^2(F_o^2)+(AP)^2+BP]^{-1}$, where $P= (F_o^2+2F_c^2)/3$. Agreement factors ($R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ and GOF = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ are cited, where n is the number of reflections and p the total number of parameters refined). All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were localized from difference Fourier synthesis and refined with constrains to the bonded atoms.

$C_{37}H_{34}NO_9PS$, M = 699.68, F(000) = 732 e, triclinic, P-1 (No. 2), Z = 2, T = 100(2) K, a = 10.7430(4), b = 10.8875(4), c = 15.1457(9) Å, α = 105.338(4), β = 96.991(4), γ = 99.420(3) °, V = 1659.83(13) Å^3; D_c = 1.400 g cm^{-3}; $\sin\theta/\lambda_{max}$ = 0.6497; N(unique) = 7595 (merged from 38528, R_{int} = 0.0744, R_{sig} = 0.0930), N_o ($I > 2\ \sigma(I)$) = 4587; R = 0.1188, $wR2$ = 0.3575 (A,B = 0.06, 42.5), GOF = 1.006; $|\Delta\rho_{max}|$ = 1.5(2) e Å^{-3}, CCDC 715538.

Dimethyl 2-(N-Benzensulfonyl-N-2,6 Dimethyl phenyl-3-yl)-3-(Triphenoxyphosphanylidene) Butandioate (4c)

IR (KBr) (ν_{max}, cm^{-1}): 1745, 1655 (C=O). NMR (500.1 MHz, $CDCl_3$): 2.4 and 2.6 (2 CH3), 3.2 and 3.8 (6H, 2s, 2O*CH*$_3$), 6.2 (1H, d, $^3J_{PH}$ = 6.0 Hz, P$^+$-C$^-$-C*H*), 6.90-7.20 (23H$_{arom}$).

Dimethyl-N-(Phenylsulfonamino-N-yl)-3-(Diphenoxyphosphoryl)Butanedioate (5a)

Colorless crystals, 0.53 g, yield 70%, m.p. 125-127 °C. IR (KBr) (ν_{max}, cm^{-1}): 2946 (SO_2), 1745, 1638 (2 C=O of esters), 1588 (C=C). MS, (*m/z*, %): 609 (M$^+$, 100). Anal. Calcd for $C_{30}H_{28}NO_9PS$ C, 59.11; H, 4.63; N, 2.30; Found: C, 59.18; H, 4.71; N, 2.24. ^{1}H NMR (500.1 MHz, $CDCl_3$): 3.6 (s, 3H, OCH_3), 3.8(s, 3H, OCH_3), 3.99 (dd, 1H, $^2J_{PH}$ = 22.5 Hz, $^3J_{HH}$ = 11.5 Hz), 5.9 (dd, 1H, $^3J_{PH}$ = 8.8 Hz, $^3J_{HH}$ = 11.5 Hz), 7.0 - 7.4 (m, 20H, Aromatic region). ^{13}C NMR (75 MHz, $CDCl_3$): δ 48.4 (d, $^1J_{CP}$ = 130.5 Hz, P-^{13}CH), 52.6, 53.2 (2×s, 2OCH_3), 60.9 (d, $^2J_{CP}$ = 2.6 Hz, P-CH-^{13}CH), 120.2 (d, $^3J_{CP}$ = 4.5 Hz, C_{ortho} of C_6H_5) 120.6, 120.7 (d, $^3J_{CP}$ = 4.5 Hz, C_{ortho} of C_6H_5), 125.6, 125.7 (2 C_{para} of 2C_6H_5), 128.4, 128.5 (2C_{meta} of 2C_6H_5), 129.3, 129.6, 129.7, 129.9, 133.1 135, 139, 150.0 (d, $^2J_{CP}$ = 9.6 Hz, C_{ipso} of C_6H_5), 150.2 (d, $^3J_{CP}$ = 9.4 Hz, C_{ipso} of C_6H_5), 166.0 (d $^2J_{CP}$ = 6.7 Hz, C=O ester), 168.4 (s, C=O ester), ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 11.5 [-$(PhO)_2{}^{31}PO$].

Dimethyl-N-(Methylphenylsulfonamino-N-yl)-3-(Diphenoxyphosphoryl)Butanedioate (5b)

Colorless crystals, 0.53 g, yield 70%, m.p. 125-127 °C. IR (KBr) (ν_{max}, cm^{-1}): 2946 (SO_2), 1745, 1638 (2 C=O of esters), 1588 (C=C). MS, (*m/z*, %): 623 (M$^+$, 80), 530 (M$^+$-OPh, 40). Anal. Calcd for $C_{31}H_{30}NO_9PS$ C, 59.71; H, 4.85; N, 2.25;, Found: C, 59.80; H, 4.80; N, 2.19.

^{1}H NMR (500.1 MHz, $CDCl_3$): 2.3 (s, 3H, -CH_3), 3.6 (s, 3H, OCH_3), 3.8 (s, 3H, OCH_3), 3.99 (dd, 1H, $^2J_{PH}$ = 22.5 Hz, $^3J_{HH}$ = 11.5 Hz), 5.9 (dd, 1H, $^3J_{PH}$ = 8.8 Hz, $^3J_{HH}$ = 11.5 Hz), 7.0 - 7.4 (m, 19H, Aromatic region). ^{13}C NMR (75 MHz, $CDCl_3$): δ 48.4 (d, $^1J_{CP}$ = 130.5 Hz, P-^{13}CH), 52.6, 53.2 (2×s, 2OCH_3), 60.9 (d, $^2J_{CP}$ = 2.6 Hz, P-CH-^{13}CH), 120.2 (d, $^3J_{CP}$ = 4.5 Hz, C_{ortho} of C_6H_5) 120.6, 120.7 (d, $^3J_{CP}$ = 4.5 Hz, C_{ortho} of C_6H_5), 125.6, 125.7 (2 C_{para} of 2C_6H_5), 128.4, 128.5 (2C_{meta} of 2C_6H_5), 129.3, 129.6, 129.7, 129.9, 133.1 135, 139, 150.0 (d, $^2J_{CP}$ = 9.6 Hz, C_{ipso} of C_6H_5), 150.2 (d, $^3J_{CP}$ = 9.4 Hz, C_{ipso} of C_6H_5), 166.0 (d $^2J_{CP}$ = 6.7 Hz, C=O ester), 168.4 (s, C=O ester), ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 11.8 [-$(PhO)_2{}^{31}PO$].

Dimethyl-N-(1,6-Dimethylphenylsulfonamino-N-yl)-3-(Diphenoxyphosphoryl) Butenedioate (5c)

Colurless crystals, 0.53 g, yield 70%, m.p. 168-170 °C. IR (KBr) (ν_{max}, cm^{-1}): 2951 (SO_2), 1781 and 1750 (2 C=O of esters), 1591 (C=C). MS, (*m/z*, %): 637 (M$^+$, 80), 544 (M$^+$-OPh, 95), 45160 (M$^+$-2Oph, 55). Anal. Calcd for $C_{32}H_{32}NO_9PS$ C, 60.28; H, 5.06; N, 2.20; Found: C, 60.65; H, 5.40; N, 2.18. ^{1}H NMR (500.1 MHz, $CDCl_3$): 1.78, 1.79 (2×s, 6H, 2CH_3), 3.5(s, 3H, OCH_3), 3.6 (s, 3H, OCH_3), 3.75 (dd, 1H, $^2J_{PH}$ = 17 Hz, $^3J_{HH}$ = 12 Hz), 5.7 (dd, 1H, $^3J_{PH}$ = 15 Hz, $^3J_{HH}$ = 1.5 Hz), 6.9-7.7 (m, 18H, Aromatic region). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.7, 19.7 (2×s, 2CH_3), 46.5 (d, $^1J_{CP}$ = 130.9 Hz, P-^{13}CH), 52.6, 52.9 (2×s, 2OCH_3), 60.4 (d, $^2J_{CP}$ = 4 Hz, P-CH-^{13}CH), 120.3 (d, $^3J_{CP}$ = 4.9 Hz, C_{ortho} of C_6H_5), 120.6, 121 (d, $^3J_{CP}$ = 4.3 Hz, C_{ortho} of C_6H_5), 125.5, 125.6 (2 C_{para} of 2C_6H_5), 128.4, 129.0 (2C_{meta} of 2C_6H_5), 129.4, 129.5, 129.8, 130.1, 132.9, 134.2, 137.9, 140.1, 141.9, 142.4, 149.9 (d, $^2J_{CP}$ = 7.7 Hz, C_{ipso} of C_6H_5), 150.5(d, $^3J_{CP}$ = 9.5 Hz, C_{ipso} of C_6H_5), 165.3 (d $^2J_{CP}$ = 5.5 Hz, C=O ester), 169.3 (s, C=O ester).

X-Ray Crystallography (5c): Crystal/Refinement Details

The X-ray diffracted intensities were measured from a single crystal (**5c**) of 0.33 x 0.23 x 0.11 mm at about 100 K on an Oxford Diffraction Xcalibur-S CCDC diffractometer using monochromatized Mo-K_α (λ = 0.71073 Å.) Data were corrected for Lorentz and polarization effects and absorption correction applied using multiple symmetry equivalent reflections. The structure were solved by direct method and refined on F^2 using SHELX-97 crystallographic package. A full matrix least-squares refinement procedure was used, minimizing $w(F_o^2-F_c^2)$, with $w = [\sigma^2(F_o^2)+(AP)^2+BP]^{-1}$, where $P= (F_o^2+2F_c^2)/3$. Agreement factors ($R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ and GOF = $\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ are cited, where n is the number of reflections and p the total number of parameters refined). All non-hydrogen atoms were refined anisotropically using all reflections. Positions of hydrogen atoms were localized from difference Fourier synthesis and their atomic parameters were constrained to the bonded atoms during refinement.

$C_{32}H_{32}NO_9PS$, M = 637.62, F(000) = 1336 e, triclinic, P-1 (No. 2), Z = 4, T = 100(2) K, a = 8.2746(1), b = 16.2970(2), c = 23.2316(4) Å, α = 80.451(1), β = 89.518(1), λ= 87.915(1) °, V = 3087.35(8) Å^3; D_c = 1.372 g cm^{-3}; μ_{Mo} = 0.213 mm^{-1}; $\sin\theta/\lambda_{max}$ = 0.7035; N(unique) = 17954 (merged from 91069, R_{int} = 0.0516, R_{sig} = 0.0669), N_o ($I > 2\ \sigma(I)$) = 12181; R = 0.0690, $wR2$ = 0.1781 (A,B = 0.04, 4.7), GOF = 1.002; $|\Delta\rho_{max}|$ = 0.89(8) e Å^{-3}, CCDC 715537.

General Procedure for Preparation of Compound 7a

To a magnetically stirred solution of 2-benzoxazolinone (0.28 g, 2mmol) and triphenylphosphite (0.62 g, 2 mmol) in 10 mL of dry diethyl ether, dimethyl acetylenedicarboxylate (0.28 g, 2 mmol) was added slowly. After approximately 2-3

h stirring at room temperature, the product was filtered and washed with cold diethyl ether (3×5 mL) and it was obtained as:

Dimethyl 2-(2-Oxo-2,3-Dihydro-1,3-Benzoxazol-3-yl)-3-(Triphenoxyphosphanylidene)Butandioate (7a)

White powder, yield 92%, mp 126-128 °C, IR (KBr) (ν_{max}, cm^{-1}): 1766, 1748 and 1661 (C=O). MS, (*m/z*, %): 587(M^+, 4), 494 (M^+- OPh, 87), 401(M^+-2Oph, 74), 310 ($P(OPh)_3$, 59). Anal. Calcd for $C_{31}H_{26}NO_9P$ C, 63.41; H, 4.52; N, 2.37, Found: C, 63.37; H, 4.43; N, 2.40. ^{1}H NMR (500.1 MHz, $CDCl_3$): 3.57 and 3.65 (6H, 2s, 2O*CH*$_3$), 6.02 (1H, d, $^3J_{PH}$ = 17.0 Hz, P^+-C^--C*H*), 6.91-7.21 (19H$_{arom}$, $3C_6H_5$ and $C_7H_4NO_2$). ^{13}C NMR (125.8 MHz, $CDCl_3$), δ_C 44.79 (d, $^1J_{PC}$ = 230.2 Hz P^+-C^-), 50.44 and 52.60 (2O*C*H$_3$), 55.18 (d, $^2J_{PC}$ = 13.8 Hz, P^+-C^--*C*H), 109.07 and 112.98 (2C, $C_7H_4NO_2$), 120.08 (d, $^3J_{PC}$ = 4.5 Hz, C_{ortho}), 121.71 and 123.82 (2C, $C_7H_4NO_2$), 126.08 (C_{para}), 129.34 (1C, $C_7H_4NO_2$), 129.83 (C_{metha}), 142.23 (1C, $C_7H_4NO_2$), 149.68 (d, $^2J_{PC}$ =7.4 Hz, C_{ipso}), 154.32 (1C, $C_7H_4NO_2$), 168.27 (d, $^2J_{PC}$ = 21.4 Hz, C=O), 169.24 (d, $^3J_{PC}$ = 17.6 Hz, C=O): ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 41.88 [$(PhO)_3P^+$-C^-].

Diethyl 2-(2-Oxo-2,3-Dihydro-1,3-Benzoxazol-3-yl)-3-(Triphenoxyphosphanylidene)Butandioate (7b)

White powder, yield 90%; mp 139-141 °C, IR (KBr) (ν_{max}, cm^{-1}): 1766, 1740 and 1659 (C=O). Anal. Calcd for $C_{33}H_{30}NO_9P$ C, 63.92; H, 4.95; N, 2.31, Found: C, 64.39; H, 4.88; N, 2.28. ^{1}H NMR (500.1 MHz, $CDCl_3$): 1.14 and 1.18 (6H, 2t, $^3J_{HH}$ = 6.5 Hz 2OCH$_2$*CH*$_3$), 4.03 and 4.15 (4H, m, 2ABX$_3$ system 2O*CH*$_2$CH$_3$), 6.03 (1H, d, $^3J_{PH}$ = 16.6 Hz, P^+-C^--*CH*), 6.90-7.18 (19H$_{arom}$, m, $3C_6H_5$ and $C_7H_4NO_2$). ^{13}C NMR (125.8 MHz, $CDCl_3$), δ_C 14.11 and 14.84 (2OCH$_2$*CH*$_3$), 44.90 (d, $^1J_{PC}$ = 228.8 Hz, P^+-C^-), 55.28 (d, $^2J_{PC}$ = 13.5 Hz, P^+-C^--*CH*), 59.12 and 61.51 (2O*CH*$_2$CH$_3$), 108.98 and 113.14 (2C, $C_7H_4NO_2$), 119.93 (d, $^3J_{PC}$ = 5.3 Hz C_{ortho}), 121.65 and 123.75 (2C, $C_7H_4NO_2$), 126.07 (C_{para}), 129.43 (1C, $C_7H_4NO_2$), 129.83 (C_{metha}), 142.23 (1C, $C_7H_4NO_2$), 149.66 (d, $^2J_{PC}$ = 7.2 Hz, C_{ipso}), 154.55 (1C, $C_7H_4NO_2$), 167.98 (d, $^2J_{PC}$ = 18.9 Hz, C=O), 168.72 (d, $^3J_{PC}$ = 18.1 Hz, C=O): ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 42.90 [$(PhO)_3P^+$-C^-].

Ditert-Buthyl 2-(2-Oxo-2,3-Dihydro-1,3-Benzoxazol-3-yl)-3-(Triphenoxyphosphanylidene)Butandioate (7c)

White powder, yield 85%; mp 145-147 °C, IR (KBr) (ν_{max}, cm^{-1}): 1766, 1736 and 1661 (C=O). MS, (*m/z*, %): 671 (M^+, 2), 577 (M^+-OPh, 35), 485 (M^+-2Oph, 43), 310 ((OPh)$_3$P, 52): Anal. Calcd for $C_{37}H_{38}NO_9PC$, 65.97; H, 5.73; N, 2.15, Found: C, 66.17; H, 5.66; N, 2.09. ^{1}H NMR (500.1 MHz, $CDCl_3$): 1.38 and 1.42 (18H, 2s, 2 OC(*CH*$_3$)$_3$), 5.96 (1H, d, $^3J_{PH}$ = 16.2 Hz, P^+-C^--*CH*), 6.91-7.26 (19H$_{arom}$, m, $3C_6H_5$ and $C_7H_4NO_2$). ^{13}C NMR (125.8 MHz, $CDCl_3$), δ_C 28.12 and 28.64 (2s, 2OC(*CH*$_3$)3), 45.72 (d, $^1J_{PC}$ = 227.5 Hz, P^+-*C*$^-$), 55.81 (d, $^2J_{PC}$ = 13.9 Hz, P^+-C^--*C*H), 78.81 and 81.67 (2s, 2O*C*(CH$_3$)3), 108.92 and 113.41 (2C, $C_7H_4NO_2$), 119.76 (d, $^3J_{PC}$ = 5.5 Hz, C_{ortho}), 121.53 and 123.71 (2C, $C_7H_4NO_2$), 125.74 (C_{para}), 29.55 (1C, $C_7H_4NO_2$), 129.77 (C_{metha}), 142.19 (1C, $C_7H_4NO_2$), 149.64 (d, $^2J_{PC}$ = 6.7 Hz, C_{ipso}), 154.68 (1C, $C_7H_4NO_2$), 167.30 (d, $^2J_{PC}$ = 20.2 Hz, C=O), 167.49 (d, $^3J_{PC}$ =18.7 Hz, C=O): ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 41.09 [$(PhO)_3P^+$-C^-].

Dimethyl 2-(2-Thioxo-2, 3-Dihydro-1, 3-Benzoxazole-3-yl)-3-(Triphenoxyphosphanylidene)Succinate (7d)

White powder, yield 97%; mp 136-138 °C, IR (KBr) (ν_{max}, cm^{-1}): 1751 and 1666 (C=O). MS, (*m/z*, %): 603 (M^+, 2), 510 (M^+-OPh, 76), 417 (M^+-2Oph, 65), 310 ($P(OPh)_3$, 50). Anal. Calcd for $C_{31}H_{26}NO_8PS$ C, 61.57; H, 4.28; N, 2.39, Found: C, 61.69; H, 4.31; N, 2.32. ^{1}H NMR (500.1 MHz, $CDCl_3$): 3.58 and 3.68 (6H, 2s, 2O*CH*$_3$), 6.84 (1H, d, $^3J_{PH}$ = 19.8 Hz, P^+-C^--C*H*), 6.90-7.32 (19H$_{arom}$, m, $3C_6H_5$ and C_7H_4NOS). ^{13}C NMR (125.8 MHz, $CDCl_3$), δ_C 45.11 (d, $^1J_{PC}$ = 225.2 Hz, P^+-*C*$^-$), 53.16 and 53.47 (2O*C*H$_3$), 53.63 (d, $^2J_{PC}$ = 11.3 Hz, P^+-C^--*C*H), 110.28 and 110.51 (2C, C_7H_4NOS), 120.66 (d, $^3J_{PC}$ = 4.7 Hz, C_{ortho}), 124.51 and 125.20 (2C, C_7H_4NOS), 125.84 (C_{para}), 129.92 (C_{metha}), 130.12 and 147.16 (2C, C_7H_4NOS), 150.08 (d, $^2J_{PC}$ = 7.3 Hz, C_{ipso}), 167.33 (d, $^2J_{PC}$ = 20.5 Hz, C=O), 168.53 (d, $^3J_{PC}$ =17.9 Hz, C=O), 179.87(1C, C_7H_4NOS) : ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 42.43 [$(PhO)_3P^+$-C^-].

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 729585, 715538 and 715537 for **4a**, **4b** and **5c** respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk), or *via* www.ccdc.cam.ac.uk/data_request/cif

ACKNOWLEDGEMENTS

We gratefully acknowledge financial support from the Research Council of Gonbad High Education Center and great collaboration of Sistan & Baluchestan University and the University of Western Australia (UWA).

REFERENCES

[1] Cambridge, D.E.C. Phosphorus, *An Outline of Chemistry, Biochemistry and Uses*. Elsevier, Amsterdam, **1995**.

[2] Yavari, I.; Esmaili, A.A.; Ramazani, A.; Bolbol-Amiri, A.R. (1997) A facila route to functionalized 1-arylsulfonyl-1,2-dihydroquinolines. *Monatsch Chem.*, **1997**, *128*, 927-973.

[3] Yavari, I.; Islami, M.R. Vinyltriphenylphosphonium salt mediated serendipitous synthesis of a functionalized pyrroloisoindole derivative. New synthesis of trimethyl 5- arylpyrrole-2,3,4-tricarboxylates. *J. Chem. Res. (S)*, **1998**, 166-167.

[4] Ramazani, A.; Bodaghi, A. One-pot, four-component synthesis of dialkyl [indane-1,3-dione-2-ylidene]alkoxysuccinates. *Tetrahedron Lett.*, **2000**, *41*, 567-568.

[5] Kolodiazhnyi, O.I.; Schmutzler, R. Synthesis and properties of phosphorus ylides containing fluorine atoms bonded to phosphorus. *Synlett.*, **2001**, *7*, 1065-1078.

[6] Wang, Z.G.; Zhang, G.T.; Guzei, I.; Verkade, J.G. PhCH=P(MeNCH$_2$CH$_2$)$_3$N: A Novel ylide for quantitative *E* selectivity in the wittig reaction. *J. Org. Chem.*, **2001**, 66, 3521-3524.

[7] Maghsoodlou, M.T.; Hazeri, N.; Habibi-Khorasani, S.M.; Afshari, G.; Nassiri, M. A facial synthesis of stable heterocyclic fused ring phosphorus ylides. *J. Chem. Res.*, **2005**, 727-728.

[8] Johnson, A.W. *Ylide Chemistry*. Academic Press, New York, **1966**.

[9] Yavari, I.; Asghari, V. Stereoselective synthesis of highly functionalized cyclobutenes. A facile route to electron-deficient 1,3-dienes. *Tetrahedron*, **1999**, *55*, 11853-11858.

[10] Yavari, I,; Adib M. Efficient synthesis of 5,6,7-trisubstituted 1*H*-pyrrolizines. *Tetrahedron*, **2001**, *57*, 5873-5878.

[11] Yavari, I.; Baharfar, R. New one-pot synthesis of tetra-alkoxycarbonylallylidenetriphenylphosphoranes. *Tetrahedron Lett.*, **1998**, *39*, 1051.

[12] Hasani, Z.; Islami, M.R.; Sheibani, H.; Kalantari, M.; Saidi, K. A facile one-pot method for preparation of succinic esters containing several functional groups. *Arkivoc.*, **2006**, *I*, 89-94.

[13] Yavari, I.; Islami, M.R.; Bijanzadeh, H.R. A facial synthesis of diastereoisomeric 1,4- diionic organophosphorus compounds. *Tetrahedron*, **1999**, *55*, 5547-5554.

[14] Yavari, I.; Maghsoodlou, M.T. A facial synthesis of stable 1,4-diionic phosphorus compounds. *Tetrahedron Lett.*, **1998**, *39*, 4579-4580.

[15] Yavari, I.; Aghazadeh, M.; Tafazzoli, M. Triphenylphosphine-Catalyzed Simple Synthesis of Dimethyl 1-Aryl-4-ethoxy-5-oxo-4,5-dihydro-1 H -pyrrole-2,3-dicarboxylates. *Phosphorus, Sulfur and Silicon*, **2002**, *177*, 1101-1107.

[16] Ramazani, A.; Kazemizadeh, A.R.; Ahmadi, E.; Noshiranzadeh, N.; Souldozi, A. Synthesis and reactions of stabilized phosphorus ylides. *Curr. Org. Chem.*, **2008**, *12*, 59-82.

[17] Kalantari, M.; Islami, M.R.; Hasani, Z.; Saidi, K. Synthesis of dimethyl-1-(trifluoromethyl)-3H-pyrrolizine-2,3-dicarboxylate using phosphorus compounds. *Arkivoc*, **2006**, (x), 55.

[18] Islami, M.R.; Mollazehi, F.; Sheibani, H. (2005) Serendipitous synthesis of 1,4-benzothiazin derivatives using 2-[(2-aminophenyl) disulfonyl aniline. *Arkivoc*, **2005**, (xy), 25-29.

[19] Kolodiazhnyi, O.I. *Phosphorus Ylides, Chemistry and Application in Organic Synthesis*. Wiley-VCH, New York, **1999**.

[20] Maghsoodlou, M.T.; Hazeri, N.; Habibi-Khorasani, S.M.; Kakaei, R.; Nassiri, M. An efficient synthesis of stable phosphorus ylides derived from pyrazole and indazole. *Phosphorus, Sulfur and Silicon*, **2006**, *181*, 25-30.

[21] Yavari, I.; Djahaniani, H.; Maghsoodlou, M.T.; Hazeri, N. Vinylphosphonium salt mediated efficient synthesis of dialkyl 1H-pyrrolizine-2,3-dicarboxylates. *J. Chem. Res. (S)*, **1999**, 382-383.

[22] Yavari, I.; Bayat, M.; Maghsoodlou, M.T.; Hazeri, N. A simple synthesis of stable phosphoranes derived from imides or acetanilide derivatives. *Phosphorus, Sulfur and Silicon*, **2002**, *177*, 2599-2610.

[23] Yavari, I.; Maghsoodlou, M.T.; Djahaniani, H.; Hazeri, N. A facile synthesis of stable heterocyclic phosphorus ylides. *J. Chem. Res., (S)*, **1999**, 216-217.

[24] Maghsoodlou, M.T.; Hazeri, N.; Habibi-Khorasani, S.M.; Nassiri, M.; Marandi, G.; Afshari, G.; Niroumand, U. An efficient synthesis of stable sulfur-containing phosphoranes derived from 2-mercapto-1-methylimidazole and 2-thiazoline-2-thiol. *J. Sulfur Chem.*, **2005**, *26*, 261-265.

[25] Maghsoodlou, M.T.; Habibi-Khorasani, S.M.; Hazeri, N.; Nassiri, M.; Kakaei, R.; Marandi, G. A simple synthesis of stable phosphoranes derived from imidazole derivatives. *Phosphorus, Sulfur and Silicon*, **2006**, *181*, 553-560.

[26] Habibi-Khorasani, S.M.; Maghsoodlou, M.T.; Hazeri, N.; Nassiri, M.; Marandi, G.; Shahzadeh, A.G. A facile synthesis of stable phosphorus ylides derived from harmin, harman, and carbazole. *Phosphorus, Sulfur and Silicon*, **2006**, *181*, 567-572.

[27] Maghsoodlou, M.T.; Hazeri, N.; Habibi-Khorasani, S.M.; Heydari, R.; Nassiri, M.; Marandi, G.; Moeeni, Z.; Niromand, U.; Eskandari-Torbaghan, Z. An Efficient Synthesis of Stable Phosphorus Ylides Derived from Triphenylphosphine, Dialkyl Acetylenedicarboxylates, and an NH-Acid. *Phosphorus, Sulfur and Silicon*, **2006**, *181*, 865-877.

[28] Saghatforoush, L.; Maghsoodlou, M.T.; Aminkhani, A.; Marandi, G.; Kabiri, R. One-pot synthesis of stable phosphonium ylides using 2-mercaptopyrimidine derivatives. *J. Sulfur Chem.*, **2006**, *27*, 583-588.

[29] Maghsoodlou, M.T.; Hazeri, N.; Habibi-Khorasani, S.M.; Saghatforoush, L.; Rofouei, M.K.; Rezaie, M. Diastereoselective synthesis of phosphonato esters by reaction between triphenylphosphite and acetylenic esters in the presence of NH-acid compounds. *Arkivoc*, **2006**, xiii, 117-123.

[30] Maghsoodlou, M.T.; Habibi-Khorasani, S.M.; Rofouei, M.K.; Adhamdoust, S.R.; Nassiri, M. Triphenylphosphite as a good reagent for the diasteroselective synthesis of phosphonate esters. *Arkivoc.*, **2006**, xii, 145-151.

[31] George, M.; Khetan, V.S.K.; Gupta, R.K. *Adv. Heterocycl Chem.*, **1976**, 19, 354.

[32] Burgada, R.; Leroux, Y.; Zabloka, M.; Elkhoshnieh, Y.U. Synthese et structure d'un trialcoxy-1,1,1 phosphole$_v$ premier modele pentacoordine contant cycle phosphole. *Tetrahedron Lett.*, **1981**, 22, 3533-3536.

[33] Hudson, H.R. The Chemistry of organophosphorus compounds, In: Hantely, F.R.; Ed.; Primary, Secondary and Tertiary Phosphines, Polyphosphines and Heterocyclic Organophosphorus(III) Compounds, A Synthesis of Dialkyl Phosphorylsuccinates, Wiley, New York, **1990**, Vol. 1. p. 1271.

[34] Gunther, H. *NMR Spectroscopy*, 2nd edn, Wiley, New York, 1995, ch. 9.

[35] Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd edn, VCH, New York, 1990, p.250.

[36] Tebby, J.C. In Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis, eds. Verkedeand JG Quin, LD, VCH Publishers, Weinheim, 1987; Ch. *1*, pp. 1-60.

[37] Silverstein, R.M.; Bassler, C.G.; Morrill, T.C. *Spectroscopic Identification of Organic Compounds*. 5th edn, Wiley, New York, **1992**.

Received: May 15, 2010 **Revised: July 9, 2010** **Accepted: July 12, 2010**