Iranian Journal of Organic Chemistry 2 (2009) 92-98

A facile synthesis of diastereoisomeric stable 1,4-diionic and also phosphorus ylides compounds contaning sulfur through the reaction between 1,3-dicarbonyl compounds with activated acetylenic esters in the presence of triphenylphosphine

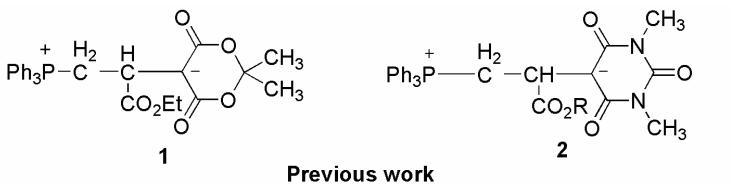
Malek Taher Maghsoodlou, Reza Heydari, Sayyed Mostafa Habibi Khorassani,* Mahmoud Nassiri, Jaber Salehzadeh, Sakineh Mollaee Poor and Mohammad Amin Kazemian
Department of Chemistry, the University of Sistan and Balouchestan, P. O. Box 98135-674, Zahedan, Iran

Abstract: The addition of triphenylphosphine to dialkyl acetylenedicarboxylates in the presence of 1,3-diethyl-2-thiobarbituric acid, cyclohexanone-2-carboxylate or 2-acetylcyclopentanone led to highly functionalized 1,4-diionic organophosphorus compounds and also stable phosphorus ylides respectively. These thio betaines possess two vicinal stereogenic centers and exist as a mixture of two diastereoisomers. The stable phosphorus ylides also 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.

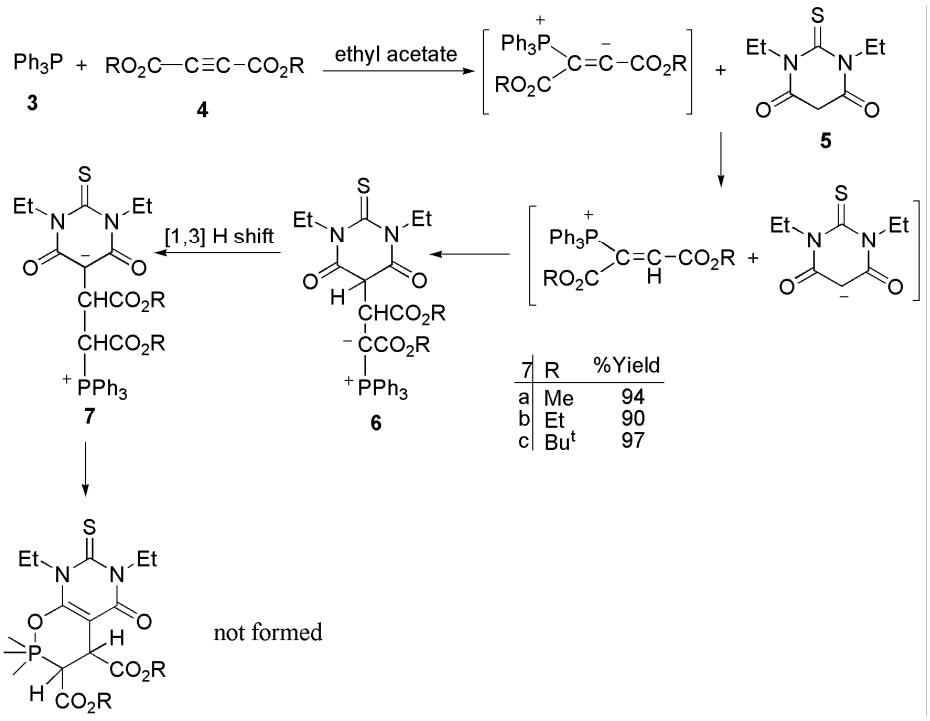
Keywords: Ttriphenylphosphine, Acetylenic ester; 1,3-Dicarbonyl compounds; 1,4-Diionic phosphorus compounds; Stable phosphorus ylides; Diastereoisomer.

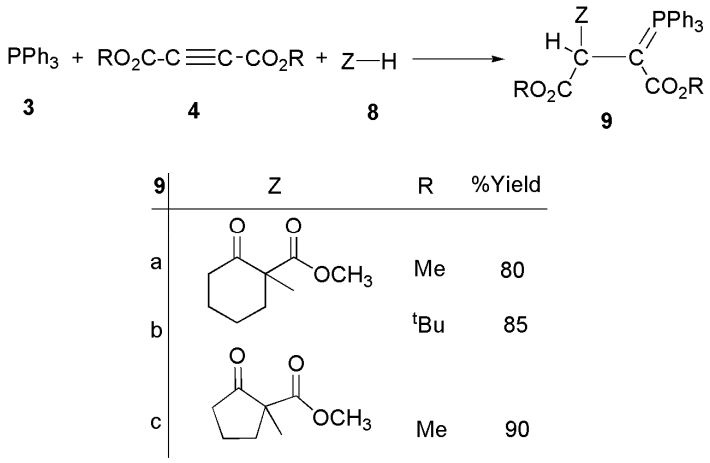
Introduction

In recent years there has been increasing interest in the synthesis of organophosphorus compounds, i.e. those bearing a carbon atom bound directly to a phosphorus atom [1-18] and [30-35]. This interest has resulted from the recognition of the value of such compounds in a wide range of industrial, biological and chemical synthetic aspects [28, 29]. As a result, a large number of methods have appeared novel synthesis of organophosphorus which involve 1,4-diionic phosphorus compounds as elusive transient species [5,19]. In all of the reactions in which this diionic system is postulated, the betaine cannot be isolated but appears to occur as an intermediate on the pathway to an observed product. We have previously described [20-22] the synthesis of stable 1,4-diionic phosphorus compounds **1** from the reaction between triphenylphosphine and ethyl propiolate in the presence of CH-acids. With the purpose of preparation of betaines having two vicinal stereogenic center, such as **2** (see Scheme 1, previous work), The reaction between triphenyl- phosphine **3** and dialkyl acetylenedicarboxylates **4** with 1,3-diethyl-2-thiobarbituri acid **5** was undertaken for generation of 1,4-diionic **7** while stable phosphorus ylides **9** were obtained from reactions between **3**, **4** and **8** in excellent yields (See scheme 1). The thiobarbituric acid moiety and its derivatives have the important pharmaceutical property and they have been used for medicinal chemistry purposes [23].



*Corresponding author. Fax: +(98) 351 8210644; E-mail: *smhabibius@yahoo.com*





Scheme 1

Results and discussion

Reaction between **3**, **4** and **5** produces the hitherto unknown butanedioates **7a-c** in 90-97% yield. All the compounds are stable crystalline solids whose structure is fully supported by elemental analyses and IR, ^{1}H, ^{13}C and ^{31}P NMR spectra and mass spectroscopy data. The mass spectra of these 1:1:1 adducts displayed fairly weak molecular ion peaks. Initial fragmentation involved the loss of ester moieties and scission of the ring. The structure **7a** with addition of six-membered ring as an alternative structure instead of **7** is unlikely because it requires several chemical shift coincidences in the ^{1}H and ^{13}C NMR spectra hence we were to expect a doublet at about δ 160 for the C-O-P moiety in the ^{13}C NMR spectra. Structure **7** was further confirmed by the ^{31}P NMR spectroscopic data (δ=23-25) which is in an agreement with the presence of a Ph_3P^+-C grouping [24,25]. On the basis of the chemistry of trivalent phosphorus nucleophiles [1-5] it is reasonable to assume

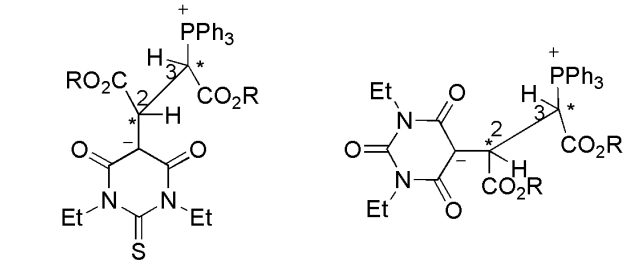
that compound **7** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by CH-acid **5**. Then, the positively charged ion is attacked by the enolate anion of the CH-acid to generate ylide **6**. Compound **6** apparently isomerizes, under the reaction conditions, to produce the 1,4-diionic compound **7**.

The ^{1}H NMR (500 MHz) spectra of compounds **7a-c** displayed signal for vicinal methine protons at δ 4.81-5.91 which appear as two sets of double of doublets for the major and minor diastereoisomers. The vicinal proton-proton coupling constant ($^3J_{HH}$) as a function of torsional angle can be obtained from the Karplus equation [26a,b]. Typically, J_{gauche} varies between 1.5 and 5 Hz and J_{anti} between 9 and 14 Hz. Observation of $^3J_{HH}$ 10.2-12.1 Hz for the vicinal protons in major and minor diastereoisomers of compounds **7a-c** indicates an anti arrangement for these protons. The assignments of the (2S, 3S)-7 and (2R, 3S)-7 configurations of **7a-c** are based on the three-bond carbon-phosphorus coupling, $^3J_{PC}$. Vicinal carbon-phosphorus coupling depends on configuration, as expected, *trans* couplings being larger than *cis* ones. The Karplus relation can be derived from the data for organophosphorus compounds with tetra- and penta- valent phosphorus [27]. The observation of $^3J_{PC}$ of 11-15 Hz for the $C(CO)_2$ group, is in a good agreement with the (2R*, 3R*)-7 for the major diastereoisomer (See experimental section). While measurement of $^3J_{PC}$ of 18-20 Hz for the ester C=O group, is in accord with the (2R*, 3S*)-7 for the minor diastereoisomer (See scheme 2).

On the other hand the reaction of methyl cyclohexanone-2-carboxylate or 2-acetylcyclopentanone **8** with dialkylacetylenedicarboxylates in the presence of triphenylphosphine were proceeded in a mixture of ethyl acetate and n-hexane (2:1) solvent to generate stable phosphorus ylides **9** within 30 minutes at ambient temperature (see Scheme 3). The ^{1}H, ^{13}C, and ^{31}P NMR spectra of ylides **9a**, **9b** and **9c** are consistent with the presence of two isomers. The ylides moiety of these compounds are strongly conjugated with the adjacent carbonyl group and rotation around the partial double bond in (*E*)-**9** and (*Z*)-**9** geometrical isomers is slow on the NMR time scale at ambient temperature (Table 1).

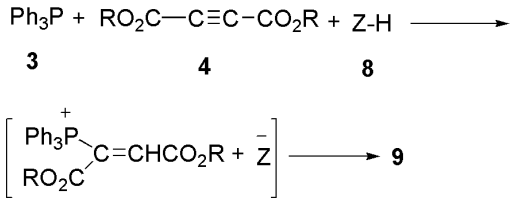
On the basis of the literature data [2,3], it is postulated that phosphorus ylide **9** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the CH-acid to form phosphoranes **9** (see Scheme 1).

In conclusion, we have found that the reaction between dialkyl acetylenedicarboxylates with 1,3-diethyl-2-thiobarbituric acid, cyclohexanone-2-carboxylate or 2-acetylcyclopentanone in the presence of triphenylphosphine leads to the facile synthesis of higly functionalized 1,4-diionic organophosphorus compounds **7a-c** and also stable phosphorus ylides **9a-c** in excellent yields.



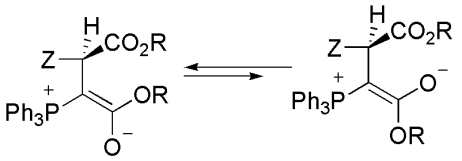
M (2R*, 3R*)-**7**a (or 2S*, 3S*) m (2R*, 3S*)-**7**a (or 2S*, 3R*)

Scheme 2



Scheme 3

Table 1. Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts (δ in ppm) and coupling constants (*J* in Hz) for H-2, OR, CO_2R, C-2, and C-3, in the major (M) and minor (m) diastereoisomers of compounds **9a-c**.



Compound	Isomer (%)	^{1}H NMR data			^{13}C NMR data		^{31}P NMR
		H-2 ($^{3}J_{PH}$)	OR	CO_2R	C-2 ($^{2}J_{PC}$)	C-3 ($^{1}J_{PC}$)	
9a	M (55)	3.46(12.1)	3.20	3.67	47.48(14.2)	37.62(123.7)	24.84
9a	m (45)	3.51(15.3)	3.67	3.70	46.22(12.8)	38.80(122.1)	25.29
9b	M (70)	3.50(19.8)	0.89	1.50	48.15(14.6)	36.62(124.1)	23.24
9b	m (30)	3.44(22.2)	1.40	1.51	46.37(14.8)	37.74(123.9)	25.08
9c	M (56)	3.54(12.5)	2.87	3.74	49.03(13.3)	39.14(121.9)	26.12
9c	m (44)	3.50(7.4)	2.94	3.69	49.80(13.5)	40.56(122.3)	25.39

Experimental

Dialkyl acetylenedicarboxylates, 1,3-diethyl-2-thiobarbituric acid cyclohexanone-2-carboxylate and 2-acetylcyclopentanone were purchased from Fluka (Buchs, Switzerland) and used without further purification. Melting points and IR spectra of all compounds were measured on an Electrotermal 9100 apparatus and a Shimadzu IR-460 spectrometer respectively. Elemental analysis for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. Also the ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a BRUKER DRX-500 AVANCE spectrometer at 500, 125.8 and 202.5 MHz, respectively. In addition, the mass spectra were obtained from a Finigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

Preparation of (2*R**, 3*R**) 1,3-diethyl-4,6-dioxo-2-thioxo-5-[2-(triphenylphosphonio)-1,2-bis(methoxycarbonyl)ethyl] tetrahydropyrimidin-5-ide (7a).

General procedure:

To a magnetically stirred solution of triphenylphosphine (0.26g, 1mmol) and 1,3-diethyl-2-thiobarbituric acid (0.2g, 1mmol) in ethyl acetate (5mL) was added, dropwise, a mixture of dimethyl acetylene-dicarboxylate (0.14g or 1mmol) in ethyl acetate (2mL) over 4min. After 40 min stiring at room temperature, the product was filtered and washed with cold diethyl ether (3×5 mL) to extract a cream powder. Yield 0.57g, 94%. m.p 160-162°C; IR (KBr) (ν_{max}, cm^{-1}): 1734, 1741 and 1749 (C=O). MS, m/z (%): 604 (M^{+}, 3), 546 (M-2Et, 42), 486 (M-2CO_2Me, 37), 406 (M-$C_8H_{10}N_2O_2S$, 27), 262 (PPh_3, 81), 183 (PPh_2, 100), 108 (PPh, 42), 77 (Ph, 29). Anal. Calcd. for $C_{32}H_{33}O_6N_2SP$ (604): C, 63.58; H, 5.46; N, 4.64 %. Found: C, 63.61; H, 5.50; N, 4.60%.

Major isomer-7a : ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.29 (6H, t, $^{3}J_{HH}$=6.9 Hz 2NCH_2CH_3) , 3.18, 3.30 (6H, 2s, 2OCH_3), 4.56 (4H, m, 2ABX_3 system 2NCH_2CH_3), 5.02 (1H, dd, $^{3}J_{HH}$=10.5 Hz and $^{3}J_{PH}$=6.6 Hz, P-CH-C*H*), 5.80 (1H, dd, $^{3}J_{HH}$=10.5 Hz and $^{2}J_{PH}$=14.5 Hz, P-C*H*-CH), 7.53-7.87 ($15H_{aro}$, m, $3C_6H_5$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 12.78 (2NCH_2CH_3), 41.55 and 41.60 (2NCH_2), 42.54 (d, $^{2}J_{PC}$= 4.7 Hz, P-CH-*C*H), 43.33 (d, $^{1}J_{PC}$=41.6 Hz, P-*C*H), 52.71 and 52.93 (2OCH_3), 87.71 (d, $^{3}J_{PC}$=11.2 Hz, P-C-C-*C*), 120.76 (d, $^{1}J_{PC}$= 88.0 Hz, C_{ipso}), 129.54 (d, $^{3}J_{PC}$=12.9 Hz, C_{meta}), 134.12 (C_{para}), 134.28 (d, $^{2}J_{PC}$=9.5 Hz, C_{ortho}), 161.14 (O=*C*-C-*C*=O), 166.88 and 173.74 (2C=O, ester), 176.09 (C=S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 24.28 ($(Ph)_3P^{+}$-C).

Minor isomer-7a : ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.17 (6H, t, $^{3}J_{HH}$=6.9 Hz 2NCH_2CH_3) , 3.31, 3.59 (6H, 2s, 2OCH_3), 4.20 (4H, m, 2ABX_3 system 2NCH_2CH_3), 5.09 (1H, dd, $^{3}J_{HH}$=11.3 Hz and $^{3}J_{PH}$=7.0 Hz, P-CH-C*H*), 5.84 (1H, dd, $^{3}J_{HH}$=11.3 Hz and $^{2}J_{PH}$=15.2 Hz, P-C*H*-CH), 7.53-7.87 ($15H_{aro}$, m, $3C_6H_5$); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 12.78 (2NCH_2CH_3), 42.01 and 42.18 (2NCH_2), 42.46 (P-CH-*C*H), 43.18 (d, $^{1}J_{PC}$=50.8 Hz, P-CH), 52.55 and 52.71 (2OCH_3), 87.99 (d, $^{3}J_{PC}$=2.5 Hz, P-C-C-*C*), 120.78 (d, $^{1}J_{PC}$= 86.3 Hz, C_{ipso}), 129.51 (d, $^{3}J_{PC}$=12.9 Hz, C_{meta}), 134.08 (C_{para}), 134.28 (d, $^{2}J_{PC}$ 9.5 Hz, C_{ortho}), 161.03 (O=*C*-C-*C*=O), 167.33 (d, $^{2}J_{PC}$=1.7 Hz, C=O, ester), 173.17 (d, $^{3}J_{PC}$=18.0 Hz, C=O, ester),

175.69 (C=S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.97 ($(Ph)_3P^+$-C).

(2*R, 3*R**)1,3-Diethyl-4,6-dioxo-2-thioxo-5-[2-(triphenylphosphonio)-1,2- bis(ethoxy carbonyl)ethyl] tetrahydropyrimidin-5-ide (7b).**

White powder. Yield 0.57g, 90%. m.p 162-164°C ; IR (KBr) (ν_{max}, cm^{-1}): 1728, 1735 and 1746 (C=O). MS, m/z (%): 632 (M^+, 5), 574 (M-2Et, 23), 486 (M-2CO_2Et, 36), 449 (M-PPh_2, 49), 262 (PPh_3, 100), 262 (PPh_2, 96), 183 (PPh, 52), 77 (Ph, 28). Anal. Calcd. for $C_{34}H_{37}O_6N_2SP$ (632): C, 64.56; H, 5.85; N, 4.43 %. Found: C, 63.87; H, 6.04; N, 4.51 %.

Major isomer-7b : ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.87-1.32 (12H, m, 2OCH_2*CH_3* and 2NCH_2*CH_3*), 3.61 and 3.78 (4H, 2m, 2ABX_3 system, 2O*CH_2*CH_3), 4.61 (4H, m, ABX_3 system 2N*CH_2*CH_3), 5.29 (1H_{bro}, P-CH-C*H*), 5.66 (1H_{bro}, P-C*H*-CH), 7.48-7.90 (15H_{aro}, m, 3C_6H_5); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 12.72 (2NCH_2*CH_3*), 13.56 and 13.79 (2OCH_2*CH_3*), 41.60 and 41.66 (2NCH_2), 42.58 (d, $^2J_{PC}$= 4.5 Hz, P-CH-*C*H), 43.38 (d, $^1J_{PC}$=43.3 Hz, P-*C*H), 61.81 and 62.62 (2O*CH_2*CH_3), 88.52 (d, $^3J_{PC}$=12.0 Hz, P-C-C-*C*), 121.32 (d, $^1J_{PC}$= 88.3 Hz, C_{ipso}), 129.50 (d, $^3J_{PC}$=12.9 Hz, C_{meta}), 133.87 (d, $^4J_{PC}$=2.6 Hz, C_{para}), 134.35 (d, $^2J_{PC}$=9.7 Hz, C_{ortho}), 161.00 (O=*C*-C-*C*=O), 166.88 and 173.74 (2C=O, ester), 176.05 (C=S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 24.28 ($(Ph)_3P^+$-C).

Minor isomer-7b: ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.87-1.32 (12H, m, 2OCH_2*CH_3* and 2NCH_2*CH_3*), 3.61 and 3.78 (4H, 2m, 2ABX_3 system, 2O*CH_2*CH_3), 4.21 (4H, m, ABX_3 system, 2N*CH_2*CH_3), 5.07 (1H, dd, $^3J_{HH}$=11.0 Hz and $^3J_{PH}$=6.0 Hz, P-CH-C*H*), 5.90 (1H, dd, $^3J_{HH}$=11.0 Hz and $^3J_{PH}$=13.2 Hz, P-C*H*-CH), 7.48-7.90 (15H_{aro}, m, 3C_6H_5); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.31 (2NCH_2*CH_3*), 14.05 and 14.19 (OCH_2*CH_3*), 41.91 and 41.98 (2NCH_2), 42.49 (d, $^2J_{PC}$=4.6 Hz, P-CH-*C*H), 42.66 (d, $^1J_{PC}$=50.3 Hz, P-CH), 61.33 and 62.23 (2O*CH_2*CH_3), 88 .67 (d, $^3J_{PC}$=2.3 Hz, P-C-C-*C*), 118.02 (d, $^1J_{PC}$= 86.3 Hz, C_{ipso}), 129.45 (d, $^3J_{PC}$=12.9 Hz, C_{meta}), 133.87 (d, $^4J_{PC}$=2.6 Hz, C_{para}), 134.28 (d, $^2J_{PC}$ 9.2 Hz, C_{ortho}), 161.00 (O=*C*-C-*C*=O), 166.64 (d, $^2J_{PC}$=1.6 Hz, C=O, ester), 172.60 (d, $^3J_{PC}$=18.0 Hz, C=O, ester), 175.66 (C=S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.94 ($(Ph)_3P^+$-C).

(2*R, 3*R**) 1,3-Diethyl-4,6-dioxo-2-thioxo-5-[2-(triphenylphosphonio)-1,2- bis(tert-butoxy carbonyl)ethyl] tetrahydropyrimidin-5-ide (7c).**

white powder. yield 0.67g, 97%. m.p 176-178°C ; IR (KBr) (ν_{max}, cm^{-1}): 1724, 1732 and 1743 (C=O). MS, m/z (%): 688 (M^+, 4), 615 (M-$OCMe_3$, 34), 587 (M-CO_2CMe_3, 29), 490 (M-$C_8H_{10}N_2O_2S$, 46), 262 (PPh_3, 100), 183 (PPh_2, 82), 108 (PPh, 36), 77 (Ph, 27). Anal. Calcd. for $C_{38}H_{45}O_6N_2SP$ (688): C, 66.28; H,6.54; N, 4.07 %. Found: C, 67.32; H, 6.61; N, 3.95 %.

Major isomer-7c : ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.94 and 0.99 (18H, 2s, 2C*Me*3), 1.07-1.23 (6H_{bro}, 2NCH_2*CH_3*), 4.56 (4H_{bro}, 2N*CH_2*CH_3), 4.85 (1H, dd, $^3J_{HH}$=10.4 Hz, $^3J_{PH}$=6.2 HZ, P-CH-C*H*), 5.64 (1H, dd, $^3J_{HH}$=10.4 Hz, $^2J_{PH}$=13.9 Hz, P-C*H*-CH), 7.43-7.85 (15H_{aro}, m, 3C_6H_5); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 12.70 (2NCH_2*CH_3*), 27.05 and 27.36 (2s, 2C*Me*3), 41.31 and 42.17 (2NCH_2), 42.42 (d, $^2J_{PC}$= 4.7 Hz, P-CH-*C*H), 43.45 (d, $^1J_{PC}$=42.9 Hz, P-*C*H), 81.63 and 84.01 (2C, 2O*C*Me_3), 88.36 (d, $^3J_{PC}$=11.9 Hz, P-C-C-*C*), 122.23 (d, $^1J_{PC}$= 88.9 Hz, C_{ipso}), 129.26 (d, $^3J_{PC}$=12.8 Hz, C_{meta}), 133.43 (C_{para}), 134.41 (d, $^2J_{PC}$=9.6 Hz, C_{ortho}), 160.99 (O=*C*-C-*C*=O), 165.52 and 172.76 (2C=O, ester), 175.75 (C=S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 25.17 ($(Ph)_3P^+$-C).

Minor isomer-7c : ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 1.02 and 1.27 (18H, 2s, 2C*Me*3), 1.07-1.23 (6H_{bro}, 2NCH_2*CH_3*), 4.18 (4H_{bro}, 2N*CH_2*CH_3), 5.15 (1H, dd, $^3J_{HH}$=10.7 Hz, and $^3J_{PH}$=6.5 Hz, P-CH-C*H*), 5.76 (1H, dd, $^3J_{HH}$=10.7 Hz, and $^2J_{PH}$=15.7 Hz, P-C*H*-CH), 7.43-7.85 (15H_{aro}, m, 3C_6H_5); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 12.70 (2NCH_2*CH_3*), 27.14 and 27.74 (2s, 2C*Me*3), 41.63 and 41.71 (2NCH_2), 42.47 (P-CH-*C*H), 42.84 (d, $^1J_{PC}$=49.8 Hz, P-CH), 80.63 and 83.62 (2C, 2O*C*Me_3), 88.57 (d, $^3J_{PC}$=2.1 Hz, P-C-C-*C*), 118.49 (d, $^1J_{PC}$= 85.2 Hz, C_{ipso}), 129.33 (d, $^3J_{PC}$=12.9 Hz, C_{meta}), 133.43 (C_{para}), 134.48 (d, $^2J_{PC}$ 9.6 Hz, C_{ortho}), 160.79 (O=*C*-C-*C*=O), 165.09 (d, $^2J_{PC}$=1.7 Hz, C=O, ester), 171.82 (d, $^3J_{PC}$=18.1 Hz, C=O, ester), 175.45 (C=S). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 25.31 ($(Ph)_3P^+$-C).

Preparation of dimethyl-2-(methyl cyclohexanone-2-carboxylate-2-yl)-3-(triphenylphosphanylidene) succinate (9a).

General Procedure:

To a magnetically stirred solution of methyl cyclohexanone-2-carboxylate (0.16 g , 1 mmol) and triphenylphosphine (0.26 g , 1 mmol) in mixture of ethyl acetate and n-hexane (2:1) was added, dropwise, a mixture of dimethyl acetylenedicarboxylate (0.14 g, 1 mmol) in 3 mL of ethyl acetate at -5°C over 10 min. After approximately 30 minute stirring at room temperature, the product was filtered and washed with cold diethyl ether (3 ×5 mL) and was finally obtained as white powder, 0.45 g, yield 80%, m.p 175-177°C,

IR(KBr) (ν_{max}, cm^{-1}): 1725 and 1628 (4 C=O). MS (*m/z*, %): 501 (M^+-CO_2Me, 7), 405 (M^+-$C_8H_{11}O_3$, 82), 262 (PPh_3, 32), 183 (PPh_2, 54), 108 (PPh, 31), 77 (Ph, 42), 59 (CO_2Me, 100). Anal. Calcd. For $C_{32}H_{33}O_7P$ (560): C, 68.57; H, 5.89 %. Found: C, 70.12; H, 5.68; %.

Major isomer (*E*)-**9a** (55%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.59-2.74 (8H, 4 CH_2), 2.90 and 3.20 (6H, 2s, 2 OCH_3), 3.46 (1H, d, $^3J_{PH}$=12.1 Hz, P-C-CH), 3.67 (3H, s, OCH_3), 7.50-7.86 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 23.07, 24.45, 31.06 and 40.98 (4 CH_2), 37.62 (d, $^1J_{PC}$=123.7 Hz, P=C), 47.48 (d, $^2J_{PC}$=14.2 Hz, P-C-*CH*), 48.47, 51.61 and 52.20 (3 OCH_3), 66.01 (d, $^3J_{PC}$=4.6 Hz, P-C-C-*C*), 126.85 (d, $^1J_{PC}$=91.0 Hz, C_{ipso}), 128.40 (d, $^3J_{PC}$=12.08 Hz, C_{meta}), 131.79 (C_{para}), 133.84 (d, $^2J_{PC}$=9.6 Hz, C_{ortho}), 170.01 (d, $^2J_{PC}$=13.3 Hz, P-C-*C*), 174.46 (d, $^3J_{PC}$=5.8 Hz, C=O), 205.85 and 207.99 (2 C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24.84 (Ph_3P^+-C).

Minor isomer (*Z*)-**9a** (45%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.59-2.74 (8H, 4 CH_2), 2.90 (3H, s, OCH_3), 3.51 (1H, d, $^3J_{PH}$=15.3 Hz, P-C-CH), 3.67 and 3.70 (6H, 2s, 2 OCH_3), 7.50-7.86 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 23.12, 24.63, 32.88 and 40.98 (4 CH_2), 38.80 (d, $^1J_{PC}$=122.1 Hz, P=C), 46.22 (d, $^2J_{PC}$=12.8 Hz, P-C-*CH*), 48.54, 51.45 and 52.30 (3 OCH_3), 65.40 (d, $^3J_{PC}$=4.5 Hz, P-C-C-*C*), 126.40 (d, $^1J_{PC}$=90.3 Hz, C_{ipso}), 128.44 (d, $^3J_{PC}$=12.8 Hz, C_{meta}), 131.79 (C_{para}), 133.84 (d, $^2J_{PC}$=9.6 Hz, C_{ortho}), 169.65 (d, $^2J_{PC}$=12.8 Hz, P-C-C), 174.88 (d, $^3J_{PC}$=5.1 Hz, C=O), 205.83 and 208.40 (2 C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 25.29 (Ph_3P^+-C).

Di-tert-buthyl-2-(methyl cyclohexanone-2-carboxylate-2-yl)-3-(triphenylphosphanylidene) succinate (**9b**).
White crystals, 0.55 g, yield 85%, m.p 150-152 ºC, IR (ν_{max}, cm^{-1}): 1733, 1634 (4 C=O). MS, (m/z, %): 644 (M^+, 15), 543 (M^+-CO_2Me_3, 25), 489 (M^+-$C_8H_{11}O_3$, 61), 262 (PPh_3, 50), 183 (PPh_2, 45), 108 (PPh, 20), 77 (Ph, 16), 57 (M^+-CMe_3, 56). Anal. Calcd. For $C_{38}H_{45}O_7P$ (644): C, 70.81; H, 6.99 %. Found: C, 71.87; H, 6.73 %.

Major isomer (*E*)-**9b** (70%): ^{1}H NMR (500.1 MHz, $CDCl_3$), δ 0.89 and 1.50 (18H, 2s, 2 CMe_3), 1.69-2.92 (8H, 4 CH_2), 3.11 (3H, s, OCH_3), 3.50 (1H, d, $^3J_{PH}$=19.8 Hz, P-C-CH), 7.44-7.842 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$), δ 23.28 and 24.40 (2 CH_2), 28.21 and 28.42 (2s, 2 CMe_3), 31.11 (CH_2), 36.62 (d, $^1J_{PC}$=124.1 Hz, P=C), 40.93 (CH_2), 48.15 (d, $^2J_{PC}$=14.6 Hz, P-C-*CH*), 52.01 (OCH_3), 66.26 (d, $^3J_{PC}$=3.6 Hz, P-C-C-*C*), 79.74 and 81.61 (2s, 2 $OCMe_3$), 126.27 (d, $^1J_{PC}$=91.8 Hz, C_{ipso}), 128.04 (d, $^3J_{PC}$=12.0 Hz, C_{meta}), 131.53 (C_{para}), 132.03 (d, $^2J_{PC}$=10.0 Hz, C_{ortho}), 168.80 (d, $^2J_{PC}$=13.0 Hz, P-C-*CH*), 172.79 (d, $^3J_{PC}$=7 Hz, C=O), 205.54 and 206.10 (2 C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 23.24 (Ph_3P^+-C).

Minor isomer (*Z*)-**9b** (30%): ^{1}H NMR (500.1 MHz, $CDCl_3$), δ 1.40 and 1.51 (18H, 2s, 2 CMe_3), 1.69-2.92 (8H, 4 CH_2), 3.10 (3H, s, OCH_3), 3.44 (1H, d, $^3J_{PH}$=22.2 Hz, P-C-CH), 7.44-7.82 (15H, m, 3 C_6H_5). ^{13}C NMR (125.76 MHz, $CDCl_3$), δ 23.31 and 24.82, (2 CH_2), 27.95 and 28.80 (2s, 2 CMe_3), 30.76 (CH_2), 37.74 (d, $^1J_{PC}$=123.9 Hz, P=C), 41.07 (CH_2), 46.37 (d, $^2J_{PC}$=14.8 Hz, P-C-*CH*), 52.01 (OCH_3), 61.54 (d, $^3J_{PC}$=4.6 Hz, P-C-C-*C*), 79.64 and 81.70 (2s, 2 $OCMe_3$), 125.00 (d, $^1J_{PC}$=91.6 Hz, C_{ipso}), 128.48 (d, $^3J_{PC}$=12.1 Hz, C_{meta}), 131.53 (C_{para}), 131.87 (d, $^2J_{PC}$=5.8 Hz, C_{ortho}), 168.24 (d, $^2J_{PC}$=13.1 Hz, P-C-*CH*), 172.30 (d, $^3J_{PC}$=7.2 Hz, C=O), 205.33 and 206.41 (2 C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 25.08 (Ph_3P^+-C).

Dimethyl -2-(2-acetylcyclopentanone-2yl)-3-(triphenylphosphanylidene) succinate (**9c**).
White crystals, 0.48 g, yield 90%, m.p 160-162 ºC, IR (ν_{max}, cm^{-1}): 1725, 1700 and 1628 (4 C=O); MS, (m/z, %): 530 (M^+, 9), 405 (M^+-$C_7H_9O_2$, 77), 277 (M^+-PPh_3 and CH_3, 77), 262 (PPh_3, 21), 209 (M^+-PPh_3 and CO_2CH_3, 28), 183 (PPh_2, 40), 108 (PPh, 17), 77 (Ph, 43), 59 (CO_2CH_3, 22), 43 (CO_2CH_3, 100). Anal. Calcd. For $C_{31}H_{31}O_7P$ (530): C, 70.19; H, 5.85 %. Found: C, 68.73; H, 6.07 %.

Major isomer (*E*)-**9c** (56%): ^{1}H NMR (500.1 MHz, $CDCl_3$), δ 1.47-2.19 (6H, 3 CH_2), 1.68 (3H, s, CH_3), 2.87 (3H, s, OCH_3), 3.54 (1H, d, $^3J_{PH}$=12.5 Hz, P-C-CH), 3.74 (3H, s, OCH_3), 7.51-7.85 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$), δ 25.43 and 27.60 (2 CH_2), 29.10 (CH_3), 37.69 (CH_2), 39.14 (d, $^1J_{PC}$=121.9 Hz, P=C), 48.60 and 51.91 (2 OCH_3), 49.03 (d, $^2J_{PC}$=13.3 Hz, P-C-*CH*), 74.30 (d, $^3J_{PC}$=3.7 Hz, P-C-C-*C*), 127.47 (d, $^1J_{PC}$=92.0 Hz, C_{ipso}), 128.4 (d, $^3J_{PC}$=12.1 Hz, C_{meta}), 131.90 (C_{para}), 133.9 (d, $^2J_{PC}$=9.4 Hz, C_{ortho}), 170.35 (d, $^2J_{PC}$=13.3 Hz, C=O), 174.23 (d, $^3J_{PC}$=5.3 Hz, C=O), 202.76 and 215.13 (2 C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 26.12 (Ph_3P^+-C).

Minor isomer (*Z*)-**9c** (44%): ^{1}H NMR (500.1 MHz, $CDCl_3$), δ 1.47-2.19 (6H, 3 CH_2), 1.68 (3H, s, CH_3), 2.94 (3H, s, OCH_3), 3.50 (1H, d, $^3J_{PH}$=7.4 Hz, P-C-CH), 3.69 (3H, s, OCH_3), 7.51-7.85 (15H, m, 3 C_6H_5). ^{13}C NMR (125.76 MHz, $CDCl_3$), δ 25.43 and 28.53 (2

CH_2), 29.75 (CH_3), 38.99 (CH_2), 40.56 (d, $^1J_{PC}$=122.3 Hz, P=C), 48.65 and 51.87 (2 OCH_3), 49.80 (d, $^2J_{PC}$=13.5 Hz, P-C-*CH*), 73.93 (d, $^3J_{PC}$=3.4 Hz, P-C-C-*C*), 126.93 (d, $^1J_{PC}$=91.7 Hz, C_{ipso}), 128.5 (d, $^3J_{PC}$=11.9 Hz, C_{meta}), 131.95 (C_{para}), 133.9 (d, $^2J_{PC}$=9.4 Hz, C_{ortho}), 169.78 (d, $^2J_{PC}$=12.1 Hz, C=O), 174.97 (d, $^3J_{PC}$=6.6 Hz, C=O), 203.65 and 216.11 (2 C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 25.39 (Ph_3P^+-C).

Acknowledgements

We gratefully acknowledge financial support from the Research Council of University of Sistan and Balouchestan.

References

[1] Cobridge. D. E. C. *Phosphorus, an Outline of Chemistry, Biochemistry and Uses*, 5th ed (Elsevier, Amsterdam, 1995).
[2] Engel, R. *Synthesis of Carbon-Phosphorus Bonds* (CRC Press, Boca Raton, FL, 1998).
[3] Cadogan, J. I. G. *Organophosphorus Reagents in Organic Synthesis* (Academic Press, New York, 1979).
[4] Kolodiazhnyi, O. I. *Russ. Chem.* **1997**, *66*, 225.
[5] Bestman H.J. and Vostrowsky, O. *Top. Curr. Chem.* **1983**, *109***,** 85.
[6] Hassani, Z.; Islami, M. R.; Sheibani, H.; Kalantari M. and Saidi, K. *Arkivoc* **2006**, (*i*), 89.
[7] Islami, M. R.; Mollazehi, F.; Badiei A. and Sheibani, H. *Arkivoc* **2006**, (*xv*), 25.
[8] Kalantari, M.; Islami, M. R.; Hassani Z. and Saidi, K. *Arkivoc* **2006,** (*x*), 55.
[9] Yavari I. and Feiz-Javadian, F. *Phosphorus, Sulfur, and Silicon* **2006**, *181*, 1011.
[10] Adib M. and Sayahi, M. H. *Monatshefte* **2006**, *137*, 207.
[11] Maghsoodlou, M. T.; Hazeri, N.; Habibi-Khorasani, S. M.; Ghulme Shahzadeh, A. and Nassiri, M. *Phosphorus, Sulfur, and Silicon* **2006**, *181*, 913.
[12] Maghsoodlou, M. T.; Hazeri, N.; Habibi-Khorasani, S. M.; Nassiri, M.; Marandi, G.; Afshari G. and Niroumand, U. *Sulfur Cehmistry* **2005**, *26*, 261.
[13] Maghsoodlou, M. T.; Hazeri, N.; Habibi-Khorasani, S. M.; Afshari G. and Nassiri, M. *J. Chem. Res.* **2005**, 727.
[14] Esmaeili, A. A.; Islami M. R. and Kardan-Moghaddam, G. R. *Phosphorus, Sulfur, and Silicon* **2006**, *181*, 527.
[15] Maghsoodlou, M. T.; Habibi-Khorasani, S. M.; Rofouei, M. K.; Adhamdoust, S. R. and Nassiri, M. *Arkivoc* **2006** (*xii*), 145.
[16] Maghsoodlou, M. T.; Hazeri, N.; Habibi-Khorasani, S. M.; Rofouei M. K. and Rezaie, M. *Arkivoc* **2006**, (*xiii*), 117.
[17] Maghsoodlou, M. T.; Hazeri, N.; Habibi-Khorasani, S. M.; Afshari G. and Nassiri, M. *J. Chem. Res.* **2005**, 727.
[18] Hazeri, N.; Habibi-Khorasani, S. M.; Maghsoodlou, M. T.; Marandi, G.; Nassiri, M. and Ghulme Shahzadeh, A. *J. Chem. Res.* **2006**, 215.
[19] Bestman, H. J. and Gross, A. *Tetrahedron lett*. **1997**, *38*, 4765, Bestman, H. J. and Zimmermann, R. *Top. Curr. Chem*. **1971**, *20*, 88.
[20] Yavari, I. and Maghsoodlou, M.T. *Tetrahedron Lett.* **1998**, *39*, 4579.
[21] Yavari, I.; Islami M. R. and H. R. Bijanzadeh, *Tetrahedron* **1999**, *55*, 5547.
[22] Shaabani, A.; Teimouri, M. B.; Yavari, I.; Norouzi Arasi, H. and Bijanzadeh, H. R. *Fluorine Chemistry* **2000**, *103*, 155.
[23] Roth, H. J. and Kleemann, A. *Pharmaceutical Chemistry* (Ellis Horwood, London, 1988).
[24] Tobby, J. C. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, Verkede J. G. and Quin, J. D. (Eds), VCH Publishers, 1987 Weinheim Ch 1, pp 1-60.
[25] Ludeman, S. M.; Bartlett, D. L. and Zon, G. *J. Org. Chem*. **1979**, *44*, 1163.
[26] (a) Karplus, M. *J. Am. Chem. Soc*. **1963**, *88*, 2870, (b) Haasnoot, C. A. G.; Leew, F. A. A. A. and Altona, C. *Tetrahedron* **1980**, *36*, 2783.
[27] Breitmaier E. and Volter, W. *Carbon-13 NMR Spectroscopy*, 3rd ed., VCH Publisher: New York, 1990 pp. 250-254.
[28] Moonen, K.; Van Meenen, E.; Verwee A. and Stevens, C. V. *Angew. Chem. Int. Ed*. **2005**, *44*, 7407.
[29] Moonen, K.; Laureyn I. and Stevens, C.V. *Chem. Rev*. **2004**, 104, 6177.
[30] Maghsoodlou, M. T.; Hazeri, N.; Habibi-Khorasani, S. M.; Moeeni, Z.; Marandi, G.; Lashkari, M.; Ghasemzadeh, M. and Bijanzadeh, H. R. *J. Chem. Res*. **2007**, 566.
[31] Baharfar, R.; Heydari, A. and Saffarian, N. *J. Chem. Res*. **2001**, 72.
[32] Teimouri, M. B. and Bazhrang, R. *J. Chem. Res*. **2005**, 50.
[33] Shaabani A. and Sadeghi Nejat, F. *J. Chem. Res.* **1998**, 584.

[34] Ramazani A. and Esmaili, A. *J. Chem. Res*. **1997**, 208.
[35] Anary-Abbasinejad, M.; Anaraki-Ardakani, H.; Dehghan, A.; Hassanabadi, A. and Seyed-mir, M. R. *J. Chem. Res*. **2007**, 574.